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Numerical simulation of two stage combustor

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Abstract

Global environmental problems are a function of the human desire to use energy as an ever increasing power source. The link between usage and quality of life is now a proven fact. For this reason a more efficiency combustion process and low-emission fuels are the global aim of the combustion research field. The objective of this work is the CFD simulation of a two stage combustor burning coal in different operating condition, The overall equivalence ratio is 0.165 on the rich side and the thermal power is 150 kW. To carry out the simulation the solver Fluent was used to solve the Navier-Stokes and energy equations, the Reynolds Stress Model (RSM) has been used to close the system. The combustion process has been modelled by the PDF approach, which solves transport equation for the mixture fractions. From the results it is possible to notice as in the first chamber the gasification process is carried out, followed by the combustion reaction of char in the second chamber. The peak temperature location and the overall temperature field are influenced by the air split ratio used.

Introduction

Nowadays power production is strongly linked with environmental pollution; in fact a larger amount of power is generated by the combustion of fossil fuels. During the combustion process gas such as CO₂ is released into the atmosphere and consequently increases in greenhouse gas occur. To contrast this behaviour new fuels are used in the power generation; these fuels are usually of a renewable type such as biomass. Biomass involves many different waste products that range from almond shells to sewage sludge. Usually biomass gives zero net CO₂ production [1,2,3,4], meaning that during growth they accumulates the same amount of CO₂ as is released during combustion. Biomass materials have lower heating value with respect of fossil fuels like coal, and higher content of volatile matter. For this reason biomass can be blended with coal to produce useful alternatives for large scale power plant.

This study highlights the first stage of developing a novel slagging model suitable for predicting the impaction rate for different coal and biomass blend. A CFD tool has been used to understand the coal combustion in different operating condition on a research rig developed for coal – biomass co-combustion. The simulation has been performed on a model of a novel inverted cyclone gasifier, the geometry of which is shown in figure 1. The boiler has two chambers: in the first, the volatilisation takes place, during this phase CO and CH₄ are released in the chamber. In the first chamber there is an air inlet, through which the air is injected tangentially to the chamber wall and a transfer duct to connect the two chambers. In order to provide high residence time, required by the gasification pyrolysis process, a swirl motion is imparted into the flow stream. The second chamber was designed to achieve the complete combustion process, for this reason secondary air inlet is provided. Secondary air is also fired tangentially to create a cyclonic flow.

For the simulation, a grid of about 200,000 hexahedral cells has been created; Fluent 6.0 code has been used to carry out the CFD calculations, the gas – phase conservation equations are treated in Eulerian fashion as reported [5]. In this study the SIMPLE algorithm is used for the pressure – velocity coupling to solve continuity and momentum equation. The particle – phase equation is treated in Lagrangian fashion, the stochastic tracking of the assumed sphere particles was also included using a Direct Random Walking (DRW) model. The RSM (Reynolds Stress Model) and P1 radiation models have been employed in this simulation.

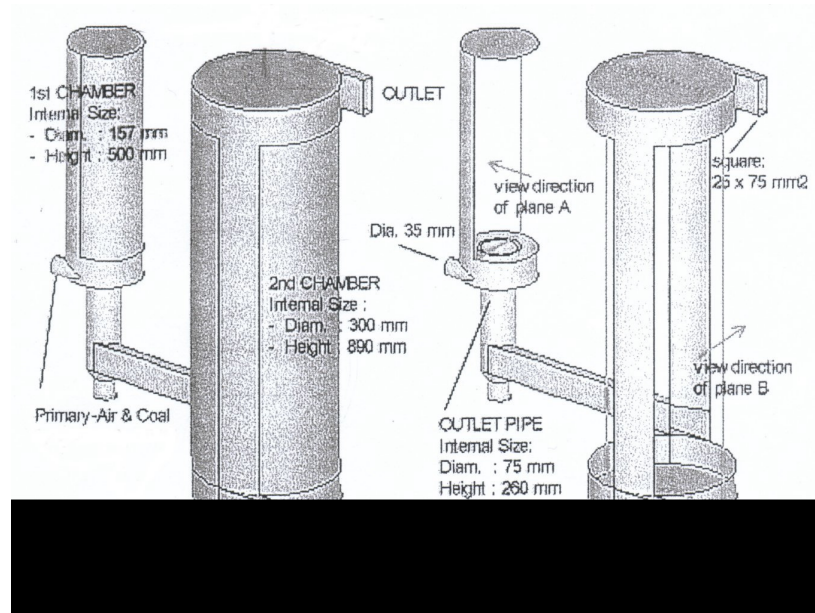


Figure 1: Geometry of the research rig.

This study has used two approaches of Fluent's capability. The first approach is used to model the heterogeneous reaction of solid fuel and oxidant. The second approach is the Probability Density Function (PDF) that is used to compute the defined species composition and properties as a results of the gaseous turbulent reaction. For the simulation three different operating conditions have been used. These conditions were concerned about the split ratio between the primary and secondary air flow rate, while the overall fuel/air ratio remains the same. Table1 and 2 highlight the air and operating conditions respectively:

	Primary	Secondary
Case A	50%	50%
Case B	100%	0%
Case C	34%	66%

Table 1: air split ratios

	Case A,B & C
Coal feeding (kg/s)	0.00416667
Air mass rate (kg/s)	0.0075425
Air inlet temperature (K)	300
Turbulence intensity at inlets	10%

Table 2: operating conditions

The overall equivalence ratio is $\phi = 0.165$ on the rich side. The coal used for this simulation is Colombian, the proximate and ultimate analysis of the coal has been used to build the pdf table. More details about the coal characteristics have been previously reported [6].

Numerical results

The temperatures calculated by fluent for all the cases analysed are reported in Table 3. These are the mean value.

Mean temperature (K)				
	First chamber	Outlet pipe	Ducting	Second chamber
Case A	1200	1200	1300	1200
Case B	1100	1600	1500	1300
Case C	1300	1200	1300	1500

Table 3: static temperature for three cases

The mean temperature in the first chamber is similar in all the three cases, this is due to the beginning of the reaction. For the outlet pipe it is possible to notice as in case B, it has the higher temperature, due to the higher equivalence ratio used in this case, hence for the other cases the amount of primary air is almost the same. In the ducting connecting the two chamber the temperature is almost constant for the case A and C, while for case B it begins to reduce due to the reason that the combustion process has used all the oxygen available and now the combustion products begin to cool. This is evident in the second chamber where the temperature is lower. In the case A the temperature in the second chamber is almost constant. Case C shows an increment in the mean temperature due to the injection of new air.

Range velocity (m/s)				
	First chamber	Outlet pipe	Ducting	Second chamber
Case A	0 ÷ 8.4	5.6 ÷ 8.4	11 ÷ 19	0 ÷ 8.4
Case B	0 ÷ 11	11 ÷ 16	17 ÷ 91	0 ÷ 25
Case C	0 ÷ 7	3 ÷ 8	8 ÷ 17	0 ÷ 10

Table 4: velocity field for three cases

Table 4 shows the velocity range in the main rig structure for the three cases analysed, the cases A and C are quite similar this is due to the similar air flow rate injected by means of the two air inlet, instead in case B the velocity are higher due to the higher primary air flow rate and to the higher mean temperature reached. In all cases the maximum velocity is located in the transfer ducting connecting the two chambers, this is due to the minimum section area in this zone.

For the species present in the combustion process it is possible to notice the following:

- CO: maximum value is the same in three cases analysed. In cases A and B the maximum value is located in the first chamber, however for case C the mass fraction of CO spreads in to two chambers.
- CO₂: this component is located in reaction zone. In cases A and B it is possible to notice the presence of CO₂ in the first chamber and in the bottom of the second chamber where new air is injected to complete the combustion reaction. For case C the CO₂ in the second chamber is lower than that in the previous cases because the reaction is almost completed before to reach the second chamber and new air is not injected.
- H₂O: the diagram of this component is similar to the CO₂ diagram, being this specie one of the main combustion products.
- O₂: oxygen is rapidly used in the combustion process and it is located near the air inlets, in case B it is not present in the second chamber because new air has not been injected

	Average residence time (sec)			Standard deviation		
	10 µm	45 µm	150 µm	10 µm	45 µm	150 µm
Case A	3.47	6.71	12.6	5.23	5.92	6.99
Case B	2.72	7.84	14.5	3.3	6.4	7.4
Case C	1.97	2.59	16	1.7	0.81	7.02

Table 5: residence time

The residence time calculated by Fluent for the cases simulated are highlighted in table 5. In the table the mean value and the standard deviation are indicated, these values have been calculated on 200 particles tracked, 10 μm is the minimum particle diameter, 150 μm the maximum and 45 μm the Rosin-Rammler mean diameter.

Conclusions and Future works

The aim of this study was to analyse the fluid-dynamics and thermal behaviour of the two stage combustor research rig. The main effect studied has been the air split ratio between the two air inlets available on the rig and its influence on particles residence time and thermal field. The following conclusions can be drawn:

- The analysis shows that the maximum temperature was similar for the three cases studied, reaching a value of 1300 – 1400 K. It is noted that the overall equivalence ratio was the same in all cases analysed.
- The wall temperatures are similar in all cases and ranges from 1200 to 1400 K.
- The velocity field calculated by fluent is more influenced by the different split ratio used. These differences are visible in zones where the section reduces and to the bottom of the second chamber where the secondary air inlet is located and the end of the ducting connecting the chambers.
- For cases A and B pyrolysis is completed within the first chamber as indicated by the CO contours. With case c the pyrolysis reaction is not completed until the start of the second chamber.
- The CO₂ and H₂O contours have been used to localize the reaction zone, positioned mainly to the bottom of the first chamber (cases A, B and C) and near the wall to the bottom of the second chamber (case A and B).
- The oxygen contour shows the presence of air that has not been consumed by the combustion reaction and in all cases the concentration reduces rapidly due to the rich conditions analysed.

Future development will include fragmentation model to predict better the particle history and combustion behaviour that will be linked to a slag/temperature/time correlation will be used.

Acknowledgment

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Influence of Fuel Density on the Conversion Rate of a Fixed Biofuel Bed Operated in a Counter-Current Mode

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ABSTRACT

The influence of fuel density on the conversion rate of a fixed biofuel bed operated in a counter-current mode has been investigated by a recently published fixed bed combustion model. In agreement with previous experimental experience the result from the model calculations shows that the fuel density has a very small influence on the conversion rate.

INTRODUCTION

Measurements [1] show that the conversion rate of a fixed biofuel bed operated in a counter-current mode (conversion front propagates towards air flow) is not much affected by a change in fuel density, which is somewhat surprising, since the conversion behaviour of the single particles constituting the bed could be expected to differ depending to their density. The conversion rate is defined as the mass of moisture and volatiles, which is released per unit time and unit area related to kg dry fuel inside a reaction front that propagates with constant velocity through a fuel bed. The present work investigates how the conversion of the bed is affected by a change in the fuel density, using a recently published fixed bed combustion model [2,3], which, in addition to other combustion processes, accounts for the conversion behaviour of the single particles constituting the bed.

SPECIFIC OBJECTIVES

Solid fuel combustion in a grate furnace takes place in a fixed fuel bed, interacting with the freeboard and the grate. This behaviour is treated by a one-dimensional model [2,3] of a fuel batch. The principle features of the model are as follows; the fuel bed consists of gas and solid phases. Two fictitious boundary surfaces, representing the grate and the freeboard, limit the bed. The solid phase consists of equally sized particles of optional shape. The model can be applied to batch-fired combustors, which is of interest in the present work, but it can also handle continuously operating co-current or counter-current combustors, moving grates and, with some modifications, downdraft gasifiers. Applied to a moving grate in a cross-current mode of operation, the model describes the combustion of a rigid fuel batch transported along the grate, where time is translated to distance along the grate. The combustion system is modelled by conservation of mass, momentum, energy and species in the gas and solid phases, regarded as one-dimensional continua. To account for thermally thick particles, the source terms that express the conversion of the solid phase must be treated by a separate particle model. Here, such a particle model [4] describes the detailed behaviour of the discrete particles of the solid phase. The model treats the particles in one dimension and calculates the temperature wave and the release of moisture and volatiles within the particles. A separate momentum equation does not appear if one assumes that gravity, kinetic energy and pressure

change are negligible. Because of this simplification, transient behaviour of the gas flow cannot be treated, and the gas phase equations are solved for steady state. The simplification is motivated by the small pressure drop over the fuel bed and the short residence time of the gas inside the bed compared to the conversion time of the solid phase. The bed voidage is assumed to be constant and the absorption of radiation in the gas is negligible. These assumptions are similar to those made in most other models of counter-current conversion [5-10]. In contrast to common assumptions made in other models, the derivation of the present model [2,3] includes irregularly shaped, shrinking, thermally large particles, elutriation of solids, solids mixing in the bed expressed as dispersion and heat transport by diffusion of gas species or by dispersion of solids. The correlations for mixing rate Eq (1), effective molecular diffusion Eq (2) [11] and effective thermal conductivity of the bed Eq (3) [11] are modified from the formulation in [2,3] as follows:

$$R_{mix} = 0.63 \left(\frac{1.75U(1-\varepsilon)}{\varepsilon d_h} \right) \min \left(\frac{C_i}{\Omega_i}, \frac{C_{O_2}}{\Omega_{O_2}} \right) \quad (1)$$

$$D_{eff} = 0.8D + 0.5d_h U / \varepsilon \quad (2)$$

$$k_{eff} = 0.8k + 0.5d_h c_p \rho U / \varepsilon \quad (3)$$

Where R_{mix} is mixing rate of gas, U superficial gas velocity, ε bed voidage, d_h hydraulic particle diameter. The following quantities are related to the gas: C concentration, Ω stoichiometric coefficient, D molecular diffusivity, k thermal conductivity, c_p specific heat and ρ is density. Index i refers to combustible gas and O_2 to oxygen. The mixing rate is expressed as equivalent to the form resistance of a particle bed. The deflection of the gas flow caused by the particles enhances the dispersion and is included together with molecular diffusion and thermal conductivity.

RESULT AND DISCUSSION

Combustion in a packed fuel bed has been investigated. The bed contained initially cylindrical wood particles having a diameter of 8 mm, a length of 25 mm and a moisture content as received of 10 %. The particle size and moisture content are common values for wood pellets. Four densities, covering a typical range for fuels, were chosen: 300 kg/m³ corresponding to a very light wood species, 430 kg/m³ - normal wood, 800 kg/m³ - very dense wood and 1100 kg/m³ corresponding to wood pellets. The fuel bed was fed from the end opposite to that of ignition, making combustion propagate towards the air stream that had a flow rate of 0.05 m³/s·m², corresponding to substoichiometric conditions. Fig 1 shows the resulting conversion rate of volatiles and moisture related to dry fuel: the rate is nearly independent of fuel density, which is in agreement with experiences from experiments. However, a weakly increasing trend with increasing density can be observed, less than 3% over the density range.

The temperature profiles of the gas and the surface of the fuel particles along the height of the reaction front are shown in the diagram to the left in Fig 2. All profiles in Fig 2 are shifted so that the position where the temperature of the solid surface attains 500°C is the same in all cases. The adjustment is small because the temperature profiles are almost identical for the various densities. The only visible difference is that the maximum temperature increases slightly both for the gas and the solid surface (less than 15°C in the present density range) with decreasing density. This is caused by the slightly slower conversion rate for smaller densities (Fig 1), which moves the condition for combustion somewhat closer to stoichiometry. The diagram to the right in Fig 2 shows relative moisture, volatile and char contents along the height of the reaction front. The relative positions of drying,

devolatilisation and char combustion in the reaction front differ somewhat with density. The trend is that an increase of density shifts the conversion of the fuel slightly toward the entering air. The figure also shows that at the present particle size, drying, devolatilisation and char combustion are separated from each other, which would make it possible to use a less detailed description of the conversion of the single particles than the one used here.

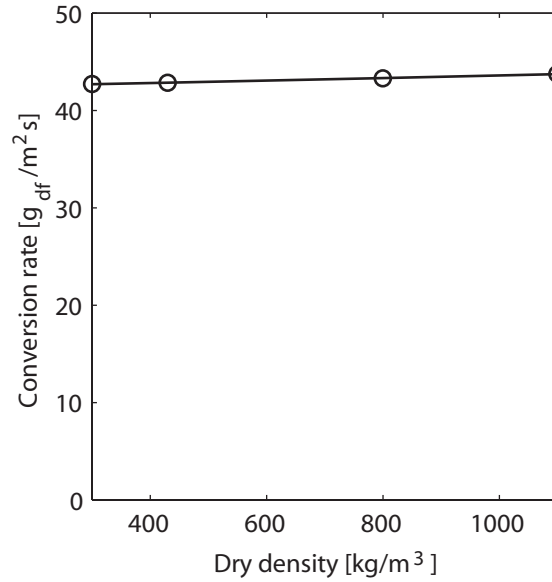


Fig. 1 Conversion rate of moisture and volatiles related to the dry fuel as a function of fuel density.

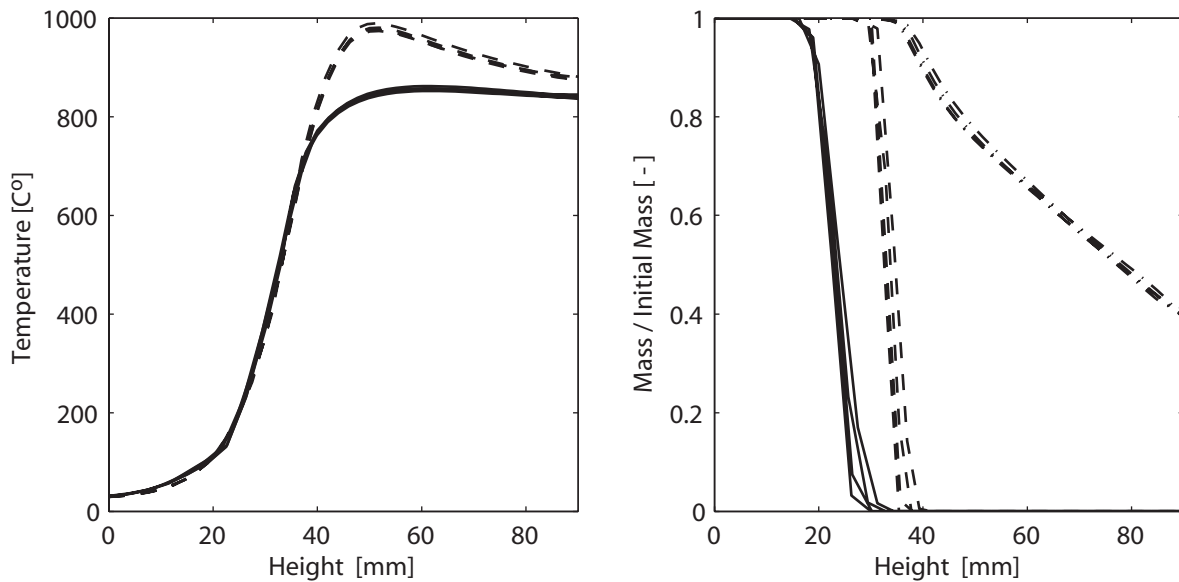


Fig. 2 Right diagram, temperature of gas (dashed lines) and surface of the fuel particles (solid lines) along the height of the reaction front. Left diagram, moisture (solid lines), volatiles (dashed lines) and char (dashed dotted line) along the height of the reaction front.

CONCLUSIONS

The model calculations confirm what has been observed previously in experiments: an increase of fuel density does not have any significant effect on the conversion rate if the conversion rate is related to the mass loss per unit time and cross sectional area of the bed. Of course, the velocity of the combustion front down through the bed of a low density fuel will be higher than that of a high density fuel. The model also shows that inside of the reaction front there is no significant difference in the combustion behaviour with a change of density, only a small shift in the location of the conversion of moisture, volatiles and char can be observed. This means that experiences from one fuel density can be used directly for similar fuels with different densities.

ACKNOWLEDGEMENTS

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A Procedure for Particulate Emission Characterization During Fluidized Bed Combustion of Solid Fuels

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INTRODUCTION

The combustion of fossil and alternative (biomass, waste-derived) fuels is experiencing renewed interest. In this respect, the characterization of fine particle emissions from combustion sources represents one of the main issues. Recent studies have highlighted that emissions of very fine particles (in the micronic-submicronic range) during fluidized bed combustion of fossil and biomass fuels cannot be ruled out when assessing the actual environmental impact of the operation.

Aim of this work is to set up a procedure to evaluate the expected amount of fine particles escaping BFB's and CFB's combustors. The procedure is based on the operation of a 40mm ID bench scale fluidized bed combustor to characterize elutriated material down to 0.5µm particle size. Bed material was also drained and analyzed in order to characterize coarser ash separated from bed inert material. Data are worked out to obtain the so-called Primary Ash Particle Size Distribution (PAPSD) of the solid fuel (2, 4).

Preliminary tests have been carried out to test the reliability and reproducibility of the procedure. Application of the proposed technique to two bituminous coals (a Polish and a South African coal) has been directed to underline how coals of similar rank may differ as regards the fate of ash. In particular, it is shown that a significant fraction of ash remaining after Polish coal burn-out has size comparable to, or slightly smaller than, the parent fuel particle size. On the contrary, the South African coal used in this study yields mostly fine ash particles whose size is comparable with typical cyclone cut-off (3).

EXPERIMENTAL APPARATUS AND MATERIALS

Figure 1 reports the sketches of the experimental apparatus previously used by Chirone et al. (1) (fig.1A), and that used in the framework of the present study (fig.1B). Both are 41mm ID stainless steel fluidized bed combustors equipped with a gas pre-heater (600 mm height) and a gas distributor made of a stainless steel nets plate. The reactor height is 1m for combustor A and 0.4m for combustor B. Fly ashes are collected by means of sintered brass filters (average porosity larger than 40µm) in (A) and by means of a purposely designed device consisting of a glass fiber filter in (B). The collecting efficiency of this device was tested comparing results obtained using an Andersen probe under the same experimental conditions. The Andersen probe included a first stage for coarse (>20-15 µm) particle separation, followed by a set of ten glass fiber filters. The new collecting device adopts the same first separation stage, followed by a two-stage glass fiber filter. The size distribution of the fine solids settled on the filter has been characterized by means of a laser particle size analyzer. A data acquisition unit is used to process signals from pressure transducers and on line gas analyzers (O₂, CO, CO₂, SO₂, NO_x e CH₄). Electrical heaters keep the reactor at a temperature of 850°C. The bed was made of 180g of quartz in the size range 500–600µm kept at the minimum fluidization at the bed temperature. Table 1 reports the main characteristics of the fuels.

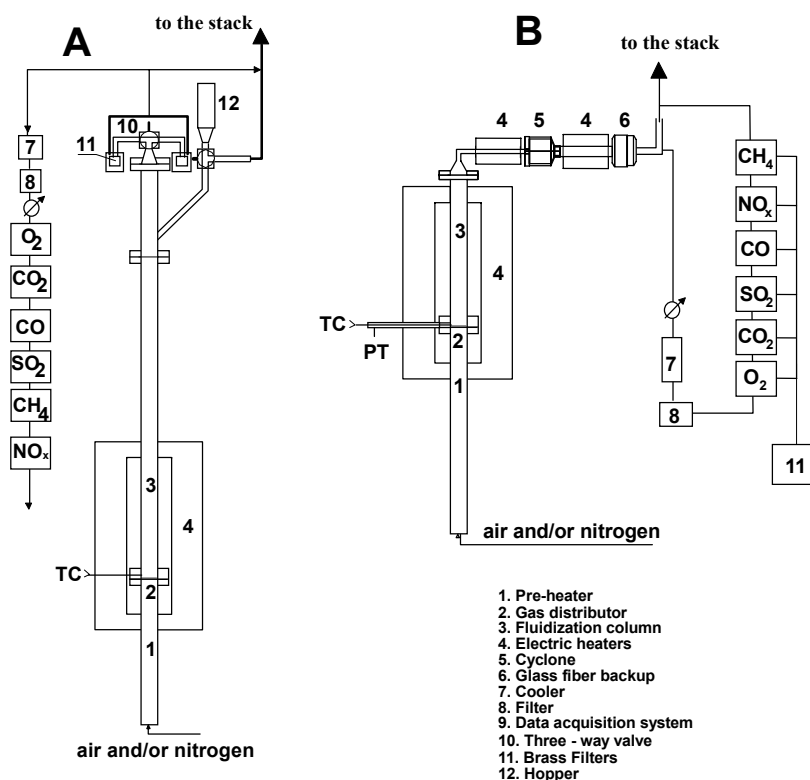


Figure 1 Experimental apparatus

Fuel	Polish	South African
Proximate analysis, % (as received)		
Moisture	2.9	7.4
Ash	5.9	13.9
Volatile Matter	29.0	22.8
Fixed Carbon	62.2	55.9
Ultimate analysis, % (dry basis)		
Carbon	75.4	66.5
Hydrogen	5.4	4.4
Nitrogen	1.3	1.2
Sulfur	0.4	0.6
Chlorine	0.2	0.1
Oxygen	11.4	13.3
Ash	5.9	13.9
Low calorific value (MJ/kg)	31.94	27.45

Table I Characteristics of the coals used.

Procedure

The procedure consists of the following sequence of steps:

1. Devolatilization (in nitrogen) followed by combustion (in air) of about 10-20g of fuel, corresponding to about 80-160 coal particles respectively, in the size range 4760-6350 μ m, until complete burnout. Gas superficial velocity is kept at the value U_1 (0.15m/s) slightly larger than the incipient fluidization velocity of the bed. Combustion is carried out at 850°C. Collection of fly ashes at the exhaust is performed in this stage.
2. Elutriation of ashes from the bed at gas superficial velocity U_2 , 2-3 times larger than U_1

but far smaller than the terminal velocity of bed inert material ($U_t = 2\text{m/s}$). Elutriated material is collected also during this stage.

3. Retrieval of coarse ash by discharge the bed material (quartz + ash). Separation of ash material from the inert material of the bed by sieving and its further characterization is performed after this stage.

The operating procedure has been optimized considering the following requirements:

- a) surface wear must not be exceedingly large to give rise to extensive secondary attrition of ash particles;
- b) combustion time must be small in order to minimize the occurrence of secondary attrition of ash particles during burn off;
- c) the coal/char particle temperature must not be high to the point of giving rise to ash sintering.

During Step 1 finer carbon and ash particles, generated during the combustion stage, are collected in the probe. During Step 2 the combustor acts like an elutriator, with the aim of collecting at the exhaust ash particles (not elutriated during Step 1) whose sizes are smaller than the bed inert material.

Constraints b) (which would call for severely oxidizing conditions) and c) (that would rather call for mild oxidation) have been reconciled by operating in air at 850°C under conditions that apparently did not bring about ash sintering. This was confirmed by the steadiness of fluidization parameters and by the particle analysis of the ashes collected in the first stage of the Andersen probe and those discharged from the bed.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 shows the fractional ash reporting to bottom and fly ash, as obtained in experiments with the two experimental configurations A and B. Whatever the experimental configuration used, the amount of bottom ashes ($d_p > 150\ \mu\text{m}$) obtained for each coal is nearly the same: 36% vs. 47% and 62% vs. 70% for South African and Polish coal respectively. On the contrary the amount of fly ashes is significantly different: 6% vs. 52% and 2% vs. 27% for South African and Polish coal respectively. These findings highlight that a large fraction of fine particles are not captured when burn-out is carried out in combustor A. This may be related to: i) possible adhesion of fly ash onto the relatively cold wall of the reactor; ii) inadequacy of the fine collection system to capture particles finer than $50\ \mu\text{m}$. On the contrary, the ash balance (in versus out) is extremely good (maximum error $\pm 2\%$) when using

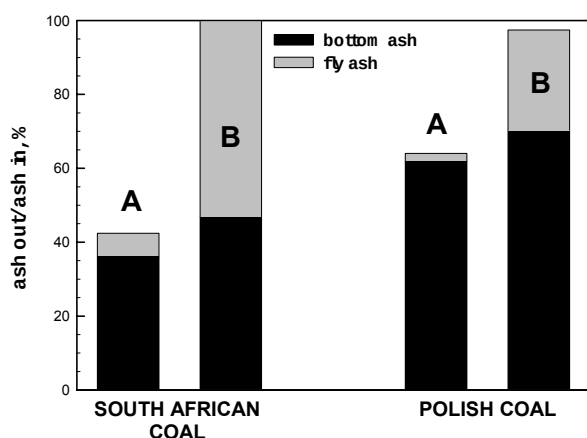


Figure 2 Ashes balance of the coals tested.

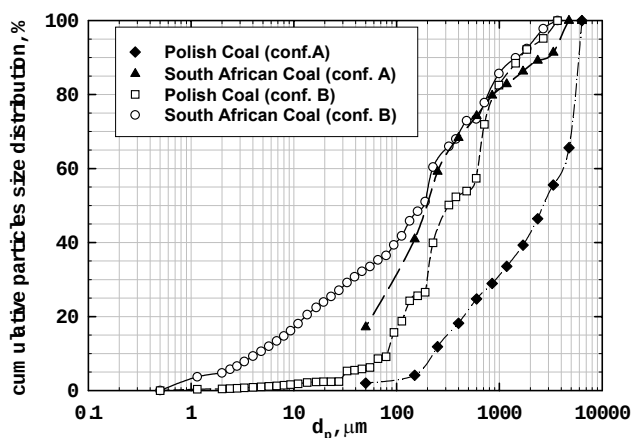


Figure 3 Comparison of PAPSD of the coals tested.

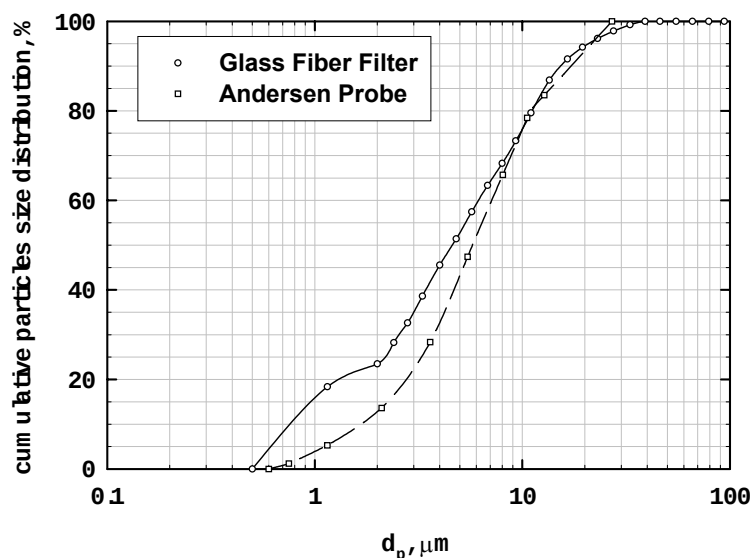


Figure 4 Fine particle collected by means of glass fiber filter and Andersen probe.

Figure 4 compares the cumulative size distributions of fine particles obtained by using either the Andersen probe (dotted line) or the glass fiber filter collection device (solid line). It can be observed that the two curves lie close to each other. Fine particle characterization based on the use of the glass fiber filter, followed by laser-diffraction granulometry, enabled more thorough characterization of the particle population finer than about $5\mu\text{m}$, due to the better ability of the laser diffractometer to resolve particle sizes compared with the Andersen probe. Moreover, the glass fiber filter collection device is much handier and more reliable than the Andersen probe.

CONCLUSIONS

- i) An upgrade of the procedure for the characterization of the extent and particle size distribution of ash generated upon solid fuel burn-off in fluidized beds has been presented.
- ii) The procedure, based on the operation of a 40mm ID bench scale fluidized bed combustor with careful design of fine particle collection at the exhaust, enables the characterization of elutriated material down to $0.5\mu\text{m}$ particle size.
- iii) An alternative device to the Andersen probe for collection of elutriated fine particles has been tested. The device is easier to use and is characterized by better sensitivity to the smaller particle sizes.

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combustor B, which is characterized by a shorter freeboard, a higher freeboard temperature and a more efficient fines collection system.

Figure 3 reports the comparison between particle sizes distribution of primary ash (PAPSD) obtained with the two experimental configurations. Analysis of cumulative distributions highlights that the contribution of fine particles is significant: particles whose size is less than $50\mu\text{m}$ account for about 30% and 10% of the whole ash for South African and Polish coals respectively.

Transversal Segregation of Gaseous Species During FB Combustion of a Biomass Fuel

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INTRODUCTION

Poor axial uniformity is experienced during FB combustion of fuels having a large content of volatiles (biomass, plastics, wastes). In fact, the fuel particles tend to segregate at the bed surface during the devolatilization stage, as a consequence of the generation of endogenous bubbles around the particles and the lifting action up to the bed surface [1]. Therefore, a significant amount of volatile matter effectively bypasses the bed and is released and burns directly in the freeboard, resulting in a considerable temperature increase in this region.

In addition, radial segregation of volatile matter is usually associated to a single point fuel feeding in FB combustors. It leads to poor transversal mixing between fuel and air, which in turn favors the establishment of radial profiles of concentration and delays fuel conversion. Both the location of the fuel entry port as well as the bed fluid-dynamics influence the extent of the transversal segregation. Although studies on segregation phenomena associated to volatile matter release in fluidized beds are already available in literature for fossil and biomass fuels [1-3], a lack of information still persists concerning the distribution of chemical species along the cross section, both inside the bed and in the splashing region, when changing the operating conditions. The aim of the present work is to provide some insight on this issue.

An experimental study has been carried out in a pilot scale fluidized bed facility fed with a biomass fuel. Results of transversal gas concentration together with a theoretical assessments on the role played by dispersion mechanisms are presented and discussed in the paper.

EXPERIMENTAL

A bubbling fluidized bed combustor with a 370 mm ID fluidization column has been used to carry out steady state combustion tests under atmospheric conditions. The 200 kW facility is sketched in Figure 1. The distributor sustains bed materials allocated in the intermediate section, which is equipped with several access ports. The heat exchange is accomplished thanks to an array of horizontal bayonet-type pipes whose adjustable penetration into the bed controls the heat removal rate. The higher section of the fluidization column (freeboard) is fitted with several ports for temperature, pressure and gas concentration probes. Two cyclones are used for flue gas de-dusting. The entire vessel is thermally insulated by means of ceramic wool. A propane burner is used for start-up by directly heating fluidized bed materials. The fuel is dosed by means of a screw type metering device and passed to a feeding line

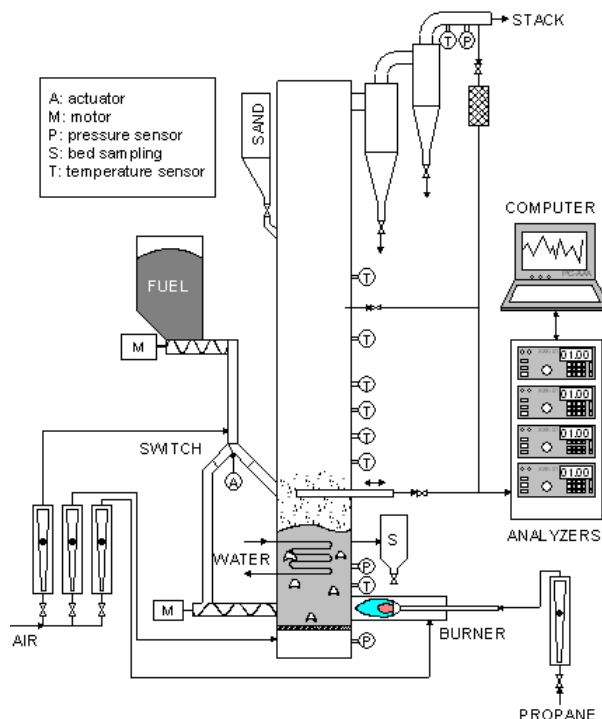


Fig. 1: Scheme of the fluidized bed combustor

Table 1: Properties of pine-seed shells

Particle size, mm	10÷30	Ash analysis (dry basis)	ppm
Density, kg m ⁻³	1200	Ca	5700
LHV (dry basis), kJ kg ⁻¹	15200	K	1500
Proximate analysis	%	Mg	350
Volatiles, %	59.6	Na	230
Fixed carbon, %	26.6	Fe	160
Ash, %	0.8	Al	80
Moisture, %	13.0	Cu	15
Ultimate analysis (dry basis)	%	Ni	10
Carbon, %	48.5	Zn	7
Hydrogen, %	6.1	Mn	6
Nitrogen, %	0.2	V	3
Sulfur, %	< 0.1	Pb	3
Oxygen, %	44.3	Co	<1
Ash, %	0.9	Ba	<1

size) has been used as inert material during combustion tests of a biomass fuel (pine-seeds shells). Physical properties and chemical analysis of the fuel are reported in Table 1.

EXPERIMENTAL RESULTS

Figure 2 reports the concentration profiles of CO₂ (Fig 2-A) and CO (Fig 2-B) obtained with the horizontally movable probe during two steady state tests carried out at same operating conditions but with different feeding options (U-bed/O-bed). It must be remarked that the abscissa zero corresponds to the fuel entry side of the bed for both feeding options. The CO₂ curve for U-bed option has a pronounced decreasing trend and the measured value changes from 13.4% to 11.6% at the opposite sides along the diameter. In contrast, the CO₂ measurements for over-bed feeding are restricted in a small band with an absolute oscillation of about 0.5%. As far as carbon monoxide is concerned, similar average values were measured (around 1.0%) for both feeding options, indicating that a fraction of the combustion is further demanded to the freeboard. Again, the U-bed curve exhibits a more pronounced decrease.

Figure 3 shows concentration profiles of CO₂ and CO for submerged feeding for different fluidization velocities. CO₂ profiles still decrease along the diameter, even if a non-monotone dependence in the relative position of the curves is noted passing from the lowest to the highest value of U. Since U has a combined effect on the expanded bed height, residence time and the internal mixing in the bed, the observed non trivial change of the measured properties could be partially explained. It is worth noting that at the highest fluidization velocity the expanded bed height exceeds 1 m, so the gas probe might be immersed in the fluidized bed. Carbon monoxide concentration is progressively increased passing from an average value of 1% to 2%, at fluidization velocity of 0.97 and 1.37 m/s, respectively. The profile declines along the diameter with almost equal slope in all three cases.

Figure 4 shows the effect of the global excess air on the concentration profiles of both chemical species. Results are fully congruent with the change of the oxygen partial pressure. At $\epsilon=1.15$, the decrease of CO₂ is paralleled by the increase of CO (around 0.6%) along the entire column diameter. Again, declining curves for both CO₂ and CO are shown in Fig 4.

On the whole, the analysis of experimental results here presented demonstrates that gas concentrations are not uniform along the combustion diameter as a consequence of the single-point fuel feeding. The switch from O-bed to U-bed feeding as well as the decrease of the ex-

that switches the particle flow to an O-bed port or, alternatively, to an U-bed conveyer, located respectively at 950 mm and 125 mm above the distributor.

A horizontal cooled probe is installed at an elevation of 1024 mm above the distributor and allows gas suction for analysis at different penetrations along the diameter of the fluidization column. The probe is equipped with a stainless steel sintered tip to prevent capture of fine particulate. At steady state, radial profiles of gaseous species (O₂, CO₂, CO, N₂O and NO) are on-line taken and recorded.

Silica sand (725 μ m nominal

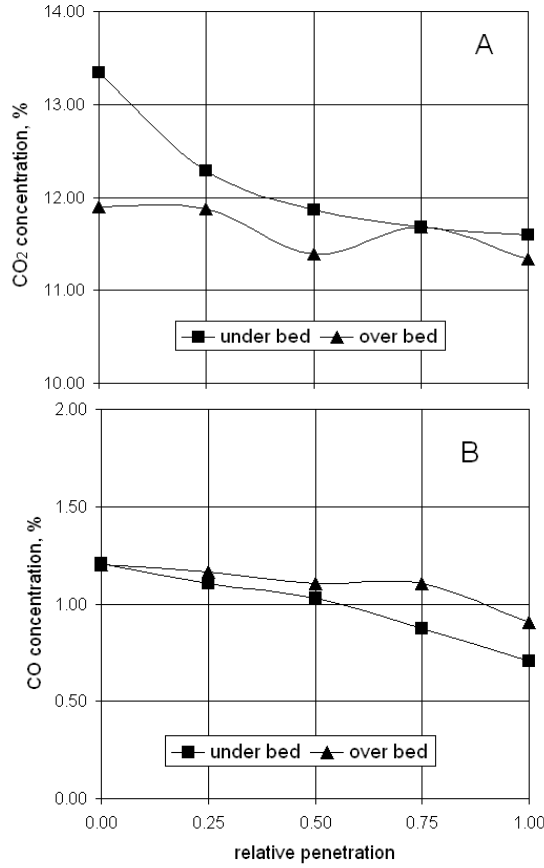


Fig. 2: concentration profiles of CO_2 (A) and CO (B) for U-bed and O-bed feeding $T=850^\circ\text{C}$, $U=0.97$ m/s, $e=1.25$

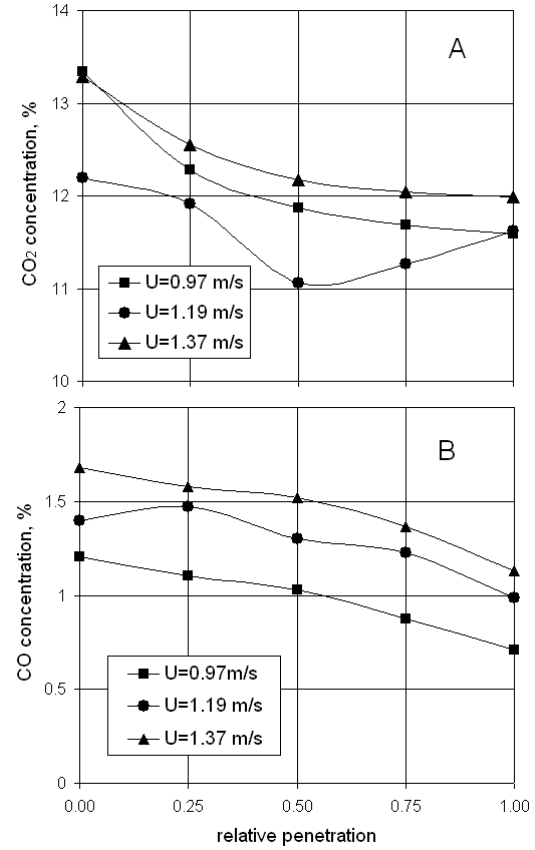


Fig. 3: concentration profiles of CO_2 (A) and CO (B) for different fluidization velocities U-bed, $T=850^\circ\text{C}$, $e=1.25$

cess air ratio seem to emphasize the loss of uniformity. Also, the augmentation of fluidization velocity, which has multiple effects on bed fluid-dynamics, appears to be ineffective in order to reduce transversal non-uniformity.

THEORETICAL ASSESSMENT

Analysis of the radial segregation results can be carried out in the light of the following three characteristic times: i) particle (or volatile bubble) rise time from the fuel feeding point to the bed surface; ii) particle (or volatiles) radial dispersion time along the bed radius; iii) particle devolatilization time.

The particle rise time to the bed surface depends on the segregation pattern of the fuel, as observed by Fiorentino et al. [1]. Hydrodynamic interactions between the devolatilizing fuel particle and the surrounding fluidized suspension induce segregation mechanisms different from those typical of mixtures of inert particles. In fact, the released volatiles form endogenous bubbles around the particles, lifting the fuel particles to the bed surface. For the biomass at hand the devolatilizing particle can be assumed to rise with the volatile bubble at an approximately constant velocity given by [4]:

$$v_r = v_r^\infty + (U - U_{mf}) \quad (1)$$

where v_r^∞ is the particle rise velocity under incipient fluidization conditions, experimentally determined to be about 0.3 m/s. The characteristic particle rise time to the bed surface is:

$$\tau_r = \frac{h_{bed}}{v_r} \quad (2)$$

where h_{bed} is the bed height above the fuel injection port. On the other hand, the radial dispersion velocity of the fuel particles is estimated to be:

$$v_d = \frac{D_r}{d_{bed}} \quad (3)$$

where D_r is the radial dispersion coefficient and d_{bed} the bed inner diameter. The characteristic particle radial dispersion time is:

$$\tau_d = \frac{d_{bed}}{v_d} \quad (4)$$

Finally, the characteristic particle devolatilization time (τ_v) of the pine seed shells has been determined experimentally at $T=850^\circ\text{C}$ [5].

Table 2 reports the calculated characteristic times at the three different fluidization velocities investigated. Values for the volatiles radial dispersion coefficient have been estimated extrapolating data reported by Stubington and Clough [6]. It is interesting to note that fuel particles rise at the bed surface in a very short time (around 1 s). During this time only few of the volatiles have been released from the particle, most of them being released directly in the splashing region. Characteristic radial dispersion times are more than one order of magnitude larger than typical rise times, indicating that inside the bed volatiles distribution is far from being well mixed in the radial direction. Further, estimated radial dispersion times are of the same order of magnitude, but slightly larger than the particle devolatilization time. On the whole, the following picture emerges: once injected in the bed the fuel particles rapidly rise with the emitted volatiles to the bed surface with only limited radial penetration. Once on the bed surface most of the volatiles are emitted while the particles move laterally. Radial dispersion is, however, sufficiently slow to give rise to significant gas concentration gradients along the bed diameter. As regards over-bed fuel feeding, even if a larger radial penetration might be expected during the particles falling from the fuel port, the same reasoning applies, indicating that significant gas concentration gradients along the bed diameter should be expected also in this case. Experimental data shown in Figs. 2-4 seem to well fit to the above picture from a qualitative point of view.

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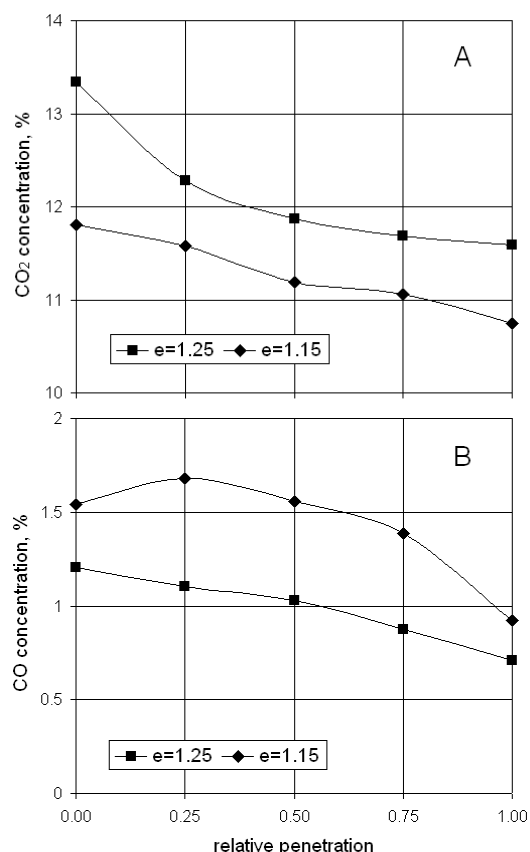


Fig. 4: concentration profiles of CO_2 (A) and CO (B) for different excess air factor U -bed, $T=850^\circ\text{C}$, $U=0.97 \text{ m/s}$

Table 2: Characteristic times.

U	0.97 m/s	1.19 m/s	1.37 m/s
t_r	0.9 s	0.8 s	1.0 s
t_d	27 s	20 s	14 s
t_v	10 s	10 s	10 s

Velocity measurements and sampling inside a wood open fire-place to optimize the combustion performances

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INTRODUCTION

Wood combustion is one of the main objectives in burning renewable sources [1]. The interest in expanding this market, while reducing the environmental impact lead the manufacturers of different wood stoves to optimize the combustion chamber reducing pollutant emission and increasing global efficiency.

The design of these stoves is still empirical and it is based on the know-how of the industrial partners. The aim of this paper is to present how it was possible to optimize the heat exchange inside a wood open fire place using recent Laser Doppler Anemometry equipment. Moreover, samplings of the flue gas were performed in different operation condition and at different delay from the wood charge in order to measure the particulate emission.

EXPERIMENTAL SET-UP

The product presents itself as a classical wood stove, whose wall are used as heat exchanger for the heating water circuit. Those stoves are divided in two parts: the combustion chamber, where wood is inserted, and on the top of the stove is inserted the water/exhaust gas exchanger also for heating. Moreover, there are two independent water circuits for heating and sanitary water. The figure 1 represents a typical wood open fire place.



Fig. 1 View of classical wood open fire place.

Two different prototypes were designed and equipped with optical accesses. The combustion chamber geometry is the same for both the stoves while the water/exhaust gas exchanger geometry was modified. The figure 2 presents the two configurations of the exchanger.

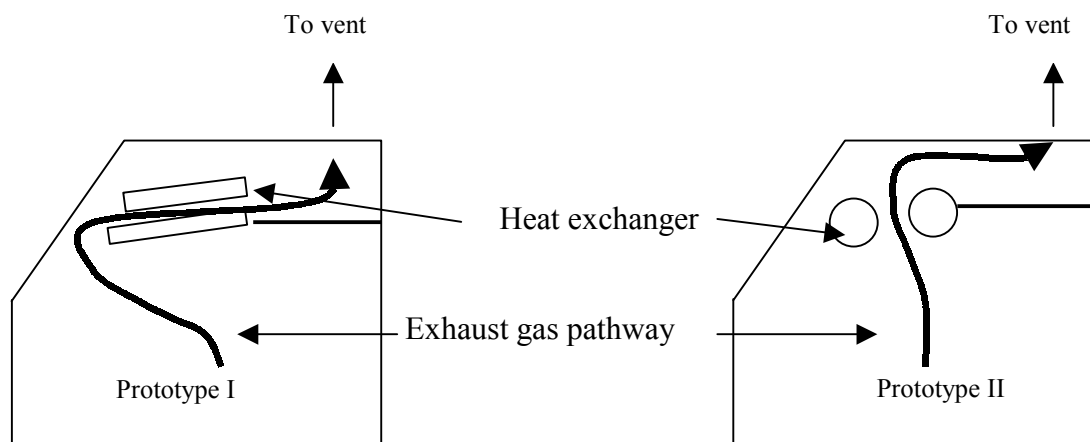


Fig. 2 Partial cross-section of the wood stoves with the heat exchanger.

The two stoves were prepared according to the UNI norm [2] in order to calculate the global efficiency. Moreover, following the norms, it was possible to compare the performances of the stoves keeping constant the combustion parameters and the operative conditions. Continuous temperature measurements of the water circuit and at the exhaust were performed. Stable gases (CO , CO_2 , NO_x , HC , O_2) were measured every five minutes. 2 D velocity profiles were obtained using a DANTEC BSA Phase Doppler Particle Analyzer configured for back scattering measurements. Measurements were performed along a wood charge of 10 kg. The duration of a wood combustion charge was about 50 minutes. Wood had relative moisture of 30% and a net heating value of 2800 kcal/kg.

RESULTS AND DISCUSSIONS

The figure 3 represents a typical differential temperature ($T_{\text{out}} - T_{\text{in}}$) profile during a combustion charge. The dot lines represent the range of acceptable value for efficiency calculation.

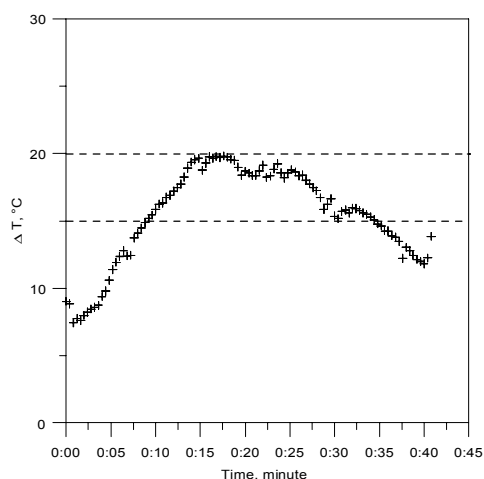


Fig. 3 Typical differential temperature profile.

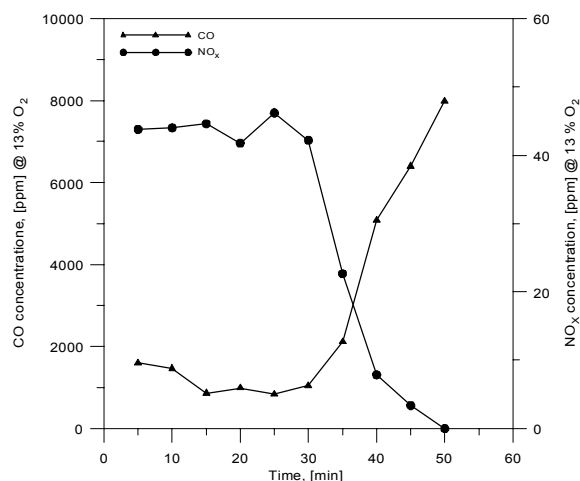


Fig. 4 Typical gas profiles.

Figures 3 and 4 are representative of both prototypes since there were no significant profile differences between the two prototypes. In fact, the global efficiency of prototype I is 74.4% while for the second one it is about 74.8%. For both the stoves there is a sharp increase of the CO emission after about 30 min from the wood charge, while NO_x concentration at the stack is about 40 ppm for the first 30 min. NO_x emissions are mainly due to nitrogen present in the wood. The total soot emissions of both prototypes have similar value of 60 mg/Nm^3 . The average exhaust gas temperature was about 250°C .

An interesting result concerns the heating rise time of the water. In fact, the starting conditions are important for such products. We measured the time elapsed for the water to pass from 15°C to 60°C . For the first prototype this time is about 1 hr, while for the second prototype (with cylindrical exchanger) this time is about 25 min. This phenomenon can be explained by the different geometry of the water/gas exchanger and their position respect to the combustion place.

A complementary explanation could be given by the velocity study. Indeed, the study concerned the measurement of the velocity flow fields in the front panel, the rear panel and lateral panel of the prototypes (fig. 5) in order to get information about the heat exchange between exhaust gases and the water exchanger.

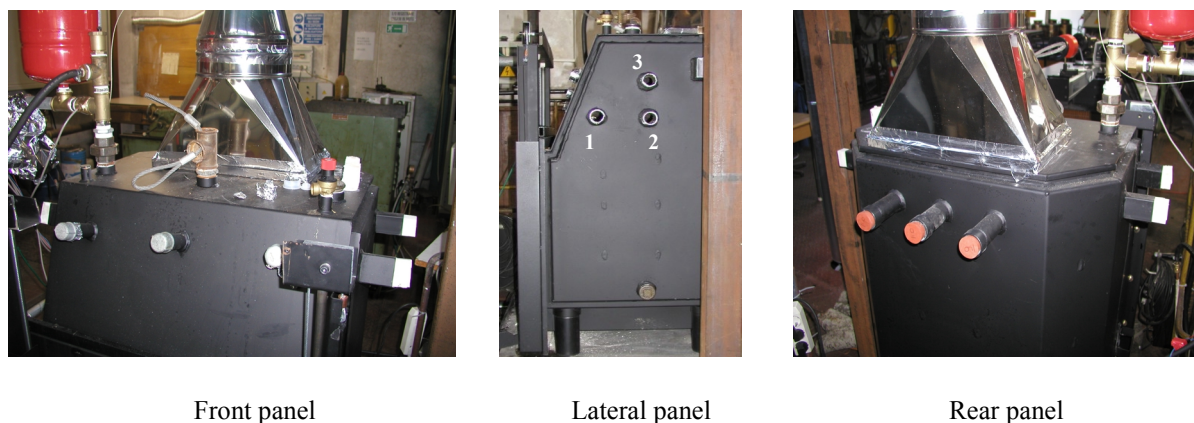


Fig. 5 View of the optical accesses of the prototypes.

The 2D velocity profiles were measured in back scattering at different depths inside the stove. The measurements obtained viewing from the rear panel are not presented here since they are similar for both prototypes and are not relevant. The analysis of the front panel measurements indicates that the gases pathways are different for the two prototypes. In fact, for the first prototype, an important part of the flue gas passes between the exchanger and the external wall as presented in figure 6, while for the second prototype most part of the gases passes between the two cylinders.

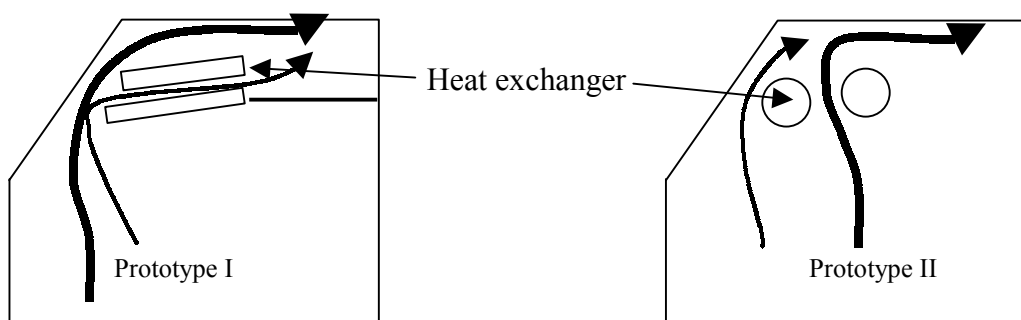


Fig. 6 Scheme of the combustion gases pathway.

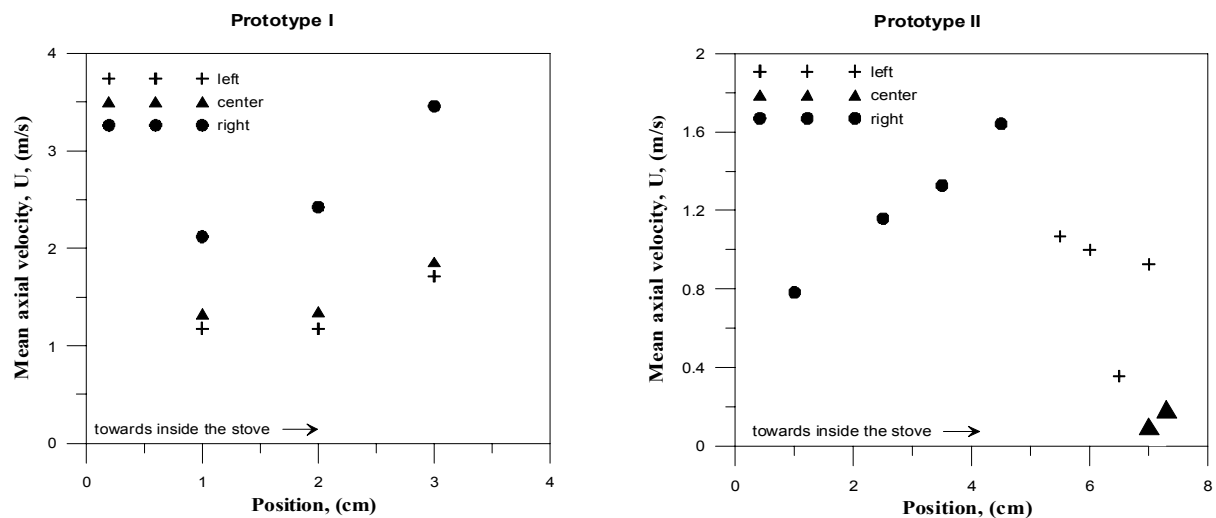


Fig. 7 Mean axial velocity profiles obtained on the front panel.

Figure 7 evidences that, for the prototype I, gases pass regularly between the external wall of the stove, while for the second prototype gases are detected only on the right part and partially on the left part of the stove. The results obtained on the lateral panel presented in figure 8 confirm the gases pathway hypothesis for prototype II. No results are available for the prototype I due to the impossibility to insert optical accesses.

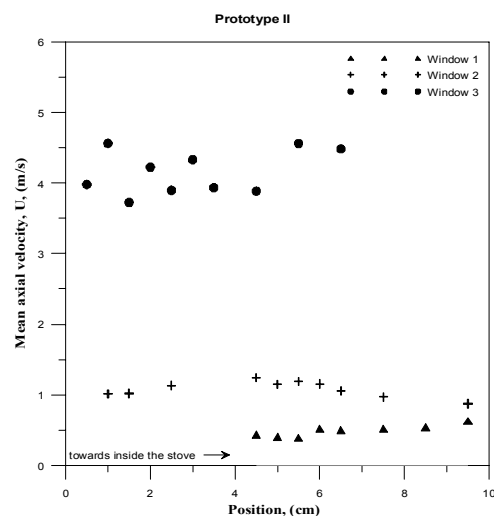


Fig.8 Mean axial velocity profiles obtained on the lateral panel.

CONCLUSIVE REMARKS

The optimization of the geometry and heat exchanger of a wood open fire-place was performed using Phase Doppler Anemometry. Gas sampling analysis evidenced that the global efficiency depends only on combustion chamber and not on heat exchanger. The global efficiency of such product is about 75 %. This work also evidenced that position of the exchanger respect to the flame is important for heat exchange.

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REACTION PATHWAYS AND KINETICS OF COAL COMBUSTION

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Analysis of coal combustion is most commonly carried out under the assumption that coal pyrolysis and char burn-out are strictly sequential steps. However more complex mechanistic frameworks might be required, embodying one or more of the following features:

- a) combustion of the raw coal can - under some circumstances - occur prior to pyrolysis;
- b) the pyrolytic processes can be themselves enhanced by heterogeneous oxidation (oxidative pyrolysis);
- c) transient build-up of carbon oxides on the surface of coal (oxygen chemisorption) is a key step in carbon combustion;
- d) heat treatment reduces the char reactivity (thermal annealing) and its propensity to chemisorb oxygen.

The present paper aims at the assessment of the relevance of these processes across the temperature ranges of practical interest. The order of magnitude of their kinetics has been evaluated with reference to a South African bituminous coal. A novel procedure based on thermogravimetric analysis has been designed and used for the purpose.

Topical area: combustion of solid fuels

Key-words: coal, combustion, kinetics

INTRODUCTION

As a coal particle is exposed to a combustion environment, either of two cases may apply:

- oxygen is unable to reach the coal surface during the heat-up/devolatilization stage, due to ablative effects. In this case coal pyrolysis and char combustion can be considered as strictly serial processes.
- oxygen is able to reach the coal particle surface during the early particle heat-up period. In this case additional reactive processes may onset and compete with pyrolysis and char combustion. Such processes include: 1.abstraction of volatile matter via oxygen promoted bond cleavage (oxidative pyrolysis)[1,2], 2. heterogeneous oxidation of coal, 3.transient build up of carbon oxides (oxygen chemisorption)[3-4].

In the late char burn off, the residual char combustion competes instead with thermally induced solid state reactions, responsible of char microstructure modifications which result into char deactivation (thermal annealing) [5-7].

The emerging picture is that, depending on process parameters and coal properties, combustion of coal proceeds from its beginning to its very end through a network of series-parallel reactions, in which heterogeneous oxidation and purely thermally activated processes compete with one another. The scope of the present paper is to perform an order of magnitude comparison of the rate of each of the above mentioned processes. This goal will be pursued with reference to a medium rank, high inertinite South African bituminous coal. The kinetics of pyrolysis, oxidative pyrolysis, char combustion and thermal annealing of South African coal were obtained in previous works [2,5-6]. A new set of thermogravimetric experiments was directed to assess the rate of chemisorption of oxygen on coal and char.

EXPERIMENTAL

The coal was ground and sieved to 100-150 μ m, degassed in a vacuum chamber and kept under vacuum prior to any analysis. Char samples were prepared in nitrogen under different heat treatment conditions and then degassed at 850°C for 2-3 min prior to any analysis.

Thermogravimetric experiments, degassing of chars and preparation of chars at temperatures up to 1400°C were carried out in a PL1000M1500 thermogravimetric analyzer. The residence time of gases in the hot zone of the furnace was of less than 1s. The preparation of char samples at 1600°C and 2000°C was carried out in a heated-strip reactor [5] with heating rate of 10⁶°C/min

Approximately 2mg of coal or heat treated char were heated in nitrogen to the desired combustion test in less than 30s. The gas flow was then switched from nitrogen to air. Isothermal combustion temperature was set to values in the range 240-360°C in coal combustion experiments, it was set to 450°C in char combustion experiments. The flue gas was analysed for its CO and CO₂ content by an on-line NDIR analyser.

The results of the gas analysis (GA) have been worked out in order to calculate the rate of change of carbon conversion degree $(df/dt)_{GA}$ according to the expression:

$$\left. \frac{df}{dt} \right|_{GA} = \frac{\dot{n}_{CO} + \dot{n}_{CO_2}}{w_o - w_{ash}} \cdot 12 \quad (1)$$

where $\dot{n}_{CO}$ and $\dot{n}_{CO_2}$ are the moles of CO and CO₂ released as combustion products in the unit time, 12 is the molecular weight of carbon expressed in g/mol, w_o is the mass of the coal or char at the beginning of the experiment and w_{ash} is the ash mass, measured at the end of the combustion experiment.

The carbon conversion degree f_{GA} has been obtained from the results of gas analysis by integrating equation (3):

$$f_{GA}(t) = \int_0^t \frac{\dot{n}_{CO} + \dot{n}_{CO_2}}{w_o - w_{ash}} \cdot 12 \cdot dt \quad (2)$$

The results of the isothermal thermogravimetrics experiments (TG) have also been worked out to evaluate the carbon conversion degree f_{TG} and the instantaneous reactivity $(df/dt)_{TG}$ as a function of time. It has been assumed that at a given time t , the weight measured by the thermogravimetric apparatus is the sum of the actual mass of carbon ($w_c(t)$) and of the mass of oxygen chemisorbed on the carbon surface:

$$w(t) = w_c(t) + 32 \cdot n_{O_2}(t) \quad (3)$$

where $n_{O_2}(t)$ are the moles of oxygen chemisorbed on the carbon surface at a given time and 32 is the molecular weight of oxygen in g/mol. As a consequence the carbon conversion degree measured and the reaction rate measured by thermobalance have been calculated by the following expressions:

$$f_{TG}(t) = \frac{w_o - w(t)}{w_o - w_{ash}} = \frac{w_o - w_c(t) - 32 \cdot n_{O_2}(t)}{w_o - w_{ash}} \quad (4)$$

$$\left(\frac{df}{dt} \right)_{TG} = - \frac{d \left(\frac{w_o - w_c}{w_o - w_{ash}} \right)}{dt} = - \frac{32}{w_o - w_{ash}} \cdot \frac{dn_{O_2}}{dt} \quad (5)$$

where $\frac{dn_{O_2}}{dt}$ is the net rate of oxygen chemisorption on the carbon surface.

It can be observed that the rate of release of combustion products must equal the rate of carbon consumption, therefore:

$$\frac{d \left(\frac{w_o - w_c}{w_o - w_{ash}} \right)}{dt} = \left(\frac{df}{dt} \right)_{GA} \quad (6)$$

Substitution of eq. (6) in eq. (5) leads to the following relations:

$$\left(\frac{df}{dt}\right)_{GA} - \left(\frac{df}{dt}\right)_{TG} = \frac{32}{w_o - w_\infty} \cdot \frac{dn_{O_2}}{dt} \quad (7)$$

$$\Delta f = f_{GA}(t) - f_{TG}(t) = \frac{32n_{O_2}(t)}{w_o - w_\infty} \quad (8)$$

The difference between the rate of carbon conversion measured by GA and TG vanishes at a time t^* when the net rate of oxygen chemisorption becomes null. The difference between the carbon conversion degree measured by GA and TG increases up to time t^* , when it reaches the value of Δf^* . The ratio of $\Delta f^*/t^*$ has been assumed as an indication of the average rate of oxygen chemisorption in the time interval $0-t^*$

RESULTS

Figure 1 shows a typical curve of instantaneous reactivity versus time obtained from coal combustion experiments. The figure refers in particular to the reaction temperature of 300°C. It can be observed that the reactivity obtained on the basis of the analysis of CO and CO₂ in the product gas ($(df/dt)_{GA}$) is initially very high and decreases monotonically. Differently, the reactivity obtained on the basis of the thermogravimetric analysis ($(df/dt)_{TG}$) passes through a maximum. The two reactivity curves merge after a time of reaction $t^* \cong 40$ min. This behaviour suggests that transient build up of oxygen is active in the first stages of reaction. After the time t^* a steady value of oxygen is reached on the carbon surface.

Regression analysis over data points of the rate of oxygen chemisorption averaged over time t^* (i.e. $\frac{\Delta f^*}{t^*} \frac{1}{1-f^*}$) yields a value of activation energy of 67 kJ/mol and of the pre-exponential factor of $1.2 \cdot 10^3 \text{ min}^{-1}$. The activation energy for coal combustion obtained from gas analysis and from the weight loss are respectively 96 kJ/mol and 84 kJ/mol, the preexponential factor is $5 \cdot 10^6 \text{ min}^{-1}$ for both.

The same technique has been applied to chars prepared under different heat treatment conditions. Results of Δf^* and t^* obtained for these chars are reported in table 1. Notably, the Δf^* values, indicative of oxygen build up in the early stages of combustion, range between 0-9%, while the equilibration time t^* is in the range 11- 115 min. The char sample with the highest propensity to chemisorb oxygen is the char prepared at 900°C for 1 min. This propensity decreases for more severe heat treatments and is negligible for chars heat treated above 1200°C for a prolonged time of 30 min. Altogether results show that transient build up of oxygen takes place in the early stages of combustion only for chars heat treated under relatively mild conditions, while chars heat treated above 1200°C for a prolonged time experience no oxygen build up at all.

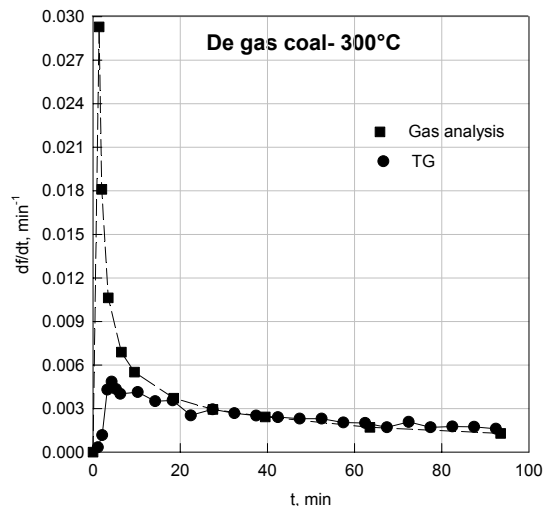


Figure 1 Isothermal coal combustion at 300°C

Table 1. Rate of oxygen chemisorption at 450°C on heat treated char

	t^*, min	Δf^*	$\Delta f^*/t^* \text{ min}^{-1}$
FB-char	30	2.45	0.082
900 1min	11	8.5	0.77
1600 1s	12	4	0.33
2000 0.35s	114	6.8	0.06
2000 2s	115	1.46	0.013
1200 30min	0	0	0
1400 30min	0	0	0

FB char: produced in FB reactor at 850°C

COMPARISON OF THE RATE OF DIFFERENT REACTIVE PROCESSES

Figure 2 reports, as Arrhenius plots, the rates of the different reactive processes that might be relevant to coal combustion. At temperatures below 400°C the fastest processes are oxygen chemisorption and coal combustion. At about 400°C pyrolysis becomes the dominant process. The rate of oxidative pyrolysis is intermediate between that of oxygen chemisorption/coal combustion and inert pyrolysis. The rate of oxygen chemisorption at 450°C on char can be faster or slower than the other processes depending on the severity of heat treatment conditions of the char. Thermal annealing is slower than all the other processes at low and medium temperature. In the absence of diffusional limitations thermal annealing becomes faster than char combustion above 1700°C, however, when combustion takes place under diffusion limited regime, the rate of thermal annealing and that of char combustion become comparable at lower temperatures (around 1400°C for particles of 10mm). The relevance of heterogeneous oxidative processes versus purely thermally activated processes is obviously further affected by the accessibility of carbon particles to oxygen, depending on a combination of ablative/diffusive/convective processes around the particles. These processes are critically dependent on particle size and on the combustion environment.

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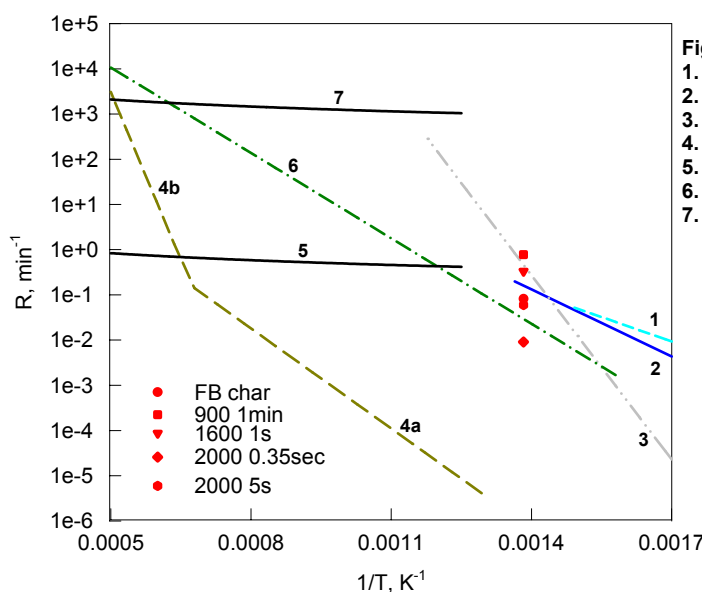


Figure 2. Rates of :
1. Oxygen chemisorption on coal
2. Coal combustion
3. Inert pyrolysis
4. (a+b) Thermal annealing
5. Char combustion under diffusion regime, d=10mm
6. Char combustion under kinetic control
7. Char combustion under diffusion regime, d=500micron

Figure 2. Comparison of reaction rates

TG-FTIR analysis of biomass and biomass components during devolatilisation

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INTRODUCTION

The behaviour of biomass materials during devolatilisation has been often referred to the behaviour of chemical components, namely, cellulose, hemicellulose and lignin, and this was validated with thermogravimetric analysis [1,2]. Generally, experimental investigations revealed no interaction among components in biomass materials, as well as in composite materials or blends [3,4]. TG-FTIR analysis applied to the evolution of compounds from the pyrolysis of biomasses is relatively recent [5,6]. This provides important information on the devolatilisation of fuels, that is the identification of major volatile species during the devolatilisation. The knowledge of the species released is fundamental to establish the quality of the gas in energetic terms, in the gasification process. The individuation of the optimal range of temperature for the release of a specific volatile compound allows for the assessment of the applicability of a pyrolysis process with the aim of chemical recovery. Also, kinetics for each volatile species can be obtained and these are basic parameters for design and modelling purposes (combustion and gasification processes).

In this work, the results of TG-FTIR analysis of different biomass materials are compared with the results obtained for the chemical components. Light gases are easily detected and a quantitative balance can be drawn considering the devolatilisation of the biomass as the sum of the contributions of all components which are supposed to devolatilise independently from each other. As a matter of fact, more complex organic compounds are hardly distinguished but can be grouped in several classes of organic species. In these cases, different compounds can be ascribed to the devolatilisation of components in different temperature ranges from a qualitative point of view.

EXPERIMENTAL

Analyses of materials used in this work (namely, wood pellets, hazelnut shells, olive and cacao residues) can be found elsewhere [7]. Furthermore, commercial components are used: cellulose Avicel, lignin from olive residue and xylan from birchwood, representative of hemicellulose component.

Thermogravimetric (TG) data are obtained using a Netzsch STA 409/C thermoanalyzer. A constant heating rate of 20°C/min is used in all experimental runs. Typical sample weights of 15 mg are employed. Experimental runs are carried out using a purge gas flow (60 ml/min) of pure nitrogen. FTIR measurements are carried out using a Bruker Equinox 55 spectrometer equipped with DTGS and MCT detectors.

TG-FTIR simultaneous measurements for the on-line analysis of volatile compounds formed during TG runs are carried out coupling the FTIR spectrometer to the Netzsch TG. The transfer line and the head of the TG balance are heated at a constant temperature of 200°C to limit the condensation of volatile decomposition products. FTIR measurements are carried out with a MCT detector. Major details can be found elsewhere [8].

RESULTS

TG results

The derivative TG curves of biomass and biomass components are shown in figure 1. The devolatilisation behaviour is very similar for all lignin-cellulosic materials studied. Biomass devolatilisation starts approximately at 200°C (that is 150°C less than traditional coals) and, generally, ends at 420-450°C. In all cases, the dtg peak has a composite shape and this is ascribed to the decomposition of main chemical components. Hemicellulose is the most reactive, cellulose exhibits a narrow range of devolatilisation (with maximum at 354°C), whereas lignin decomposes in a very wide range of temperature. The global weight loss (at 1000°C and 20°C/min) is 74.2, 86.8 and 60.2%, respectively. The different reactivity and volatile release determine the devolatilisation of lignin-cellulosic materials according to their chemical composition: this conclusion will be discussed in the next section.

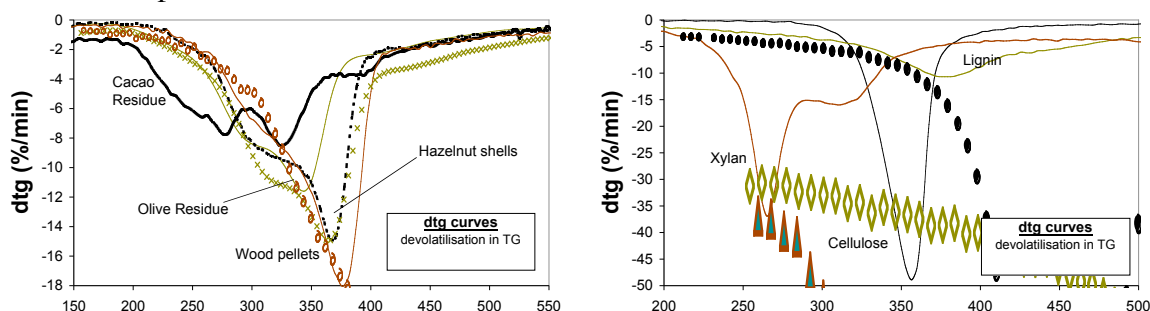


Fig. 1 dtg curves for biomass and biomass components

FTIR results

TG/FTIR analysis for biomass components and lignin-cellulosic materials can be difficult because all volatiles species are released in a very narrow range of temperature. Furthermore, the variety of compounds released makes quite complicated the individuation of single species. However, some important conclusions can be drawn also from a qualitative point of view. Generally, the major quantity and variety of gases released occur during the main devolatilisation step and this can be verified in figure 2 for biomass components and a biomass material (namely, wood pellets), comparing the FTIR profiles of different species with the dtg curve. CO_2 , CO , H_2O , CH_4 can be easily identified. Also, CH_3OH and HCOOH can be detected. In all these cases, IR profiles have a quantitative significance, even if concentration values can not be furnished at present. More complicated organic compounds can be only grouped in classes, as hydrocarbon (CH_n) and carbonyl compounds (C=O), with specific ranges of integration of IR spectra (details in [8]). Peaks of different gases are not directly and quantitatively comparable among them because the integrated absorbance is proportional to the concentration of single volatile species in the gas released, but the proportional constant differs from one compound to another. This is the reason why the profile of some gaseous species are magnified for an arbitrary factor just to get a better visualisation of curves in figure 2. However, qualitative information on the temperature range and the evolution behaviour for each compound can be obtained.

IR profiles of CH_3OH and CH_4 released are reported in figure 3 for all materials and biomass components. In these cases, the analysis gains a quantitative importance. In fact, they are defined chemical species with a well identified IR spectrum. Furthermore, the integrated absorbance is normalised for all materials, that is reported to the same initial sample mass in the same conditions. Therefore, the integrated absorbance reported in figure 3 is directly proportional to the CH_3OH or CH_4 concentration in the gas released during the devolatilisation and peaks of different materials can be quantitatively compared.

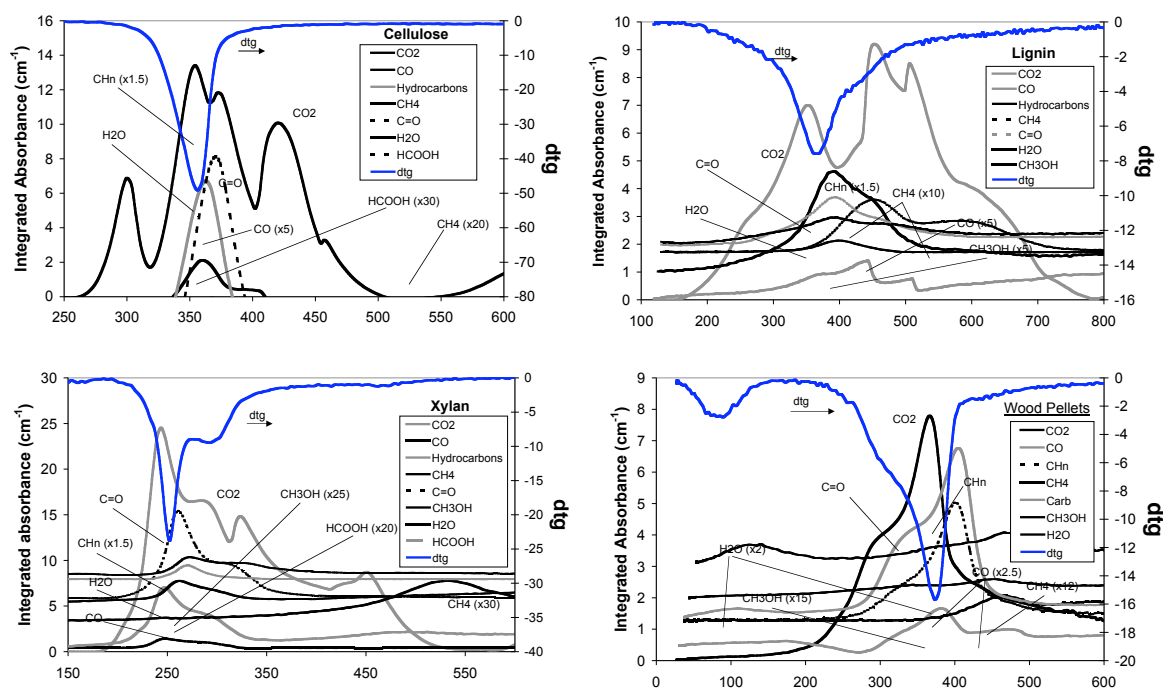


Fig. 2 FTIR profiles and dtg curves for biomass components and a biomass material.

CH_3OH is released during the devolatilisation of xylan and lignin (with different temperature ranges, 243 and 366°C for the maximum, respectively), whereas it was not detectable during cellulose decomposition. As for lignin-cellulosic materials, a significant trend can be noticed with two temperature ranges of release and this is ascribed to the decomposition of both components. A quantitative approach will be discussed in the next section.

The release of CH_4 occurs at higher temperatures respect to the main devolatilisation, as already observable in figure 2. Cellulose releases a smaller amount of CH_4 respect to xylan (but with a similar temperature range and shape of the peak) and lignin, which actually exhibits a composite peak with an important sub-peak at a relatively lower temperature. Most biomass materials show a profile shape which can be qualitatively reported to the components and this depends on the initial chemical composition.

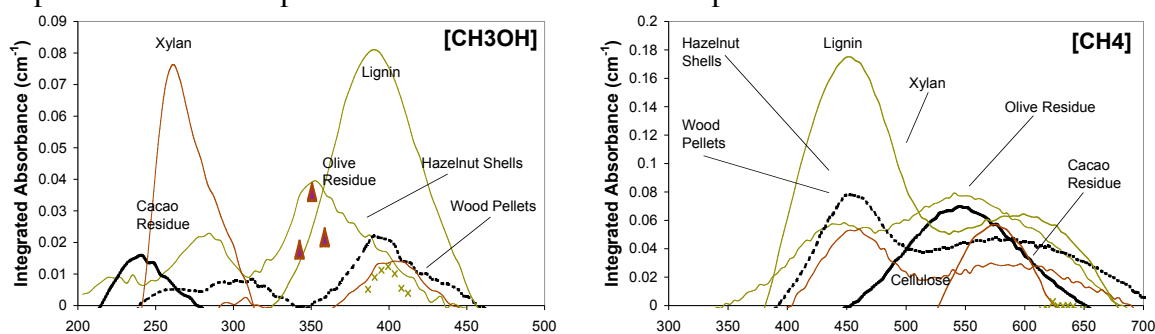


Fig. 3 FTIR profiles of CH_3OH and CH_4 for biomass and biomass components.

DISCUSSION

A weighted sum of the TG curves for each component allows the devolatilisation of lignin-cellulosic materials to be obtained according to the following equation:

$$Y_{\text{biom}} = Y_{\text{cell}}x_{\text{cell}} + Y_{\text{hemi}}x_{\text{hemi}} + Y_{\text{lign}}x_{\text{lign}} \quad (1)$$

where Y is the amount of volatile released, x is the weight fraction of a component in the biomass and the subscripts biom, cell, hemi and lign mean biomass, cellulose, hemicellulose and lignin, respectively. The application of this equation to materials tested in this work gives theoretical values in good agreement with experimental results obtained from TG analysis. Some examples are shown in figure 4, for wood pellets and hazelnut shells. The most important discrepancy is imputable to the xylan decomposition: in fact, its reactivity is higher than all biomass materials. However, maximum differences of 5% can be observed.

Equation 1 can be also applied to the release of each gaseous species released and experimental IR profiles can be compared to theoretical ones obtained considering the components acting independently. For instance, the case of the release of CH_3OH for wood pellets and hazelnut shells is reported in figure 4 with a quite good agreement. In particular, the humps in the IR profiles are attributed to the decomposition of xylan and lignin at low and high temperature, respectively.

In conclusion, TG-FTIR analysis has a good potential to provide valuable parameters for predictive modelling of biomass pyrolysis. However, more work is needed to optimise the experimental technique, to better utilise the rich information obtained from this analysis and to quantitatively validate simple and useful correlations for practical applications.

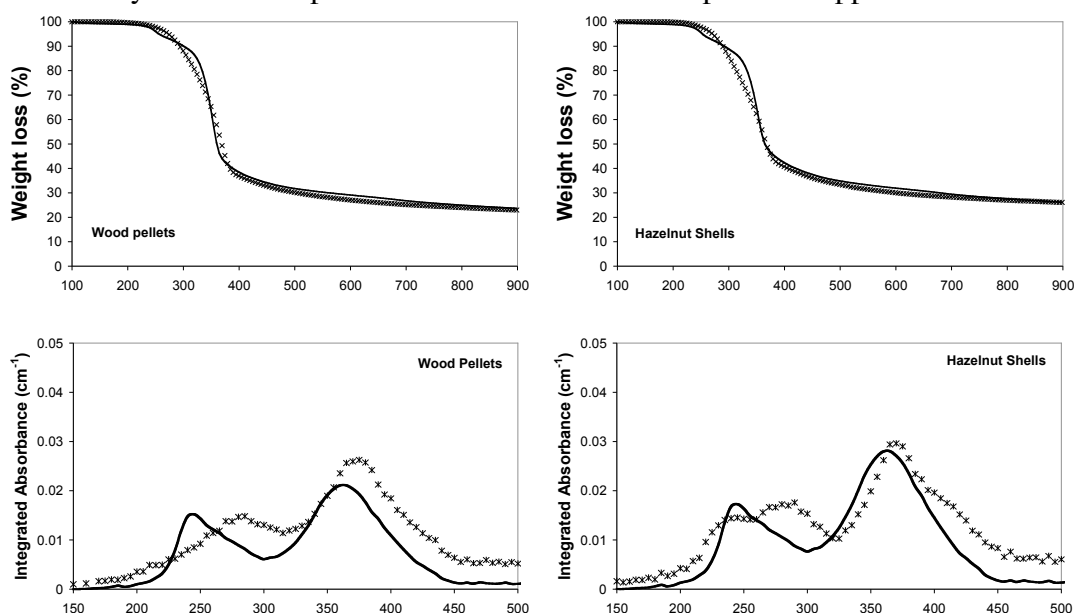


Fig. 4 Comparison of experimental (symbols) and theoretical (continuous lines obtained using equation 1) TG weight loss curves and CH_3OH FTIR profiles for wood pellets and hazelnut shells.

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Properties of chars obtained by fast pyrolysis of secondary fuels

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INTRODUCTION

The characterisation of chars from alternative fuels is a fundamental step in processes where the morphological structure of the solid particle has an important role on the efficiency, i.e. combustion and gasification [1-3]. A deep understanding of related thermal treatment mechanisms is required in order to achieve a high combustion efficiency and to effectively design and operate the combustion system. The basic step is considering a single particle inserted in a reactor with a determined thermal history. The inter-related events through which single particles of solid fuel undergo during a thermal treatment are heating up, drying, devolatilisation and oxidation of both volatile and solid products. Size and structural variations (porosity evolution, swelling, fragmentation) occurring during all phases in thermal processes have a strong influence on each mechanism, especially when diffusion phenomena play a crucial role (char oxidation and gasification).

The objective of this work is the characterisation of chars from alternative fuels obtained by fast pyrolysis. The solid residue characteristics depend strongly on the conditions used during the devolatilisation, i.e. the heating rate (HR), the maximum temperature experienced, the residence time at this temperature and the gaseous atmosphere [4]. Therefore, it is important to develop and test methods to study chars obtained in severe thermal conditions (high temperature and high HR) in order to provide relevant information for practical applications and comprehensive modelling. Significant results are reported as for density, shape, size and structure of the particle which influence the combustion behaviour.

EXPERIMENTAL

Materials

Lignin-cellulosic materials (namely, olive residue, wood pellets, hazelnut shells, cacao residue), a paper sludge, two low volatile coals (coal Qiyi and Tower) and a high volatile coal (coal Kema) are used as starting materials to obtain the chars. The ultimate and proximate analyses and the heating value of all materials are listed in Table 1.

Char Production

Chars are obtained by fast pyrolysis of materials in a wire mesh reactor (Pyroprobe CDS-2000). This is a commercial reactor which performs severe thermal conditions: the nominal HR is 20000°C/s, the maximum temperature is 1400°C. Generally, a sample of 2-3 mg is dried at 105°C in a flowrate of nitrogen, then the most severe conditions are programmed till the maximum devolatilisation conversion. From modelling investigations [4], values on the order of 1000-2000°C/s can be actually expected as for the effective HR of the sample.

Char Analysis

Solid residues obtained after fast pyrolysis are analysed using an Electro-Dynamic Thermo-

Gravimetric (EDTG) balance. It consists of a chamber, where an electric field is generated capable of suspending a single particle, and various external devices allowing the fuel or char particle to be visualised. Single particles are injected in the chamber and captured by the electrostatic force. The EDTG analyser is used to evaluate the size, the shape and the density of char particles: they are compared with the respective properties of parent materials, so that providing interesting information on the structural variations occurred after the devolatilisation. This is a time consuming analysis, due to the high number of tests required to represent a significant number of particles from a statistical point of view (usually 20-30). A laser beam can be used in the EDTG balance to heat the particle and study the devolatilisation behaviour from the temperature-time traces obtained from two pyrometers. In this case a very high heating rate (on the order of 10^5 °C/s) can be achieved. Finally, a SEM analysis is carried out in order to qualitatively define the morphological variations occurred on solid residues and to explain the main results obtained from the previous analysis.

Fuel	Ultimate analysis (% d.a.f.)				Proximate analysis (%)			ash	HV (MJ/kg)
	C	H	N	S	Mois.	VM	FC		
Olive residue (LC)	51.2	6.7	0.83	0.05	14	67.4	17.6	1.0	20.1
Wood pellets (LC)	49.4	6.1	0.99	0.16	6.9	71.7	19.4	2.1	19
Cacao residue (LC)	47	6	2.6	0.23	10.6	64.2	18.3	6.9	17.9
Hazelnut shell (LC)	51	5.4	1.30	-	7	73	18.8	1.2	n.d.
Paper sludge (W)	24.3	3.4	0.51	0.01	55	22.6	1.4	21.3	5.1
Coal Kema (C)	71.4	4.5	1.12	0.81	5.7	28.7	52.6	13	28.7
Coal Tower (LVC)	87.3	3.6	1.3	0.2	dry	8.9	85.8	5.3	34
Coal Qiyi (LVC)	75.2	3.6	1.3	0.2	dry	12.8	70.4	16.8	30

Table 1. Ultimate and proximate analyses and heating value of lignin-cellulosic fuels (LC), wastes (W), traditional coals (C) and low volatile coals (LVC).

RESULTS AND DISCUSSION

The approach developed and applied for the characterisation of high HR chars is schematically described in figure 1. Details for the evaluation of each properties will be given in the following subsections. In general, distributed values are obtained from EDTG analyses, depending on the number of particles tested. The average values are reported in table 2. In this work, the devolatilisation study in the EDTG balance is used only to evaluate the specific heat of the char, whereas other information (onset temperature, kinetics, etc.) can be found elsewhere [4].

Evaluation of the specific heat of chars

The specific heat of three different fuels has been evaluated from the temperature-time traces during the devolatilisation in the EDTG balance. A simple energy balance during the cooling step allows the cp of the solid residue after a very high HR devolatilisation to be obtained. It is worth noting that in this case, the specific heat listed in table 2 is referred to EDTG chars (that is directly obtained after a rapid devolatilisation of the particle heated with the laser), whereas the other properties (size, shape and density) are reported for Pyroprobe chars.

Size variations

The dimension of the particle is directly measured from the visualisation device of the EDTG analyser. The main dimensions are acquired with an error between 2 and 5%, depending on the dimension and the optical components. An equivalent spherical diameter (Dse) can be calculated assuming the particle as an ellipsoid, thus from the equatorial (Dx) and the axial (Dy) diameters. The diameter slightly decreases for all coals (table 2), with a larger decrease for the high VM coal Kema. Generally, the size decreases also for biomass materials with

important reductions (as for wood pellets and hazelnut shells), whereas for some residues it can also increase (cacao residue). In this cases, it is important to evaluate also the shape of the particles, because an equivalent spherical diameter can not be suitable for particles which exhibit a cylindrical shape.

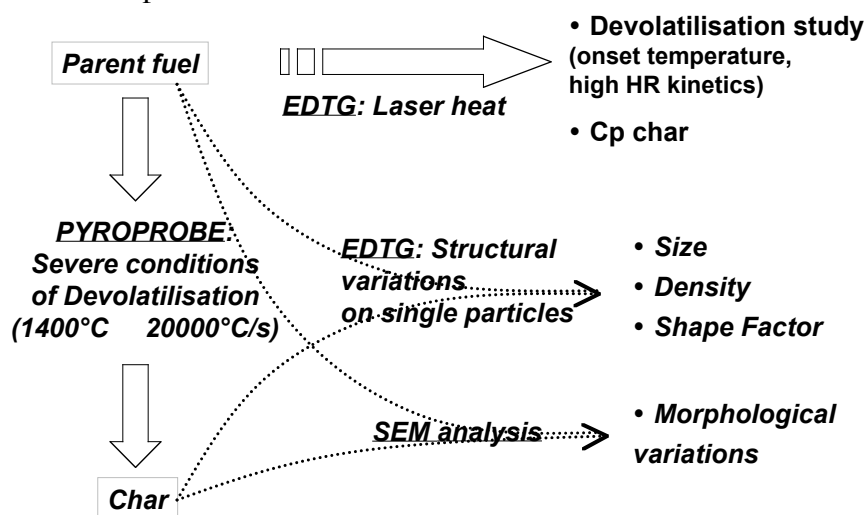


Fig. 1 Scheme of the experimental procedure.

Material	Cp (kJ / kg K)	Dse (µm)		SF		Density (g/cm ³)	
	high HR char	parent mat.	high HR char	parent mat.	high HR char	parent mat.	high HR char
coal Kema	1.20	72.4	63.5	90.4	35.2	1.486	1.027
coal Tower	nd	61.7	60.4	87.8	35.1	1.633	1.258
coal Qiyi	1.32	64.4	62.8	87.4	35.1	1.565	1.215
olive residue	nd	99.9	98.2	99.7	44.8	0.535	0.794
wood pellets	1.12	139.1	114.1	77.8	45.4	0.826	0.841
hazelnut shells	nd	173.6	131.5	135.2	41.3	0.159	0.98
cacao residue	nd	132.4	139.2	142.2	42.0	0.581	0.762
paper sludge	nd	149.9	103.2	78.2	45.6	0.645	0.846

Table 2. Average values of specific heat, spherical equivalent diameter (Dse), shape factor (SF) and density of particles of high heating rate chars and parent materials.

Shape variations

Different shapes can be observed during the analysis of the particles and this represents a further important parameter in the characterisation of chars and parent materials. Different classes can be defined depending on the sphericity/cylindrical form and the irregularity of the perimeter. For all classes, the appropriate perimeter (P), area (S) and volume (V) can be geometrically calculated. The Shape Factor SF is defined as the S on P ratio. In all cases, SF decreases (see table 2) and this denotes a more spherical shape in the char particles comparing with the parent material. The reduction is very pronounced for some biomass fuels and this is the result of swelling phenomena due to the release of volatiles during the rapid heating of the particle in the devolatilisation step.

Density variations

The density of a particle is evaluated in the EDTG analyser according to the imposed flow technique [5]. Variations in the gas flowrate determine different values of the drag force: for limited gas velocity (Stokes regime) the particle is maintained levitated by an appropriate value of the electric voltage. At the equilibrium, the drag force (F_a), the gravity force (mg , where m is the mass of the particle) and the force due to the electric field (E) can be written according to the following balance:

$$mg = qE + F_a \quad (1)$$

where q is the electrostatic charge on the particle. The value of the density can be calculated from m and the volume of the particle. Major details can be found elsewhere [4]. The density decreases for all coals, whereas it increases for biomass fuels (see table 2).

In order to shed light on this result, a SEM analysis has been carried to assess the effect of morphological variations between the parent material and the char for a biomass and a low volatile coal. Also, the density has been evaluated from EDTG balance for solid residues at different degrees of devolatilisation. Results are reported in figure 2. The linear trend in the density reduction for the low volatile coal is consistent with a constant diameter model: the release and, thus, the weight loss during the devolatilisation step decreases the density leaving a higher porosity, but with minor variations in the size (as noticed above). SEM analysis confirm this hypothesis (see figure 2). Vice versa, for biomass fuels, the density increase can not be explained with a constant diameter model, but a different mechanism should be supposed. In this case, the volatile release is very important (mostly, more than 70%) so that the structure of the solid residue is completely different comparing with the parent material. Agglomeration phenomena due to the softening of the material during the heating up can produce a more compact structure (caused by the melting and resolidification of the material): this increases the density diminishing the microporosity as observed from SEM images in figure 2.

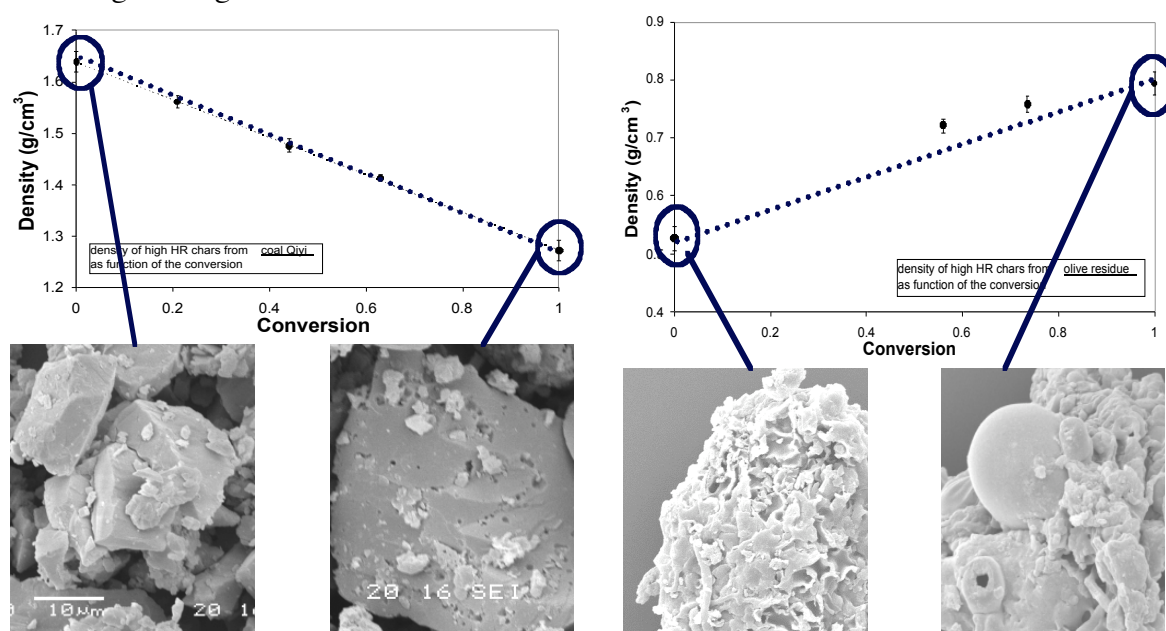


Fig. 2 Density of solid residues from a low volatile coal (coal Qiyi) and a biomass fuel (olive residue) as function of the devolatilisation conversion (in Pyroprobe) and SEM analysis of the extreme cases.

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The Influence of the Devolatilisation Rate on the Reactivity of Chars from a Coal, a Biomass and their Blend.

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INTRODUCTION

In the last decade a growing concern has been registered towards the study of biomass combustion [1]. Biomass represents, after oil and coal, the third most important world energy source and certainly the major energy resource for developing countries. With respect to fossil fuels it is renewable and, hence, does not contribute to the increase of the CO₂ global emission since the CO₂ released during the combustion has been already recently absorbed by the plant during its growth [2]. Therefore, a growing use of biomass may allow the reduction of CO₂ concentration increase in the atmosphere, which seems to contribute at least partially the green house effect. However, the complete substitution of fossil fuels with biomass in existing plants is not feasible because of the marked differences between the combustion behaviour of the former and the latter in terms of volatiles and mineral matter content, and of chars reactivity. It appears possible, however, to substitute a small percentage (i.e. 5-10 wt %) of the fossil fuel with biomass without significantly modify the fuel physico-chemical characteristics and, therefore, its combustion behaviour. In any event, in the view of such a use of the biomass it is recommendable that it has a relatively high carbon/nitrogen ratio, a low humidity content (less than 30 wt%) and, consequently, an adequate heating value [3].

It is well known that fly ashes leaving industrial boilers contain significant amounts of unburned carbon [3]. This could be due to a number of reasons: i) loss of reactivity of the char as the combustion proceeds [4]; ii) the presence in the char of mineral matter and/or of different organic phases with different reactivity [5]; iii) the extremely high heating rate at which the fuel is subjected at its entry in the combustion chamber. Specifically, coal powder injected in the combustion chamber of industrial boilers withstands to pyrolysis in times of the order of 1/10 s or less and the correspondent heating rate is between 10³ and 10⁴ K/s.

This work aimed at analysing the combustion behaviour of devolatilised samples of a coal, of a biomass and of their blend produced at low (20 K/min) and high (10³ K/s) pyrolysis rates.

Table 1: typical composition of olive residue.

content	wt %
humidity	8-9
carbon	47-50
hydrogen	6.3-6.8
nitrogen	0.9-1.5
sulphur	0.1-0.25
oxygen	31-41
ash	1.4

To this end chars of the cited samples were obtained, by a N₂ flow TG apparatus (for the low pyrolysis rate) and by a specifically designed high temperature wire mesh reactor (HTWMR) (for the high pyrolysis rate), and their reactivity tested by air flow TG analysis. The results are discussed.

EXPERIMENTAL

Two materials were employed in the experiments: a bituminous coal and olive residue after olive oil production. The typical elemental composition of olive residue is shown in table 1 while the characteristics of the employed coal are reported in table 2. The two materials and a blend of them (10 wt % of biomass) were dried at 383 K for 12 h, then thoroughly pounded in an electric mortar in size below 45 µm. Specific surface area (S.S.A.) measurements were performed by a Sorptometer 1040 "Kelvin" (Costech International) on fresh pounded samples and on such samples after pyrolysis. Slow pyrolysis of the samples was carried out by a thermogravimetric apparatus (Q 500 TA Instruments) in N₂ flow at an heating rate of 20 K/min and up to 1273

K. Fast pyrolysis of the samples was, instead, carried out in a specifically designed high temperature wire mesh reactor (HTWMR) equipped with a Marathon MR1SBCF two color pyrometer (Raytec) with a response time of 10 ms and a measurable temperature range

Table 2: coal ultimate and proximate analysis

Ultimate analysis	wt %
carbon	71.43
hydrogen	4.47
sulphur	0.81
chlorine	0.27
nitrogen	1.12
oxygen	8.13
ash	13.78
Proximate analysis	
fixed carbon	52.60
volatiles	28.73
humidity	5.68
ash	12.99

between 973 and 2073 K. Further details of the apparatus are reported elsewhere [6]. The reactor chamber was flushed with N₂ flow for 15 min before each test then the electric current was allowed to pass through the wire mesh and the sample temperature was brought at 1273 K at a rate of 10³ K/s. The sample was also maintained at such a temperature for 5 s. During all the test the N₂ flow was kept constant. The reactivity of fresh and pyrolysed (slowly or fast) samples was evaluated by air flow thermogravimetric analysis in the mentioned TG apparatus at an heating rate of 10 K/min from ambient temperature up to 1253 K.

RESULTS

Volatiles content of the various samples, determined by fast and slow pyrolysis, are reported in table 3. As

Table 3: samples volatiles content measured by slow and fast pyrolysis and S.S.A. of fresh and fast pyrolysed samples.

Sample	Volatiles (wt %)		S.S.A., m ² /g	
	fast pyrolysis	slow pyrolysis		
coal	43	33	5	26
olive residue	83	81	1	14
blend	42	33	3	25

expected, with both high and low pyrolysis rate the quantities of volatiles of the biomass result much higher than that of the coal and, in addition, the blend volatiles amounts are very close to that of the coal. Differences are found between the volatiles

determined by slow and fast pyrolysis. Such differences are relevant for the coal and the blend and much less significant for the biomass (table 3). In the same table the results of S.S.A. measurements carried out on the fresh and the fast pyrolysed samples are also reported. It appears that fresh coal and biomass and the correspondent blend have S.S.A. of the same order of magnitude. The same result is obtained after pyrolysis. However, pyrolysis increases the S.S.A. of each sample of an order of magnitude. In any case, the values of S.S.A. pertaining to the blends are intermediate between that of the parent materials although closer to that of the coal.

Air flow TG tests of the fresh samples (not reported here) showed that biomass starts to loose weight at low temperature (450 K), presents two DTG peaks (at 600 and 680 K) and the combustion ends at 770 K. Coal presents a single DTG peak at 760 K with a shoulder at 670 K, due to the combustion of volatiles, and a combustion end temperature of 870 K. The combustion behaviour of the blend is intermediate but, as expected on the basis of the relative amounts of the components in the blend, very close to that of the coal.

Coal char obtained by pyrolysis at 10³ K/s (Fig. 1) appears less reactive than that produced at 20 K/min (Fig. 2) its DTG curve and the correspondent peak resulting shifted 25 K towards higher temperatures. However, the combustion end temperatures of both samples are coincident (cfr. Fig. 1 and 2). With respect to the fresh coal in the pyrolysed coals the volatiles are absent and, also, the chars burn more slowly than the heavy portion of the coal leading to a 50 K increase of the combustion end temperature.

The comparison between the biomass chars, obtained at the two pyrolysis rates, shows that the char obtained at 10³ K/s (Fig. 1) appears more reactive, the DTG peak temperature and the

combustion end temperature being lower (20 K and 50 K, respectively) than those pertaining to the char produced at 20 K/min (Fig. 2). In addition, this latter sample shows a double peak DTG curve, which recalls that shown by the fresh biomass. This feature influence, also, the

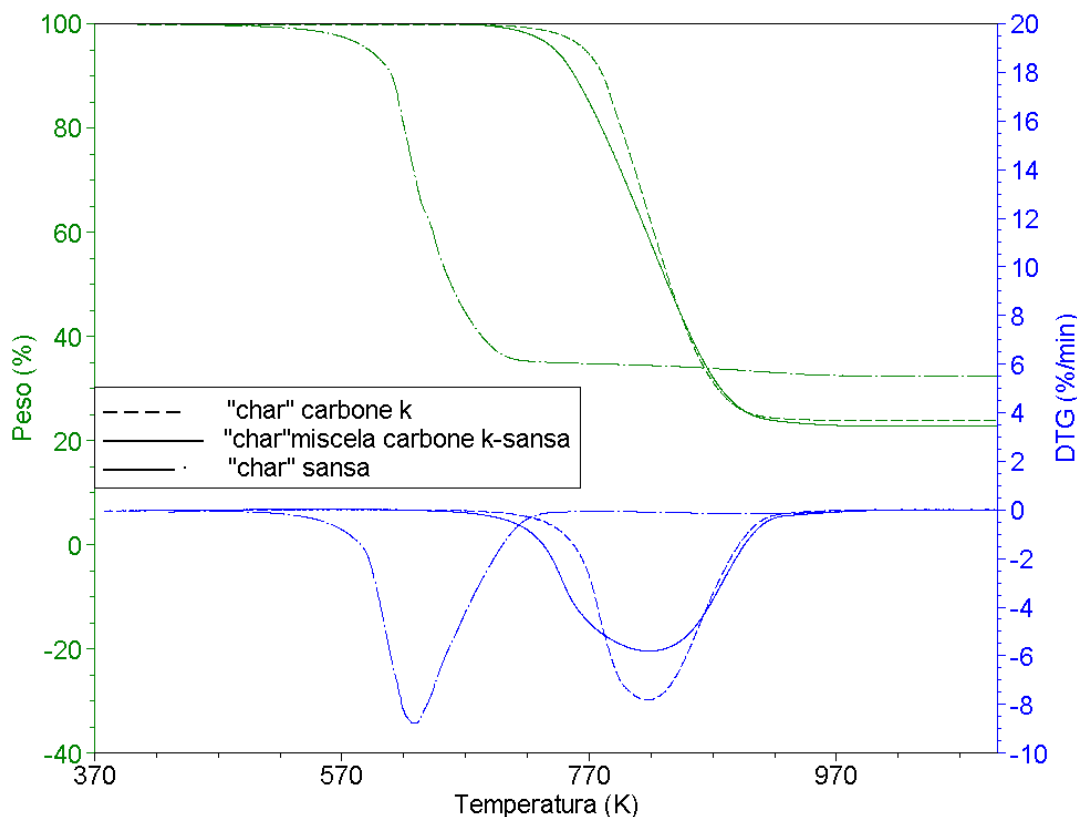


Fig. 1 Results of TG analysis of the chars of coal of biomass and of their blend obtained by pyrolysis at 10^3 K/s.

behaviour of the blend char. Indeed, the effect of the double DTG peak of the slowly pyrolysed biomass (Fig. 2) is evident in the DTG profile of the blend in Fig. 2. Actually, a shoulder at temperature higher than that of the peak is visible in the DTG curve of the blend char. This shoulder determines a combustion end temperature of this sample higher than that pertaining to the correspondent 10^3 K/s pyrolysed sample (cfr. Fig. 1 and 2). It is worth noting, however, that the second peak of the DTG curve pertaining to the biomass char (pyrolysed at 20 K/min) occurs at 740 K while the shoulder of the DTG curve of the correspondent blend char verifies at 910 K (Fig. 2). In addition, the DTG peak temperature is 30 K lower for the sample obtained at lower pyrolysis rate.

Summarising, in the case of coal with respect to the slow pyrolysis rate the high pyrolysis rate gives rise to a markedly larger volatile release, a less reactive char but a combustion end temperature practically coincident with that of the slowly pyrolysed coal char. For both chars, however, the combustion end temperature is markedly higher than that of the fresh coal. In the case of the biomass the high pyrolysis rate determines a slight increase of volatiles release and a more reactive char in terms of both DTG peak temperature and combustion end temperature. In the case of the blend (10 wt% biomass) the high pyrolysis rate gives rise to a significantly higher volatiles release, a decrease of the reactivity (in terms of combustion start temperature and DTG peak temperature) but also an increase of reactivity (in terms of combustion end temperature). This latter phenomenon seems to be attributable to the influence of the biomass char on the combustion behaviour of the blend in spite of the fact that the biomass char, when tested alone, results to be already burned off at 800 K and that

the amount of biomass char in the blend after devolatilisation should be not more than 3.5 wt%. This would suggest that the influence of the mineral matter contained

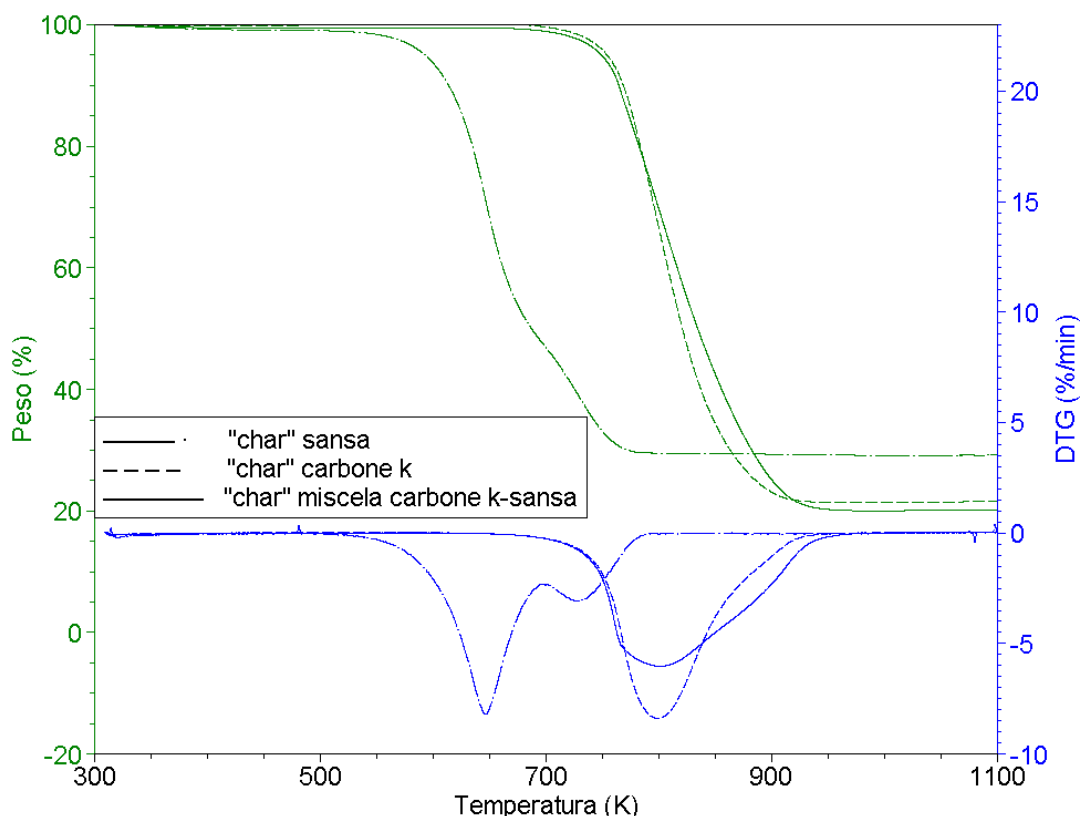


Fig. 2 Results of TG analysis of the chars of coal of biomass and of their blend obtained by pyrolysis at 20 K/min.

in the char rather than that of the organic components of the char itself determines the observed behaviour. In any event, this is a matter to be further investigated.

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An Integrated Kinetic Based Modelling Approach to Alkali-Salt Formation and Deposition in Pf Boilers

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INTRODUCTION

In the present study a numerical approach to the simulation of boiler conditions was extended to both explain and evaluate the vapour phase chemistry of alkali and chlorine and the alkali salt deposition mechanisms on heat transfer surfaces of the convection pass. The modelling methodology is based on an integrated use of different simulation tools: CFD (IPSE), PROATESTM and Chemical Engineering Models (RNA). A first study on the impact of different blending of coal and RDF on a real plant is presented, showing that the numerical approach can be used to predict the increase of alkali salt deposition on superheater tube banks.

NUMERICAL MODELS

At present ENEL numerical approach to the simulation of boiler conditions consists in a CFD code (IPSE) for the 3D simulation of the main chemical and physical conditions of the fluid flows inside industrial combustion chambers, in the PROATESTM code providing a mono-dimensional model of the convection pass which determines heat exchanges between gas and boiler steam, gas and metal temperature and in a subsequent schematisation of the modelled volume with a chemical engineering model called Reactor Network Analysis (RNA).

The latter consists of an equivalent network of ideal, perfectly stirred, reactors extracted from the results of CFD simulation by an automatic zoning algorithm. Detailed reaction mechanisms are then applied over the reactor network and a more accurate calculation of the combustion yields is performed. The Reactor Network Analysis is based on a mechanistic approach to the combustion chemistry. Until now it was applied for the prediction of pollutant emission of gaseous species (NO_x, SO_x, CO, H₂S) using detailed reaction schemes; recently it was extended to include the calculation of char oxidation.

A scheme of the approach that was developed for predicting the formation and deposition of alkali-salt in pulverised coal fired boilers is the following:

- ✓ A three-dimensional model of the combustion chamber was performed to predict local temperatures, heat fluxes, flow rates, char burnout and concentrations of main species. This was achieved employing IPSE CFD code, which solves steady, three-dimensional, turbulent flow, heat transfer, and chemistry of pulverised coal combustion [1].
- ✓ The convection pass was schematised with a mono-dimensional model which utilises PROATESTM code for calculating all the mass and heat exchanges between the gas and boiler fluids [2].

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- ✓ A chemical engineering model of the boiler was provided. For the combustion chamber it consists of an equivalent network of idealised reactor elements (up to 500) extracted from the results of CFD simulation by an automatic zoning algorithm [3]. For the convection pass the chemical reactor model was designed following the same schematisation adopted by PROATESTM.
- ✓ Detailed reaction mechanisms including (NO_x, SO_x, Chlorine and Alkali) was applied over the reactor network (RNA) and a more accurate calculation of the combustion yields was performed.
- ✓ Mass transfer rates of the alkali-salt deposition on the heat exchanger surfaces in the convective pass was calculated evaluating the occurring mechanisms.

MODELLED CASE

The modelled plant is a 320 MWe tangentially coal-fired dry-bottom boiler. The boiler is equipped with 20 tangential burners and a combustion system designed to reduce the formation of nitrogen oxides. A deeper description of the combustion configuration may be found in [4]. For the CFD flow calculation the IPSE code [5] was used. The finest grid adopted was an orthogonal, structured mesh with non uniform pitch with 99180 computational cells (38 x 29 x 90). The numerical strategy adopted for coupling the various submodels for turbulence, heat transfer, radiation and pressure was that exposed in previous works [5]. In particular the solution of the conservation equation, including convective and diffusion terms, has been computed for each chemical species present in the system. The reaction rates, that appear as source terms, were computed from the Arrhenius kinetic rate expression which considers both the forward and backward rate constant for reactions. The chemical model of coal combustion adopted by CFD was obtained coupling a simplified kinetic scheme [3] for the hydrocarbon gas species, with a reaction for the volatile release (CO, CO₂, H₂O, H₂, CH₄, TAR) from coal and a reaction for the oxidation of char particles. For the latter 12 size classes of diameter have been considered. The results of CFD simulations have been validated against measurements of thermal fluxes on the fire side walls and measurements of temperature and concentration of O₂ and CO acquired with a suction pyrometer on a section above the nose.

Running the post-processing code of CFD outputs with rezoning algorithms it has been produced a subdivision of the modelled volume in 550 homogeneous zones generating a Chemical Reactor Network. Then the combustion yields have been recalculated with a detailed kinetic mechanism. The kinetic mechanism (3003 reactions of 174 species) was constructed adding a module for Na and K chemistry interacting with Cl to the assessed comprehensive detailed scheme describing hydrocarbon combustion chemistry and pollutant formation (NO_x and SO_x) adopted in previous works [6,7].

The kinetic module adopted for describing alkali chlorination is presented in a previous work [8]. It has been derived after collecting and examining kinetic and thermodynamic data available in literature and in scientific databases.

In this mechanism the reaction paths leading to the formation of oxides and sulphates have not been considered. The former, because the formation of alkali oxides has a secondary relevance in the environment inside industrial boilers (as can be shown also by equilibrium calculations), the latter because there is still much uncertainty whether sulphation occurs homogeneously in the gas phase or heterogeneously on the tube and particle surfaces [9]. As concerns of HCl and its products, Dryer and co-workers' kinetic submechanism was taken directly from the literature and used without modification [10].

RESULTS

The modelling of Fusina plant was started, applying the CFD+RNA approach for predicting

the impact of coal-RDF co-firing in terms of flue gas composition and deposition of alkali on tube banks of the convection pass. Simulations for three fuel feeds have been performed: only SA Coal (for which the input level of volatile alkalis was derived from the balance of measured chloride enrichment of ashes) and two blends SA Coal + 3 t/h RDF, S.A. Coal + 9 t/h RDF. All the alkalis contained in RDF were assumed volatile. In Figure 1 is shown the change of alkali and chlorine level in the fuel produced by the blending.

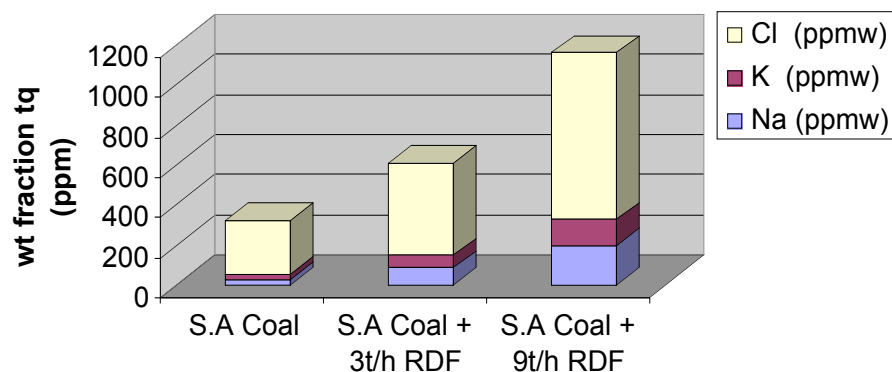


Fig. 1 Input level of volatile alkalis and chlorides for the simulated coal-RDF blends.

On the first the kinetic calculation was performed for the combustion chamber yielding a detailed representation of the interconversion of the species of interest. In particular it was shown as alkali hydroxides are present mainly in the burner zone, while alkali chlorides prevail in the post-flame zone (after nose). Further it was seen that the molar fraction of HCl always exceeded the alkali one.

As following step, the stream exiting from the furnace was given to the reactor model of the convection pass and then the alkali-salt deposition on the heat exchanger surfaces was calculated evaluating the occurring mechanisms.

The calculation of the mass transfer rates of the alkali-salt deposition requires on the first a qualitative analysis of which mechanism occurs along the convective pass, and then a quantitative evaluation adopting suitable models. For the studied case the qualitative analysis has shown that the dominant mechanism of alkali chloride deposition on tube banks is vapour diffusion followed by condensation on heat exchange surfaces. While the banks where homogeneous and heterogeneous condensation may occur are the last and the economiser, leading respectively to aerosol formation and fly ash enrichment in the flue gas main stream.

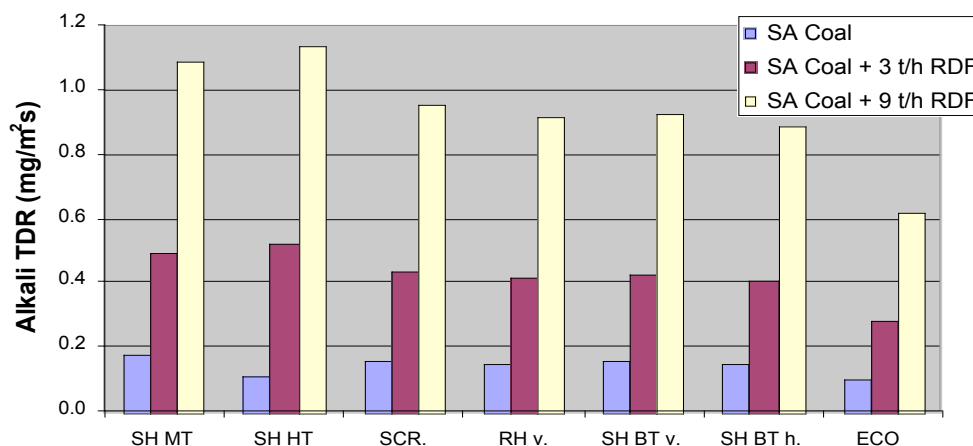


Fig. 2 Deposition rates of alkali vapours calculated for the different sections of the convection pass and for different RDF shares in the fuel.

The deposition rate by vapour condensation on tube banks is evaluated assuming analogy between heat and mass transfer [11], while the diffusion coefficients are evaluated according to Chapman-Enskog theory [8]. The calculated mass transfer rates of the alkali chlorides, shown in Fig 2, are of realistic order of magnitude, resulting in an increase of about five times for the deposition rate in the case of co-combustion with 9 t/h of RDF share respect to the normal operation. The deposition rate calculated for the normal operation case is reasonable, if compared to measurement acquired on boilers of similar operating conditions. Further assessment of the co-combustion predictions will be derived from ongoing measurement in a full size boiler.

CONCLUSION

The developments of a model for predicting alkali salt deposition in the convection pass of a recovery boiler are presented. Modelling can be used qualitatively to understand problems with fouling and corrosion, that can arise when coal is blended with RDF or bio-fuels, and make more effective use of convection surface and sootblowing. With greater validation, the model will be a useful engineering tool for anticipating mineral matter behaviour with changes in fuel composition, operating conditions, and design. In future works, in order to elaborate a comprehensive model for deposition phenomena, it will be necessary to clarify the sulphation kinetic mechanisms of alkali species that at the moment are not clearly understood. Moreover it will be necessary to estimate the reactions between vapour phase alkali compounds and silicates present into fly ash particles. The overall task is the construction of an integrated model that, starting from the fed coal analysis and boiler geometry, quantifies the fly ash composition and size distribution and evaluate the deposits growth resulting from the condensation of inorganic volatile species and fly ash deposition

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Turbulent flames with realistic thermal expansion of burning matter

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INTRODUCTION

The role of the hydrodynamic flame instability (the Darrieus-Landau or DL instability) for premixed turbulent burning in gas turbines and car engines has been widely discussed, but the final answer still remains unknown [1-3]. For a long time it was supposed that the instability influence is minor [1,4]. Now there is mounting evidence that the DL instability is of primary importance for turbulent burning in the flamelet regime, and sometimes this effect may even dominate [5-10]. Of course, this evidence is rather indirect, and one needs a more quantitative investigation to compare the role of external turbulence and the intrinsic flame instability. Unfortunately, direct numerical simulations cannot help in this case, since the characteristic length scale of the flow (10 – 100) cm exceeds the typical flame thickness ($10^{-4} - 10^{-3}$) cm by many orders of magnitude. Renormalization analysis [11,12] may work better when such a large number of different length scales is involved in the problem. The original papers [11,12] developed the renormalization ideas in the artificial context of a flame with zero thermal expansion, when the densities of the fuel mixture ρ_f and the burnt gas ρ_b are the same, i.e. the expansion factor $\Theta \equiv \rho_f / \rho_b$ is equal unity $\Theta = 1$. However, the assumption of $\Theta = 1$ is quite far from reality. Instead, laboratory and industrial combustion is accompanied by rather strong expansion of burning gaseous mixture $\Theta = 5 - 8$. As a matter of fact, it is the density drop that causes the DL instability, and the larger the expansion factor Θ , the stronger the instability [1-3].

In the present paper we expand the ideas of the works [11,12] to the case of a flame front strongly corrugated both by the external turbulence and the DL instability in the flamelet regime of burning. Assuming self-similar properties of the corrugated flame dynamics we find analytical formulas for the propagation velocity of a strongly turbulent flame. We demonstrate that the DL instability is of principal importance when the integral turbulent length scale is much larger than the cut off wavelength of the instability.

TURBULENCE AND THE DL INSTABILITY WORK SEPARATELY

According to the well-known Clavin-Williams formula [13] obtained in the case of no thermal expansion $\Theta = 1$ and zero flame thickness, weak turbulence increases velocity of flame propagation U_w in comparison with the planar flame velocity U_f as $\Delta U = U_w - U_f$,

$$\Delta U / U_f = U_{rms}^2 / U_f^2, \quad (1)$$

where $U_{rms} = u_{rms}(L_t)$, u_{rms} is the turbulent rms-velocity depending on the characteristic length scale λ , and L_t is the integral length scale of the turbulent flow. Equation (1) may be also presented with the help of spectral density $\varepsilon_t(k)$ of the turbulent kinetic energy

$$\Delta U / U_f = U_f^{-2} \int_{k_t}^{k_v} \varepsilon_t(k) dk \quad \text{with} \quad u_{rms}^2 = \int_k^{k_v} \varepsilon_t(k) dk, \quad (2)$$

where $k_t = 2\pi / L_t$ and $k_v = 2\pi / L_v$ are the wave numbers corresponding to the integral and Kolmogorov (dissipation) length scales, L_t and L_v , the former being usually much larger than the latter $L_t \gg L_v$, $k_t \ll k_v$. In the case of the Kolmogorov turbulent spectrum $\varepsilon_t(k) \propto k^{-5/3}$ we find $\varepsilon_t(k) = (2/3)U_{rms}^2 k_t^{2/3} k^{-5/3}$. Equation (1) has been extrapolated to the case of a strongly turbulent flame assuming self-similar properties of the corrugated front [12]. Following [12] we decompose the spectrum of turbulent flame wrinkles into narrow bands, each of them providing similar small increase of the flame front velocity determined by Eqs. (1), (2). Let us designate the velocity of flame propagation corresponding to the wrinkles with the wave numbers above k by $U = U(k)$ and rewrite Eq. (2) in the form

$$dU / U = -\varepsilon_t(k) dk / U^2. \quad (3)$$

Integrating Eq. (3) over the whole turbulent spectrum one obtains the propagation velocity U_w of a strongly corrugated flame with zero thermal expansion $\Theta = 1$, [12]

$$U_w^2 = U_f^2 + 2U_{rms}^2. \quad (4)$$

Let us consider similar scale-invariant formulas for the case of a flame front corrugated because of the DL instability only, when there is no external turbulence. It has been obtained experimentally [5,6] that a corrugated spherical flame front unstable according to the DL mechanism accelerates with the velocity of flame propagation U_w depending on the characteristic length scale of the hydrodynamic motion λ as $U_w = U_f (\lambda / \lambda_c)^D$, where λ_c is the cut off wavelength of the DL instability proportional to the flame thickness, and $2 + D$ has been interpreted as fractal dimension of the flame front. According to the experimental measurements [5,6] the fractal excess is approximately $D \approx 1/3$ for all investigated laboratory flames. Assuming self-similar properties of the fractal cascade we should expect that the “intermediate” velocity of flame propagation $U = U(k)$ produced by the wrinkles with wave numbers in between k and $k_c = 2\pi / \lambda_c$ depends on k as

$$U = U_f (k / k_c)^{-D}. \quad (5)$$

The last equation may be also presented in the differential form similar to Eq. (3)

$$dU / U = -\varepsilon_{dl}(k) dk \quad (6)$$

with $\varepsilon_{dl} = D / k$ for $k < k_c$ and $\varepsilon_{dl} = 0$ when $k \geq k_c$.

TURBULENCE AND THE DL INSTABILITY WORK TOGETHER

In general, when a flame front with realistic thermal expansion propagates in a turbulent flow, then both the DL instability and external turbulence contribute to the velocity increase. In that case the velocity increase depends both on the scaled turbulent intensity U_{rms} / U_f and on the intrinsic flame parameters $\Delta U / U_f = F(U_{rms} / U_f; \Theta; \dots)$. When turbulence is weak, then the last formula may be reduced to

$$\Delta U / U_f = C_{dl} + C_t U_{rms}^2 / U_f^2, \quad (7)$$

where the coefficients C_{dl} and C_t depend on intrinsic flame parameters. Obviously, the first term in Eq. (7), C_{dl} , describes the velocity increase due to the DL instability only. The second term describes flame response to external turbulence. If flame propagates perpendicular to the axes of turbulent vortices, then the factor C_t is determined by the so-called turbulence-induced solution and equals

$$C_t = (\Theta + 1)^{-1} \frac{16\Theta^3}{4\Theta^2 + (\Theta^2 + 1)^2} \quad (8)$$

in the case of a flame of zero thickness [14]. According to Eq. (8) we have $C_t = 0.2 - 0.4$ for $\Theta = 5 - 8$. Still, preliminary evaluations show that finite flame thickness may increase the coefficient C_t approximately twice. Besides, the effect of flame propagation along the vortex axis contributes also to the coefficient C_t [15]. Thus, at present it is reasonable to treat C_t as a factor close to unity. Taking into account (3), (6), (7) and assuming scale-invariance of flame dynamics, we find the increase of the turbulent flame velocity produced by one narrow band in the turbulent spectrum

$$dU/U = -\varepsilon_{dl}(k) dk - C_t \frac{\varepsilon_t(k)}{U^2} dk, \quad (9)$$

or

$$\frac{1}{2} \frac{d}{dk}(U^2) = -\varepsilon_{dl}(k)U^2 - C_t \varepsilon_t(k). \quad (10)$$

We came to a linear differential equation with coefficients depending on the variable, Eq. (10), which may be solved analytically by a standard method. Below we will consider the solution to Eq. (10) for the most typical case of the DL cut off wave number smaller than the Kolmogorov cut off $k_t < k_c < k_v$ and for the excess of the fractal flame dimension $D = 1/3$. A more general solution to Eq. (19) is presented in [14].

To find the solution to Eq. (19) we have to consider separately two domains of large and small wave numbers (short and long wavelengths), $k_c < k < k_v$ and $k_t < k < k_c$, respectively. Solution to Eq. (10) in the domain $k < k_c$ may be written as

$$U^2 = C_1 \left(\frac{k}{k_c} \right)^{-2D} + 2C_t k^{-2D} \int_k^{k_c} \eta^{2D} \varepsilon_t(\eta) d\eta, \quad (11)$$

where the integration constant is determined by the solution in the domain of short wavelength $C_1 = U^2(k_c)$. It has been shown in [10,16] that flame response to external turbulence is quite different for large and small wave numbers. Because of the strong thermal suppression the harmonics of external turbulence with large wave numbers $k > k_c$ (small wavelength $\lambda < \lambda_c$) wrinkle the flame front only slightly and produce almost no increase in the flame velocity $U(k_c) \approx U_f$ providing the integration constant of Eq. (11) $C_1 \approx U_f^2$. Of course, such a conclusion holds only for moderate turbulent intensity, which does not modify the inner structure of a flame front. When the inner flame structure is modified, then we go over from the flamelet regime of turbulent burning to the regime of thickened flames, which is beyond the scope of the present paper.

Then in the case of Kolmogorov turbulence $\varepsilon_t(k) \propto k^{-5/3}$ and $D = 1/3$ we find from (11)

$$U^2 = U_f^2 \left(\frac{k}{k_c} \right)^{-2/3} + \frac{4}{3} C_t U_{rms}^2 \left(\frac{k}{k_t} \right)^{-2/3} \ln(k_c / k), \quad (12)$$

or

$$U_w^2 = U_f^2 \left(\frac{L_t}{\lambda_c} \right)^{2/3} + \frac{4}{3} C_t U_{rms}^2 \ln(L_t / \lambda_c). \quad (13)$$

When turbulent intensity is zero $U_{rms} = 0$, then Eq. (13) goes over to the velocity increase produced by the DL instability only. Comparing the second terms in the velocity increase in Eq. (4) and Eq. (13) (the terms related to the external turbulence) we can see that the turbulent term in Eq. (13) is multiplied now by a large factor $\ln(L_t / \lambda_c)$, which makes the influence of external turbulence much stronger in the presence of the strong DL instability.

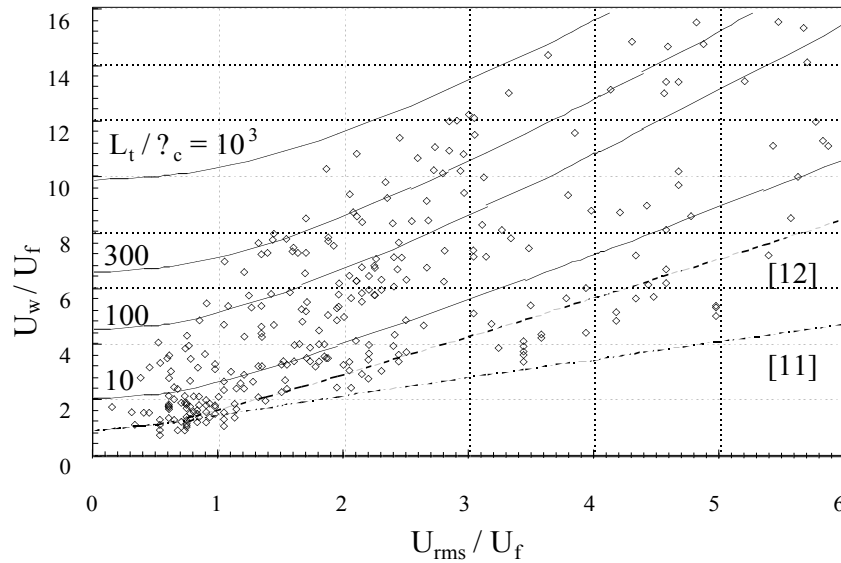


Fig. 1. Turbulent flame velocity vs the turbulence intensity for different integral turbulent length scales $L_t / \lambda_c = 10 - 10^3$ (solid lines). The dashed and dashed-dotted lines show the results [12] and [11], respectively. The markers show the experimental results [4].

The velocity increase Eq. (13) is presented in Fig. 1 for the parameter domain $L_t / \lambda_c = 10 - 10^3$ typical for the combustion experiments [4]; the experimental results are shown by the markers. As we can see, the DL instability is of principle importance when the characteristic length scale of the flow (the integral turbulent length scale) exceeds the cut off wavelength of the instability considerably. The obtained analytical results agree rather well with experiments. Still, in order to perform a careful quantitative comparison one has to take into account details of a particular experiment.

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Mixture Preheating Effects in a Bluff-Body Burner

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ABSTRACT

We simulate by means of Large Eddy Simulation a premixed burner consisting in a straight channel (rectangular cross-section) with a prismatic bluff-body (triangular cross-section). In a previous work we simulated this burner without preheating the mixture; we showed the importance of simulating the side wall confinement effect to correctly predict the shortening of the wake and the wall heat transfer. In this paper we simulate the same burner operated with a preheated mixture to show the effect of preheating on flame stabilization and on turbulence – chemistry interaction. We simulate both simple mixing and reacting cases; results are compared with the experimental data. The time-dependent LES results show three-dimensional vortex structures periodically shortening the recirculation zone downstream of the bluff-body and entraining fresh mixture into the hot recirculating region.

INTRODUCTION

A method widely used in combustor to hold and stabilize a turbulent flame consists of creating a recirculation region where oxidation kinetics has sufficient time to burn most or all the fuel. A backward-facing step or a bluff-body are typical flameholder geometries. Combustors with bluff-body flameholders, such that analysed in the present study, are characterized by a shear layer where vortices are shed due to Kelvin-Helmholtz instability [1]. This shear layer separates the regions of high speed fresh mixture from the wake region of lower speed hot products. Turbulence enhances mixing downstream of the bluff-body, stabilizing the flame in an unsteady manner.

We numerically simulate a premixed bluff-body burner built and instrumented by VOLVO-FLYGMOTOR [2,3]. The purpose is to investigate how a flameholder works. We perform LES simulations of the turbulent reacting flow to capture its dynamics; we use the Fractal Model (FM) [4,5] as SGS model for turbulence and chemical kinetics closure. Comparison of numerical results with experimental data validate again the FM itself.

TEST CASE

The burner is a straight channel with a rectangular cross section; the inlet section is used for flow straightening, turbulence control and for fuel and seeding injection. The air entering in the inlet section is distributed over the cross-section by a critical plate that isolates the combustor acoustically from the air supply system. The combustor section ends in a circular duct with a large diameter. The flame is stabilized by means of a typical V-Flameholder whose height is $0.04m$ and width is $0.24m$; this flameholder is centered in the channel, $0.682m$ upstream of combustor exit. A detailed description of the combustor is given in [3].

The fuel is a mixture of propane and air at $600K$ and $\phi = 0.65$ (equivalence ratio); the operative pressure is $1atm$ and the initial combustor pressure is $100KPa$. The inlet flow velocity before bluff-body is $U_{bulk} = 37m/s$, the airflow $0.6Kg/s$ and the Reynolds number $Re = 28000$ based on the hydraulic diameter. This flow condition has been experimentally studied only in the reactive case in [2,3].

NUMERICS

The numerical simulation is made by a 3-D code developed for turbulent, reacting, unsteady flows at low Mach number, parallelized using the MPI procedures. The finite difference numerical scheme is explicit, third order accurate in time and second in space.

Our computational domain starts just downstream of the bluff-body and ends before the sudden expansion in the final part of the combustor; dimensions are $0.24m \times 0.12m \times 0.5m$ (spanwise, height, length). The grid (100x100x150 nodes along X, Y and Z) is structured with nodes uniformly distributed in the X and Y directions; nodes along Z are stretched, the grid becoming coarser towards the burner exit.

Walls are adiabatic and viscous. At the outlet we use the NSCBC (Navier-Stokes Characteristic Boundary Conditions) method [6]; it is particularly useful because it reduce numerical reflection of acoustics waves. At the inlet section we impose the three components of velocity, the flow temperature and composition; pressure is extrapolated by the internal domain. The velocity profile has been derived from a previous simulation that took into account the whole bluff-body triangular shape.

At the start-up of the nonreactive simulation the mixture enters into the burner filled with still air. Transition to turbulence is forced overimposing some disturbances turned off after transition. After we used the nonreactive developed flow as initial condition for the reactive simulation. We ignited the mixture by using a fast chemistry approach, then switched to the two step mechanism proposed in [7].

The SGS model adopted is the Fractal Model, described in [4,5].

RESULTS

Nonreactive Case

We simulated the nonreactive flow to show the effects of combustion on turbulent structures and turbulence dynamics.

Results show that the flow is characterized by a recirculation zone downstream of the bluff-body. The recirculation zone is long approximately $z = 0.09m$ and consists of two counter-rotating vortices asymmetrically shed from the flame-holder edges. These vortices are quickly dissipated after shedding and cause oscillation in the wake. The wake oscillation has a characteristic frequency $f = 522Hz$, whilst the shedding frequency of the two asymmetric vortices is $f = 261Hz$. The shedding Strouhal number ($St = f \cdot h / U_{in}$, where h is the bluff-body height and U_{in} is the inlet velocity) estimated from our simulation is $St = 0.282$. We note that in the actual preheated flow, the Strouhal number and frequency are higher than in the non-preheated flow; in fact, results in [8] show $St = 0.25$ and $f = 105 Hz$ for the nonpreheated flow.

Figure 1 shows an instantaneous axial velocity field in the middle plane of the burner; the streamlines show the coherent structures shed by the bluff-body. The recirculation zone dynamics is not symmetric in the spanwise direction.

The time averaged flow field reported in Fig. 2 is obtained by means of 40 sampled fields corresponding to a time window of 0.067s. The average recirculation zone is characterized by two symmetric counter-rotating vortices whilst instantaneously it has only one eddy (see Fig. 1).

Reactive Case

Starting from the nonreactive simulation we ignited the mixture. Due to combustion the recirculation zone topology and dynamics change (see Fig. 3): its length is approximately $z = 0.14m$, greater than the nonreactive case, and it is characterized by two counter-rotating vortices that pulse asymmetrically without being shed (whilst the nonreactive flow experienced asymmetric shedding). The two eddies stretch each other, produce intense mixing of hot combustion products and fresh mixture and bring them towards the bluff-body; the residence time and temperature are high enough for chemical reactions to take place. Therefore the wake is a hot spot anchoring the flame. Downstream of the bluff-body out of

the reacting zone the flow accelerates up to 50-60 m/s as in the nonreactive flow; acceleration is larger in the wake.

Figure 3 shows an instantaneous temperature field and some streamlines in the middle plane of the burner. Temperature is maximum in the recirculation zone that anchors the flame. The stretching of the two main eddies produces other small structures not present in the time averaged flowfield shown in Fig. 4.

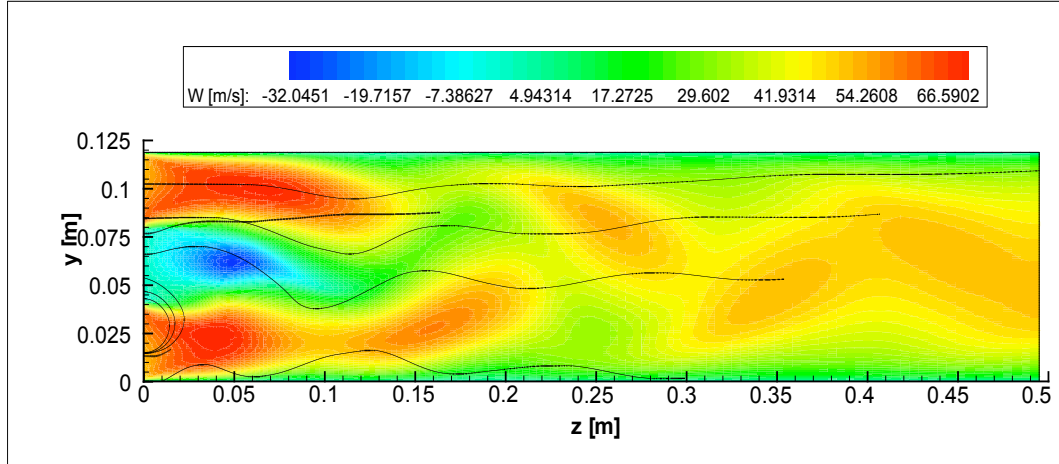


Fig. 1: Instantaneous axial velocity field and streamlines in the nonreactive case.

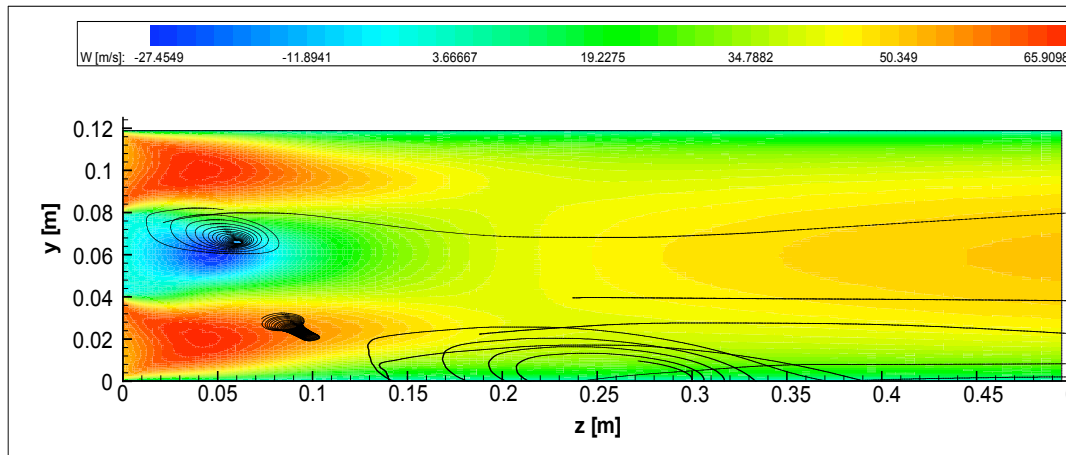


Fig. 2: Time averaged axial velocity field and streamlines in the nonreactive case.

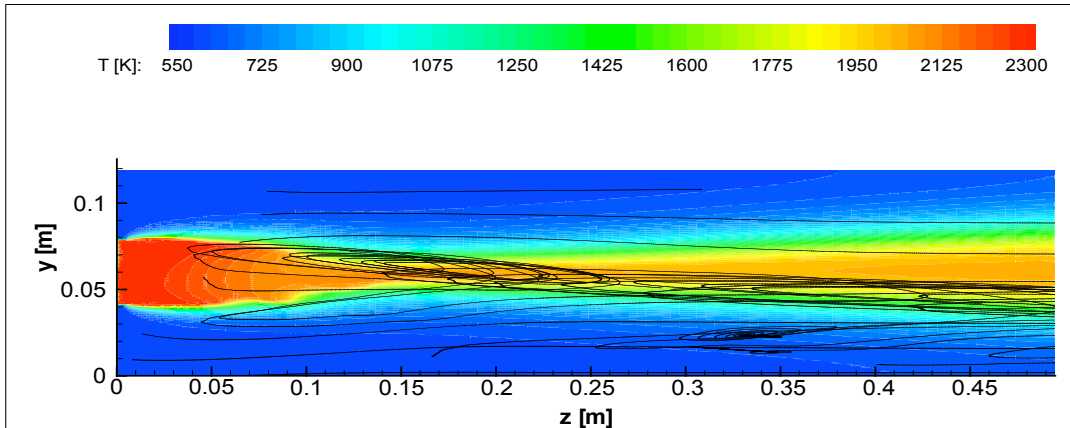


Fig. 3: Instantaneous temperature field and streamlines in the reactive case.

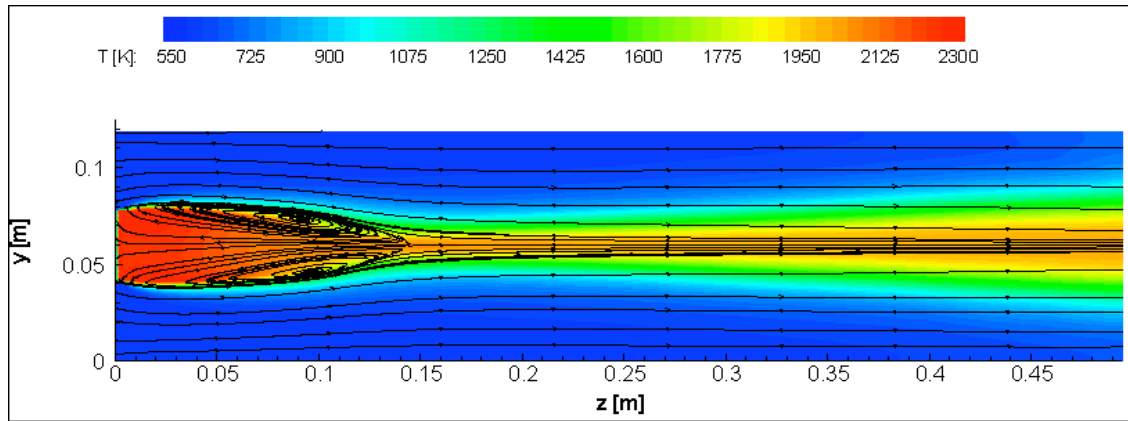


Fig. 4: Time averaged temperature field and streamlines in the reactive case.

Looking at the three-dimensional structure of the recirculation zone we note that its length is greater in the middle plane of the burner due to the side walls effect; therefore the main anchoring is achieved at the center, where the largest heat release takes place. Expansion at this location produces lateral motion of the flow from the side walls towards the center, as shown in Fig. 5. This effect is less evident in the nonreactive simulation.

We note that the actual preheated case does not experience any shedding; the wake oscillates at frequency less than 30 Hz . Instead, nonpreheated flow of a slightly lean mixture at slower inlet velocity in the same burner [8] has characterized by a symmetric shedding at 105 Hz and $St = 0.33$.

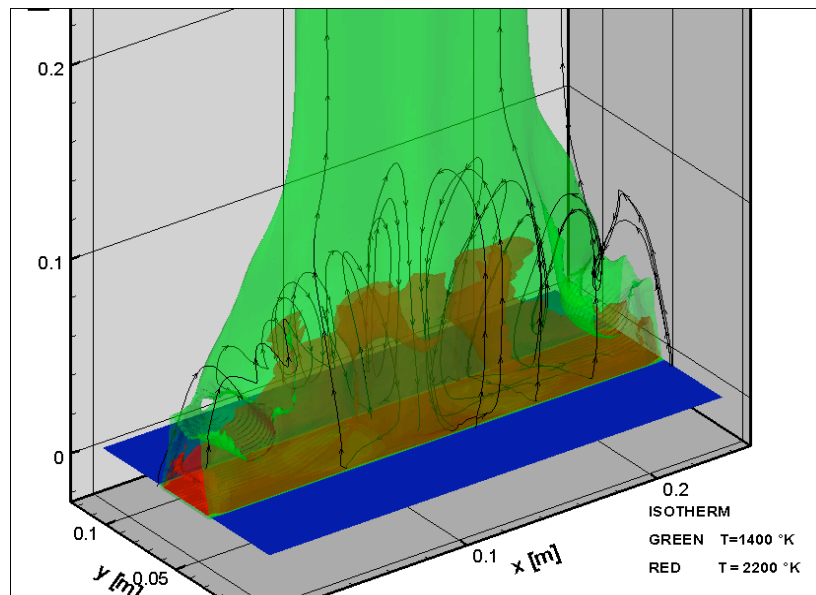


Fig. 5: Instantaneous temperature iso-surfaces and streamlines for the reactive case.

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Modeling Turbulent Reacting Near-Wall Flow

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ABSTRACT

A premixed flame in a turbulent low-Reynolds-number Couette flow has been modeled using the Eddy Dissipation Concept (EDC) for turbulent combustion in conjunction with finite-rate chemistry. The results were compared with direct numerical simulation (DNS) data. The behavior of the standard EDC is shown for both an adiabatic flame and a wall-interacting flame. A proposed low-Reynolds-number version of the EDC shows promising results for this turbulent reacting near-wall flow.

INTRODUCTION

A reacting turbulent flow is strongly influenced by the presence of walls. Close to a wall, the turbulence Reynolds number is, in general, low. To account for such low-Reynolds-number effects, the EDC must be modified. In the present work, the EDC was modified by employing low-Reynolds-number functions similar to those widely used in turbulence modeling of non-reacting flows. This modification was tested on the low-Reynolds-number flame by Alshaalan and Rutland [1, 2]. They presented DNS results of a premixed flame in a turbulent Couette flow by using a single-step chemical mechanism.

MODELING

In EDC, for a single-step reaction, F (Fuel) $\rightarrow$ P (Product), the mean chemical reaction term for the fuel mass fraction can be expressed as [3]

$$-\overline{R}_F = \overline{\rho} \frac{\gamma_\lambda^2}{\tau^*} (Y_F^\circ - Y_F^*), \quad (1)$$

In the standard high-Reynolds-number version of EDC, the mass fraction of fine-structure regions and the reactor residence time is expressed as

$$\gamma_\lambda = 2.1 \left(\frac{\nu \tilde{\varepsilon}}{\tilde{k}^2} \right)^{1/4} \quad \text{and} \quad \tau^* = 0.4 \left(\frac{\nu}{\tilde{\varepsilon}} \right)^{1/4}. \quad (2)$$

The superscripts $^\circ$ represents the surroundings and * represents the fine structures (the values into and out of the reactor). The fine-structure mass fraction, Y_F^* , was found by finite-rate chemistry calculations. Here, a single-step Arrhenius expression (the same as in the DNS calculations) was used to find the specific fuel reaction rate for the reactor.

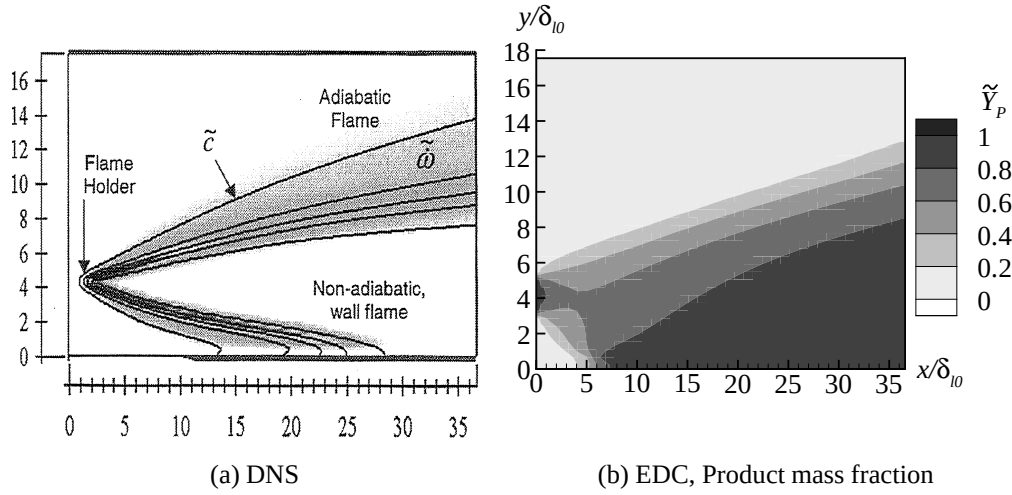


Figure 1: DNS flame picture [2] versus EDC modeled flame

For a turbulent near-wall flow, γ_λ might follow another distribution than the standard expression in Eq. 2 near the wall. For instance [7]

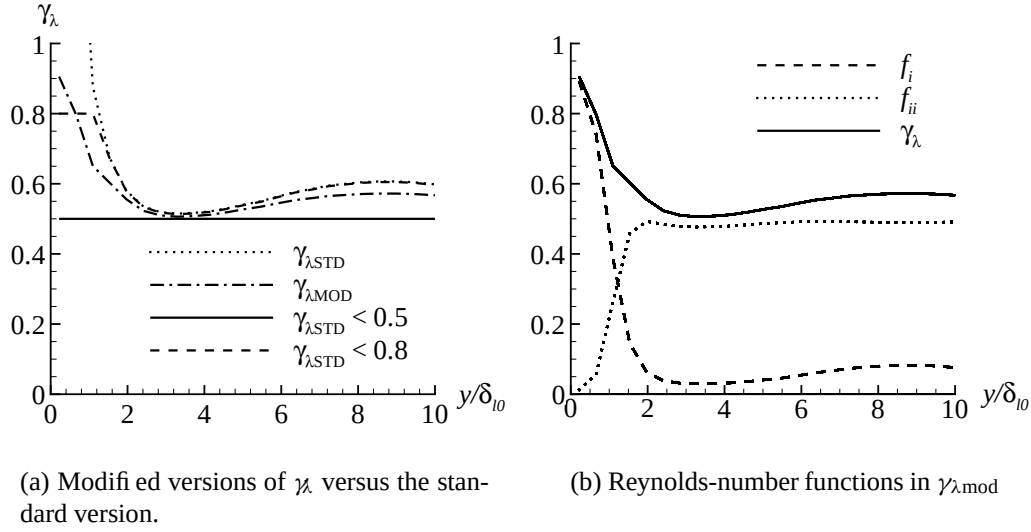
$$\gamma_\lambda = \underbrace{\left(1 - f_1^{1/2} f'_\mu\right)}_{(fi)} + \underbrace{f_2 f_\mu 2.1 \left(\nu \tilde{\varepsilon} / k^2\right)^{1/4}}_{(fii)}, \quad (3)$$

where $f_\mu = \exp(-3.4/(1 + Re_T/50)^2)$ is the Reynolds-number function by Launder and Sharma [5], $f'_\mu = f_\mu^{1.4/3.4}$, $f_1 = Re_T/(Re_T + 0.5)$, $f_2 = Re_T/(Re_T + 1.0)$, and $Re_T = k^2/(\nu \varepsilon)$. When approaching a wall, γ_λ in Eq. 3 approaches unity [7] which means that all of the flow is approaching the fine-structure state. For larger Reynolds numbers ($Re_T > 300$), γ_λ in Eq. 3 will approach the expression in Eq. 2. Based on this assumption, it can be shown that, in conjunction with finite-rate chemistry calculations, the mean chemical reaction rate approaches the reactor reaction rate at the wall. This means that the limiting value of EDC at a wall is a laminar reactor.

Mass-weighted Reynolds-averaged equations were solved for energy, and fuel mass fraction. For these equations, the general gradient model was used with a turbulence diffusivity modeled by a constant turbulence Prandtl or Schmidt number, $\sigma_h = \sigma_Y$. Heat-release effects were not modeled as an attempt to minimize uncertainties in the calculations, since it will serve to decouple the fluid dynamics and the flame. The fluid dynamics data were taken from the DNS results [1]. Hence, the momentum and turbulence equations were not solved. As an effect, the heat released from the flame will have no effect on the flow (which was held constant like the DNS flow).

CASE DESCRIPTION

The flame configuration is shown in Fig. 1(a), The flame is premixed and similar to a methane-air combustion near the lean flammability limit. It is V shaped and held in position by a flame holder, where one branch of the flame is far away from the wall, and the other branch is interacting with the cold lower stationary wall. The Reynolds number based on the half channel width and the mean velocity was $Re_H = 504$.


 Figure 2: The modified γ_λ and the Reynolds-number functions.

RESULTS AND DISCUSSION

The predictions were performed using the general-purpose CFD code Spider. Spider is an elliptic solver which is based on finite volumes and non-orthogonal curvilinear computational mesh. A two-dimensional 42×42 Cartesian mesh was employed in the present calculations. Figure 1(b) shows contour profiles of the product mass fraction $\tilde{Y}_P = 1 - \tilde{Y}_F$ from the calculations using the modified γ_λ in Eq. 3. Note that the inlet boundary coincides with the axial location $x/\delta_{l0} \approx 2$ in the DNS calculations (cf. Fig. 1(a)).

The upper branch seemed to spread at a reasonable rate, whereas the wall flame was spread too fast towards the wall compared to the DNS flame (Fig. 1(a)). The exclusion of the effects due to heat release will have some effect on the underprediction of the wall flame. Since density was held constant in the present computations, the heat released from the flame had no effect on the flow. The expansion from the flame would probably push it away from the wall. This can also be seen in the DNS flame (Fig. 1(a)). The deflection of the branches is probably due to the heat release. In the EDC predictions, the branches follows a straight line, which shows that there are no heat-release effects. Also, uncertainties in the inlet conditions may lead to some discrepancies. The eddy viscosity in the gradient models was adjusted for the low-Reynolds-number effects close to the wall by employing the Reynolds-number-function by Jones and Launder [4]. Other functions (such as the one by Launder and Sharma in Eq. 3) gave similar results. This indicated that the diffusion model provided sufficient accuracy for the present case.

For high-Reynolds number flows, a certain upper limit, $\gamma_\lambda < 0.5$, is normally introduced to avoid excessive reaction rates in the low-Reynolds-number regime (e.g. near walls). From these considerations, and since the presumptions of the standard model were broken for the present flow, the effects of introducing two different upper limits on γ_λ were investigated and compared to the results from using the modified version in Eq. 3. First, an upper limit of 0.5 was applied for γ_λ . Second, an upper limit of 0.8

was introduced since it was found that γ_λ was greater than 0.5 for most of the flow. Previous work have indicated that $\gamma_\lambda > 0.5$ may be unrealistic. However, the present work showed that allowing γ_λ to increase above this value gave more reasonable results for most of the flame (cf. Fig. 2(a)). Introducing $\gamma_\lambda < 0.5$ gave less reasonable results for the flame away from the wall, but predicted a more reasonable wall flame than the other two approaches. For this case, the reaction rate for the rest of the flow was more underpredicted than for the other cases. Introducing $\gamma_\lambda < 0.8$ gave more reasonable results for the flame away from the wall, but over-predicted the reaction rate towards the wall. The proposed model in Eq. 3 seemed to give more reasonable results for the wall flame compared to $\gamma_\lambda < 0.8$, otherwise these two cases gave almost similar results. Compared to the $\gamma_\lambda < 0.5$ case, the proposed version gave a more reasonable flame away from the wall, but the wall flame was spread even faster towards the wall. This was due to the higher rate of γ_λ near the wall (cf. Fig. 2(a)).

Figure 2(a) shows that the Reynolds-number functions kept γ_λ at a somewhat lower level than the standard γ_λ . The modified γ_λ increased towards unity when approaching the wall. It seems as if the modified version held γ_λ at a more reasonable level in the buffer region (the region $1 < y/\delta_{l0} < 2$) compared to the $\gamma_\lambda < 0.8$ case. The plot of the Reynolds-number functions in the proposed modification of γ_λ (Fig. 2(b)), shows that they behave as expected and as discussed in [7]. Thus, this might be a possible path towards an extended EDC capable of predicting turbulent reacting near-wall flows.

CONCLUSIONS

The behavior of EDC in conjunction with finite-rate chemistry, for a turbulent premixed flame interacting with a wall, including low-Reynolds-number effects, was shown and compared to DNS results. The predictions show that the proposed low-Reynolds-number version of EDC might be a way to extend the model to turbulent reacting flows near walls.

ACKNOWLEDGEMENTS

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A Time-scale Analysis of Hydrogen Mixtures Combustion under Diluted Condition

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INTRODUCTION

Several applications of the mild combustion technique are currently being proposed with the aim of employing it in the different fields of the process industry as well as to various types of energy production and conversion plants. One of the most interesting is the accomplishment of gas-turbine systems where the numerous and peculiar advantages of this combustion modality are particularly desirable. However the present state of understanding of the mechanisms by which the mild combustion regime establishes and maintains stably needs some further analysis to prove the successful application to gas turbines and to different fuels. To this end some recent studies addressing the necessity of a deeper insight in the physical and kinetic aspects have pointed out on one side the fundamental role of the ignition chemistry of the fuel [1], on the other side the relevance of internal recirculation patterns and hence of a proper choice of both the geometry of the combustion chamber and the inlet velocities of fuel and air [2]. In particular the possibility of achieving a mild condition even starting from the reactants at ambient temperature has been experimentally demonstrated, thus giving evidence to the fact that the instauration of this kind of regime is possible provided that the chemical time scale inside the combustion chamber is comparable to the time scale of the flow, being this the condition that leads to the perfectly stirred configuration [3].

In the perspective of the exploitation of hydrogen and hydrogen containing mixture as novel fuels, over which there is increasing attention as future energy vectors to solve pollution related problems and to meet energy savings requirements, our work focuses on a time scale analysis of the two competing phenomena, i. e. oxidation kinetics and mixing process between fuel and oxidant streams. Being able to quantify the degree of interaction between them is indeed the key to choose the proper design parameters in order to avoid falling into the instable flame region which has been experimentally drawn only for a few fuels, such as methane [4].

The analysis presented by Oberlack [7] points out that the steady-state temperature in the mild regime depends monotonically on the Damköhler number, which was based on the residence time inside a perfectly stirred reactor. To simulate turbulence fluctuations a statistical perturbation of this parameter was introduced and to allow simple calculations a one-step kinetics was assumed. In this work it is also methane considered.

Our object was that of numerically drawing the limits of the probable stable mild operation for CO/H₂ – air and H₂ – air, for which no experimental diagram have been presented yet. The issue seemed us worth discussing in light of the considerable difference in the ignition kinetics between methane and hydrogen. Moreover some experimental data on diluted hydrogen – air combustion in counter-flowing configuration have revealed a significant deviation of the temperature vs Damköhler number curve from the S-shape [6].

CALCULATION METHOD

The simplest approach to the problem was that of performing numerical simulations of the combustion of H₂-air, CO/H₂-air under diluted conditions by means of the Partially Stirred

Reactor model available in the Chemkin 3.7 package. It has been experimentally demonstrated that the main process parameters in the mild regime can be reasonably predicted with the assumption of the perfectly stirred reactor model [3]. Actually a significant deviation exists from this ideal behaviour, due to the non-ideal mixed state of the reactants in a diffusive burner, so that information on the fluid dynamic behaviour is required. The PASR model enables us to account for the turbulence-chemistry interactions, without the need of spatially solving the fluid-dynamic field, as well as to adopt extensive kinetic mechanisms. The effect of turbulence is simply represented by a frequency of mixing, which is related to turbulent scalar dissipation rate and hence directly comparable with values from CFD computations. This has obviously a limitation, in that for each calculation we are representing a complex fluid dynamic field using a single value of the scalar dissipation rate. Nonetheless this is an effective tool for our stability analysis, in so much as the hypothesis of homogeneous and isotropic turbulence holds in the fine scales where the chemical reactions take place.

The mean thermo-chemical properties inside the reactor are assumed to be spatially homogeneous but imperfectly mixed at the molecular level. Composition and temperature are described by a probability density function which is derived from the joint velocity-composition PDF [5]. The solution for the density-weighted $P(\psi, t)$ is found by means of a Monte Carlo method, for which we adopted a large number of particles (more than 2000) in order to minimize statistical errors. With reference to the micro-mixing model we choose the IEM model. Several studies dealt with the performance of different mixing models, namely the Curl model, the modified Curl model and IEM model, and it was shown the full agreement between the results obtained with all these.

BOUNDARY CONDITIONS

We selected a reference value of 100 KW for the power of the burner, since an experimental facility suited for this size of combustors is currently under construction in our laboratory.

We considered two different fuel mixtures, one is composed of a 50% vol. of H₂ in N₂, the other is CO/H₂/N₂ in proportion 28/32/40 % vol., which can be representative of a syngas type fuel. The oxidant is vitiated air, whose composition results from the dilution of atmospheric air with the burned gas of a stoichiometric fuel-air mixture, so that also a value of the recirculation ratio can be assigned. As a matter of fact between fresh air and flue gases we assumed the simplified hypothesis of their instantaneous mixing down to the molecular level, considering that the transport phenomena related to the mixing between fuel species and oxidant species are the most limiting ones.

The kinetic scheme comprehends 17 chemical species and 58 reactions, which account for the NO_x formation-destruction paths fully.

RESULTS

Three values for the residence time were considered: 10 ms, 100 ms and 1 s. The mixing time was made to vary between 1E-5 and 1E-1 s so as to span the more relevant values expected in practical devices.

The steady state adiabatic temperatures of the reactor are reported in Figure 1 for the case of CO/H₂/N₂ as fuel. The same series of calculation has been performed with H₂/N₂ as fuel. For this latter mixture the computation has been carried out also at 20 bar.

Based on the above-mentioned fluid dynamics times, two distinct Damköhler numbers can be defined [8]: $Da_{mix} = \tau_{mix}/\tau_{chem}$ and $Da_{res} = \tau_{res}/\tau_{chem}$. The characteristic chemical time was calculated as the time delay corresponding to a 100 K increment in the initial temperature of the premixed reactants. The Da_{res} number ranges from a minimum value of 10 to a maximum of 10000, while the Da_{mix} number varies between 0.01 and 1000.

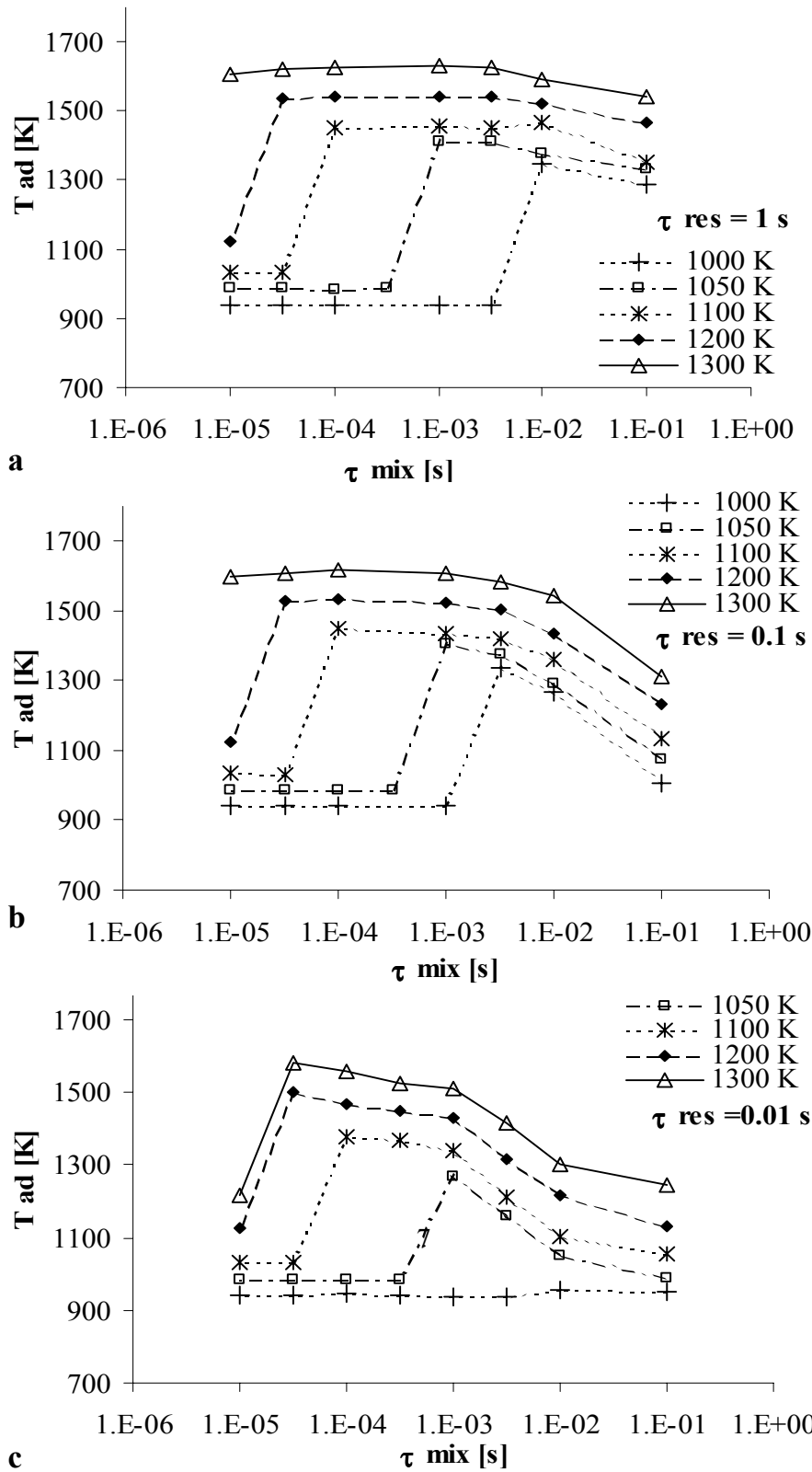


Fig. 1 Reactor temperature [K] versus mixing time [s] for different values of the oxidant pre-heating temperature. The fuel is a 28/32/40 [vol.%] mixture of CO/H₂/N₂. The equivalence ratio is unitary. O₂ molar fraction is equal to 6 % in the oxidant stream.

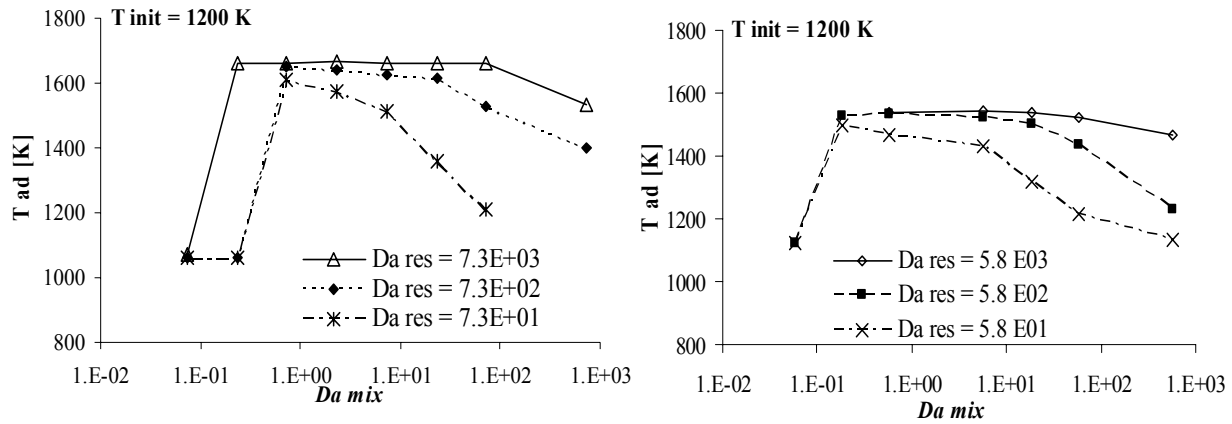


Fig. 2 Reactor temperature vs mixing-time-based Damköhler number. Right side: H₂/N₂. Left side: CO/H₂/N₂.

In these interval we could point out the conditions in which a strong turbulence-chemistry interaction exists as is the case at the lower initial temperatures of the reactants and with the lower residence times. Higher initial temperatures, as well as longer residence times, lead to a greater stability. With a temperature pre-heating of 1200 K and a residence time of 100 ms, the combustion process becomes nearly insensitive to the turbulence fluctuations, even for extremely high strain rates, whereas a conventional flame would extinguish.

In the case of the H₂/N₂ mixture the same behaviour can be observed (figure 2), except for a slightly more extended interval of stability over the mixing time. As a matter of fact the degree of dilution of the fuel itself and of the oxidant stream is so high that the characteristic chemical time is of the same order of magnitude of the syngas-type fuel above considered.

As far as the pressure effect is considered, the stability region becomes slightly narrower with increased pressure.

CONCLUSIONS

We have reported a numerical analysis of the turbulence-chemistry interactions in the combustion of CO/H₂ and H₂/N₂ mixtures under diluted condition. Due to the relatively long chemical times of the diluted combustion quite long residence times, if compared to those in the conventional systems, are requested. Instabilities are then avoided even when the strain rate ($\sim 1/\tau_{\text{mix}}$) is greater than 10 E4.

The present analysis needs now to be extended with regard to the fuel composition, by considering richer-in-H₂ mixtures, and to the pressure, in order to obtain a more complete evaluation for the conditions of interest for gas turbine applications. The results of our calculations are relevant in the preliminary evaluation of possible flow patterns and geometrical configuration for combustion chambers, in which mild combustion of H₂-containing fuels can be successfully accomplished.

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Boundary conditions in subsonic compressible Navier-Stokes flows

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ABSTRACT

In the present work the boundary condition problem for subsonic compressible reacting flows is addressed. In particular, the focus is set on local boundary condition models based on the application of the one-dimensional theory of the characteristics to the Favre-averaged Navier-Stokes equations, coupled with EDC combustion model, for both time-dependent and steady-state numerical simulations. For the latter typology of problems the “absorbing” layer concept has been coupled with the aforementioned characteristic-based models.

The models presented in this paper, developed in the frame of a Finite Volume in-house code, have been tested on a time-dependent reacting case, where the combusting region crosses the boundary without introducing any sensible disturbance in the computational domain. Also, the application of the boundary models to one steady-state reacting problem is presented.

NON REFLECTING BOUNDARY CONDITIONS

The proper specification of boundary conditions is a crucial problem in the numerical solution of low-Mach compressible flow fields. The Navier-Stokes equations require one boundary condition at subsonic outflow boundary 0, usually the static pressure. Although this leads to a well posed problem, it also generates pressure disturbance reflections in the domain, thus affecting the convergence to steady-state solution. The most cost-efficient way to deal with this problem is the specification of a suitable non reflecting boundary condition; in the present work the focus has been put on local boundary techniques.

A mathematical treatment for non-reflecting boundaries in hyperbolic equations has been developed by 0. Because the Navier-Stokes equations are non-linear and non-hyperbolic, the results of the aforementioned paper cannot be applied directly. From the analysis of the linearized inviscid equations, based on the work from 0, in 0 a non-reflecting characteristic-based boundary condition for the non-linear one dimensional inviscid Navier-Stokes equations is obtained:

$$\frac{\partial p}{\partial t} - \rho c \frac{\partial u}{\partial t} = 0 \quad (1)$$

It has been shown that outgoing waves produce no reflections if the boundary treatment in 0 is adopted. It is worth to notice that the steady state solution is dependent on the initial data and, therefore, this treatment may be unsatisfactory if a steady-state solution is sought. A further development of the work in 0 can be found in 0, 0. In particular, a non reflecting boundary condition technique is proposed for problems focused on the steady-state solution:

$$\frac{\partial p}{\partial t} - \rho c \frac{\partial u}{\partial t} + \alpha(p - p_{\infty}) = 0. \quad (2)$$

The introduction of the term $\alpha(p - p_{\infty})$ accounts for the physical feedback that the non-

modelled region outside the computational domain exercise on the computational domain itself. The optimal value for α is case dependent. As far as the inlet boundary condition is concerned, in 0 a zero-th order extrapolation of the outgoing characteristic variable for the linearized system of equations is introduced:

$$\Delta p - \rho c \Delta u = 0. \quad (3)$$

In the present work the equations (2) and (3) have been used for simulations focused on the attainment of steady state solution, while the equations (1) and (3) have been used for simulations focused on transient phenomena. Also, the absorbing layer concept has been implemented in the same frame. In particular a fourth-order filter, based on the Rhie and Chow filter (0), has been adopted in a buffer region along the wall boundaries:

$$\frac{\partial \phi}{\partial t} = RHS(\phi) + F(\phi), \quad (4)$$

where RHS is the usual right hand side of the governing equations and F is the filter. The fourth-order filter has the following form:

$$F(\phi) = A \frac{\Delta x^4}{\Delta t} \frac{\partial^4 \phi}{\partial x^4}, \quad (5)$$

where Δx is the size of the cell, Δt is the time step and A is the filter constant.

TEST CASES

The test cases presented in this section are:

- the unsteady compressible reacting simulation of a two dimensional channel, with the focus being put on the interaction between flame front region and non reflecting boundary;
- the transient compressible reacting simulation of a two dimensional combustor, with the focus being put on the attainment of a steady-state solution.

In the presented test cases the EDC combustion model (0, 0, 0) coupled with the infinitely fast chemistry assumption has been adopted. All cases have been solved with a fourth order Runge-Kutta solver, with a fixed CFL=1.0

Two dimensional unsteady reacting channel

In Figure 1 the two dimensional reacting channel geometry and case set-up are presented:

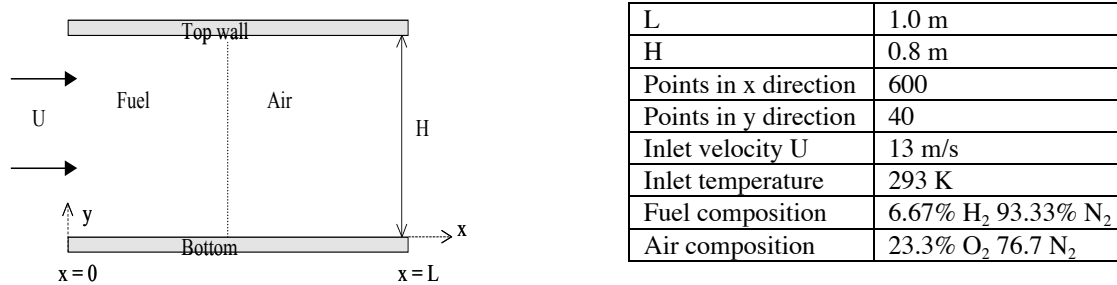


Figure 1: 2 dimensional reacting channel geometry and set-up

In Figure 2 the density profiles at longitudinal centreline are presented, while in Figure 3 the temperature profiles at longitudinal centreline are presented. It can be noticed that the flame front, corresponding to the low density region, appears to cross the outlet boundary without any major reflections.

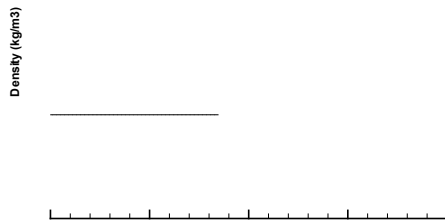


Figure 2: Density profiles at center line

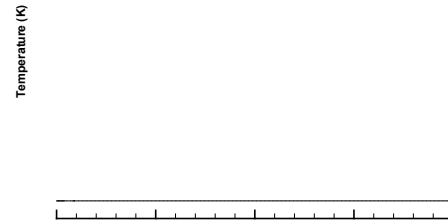


Figure 3: Temperature profiles at center line

Two dimensional combustor

In **Figure 4** the two dimensional combustor geometry and case set-up are presented:

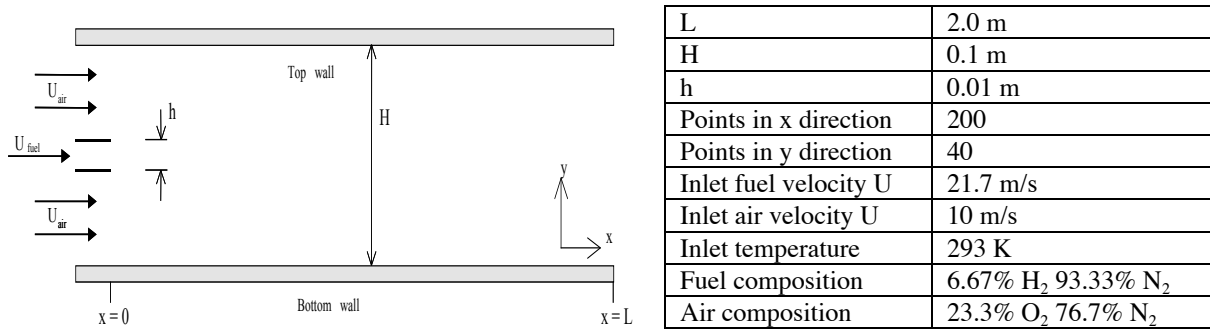


Figure 4: 2 dimensional combustor geometry and set-up

In the presented simulation an absorbing layer with variable filter constant has been modelled on each wall, with a thickness of 12.5 millimetres, and on the inlet, with a thickness of 30 millimetres. The absorbing layer efficiently smoothes out the fluctuations near the walls and the inlet of the y component of velocity and the adoption of variable filter constant allows the attainment of accurate solutions in the far-from-wall region. In Figure 5 the temperature contours are presented.

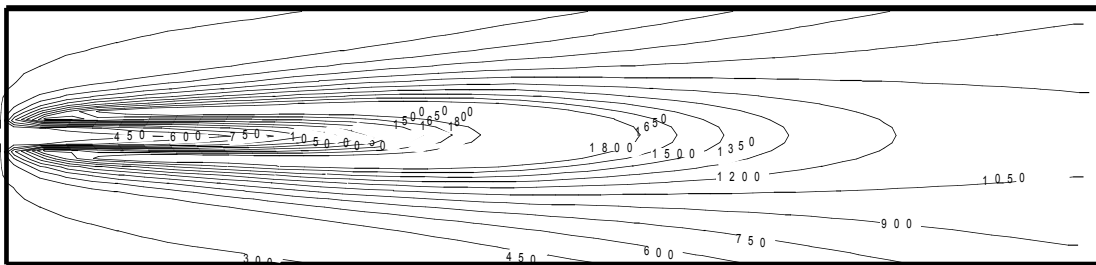


Figure 5: Temperature contours

In Table 1 the convergence characteristics of the presented case are shown:

Table 1: Convergence characteristics

Boundary condition type	Time steps to convergence
-------------------------	---------------------------

Reflecting BC's	no convergence after 400000 time steps
Non reflecting BC's w/o absorbing layer	167000
Non reflecting BC's w absorbing layer	60000

In the simulations with non reflecting boundary conditions a value of 0.2 was used for the parameter α .

CONCLUSIONS

In the present work two boundary condition models, based on the one dimensional theory of the characteristics, are applied to reacting low Mach compressible flows. Also, the absorbing layer concept has been adopted as a mean to damp pressure disturbances in the cases where a steady state solution is sought.

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RANS, LES and Hybrid RANS/LES Turbulent Premixed Combustion TFC Model

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Introduction

The problem of premixed combustion modeling at developed turbulence and fast chemistry for prediction of averaged combustion rates and species fluxes is so called *turbulent combustion challenge*. Two main reasons are at the base of the challenging problem:

- Instantaneous combustion takes place in thin flame sheets with non-laminar flamelets and developed wrinkle structures depending on unresolved by model equations small-scale turbulence-chemistry coupling.
- The progress variable flux (and hence the heat and chemical species fluxes) in premixed flames is as a rule counter-gradient in the most part of flame with transition from the gradient transport along the flame in spite of observed increasing flame brush.

In the TFC (turbulent flame closure) model resolution of this difficulty is based in fact on developed Kolmogorov ideas successfully used in turbulence modeling. Realization of them has specifics in the cases RANS, LES and hybrid RANS/LES formulations of the model.

RANS TFC combustion model formulation

We assume that not only Kolmogorov small-scale turbulence[1] controlling in our model the transport in the thickened flamelets is equilibrium but also equilibrium is the hydrodynamics structure of small-scale flamelet wrinkles giving at strong turbulence the main contribution in the sheet area. So there are equilibrium thickened flamelet speed $S_f > S_L$, width $\delta_f > \delta_L$, the dimensionless flamelet sheet area $(\bar{F}/F_0)$ and hence $U_t = U_f(\bar{F}/F_0)$ are controlled by large-scale turbulent parameters u' , L and the characteristic chemical time $\tau_{ch} = \chi/S_L^2$ (χ is the molecular heat transfer coefficient).

The TFC model [2, 3] yields the theoretical expressions for these parameters:

$$U_f \approx u' \cdot Da^{-1/2}, \delta_f \approx L \cdot Da^{-3/2}, u'_f \approx u' \cdot Da^{-1/2}, \chi_f \approx D_t(Da)^{-2}, (\bar{F}/F_0) \approx (Da)^{3/4} \quad (1)$$

and the final expression for the flame speed U_t that is used directly for the equation closure

$$U_t = U_f(\bar{F}/F_0) = A \cdot u' \cdot Da^{1/4} = A \cdot u'^{3/4} S_L^{1/2} \chi^{-1/4} L^{1/4} \quad (2)$$

The exact unclosed the progress variable Favre averaged $\tilde{c}$ – equation (Eq.3) and the model TFC equation (Eq.4) are the following:

$$\begin{aligned} \frac{\partial \bar{\rho} \tilde{c}}{\partial t} + \frac{\partial \bar{\rho} \tilde{u}_i \tilde{c}}{\partial x_i} &= - \frac{\partial \overline{\rho u_i'' c''}}{\partial x_i} + \bar{\rho} \tilde{W} \quad (3) \\ &\quad \downarrow \quad \quad \quad \downarrow \quad \quad \quad \downarrow \\ \frac{\partial \bar{\rho} \tilde{c}}{\partial t} + \frac{\partial \bar{\rho} \tilde{u}_i \tilde{c}}{\partial x_i} &= \frac{\partial}{\partial x_i} \left(\bar{\rho} D_t \frac{\partial \tilde{c}}{\partial x_i} \right) + \rho_u U_t |\nabla \tilde{c}| \quad (4) \\ &\quad \downarrow \quad \quad \quad \downarrow \quad \quad \quad \downarrow \\ &\quad \text{GTD} \quad \quad \quad \text{CGT} \quad \quad \quad \text{Actual source} \quad \quad \quad \text{Model source} \end{aligned}$$

In Equations $Da = \tau_t / \tau_{ch} \gg 1$ is the Damköhler number, $\tau_t = L / u'$ is the characteristic turbulent time, u'_f and χ_f are the characteristic turbulent pulsation and turbulent transport inside the flamelet, $D_t \approx u' L$ is the turbulent diffusion coefficient. Empirical parameter $A \approx 0.5$ is approximately the same for tested in [4] gas fuels CH_4 , C_2H_6 , C_3H_8 and H_2 .

Though the final aim of turbulent combustion modeling in the context of the $\tilde{c}$ variable is to simulate all variables of the unclosed equation (Eq.(1)), i.e. fields of Favre or Reynolds averaged $\tilde{c}$, the flux $\overline{\rho u_i c}$, $\bar{\rho}$, $\tilde{u}_i$, the reaction (source) term $\bar{\rho \tilde{W}} = \bar{\rho \tilde{W}}$ (and hence also $\tilde{T}$ and the main species $\tilde{Y}_i$ that ignoring contribution from thin flamelet sheet are equal to $\tilde{T} = T_u(1 - \tilde{c}) + T_b \tilde{c}$ and $\tilde{Y}_i = Y_{ui}(1 - \tilde{c}) + Y_{bi} \tilde{c}$ where indexes "u" and "b" refer to unburned (cold reactants, $\tilde{c} = 0$) and burned (chemically equilibrium products, $\tilde{c} = 1$) gases. The model TFC equation Eq. (4) used in simulations together with the "k-ε" turbulence model equations describes directly only the fields of the density $\bar{\rho}(\vec{x}, t)$, velocity $\tilde{u}(\vec{x}, t)$ and the progress variable $\tilde{c}(\vec{x}, t)$ (and hence the fields of $\tilde{T}(\vec{x}, t)$ and $\tilde{Y}_i(\vec{x}, t)$). Obviously Eq. (4) does not describe actual transport and source in Eq. 3 as the transport $\overline{\rho u_i c}$ was presented as a sum of the gradient turbulent diffusion (GTD) and the pressure driven counter-gradient transport (CGT) and the latter was included in the model source term [3]. We developed a gasdynamics model for CGT assuming that total pressure of cold reactants is constant in flame that gave an opportunity to estimate the actual flux $\overline{\rho u_i c}$ and source $\bar{\rho \tilde{W}}$ [5].

LES TFC combustion model formulation

In large eddy simulations (LES) of the premixed flamelet combustion we describe obviously not the actual instantaneous thickened flamelet sheet but an instantaneous smoothed (averaged on the subgrid level) flame sheet. The turbulence controlling this flame characteristics is the subgrid turbulence and its parameters depend also on used mesh size Δ . In principle two main ideas could be used for estimation of the subgrid turbulence. The first is based on the Kolmogorov idea of equilibrium of the small-scale turbulence that is controlled by the large scale turbulence. The second idea proposed by Smagorinsky connected the turbulence parameters with local characteristics of the smoothed velocity field.

Assuming well known Kolmogorov equilibrium inertial interval $E(k) = C \varepsilon^{2/3} k^{-5/3}$ [1] we can estimate the turbulent subgrid turbulent velocity and scale

$$u'_\Delta \approx \int_{1/\Delta}^{\infty} E(k) dk \approx \varepsilon^{1/3} \Delta^{1/3}, \quad L_\Delta \approx \int_{1/\Delta}^{\infty} k^{-1} E(k) dk / \int_{1/\Delta}^{\infty} E(k) dk \approx \Delta \quad (5)$$

and hence the subgrid turbulent transport coefficients are equal to

$$D_\Delta \approx \nu_\Delta \approx \chi_\Delta \approx u'_\Delta L_\Delta \approx \varepsilon^{1/3} \Delta^{4/3} \quad (6)$$

Using for estimation of the subgrid flame speed these turbulent parameters and applying them in Eq.(2) we have the expression for the flame speed in the model LES equation

$$U_t^\Delta = U_f(\bar{F}_\Delta / F_0) = A^* u'_\Delta S_L^{1/2} \chi^{-1/4} \Delta^{1/4} [\approx U_t(\Delta / L)^{1/2}] \quad (7)$$

We notice that justification of Eq. (7) is worse than Eq. (2). The difficulty in using in LES these estimations is connected with the fact that we do not know the field of averaged dissipation rate $\varepsilon(\vec{x}, t)$. So in actual LES for estimation of the subgrid turbulence is widely used in fact Plandtl type model Smagorinsky model[6] that connected this turbulence with the resolved in LES strain-rate tensor $\tilde{S}_{ij}$ and the mesh size Δ

$$u'_\Delta \approx \Delta |\tilde{S}|, \quad D_\Delta \approx \nu_\Delta = (c_s^\Delta \Delta)^2 |\tilde{S}|, \quad |\tilde{S}| \equiv (2\tilde{S}_{ij}\tilde{S}_{ij})^{1/2}. \quad (8)$$

Hybrid RANS/LES TFC combustion model formulation

Described in previous two paragraphs RANS and LES formulations of the TFC model is presented, for example, in the commercial codes Fluent. Here we present the RANS/LES approach. The main idea: not LES instead of RANS simulation but together. Namely the first step is RANS simulation, the second step is LES using RANS fields of the turbulent energy $\tilde{k}(\vec{x}, t)$ and the dissipation $\tilde{\varepsilon}(\vec{x}, t)$ for estimation in LES the subgrid transport coefficient and the combustion rate. Motivation is the following. RANS is more appropriate for simulations of the averaged fields and justifiably models combustion rates using the Kolmogorov ideas of equilibrium. But in spite of less justified combustion rates modelling LES have obvious advantages as it describes more realistic hydrodynamics including the large-scale vortex structure. The combustion model equations used for simulations presented below together with the standard " $k - \varepsilon$ " model were the following:

$$\frac{\partial \tilde{\rho} \tilde{c}}{\partial t} + \frac{\partial \tilde{\rho} \tilde{u}_i \tilde{c}}{\partial x_i} = \frac{\partial}{\partial x_i} (\tilde{\rho} D \frac{\partial \tilde{c}}{\partial x_i}) + 0.3 \rho_u \tilde{k}^{3/4} \tilde{\varepsilon}^{-1/4} \chi^{-1/4} S_L |\nabla \tilde{c}| \quad (9)$$

where in RANS simulation $D = D_t = 0.09 \tilde{k}^2 / \tilde{\varepsilon}$ and in LES $D = D_\Delta = 0.05 \tilde{\varepsilon}^{1/3} \Delta^{4/3}$. In simulations we assume the model source the same in RANS simulations and LES i. e. we ignore the effect of smooth wrinkles in LES U_t and it gave an opportunity to yield additional empirical constant using in LES Eq. 7.

In figures we show result of simulations for the P. Moreau experimental test case [7]. Fig.1 demonstrate reasonable agreement between RANS simulation (lines of $\tilde{c} = const$ and profiles $\tilde{c}(y)$) and associated LES P. Moreau (1977) experiment (comparison of RANS simulation with the experimental data was published in [8]). Fig.2 show $\tilde{c}$ – and $\tilde{z}$ – fluxes in y direction obtained directly from LES. These direct results (without transport modeling) means: In the same cross sections of the flame $\tilde{z}$ – flux (turbulent diffusion) is gradient while $\tilde{c}$ – flux is counter-gradient. In spite of it the flame brush ($\tilde{c} = const$ lines) in LES has increasing width that is in agreement with RANS simulation obtained using " $k - \varepsilon$ " model.

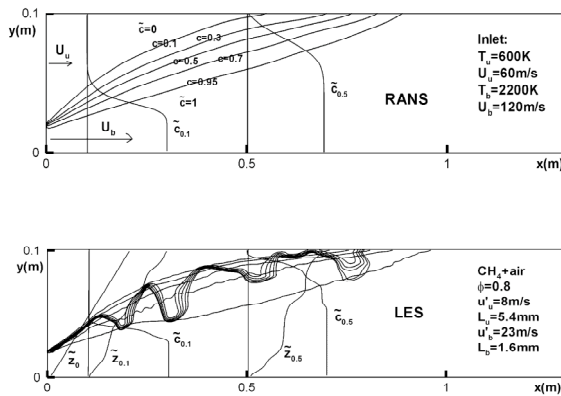


Fig.1: Instantaneous and averaged lines and profiles of $\tilde{c}$ and the passive concentration $\tilde{z}$

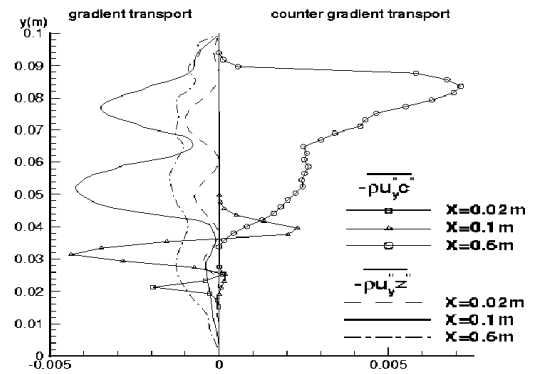


Fig.2: Transport term of $\tilde{c}$ and $\tilde{z}$ in y direction

We present also numerical RANS/LES of combustion behind a stabilizer, Fig.3 [9]. The model is able to resolve vortex shedding giving good estimation of the width of circulation zone. Parameters of the reactants are: $u = 18m/s$, $T = 288K$, $\Phi = 0.65$.

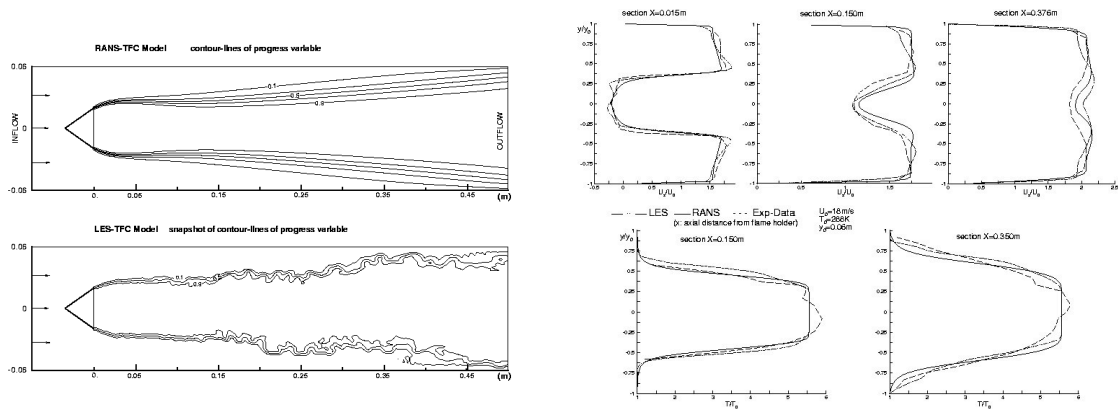


Fig3 Contour-lines from RANS and instantaneous LES and comparison with the experiment

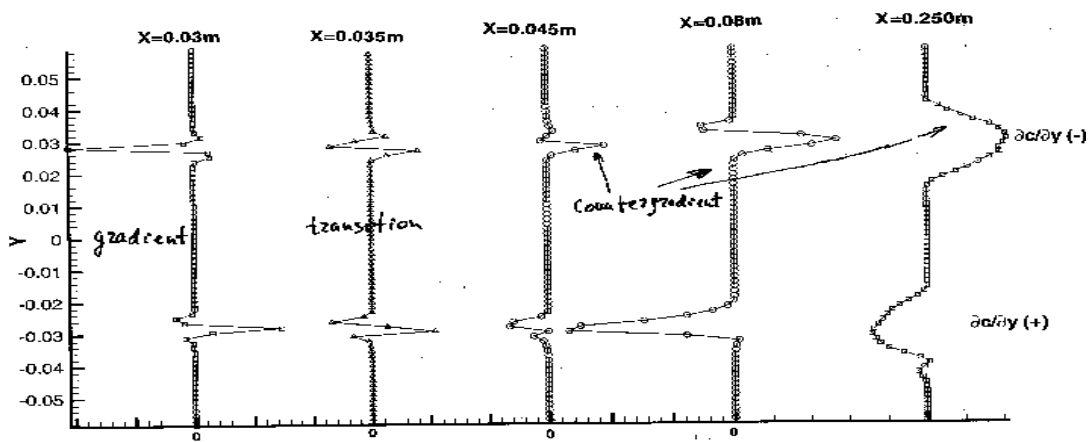


Fig. 4 Transition from gradient to counter-gradient transport of the flux $\overline{\rho u_y'' c}$ along the flame (x is the distance of the section from the flame holder)

Conclusion

We believe that developed hybrid method for premixed flames yielding both RANS averaged fields and LES filtered instantaneous fields could be effective for modeling of gasturbine combustion including (in future) prediction of the unsteady combustion regimes. This method could be useful for RANS simulation of the averaged ICE cycle with further prediction of cyclic variations using LES base on the results of RANS simulation.

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Numerical Simulation of a Hydrogen Nonpremixed Turbulent Flame

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ABSTRACT

A non-premixed hydrogen-air burner is numerically simulated in this work. The burner, arranged vertically, is of annular type, consisting in a central fuel tube and a two concentric air tubes with different velocities. The Reynolds number, based on the fuel jet, is 8830, which correspond to a velocity of 100m/s. A large-eddy simulation has been applied to the calculation, using a conserved scalar formalism; the filtered Navier-Stokes equations have been closed using the Smagorinsky-Lilly SGS model. An assumption of equilibrium chemistry has been employed to express the thermo-chemical variables as function of conserved scalar. The time-dependent LES results of the thermal-fluid-dynamic fields show periodical separation of flame tip. The observation suggest that buoyancy forces have significant impact also in turbulent flames. Finally the LES results are compared with RANS computations and experimental data [1].

INTRODUCTION

Motivation

The objective of this work is to understand both mean and instantaneous (time-dependent) structure of a non-premixed turbulent flame in a simple coflow configuration.

Large-eddy simulation (LES) is a method of great potential for the simulation of turbulent flows because fluctuations are resolved down to the filter width.

The treatment of the chemical source term in the filtered species transport equation can be avoided using a conserved scalar formalism in the case of non-premixed combustion [2]. The mixture fraction as well as the thermochemical state of the fluid is obtained from this scalar by means of the chemical equilibrium approaches.

The extension of LES to reacting flows, under conserved scalar formalism, allows to observe some important physical aspects of combustion processes.

Burner configuration

The hydrogen flame of the present study has been experimentally investigated in a previous work [1], providing accurate velocity and temperature measurements in near-field region. The burner consist of a central fuel tube (inner diameter: $d_{i1}=9.45mm$) and a concentric air tube (inner diameter: $d_{i2}=26.92mm$) centred in a vertical pseudo-circular test section (inner diameter: $D=150mm$) through which external air is supplied. Hydrogen is the fuel, discharging at 100m/s (mean jet velocity), so the Reynolds number, based on the fuel jet, is

8830. The mean air velocity at the exit of air tube is 20m/s, and the velocity of external air is 4m/s.

Computational domain and boundary conditions.

The LES has been carried out on a cylindrical computational domain (diameter: $D=150mm$, length: $L=800mm$). The numerical grid was unstructured and had a total of almost 450 000 cells. The highest grid resolution was near the fuel exit to better resolve the gradients in this area, and got coarse downstream and outwards.

The mean velocity profile measured in the test experiments at axial position $x=1.5mm$ was enforced at the boundary corresponding to the nozzle exit plane. The turbulence intensity was assumed constant, but different for each inlet flow condition. Reactants are injected into the burner at 300K. A Reynolds Averaged Navier-Stokes (RANS) simulation was also conducted for comparison with LES. The RANS computational domain was two-dimensional (75mm X 1m), the grid was unstructured and had almost 26 000 cells.

RESULTS AND DISCUSSION

Mean Thermal Structure

The mean thermal field from LES calculation show a flame shorter than in the RANS calculation with a great thermal spreading after the (mean) tip of the flame. The temperatures predicted by LES are generally lower; higher temperatures are reached in the near field area, instead that near the flame tip as in RANS. Radial profiles of temperature from LES agree well with experimental data except in a little region close to the nozzle. In this area the predicted peak temperatures in both LES and RANS calculation are too low. This disagreement is due to local low grid resolution. A new RANS simulation of the nozzle area, with grown resolution, has shown a hot point on the lip of the fuel tube. This little burning zone, allowed by low velocity and high hydrogen diffusion, work as a spark for the mixture reducing the ignition delay.

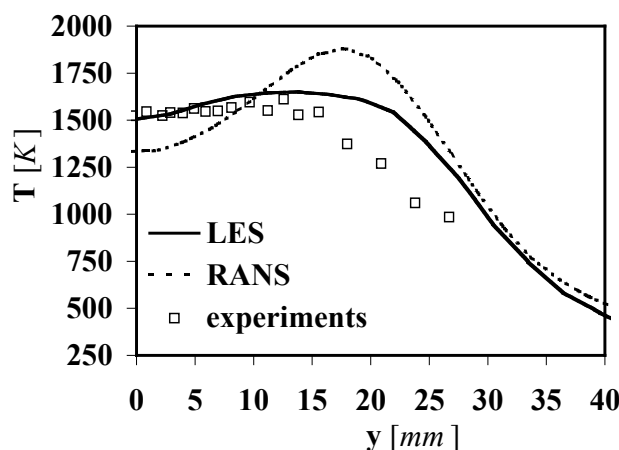


Fig. 1 Radial profiles of mean temperature at $x/d=24$.

Mean Velocity Field

The mean axial velocity profile along the axis predicted by LES are in close agreement with experimental data. The computation shows an initial area ($0 < x < 5d$) where axial velocity is nearly constant then the axial velocity decays with steep gradient. For $x/d > 20$ the expansion

of the fluid due to combustion becomes more important than the spreading of momentum, so axial velocity begins to grow slowly. Thus, the flow field can be split in a momentum controlled area ($0 < x/d < 20$) and a buoyancy controlled area ($x/d > 20$). The transition zone is quite well detected by the *flame Froude number* that quantifies the relative importance of inertial forces respect to gravity forces; the Froude number is $O(1)$ in buoyancy controlled area and $O(100)$ in momentum dominated area.

This aspect is not predicted by RANS simulation leading to large difference in mean exit velocity.

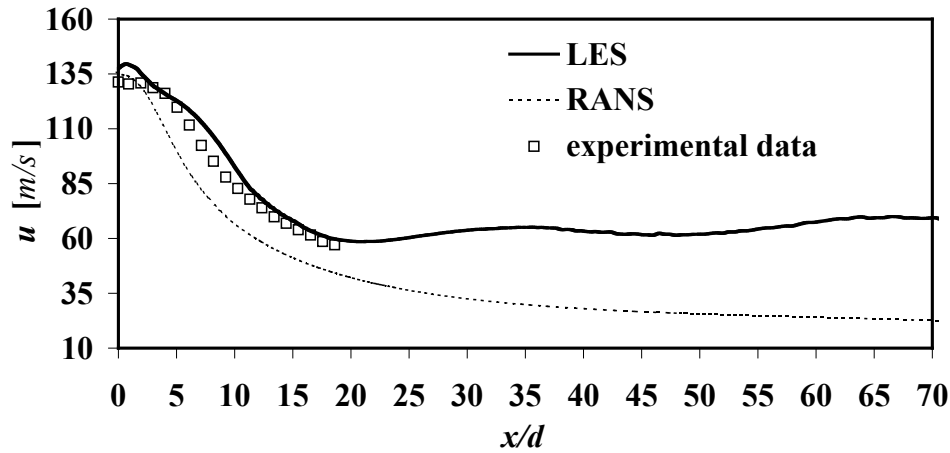


Fig. 2 Axial profiles of mean axial velocity.

Time-dependent structure

Jet flows with density inhomogeneity are characterized by large scale buoyancy structures [3]. These buoyancy induced instabilities are very significant even in this fully turbulent flame.

The time-dependent LES results of the thermal-fluid-dynamic fields show periodic separation of flame tip. These separated large-scale structures are then convected downstream,

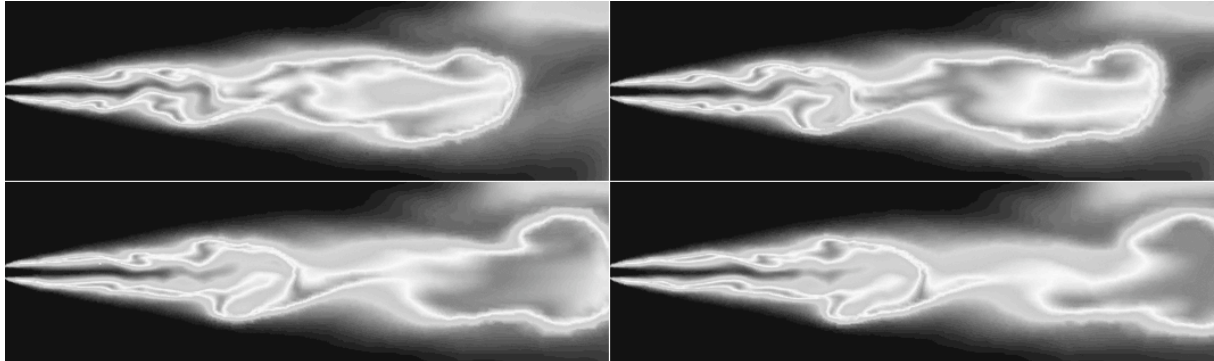


Fig. 3 Time-dependent thermal field showing separation of flame tip.

interacting with the combustion process.

Looking at an axial section of the flow, we note a series of counter-rotating vortex structures very close to the nozzle; they grow in size while convected downstream. The size of this structures is very similar to the radial dimension of the flame. When the induced oscillations become greater and more irregular, the axial velocity can be locally substantially reduced. In the region of the flame where hydrogen flux is reduced, the flame front move inward in the direction of the fuel. The pocket of unburned hydrogen trapped downstream by the contraction, is very light, because of the very low hydrogen density and high temperature. So

this pocket quickly accelerates leaving the rest of the flame. These large reacting structures cause intense mixing in the last part of the burner, explaining the even mean thermal field observed there.

The counter-rotating vortices arising just out of the nozzle are the axial section of a three-dimensional helicoidal structure [4], that we identified by means of an iso-helicity surface, $He = \mathbf{u} \cdot \boldsymbol{\omega}$ being the helicity. This structure is very regular and well-defined in the momentum controlled area, then suddenly disappears after the transition in buoyancy controlled area.

The correlation between flame surface stretching and local temperature has been observed by the analysis of the time-dependent behaviour of the flame. Specifically the strain rate

$$\hat{\Gamma} = \frac{1}{A} \frac{\partial A}{\partial t}$$

was chosen as the parameter for the flame stretching evaluation, showing the connections between temperature and strain-rate profiles along two lines parallel to the flame front and located inside and outside the flame.

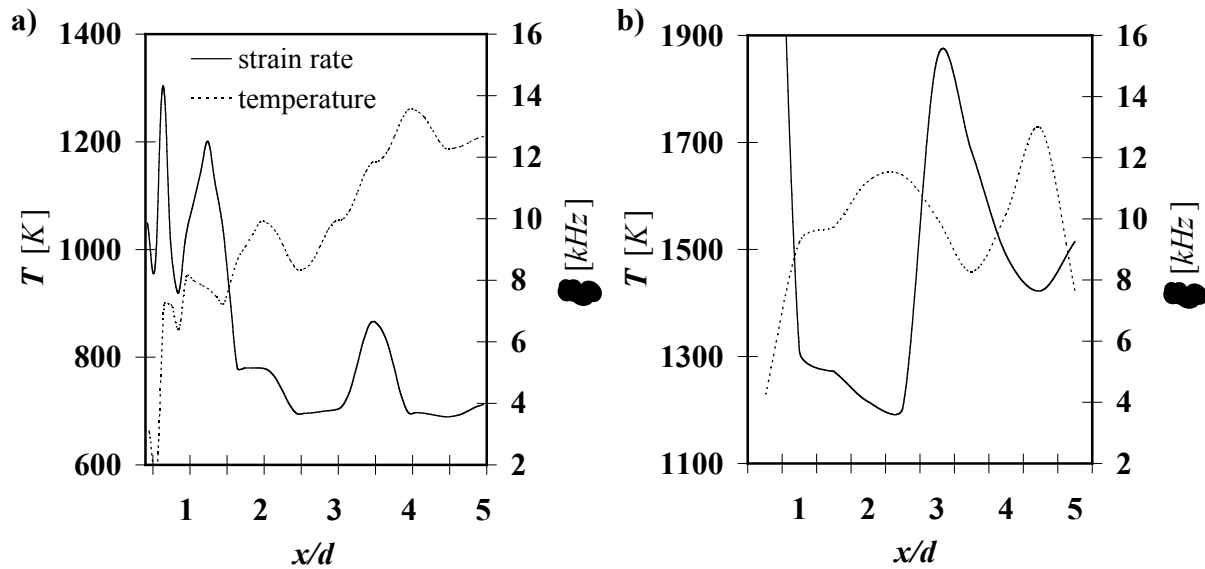


Fig. 4 Correlation between temperature and strain rate variations inside (a) and outside (b) the flame.

On the external line strain rate and temperature variations have the same sign; instead on the inner line the two signals have an opposed phase. This difference is probably due to the effect of the vortex-flame interactions.

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Interactions Between Acoustic Waves and Turbulent Combustion with the Eddy Dissipation Concept

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INTRODUCTION

The present work is aimed to the study of the physical and numerical behaviour of pressure waves observed in combustion instabilities. The acoustic interaction between heat release and acoustic modes occurs in fact to be at the core of combustion instabilities growth. Unstable heat release affects the flow by suddenly changing fluid temperature and density. These changes give rise to pressure waves travelling through the field. Since the effect of the heat release in premixed flames can be approximated as sequel of pulses, it will induce waves with different wave lengths (spanning, in the ideal case, the whole spectrum) flowing at the same speed. By numerically solving the problem, the waves speed, close to the speed of sound for small Mach number, will not be independent on the frequency as it is physically [1]. The effect of pressure waves on the Eddy Dissipation Concept for turbulent combustion (EDC) [2,3] was investigated in order to observe if the model was qualitatively and quantitatively sensible to such effects.

PHASE-SPEED EFFECTS, ALIASING, AND DISCRETISATION

Initial tests were conducted to investigate the differences between numerical solution and real behaviour. Fourier analysis of the linearised viscous convection equation [1] showed that even for a conservative scheme the numerical speed of sound will differ from the physical one. The proper numerical mesh must be very small to obtain a good accuracy. It also became clear that the numerical speed of the waves for a given mesh depends on their frequency. For the non-linear cases, specific mesh sensitivity tests have to be performed. Furthermore, tests were conducted to clarify the necessary grid refinement to avoid aliasing.

To test the wave speed dependency in FLUENT™, a simple 2D channel was simulated. A rectangular field 0.5m_0.05m was discretised with a mesh consisting of 500_50 square finite volumes [4]. The fluid was assumed to follow the ideal-gas law, and the turbulence was described by a Reynolds-stress-equation (RSE) model [5]. The inlet boundary condition was a total pressure sinusoidally varying in time. Various frequencies and amplitudes have been tested to assess their influence on the wave speed in the range observed in real combustor (0.1–10 kHz). The outlet pressure was fixed. The time integration was performed by a second-order implicit algorithm, with a second-order upwind stabilization method to discretise the space coordinate. The time step of $2.5 \cdot 10^{-6}$ s corresponded to a Courant number of 0.1, and the solution was observed after 200 time steps. As expected, the velocity was close to the local speed of sound (330 m/s). However, the speed of the waves was slightly dependent on their frequency, increasing from 360 m/s at 100 Hz to 390 m/s at 10 kHz.

THE EFFECT OF PRESSURE WAVES ON MODELLED TURBULENCE

Magnussen's EDC [2,3] is a widely used approach used to link the dynamics of the small scales where combustion occurs, with the features of the mean flow. It provides a connection based on the modelled turbulence quantities of the flow. Tests were performed to clarify how acoustic disturbances affect the model. It turned out that the turbulence kinetic energy and its dissipation rate were not strongly influenced by pressure waves. Results are plotted (Figure 1) along the streamwise centre-line of the channel.

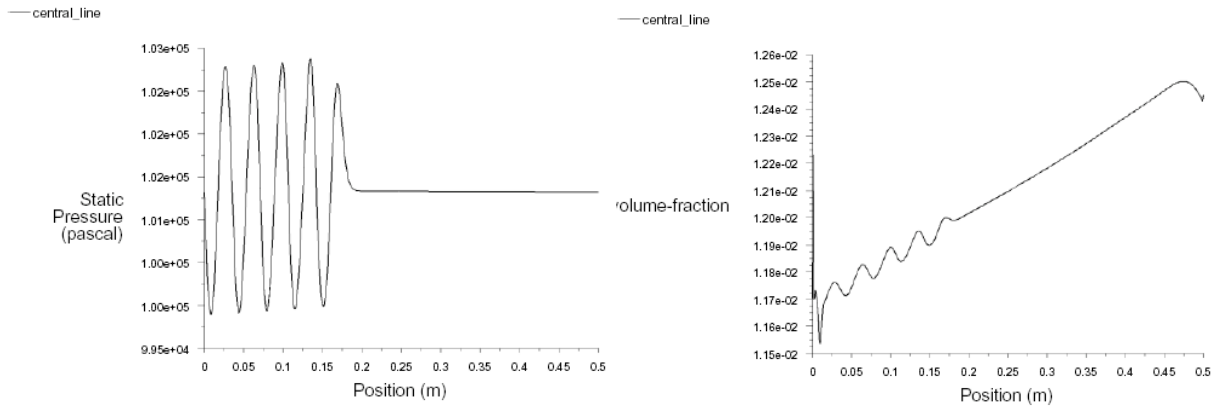


Figure 1: Pressure (left) and EDC fine-structure mass fraction (right).

The pressure shows the expected behaviour, oscillation with a frequency of 10 kHz was introduced as inlet boundary condition. The wave travels at the local sound speed. As expected the effects on the turbulence quantities were weak. This effect should be transferred through the (closed) production term and the (modelled) pressure-strain correlation in the RSE. Both effects appeared to be weak. As the efforts on RSE modeling have primarily been devoted to model the redistributive actions of the pressure-strain correlation, the pressure-wave effects are still to be worked out.

THERMAL SHOCK IN A DUCT FLOW

In real combustors the mechanisms at the core of the amplification phenomenon is the heat release unsteadiness, which provides the energy to the system. This leads to self excited acoustic modes growing until they reach a non linear limit loop. In turbulent combustion, changes in the mixing rate will modify the turbulent velocity of the flame leading to unsteady heat release within the flow field. The local temperature suddenly increases as the flame front is moving and hot spots induce pressure and density variations. The effect of a hot spot was simulated in order to understand how the pressure field is influenced.

Unsteady heat release is known to be a source of sound, and a simple model has been derived for plane waves. Provided that the reactants and products behave as perfect gases and there is no molecular change during the chemical reaction, combining the energy equation with the linearised momentum equation one obtains the inhomogeneous wave equation, the term on the RHS describing how unsteady heat generates pressure waves.

$$\frac{1}{\bar{c}^2} \frac{\partial^2 p'}{\partial t^2} - \frac{\partial^2 p'}{\partial x^2} = \frac{(\gamma-1)}{c^2} \frac{\partial q}{\partial t}$$

The mean flow has two main consequences: it affects the speed of the acoustic waves, which then travel downstream with speed $c+u$ and upstream $c-u$. On the other hand the equations of

mass, momentum and energy are coupled leading to the convection of linear waves of entropy and vorticity.

Combustion unsteadiness has been emulated by patching the flow field with a high temperature spots and following the solution in time. The hot spot acts like a step in the flow domain, and it is convected downstream by the mean velocity. The result is pressure waves travelling in both directions.

NUMERICAL MODELLING

The flow field was the same rectangular 2D channel (0.5m_0.05m) described. In this case, the temperature of a thick layer composed by 5 cell rows (5 mm) situated at the middle of the channel was patched in order to simulate the effect of a hot spot. The case was simulated at different conditions of flow rate, inlet temperature and pressure, and with different spot temperature. The solution showed how the hot spot was convected approximately at the local flow speed, while pressure waves are convected at the sound speed. The flow was compressible (ideal gas law) and turbulent. The turbulent model adopted was an RSE model [5] with a quadratic model for the pressure-strain correlation. The upstream stabilisation scheme adopted was again the second order upwind, and the QUICK scheme was been tested as well.

The flow field without the hot spot was simulated to a steady solution. Then the temperature field of the converged solution was patched with a higher temperature in the central zone and the fluid-dynamics fields obtained was used as initial condition of the unsteady computation. The spatial resolution had first been found not be affected by aliasing in the initial tests, while the time step was 10^{-6} s.

BEHAVIOUR OF THE PRESSURE WAVES

The hot spot induces pressured waves on a wide spectrum, which were convected at the local sound speed and reflected by the boundaries. By sampling the pressure at the middle of the channel, it was possible to identify the modes and observe the error due to the phase speed (*Figure 2*). At high frequency the difference between numerical and theoretical frequency becomes appreciable. For the 12th mode, the theoretical frequency was 3690 Hz, whereas the measured one is about 4.2 kHz. This error is coherent to the value reported from the initial tests.

By observing the pressure spectrum over the whole attenuation range, it is also possible to observe how the dissipation acts.

The damping becomes appreciable at a frequency which is very close to the Taylor frequency, while the modes seem to be completely damped at a frequency close to the Kolmogorov scales (*Figure 2* (right)) corresponding in this case to a frequency of 24 kHz. The Taylor frequency, 0.258 times the Kolmogorov frequency, was 6.2 kHz.

EFFECT ON THE COMBUSTION MODELLING

The analysis showed that it is possible to simulate the acoustic modes with good accuracy and to catch their attenuation. Therefore it needs to be investigated how the turbulence model and consequently the combustion model (EDC) take them into account. In the presented case, particularly the FFT analysis showed that the pressure waves have only marginal effect on turbulence quantities. This may be attributed to the circumstance that available turbulence models are not developed to deal with pressure waves.

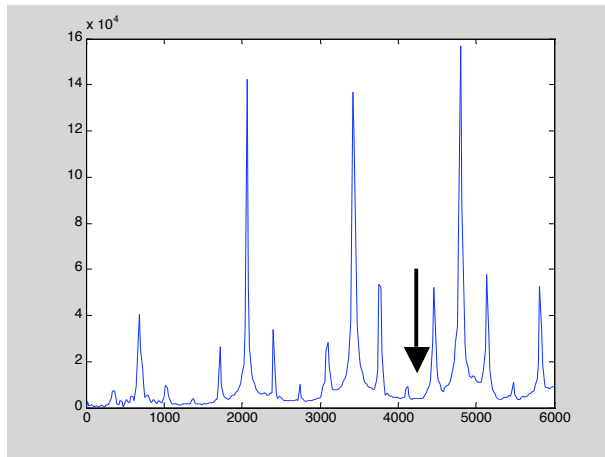


Figure 2: Fast-Fourier-transfer analysis (left) and Power spectrum (right) of pressure.

CONCLUSION

Simulation of problems including pressure oscillation with FVM requires care in order to limit error due to the phase speed and aliasing. Mesh dependency tests have to be performed in order to ensure good accuracy in the frequency spectrum of the problem. The use of RSE turbulence model with an accurate pressure strain correlation leads to reasonable results showing coherent energy spectra. In particular a discrete energy cascade seems to rule the attenuation of acoustics (*Figure 2*). This cascade has only marginal effect on k and ϵ and therefore on the volume fraction. The effect is that the combustion rate is only weakly influenced by pressure oscillations.

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Unsteady Characterization of a $CH_4/H_2/Air$ Turbulent Non-Premixed Flame

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ABSTRACT

The bluff-body burner analyzed in this work is a good test case to validate *LES* models: it has a simple geometry, with well defined boundary conditions; it has complex flow patterns similar to those found in practical combustors; and it involves complex physics related to flame stabilization, localized extinctions and reignition zones, providing a mean to analyze chemistry - turbulence coupling.

In this paper we perform *LES* of the proposed $CH_4/H_2/Air$ turbulent nonpremixed flame using the *Fractal Model* as *SGS* model as *SGS* closure for turbulent combustion. Results show that the flame is strongly unsteady and three-dimensional, mainly within the recirculation zone. Irregular eddies are shed from the jet at different high frequencies, while larger structures are shed from the outer edge at regular lower frequency. Intense stretching in the neck region of the flame produces local extinction. Although the fast chemistry used in the simulation is a too crude assumption, resulting in a flame shorter than the actual one, results evidence complex interaction between chemistry and turbulence.

TEST CASE AND NUMERICAL SIMULATION

In this work we analyze the bluff-body burner studied experimentally at the University of Sydney [1]-[5]. The burner consists of a 50 mm diameter (D_B) bluff-body with a 3.6 mm central fuel jet (D_j). The burner is unconfined and centred in a wind tunnel where air with a free stream turbulence of around 2% flows. The central jet is a fuel mixture 1/1 (in volume) of CH_4/H_2 at 118 m/s (bulk velocity) and the coaxial jet is air at 40 m/s.

We performed *LES* simulation of the bluff-body flame chosen by using the *FM* [7, 8] as *SGS* model for turbulent combustion. We used our own code parallelized using the *MPI* procedures. We implemented a third-order Runge-Kutta explicit time-stepping scheme and second-order central differencing to numerically integrate the compressible, reactive, Navier-Stokes equations. In this way we can take into account acoustics effect. The stability conditions impose 10^{-8} s as time step, increasing the computational time but allowing to resolve the high frequencies typical of chemical reactions.

Our calculation domain has three zones: the main zone, where combustion takes place, has the exit at 400 mm downstream of the bluff-body face; the other two inlet zones are 50 mm long. The radial extension is 75 mm ($3D_B/2$), where the coflowing air is undisturbed on the base of the experimental measurements. The grid is structured. The number of grid nodes are $306 \times 126 \times 32$, $80 \times 11 \times 32$ and $80 \times 56 \times 32$, respectively for the main combustion zone, the fuel inlet zone and the coflow air zone. Numerical simulations shown in [5] have inlet conditions specified 100 mm upstream of the face of the bluff-body; the computational domain is extended 300 mm downstream of the bluff-body and has a radial extension of 70 mm from the axis.

As boundary conditions we assumed the *NSCBC* method [6] (Navier-Stokes Characteristic Boundary Conditions) at the inlet and outlet; this method is necessary particularly at the outlet because it avoids large reflections of acoustics waves inside the numerical domain. At the outlet the pressure relaxes to 1 *atm*. At the inlet we specified velocity, temperature and composition. We stress that the experimentalists provided only bulk velocities and profiles downstream of the exit; these data are not sufficient for good specification of the *LES* problem at the inlet. At the maximum radial distance from the axis we assumed a slip condition; this assumption is a crude simplification because it makes the simulated flow confined, whilst in fact it is not.

We started the simulation with an initial still air field and forced transition to turbulence overimposing some disturbances, turned off after transition.

All molecular transport properties, except mass diffusivities, are calculated by means of kinetic theory and using look-up tables and interpolation technique to reduce computation time. We assumed the same diffusivity for all the species and calculated it by means of a constant Schmidt number.

In our calculations we estimate chemistry in the crudest way; in particular, for hydrogen oxidation we assumed fast chemistry controlled by subgrid turbulent mixing, according to *EDC* [9], and for methane oxidation we assumed the single step mechanism of Westbrook and Dryer [10].

RESULTS

The flame is characterized by a stabilizing recirculation zone followed by a neck zone and then by a burnout region further downstream where the flame propagates in a jet-like manner. Experiments show that the flame is very stable and has a visible length of $\sim 20 D_B$ ($\sim 1 m$); measurements are only taken at axial locations extending to $2.4 D_B$ [2]. The recirculation zone extends to $\sim 1.6 D_B$ ($\sim 80 mm$).

We want to stress that due to the fast oxidation mechanisms assumed, our simulated flame will be inevitably shorter than the actual one; in fact, chemical reactions happen within $\sim 300 mm$ from the injection in our simulation. Another point to stress is that we used a too short time window ($\sim 6 ms$) for statistics, i.e., for computing averaged quantities and *RMS* fluctuations; the lack of symmetry our average field marks this point.

A time averaged view of the recirculation zone obtained from measurements indicates the existence of one large vortex on the outer edge and a second narrower vortex close to the jet centerline [1]. The structure of the recirculation zone is similar to that found in isothermal bluff-body flows at relatively low jet momentum [2], and to that we have already found in other bluff-body flames [8].

Looking at our computed averaged field we noted the two vortices, but they have roughly the same size; the length of our averaged recirculation zone is $\sim 1 D_B$, smaller than the experimental one, $\sim 1.6 D_B$. The disagreement in the average picture is probably due to the too small time window ($\sim 6 \cdot 10^{-3} s$) that we used for statistics. We stress that, in fact, some instantaneous fields (see Fig. 1) are in better agreement with experimental data: the eddies constituting the instantaneous recirculation zone extend up to $\sim 1.6 D_B$.

Our simulation shows that the recirculation zone has a complex dynamics. The outer toroidal vortex is initially symmetric (see Fig. 1). The evolution of the inner recirculation zone is strongly three-dimensional due to irregular eddies shed from the edge of the jet at high

frequencies ($\sim 790 \div 1600 \text{ Hz}$); these eddies enlarge and break themselves into smaller eddies, pushing the outer vortex downstream. While the outer initially regular vortex is being shed, it is strongly deformed by the inner eddies, and its shedding becomes asymmetric with a frequency of $O(100) \text{ Hz}$. Outer vortex rotates from the air side towards the center of the burner and produces entrainment of the recirculated flow into the air stream; the fuel-air mixing within the recirculation zone is mainly controlled by the inner eddies.

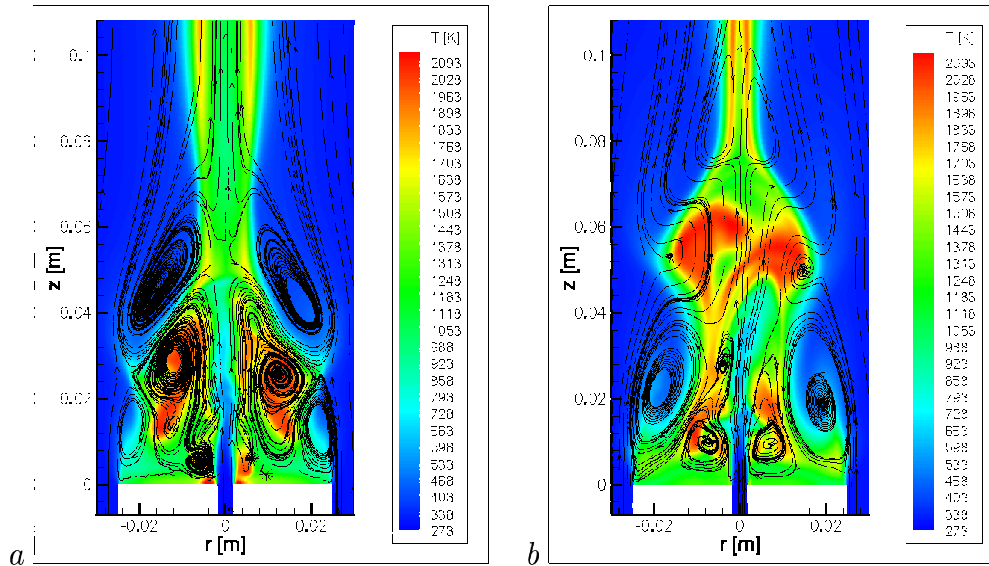


Fig. 1: Instantaneous temperature distributions and streamlines inside the recirculation zone downstream of the bluff-body. The delay time between the two frames *a* and *b* is $\sim 1.9 \cdot 10^{-3} \text{ s}$.

Some irregular rolling eddies, without a regular shedding frequency, have been also experimentally identified on the inner edge of the outer vortex [4]. Experiments [4] also revealed that from the outer edge of the burner there are regular, periodic coherent structures shed at a certain frequency, not reported in [4]. The outer large vortex is intermittent at this operating condition, affecting mainly the flame stability and burning pattern.

In the outer region the gradients are very steep and the scalar dissipation rates are high; the missing of OH in the instantaneous *LIF* images in [4] indicates that the flame is intermittent close to the burner exit within the recirculation zone and sometimes is lifted from the jet exit plane [3]; this is in agreement with Fig. 1. Moreover, the high instantaneous velocity gradients across the boundaries of the adjacent large scale structures produce an increase of turbulence levels inside the recirculation zone, as measured in [11].

Instantaneous temperature fields show simultaneous reaction zones within the recirculation zone due to the strong three-dimensional mixing of the inner vortices. This is confirmed by instantaneous measurements of reactive scalars within the recirculation zone [4]. Unsteady results show eddies stretching the flame; the separated reaction zones are convected downstream, and close to the end of the recirculation zone they merge into one, broad and distributed, with some islands of unreacted fresh mixture or cooled combustion products; this is confirmed by experiments [4]. After this broad reacting zone becomes a flat front at $z \sim 1.8 D_B$; unburnt reactants burn inside this front while it propagates downstream; this makes downstream jet region leaner, resulting in the radial approaching of the conical jet flame front close to the axis. Intense

stretching develops in the neck zone of the flame after the passage of the flat front, leading to local extinction and temperature decreasing.

CONCLUSIONS

The bluff-body flame analyzed has a stabilizing recirculation zone, a neck zone and a burnout region where the flame propagates in a jet-like manner. *LES* results show that the flame is strongly unsteady and three-dimensional, mainly within the recirculation zone. Irregular eddies are shed from the jet at different high frequencies, mainly controlling fuel-air mixing, while larger structures are shed from the outer edge at regular frequency.

It seems that the discrepancy between the calculations at the moment available in literature and the measurements at downstream locations in the jet and flame, may be due to vortex shedding on the outer (air side) edge of the recirculating region. In our *LES* simulation we capture the flow dynamics, but our fast oxidation mechanisms are too crude to well predict experimental data; in particular, our flame is shorter than the actual one. However, results evidence complex interaction between chemistry and turbulence, showing also local extinction due to intense stretching in the neck region of the flame.

The average picture reported in this paper suffers of a too small time window ($\sim 6 \cdot 10^{-3}$ s) used for statistics. The lack of symmetry indicates this point, and, in fact, some instantaneous fields are in better agreement with experimental data.

Moreover, the data provided by the experimentalists are not sufficient to accurately specify the inlet boundary conditions of the *LES* problem.

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Modeling Explosion In Compartmented Vessels

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INTRODUCTION

Linked vessel configuration is very common in industrial equipment (reactors and tanks interconnected, mines, electrical equipment casings, buildings). In these configurations, accidental explosions give rise to unexpected high pressure and rate of pressure rise. This phenomenon is called “pressure piling” and its occurrence is a relevant issue of industrial safety. Several models [1-4] and experiments [1,5-9] were proposed in the literature, showing that geometric characteristics (e.g. connecting tube diameter, ratio of volumes of connected vessels) influence strongly the phenomenon. So far, most of the models developed to study pressure piling are semi-empirical [1-3], generally using a “turbulisation factor” (χ) to take into account the interaction between flame and turbulent flow field. Their applicability is restricted to the specific experimental conditions. Indeed, explosion is an intrinsically unsteady phenomenon, which is strongly influenced by the feedback between flame and flow-field and the reproduction of explosions has to deal with the effects of the unsteady interaction of flame propagation and geometry. An alternative approach is based on Computational Fluid Dynamic (CFD) codes, which solve the set of Navier-Stokes equations unless simulating explosions in medium and large scales, for which solution of unsteady RANS equations is necessary. Maremonti et al (1999) [4] used a commercial CFD code specifically developed for simulating gas explosions, based on the well known quasi-laminar approach and the Eddy-Dissipation combustion model to reproduce pressure piling in a medium scale apparatus, provided that some parameters are adjusted to reproduce the experimental behaviour. Indeed, whatever the CFD code, no universal chemical model has been developed for the combustion regimes (laminar, flamelet, corrugated, well mixed, distributed regime). This aspect is relevant if considering that during explosion more different combustion regimes can occur, even at the same time. In the present paper, a CFD model is developed in which the combustion models adapt to the specific combustion regime arising during the explosion occurring in the interconnected vessels. The model has been directly validated by means of a blind test carried out with the experimental findings of Singh (1977) [1], showing the ability of the models in reproducing the phenomenon of pressure piling.

THE MODEL

The developed model is based on the solution of unsteady Reynolds average energy, momentum and mass balances equations. A k - ϵ model is used for turbulence. The evaluation of the mean reaction rate was performed by using the appropriate combustion model for any of the combustion regime present during the explosion. Indeed, the turbulence induced by gas expansion and geometry during explosions is likely to evolve towards very high values starting from zero. As a consequence, transition from laminar flame to turbulent flame regime may occur. According to the characteristic lengths, turbulence and chemical times, it's possible to identify the combustion regimes both in the two vessels and in the tube: the characteristic values of the ratio between the integral length (L) and the laminar flame thickness (δ) for the first vessel is 1000, for the tube is 180 and for the second vessel is 300. Following the Borghi diagram [11], these L/δ values suggest the flame propagation can occur

following a laminar regime, a wrinkled regime, and a flamelet or corrugated regime, depending on the intensity of turbulence u' through its ratio with the laminar burning velocity (S_L). So far, no universal correlation valid for all these combustion regimes exist. Hence, three different combustion models were implemented, depending on the turbulence local intensity, and the transition were performed by checking the value of u'/S_L and Ka number ($Ka = (l_l / l_k)^2$ where l_l is the laminar flame thickness and l_k is the Kolmogorov length). The initial laminar flame propagation was described by means of a phenomenological approach because of the onerous computational effort required for the use of the Arrhenius equation. Hence, the combustion rate has the classical dependence on the laminar burning velocity S_L . The flamelet regime was described by the model of Cant (1990) [12] recently improved by Abu-Orf & Cant (2000) [13] to reproduce correctly the reaction rate at the wall boundaries. Finally, the distributed reaction regime was described by the equation of Gülder (1990) [14] which adopts a turbulent flame speed, function of Damkholer and Reynolds number.

RESULTS AND DISCUSSION

The solution of the resulting model was performed by means of the commercial CFD-ACE+ solver [15] In order to validate the model, the numerical results were compared with the results obtained by Singh (1977) [1] for two cylindrical vessels interconnected by a tube filled by stoichiometric propane-air mixture. The ignition vessel has a volume $V_I = 5.5 \text{ m}^3$. A sketch of the set-up is reported in Fig. 1. In the same figure, the position of gauges where pressure histories were measured by Singh and compared with numerical results is reported.

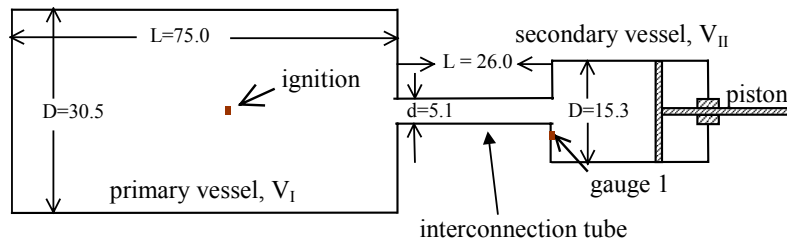


Fig. 1 Experimental configuration of Singh (1977) [1] reproduced in the simulation. Internal diameter: d_I : 30.5cm; d_{II} : 15.3cm. Tube: $L=26\text{cm}$, $d=5.1 \text{ cm}$..

Singh (1977) performed experiments in the two vessels configuration by measuring the pressure reached in the second vessel when flame enters the second vessel (P_1) and the second vessel pressure peak (P_k) in the position gauge 1. For the simulation, a 2D numerical domain has been set and square cells with an average size of 1cm were used.

The simulations were performed assuming a stoichiometric propane-air mixture at atmospheric pressure and temperature as initial conditions. Ignition was performed by assuming a hot spot at 2000K for the 4 cells located in the centre of the first vessel (Fig.1). Singh (1977) [1] has not reported any pressure time history and thus the validation was performed by only comparing the values of pressure P_1 and P_k at the time (t_1 and t_k) at which these values were reached. The numerical temporal pressure profiles as calculated in the first and the second vessel are shown in Fig. 2A for the specific case of $VR=V_I/V_{II}=14$ and tube diameter equals to 0.051m.

The agreement between the computed and the measured pressure values P_k and P_1 is satisfactory. When the flame enters the second vessel tube ($t \approx 82 \text{ ms}$) the pressure in the second vessel starts to rise faster and pressure piling occurs: the peak pressure in the second vessel is higher than the thermodynamic value corresponding to initial atmospheric conditions ($P = 8.5 \text{ bar g}$, $T = 2600 \text{ K}$). After about 100 ms, the pressure value reaches its

thermodynamic value. In Fig. 2B, the u'/S_l ratio is plotted as a function of time to indicate the occurring combustion regime.

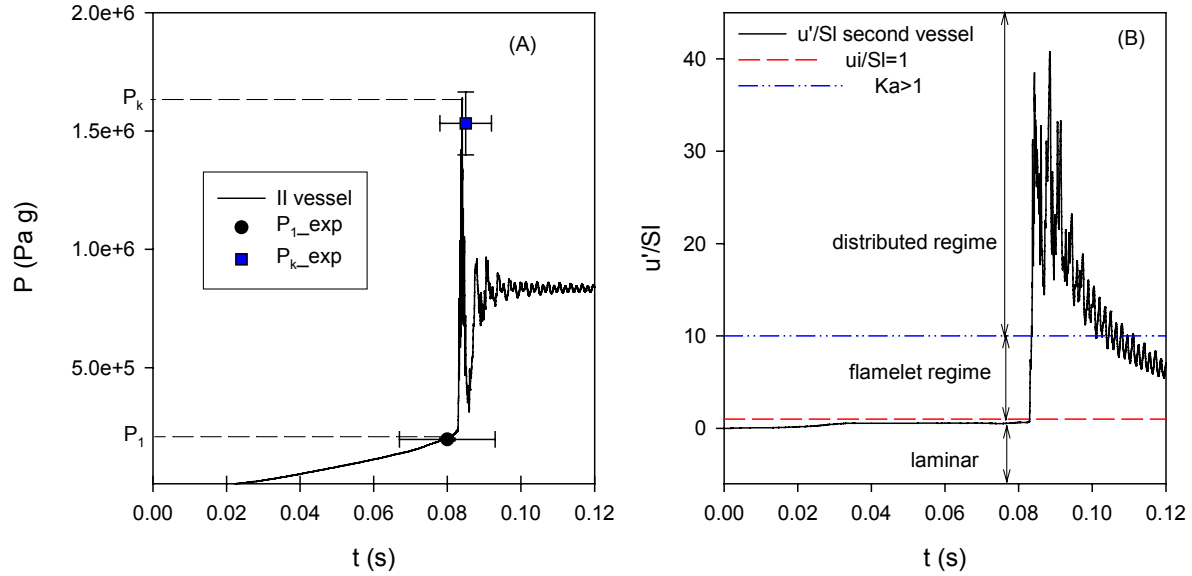


Fig. 2 Pressure (A) and u'/S_l ratio with respect to time as calculated in the first and in the second vessel. $VR=14$, $d=0.051$ m. Symbols: experimental data of Singh (1977) [1].

As shown in the plot, u'/S_l is always lower than one at $t < 82$ ms, before the flame enters in the tube. This result suggests that flame propagation in the first vessel occurs at laminar condition. When the flame enters in the tube ($t = 82$ ms), u'/S_l starts to increase, hence becoming higher than unity: the combustion regime is a flamelet corrugated regime. The increase of turbulence intensity is due to the interaction of flame and flow-field in the restriction area from the first vessel to the tube. After about 1 ms, the flame enters in the second vessel and the turbulence intensity increases further. The value of Ka is higher than one thus shifting to the distributed reaction zone. This result points out that in the second vessel turbulent flame propagation occurs, leading to a very low reaction time.

During flame propagation in the first vessel, unburned gases are pushed from the first vessel to the second (jet injection), thus producing turbulence and giving rise to a jet ignition in the second vessel. Of course, the mass flux increases the pressure in the second vessel; hence, when the flame enters the second vessel, ignition occurs at an initial pressure (P_1) which is higher than the atmospheric value. As a consequence, it is not surprising that a peak pressure P_k higher than the thermodynamic value is observed.

Pressure piling phenomenon is strongly affected by the competition between reaction time and venting time (through the connecting tube) and by pre-compression in the second vessel. The ratio of reaction time to venting time is often reported in the literature as the Bradley number (Br) for flame propagation at laminar conditions and turbulent Bradley number (Br_t) for turbulent flame propagation [16]:

$$Br_t = 0.21 \sqrt{\frac{E_o}{\gamma_{u,o}}} \frac{\mu}{\chi} Br \quad (3)$$

where E_o is the expansion factor, $\gamma_{u,o}$ is the specific heat ratio for the unburned fuel at initial condition, μ is the “discharge coefficient” and Br is:

$$Br = \frac{A_v c_o}{V^{2/3} S_{u,o} (E_o - 1)} \quad (4)$$

where A_v is the vent ratio (the tube section), c_o is the ambient sound speed, V is vessel volume, and $S_{u,o}$ is the laminar burning velocity at ambient condition. The parameter χ takes into account the effect of turbulence on flame propagation: the higher the turbulence, the higher χ , the lower is the value of Br_t (i.e. the reaction time). In the first vessel, the flame propagation is nearly laminar and the reaction to venting time is equal to Br , which was calculated as about one: venting time and reaction time are of the same order of magnitude. In the second vessel, the turbulence induced by jet injection and by the subsequent jet ignition causes a strong decrease of the reaction time: gases do not have the time to vent through the tube because reaction is much faster (the violence of explosion) and the explosion occurs much more as in a closed vessel rather than in an open vessel interconnected to a duct. The pressure peak is the result of both violence of explosion and pre-compression. The pre-compression induced by the mass flux from the first vessel to the second vessel, allows a pressure before ignition higher than the atmospheric one. In conclusion, for very low Br_t , the peak pressure in interconnected vessel has the value of pressure which would be reached during flame propagation in a closed vessel starting from P_1 . More generally, the value of the peak pressure is higher than the thermodynamic pressure value starting from atmospheric pressure ($P_t = 8.5$ bar g) but it is lower than that at P_1 (e.g., if $P_1 = 2$ bar, $P_t = 18.7$ bar).

CONCLUSIONS

In the present paper a CFD model was developed and validated against experimental results without any adjustable parameter. A regime-specific combustion model was developed. Simulation results showed that main factors affecting pressure piling are the pre-compression and the reaction to venting time ratio (Br_t) in the second vessel. Mitigation of pressure piling is obtained increasing the value of Br_t , i.e. a reduction of the turbulence induced by the flame propagation by changing the vessel geometry. If low reaction times are considered, peak pressure can be still avoided by reducing pre-compression effects.

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Pollutant Emissions from Diffusion Flames with an Integrated CFD Procedure

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INTRODUCTION

Although the continuous development of detailed reaction schemes and the improvement of CFD tools, nowadays the prediction of pollutants emissions from combustion systems represents an open research field. The analysis of experimental burners helps the definition of new methodologies, useful to minimize the environmental impact of industrial devices.

This paper deals with the evaluation of pollutant emissions from a test case burner involving a very detailed and comprehensive reaction scheme, starting from CFD calculations. The first part of the work is focused on the simulation of a $\text{CH}_4\text{-H}_2$ (1:1 vol.)/air flame with a fuel inlet velocity of 118 m/s, using the commercial code FLUENT6. Some modifications of the usually adopted models for the representation of the turbulence-kinetics interaction are introduced. NO_x emissions are then evaluated by post-processing the flow and temperature fields, as predicted by CFD.

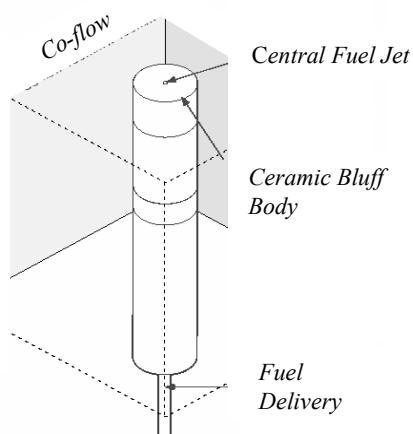


Fig.1 The burner geometry [1]

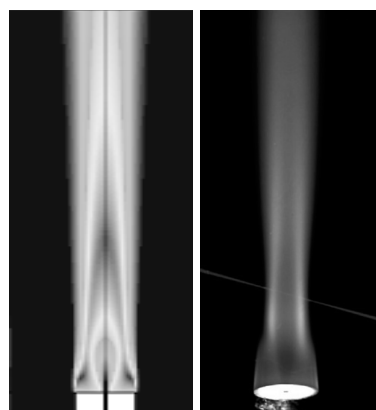


Fig.2 Favre-average temperature. Left side: simulation, right side: exp. measurements[1]

EXPERIMENT

The experimental work developed by two teams, respectively Sidney University and Sandia National Laboratories [1] is focused on the analysis of an unconfined flame, fed with a mixing of natural gas and hydrogen.

As shown in figure 1, the burner is composed by a central conduct with a diameter of 3.6mm for the fuel jet, situated within a ceramic tube (the bluff-body) of 50 mm. The fresh air comes from a square inlet (the wind tunnel), which confines the flame development. The flame was investigated through not intrusive technique (laser).

SIMULATION

Mathematical modeling

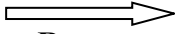
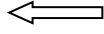
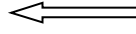
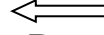
The flame was simulated in the steady state in cylindrical-polar coordinates using a 2D non-uniform unstructured mesh composed by 45,000 cells. For the spatial resolution the First-

Order Upwind Scheme was adopted. The algorithms PRESTO and SIMPLE are respectively used for the pressure interpolation and for the coupling of pressure and velocity. The radiative heat transfer of the unconfined flames is calculated with the P1 model. The instantaneous Navier-Stokes equations are manipulated to deal with the fluctuating quantities of the turbulence state. Turbulent models (Standard k- ϵ and RSM) are then used to close the equation system.

The interaction between turbulence and chemistry is often handled through the Finite Rate-Eddy-Dissipation Model (FR-ED). The controlling rate is assumed the slower between the kinetic values and turbulent mixing rate. It means that both the Arrhenius and the Eddy-Dissipation rates are calculated for the forward and the reverse reaction separately. In particular conditions, this approach can lead to strong deviations.

Let's assume a chemical reaction $A+B \rightleftharpoons C+D$, kinetically favorite in the forward direction. In the example of table 1, turbulent mixing rate favors the reverse reaction. The application of the FR-ED concept separately to the direct and reverse reaction can produce a net rate opposite to the kinetic indications. On the contrary, it seems better to first evaluate the net kinetic rate and only then to apply the FR-ED concept comparing this net rate with the corresponding forward or reverse turbulent mixing rate. In this way the example of table 1 will bring to conclusion in line with kinetics. A UDF (User-Defined-Function) was then implemented in the code to modify the turbulence-chemistry interaction following this approach.

Table 1. Example of Finite Rate-Eddy-Dissipation Model (FR-ED) and modified FR-ED

	Forward rate A+B	Reverse rate C+D	Net rate
Kinetics	 $R_{K,f}$	 $R_{K,r}$	 $R_{KIN}=R_{K,f}-R_{K,r}$
Turbulent Mixing	 $R_{T,f}$	 $R_{T,r}$	
FR-ED	 $R_{T,f}$	 $R_{K,r}$	 $R_{ED}=R_{T,f}-R_{K,r}$
Modified FR-ED	 $R_{ED-M}=\min(R_{KIN}, R_{T,f})$		

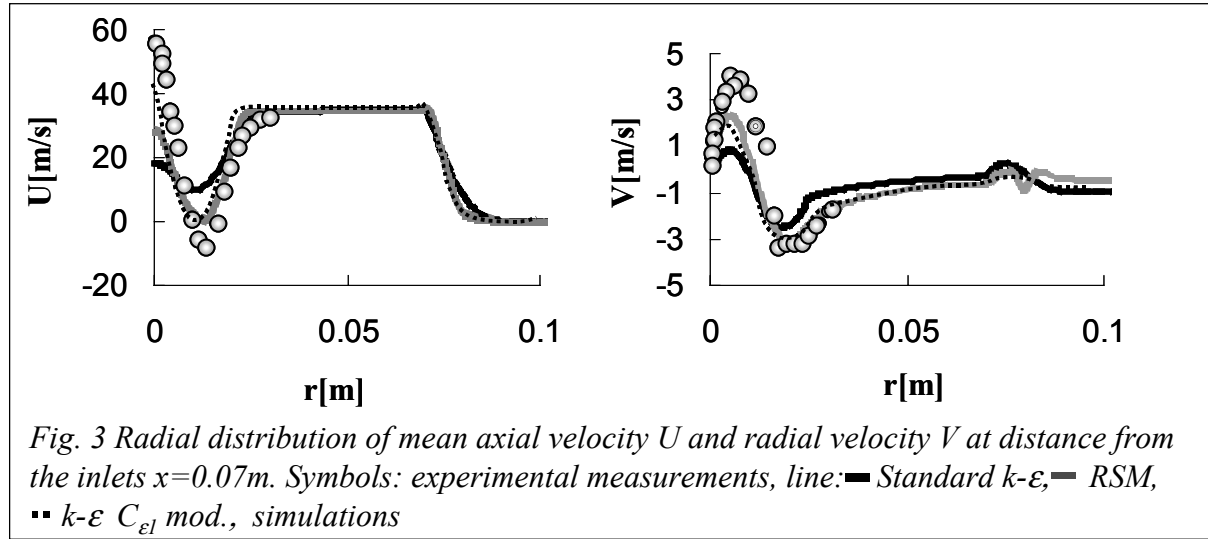
RESULT AND DISCUSSION

CFD simulations

A first series of simulations was generated to determine the appropriate turbulence model. In particular 3 models were tested: Standard k- ϵ , RSM and a Modified k- ϵ version. All of them show a similar flow pattern, with a flame shape close to the real one (Fig.2). The flame can be divided into three separated zones: the recirculation, the neck and the jet-like propagation zone.

The Standard k- ϵ model has known shortcoming for predicting round jets. In particular, the standard k- ϵ model overpredicts the decay rate and the spreading rate of a round jet. Modifications suggested by McGuirk and Rodi [2] for the parameter $C_{\epsilon 1}$ lead to a value of 1.60 for self-similar round jets. The improvement in the prediction of the flow with $C_{\epsilon 1}$ modification is evident from the comparison shown in figure 3. Both axial (U) and radial (V) calculated velocity profiles agree much better with the experimental data. In the following, the

analysis of the kinetics-turbulence interaction was then developed using the $C_{\epsilon I}$ modified k- ϵ model, which also induces a better stability than RSM during the iterative process. The simplified chemical kinetics scheme of Jones-Lindstedt [3] was used to describe the combustion process in terms of 7 species (CH_4 , H_2 , CO , CO_2 , H_2O , O_2 and N_2 as inert).



Being the profile of T and H_2O very similar (figure 4) it is evident that the exothermicity of the process is generated for the most part by the complete oxidation of H_2 to H_2O . The slight overprediction of the thermal level of the flame is due to the overestimation of the H_2O production. This deviation is much more evident using the FR-ED Model.

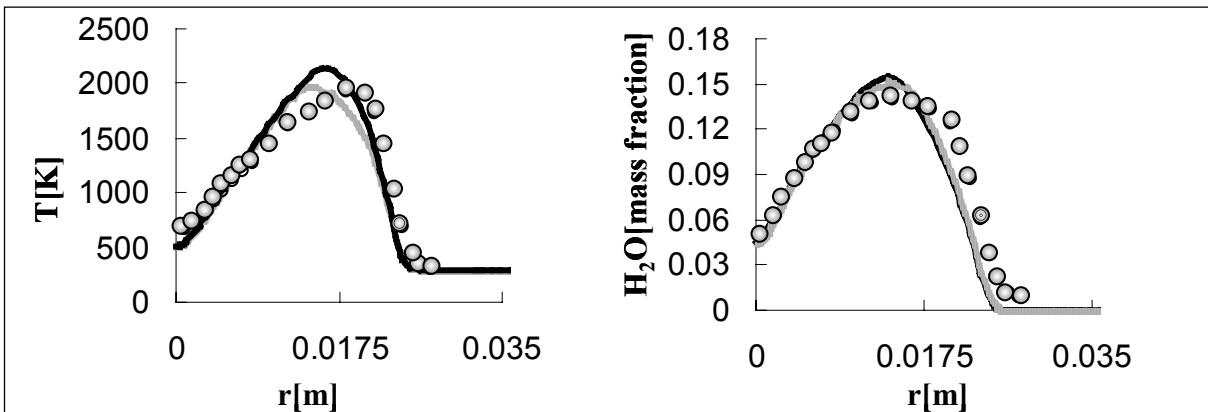


Fig. 4 Radial distribution of mean temperature T and H_2O mass fraction at distance from the inlets $x=0.045\text{m}$. Symbols: exp. measurements, line: — FR-ED M, - - UDF simulations

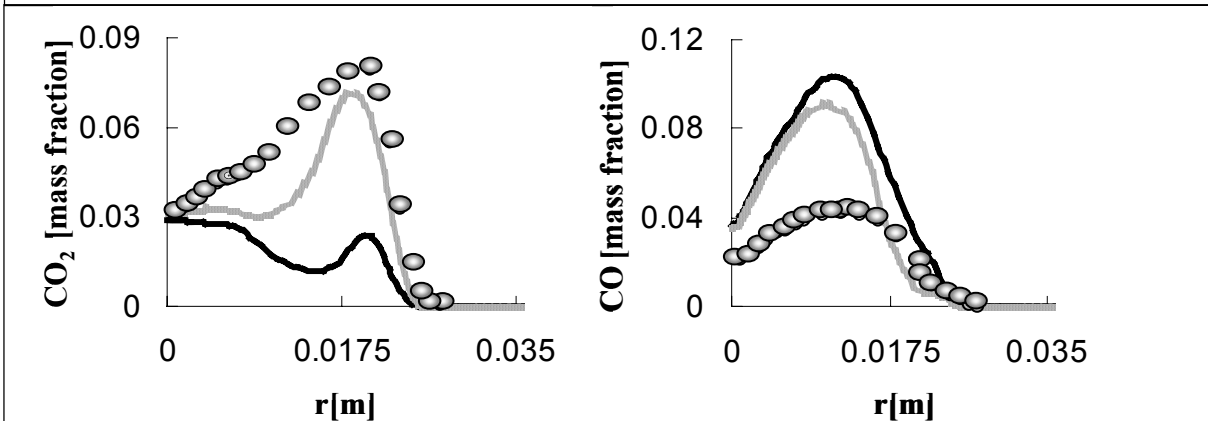
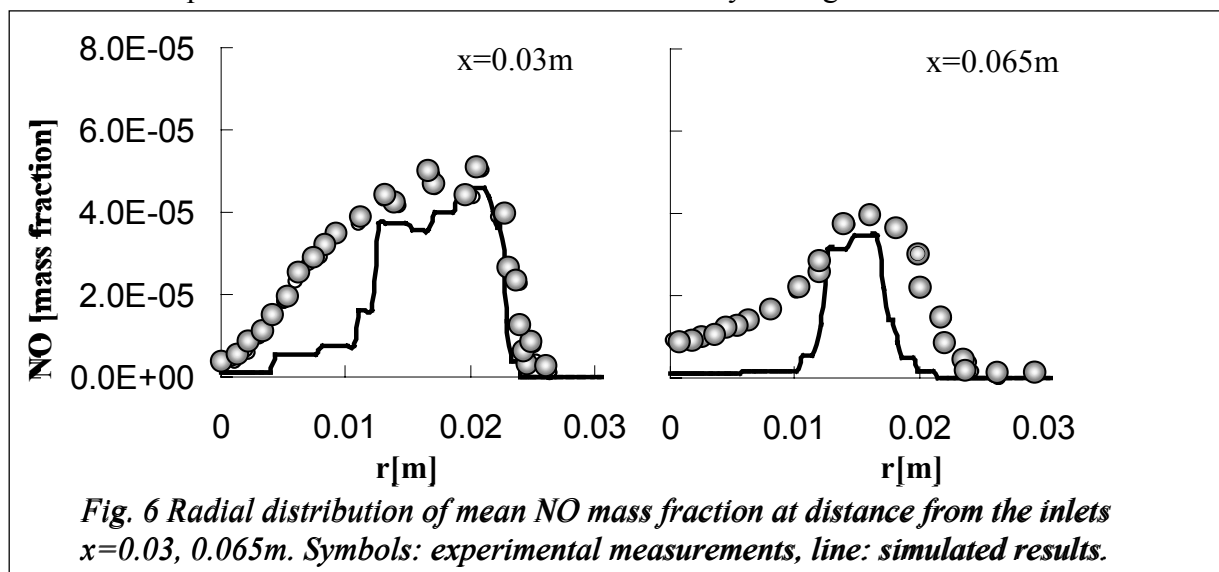


Fig. 5 Radial distribution of mean temperature CO_2 and CO mass fraction at distance from the inlets $x=0.045\text{m}$. Symbols: exp. measurements, line: — FR-ED M, - - UDF simulations

Significant improvements of the prediction of CO and CO₂ formation were provided by the modification of the FR-ED model. In particular the use of UDF shifts the CO-CO₂ ratio towards carbon dioxide.

NO_x emissions

Because of the computational limits, the detailed chemistry of NO_x formation cannot be used in the CFD codes. For this reason, a chemical post-processor was adopted on the basis of the flow, thermal and stoichiometry fields obtained from the CFD calculations. This multi-zone method or SFIRN processor [4] clusters the grid cells and builds up an equivalent and simplified network of ideal reactors. The simulations have been carried out using a general program (DSMOKE) and referring to a comprehensive detailed kinetic scheme involving about 1,600 reactions with 100 species [5]. Figure 6 shows the good agreement between the experimental and the calculated NO concentration in the flame. Being fuel a CH₄-H₂ mixture (free from N₂), NO_x production is only due to thermal and prompt mechanism. In fact the NO concentration peak is located in the zone characterized by the highest T levels.



CONCLUSIONS

The modification of the turbulence-kinetics interaction for the reactions definition, as well as the modification of the k- ϵ model parameter $C_{\epsilon l}$ allows improving the CFD prediction. This work demonstrates the capability of the adopted SFIRN procedure to predict NO_x formation not only at the boiler exit but also at the burner scale and directly inside the flame.

Acknowledgments

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EXPERIMENTAL AND NUMERICAL ANALYSIS UPON A NATURAL GAS SWIRL COMBUSTOR

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1 –INTRODUCTION AND EXPERIMENTAL SET-UP

One of the most promising technologies used to improve conventional combustion performances is based on the optimisation of the mixing process among fuel, air and hot flue gases. It is well known that, independently from the combustion technology used, any improvement of combustion performance relative to pollutant formation, stability and overall efficiency requires a careful study of the mechanism of mixing and entrainment in high turbulent reacting flows, especially in the presence of swirl motion. In fact, swirl is imparted to the air flow in order to increase fuel-air mixing and improve flame stabilization.

This paper reports on the main results of the characterisation of reactive thermo-fluid dynamic field developed by a natural gas swirl burner, equipped with an axial + tangential entry swirl generator (swirl number of the air stream fed to the burner=0.82) and with fuel injection coaxial to the air stream (Fig. 1). This burner has been selected for both experimental analysis and numerical simulation, presenting a geometry similar to that used in typical industrial appliances, but simple enough to allow a continuous match between experimental data and results from CFD simulations.

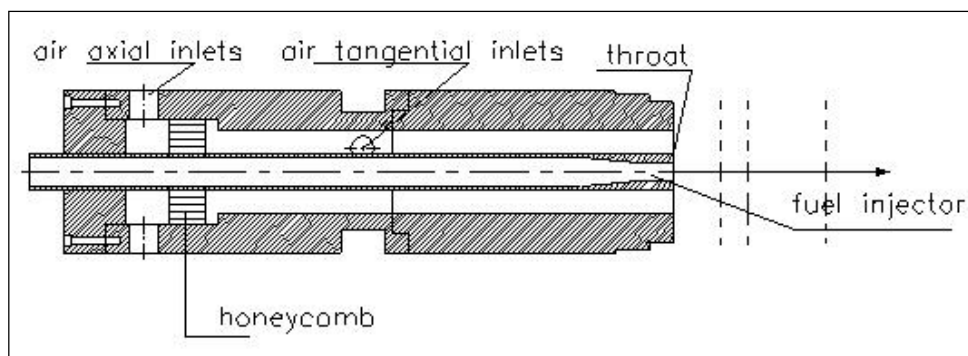


Fig. 1: schematic view of the investigated burner.

Natural gas is supplied through a central pipe with an axial injection nozzle, 8 mm diameter, derived from a real burner injector design. The inner pipe has an outer diameter of 15 mm and is located concentrically in the outer pipe of inner radius $R_b = 18$ mm. The tangential and axial air and the fuel flow rates are measured and stabilized by calibrated thermal mass flowmeters and controllers. The burner is fed by natural gas provided by the network distributor in the Bovisa laboratory area (90% methane, 4% ethane, 1.5% propane, 4% N_2 and a small percentage of higher hydrocarbons). It works in lean condition (equivalence ratio=0.68) with an input thermal power=17 kW. The main operating conditions of the combustor are resumed in Tab. 1

Air flow rate [g/s]	8.8
Air mean velocity efflux v_{air} [m/s]	8.7
Reynolds number of air jet	20700
Natural gas flow rate [g/s]	0.35
Natural gas mean velocity efflux v_f [m/s]	10.7
Reynolds number of natural gas jet	5600
Input thermal power [kW]	17
Air swirl number S	0.82
Fuel/Air Momentum ratio MR	0.91
Fuel/Air Equivalence ratio Φ	0.68

Tab. 1: main operating conditions of the investigated burner.

Experimental analysis of the flame confined by a quartz combustion chamber (internal diameter=192 mm) has been performed by means of laser Doppler anemometry for velocity measurements and thin thermocouples for temperature characterization.

2 - NUMERICAL INVESTIGATIONS

The numerical investigations were performed using the commercial CFD code FLUENT 6.0. The algorithms PRESTO and SIMPLE [1] were respectively used for the pressure interpolation and for the coupling of pressure and velocity. Thermal radiation is included in the simulation using the P1 model [2]: combustion chamber wall emissivity has been set to 0.85. A two standard equations k- ϵ model was used to model turbulence, and the Standard-Wall-Functions for the wall treatment. The natural gas oxidation was described using a simplified chemical kinetics scheme composed of 4 reactions (1-4)[3]. Three other reactions (5-7) were introduced to take into account the partial oxidation of heavier alkanes C_2H_6 , C_3H_8 , C_4H_{10} to CO which are present in the fuel feeding:

Tab. 2: Reaction scheme [kmol-m-s-kJ-K] ($R_i = AT^\beta \exp(-Ea/RT) \prod C_i^{\alpha_i}$)

Expression	A	Ea	β	α_i	n°
$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$	4.4×10^{11}	1.256×10^5	0	$n(CH_4) = 0.5, n(O_2) = 1.25$	(1)
$CH_4 + H_2O \rightarrow CO + 3H_2$	3.0×10^8	1.256×10^5	0	$n(CH_4) = 1, n(H_2O) = 1$	(2)
$H_2 + 0.5O_2 \leftrightarrow H_2O$	2.5×10^{16}	1.67×10^5	-1	$n(H_2) = 0.5, n(O_2) = 2.25,$ $n(H_2O) = -1$	(3)
$CO + H_2O \leftrightarrow CO_2 + H_2$	2.75×10^9	8.38×10^4	0	$n(CO) = 1, n(H_2O) = 1$	(4)
$C_2H_6 + 2.5O_2 \rightarrow 2CO + 3H_2O$	7.19×10^9	1.256×10^5	0	$n(C_2H_6) = 0.1, n(O_2) = 1.65$	(5)
$C_3H_8 + 3.5O_2 \rightarrow 3CO + 4H_2O$	5.62×10^9	1.256×10^5	0	$n(C_3H_8) = 0.1, n(O_2) = 1.65$	(6)
$C_4H_{10} + 4.5O_2 \rightarrow 4CO + 5H_2O$	5.62×10^9	1.256×10^5	0	$n(C_4H_{10}) = 0.1, n(O_2) = 1.65$	(7)

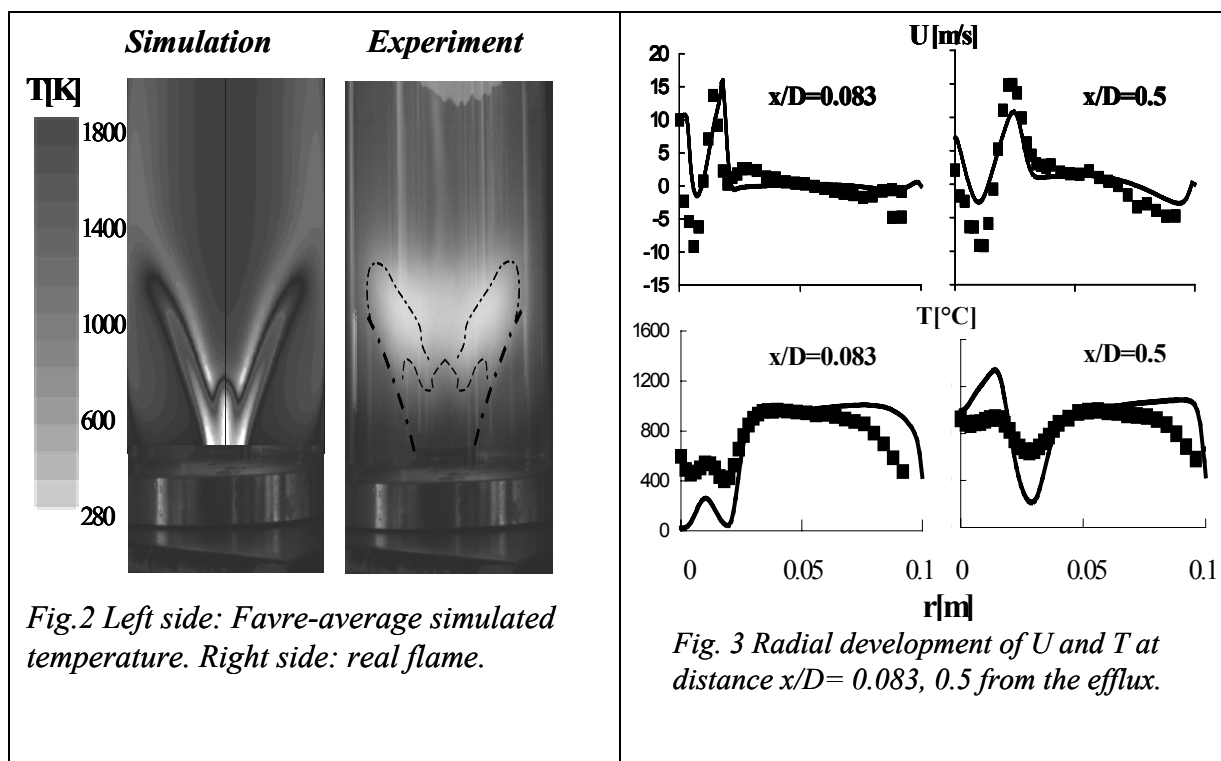
The analysis of non-premixed turbulent flames requires a suitable scheme for coupling the turbulent mixing and the reactions of major species. Usually the finite rate/eddy breakup combustion model is adopted. Being R_i^A the reaction rate from Arrhenius expression, R_i^R and R_i^P the turbulent mixing pointer for reactants and products, this model assumes the smallest rate among R_i , R_i^R and R_i^P as the governing rate. This is done separately for the forward and the reverse rates, ignoring the differences in the Arrhenius expression rate of the two reactions, when the controlling step is the mixing rate of the species

3 – RESULTS AND DISCUSSION

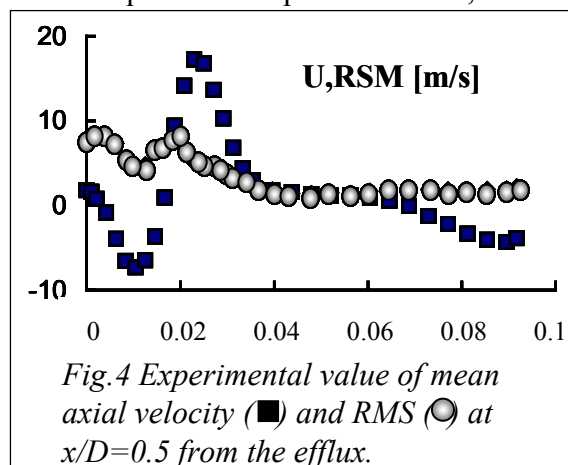
During the first part of the work the numerical simulation of the swirled combustor was

carried out on an axi-symmetric domain. A non-uniform unstructured mesh composed by 21,000 cells was used. The computational grid was adapted close to the reactants efflux where the conditions are more critical (intense turbulent mixing process and variables gradients). Tests performed previously [4] with finer grids demonstrate that the quality of the prediction does not improve enhancing the number of cells used.

From Fig. 2 the simulated thermal field and the image of the investigated flame show a very similar shape: moreover the flame shows the classical bulb morphology, typical of high swirl processes.



Under a quantitative point of view, from the comparison of the mean axial velocity and temperature radial profiles (at different distances x/D from the efflux, where D =air duct diameter=36 mm) in Fig. 3, the numerical results do not satisfactory agree with the experimental data, in particular in the zone nearest to the axis, in which the code seems to under-predict the mixing rate of the two coaxial streams, giving rise to higher segregation of the central fuel jet with respect to the experimental measurements. As a consequence, the code under-estimates also the development of the central recirculation zone due to the high swirl effect, which can



induce hot gases opposed flow with respect to the central fuel jet penetration. These differences are probably due to the strong fluctuations that characterize the not completely developed turbulent flow ($Re \approx 5600$) of the central fuel jet, as shown in Fig. 4, which presents the measured radial profile of mean axial velocity and turbulence intensity at a distance

$x/D=0.5$. In this figure, it is evident that the fluctuating component, especially in the zone close to the burner axis, is of the same order of the mean value.

This not predictable turbulence intensity close to the burner axis can induce higher mixing rate of the two coaxial streams, also with hot burned gases recirculating in the central region developed by swirl, increasing the gas inlet temperature to values much higher than the inlet value of 300 K.

Being the turbulence effects so marked, their influence must be evaluated in a 3D simulation. Therefore, the agreement with the experimental data was improved using the computational grid shown in figure 5 composed of 150,000 cells.

In particular, to represent the strong fluctuations near the central inlet, the natural gas feeding was tilted of 3° to simulate increase of turbulence levels and subsequent mixing and possible flame instability.

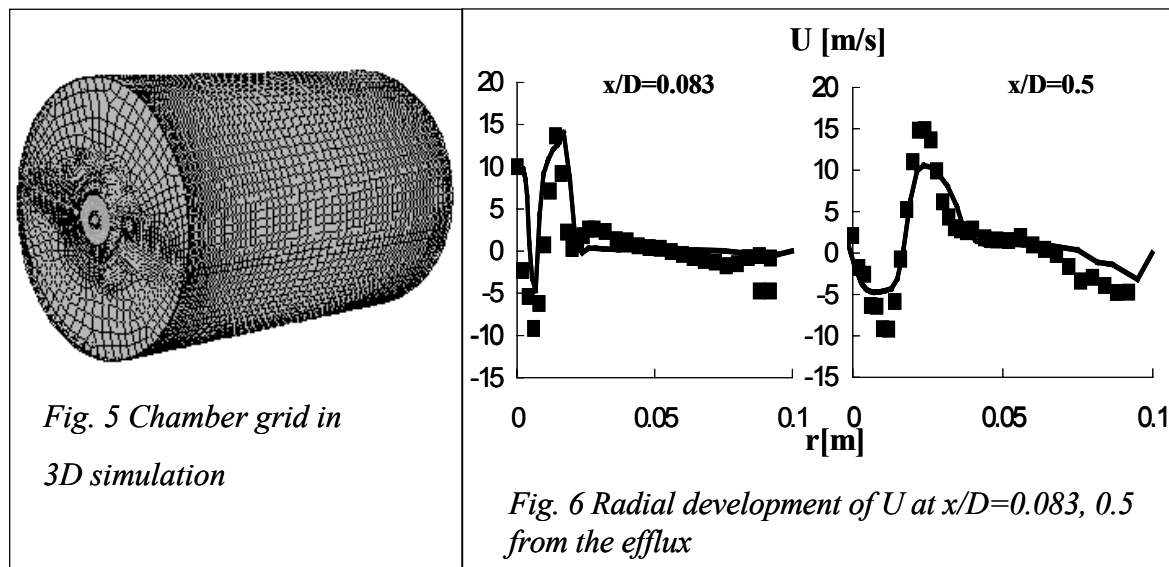


Fig. 6 shows the comparison between the experimental and calculated mean axial velocity profiles of the flame, with 3° tilting of the fuel injector. It can be observed that the agreement is good (especially for the formation and development of the recirculating region due to swirl), and the simulated solution is strongly improved.

4 – CONCLUSIONS

The work has shown some of the problematic in simulating strong swirling flames ($S \approx 0.9$). The strong turbulence generated by the application of the tangential velocity component to the fresh air incoming requires unsteady simulations to describe the turbulent phenomena that characterize such flows.

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Large Eddy Simulation of Flame Wrinkling in Turbulent Premixed Combustion

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This work investigates a flame tracking method based on the level-set G -equation, for simulation of flame wrinkling. The G -equation was derived for tracking the motion of flame front. It has been used by several authors in different applications, such as studies of hydrodynamic instabilities (see [1] and references therein); simulations of turbulent premixed flames using Reynolds averaged Navier-Stokes equations (RANS) [1-3] and large eddy simulations (LES) [4]. In the statistically stationary RANS calculations, wrinkling of the instantaneous flame front can not be simulated directly, rather, it has to be modeled. In LES, the unsteady motion of the large-scale eddies down to the inertial sub-range scales are calculated directly. The wrinkling of flame front (at least the large-scale wrinkling) may be captured in LES. Results presented in this paper indicate that not all the resolved eddies are effective in wrinkling the flame front.

The following model G -equation is used

$$\frac{\partial G}{\partial t} + u_i^{gs} \frac{\partial G}{\partial x_i} = s_{sgs} \left(\frac{\partial G}{\partial x_i} \frac{\partial G}{\partial x_i} \right)^{1/2} \quad (1)$$

Here u_i^{gs} is the LES grid resolved velocity component in x_i direction; s_{sgs} is the sub-grid scale flame surface propagation speed, which depends on several factors: the thermal-chemical properties of the reactant mixture, the flame stretch, etc.. In the G -equation (1), the effect of flow convection by the three-dimensional eddies is taken into account in terms of u_i^{gs} and effect of differential diffusion (non-unity Lewis number) and flame stretch is taken into account in terms of s_{sgs} . It is calculated here using Damköhler's model, valid at the Damköhler's large-scale turbulence limit:

$$s_{sgs} = s_L + u'_\Delta \quad (2)$$

Here s_L is the laminar burning velocity and u'_Δ is the characteristic turbulence velocity scale at the resolved grid length scale Δ .

The above equations are numerically solved together with the space-filter Navier-Stokes equations in a bluff body stabilized premixed flame configuration, known as VR-1 test rig [5], which has been studied using RANS based models [2,3]. The VR-1 test rig consists of a rectangular channel, 120mm high and 240mm wide. In the chosen test case, propane/air lean premixed mixture, at equivalence ratio 0.6 and inlet temperature 600K is introduced to the combustor. A prismatic triangular flame holder, with the side length 40mm, is used to stabilize the combustion.

Figure 1 shows the instantaneous flame surface denoted by $G=0$. The large scale wrinkling is clearly seen in both the streamwise and spanwise directions. From the top view

figure (1c) one can see there are several ‘holes’ which is the place where the flame surface attached to the walls. Two flame surfaces are shown in the figure (see 1a, 1b). The two flame surfaces are originated from (physically stabilized by) a flame holder which is placed at the left hand side of the figure. From the side view figure (see 1b, 1a) one can see that most of the wrinkling scales is of length of the flame holder height which is typically of integral length scale. The top view figure shows that in the spanwise direction there are about 6 wrinkling ‘periods’. Each of these scales is also about the flame holder height. There are some small wrinkling scales found in the top view figure (1c).

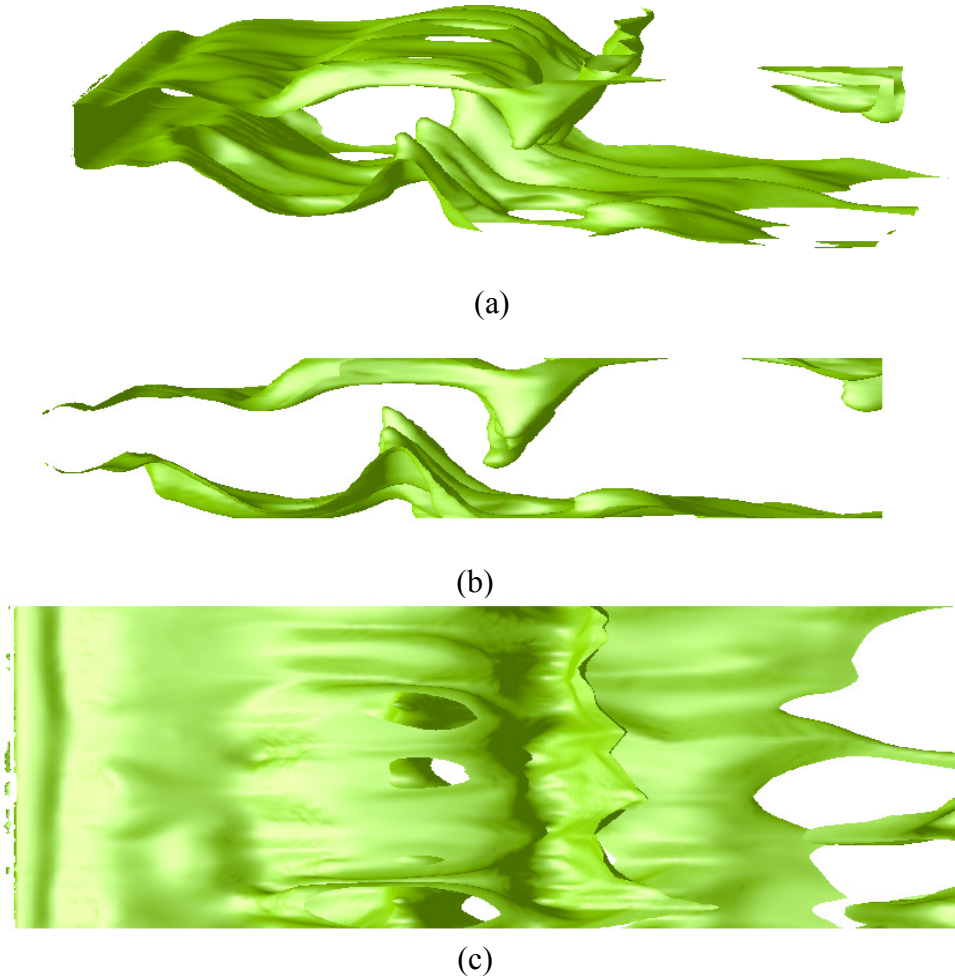


Fig. 1. An instantaneous flame front ($G=0$). (a): a 3-D view showing the resolved wrinkling scales; (b): a 2-D side view showing mainly the streamwise wrinkling; (c): a 2-D top view showing both streamwise (horizontal in the figure) and spanwise wrinkling

Figure 2 shows iso-surfaces of the three components of the instantaneous vorticity field. The iso-surface is chosen as $\omega_x = 0, \omega_y = 0, \omega_z = 0$, which are the boundaries separating clockwise rotating eddies and counter-clockwise rotation eddies. Therefore they show in certain sense the length scales of different turbulence eddies. As seen first, the resolved length scales varies in a wide range, which is a general characteristic of turbulence. The triangular shaped flame holder can also be seen in the figure. The flow is from the left hand of the figure to the right hand side. In front of the flame holder, only certain large scale eddies are found. After the flame holder much small scale eddies are found, which indicates significant

turbulence production by the bluff body. It is worthy noting that the resolved turbulent scales are highly anisotropic: the scales of eddies in the streamwise direction are much longer than the other two directions. Also noted is the vortex shedding structure after the flame holder.

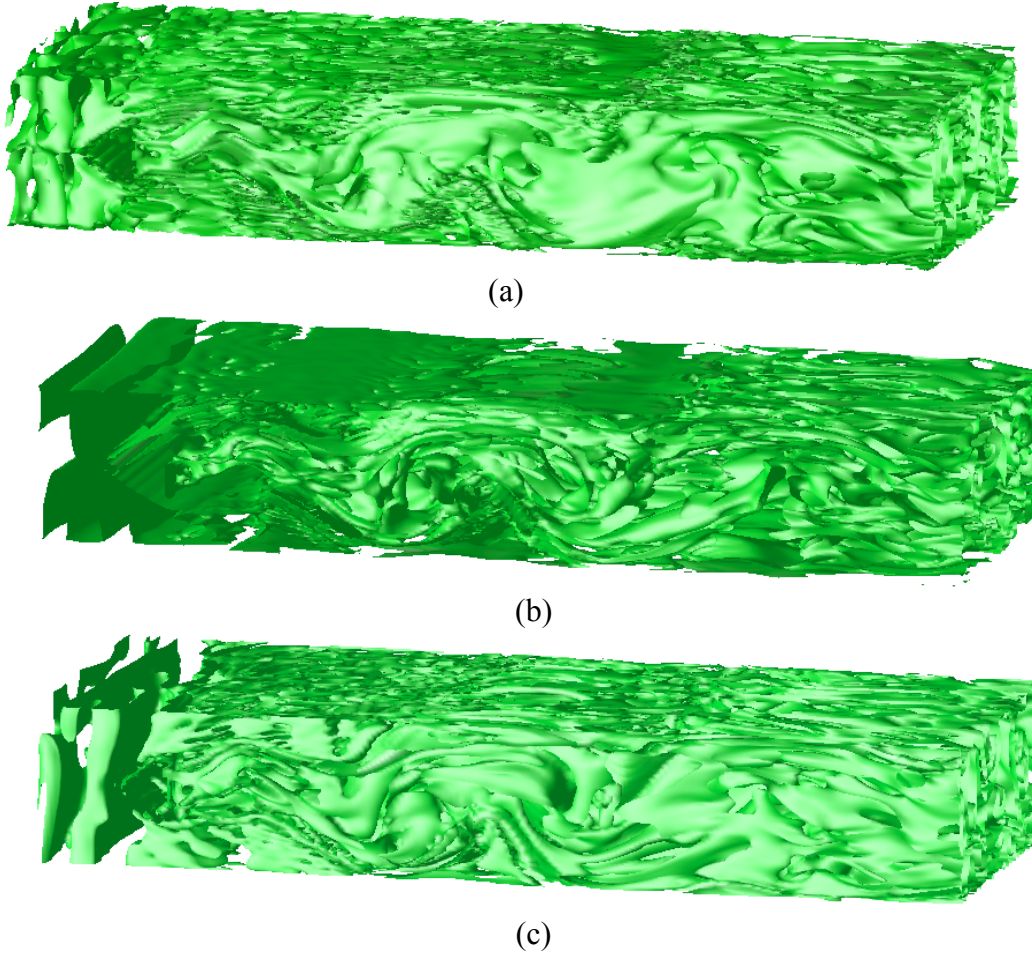


Fig. 2 Three-dimensional view of iso-surfaces of vorticity components. (a): streamwise vorticity component $\omega_x=0$, (b): vertical vorticity component $\omega_y=0$, (c): spanwise vorticity components $\omega_z=0$.

Combining Figures 1 and 2 we can find the following. First, turbulence and the flame surface is closely inter-acting each other. The flame surface shape follows closely the shape of the wake vortex shedding. The flame has a significant impact on the turbulence field. In front of the flame (left hand side of the flame surface), turbulence eddies are much finer. After the flame turbulence eddies are large. Second, although the resolved eddies scales are rich, the wrinkle size is mainly close to the integral length. Smaller scale wrinkling is not captured. A possible cause of this failure may be the lack of response of flame front to the smaller eddies.

An analysis is performed to examine the response of flame front to small disturbance. For a one-dimension flame moving following a sine wave as a function of time with a frequency ω and amplitude a , it can be shown that the $G=0$ front moves as a function of sine wave with the same frequency (with a phase delay of 90 degrees). The amplitude of the $G=0$ front fluctuation is however proportional to a/ω . This implies that the high frequency disturbance is not effective in perturbing the flame front. As a consequence, we may expect

that in LES using G -equation, the small scale eddies with short time scales are not effective in wrinkling the flame front.

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Flame Structure of Counterflow n-Heptane/Air Partially Premixed Flames

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INTRODUCTION

Liquid fuels represent perhaps the most important energy source, since they are used in numerous propulsion and energy conversion applications. The characteristics of liquid fuel combustion are extremely complex because the fuel is introduced into the combustion chamber in the form of a spray that consists of droplets with a wide size and velocity distribution, resulting in disparate vaporization rates. This non-uniform evaporation process in practical spray combustion systems is very difficult to model so that a fundamental investigation that begins from simpler configurations is very useful. Such an investigation can also facilitate the validation of theoretical/computational models through experimental measurements of flames established in such simpler configurations. However, there is a paucity of such measurements in the literature [1,2]. Although most practical liquid fuels are blends of several components, we have selected n-heptane as a surrogate fuel in this investigation for sake of simplicity.

Due to their diverse applications and fundamental relevance, partially premixed flames have been investigated extensively in recent years. Most of these studies, however, have focused on methane-air flames [1,3-9], motivated perhaps by the fact that extensive experimental data have been reported for these flames and detailed reaction mechanisms are available to model the methane-air chemistry. Except for some recent studies [1,9-13], partially premixed flames burning higher hydrocarbon fuels, especially liquid fuels, have not been investigated.

In this investigation, we report on an experimental-computational investigation of n-heptane partially premixed flames established in a counterflow burner. The objective of this study is to report detailed experimental data that can be subsequently used for the validation of computational models and reaction mechanisms involving simulations of liquid fuels in general, and n-heptane in particular.

EXPERIMENTAL APPARATUS

Experimental results have been obtained for flames established in a counterflow burner. The separation distance between the counterflow nozzles of the burner is 15 mm and the jet diameter is 27.38 mm. The fuel emerges from the bottom nozzle. A nitrogen curtain is established through an annular duct surrounding the fuel jet in order to isolate the flame from ambient disturbances. The nitrogen and burned gases are exhausted and cooled through another annular duct around the oxidizer nozzle. A detailed schematic of the experimental setup is presented in Fig. 1.

The velocities of the two streams are chosen to conform to the global strain rate [3],

$$a_g = \frac{2|V_O|}{L} \left(1 + \frac{|V_F|}{|V_O|} \sqrt{\frac{\rho_F}{\rho_O}} \right)$$

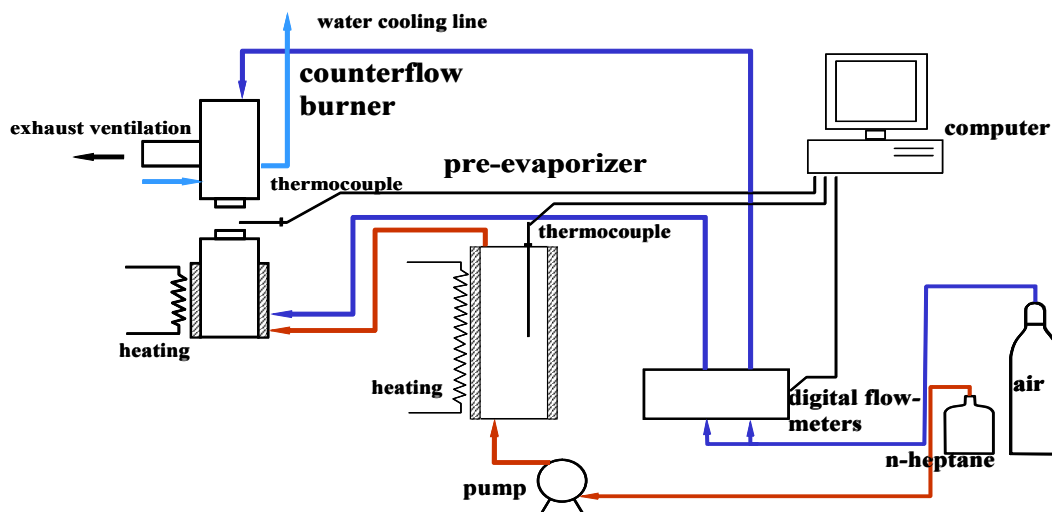


Fig. 1 Schematic of the experimental apparatus.

and to satisfy the momentum balance,

$$\rho_O V_O^2 = \rho_F V_F^2$$

The oxidizer is air at room temperature while the fuel stream consists of mixtures of nitrogen and prevaporized n-heptane. The fuel nozzle is heated and the temperature is controlled to maintain the fuel-containing stream at a 400 K temperature at the burner exit. Nitrogen and n-heptane are mixed in a prevaporizer, which consists of a stainless steel chamber that is electrically heated. The desired mass flowrate of n-heptane into the prevaporizer is maintained by a liquid pump. Half of the chamber is filled with glass beads to impede the flow, thereby increasing its residence time in the chamber and, hence, enhancing the heat transfer to the liquid fuel. The temperature of the fuel vapor exiting the chamber is monitored by a thermocouple.

Temperature profiles of various flames have been obtained using a thin Pt-Rh thermocouple with a bead diameter of 0.508 mm and wire diameter of 0.127 mm.

REACTION MECHANISM

The kinetic mechanism (SOX) used to model the flames has been developed by extending a detailed oxidation scheme which can be used for several fuels. Due to the hierarchical modularity of the mechanistic scheme, this model is based on a detailed sub-mechanism of C₁-C₄ species. Assuming analogy rules for similar reactions, only a few fundamental kinetic parameters are required for the progressive extension of the scheme towards heavier species. The resulting kinetic model of hydrocarbon oxidation from methane up to n-tetradecane consists of about 250 species and 5,000 reactions. Almost all the reactions considered in this work have been already published and the complete scheme is available upon request [14].

The subset of n-heptane oxidation reactions in the mechanism have been extensively tuned by validating experimental measurements for pure pyrolysis conditions, oxidation in a jet stirred and plug flow reactors, and on a large set of shock tube experiments [15]. The polycyclic aromatic hydrocarbons (PAHs), well known for being soot precursors, are described with large detail inside the scheme. The formation of the first aromatic rings by the C₂ and C₄ chemistry and by the resonantly stabilized radicals like propargyl and cyclopentadienyl (C₃H₃ and C₅H₅) has been carefully investigated in previous investigations [16,17]. Further growth of PAH species up to coronene (C₂₄H₁₂) is also modelled through the well known HACA mechanism (Hydrogen Abstraction Carbon Addition) [18]. The main consumption reactions of aromatics and PAHs are H abstraction reactions by H and OH radicals. This high temperature reaction

mechanism has been validated by a large amount of experimental data [16,17].

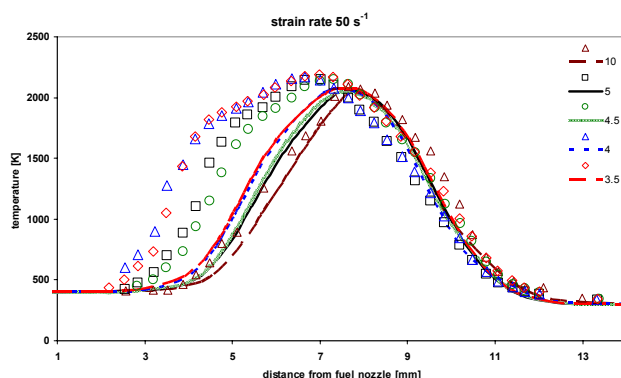


Fig. 2a Experimental (symbols) and simulated (lines) temperature profiles at a strain rate of 50 s^{-1} .

Numerical simulations have been done with OPPDIF, a program from CHEMKIN package [19] that is capable of modeling combustion between two opposed jets. The code has been modified to handle the complex reaction mechanism that was previously described, and to account for thermal radiation through the optically thin model. Thermodynamic properties were mainly obtained from Burcat [20]. Unavailable properties have been estimated by using group additivity and difference methods [21]. Transport properties have been obtained from the CHEMKIN database [22] wherever available, while unavailable data has been deduced by analogy with known species.

RESULTS AND DISCUSSION

Experiments were performed by varying the global strain rate and the equivalence ratio. Partially premixed n-heptane flames exhibit a characteristic double flame structure. There is an azure flame on the fuel side due to the partial oxidation of heptane by the air present in the fuel-rich stream. Unburned fuel and intermediate combustion species such as CO and H_2 are then carried to the blue non-premixed flame where they are oxidized by air.

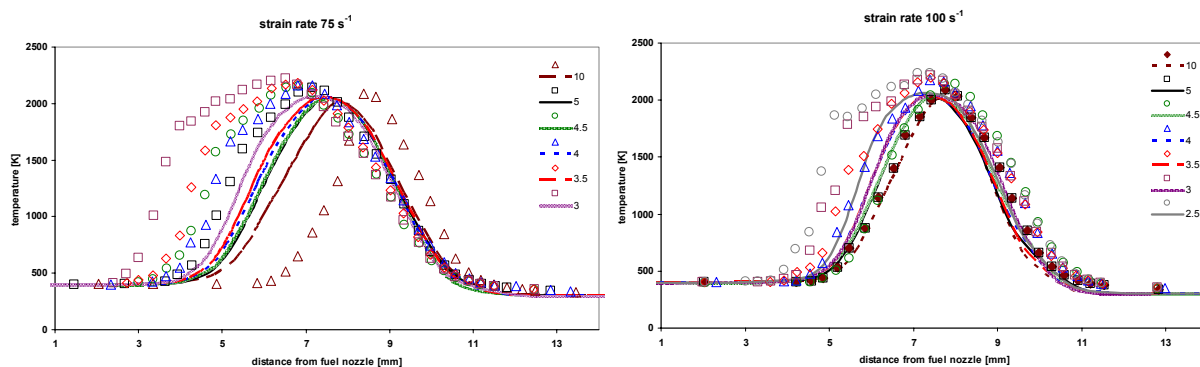


Fig. 2 Experimental (symbols) and simulated (lines) temperature profiles at a strain rate of 75 s^{-1} (b) and 100 s^{-1} (c).

We will report three sets of results for three different strain rates. For each strain rate, we will compare temperature profiles for flames established with several values of equivalence ratios ϕ of partial premixing. Figure 2a presents values of temperature for flames established at a global strain rate of 50 s^{-1} and at equivalence ratios decreasing from 10 to 3. The experimental values are compared with numerical simulations and the temperature measurements have been

corrected for radiation heat loss. The double flame structure is evident from the broad temperature profiles. Decreasing the equivalence ratio of premixing, i.e. making the fuel stream composition closer and closer to a stoichiometric mixture, the premixed flame shifts towards the fuel nozzle, and the peak temperature increases. For the case $\phi=3.0$ the oxidizer concentration is such that the premixed flame is almost attached to the fuel nozzle. The oxidizer side of temperature profile is slightly affected by the variation of equivalence ratio of premixing. The location of the non-premixed flame is unchanged, while the peak temperature slightly increases. The same trend can be observed in Figs. 2b and 2c in which similar experimental results are presented for strain rates of 75 s^{-1} and 100 s^{-1} respectively. The profiles in general become sharper at higher strain rates because flow velocities increase. The same holds for the cases $a_g=50\text{s}^{-1}$ and $\phi=3$, and $a_g=100\text{s}^{-1}$, $\phi=3.5$. The simulated profiles reflect this behavior and the peak temperature values are in good agreement with the experimental results.

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Automatic reduction of chemical mechanisms up to C₁₀ applied to RIF calculations

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ABSTRACT

An automatic reduction procedure for chemical mechanisms has been applied to reduce a complex mechanism for n-decane (105 species, 883 reactions) and used in Representative Interactive Flamelet (RIF) calculations under Diesel engine conditions. Thus the resulting reduced mechanism must reproduce the ignition as well as the development of the flamelet. The procedure uses the quasi-steady-state approximation (QSSA) through an automatic identification of steady-state species. The automatic selection is carried out according to a Level of Importance (LOI) measure obtained from the species' chemical lifetime and species sensitivity. In this manner the species are ranked according to their influence on the chemical mechanism and the species with a low LOI are considered in steady-state without introducing significant errors into the calculations.

INTRODUCTION

One of the challenges in combustion science, and any research concerning the treatment of large chemical system, is the reduction of chemical reaction mechanisms without loss of detailed information and accuracy. This is of importance for implementation of more realistic chemistry in CFD modelling without leading to unacceptable increase in the computational cost. Also, reduced mechanisms are indeed favourable when applying procedures for combining flow calculations with more complex chemistry for the predictions of gaseous and particulate emissions. One example for this is the simulation of the combustion process in a Diesel engine, using instationary representative interactive flamelets. As the demand for results using complex fuels are increasing, easy and flexible methods for reducing the large detailed mechanisms to manageable sizes are essential.

Different methods for obtaining and handling reduced mechanisms have been proposed in literature. The most commonly used are the intrinsic low dimensional manifold method (ILDM) proposed by Maas and Pope [1], and computational singular perturbation (CSP) proposed by Lam [2], and developed by Massias et al. [3]. However, they are not trivial to use, and rely to some extent on an experienced user. It has been our goal to develop a flexible reduction procedure that is automated to the extent that no prior experiences with the mechanisms are needed. Also, we have focused on developing a selection parameter for steady state species that is general in use in any combustion system. The method has been presented in a series of publications where different chemical and physical systems have been used to demonstrate the flexibility of such a method [4][5]. In the present work our objectives have been to extend the work to more challenging systems.

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We used a chemical mechanism for a mixture of n-decane and α -methylnaphthalene containing 105 species and 883 reactions, and applied it to a simulation of an igniting flamelet. This implies that the final reduced mechanism must reproduce both the ignition scenario as well as the development of a stable diffusion flame.

PHYSICAL AND CHEMICAL MODELING

The simulations are carried out using an in house code calculating the development of an igniting flamelet under given pressure and initial temperature conditions. The concept was proposed by Peters [6] and is aimed to couple chemistry with flow. Steady state combustion processes – the steady, unreactive initial mixture, and the quasi steady burning state – can be simulated by using a flamelet library, generated prior to the flow calculation. However, instationary combustion processes – ignition of a flamelet, and extinction or re-ignition processes – need to be calculated in interaction with the flow simulation, and demands the solution of the instationary flamelet equations [7]. The simulation for the current work includes the stages of the steady unreactive initial mixture, the ignition and development of the flames – the quasi-steady burning state.

The chemical mechanism is a mechanism for n-Decane/ α -methylnaphthalene mixture combustion including aromatics species needed to predict the inception and growth of soot particles. This mechanism is automatically reduced by quasi-steady-state approximations (QSSA) for species with short chemical lifetimes and/or minor influence on the chemical system. Individual species are ranked with respect to static and dynamic characteristics according to a Level Of Importance (LOI) measure [4] obtained from their chemical lifetimes in combination with a species sensitivity measure:

$$(LOI)_i = S_{T_i} \tau_i \quad (1)$$

where the species sensitivity, the sum of all reaction sensitivities of the reactions in which the species is involved, is taken towards the temperature as the ignition timing is crucial for a correct reproduction of the combustion process and emissions of pollutants such as soot and NO_x. This selection parameter thus captures species with long lifetimes but with little sensitivity on temperature – the target in the present analysis. Vice versa, species with short lifetimes but with high sensitivity will be kept in the mechanism.

A thorough study where different approaches were investigated showed that a simple maximum value of LOI accumulated over the entire calculation range in both space and time did not provide a reliable selection parameter. Typically the values in the flame exceeded the values in the pre-ignition situation. Thus, the resulting reduced mechanisms were inapplicable for reproducing the ignition of the flame satisfactory. An LOI determined at stoichiometric values that was previously found to be reliable in diffusion flame calculations was also studied, but resulted in the same selection parameters as the maximum accumulated values. This is not surprising since the point of stoichiometry in the early flame is not the point of its most reactive condition [8], and accumulated over time, the maximum values at stoichiometry thus the stable flame. This gave motivation to set the LOI at the point of maximum temperature that moves from low mixture fractions towards that of stoichiometry. However, before ignition the maximum temperature is found simply at the first grid-point on the air-side. Thus, a sensitivity parameter failed to be provided at this point. Finally, the accumulated values from the pre-ignition were investigated and found to give a reliable selection of steady-state species. This result is in agreement with earlier experience revealing that satisfactory calculations of the ignition scenario are more

sensitive to the selected steady state species. As soon as a flame has been developed, the calculations are more robust against approximate reduced mechanisms.

RESULTS

The reduced mechanisms provided by the use of the method described above are used to calculate igniting flamelets with a n-Decane/alpha-methylnaphthalene mixture as fuel at pressures $P = 50\text{-}100$ bar. The initial temperatures are set to 950-1200K on the air side and 300-700K on the fuel side. The scalar dissipation rate is set constant in time, with a bell shaped dependency on mixture fraction. It was possible to obtain a 56% reduction of the mechanism to a reduced mechanism containing 46 species. This is still a large number, and an even more reduced mechanism is desirable. This large number is a consequence of that the mechanism must predict the transition from low temperature auto-ignition chemistry to high temperature flame chemistry.

The evolution of the flame is found to be well predicted using the reduced mechanisms down the most reduced. Figure 1 shows the temperature profiles as a function of the mixture fraction at four different points in time, one just before ignition and three as the diffusion flame develops to become well established. Some deviations are found in the fuel rich region probably due to setting many of the C_2 - C_6 species to steady state. A second maximum is found to develop which is a feature also present in the detailed mechanism, but becomes significant at higher pressure. The established diffusion flame is well reproduced by the reduced mechanisms. This is also the experience we have when applying reduced mechanisms in ignition situations and diffusion flame situations separately. The reproduction of ignition is more sensitive on the employed mechanism, whereas the flame calculations need a few-step mechanism to represent the chemistry involved.

CONCLUSIONS

A set of reduced mechanisms based on a mechanism for mixtures of n-decane and α -methylnaphthalene, compiled from different sources, has been developed and tested for validity. The reduced mechanisms are validated in a similar in-house RIF-code. An acceptable agreement between the results from the full mechanism and the reduced mechanisms down a reduction of 56% in the number of species is reported. The mechanism is also tested for its robustness to changing physical conditions and found to be satisfactory. However, treatment of the algebraic equations to calculate the concentrations of steady state species in an inner iteration is needed. This procedure becomes time demanding as the number of species in steady state increases, and must be improved to achieve significant speed up also for the most reduced mechanisms for complex fuels. Such improvements can include lumping or truncation procedures.

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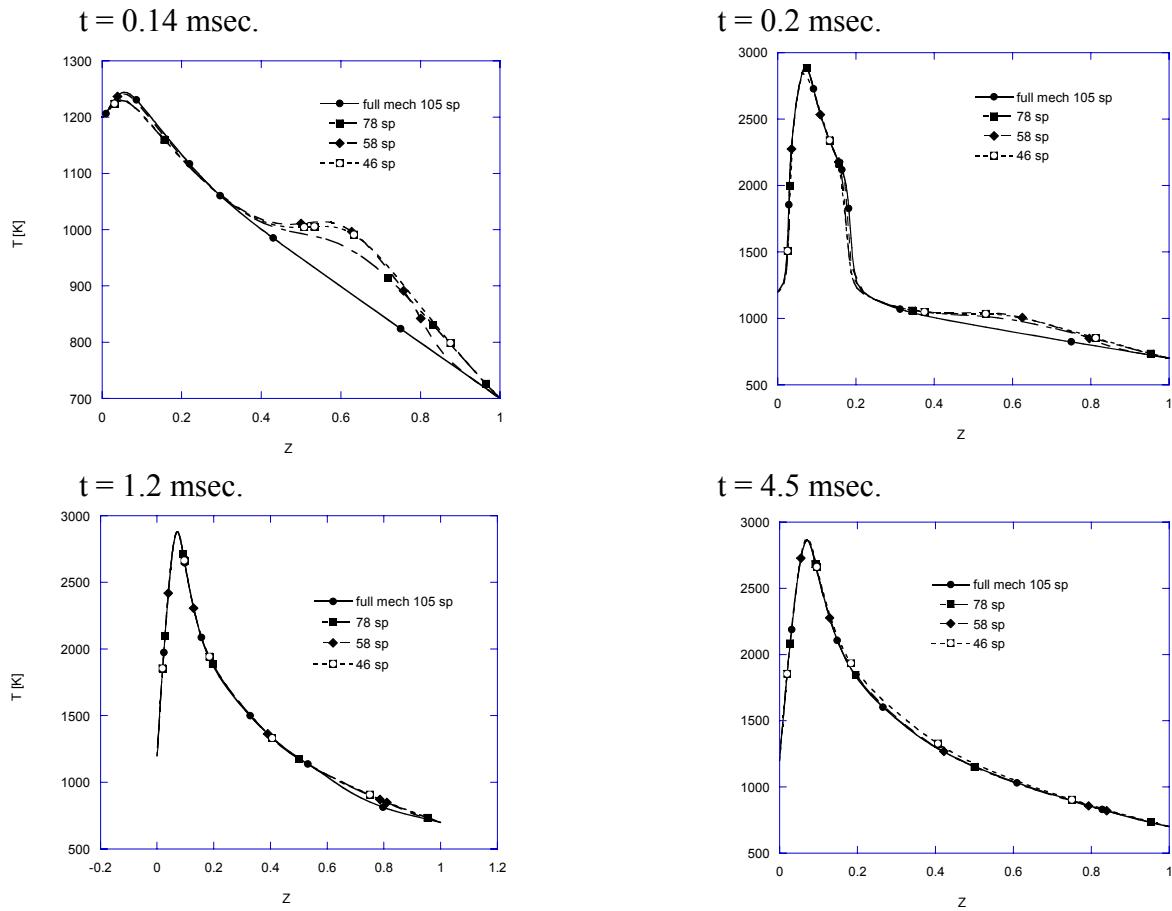


Figure 1: Maximum temperature profiles as a function of the mixture fraction for four different points in time.

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An investigation of butadiene reactions as possible source of soot precursors

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INTRODUCTION

Among the different harmful airborne species produced by fossil fuels combustion, since a few years the attention has been focused on the emission of polycyclic aromatic hydrocarbons (PAH) and soot [1]. Although there is a general agreement on the main feature of the processes involved [2], the details of the reaction mechanism are not yet completely understood. Among the possible reactions that can contribute to the formation of PAH, pathways involving butadiene can be important in various operating conditions since, because of its stability, butadiene is a significant intermediate during hydrocarbon combustion. For instance, butadiene can be thought to be involved in the formation of two-ring hydrocarbons through the addition to the phenyl radical. Then, the main goal of this work was to investigate the production of cyclic hydrocarbons from the addition of 1,3-C₄H₆ to C₆H₅. In particular, naphthalene and indene formation has been considered. Due to the lack of experimental information, all the relevant thermodynamic and kinetic parameters for the different reaction channels, shown in figure 1, were estimated through quantum chemistry.

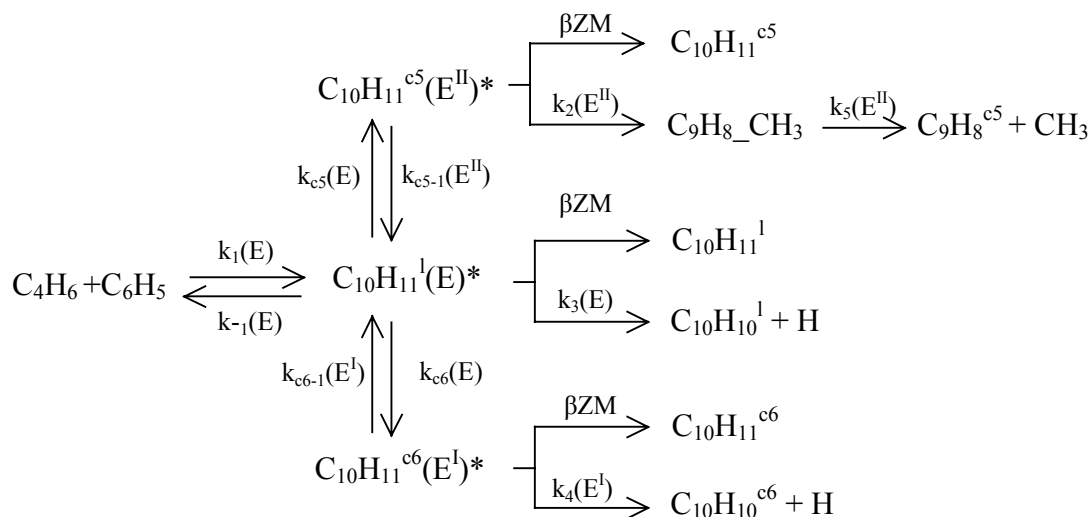


Fig. 1 Global kinetic scheme following the reaction of addition of C₄H₆ to C₆H₅.

In particular, the molecular energies of reactants, products and transition states were calculated with an approach similar to the G2MP2 method [3] from which it differs in that geometrical structures were not optimized at MP2 level, but with B3LYP functionals [4] and the 6-31g(d,p) basis set. This modification decreases the computational times and increases the accuracy of the calculated energies. All calculations were performed with the Gaussian 98

programs suite [5]. Global kinetic constants were calculated with Quantum Rice Ramsperger Kassel theory [6].

RESULTS

Evaluation of TST rate coefficients

Calculated kinetic constants for the addition of C_6H_5 to C_4H_6 to form the $C_6H_5-C_4H_6$ adduct and for its decomposition are reported in Table 1.

Table 1. Kinetic constants calculated for the addition of C_6H_5 to C_4H_6 . $k=AT^\alpha \exp(-E_a/(RT))$. Energies calculated at the G2MP2 level on geometries optimized at the B3LYP/6-31G(d,p) level. Units in kcal, s, mol and cm.

	Reaction	A_{forw}	α	$E_{a\text{forw}}$	A_{back}	α	$E_{a\text{back}}$
k1	$C_4H_6 + C_6H_5 \rightarrow C_{10}H_{11}^l$	$3.1 \cdot 10^{11}$	0.	0.	$1.7 \cdot 10^{17}$	-1.	48.9
k _{c5}	$C_{10}H_{11}^l \rightarrow C_{10}H_{11}^{c5}$	$1.3 \cdot 10^{11}$	0.	45.0	$6.1 \cdot 10^{12}$	0.	25.9
k _{c6}	$C_{10}H_{11}^l \rightarrow C_{10}H_{11}^{c6}$	$1.9 \cdot 10^{11}$	0.	24.5	$6.7 \cdot 10^{12}$	0.	20.7
k ₂	$C_{10}H_{11}^{c5} \rightarrow C_9H_8^{c5} - CH_3$	$4.0 \cdot 10^{12}$	0.	24.9	$1.6 \cdot 10^{12}$	0.	51.7
k ₃	$C_{10}H_{11}^l \rightarrow C_{10}H_{10}^l + H$	$3.8 \cdot 10^{12}$	0.	46.8	$8.1 \cdot 10^{12}$	0.	8.8
k ₄	$C_{10}H_{11}^{c6} \rightarrow C_{10}H_{10}^{c6} + H$	$7.8 \cdot 10^{12}$	0.	31.9	$3.5 \cdot 10^{12}$	0.	8.9
k ₅	$C_9H_8^{c5} - CH_3 \rightarrow C_9H_8^{c5} + CH_3$	$1.5 \cdot 10^{13}$	0.	31.5	$5.9 \cdot 10^{10}$	0.	12.1

The optimized transition state structure for this reaction is shown in fig. 2.

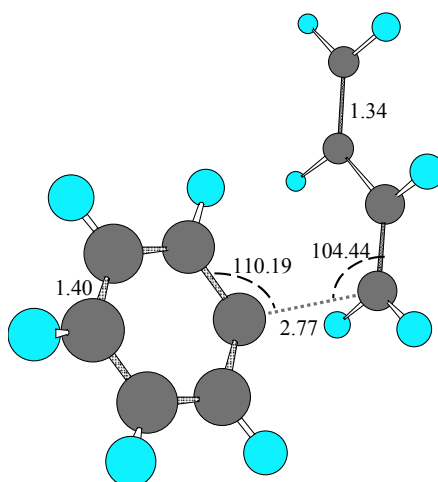


Fig. 2 Transition state structure optimized at the B3LYP/6-31G(d,p) level for the addition of C_4H_6 to C_6H_5 .

The frequencies analysis showed that at the transition state there are several small vibrational frequencies that correspond to the motions shown in figure 3. To determine which should be treated as internal rotor, we took a few points on the potential energy surface corresponding to

each rotational motion. We found that the 22.4 cm^{-1} vibrational frequency corresponds to the torsional motion around the C-C bond. Therefore it was treated as a free rotor with a mean moment of inertia $I = I_1 \cdot I_2 / (I_1 + I_2)$, being I_1 and I_2 the moments of inertia for rotation around the breaking bond of the two moieties. Two of the remaining low vibrational frequencies are hindered by a substantial energy barrier determined by the mutual repulsion between the two moieties and were therefore treated as vibrations. The remaining two were considered as hindered rotors and their partition function was calculated through the solution of their 1D Schrödinger equation using potentials calculated with quantum chemistry.

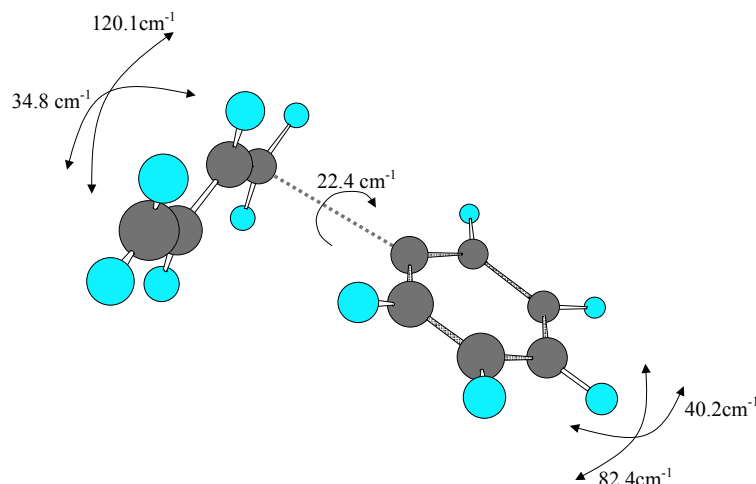


Fig. 3 Vibrations lower than 150 cm^{-1} in the transition state of the reaction $C_4H_6 + C_6H_5 \rightarrow C_4H_6 - C_6H_5$.

QRRK calculations

QRRK rate coefficients were evaluated using as input the kinetic constants calculated with quantum chemistry. The adducts, namely $C_{10}H_{11}^1$, $C_{10}H_{11}^{c6}$, and $C_{10}H_{11}^{c5}$, which are formed through the collisional stabilization reactions from the corresponding excited species, are extremely reactive and unstable, and are therefore likely to get rapidly back to the excited state and react according to the reaction pathway reported in fig. 1. This was accounted for in the QRRK calculations imposing a zero net rate of formation for such species. The rate of formation of $C_{10}H_{10}^{c6}$ and $C_9H_8^{c5}$ is reported in figure 4 as a function of the gas phase temperature.

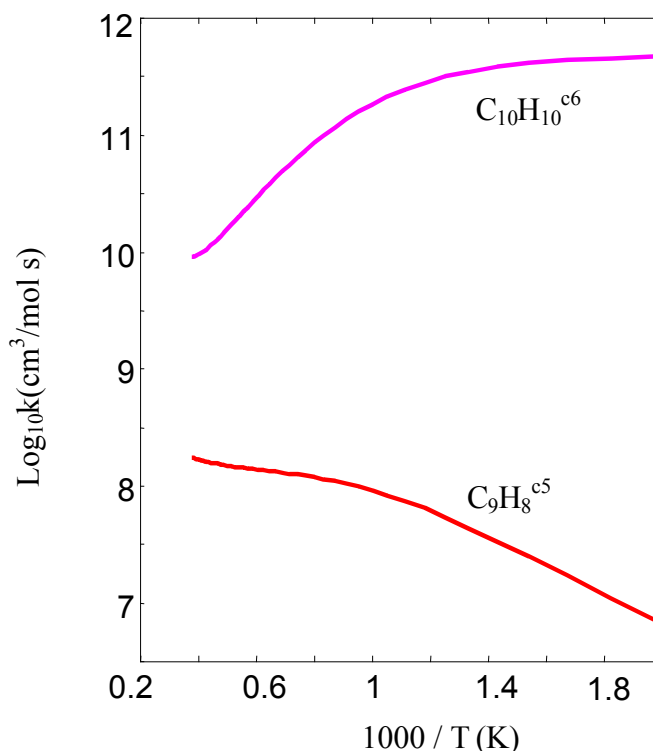


Fig. 4 Comparison between the formation of $C_9H_8^{c5}$ and $C_{10}H_{10}^{c6}$ species in the global kinetic scheme of fig. 1.

To determine whether this mechanism can contribute to the formation of naphthalene, we compared the QRRK reaction rates here calculated with those of the well known HACA mechanism [7]. The rate proposed for the addition of C_2H_2 to C_6H_5 , evaluated at 1000 K, is $1.2 \cdot 10^{11}$ mol/(cm³s), which is similar to the $3.1 \cdot 10^{11}$ mol/(cm³s) value here calculated. Therefore, it can be concluded that at least in conditions where C_4H_6 is more abundant than C_2H_2 and a not negligible amount of C_6H_5 radicals are present, a significant amount of naphthalene and indene can be formed from the direct addition of C_4H_6 to C_6H_5 .

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Detailed Mechanism for n-Heptane and iso-Octane Relevant for HCCI Engine Calculations

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ABSTRACT

A detailed mechanism for the oxidation of n-heptane and iso-octane mixture, including NO_x chemistry, has been developed and validated against the shock tube experimental data from Fieweger et al. [1, 2] for both low and high temperature regions, lean and rich fuel conditions, a range of octane numbers and pressures from 13 bar to 40 bar. In addition, the mechanism was tested using a zero dimensional HCCI model against engine experiments under a range of octane numbers and initial temperatures.

INTRODUCTION

The Homogeneous Charge Compression Ignition (HCCI) is known for its low pollutant emissions and is an important development for meeting future stricter pollution controls. This work studies the effect of elevated pressure and temperature of the n-heptane and iso-octane mixture in the developing combustion device the HCCI engine. It is done by developing and updating the existing fuel mechanism.

The major draw back of HCCI engines is its difficulty to control the ignition timing. The ignition timing in HCCI is dependent on the autoignition chemistry and not on injection timing as in Diesel engines or spark occurrence as in SI engines. A small change in the inlet conditions can vary the results dramatically. For this reason detailed reaction mechanisms for complex fuels, validated under HCCI engine conditions are needed, to simulate and understand the complex chemical processes that lead to autoignition. As a result of this development an accurate and comprehensive reaction mechanism is provided.

DETAILED MECHANISM

The construction of the detailed mechanism is systematically in accordance with Curran et al. [4] using the reaction classes and rate constants suggested by the authors as a base. Intermediate reactions, considered of low importance for the timing of ignition, are simplified substantially. The mechanism is further divided into sub-mechanisms, for lighter hydrocarbon fuels and for reaction intermediates. The detailed mechanism consists of 140 species and 1275 reactions excluding NO_x sub-mechanism and 157 species and 1547 reactions including NO_x sub-mechanism. In the present detailed mechanism all the reaction paths which are known to be pertinent from both high and low temperature kinetics are included in order to cover the full range of temperature and pressure. Pathways of the mechanism involve the fuel species, iso-octane and n-heptane, and also the lower alkene sub-mechanisms of C₇, C₆ and C₅ species (where the C₄ and below is the part of the base mechanism [5]).

Selected species isomers undergoing same reaction types were lumped. In this lumping procedure, a decision is made whether a distinction between the different isomers is necessary or not. However, a distinction was always made in the reaction coefficients (duplicate reactions with different rate coefficients). The first species that are lumped are the products from Reaction type 12 (Alkyl peroxy radical "RO₂" isomerization). Problems in calculating backward reactions of lumped reactions are avoided, since this reaction class is almost

irreversible. The rate constants of this class are found to be not sensitive for both; shock tube experimental and HCCI engine conditions. All alkenes (C_5 , C_6 , C_7 and C_8) have been lumped to either linear (C_5H_{10} , C_6H_{12} , or C_7H_{14}) or branched forms ($i-C_5H_{10}$, $i-C_6H_{12}$, $i-C_7H_{14}$ or $i-C_8H_{16}$).

Sensitivity of reaction pathways

The rate coefficients are chosen in accordance with Curran et al. [4]. Differences in the base mechanisms, and in thermodynamic data, made adjustment for some reaction rate coefficients necessary. For this a detailed sensitivity analysis on the reaction types has been performed.

Reaction type 10 (Addition of Alkyl radicals to O_2) and reaction type 23 (O_2QOOH Isomerization to Ketohydroperoxide + OH) are the most sensitive classes of reactions in terms of their reaction coefficients. We increased the rate constants of both classes by factor 4. This gave the best optimisation of the mechanism for both the shock tube experiments and the engine experiments.

Further, the base mechanism was slightly modified, to include reactions that were found to be important at low temperatures, and to include all branched species that are products of the iso-octane sub-mechanism.

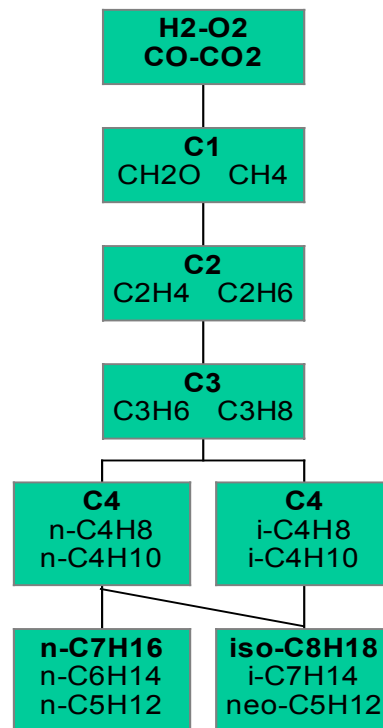


Figure 1: Mechanism

VALIDATION OF MECHANISM

The detailed n-heptane and iso-octane oxidation mechanism has been first validated against the shock tube experimental data from Fieweger et al. [1, 2]. Calculated and experimental ignition delay times have been compared at low and high temperatures. In the negative temperature regime, where the ignition occurs as a two-stage process, we compare in addition the timing of the occurrence of the low temperature oxidation. The mechanism was validated for fuel lean and rich conditions, a range of octane numbers and pressures from 13 bar to 40 bar.

Further validation was done under HCCI engine conditions. NO_x chemistry was included in the mechanism to investigate the influence of rest gas NO_x on ignition timing in HCCI engine. The validation of the mechanism was made for a range of octane numbers and initial temperatures using a zero dimensional HCCI engine model. Experimental data performed at Lund Institute of Technology on a modified Volvo TD100 engine with variable compression ratio and port injected mixture of n-heptane and iso-octane [3] was used.

Constant Volume flow model

Validation of the mechanism was made by comparison between the constant volumes flow model calculations and shock tube experiments from Fieweger et al [1, 2]. The initial temperature range from 700 to 1300 K is set for all the cases. Experiments were considered at 13 to 40 atm, fuel-air equivalence ratios (ϕ) equal to 0.5, 1.0 and 2.0, and RON numbers 0, 20, 40, 60, 80, and 100. In general, there is a good agreement between calculated and experimental ignition delay times. Results for RON 100 and RON 0, $\phi=1$, $P=40$ atm are shown in the figures 2 and 3 as an example.

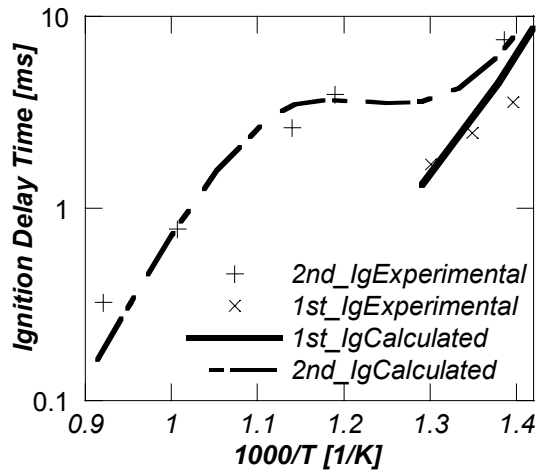


Figure 2: Ignition delay times for iso-octane at $P=40$ atm and $\phi=1.0$.

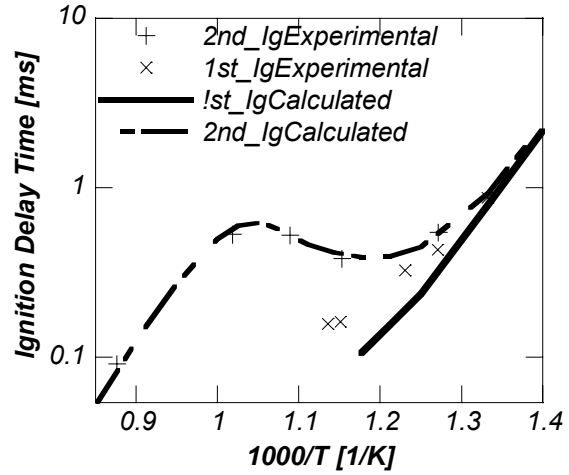


Figure 3: Ignition delay time for n-heptane at $P=40$ atm and $\phi=1.0$.

The comparison shows that both the occurrence of the low temperature oxidation reactions (1st ignition delay time) and the final excitation (2nd ignition delay time) is well predicted. The strong increase of the ignition delay with increasing temperature for n-heptane and the weak increase for iso-octane in the negative temperature regime agrees also well with the experiments.

HCCI Engine Model

The mechanism has been further validated against HCCI engine experiments using the same computer program, which was used for the constant volume calculations. For these calculations a zero-dimensional engine model was applied. The model compresses the gas to auto-ignition, using temperature and pressure at a certain crank angle position obtained from engine experiments as initial conditions. Further input parameters of the model are the air-fuel equivalence ratio (λ), the fuel and oxidizer composition, the amount of internal and external EGR, the cylinder wall temperature, the Woschni constants, the chemical kinetic mechanism for actual fuel, and the engine geometry. The output of the model is crank angle resolution, species concentration, cylinder pressure and temperature. Agreement in temperature and pressure profiles (before autoignition occurrence) can be improved by varying the initial conditions of cylinder temperature and pressure and also the air-fuel ratio.

The calculated data from the ignition code is validated against the experimental data, which was provided by Christensen et al., at Lund Institute of Technology [3]. The engine experiments were performed in a Volvo TD100 engine modified to run on one cylinder and with a secondary piston in the cylinder head giving the opportunity to vary the compression ratio. Iso-octane and n-heptane were mixed to achieve various octane numbers. The fuel was supplied via port injection. The charge temperature was varied between 30 and 130 °C. The compression ratio was adjusted between 21.4 and 10.8 in order to have an optimal point of ignition in each case. The validation of the detailed mechanism was performed for different cases of RON. Air-fuel equivalence ratio (λ) was set to 3.0 for all the cases and the engine speed were 1000 rpm. The initial pressure at inlet valve closing (IVC) for the calculations was consequently set to the measured cylinder pressure minus 0.1 bar, the wall temperature was chosen to be 490 K and EGR (5% residual gas) for all the cases. The calculated and the measured cylinder pressure for the two different cases are shown in figures 4 and 5. As we can see in the figure 4 for the RON 100 case at initial temperature of 330 K (at IVC), there is

a good agreement between the detailed mechanism and the experiments; it can be seen in cylinder pressure trace. Ignition occurs a bit early but altogether it follows the experimental data quite well especially in the low temperature region. This pattern of good agreement can be seen in other cases as well such as the case of RON 83 at initial temperature 359 K which is shown in the figure 5.

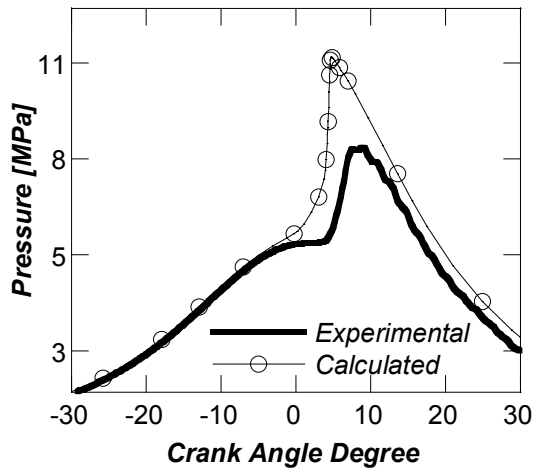


Figure4: Cylinder pressure for RON100 at initial temperature of 330K

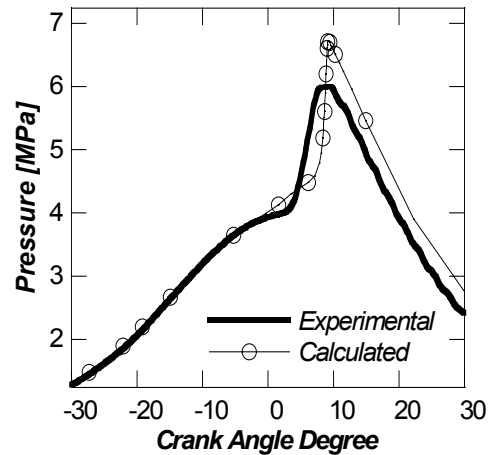


Figure5: Cylinder pressure for RON83 at initial temperature of 359K

CONCLUSION

A detailed reaction mechanism of n-heptane/iso-octane oxidation with special focus on optimising it to the HCCI engine conditions has been presented. The mechanism was constructed using a reaction type concept as used for automatic mechanism generation. The size of the mechanism is limited by making use of species lumping. The developed mechanism has been validated against the experimental data from shock tube and HCCI engine experiments. The ignition delay is well predicted for the shock tube experiments, at low and high temperatures and at low and high octane numbers. In the negative temperature regime the occurrence of low temperature oxidation reactions is well predicted. For the HCCI engine experiments there has been a significantly good agreement between model predictions and experimental data. This work provides a detailed kinetic mechanism for mixture of n-heptane and iso-octane containing a reasonable low number of the species and reactions. This item of the mechanism provides a good basis for further reduction of the mechanism, using sensitivity, reaction flow, and lifetime analysis.

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Pyrolysis and Oxidation of Cyclo-Alkanes

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Introduction

Detailed kinetic mechanisms of oxidation and combustion processes are useful tools for the evaluation of knocking tendency of the different fuels as well as for the prediction of pollutant formation in terms of PAH, soot and NO_x. Detailed kinetic schemes for methane and natural gas combustion are reliable and widely used in the scientific community. GRI Mechanism is a well known and largely diffused example. On the contrary, the kinetic knowledge and above all the availability in the scientific literature of reliable kinetic schemes for liquid fuels is scarce. Real gasolines consist of mixtures of most of the hydrocarbon isomers in the C₄-C₉ fraction possibly including also different additives. RON, MON and BRON commercial indexes are widely used in order to define the knocking propensity of the gasolines in terms of a surrogate mixture of only two primary reference fuels: iso-octane and n-heptane. Oxidation and combustion of gasoline is therefore described with detailed kinetic mechanisms of these two model fuels even if kinetic schemes with a detailed description of several isomers in the paraffin fractions have been developed in the recent years. These kinetic schemes are very detailed in the initial propagation reactions taking into account all of the different isomer species but strongly sacrifice the successive steps of the huge number of intermediate species [1].

The proper characterization and description of diesel, kerosene and jet fuels is a more difficult task. In facts, these liquid fuels consist of complex mixtures of heavy hydrocarbons, including alkane, cycloalkanes and aromatic molecules in the C₁₀-C₁₆ fraction.

As already discussed elsewhere, the definition of primary reaction classes with their reference kinetic parameters for normal and branched alkanes allows the automatic generation of detailed kinetic schemes. In this way, it is well evident that the description of pyrolysis and combustion of large alkane molecules such n-dodecane or iso-cetane becomes a feasible task [2].

This work presents and discusses some features of the kinetic behaviour of cycloalkane combustion, where larger uncertainties are still present.

Main classes of primary propagation reactions of cycloalkanes.

As already mentioned, the primary oxidation reactions of alkanes to form primary products and intermediate radicals have already been discussed in previous papers [3]. On very similar basis, it is possible to follow the reaction paths of cyclo-alkanes both for the high and low temperature oxidation mechanisms. At high temperatures, alkyl radicals from cyclo-hexane and methyl-cyclohexane undergo β -decomposition reactions to form not only cyclo-alkenes radicals but also hexenyl and heptenyl radicals, respectively. These radicals can subsequently isomerize to form the resonantly stabilized radicals of allyl type. Hexenyl, heptenyl and resonant radicals can then β -decompose to form smaller radicals and diolefines.

As usual for the low temperature reactions, oxygen addition on alkyl radicals is in competition with the H-abstraction reactions to form alkenes and HO₂[•]. The formation of peroxy radicals, without activation energy, prevails at low temperatures and this is the first step towards the usual degenerate branching path involving the following successive elementary steps:

- Isomerization of peroxy radicals ($\text{ROO}\cdot$) to form hydro-peroxy-alkyl radicals ($\text{QOOH}\cdot$).
- O_2 addition on $\text{QOOH}\cdot$ to form hydro-peroxy-alkyl-perossidic radicals ($\cdot\text{OOQOOH}$).
- Isomerization and decomposition of $\cdot\text{OOQOOH}$ to form $\text{OH}\cdot$ and a ketohydroperoxide.
- Decomposition of ketohydroperoxides to form 2 radicals.

These reactions are important at low temperatures and high pressures, since they depend on O_2 concentration. The importance of ketohydroperoxide formation lies in its very fast unimolecular decomposition reaction ($k_{\text{dec}} \approx 10^6 \exp(-42000/RT) [\text{s}^{-1}]$) with the net formation of two new radicals.

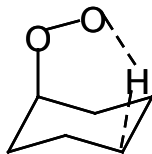


Fig.1. Two ring structure of intermediate components

At intermediate temperatures $\text{QOOH}\cdot$ radicals can also form $\text{HO}_2\cdot$ and parent alkenes or OH and carbonilic compounds (through β -decomposition reactions) or finally cyclic ethers (through a O-O homolysis reactions).

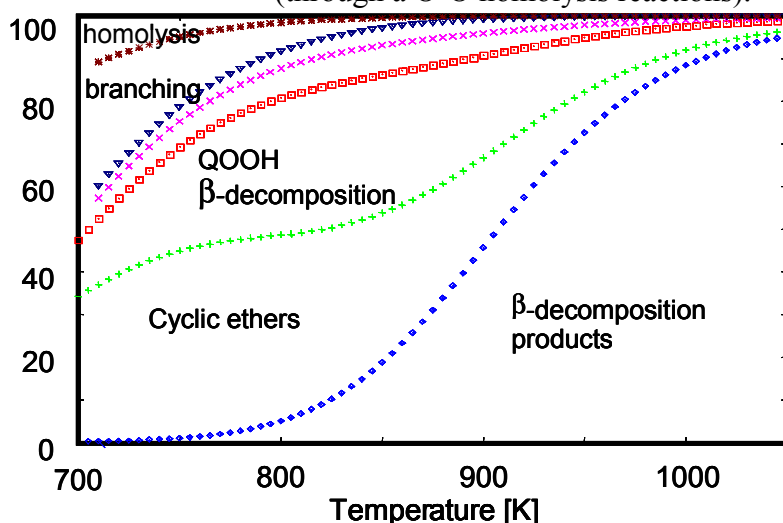


Fig. 2 Initial selectivities of primary products of MCH
Stoichiometric mixture in air at 1 atm.

A peculiar aspect of isomerization and homolysis reactions of cyclo-alkyl radicals is the possible formation of double ring intermediates. In facts, isomerization reactions of alkyl and peroxy radicals involve the formation of intermediate ring structures. Therefore, their kinetic parameters are usually evaluated on the basis of the corresponding strain energy corrections and to the number of rotors blocked in the transition state. When considering cyclo-alkane (and derived) radicals, the structure of the intermediate species presents two rings, since their original cyclic structure.

Figure 1 shows one example of the isomerization reaction of the peroxy radical of cyclo-hexane. A strain energy correction in the activation energy of 2000-3000 cal/mol is applied for the 5, 6 or 7 membered double ring intermediates. This energy value is only a very first guess and it requires a better definition with accurate '*ab initio*' calculations. No reference values are suggested in the literature. Nevertheless, the results obtained using this correction in the detailed kinetic models of both cyclo-C6 and MCH oxidation show a reasonable agreement with experimental data. From a theoretical and kinetic point of view, it is important to observe that one should expect larger corrections in the activation energy with a significant increment in the frequency factor.

Lumped reactions and extension of the oxidation scheme.

As already described for paraffins, also for cycloalkanes a lumped kinetic scheme is developed on the basis of a limited number of pseudo-species and pseudo-reactions

representative of the whole reaction path. The lumped scheme is obtained by imposing the agreement with the cumulated selectivities of primary products obtained with the detailed scheme. Fig. 2 shows the typical behavior of these selectivities at 1 atm. Higher pressures favour the branching reaction paths.

In order to show the relative reactivity of cyclo-alkanes, Fig. 3 shows the concentration of OH radical vs time for the oxidation of n-pentane, n-heptane, iso-octane, cyclo-hexane and MCH. This radical is a clear index of the system reactivity during a typical two-stage ignition process, for instance in a rapid compression machine.

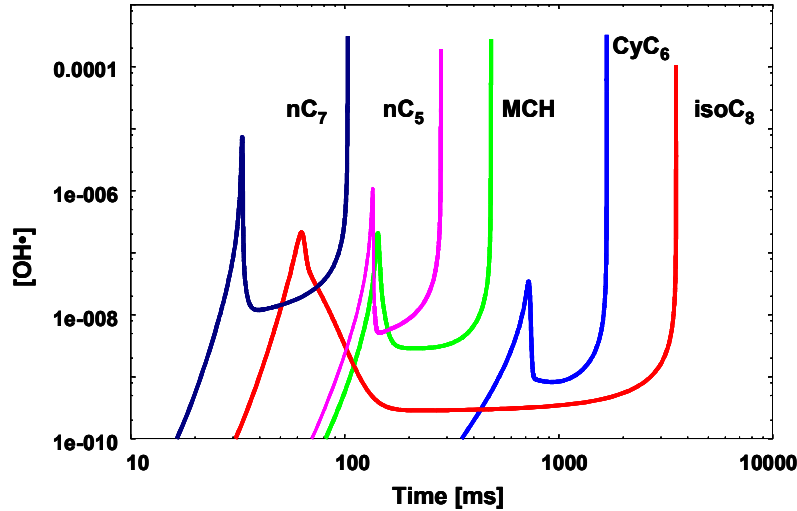


Fig. 3 OH radical concentration vs time [ms].
Stoichiometric mixtures in air at 1 atm and 660 K

According to the Octane Number (ON) of the different fuels, this plot confirms the higher reactivity of n-paraffines compared to cyclo- and branched- alkanes.

Moreover this figure indicates that the knocking tendency of the different fuels is well explained in terms of the delay time of high temperature ignitions. In facts their ON are the following:

Species	ON
n-heptane	0
n-pentane	26
MCH	83
cyclo-hexane	88
iso-octane	100

The predicted delay time of the low temperature ignition of iso-octane appears shorter than the corresponding times of the two cyclo-alkanes. These results mainly reflect the kinetic assumptions related to the isomerization reactions and it is qualitatively in line with recent experimental evidences [4].

Comparisons with experimental data

For sake of space limitations, the comparisons with experimental data will be very limited and only related to the low temperature mechanism. Fig. 4 shows behavior of cyclo-hexane oxidation in a stirred reactor. By varying the initial reactor temperature from 530 up to 600 K, model predictions of the temperature profiles along the time for different reactor temperatures agree with the experimental behavior moving from slow combustion to 3 cool flames [5]

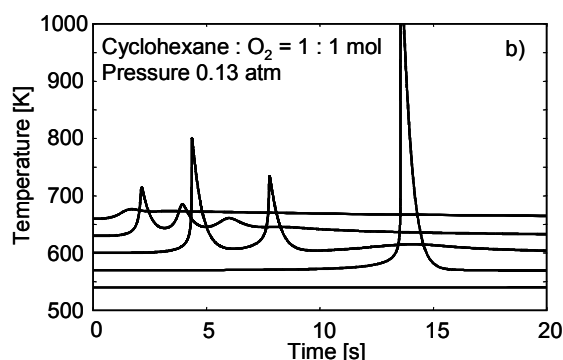


Fig. 4 Cyclohexane oxidation in a PSR. Calculated temperature profiles at different reactor temperatures vs the time.

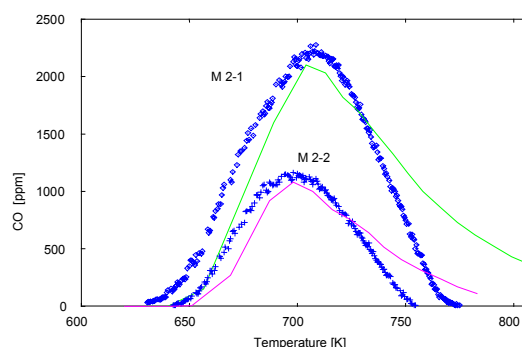


Fig. 5 Binary Mixtures n-dodecane and MCH. CO mole fractions [ppm] vs reactor temperature [K].

Recent experimental data on MCH oxidation have been obtained in a pressurized, adiabatic plug flow reactor at Drexel University [6]. These experiments analyze the low temperature reactivity of different mixtures with the CCD (Controlled Cool Down) technique. During the experiments reactor temperature decreases with a fixed cooling speed and the combustion heat allows to describe the reactivity of the system until the NTC zone. Fig. 5 shows, in terms of a CO reactivity map, the behavior of a binary mixtures with 37% of n-dodecane and 63% of MCH. Two CCD experiments were conducted with different fuel concentration. For both the experiments, model predictions well agree with the experimental measurements in terms of initial reactivity as well as in terms of the maxima CO location. The model slightly over predicts the residual reactivity of the system at intermediate temperatures (750-800 K). A large set of comparisons between model predictions and experimental measurements in the high temperature conditions was already reported elsewhere [2]

Conclusion and future developments

The proposed kinetic scheme has been successfully validated in comparison with several experimental data obtained in different devices and conditions, from the high temperature to the cool flame and low temperature ignitions. Despite these encouraging comparisons further work is needed to improve and confirm the kinetic model. Particularly, the corrections for the double rings in the transition state should be accurately evaluated by new measurements and researches in order to complete the kinetic analysis of cycloalkanes oxidation.

Acknowledgments

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Residence Time Effect on Natural Gas Combustion in a Well-Stirred Reactor

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INTRODUCTION

The use of very diluted and highly preheated reactants is the main characteristic that makes Mild Combustion [1] partially fulfill requirements of environmental politics. Temperatures reached during the oxidation process are relatively low in comparison with a traditional system and are controllable by changing the dilution degree. This allows for a reduction in pollutant emissions such as NO_x and soot. Moreover, the increase of thermal energy transfer leads a reduction of fuel demand and hence of CO₂ emission. The broad application of Mild Combustion deserves further studies in order to better characterize the influence of a high inlet temperature and a high dilution degree on the fuels oxidation. In previous works [2, 3] the attention was focused on the evaluation of the influence of high temperatures, very diluted conditions on methane oxidation kinetics by means of experimental and numerical analyses. It was carried out on a well-stirred reactor between 825K up to 1250K varying C/O feed ratio. The study pointed out a significant temperature oscillation phenomenology for a relatively wide range of temperature and C/O ratio that was classified on the basis of waveform shape. Such a dynamic behavior was only partially identified in the past in methane oxidation by means of a numerical study [4]. On the other hand, the experimental studies reported in literature, that evidenced the oscillatory behaviors in methane oxidation, were performed at lower temperatures and in batch conditions [5, 6, 7].

From a practical point of view, the presence of such oscillatory regimes, due to thermo-kinetic behavior of the system, could induce a negative phenomenology. In fact, their coupling with physical processes could give rise to high frequency oscillations in combustion chambers, generally responsible of efficiency decrease and of serious damage in gas turbine burners. Such dynamic behavior is hidden in conventional process involving methane by relatively fast oxidation kinetic that characterizes traditional gaseous fossil fuels. Moreover, activation of different kinetic pathways hypothetically responsible of oscillation could induce an increase of pollutant formation.

By extending the previous analysis on methane oxidation [2, 3], the effect of residence time on oscillation phenomenology was studied at a fixed inlet temperature.

EXPERIMENTAL SET-UP

The experiments were carried out in a spherical quartz Jet Stirred Flow Reactor (JSFR) with volume of about 100 cm³. The design of the nozzle orientation and dimensions is realized in order to have a high mixing degree for a relatively wide range of residence times [8]. The reactor is allocated in a cylindrical (0.3 m i.d.) electrically heated, ceramic fiber wall oven equipped with a temperature controller. A recirculation system provides for a homogeneous distribution of temperature in the oven.

Temperatures inside the JSFR were monitored using a silica coated wire (40µm diameter) Pt-Pt13%/Rd thermocouple. Temperatures were acquired by means of an A/D converter at a sampling rate of 50Hz, then stored and analyzed by a personal computer. Sampling and off-line analysis by means of gas-chromatography with flame ionization detection for the

determination of light hydrocarbons were performed in the chosen conditions.

The experiments were run at atmospheric pressure for temperature values ranging from 825K to 1275K and for C/O feed ratios ranging from 0.01 to 1.4. The dilution degree was 90% and the residence time τ changed from 0.5 sec towards lower values in order to evaluate its effect on methane oxidation evolution.

RESULTS AND DISCUSSION

The effect of the residence time on the oscillation behavior was experimentally analyzed for several inlet conditions. In particular Fig.1 shows the temperature temporal profiles collected at $T_{inlet}=1123K$ and $C/O=0.3$ for different τ . This was changed from 0.5 sec down to the minimum value allowed of 0.35 sec. In fact, the oven power is not enough to preheat the reactants at the required inlet temperature for residence time lower than 0.35 sec.

As it can be seen for $\tau=0.5$ sec the system evolves through a complex oscillation that was previously classified as double oscillation [2]. The first temperature peak is quite smooth. In contrast, the second one is very sharp and the system reaches its highest temperature value that is about 1390K.

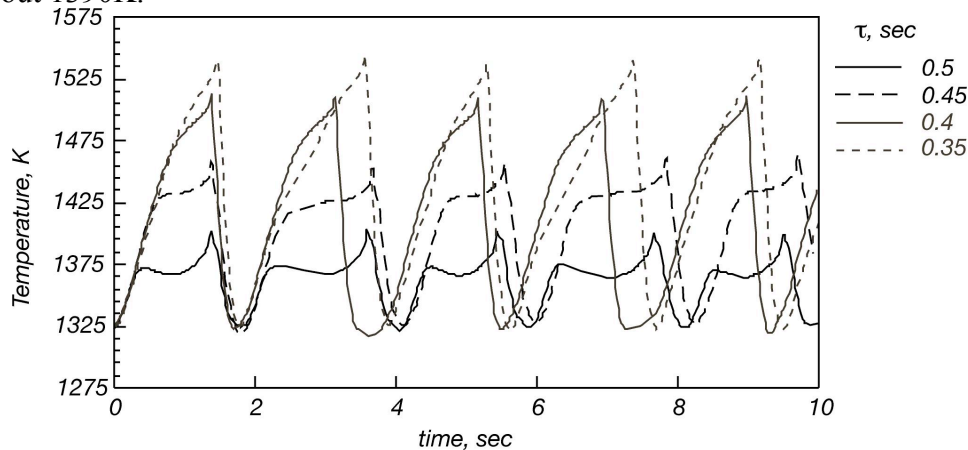


Fig. 1 Temperature temporal profiles for $CH_4/O_2/N_2$ system for $T_{inlet}=1123K$ and $C/O=0.3$ at various residence times τ .

For $\tau=0.45$ sec the oscillation typology is the same although the first peak is less pronounced. The temperature increase is higher reaching the value of about 1450K in correspondence of the second peak, whereas the frequency decreases very slightly.

A further decrease in residence time to 0.4 sec leads the two temperature peaks of double oscillation waveform to merge in a single peak that reaches the maximum value of about 1550K. The same considerations apply for the temperature oscillation detected at 0.35 sec where the reactor temperature achieves about 1540K. Moreover, also in this case passing from $\tau=0.4$ sec to $\tau=0.35$ a slight frequency decrease can be recognized.

The trend of maximum temperature occurring during the oscillation is not directly related to the variation in heat transfer. For JSFR used in the present work both the mixing and the thermal flux are related to the fluid-dynamic conditions inside the reactor. In this case, for a fixed inlet temperature, a decrease in residence time corresponds to an increase of inlet flow that in turn, leads to a higher overall heat transfer coefficient [9]. Therefore, the variation in heat transfer should affect the process by decreasing the working temperature with the residence time. The opposite trend has been pointed out during the experimental analysis.

The same phenomenology was evidenced by Gray et al. [10] by studying the ethane oxidation in a continuous well stirred reactor. Although the residence times and the temperature range

were very different from the conditions considered in the present work, the authors showed that in the cool flames region the temperature increase measured during the oscillation decreased from 40K to 14K varying τ from 15 μ sec to 60 μ sec. This temperature decrease corresponded to an increase of oxygen conversion that passed from 87% at τ 15 μ sec to 95% at τ 60 μ sec. In this work [10] the authors used a mechanically stirred reactor where the heat transfer coefficient does not depend on mass flow [11]. As a consequence, also in this case it is not responsible for the temperature dependence on residence time.

Therefore, the relation between τ and the maximum temperature achieved during oscillations could be due to the increase of mass flow rate corresponding to a decrease in residence time.

In previous works [2, 3] on the basis of comparison between experimental and numerical results it was supposed that the dynamical behavior evidenced during methane oxidation is due to the interaction between the kinetic of the methane oxidation and the thermal exchange between the reactor and the environment. Although the chain branching of the CH_4 reaction mechanism is basically due to the H_2/O_2 system, methane evolves according two main pathways that are the oxidation and the recombination channels respectively. The rate of production analysis showed [2, 3] that recombination channel acts subtracting CH_3 radicals from the oxidation channel, storing them as $\text{C}_{(2)}$ compounds. When the chain branching starts, the recombination channel releases the CH_3 radicals through the formation of acetaldehyde and its dehydrogenation until the formation of CH_3CO radicals. These, in turn, are thermally decomposed, producing CH_3 radicals and CO that feed the oxidation channel enhancing the reactivity of the system and causing the temperature increase. Therefore, the recombination channel modulates the oscillation occurrence [2, 3]. The proper radical concentrations and temperature inside the reactor, that make the chain branching reactions related to the temperature oscillations start, do not depend on inlet flows. However, when the branching starts the lower the residence time, the higher the mass flow rate and therefore, the higher the thermal power obtained. This leads to an increase of the maximum temperature reached during the oscillation. This also corresponds to a slight growth in $\text{C}_{(2)}$ concentration, such as shown by the normalized ethane and ethene/acetylene concentrations reported in Fig.2 as function of residence time.

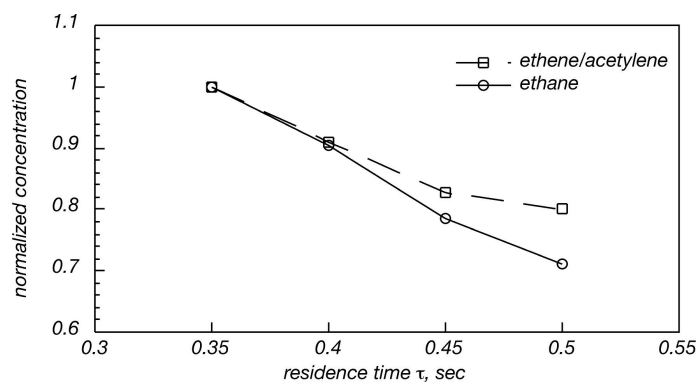


Fig. 2 Normalized concentration profiles of $\text{C}_{(2)}$ compounds as function of τ .

Such an increase could be due to the temperature effect on competition between the two different kinetic paths. In fact, the higher temperature obtained at lower residence time could improve the recombination channel. The same effect was obtained by increase the inlet temperature for a fixed residence time. This can be easily inferred on the basis of temperature profiles reported in Fig.3. They represent temperature reaction increases (ΔT) as function of

C/O for T_{inlet} equal to 1025K, 1125K, 1225K. The dashed lines individuate the region where oscillations occur, showing the minimum and the maximum temperature measured during the oscillations themselves. For the highest inlet temperature the ΔT is independent from C/O ratio and the difference between the working and inlet temperature is of about 50K for rich mixtures (C/O ≥ 0.25). Such limited temperature increase suggests that in these conditions the recombination channel is very active. Moreover, in this case it could be hypothesized that the $C_{(2)}$ compounds are not oxidized to acetaldehyde leading to the formation of CH_3 radicals, but they mainly form and accumulate as C_2H_2 . In fact for temperature values higher than 1200K the acetylene becomes a relatively stable compound [12]. Hence the reactivity of the system is dramatically lowered and the system does not reach high working temperatures.

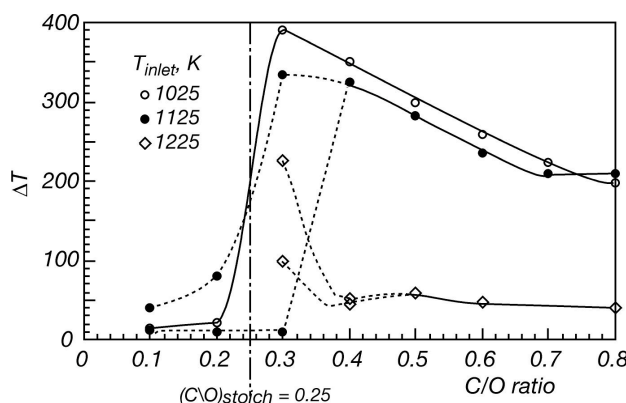


Fig. 3 Temperature increase (ΔT) for dilution of 90%, $\tau = 0.5$ sec.

CONCLUSION

It has been shown that the dynamic behavior evidenced during methane oxidation in the region of double oscillation typology are affected by the residence time considered. The experimental evidences reported in present work support the hypothesis that the oscillations occur as result of the competition between the oxidation and recombination channels present in the kinetic mechanism of methane combustion. The last one can subtract CH_3 radicals from the oxidation channel. If the recombination channel releases these radicals the system could evolve through an oscillation regime whereas if it stores them as C_2H_2 , the system evolves through a stable combustion regime characterized by a very low temperature increase.

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Reactivation of FBC Spent Sorbents by Water and Steam Hydration

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INTRODUCTION

Fluidized Bed Combustion (FBC) of sulphur-bearing fuels is accomplished with *in situ* capture of sulphur oxides by limestone-based sorbents. Sorbent sulphation patterns have been extensively investigated in the past [see e.g. 1,2]. Sulphation most typically conforms to the core-shell pattern: the reaction front in the sorbent particle divides the unreacted CaO inner core from a partly reacted less porous outer shell. The build up of the sulphated outer shell prevents complete sulphation of the unreacted CaO core, as SO₂ diffusion through the CaSO₄ layer becomes negligible over the typical process time-scales. Sorbents employed in FBC undergo comminution which can lead to changes in particle size distribution and to fines elutriation with consequences on the desulphurization process [3].

Among the techniques proposed to enhance calcium utilization, one of the most promising is the reactivation of the exhausted sorbent via water- or steam- hydration [4,5]. This process mainly implies the conversion of the unreacted CaO into Ca(OH)₂ which, having a larger molar volume, swells inside the particles leading to the formation of cracks and flaws. In this way enhanced access to SO₂ is provided upon further exposure of the reactivated sorbent to sulphur-containing atmospheres. Both techniques are attractive, as they enhance the sulphur uptake of sorbents, reduce waste disposal costs and consumption of natural resources, limit CO₂ emissions.

The aim of this experimental work was to characterize the influence of the water- and steam- hydration/reactivation processes of FB spent sorbent particles on sulphur capture ability and particles sulphation patterns, fragmentation and attrition phenomena upon resulphation in FB reactors.

EXPERIMENTAL

A laboratory scale stainless steel atmospheric FB reactor (electrically heated), 40mm ID and 1m high, was employed for sulphation, steam-reactivation and resulphation tests. Details of the reactor can be found elsewhere [3,6]. Sorbent particles (a high-calcium Italian limestone, *Massicci*) were sulphated to exhaustion at 850°C in the FB reactor, and then subjected to hydration-reactivation tests by means of water or steam (the 0.4-0.6mm particle size range was chosen for all the experiments). Water reactivation was conducted in a thermostatic bath at 25°C for a curing time of 3h (for other details, see [6]). Steam reactivation tests were carried out, at 250°C for a curing time of 3h, in the FB reactor by fluidizing the bed material, consisting of spent sorbent particles (40g), with an equimolar N₂-steam mixture. Polished cross sections of water- and steam- hydrated sorbent particles, embedded in epoxy resin, were observed under a SEM-EDX detector (for the sulphur elemental mapping) and analyzed with a Computer Controlled SEM-EDX (CCSEM-EDX) technique (for the quantitative characterization of the sulphur distribution patterns), described

in detail elsewhere [2,6]. In this context, it is only recalled that bimodal sulphur distribution functions are indicative of a core-shell sulphation pattern, while unimodal distribution functions reveal uniform sulphur distribution throughout the particles cross sections. Finally, the effect of the reactivation treatment on the particle size distribution was investigated by sieving the hydrated particles in 9 size ranges between 0-0.053mm and 0.4-0.6mm. The occurrence of further fragmentation of water- and steam- hydrated samples (re-sieved in the size range 0.4-0.6mm) upon calcination was investigated by injecting samples in the FB fluidized by air at 850°C for 5 min and then sieving the hydrated/calcined sorbent particles in the same size ranges as above.

Resulphation tests of water- and steam- hydrated samples were carried out under operating conditions resembling those of the 1st sulphation tests: batches of bed material consisted of mixtures of reactivated sorbent (25g in the size range 0.4-0.6mm) and silica sand (150g in the size range 0.85-1mm), fluidized at 0.8m/s for 180min by simulated flue gases consisting of a mixture $\text{SO}_2 + \text{N}_2 + \text{O}_2$ with a SO_2 inlet concentration of 1800ppmv. The FB reactor was equipped with a two-exit head connected to sintered brass filters (designed to allow capture of elutriated fines and characterization of the attrition rate) and with on line gas analysis (enabling calculation of the degree of calcium conversion, or sulphur uptake, as a function of time).

RESULTS AND DISCUSSION

Reactivation of spent sorbent particles

FIGURE 1 reports SEM-EDX micrographs of Water-Hydrated (WH) and Steam-Hydrated (SH) samples (for comparison the Sulphated -S- sample is also included). Inspection of FIGURE 1 reveals the establishment of a core-shell particle structure for the S sample, in line with previously reported findings [1,2]. Redistribution of sulphur between the shell and core zones for the WH sample is remarkable (similarly to [7]). Notably, sulphur redistribution was observed also for the SH sample. In order to quantitatively account for differences in the three samples, the extent of the sulphur redistribution was examined with the aid of the CCSEM-EDX technique (FIGURE 1): WH and SH samples both show a bimodal sulphur distribution pattern similar to that of the S sample, but the relative significance of the core-zone and the shell-zone peaks strongly changes. This indicates a better sulphur distribution in the particles induced by sorbent water- and steam- hydration, and provides an important pathway to sulphur uptake enhancement by spent sorbent reactivation. A mechanism for the sulphur redistribution observed in the WH sample, based on dissolution/precipitation phenomena of calcium species via the aqueous phase, was reported in [7]; it can be speculated that a similar sulphate ions migration mechanism might be at work under steam hydration conditions.

TABLE 1 reports the cumulative particle undersize distributions for WH and SH samples, whose original size (i.e., before the reactivation treatment) was 0.4-0.6mm. For the WH sample less than 5% of the particles mass was in the range 0-0.4mm after hydration, and no significant population of particles finer than 0.15mm was observed. On the contrary, more than 50% of the SH particles mass was in the range 0-0.4mm. TABLE 1 also reports the same analysis conducted on calcined WH and SH samples. A non-negligible fragmentation of both water- and steam- reactivated/calcined samples is observed upon calcination: 22% (for the WH sample) and 44% (for the SH sample) of particles were in the range 0-0.4mm, and in both cases particles finer than 0.05mm were observed. It is recalled here that, after hydration, the sorbents were re-sieved in the original size range (0.4-0.6mm) prior to FB calcination.

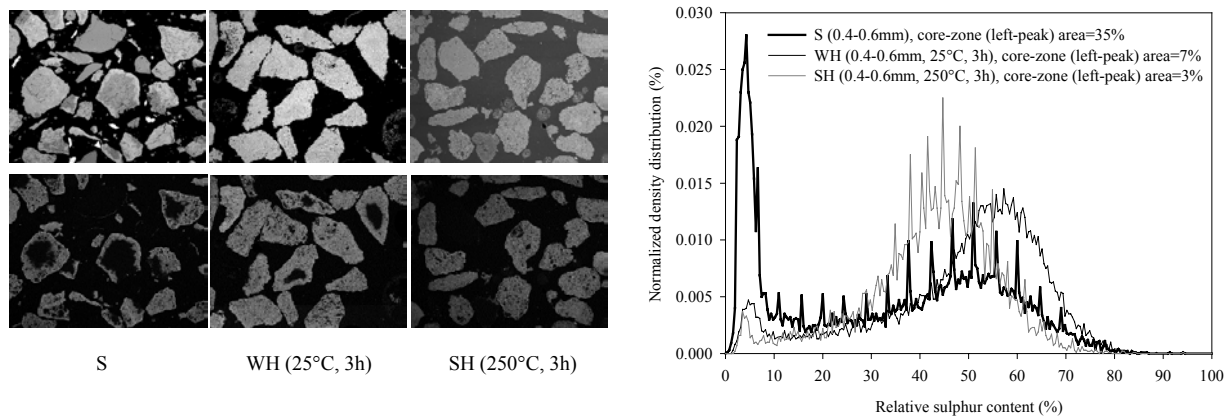


Fig. 1: SEM micrographs (left figure, upper row) and EDX sulphur maps (left figure, lower row) of cross sections of sulphated and hydrated multiparticle samples and (right figure) CCSEM-EDX analysis results.

Tab. 1: Cumulative particle undersize distributions for hydrated and hydrated/calcined samples.

particle size (mm)	WH (mean Sauter diameter=0.473mm)	SH (mean Sauter diameter=0.218mm)	calcined WH (mean Sauter diameter=0.358mm)	calcined SH (mean Sauter diameter=0.269mm)
0-0.053	0.1%	2.6%	0.7%	1.2%
0.053-0.112	0.3%	8.6%	2.6%	6.3%
0.112-0.150	0.4%	14.0%	4.0%	10.1%
0.150-0.212	0.8%	23.8%	6.3%	16.5%
0.212-0.250	1.2%	29.5%	8.2%	20.1%
0.250-0.300	2.2%	37.5%	11.8%	25.5%
0.300-0.355	3.2%	47.4%	18.1%	36.4%
0.355-0.400	4.8%	51.2%	22.0%	44.0%
0.400-0.600	100%	100%	100%	100%

Resulphation of the reactivated sorbents

FIGURE 2 reports the degree of calcium conversion (X_{Ca}) as a function of time during batch resulphation of WH and SH samples (the results achieved during the 1st sulphation test are also reported, for comparison purposes). Water- and steam- reactivation of the spent sorbents were both highly effective in promoting further sulphur uptake upon resulphation: ultimate calcium conversion degrees were 54% (for the SH sample) and 53% (for the WH sample), far larger than the value (28%) achieved during the S test. Sulphur uptake is faster for the SH sample, showing larger sulphur uptake in the first part of the resulphation test, and deactivates earlier with respect to the WH sample.

FIGURE 3 shows the fines elutriation rate $E(t)$ as a function of time during the resulphation of the WH and SH samples. Notably, data for the WH sample refer to 6h (and not 3h)-water-hydration, but in a previous investigation [6] it was found that the attrition rates of the 3h- and the 6h- water-reactivated samples were similar. For the WH sample, $E(t)$ decreases with time upon resulphation following a general trend similar to that observed during sulphation tests [3]: particle rounding off and removal of surface asperities prevail at first, then attrition is dominated by strengthening of the surface layer upon sulphation, making $E(t)$ vanishingly small in the long term as resulphation reaches completion. For the SH

sample, the trend of $E(t)$ is slightly different: attrition rate is much smaller than that of the WH sample at the beginning, but $E(t)$ decreases more slowly, overtaking the attrition rate of the WH sample. The total elutriated mass ($\int E(t)dt$) is almost the same (2.2g) in the two cases. One important key to this behaviour is represented by the consideration that steam reactivation was carried out in the FB, so that rounding off of SH particles was already effective during hydration. Once rounding off of the WH samples is over, the larger elutriation rate of the SH sample may be related to extensive particle fragmentation which increases the exposed surface per unit mass of the sorbent and enhances attrition.

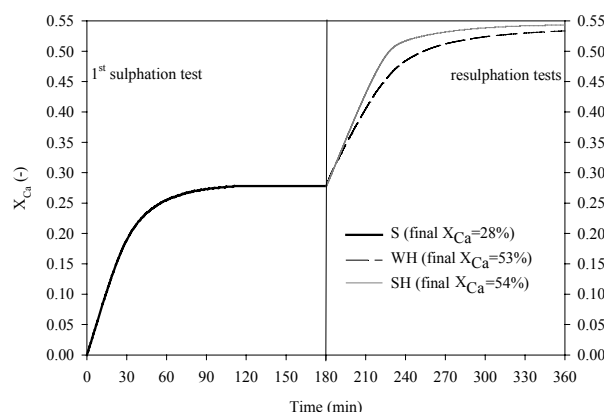


Fig. 2: Degree of calcium conversion as a function of time during sulphation and resulphation tests.

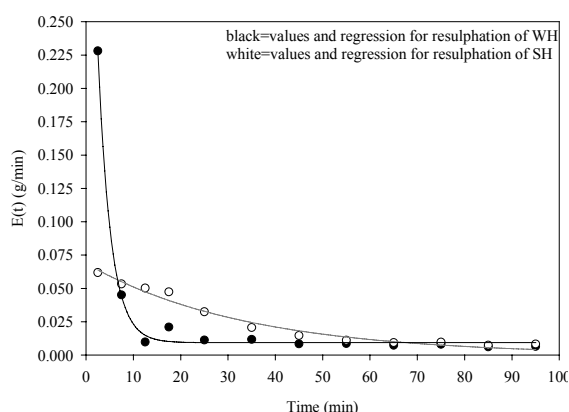


Fig. 3: Fines elutriation rate during batch resulphation of reactivated sorbents.

CONCLUSIONS

Reactivation of FB spent sorbents by hydration with either water or steam is addressed. Both water- and steam- reactivations induce a strong sulphur redistribution throughout the particles cross sections, which, in addition to the swelling/fissuring mechanism related to hydration, enhances the sulphur capture ability of the reactivated particles to comparable extents. Steam-reactivated particles are much more prone to fragmentation upon FB calcination and to attrition upon resulphation than water-reactivated sorbent.

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Fluidized Bed Pyrolysis of two Plastic Wastes

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ABSTRACT

Two commercially-available recycled polymers, a polypropylene and a polyethylene were individually pyrolysed in a laboratory scale fluidized bed reactor operated at different bed temperatures (from 550 to 750°C) and fluidizing gas velocities (0.13 and 0.28m/s). The study refers about the influence that these two key variables can have on the yield and composition of pyrolysis products, as measured by means of a specifically designed procedure. The comparison of the results, obtained for tests carried out under the same operating conditions, suggests that the two recycled polyolefins show a remarkably different behaviour.

INTRODUCTION

The term feedstock recycling describes a family of processes that convert solid plastic materials into smaller molecules that can be used as feedstock for the production of new petrochemicals and plastics. These processes constitute a remarkable improvement in the technology of plastics recycling since they can treat heterogeneous and contaminated plastics with a limited use of pre-treatments. In particular, the process of pyrolysis carried out in fluidized bed reactors appears one of the most attractive being able to obtain sufficiently high yields of valuable products (1,2,7). The very good heat and material transfer, and the consequent almost constant temperature inside the reactor, provides for a relatively uniform spectrum of products and allows short residence times at moderate temperatures (from few seconds to 1.5min). Moreover, the absence of moving parts in the hot region reduces the maintenance time and cost while the possibility to apply the process on a relatively small scale makes wider the range of investment options. The disadvantages that are not yet completely eliminated are the necessity to limit the chlorine content in the inlet stream up to about 2% and the risk of solids agglomeration in the bed, with the consequent worsening of the quality of fluidization (3,7,8).

The present study describes a series of experiments aimed to quantify the yield and the composition of products obtained during the pyrolysis of two plastic wastes.

EXPERIMENTAL

The tested materials are recycled polyethylene (PE) and polypropylene (PP) obtained from separate collection of plastic wastes. The main properties of both polymers are reported in (4, 6). The experiments were carried out in a laboratory scale bubbling fluidized bed reactor, made of high temperature austenitic stainless steel, having an internal diameter of 55mm and a total height of 0.7m. A sampling line was specifically designed and installed to collect pyrolysis gas and to recovery the heavy hydrocarbons fraction. Further details on the experimental apparatus utilized for the tests as well as on the procedure adopted for sampling and analysis can be found in (4).

RESULTS AND DISCUSSION

The Influence of Polymer-to-Particle Interactions to the Pyrolysis Process

The polymer pellet injected into the hot fluidized bed is fast heated up by a high-rate heat transfer mechanism that leads external surface up to the softening temperature. Several sand

particles stick therefore on the plastic surface, forming a polymer–sand aggregate that has the external shell made of sand particles and the internal core made of polymer not yet molten (3). When the temperature further increases, the surface of the pellet reaches the melting temperature and the polymer flows throughout the bed particles of the external shell, so forming a uniform coating over and between them. The progress of heating (i.e. the increase of temperature and/or that of residence time) leads to the cracking of the weak carbon–carbon bonds of the polymer chain, i.e. to the beginning of the pyrolysis process, which starts when the polymer has already covered the bed particles. Therefore, the primary cracking is not related to the whole molten pellet, but to a layer of polymer, which coats and adheres on the external surfaces of single sand particles. This aspect must be taken into account in the modeling of process as well as in the definition of design and operating criteria of the reactor (3). The volatiles formed during the primary reactions move throughout the dense bed and then along the freeboard region. The secondary cracking occurs in these two regions of the reactor and produces a spectrum of hydrocarbons. The amount and the type of these compounds, i.e. the yield and the composition of pyrolysis products, are affected by the bed temperature and the gas residence time in the different regions of the reactor (4).

The Influence of Bed Temperature on the Yield of Pyrolysis Products

A first series of tests were carried out for both polymers at a fixed fluidizing gas velocity, U , equal to 0.13m/s, and at different values of the bed temperatures, from 550 up to 750°C. In all the experiments, the quality of fluidization remained always good, as indicated by the time profile of pressure and as expected on the basis of previous experiments (3,5), and the products showed gas, liquid and solid compounds in different yield and composition. In particular, in the case of PE, solids were found under two forms: a large fraction of polymer only partially degraded was collected in the range 550-650°C; tar residue was instead collected from reactor walls in the whole range of tested temperatures. The solid products of PP pyrolysis were recovered by the sampling line only for a little fraction; the largest part remained stuck on the reactor walls and its amount was quantified by switching, at the end of each run, the fluidizing gas from nitrogen to air and by processing the measured contents of CO, CO₂ and C_nH_m in the flue gases. The high values of carbon-to-hydrogen molar ratios of this solid phase indicate that it should be classified as soot. Figure 1 shows a SEM picture of the solid phase for both the pyrolyzed polymers, highlighting the remarkably finer size of the elements which form the PP solid phase. The liquid yield of PE pyrolysis was substantially negligible below 600°C and just appreciable only when the process was carried out at a temperature as high as 650°C. The composition indicates a dominant content of aromatics like benzene and toluene, other compounds being styrene, xylene and polycyclic aromatic

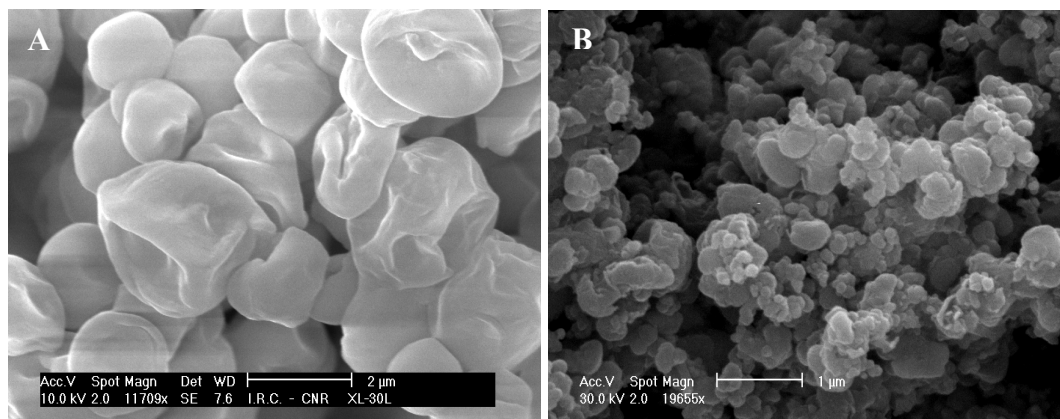


Fig. 1 Pictures of degraded PE (A) and soot particles from PP pyrolysis (B) collected in the cold trap.

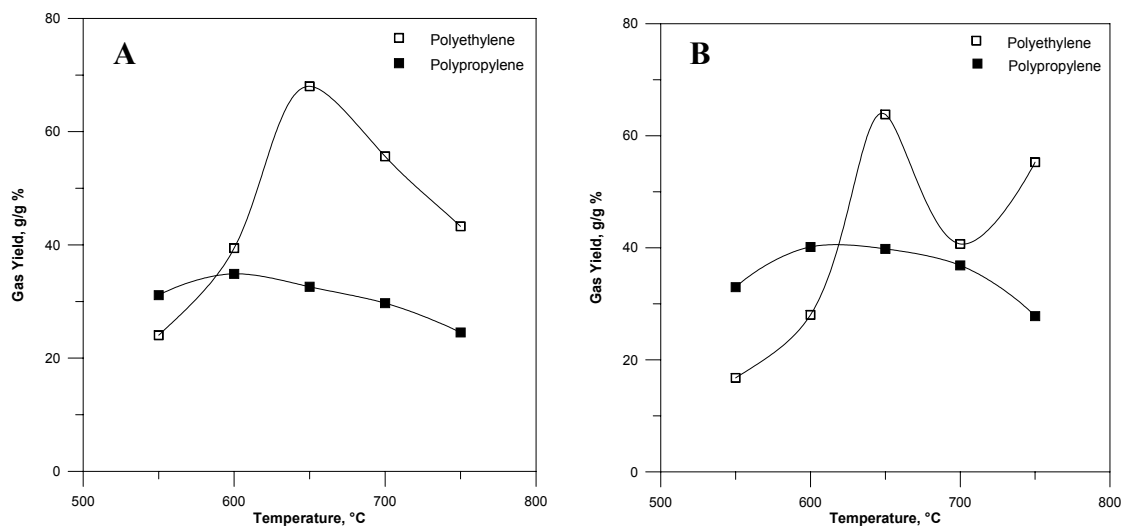


Fig. 2 Gas yield as a function of temperature at fluidizing gas velocity of 0.13m/s (A) and 0.28m/s (B).

hydrocarbons, from naphthalene to pyrene. The BTX yield had its maximum at 700°C in correspondence to the minimum yield of PAH. Generally, the PP pyrolysis products were mainly present as solid and gas phases. Only in some runs a negligible amount of a liquid phase was observed even though it was not analyzed since it fastly volatilized at ambient temperature.

The yield of obtained products, as well as their composition, depends on the reaction temperature for both polymers tested. In particular, the gaseous yield obtained from the pyrolysis of PE, expressed as grams of gaseous products for each gram of injected polymer, is strongly influenced by this key variable, with a maximum value at a temperature of 650°C (Fig. 2 A). On the contrary, the yield in gaseous products in the case of PP appears less affected by the bed temperature, ranging between 24 to 35%.

The same parameter has also a remarkable effect on the gas composition, as clearly showed by Figures 3. Ethylene and propylene were the two main components of the gas obtained

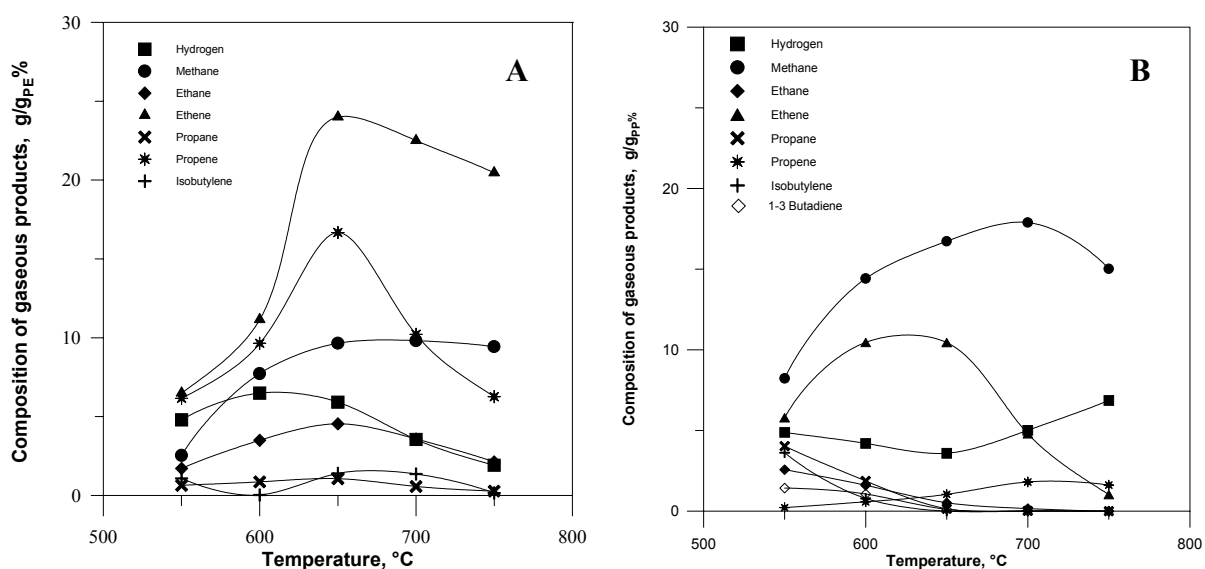


Fig. 3 Composition of gaseous fraction for polyethylene (A) and polypropylene (B) as a function of temperature at fluidizing velocity of 0.13m/s.

from the pyrolysis of polyethylene. Large amounts of these olefins (about 60wt% of the total gas yield) were obtained in almost all the range investigated, with the highest yields at 650°C. The methane yield continuously increased with the reaction temperature, whereas hydrogen yield slightly decreased. In the case of polypropylene, methane and ethylene yields resulted the highest, while the trend of hydrogen curve appears almost constant with a yield of about 5%. The propene content becomes appreciable only at temperatures higher than 650°C, having, however, a limited value as it can be expected on the basis of the thermal decomposition mechanism of polypropylene (9).

The Influence of Gas-Phase Residence Time on the Yield of Pyrolysis Products

The gas residence time inside the reactor, i.e. the time necessary to gases for moving through the bed and the freeboard and then leaving the reactor, was changed by increasing the fluidizing gas velocity from 0.13 to 0.28m/s. The residence times inside the reactor consequently decreased from about 4 to 2s, for both the polymers. It is noteworthy that the procedure, detailed and quantified in (4), was utilized in order to change the gas-phase residence time but mainly affected the time spent throughout the freeboard. The residence time in the bed is instead affected by another operating variable, the height of expanded bed, which was kept fixed in these experiments due to the small scale of the reactor used. The comparative analysis of the data collected during the tests at two fluidization velocities shows that, in the case of PE, the amount of not-degraded polymer was larger for shorter residence times, even though it again decreased as temperature increased, while the tar production resulted higher. The liquid products are again appreciable only at higher temperatures. The pyrolysis of PP, when carried out at a lower residence time, produced a lesser amount of soot and, as a consequence, a higher gas yield. The comparison between the gas yields of two polymers at a different residence time is showed in Fig. 2 B. The analysis of gas composition in the two hydrodynamic conditions tested, for both polymers, indicates a not substantial effect of the gas residence time.

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The Life Cycle Assessment of Alternative Solid Waste Management Options. A case study.

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ABSTRACT

The Life Cycle Assessment (LCA) is an internationally standardized method that has been developed from chemical engineering principles and energy analysis and it is able to account for upstream and downstream inputs and emissions related to the life cycle of a product or a service. It is generally considered the best environmental management tool that can be used to obtain an objective quantification of all the environmental impacts related with different solid waste management scenarios.

The LCA of three alternative management options relating to a situation of solid waste emergency in Italy has been developed. The extreme delicacy of the decision-making process to which the LCA results have to contribute suggested increasing the reliability of the assessment conclusions by using a high quality of data and a deepened analysis of technical processes. An analytical comparison between three selected scenarios is reported with reference to some crucial environmental impact categories. The results quantify the relative advantages and disadvantages of different management schemes and suggest some possible improvements in design and operating criteria.

INTRODUCTION AND SCOPE

The study refers to the assessment of environmental performance of alternative solid waste management options that can be used in an area of the South of Italy, the Regione Campania, where a poor solid waste management policy created a situation of heavy emergency. The area has an extension of about 13600km², 5.7 million of inhabitants and a production of municipal solid wastes equal to about 7000t/d. These were all sent to landfilling until the beginning of 2001, without any significant recourse to separate collection and thermal treatment. This short-sighted solution fast made exhausted the landfill volumes of the area, so that since 2002 no more space for restwaste dumping was available. The Italian Government created a National Committee for Waste Emergency in Campania that decided to apply as soon as possible a new waste management scheme, including seven units for RDF production from restwaste sorting, with a total capability of 8350t/d, and two units for its combustion with energy recovery, with a total capability of 1,000,000t/y.

The aim of the study was the quantification of the difference between the environmental performance of three different scenarios for solid waste disposal in the area of Regione Campania: that planned in the program of the Committee for Waste Emergency; an hypothetical scenario that continues to see the landfilling as the only possible option; a scenario where all the restwaste is mass burned without RDF preparation. The paper deals with the Life Cycle Assessment of these three solid waste management scenarios. The *primary audience* for this effort is the Italian Committee for Waste Emergency in Campania, which is interested to assess energetic and environmental profile of the current management in comparison with some integrated alternatives.

LIFE CYCLE INVENTORY

The phase of Life Cycle Inventory aimed at identifying and quantifying the environmental burdens crossing system boundaries. It resulted in an *inventory table*, i.e. a list of raw materials and energy inputs, and of individual emissions to air and water and solid waste generation, that is then utilised in the phase of impact assessment (1, 3). Details of results of this inventory phase can be found in (2).

The landfilling scenario

The type of landfill chosen as reference is equipped with high quality bottom and top barriers (e.g. made of HDPE or of another low permeability material, such as clay) for leachate containment as well as with up-to-date technologies for leachate treatments and energy recovery from biogas. A recent study which investigated all the landfills in operation in Campania until 2000 (4) indicated that the amount of the leaked leachate can be assumed as negligible. The technology selected for the treatment of collected leachate is that of reverse osmosis, which has not yet been installed in Campania but that it is considered one of the best available technologies. The biogas collection and treatment system was of high efficiency too. It was assumed that the biogas collection efficiency is equal to 55% and that the 60% of this collected biogas is burned in a gas engine with an electric conversion efficiency of 35%. The remaining 40% is sent to a flare to reduce greenhouse effect.

The RDF production and combustion scenario

The *RDF production* consists of a sorting process, which produces RDF bales and ferrous materials, and a biological treatment process, which produces a stabilized organic fraction (S.O.F.) that can be used for contaminated soil remediation. All data for the inventory of direct and avoided burdens have been obtained by averaging those measured during on-site investigations in two RDF facilities, located in Caivano and Pianodardine and having throughput of 2000 and 400t/d of restwaste, respectively.

The stage of *RDF combustion* is composed by three sections: combustion, energy recovery and flue gas treatment. The reference plant has three parallel lines, each with a capability of 27t/h and characterized by a mobile grate. The flue gas treatment is composed by a semidry scrubber for acid treatment, a fabric filter for removing fly ashes and a SCR DeNO_x that uses a catalyst to reduce NO_x and organic micro-pollutants.

The mass burn scenario

This management scenario is an alternative option to waste valorisation by recovering energy without a careful preliminary sorting process. The data were collected during technical visits to a couple of modern mass burn incinerators that are in operation since 2001 in North Italy, in the Milan area (Silla 2) and in Cremona.

The transportation stage

The distances of the main Campania towns (for a total of 168) from treatment or final disposal units have been taken into account. For the three analysed scenarios, all the possible paths for restwastes, RDF bales, sorting scraps, SOF scraps and incineration ashes have been considered. The capacity of the lorries was assumed to be always equal to 32m³. The waste density was assumed to be: 0.7t/m³ for restwaste from towns to landfills, RDF facilities or incinerators and for sorting scraps from sorting units to landfills; 1t/m³ for RDF bales from RDF facilities to incinerators; 1.2t/m³ for conditioned ashes from incinerators to landfills.

LIFE CYCLE IMPACT ASSESSMENT

The phase of life cycle impact assessment aims at quantifying the relative importance of all

environmental burdens estimated in the LCI and at aggregating them to a small set of category indicators, or, in some cases, to a single indicator (1). The following categories were assumed as principal indicators of environmental impact related to each step of restwaste life cycle: consumption of natural resources, air pollution, water pollution; quantities of solid waste generated (which is strictly related to the requirements of landfill volume).

The LCIA Results

Energy and Resource Consumption

Figure 1 shows the net energy consumptions for all the examined scenarios. The two scenarios with a thermal treatment of solid wastes show, as expected, a remarkable higher energy savings: with reference to landfilling, these savings are equal to 640% and 850%, respectively for RDF production/combustion and for mass burn combustion.

Climate Change

Figure 2 quantifies the generation of GHG (expressed as kilograms of CO₂ equivalent, for a time horizon of 100 years) for each restwaste management scenario, with the indication of contributions related to the different stages of life cycle. Note that the combustion processes present a GHG generation remarkably lower than that of landfilling scenario, mainly because the global warming potential of methane (which is generated only by the anaerobic digestion occurring in landfills) is 21 times higher than that of carbon dioxide.

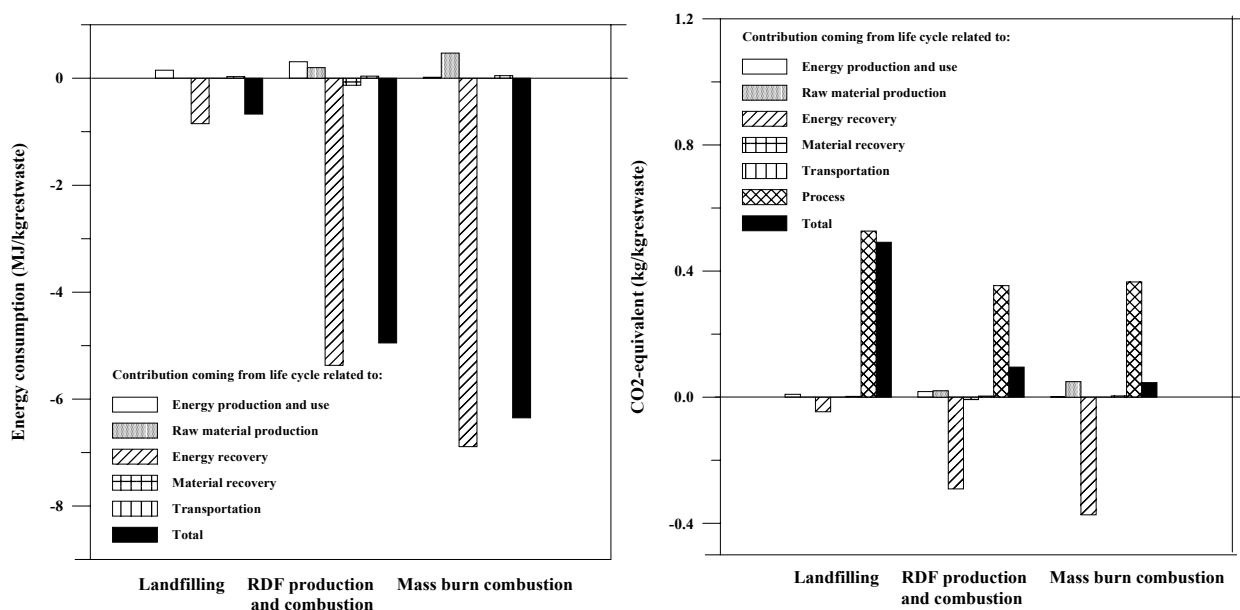


Fig. 1 The net energy consumption related to each restwaste management scenario with the indication of contributions coming from the different stages.

Fig. 2 The generation of greenhouse gases (expressed as kilograms of CO₂ equivalent) related to each restwaste management scenario with the indication of contributions coming from the different stages.

Acidification and Emissions in the Environment

The LCA study also quantified the acidification potential in terms of grams of SO₂ equivalent (5), emissions in air and water as well as solid waste productions. The results are reported in Table 1. Note that the COD and BOD values are not reported since for all the scenarios they are very low: 64mg/kg_{restwaste} and 16mg/kg_{restwaste}, respectively, for landfilling and about zero for thermal treatment scenarios. Moreover, as expected, the thermal treatment scenarios

present a very low amount of solid wastes, even though large parts of these (particularly in the case of mass burn combustion) are conditioned ashes from incineration, which require special landfills.

Overall evaluation

Table 1 summarizes the indicators of principal environmental impact categories, as evaluated for the three scenarios for restwaste management. It is immediate to note the poor environmental performances of landfill, even though a series of advantageous hypotheses were utilized in the study. An even worse overall assessment for this option is then predictable, taking in mind that LCA does not cover disamenity effects, like odour and visual pollution, destruction of the natural habitat, etc.

On the other hand, the overall performance of the waste management scheme proposed for Regione Campania appears rather satisfactory.

Impact category	Landfilling	RDF production and combustion	Mass burn combustion
Energy consumption, MJ/kg _{restwaste}	-0.67	-4.95	-6.35
Crude oil consumption, g/kg _{restwaste}	-6.32	-51.9	-68.4
Water consumption, g/kg _{restwaste}	-16.2	-69.1	<i>124.7</i>
CO ₂ -equivalent, kg/kg _{restwaste}	0.49	0.095	0.046
Air emissions of organic compounds, g/kg _{restwaste}	2.96	-1.70	-2.24
Air emissions of dusts, g/kg _{restwaste}	-0.04	0.006	<i>0.39</i>
SO ₂ -equivalent, g/kg _{restwaste}	-0.44	-3.66	-4.6
Water emissions of suspended solids, g/kg _{restwaste}	0.03	1.23	<i>6.79</i>
Occupied landfill volume, m ³ /t	1.43	0.49	0.27

Tab. 1 The indicators of principal environmental impact categories, as evaluated for the three scenarios for restwaste management. The bold types indicate the best environmental performance while the italic types indicate the worst.

CONCLUSIONS

Three alternative solid waste management options that could be used in Regione Campania, an area of the South of Italy suffering from a situation of weighty waste emergency, have been assessed by means of the internationally standardized method of Life Cycle Assessment. An analytical comparison between the three selected scenarios has been developed and quantified with reference to some crucial impact categories, like energy and material consumptions, climate change, acidification, air and water emissions, solid waste production. The results quantify the poor performance of landfilling option and validate the waste management scheme proposed for Regione Campania.

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Raman Scattering at 532 and 355 nm in Rich Flames, Including Effects from Liquid Fuel Droplets

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INTRODUCTION

Raman scattering is a powerful tool for the simultaneous detection of major species and temperature in flames, with good spatial and temporal resolution [1,2]. It is of interest because it can provide a spatially and temporally resolved, simultaneous measurement of N₂, O₂, CO₂, CO, H₂ and H₂O [3]. Fluorescence from hydrocarbons, OH, NO, carbon and other species can produce a strong background emission that makes Raman detection very difficult in certain spectral locations, when specific laser wavelengths are used. In sooting flames, particle incandescence can potentially interfere as well. These interferences can often be avoided, however, by suitable choice of excitation wavelength and detection schemes.

Our interest is to apply Raman scattering to the gas-phase flow inside a diesel simulator [4]. Liquid fuels will be injected into this simulator and they will very likely introduce strong interferences that may render impossible Raman detection during portions of the transient spray event. This is not the first time that Raman scattering has been applied to this environment, and much of the data has indeed been discarded due to interferences [2,5]. The goal in this work is to explore these problems further, in order to evaluate options and to optimize the measurement.

BACKGROUND

The optical system required for a Raman scattering measurement is straightforward. One arbitrary wavelength laser can be used (see e.g. Fig. 1). The beam is focused into the flow field of interest and the scattered light is typically collected at 90° to the beam. The collected optical signal is usually dispersed and analyzed using a spectrometer. The Raman signal is shifted in wavelength from the laser wavelength, and it is very weak relative to the Rayleigh scattered laser light. A filter that blocks scattered light at the laser wavelength is thus placed in front of the spectrometer.

The second harmonic of Nd:YAG is the most common laser wavelength for Raman studies, because the available power level is quite high (up to the J/pulse regime), and it can be used in its entirety when a pulse stretcher is implemented to avoid laser breakdown in the sample volume. Use of 532 nm, however, has several potential problems. Interference by soot incandescence near 500 nm, and the well-known C₂ interference, can both prove problematic. The C₂ interference can be caused by direct laser induced fluorescence of naturally occurring C₂, or the laser pulse can create C₂ via fragmentation of soot (even nascent soot) and then this laser-created C₂ will fluoresce. The propensity for laser breakdown is also higher in the

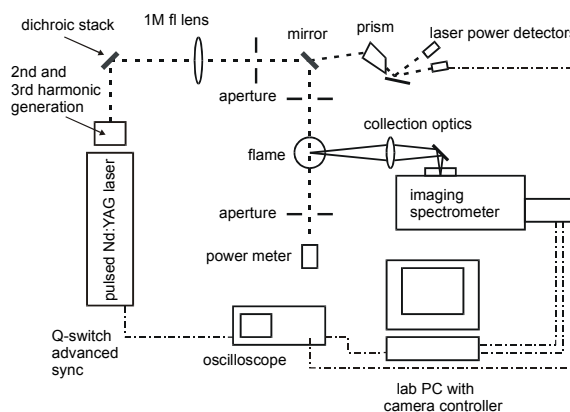


Figure 1. Basic layout for a Raman measurement.

presence of a droplet mist. Additional problems associated with the use of liquid fuels like dodecane or diesel have not been explored in detail. It would therefore be worthwhile to consider alternatives to 532 nm excitation.

The Raman cross section for a molecule is dependent upon the inverse of the wavelength to the fourth power (e.g. $1/\lambda^4$). The third harmonic of YAG (355 nm) is worthy of consideration despite reduced pulse energy, based upon this increase in the cross section. This wavelength is too long for many UV-induced fluorescence interferences and somewhat short for soot incandescence (which peaks at above 500 nm) [6,7].

In the work presented here we evaluate both 532 and 355 nm wavelengths in fuel rich propane flames, and we observe the effect of liquid fuel sprays and droplets on Raman signatures at atmospheric pressure.

EXPERIMENTS

Figure 1 contains a schematic diagram of the experiment described here. The same type of laser was used for both wavelengths; a Quanta-Ray GCR16 (10 Hz, 10 ns pulsewidth in the fundamental) in the second and third harmonics. Various pulse energy levels were investigated. The beam was focused past the measurement zone, using a 1 M focal length lens. The beam in the sample volume (diameter of about 1.3 mm for 532 nm and about 650 μ m for 355 nm) was thus converging slightly. The Raman signal was collected by $f_{\#}$ 4.8 optics and focused into a spectrometer entrance slit that was set at 300 μ m for all experiments. The spectrometer was an $f_{\#}$ 4.0 Acton Research SpectraPro-300, fitted with a Roper Scientific ICCD-1024MG-E intensified array. The spectral resolution was 1.6 nm.

Two burners were used in this study. For purely gas-phase flames, a standard McKenna premixed burner producing stable, rich flames with a nitrogen shroud flow was used. The second burner was a Perkin-Elmer aspirating burner body fitted with a water-cooled, Meeker style burner head using a stainless steel honeycomb flame stabilizer and a nitrogen shroud flow. The Perkin-Elmer burner was used primarily to study the effect on Raman spectra of mixed flames burning vaporizing liquid fuel (dodecane or commercially available diesel) with propane and air. Gas flows for both flames were supplied by frequently calibrated Brooks mass flow meters. The various flames investigated are described in Table 1. Some soot was usually observed in the measurement volume. Most Raman measurements were performed in the post flame region (15 mm above the flame front), to avoid questions about interpretation of signals from within the flame front (which is difficult to probe in these burners at 1 atmosphere anyway). The effects of pulse energy, intensifier gate width, gate delay (to observe decay of the background signal), and polarization state were investigated.

Table 1

Flame No.	burner	ϕ (propane/air)	ϕ (propane/air + dodecane)	ϕ (propane/air + diesel)
1	McKenna	2.4	none added	none added
2	Perk.-Ell.	2.3	2.7	2.9
3	Perk.-Ell.	3.2	3.8	3.4
4	Perk.-Ell.	2.3	none added	none added
5	Perk.-Ell.	5.9	none added	none added

RESULTS AND DISCUSSION

In order to compare our results to those of Meier and Keck [7], we acquired one data set with a long intensifier gate width of 100 ns, and we fixed our pulse energy at 175 mJ. Figure 2 contains the various Raman spectra from Flame 1, using a 532 nm laser beam under these conditions. In this case we have also investigated the effect of a polarizer in the collection optics. The spectrum that used no polarizer has been scaled to match the background-

subtracted N_2 Raman peak of the case where the polarizer passed the Raman, because the polarizer we used attenuates the light. Two polarization states were examined here: one that maximizes the Raman signal and one that minimizes it. Both are depicted in the figure. Because the polarizer is a sheet device, it does not have the rejection ratio of a calcite polarizer, but there is a clear loss of most of the Raman signal at the orientation that minimizes the Raman signatures. In addition, the LIF is clearly depolarized, and the polarizer orientation that passes the Raman signature improves the strength of the Raman signal relative to LIF. This effect is most pronounced just to the red of the N_2 Raman peak, where two C_2 vibrational bands can be found. Figure 2 also contains a spectrum that was acquired asynchronously with the laser trigger. In this case the intensifier gate was delayed by 20 ns after the laser pulse trigger. The same 100 ns gate width was used. One can see that the short-lived Raman spectra have been eliminated while the longer-lived LIF persists but is weaker.

Next, Raman spectra were taken at laser pulse energy levels ranging from 50 to 250 mJ, triggered synchronously with the laser. Flame 1 was used again with the 532 nm laser beam. The intensifier gate width was set to 20 ns, for better background rejection. The acquired spectra were marginally improved relative to Figure 2, but the signal-to-background ratio clearly improved with energy. No obvious soot incandescence was observed. The nitrogen data were then converted into a signal-to-background ratio and then plotted as a function of laser energy in Figure 3a.

The Raman spectrum acquired at 355 nm, using 145 mJ per pulse with a beam diameter of 650 μm in Flame 1, was similar to Figure 2. The asynchronous signal was lower than the synchronous signal by a greater margin than for the 532 nm case. It is clear, however, from the polarizer results that there is a significant laser-generated background embedded within the 355 nm Raman spectra at the synchronous gate time. Synchronous Raman spectra were then taken at laser pulse energy levels ranging from 30 to 147 mJ, with the same experimental settings. As with the 532 nm results, the signal rises much faster than the background. The nitrogen data were then converted into a signal-to-background ratio and then plotted as a function of laser energy in Figure 3b. The 355 nm signal-to-background ratios we achieve are better than those found by Meier and Keck [7], even at the same pulse energy level they used.

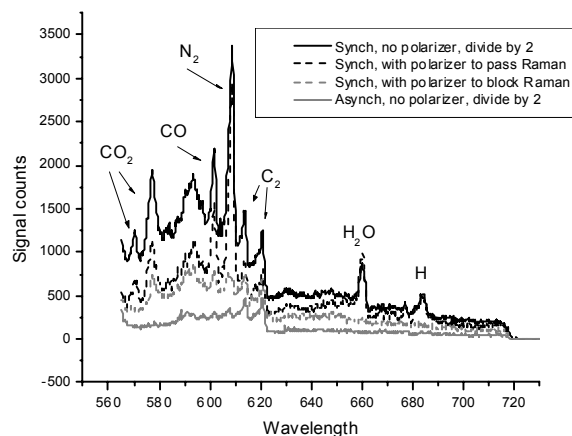


Figure 2. Flame 1, 532 nm Raman spectra taken synchronous and asynchronous (i.e. delayed) with the laser pulse. CO_2 , CO , N_2 , H_2O and H_2 features are Raman, C_2 is fluorescence.

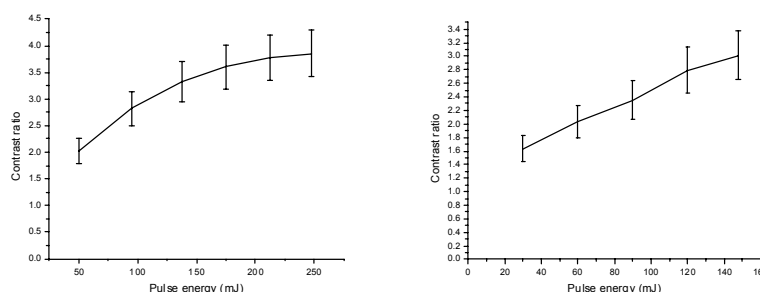


Figure 3. a. 532 nm N_2 Raman contrast ratio b. 355 nm N_2 contrast ratio

The Perkin-Elmer burner (Flames 2 - 5) measurements were performed without a polarizer. Otherwise the Raman experimental setup was unchanged. First, Raman spectra were acquired synchronous with the 532 nm laser pulse in Flame 2 using a 20ns gate and energy of 175 mJ per pulse. The spectra were what one would expect from gas-phase fueled flames at the same equivalence ratios. The asynchronous results were also predictable. This occurred because the fuel droplets evaporated fully before the flame front. The 355 nm data (145 mJ/pulse) for Flame 2 were also unsurprising. Clearly, if liquid phase fuels have evaporated and reacted, they pose no additional problem to Raman measurements. For Flame 3, two neutral density filters of OD 3 and 1 were required to reduce the signal below the detector array saturation threshold, because there was a good deal of laser breakdown at droplets that survived into the sample zone. The combined problems of droplet-related breakdown and high levels of interference at both wavelengths render this region of a spray flame impossible for Raman detection.

In order to evaluate the contribution of CH₂O and PAH, the laser was fixed at 355 nm (a wavelength known to have this problem) and no polarizer was used. Figure 4 presents spectra with gate widths of 1000 ns, taken just inside Flame 4. Here, one can see the nitrogen Raman feature, together with a structured spectrum clearly arising from formaldehyde fluorescence and several small Raman features from flame products. Spectra taken just inside Flame 5 are similar to Figure 4 but less structured. The entire spectrum is dominated by laser induced fluorescence from formaldehyde and PAH species. The nitrogen Raman line is in evidence, but no other distinguishing Raman features can be found. The 355 nm case could be used, however, for line imaging; to acquire formaldehyde fluorescence signatures near flame zones while clean Raman signatures would be observed in the post flame zone. Appearance of PAH signatures

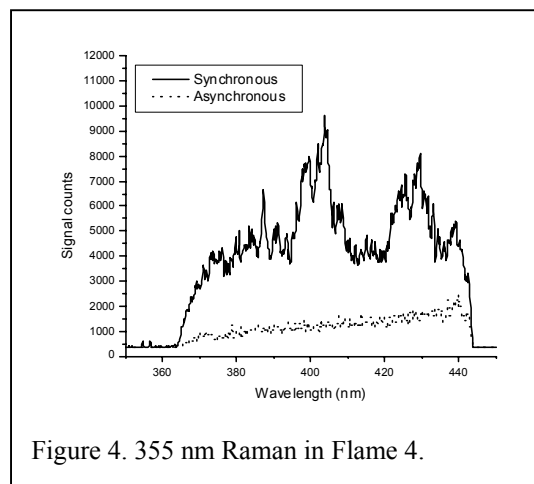


Figure 4. 355 nm Raman in Flame 4.

above the formaldehyde spectrum in specific locations could also prove useful, because they appear at high equivalence ratios.

ACKNOWLEDGEMENTS

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Ballistic Imaging for the Liquid Core of a Spray

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INTRODUCTION

We are developing a technique for imaging the near-field, liquid core in the primary breakup region of a fuel spray, under operating temperatures and pressures typical of engines. This technique, called “ballistic imaging”, has been used primarily in the medical community for imaging through tissue, but it was also used to demonstrate jet imaging [1,2].

BALLISTIC IMAGING

When light (either continuous or pulsed) passes through a highly turbid medium, some of the photons actually pass straight through without scattering, exiting the medium within roughly the same solid angle that they entered (see Figure 1a). These relatively few photons are termed “ballistic”. Because they travel the shortest path, they also exit first (see Figure 1b). A somewhat larger group of photons is called “snake-like”, because they are scattered just once or twice. They exit the medium in the same direction as the input light but with a somewhat larger solid angle than the ballistic photons. Because they travel a bit further, they exit just after the ballistic photons. Light exiting the medium that has scattered multiply has a larger photon number density, but it also is scattered into a very large solid angle and it exits last.

Due to their undisturbed path, ballistic photons retain an undistorted image of structures that may be embedded within the turbid material. If used in a shadowgram arrangement, the ballistic photons can provide diffraction limited imaging of these structures. Unfortunately, in most highly scattering and/or absorbing environments, the number of transmitted ballistic photons is often insufficient to provide the necessary signal to noise ratios (SNR) to form an image. In such a case, the snake-like photons retain slightly distorted information and can be used in imaging, together with the ballistic photons, with little degradation of resolution. In contrast, diffuse photons retain no memory of the structure within the material. If allowed to participate in the formation of an image, the various paths these multiply scattered photons take through the material will cause any image point they form to appear as if it came from an entirely different part of the object, and this will seriously degrade resolution. Unfortunately, diffuse photons are the most numerous when light is transmitted through highly scattering media. The problem of obtaining a high-resolution image through highly scattering materials is thus a matter of separating and eliminating the diffuse light from the ballistic and snake-like light. This can be done using discrimination methods that make use of the properties that are retained by the ballistic and snake-like light but are lost in multiple scattering events. As already alluded, the direction taken by transmitted light, together with exit time, can help to

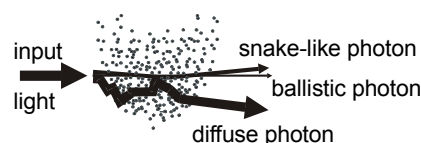


Figure 1a. Geometric schematic of ballistic imaging.

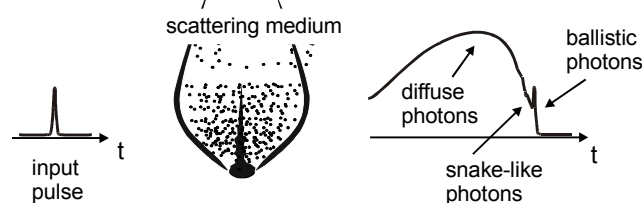


Figure 1b. Time-domain schematic of ballistic imaging with a short pulse.

segregate diffuse photons from the imaging photons. Furthermore, ballistic photons are coherent with the input light and they retain the input polarization. These attributes have also been used for ballistic imaging.

In what follows, we describe development of this time-gated ballistic imaging system, we present results from initial tests and their implications, and then describe ongoing and future work.

TIME-GATED BALLISTIC IMAGING

This work began with a comparison of ballistic imaging approaches described in the literature. This technique was developed for imaging through tissue, and unfortunately there was no standard test by which to compare the various approaches. Each research group has used various materials as scattering media, with their own standards for resolution benchmarks. For instance, one group may image a pair of crossed wires embedded in a chicken breast while another may use a resolution test chart in a medical fat-substitute. This lack of standardization makes it difficult to compare one method with another, in order to determine the most useful method for new applications such as this spray work. As a first step, therefore, we developed an imaging resolution figure of merit and used it to compare published techniques. In addition, because diesel sprays are transient, it was necessary to find a technique that could acquire rapid transients. In this case, we chose to take fast, still images of single events.

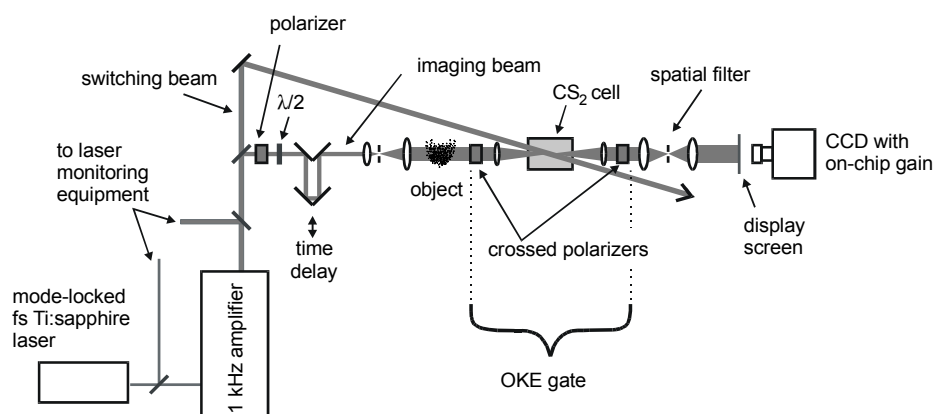


Figure 2. Layout of OKE-switched ballistic imaging system.

Based upon this evaluation, we settled upon the time-gated system shown in Figure 2. It uses an Optical Kerr Effect (OKE) gate, similar to that used Alfano and co-workers [1,2]. In order to evaluate various optical system options, we performed detailed development work that is not fully described here. It involved embedding a resolution test chart inside a cell filled with a solution of polystyrene spheres that were mixed to emulate the scattering environment of a spray. Various options were then tested against each other for best image fidelity in a single shot, until we arrived at the system described here. It is important to point out that other, more common imaging systems (e.g. shadogram) were not capable of imaging the test chart through this scattering environment. It was certainly not visible to the eye.

As shown in Figure 2, 1-kHz repetition rate Spectra-Physics Spitfire Ti:Sapphire regenerative amplifier, seeded with a Spectra-Physics Tsunami Ti:Sapphire mode-locked laser, generates 150 fs, 1mJ pulses centered at ~ 800 nm. The linearly polarized beam is split into OKE gating and imaging beams; 30% of the optical power is used as the imaging beam while the remaining power is used to create the OKE time gate.

The polarization state of the imaging beam is first cleaned up with a polarizer, because the OKE gate relies upon polarization switching. The imaging beam is then time delayed using an adjustable length delay arm. This allows one to control the delay between the arrival of the

switching and imaging pulses at the OKE gate, for optimum time gating. The imaging beam then passes through an optics train consisting of a telescope (with spatial filter) that controls the imaging beam size at the object, a system to relay the beam through the OKE switch, and a combined spatial filter/telescope for imaging onto a display screen.

As mentioned above, one signature of ballistic and snake-like photons is their directionality. Diffuse photons, on the other hand, are multiply scattered; locating their energy in a full 4π sr. One passive approach to ballistic imaging takes advantage of this fact by using a fairly hard spatial filter in the imaging beam. At first this seems like a simple and easy solution, but spatial filters also remove high spatial frequency components (the small features, including sharp edges) of the image itself. This is because the pinhole of the spatial filter must be placed at a lens focus. That focal plane is the Fourier plane, where high frequency components of the image can be found off axis. The pinhole blocks them, together with the diffuse photons, and the image is thus seriously blurred. Any optical train is a spatial filter of sorts, however, and if careful design is applied one can eliminate a good deal of the diffuse photons while preserving image fidelity. Even a spatial filter can be used (as depicted in Figure 2) if it has been shown not to degrade imaging performance itself. The system shown in Figure 2 thus has an inherent passive ballistic imaging system built into it, while maintaining good image fidelity.

Additional diffuse photons are rejected at the OE gate, which works in the following manner. When there is no switching pulse present, no image is transferred to the display screen. This is because the OKE gate uses crossed calcite polarizers. The first polarizer in the OKE gate (second polarizer used in the imaging beam) is oriented to pass the polarization orientation of the imaging beam. The second OKE polarizer is oriented normal to the first, blocking an unperturbed imaging beam. The measured extinction ratio of the polarizers is $>10^5$; without a switching pulse present there is $<10^{-5}$ transmission of the imaging beam through the second polarizer. After the first OKE polarizer, the imaging beam is focused into the Kerr active liquid (CS_2 in this case) with an F/#5 achromat, and then up-collimated with a second F/#10 achromat. At the arrival of a switching pulse, the intense electric field of the pulse causes the CS_2 dipoles in a to align along the polarization vector of the switching beam, creating temporary birefringence in the liquid. This birefringence rotates the polarization of the imaging beam, allowing most of the imaging beam ($\sim 70 - 75\%$) to pass through the second polarizer. The imaging beam time delay is adjusted while switching for maximum signal transmission through the OKE gate. This OKE induced birefringence is limited in time by either the duration of the laser pulse or the molecular response time of the Kerr medium, whichever is longer. In our case, the incident laser pulse is of much shorter duration than the molecular relaxation time of ~ 2 ps for CS_2 ; our gate time of 2 ps has been confirmed by direct measurement.

PRELIMINARY SPRAY EXPERIMENTS

As a first spray test of this imaging system, we have set up a quasi-steady water jet experiment. It uses a piston-accumulator system to provide high pressure (2,000 psi) over about 1 minute of spray time (see Figure 3). The jet under study is a stock spray nozzle modified to omit internal components that destroy the solid core. Thus, this jet approaches the simplicity of the diesel nozzle, which is typically a short length (typical l/d of 2 to 6) hole, submillimeter in diameter (100 to 300 μm), with atomization totally dependent on the conversion of pressure to velocity in the orifice. Jet diameters for nozzles that we have procured range from 0.018 to 0.031 inches (0.5

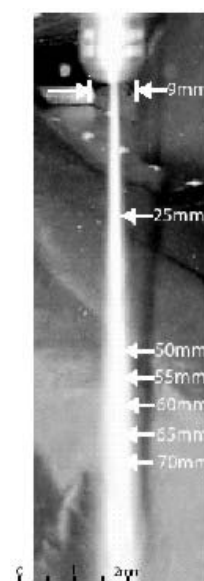


Figure 3. Water jet.

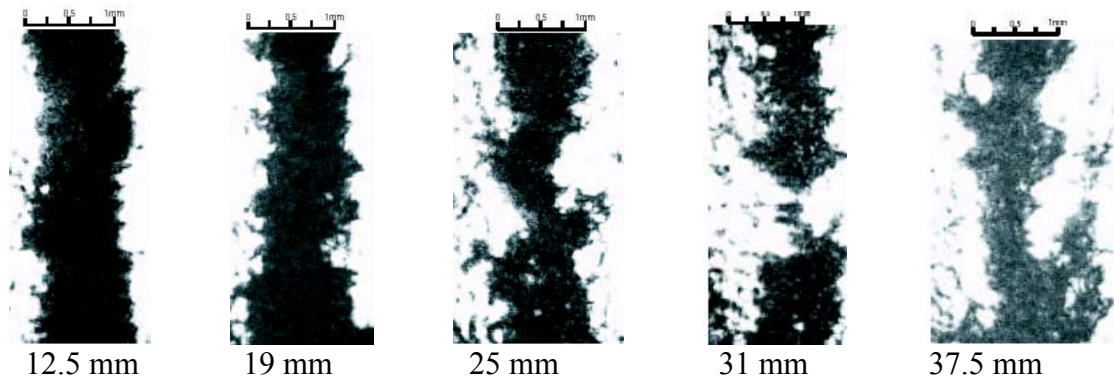


Figure 4. Ballistic images of the liquid core as a function of distance from the jet exit.

to 0.8 mm). Relevant parameters for the jet depicted include: flow rate = 1.89 l/min, fluid velocity at nozzle exit = 191.5 m/s, nozzle exit diameter = .457 mm, $We = 232736$, $Re = 102517$, $Oh = 0.00471$. These numbers put the jet well into the atomization regime. Ballistic images were acquired at various positions in the jet, as shown in Figure 4.

Figure 4 contains the first sequence of ballistic images of a liquid core in a spray. The entire spray was somewhat larger than these images, because the outer fog of droplets is not depicted here. Other, more common imaging techniques are unable to detect these structures. The resolution limit of this system is about 15-20 μm , which is larger than the smallest features of interest in sprays. The system can be improved, but these images already clearly demonstrate turbulent primary breakup of a jet, which is an important finding. The speckled features in the images are on the same scale as the resolution limit. They may be evidence of droplets, for example, or they may simply be diffraction patterns. Future work will be devoted to resolving such issues. It will likely be necessary to apply image-processing techniques to remove spurious features while retaining genuine structures.

ACKNOWLEDGEMENTS

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Studies of Flame Propagation in an SI-engine using Laser-induced Fluorescence of CH₂O

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ABSTRACT

Visualization of the unburnt fuel-air mixture has been performed in a spark-ignition engine using planar laser-induced fluorescence of formaldehyde. Formaldehyde (CH₂O) is naturally formed in the first stage of the two-stage ignition process in the end-gas, and the fluorescence was detected after excitation using the Nd:YAG-laser wavelength 355 nm. Thus the contour of the fluorescing area indicated the position of the flame front. The flame propagation was measured in each cycle by recording a fluorescence image from each of two subsequent laser pulses. The merits and limitations of this technique for engine applications are discussed.

INTRODUCTION

Still in the year 2003 the transportation sector relies heavily on the use of fossil fuels. During the last decades increasing concern has been raised regarding the fuel consumption and the emissions of combustion engines and the research have to face these aspects as well as the reliability, durability and overall performance of the engine.

In all combustion engine types the performance, fuel consumption and emission formation is strongly dependent on how the combustion process develops in time and space. In spark-ignition (SI) engines a flame kernel is formed emanating from the spark plug and propagating towards the cylinder walls. This flame propagation process is closely related to engine parameters such as fuel-air mixture and combustion chamber design, and can thus be regarded as an important link between these properties and engine performance.

Laser diagnostic methods [1] have during the last decades evolved as a powerful tool for measurements of both chemical and physical properties in the combustion chamber. For example, temperature measurements using Coherent Anti-Stokes Raman Spectroscopy (CARS) has proven to be very useful [2]. Laser-Induced Fluorescence (LIF) has been used both for visualization of radicals and of the fuel distribution by adding a suitable tracer element (see for example [3] and references therein). In laser-induced fluorescence, molecules are transferred to an excited state by incoming laser radiation. The molecules will very fast transfer back to the ground electronic state while emitting radiation – the fluorescence signal.

The addition of tracers introduces a potential source of error into the measurement situation because the combustion process may be affected. By probing a naturally occurring species this uncertainty can be circumvented. Many radicals are present at different stages and at different locations during the combustion process and some of these radicals, such as OH,

have often been used as a flame front marker. Another naturally occurring species is formaldehyde (CH_2O) that is formed in the unburnt mixture during the so called cool-flame chemistry that foregoes the real combustion. Since formaldehyde then is consumed, the presence of this species indicates unburnt areas of the combustion chamber. Formaldehyde and other species formed in the cool-flame region have also been used to detect self-ignition centers [4-6] – a process that may lead to engine knock.

In this work we have studied the flame propagation by using a double laser and camera setup and recording two images of the formaldehyde distribution during each engine cycle.

EXPERIMENTAL SETUP

Two Nd:YAG lasers were used for excitation of formaldehyde at the wavelength of 355 nm. The beams were shaped to 4 cm wide sheets using cylindrical lenses and led through a quartz ring situated at the top of the cylinder wall of the port-injected AVL 5411 single-cylinder research engine. This is illustrated in Fig. 1a. The signals were detected perpendicular to the incoming laser sheets through a piston window via an aluminium mirror located below the piston. In Fig. 1b the view through the quartz window in the hollow piston is shown and the details of the pent-roof combustion chamber is evident. The observable area was 65 mm in diameter as opposed to the bore at 83 mm. This comes from the fact that the cylinder is hollow and its steel walls partially block the view.

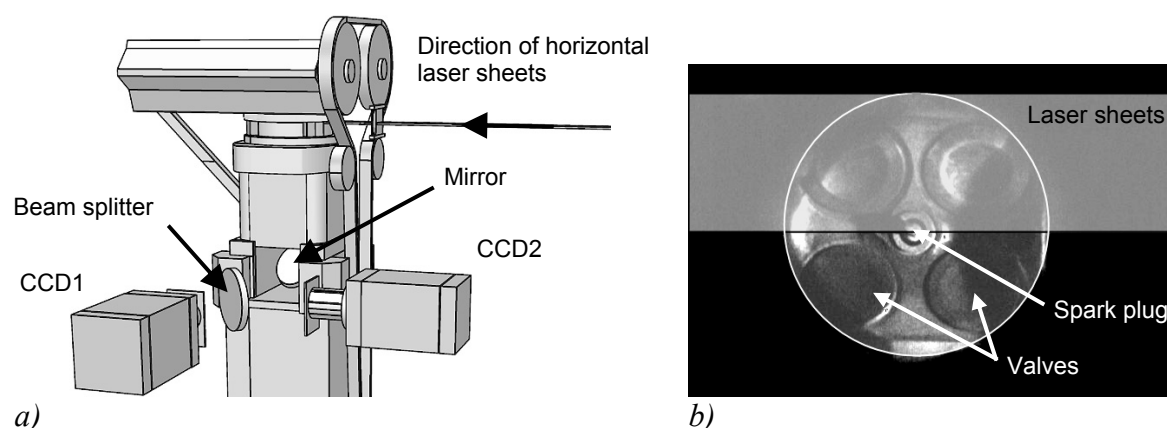


Fig. 1 a) Experimental setup. b) The view through the piston window.

The fluorescence images were captured on two separate ICCD cameras by separating the signal using a beam splitter. Two long pass filters (GG385) were used to suppress the laser wavelength. The pulse energy was 70 mJ for both lasers. The fuel consisted of a mixture of n-heptane and iso-octane (RON 60) and the engine was run at a constant speed of 1200 rpm. One advantage of the system was that the two laser-detector setups were triggered independently. This enabled us to choose time separation between recorded images arbitrarily. For measurements of flame propagation we decided to use the separation 1.5 CAD, which corresponded to 200 μs .

RESULTS

An example from a measurement series is shown in Fig. 2. The white areas are formaldehyde signal from the unburned fuel-air mixture and the dark ones correspond to the areas where the flame already have passed and consumed the formaldehyde. These images were captured at -2CAD and -0.5CAD, respectively, as indicated in the corresponding pressure trace.

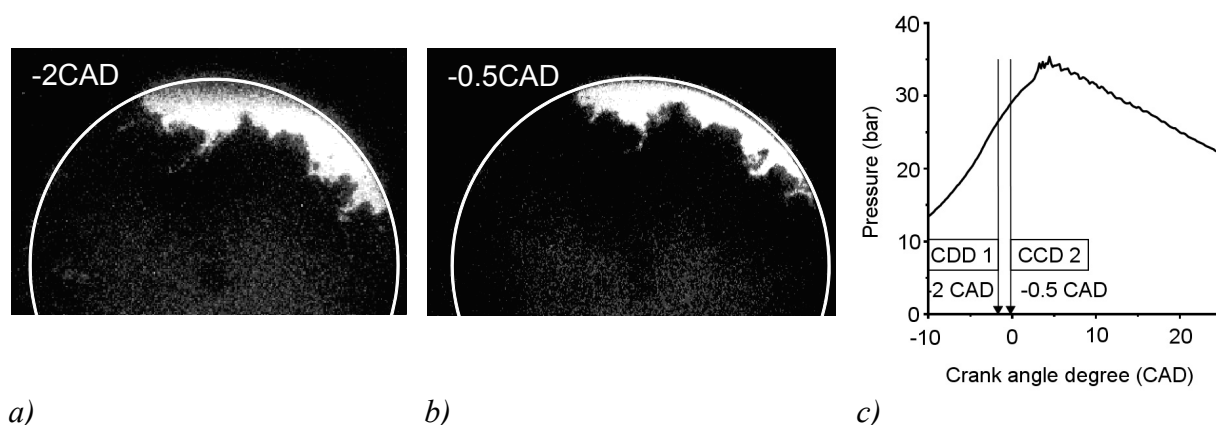


Fig. 2 a and b) Laser-induced fluorescence images of formaldehyde (white areas) in the AVL engine. c) Pressure trace for the cycle shown together with the time positions where the images were recorded. The oscillations that are observed to start at +3CAD indicate the engine knock phenomenon.

The LIF signal was studied spectrally using a spectrometer, and formaldehyde peaks were identified. The spectra looked similar to those presented in previous studies in the same engine [7], and it can not be ruled out that other molecules formed in the cool-flame chemistry contribute to the detected signals.

From image pairs such as the ones presented in Fig. 2 the average flame propagation velocity can be estimated. By using a contour recognition program and subsequently also a routine that calculates the distance between points in the two contours, the flame velocity field can be calculated. This is illustrated in Fig. 3 for the image pair in Fig. 2.

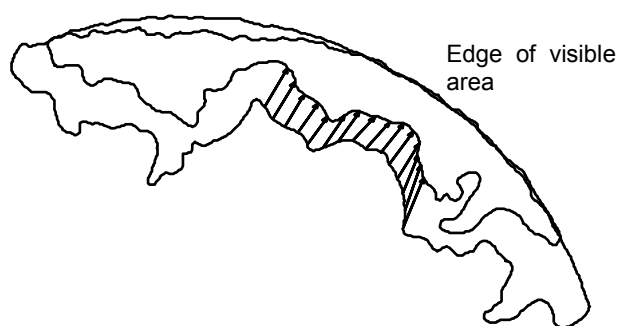


Fig. 3 The contours of the image pair from Fig. 2 along with parts of the calculated velocity field.

Using the treatment discussed above the average flame speed in the illustrated region was found to be ~ 15 m/s. Of course this assumes the third dimension (the height of the combustion chamber) to give negligible contribution to the velocity. Since a pent-roof design was used, this must not necessarily be true. However, near the edges where the formaldehyde signal most often appeared, the height of the chamber is much less than in the middle regions and the approximation of two-dimensional flame propagation is believed to be sufficient. Unfortunately the possibility of studying cycle-to-cycle variations for stable operating conditions was limited in the present measurements since the engine temperature increased during operation.

DISCUSSION

The main advantages of using formaldehyde as a flame front indicator are that it is a natural intermediate species and that it is conveniently excited using the third harmonic of an ordinary Nd:YAG laser at the wavelength 355 nm [7]. Drawbacks are that formaldehyde only is present in large enough quantities to be detected if the temperature and pressure is sufficiently high for its formation. This prevents detection of flame propagation early in the cycles. It should also be noted that the formaldehyde signals obtained during our experiments showed very good signal strength despite the fact that the wavelength 355 nm is not the optimum choice to get a strong absorption in formaldehyde.

The use of formaldehyde as a flame front marker was compared with the added fuel tracer 3-pentanone excited at the laser wavelength 266 nm. The tests showed that the signal-to-noise ratio was lower for the 3-pentanone images when using equal pulse energy in the beams. It was also found that the structures in the 3-pentanone images and the formaldehyde images coincided when the laser-detector systems were used with no time separation.

To summarize, in this work laser-induced fluorescence has been used to study flame propagation in an optical SI-engine with a real geometry pent-roof design. Species formed during the cool flame chemistry, among them formaldehyde, were probed, thus acting as a marker of the unburnt gas regions. The dual laser and detector setup made it possible to record two images with arbitrary time separation from which the flame propagation velocity could be calculated. The standard laser wavelengths used simplified the setup, and the signal-to-noise ratio was good using laser pulse energies around 70 mJ.

ACKNOWLEDGEMENTS

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Synchrotron X-ray Scattering Diagnostics for the Study of Carbon-Based Particles and their Precursors in Relation to Combustion

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INTRODUCTION

The transition from molecules to clusters or particles is a key issue to understand the mechanisms that determine particle formation during hydrocarbon combustion. Experiments by other groups have shown that nanoparticles, i.e. particles with the size around a couple of nanometers in diameter are produced in different flames [1,2]. Their properties were found to change with the conditions of combustion. The results were obtained by a combination of measurements in-situ and ex-situ.

Measurements of elastic scattering and radiation extinction in the optical ultraviolet and visible wavelength region allows the determination of characteristic sizes of particles. However, much of the sensitivity is lost what concerns the size and structure of the particles when sizes are smaller than typically 20 nm in diameter.

Radiation at wavelengths close the length of interatomic distances, should allow the molecular structures of molecules and clusters to be resolved. Small-Angle-X-ray Scattering (SAXS) [3,4], using synchrotron radiation sources, has been used to measure the size of particles around a couple of nanometers in flames [5,6], by analyzing the forward scattered radiation, i.e., in the region which normally is referred to as diffraction in classical optics.

This work, reports the first results included from a series of measurements related to a project to study molecular growth and particle formation in flames by use of the sideward X-ray scattering. This method shows stronger sensitivity to molecular structure than the forward scattering region. Experimental scattering patterns are compared with results from scattering calculations. In particular aromatic structures as evidenced from calculations should show characteristic signatures in the sideward region. The scattering pattern gives also information of the size of these molecules.

EXPERIMENTS AND CALCULATIONS

Radiation was extracted from the synchrotron ring at MAXLAB, to station D611. The beam was passed through a double crystal spectrometer (Si-111). The wavelength λ of the radiation could be tuned between 1.24 Å and 2.50 Å corresponding to 10 keV and 5 keV respectively. The spectral brightness, $\lambda/\Delta\lambda$, was 10^4 . The intensity corresponded to 10^8 - 10^9 photons s⁻¹. The radiation was horizontally polarized.

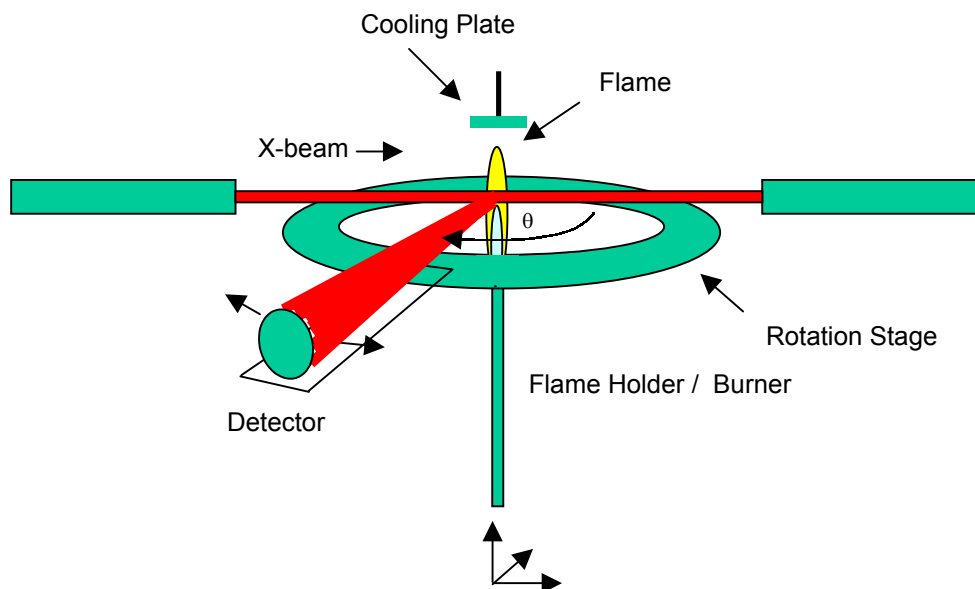


Fig.1 The experimental Set-up.

Figure 1 shows the basic components of the experimental set-up. The X-ray beam diameter was 2 mm. The positions of the flame and the cooling plate could be x-y-z translated by a computer. A detector, consisting of a scintillator and a photomultiplier tube (PMT) was attached to a rotation stage. The movement of the rotation stage and therefore the scattering angle (θ) of the detection was controlled by a computer. The detector could be rotated in the range of scattering angles $17.5^\circ \leq \theta \leq 165.5^\circ$. The output from the detector was sent by the computer to a gated integrator/boxcar averager connected to a computer A/D interface, synchronized to the movement of the rotation stage. In most of the applications the X-ray beam was modulated by a chopper and the detected signal was filtered through a lock-in amplifier.

In order to increase the signal intensity in the sideward region the rotator and burner could be rotated as one unit between 0° and 90° around the beam axis. Most of the flame measurements were obtained for an inclination of 60° . Angular scattering patterns were recorded for air, burning butane gas, ethylene/air and soot condensed on the cooling plate.

The angular distribution of the scattered radiation was calculated based on a model from dipoles centered at the atomic positions for different molecules. The atomic scattering properties were included for carbon, oxygen and nitrogen. The calculated results were then compared to the measured patterns. Figure 2 shows some results obtained from calculations. Patterns were calculated for different aromatic substances, nitrogen, oxygen ethylene and butane.

The results show that the structures of the angular patterns are related to the structural size of a molecule or a graphitic particle. The results from flame measurements contain considerable noise, however, in some case signs of structure can be found. The experiments will continue, improving the signal-to-ratio of the detected signal

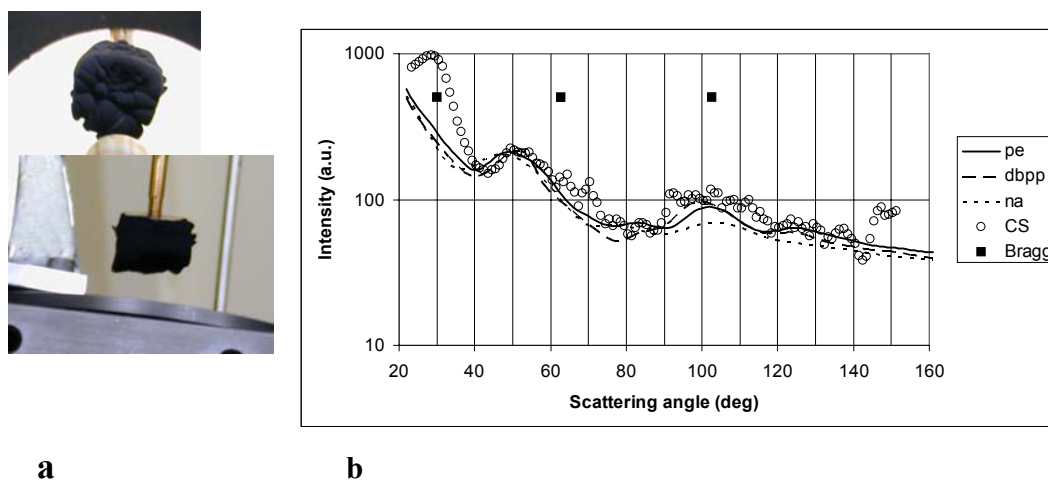


Fig.2 a) Photographs of the soot condensated on the cooling plate inserted in the flame; b) The resulting scattering pattern measured from the soot at $1.771 \text{ \AA}$ (CS) and the calculated patterns for the aromatic substances perylene (pe), dibenzo-peropyrene (dbpp), and naphthalene (na). The position of the maxima obtained from the Bragg equation [3,4] for the inter-plane distance of graphite sheets, $3.4 \text{ \AA}$, are also given.

ACKNOWLEDGEMENTS

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A Method to Avoid Spatial Laser-Wing Effects in Laser-Based Spectroscopies for Combustion Diagnostics

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INTRODUCTION

Laser spectroscopy is very successful in obtaining important information on combustion processes [1]. However, realistic characteristics of laser beams are often discarded in favor of a simpler theoretical readability of spectroscopic experiments. Among these conceptual simplifications, laser interactions are frequently thought to be point-like or spatially homogeneous. On the contrary, real laser beams are with uneven spatial profiles and the reduction to spatially unstructured beams might be inappropriate for quantitative comparisons between theory and experimental results.

One example of a spectroscopic application where probe volume effects are dominant is saturation, which has a high non-linear sensitivity to spatial changes in laser beams. Saturation is largely adopted in laser-induced fluorescence (LIF) spectroscopy. Actually, saturated LIF (SatLIF) is one of the most important techniques used to circumvent molecular quenching and laser power fluctuations [1-3]. It is also attractive for its high species detection sensitivity and it can be employed to extract number densities of molecular species [1-3]. Nonetheless, realistic choices of laser systems pose a serious experimental issue about the loss of saturation along the wings of frequency, time and space distributions of laser pulses. This loss of saturation efficiency has been termed laser-wing effect [1-3] and its spatial genesis has attracted a great deal of attention in the past decades [4]. Unfortunately, it is a matter of fact that none of the proposals to limit spatial wing contributions in the experimental data has been so successful and, nowadays, experimentalists avoid SatLIF although such a technique is declared potentially superior [5].

Salmon and Laurendeau have suggested the idea of looking for fluorescence emitted from the line traced by the spatial maximum (center-line) of laser beams with gaussian or similar profiles [6]. Wing-related flaws are indeed absent when the geometrical source of fluorescence is reduced to the center-line. To that end, Salmon and Laurendeau developed a formalism where center-line emission was derived from lateral fluorescence intensities through an Abel-like inversion. But the analysis was limited to steady-state of the so-called balanced-cross model [1], and, besides the limited application, the main disadvantage is the finite resolution needed to observe fluorescence profiles at sufficient level to work out center-line emission from Abel integral. Abel inversion suffers additionally from optical collection effects [6] that must be considered for accurate measurements. Everything considered, exact center-line detection seems an impossible task to attain in a general SatLIF experiment where collection optics have a limited resolution which is far from being fine enough to resolve the line of maximal emission. The difficulty is self-evident if it will be noticed that laser focusing (compulsory for high saturation) remarkably reduces the physical extension of the interaction volume.

In the present paper, an alternative proposal to detect center-line emission will be developed. Numerical simulations will provide the evidence of a simple approach to corrections for laser-wing contributions.

THE METHOD

Suppose to call $F(t, I)$ the saturated fluorescence emitted from the point $\mathbf{r} = (x, y, z)$ at the time t when the local laser intensity is $I(\mathbf{r}, t)$. The signal Φ emitted from the whole interaction volume is

$$\Phi(t, I_0) = k \int F(t, I(\mathbf{r}, t)) d\mathbf{r} \quad (1)$$

with I_0 the total laser intensity and k a constant determined by the measuring process. Eq. (1) can be solved by noting that fluorescence is usually collected from the laser focus [1-3] and consequently the local laser intensity (i) does not show appreciable change along the propagation direction (coincident with the z-axis), (ii) is separable in its radial, angular and time profiles and can be written in the following form

$$I(\rho, \vartheta, t) = I_0 R(\rho) \Theta(\vartheta) T(t) = I_{rad}(\rho) \Theta(\vartheta) T(t), \quad (2)$$

where functions R , Θ and T are normalized to give the total pulse energy after integration over space-time. Eq. (1) can thus be rearranged in

$$\Phi(t, I_0) = -\frac{k l}{2} \int_0^{2\pi} \int_0^{I_0 R(0)} \frac{F(t, I_{rad}, \Theta(\vartheta), T(t))}{g(I_{rad})} dI_{rad} d\vartheta, \quad (3)$$

where function g accounts for the change from ρ to I_{rad} in the integration variable. To get center-line emission it is sufficient to derive Eq. (3) with respect to I_0 . By applying Leibnitz theorem for differentiation of integrals it is then possible to find the following result

$$F(t, I(\rho = 0, t)) = -\frac{g(I_0 R(0))}{\pi k l R(0)} \frac{d\Phi(t, I_0)}{dI_0}, \quad (4)$$

where the fluorescence signal F is the center-line emission defined by $\rho = 0$. Eq. (4) is very noticeable because it says that laser-wing contribution can be totally eliminated by measuring the fluorescence signal Φ relative to the whole interaction region! A first interesting consequence of Eq. (4) arises when complete saturation holds along the center-line. Mathematically, if $F = \text{constant}$ then $\Phi \sim \text{Log}(I_0)$. The logarithmic dependence is the resultant effect of spatial laser-wings on the overall emission and this is consistent with literature results obtained for specific physical conditions [3]. The additional remark on Eq. (4) is that the relation between center-line emission F and total signal Φ remains valid even if time integration is performed. This is very important for experiments in which time sampling has been applied to SatLIF signals that have not been visualized with oscilloscopes.

NUMERICAL SIMULATION AND DISCUSSION

A numerical simulation was run to verify the reliability of the result given above. The radial dependence was chosen to be gaussian as it represents the basic spatial structure of lasers in SatLIF experiments [1-3]. The temporal shape $T(t)$ of the laser pulse was derived from the numerical solution of a Q-switched laser system generating a pulse width of about 5 ns (Fig 1a). This time scale is typical to guarantee enough laser irradiance to saturate the observed molecular transition. The dynamical model was developed for a four-level molecule

simulating the emission of the $A^2\Sigma^+(v'=0)-X^2\Pi(v''=0)$ band in hydroxyl radical with relevant quenching and rotational relaxation [6, 8, 9].

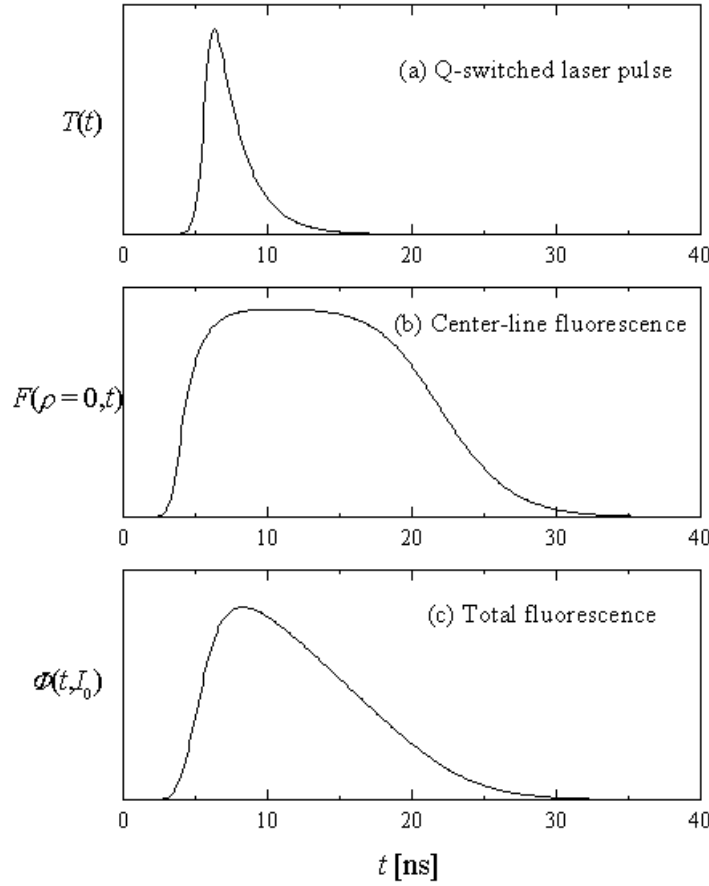


Fig. 1 Laser pulse $T(t)$ and time profiles of center-line and total fluorescence response.

The comparison between the time profiles $F(t, I(\rho = 0, t))$ and $\Phi(t, I_0)$ of SatLIF emission has been reported in Figs. 1(b) and 1(c). High saturation can be observed in Fig. 1(b) and what is remarkable is the plateau that lasts for some ns. On the contrary, Fig. 1(c) shows the loss of saturation quality expected with acquisitions of the signal Φ . The plateau has disappeared and the time structure is similar to the laser pulse but with a more enlarged time width determined by the complex interplay between molecular dynamics and time shape of the laser pulse. Nonetheless, the saturation efficiency of Fig. 1(c) might be improved by selecting a region around the spatial maximum of the laser profile. For instance, a combination of lenses and a monochromator slit has often been employed in real experiments to discriminate peaks in emitted profiles [1-3]. This kind of method was considered in the simulation by resolving the signal Φ with a slightly better spatial resolution than that found in literature. The result for the resolved total signal Φ^* is reported in Fig. 2(a). The new signal has a shape that is rather similar to Φ (Fig. 1(c)) and it is clear that laser-wings are still significant although spatial discrimination was included. According to Eq. (4), the derivative of Φ yields a much better result. In the simulation the derivative of Fig. 1(c) with respect to I_0 was calculated and the right-hand of Eq. (4) has been reported in the continuous line of Fig. 2(b). To compare this result with the exact center-line emission, some points (open circles) of the numerical solution

of Fig. 1(b) have been included in Fig. 2(b). The two results coincide and this proves graphically and numerically what has been obtained analytically in Eq. (4).

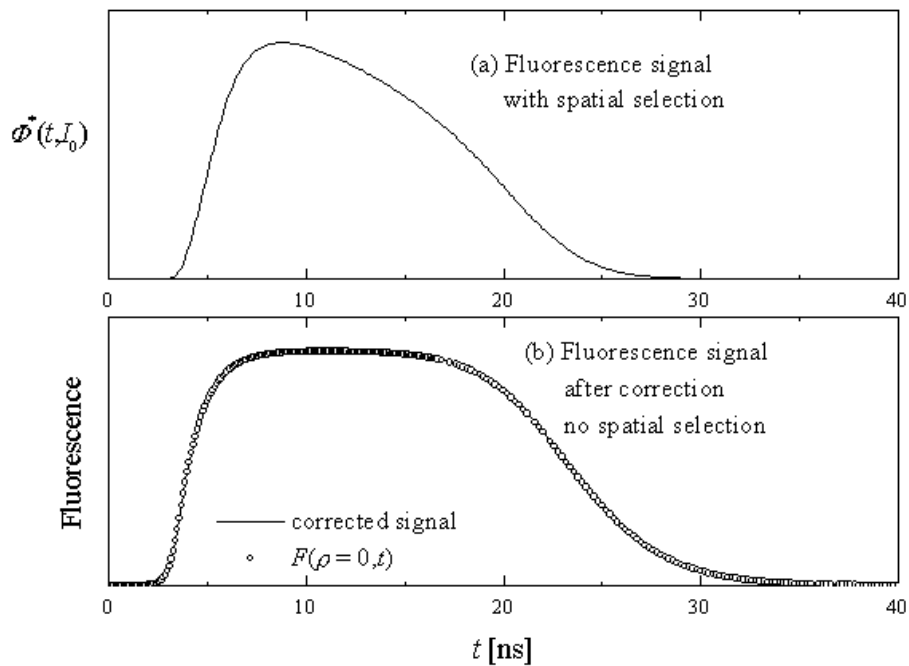


Fig. 2 Fluorescence signals with and without spatial selection. In (b), Eq. (4) has been used to obtain the corrected signal. The open circles reproduce the center-line signal F of Fig 1(b) that has been reported for comparison.

In conclusion a general method to obtain wing-free SatLIF data has been demonstrated without using the customary technique of spatial selection. The new method represents a great advance in comparison to the partialities of previous proposals found in literature. The detection of center-line established in Eq. (4) might also be useful to limit the problem of laser chemistry [1-3] because of the lower laser intensities needed to diagnose saturation.

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A NOVEL PARTICLE TRAP FOR USE WITH THE GAS QUENCHING PROBE

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ABSTRACT

A novel particle trap impactor is developed for use with the gas quenching in fluidized bed combustion conditions. At room temperature, the impactor with a nozzle of 1mm in diameter, in combination with the orifice to jet diameter ratio at 1.5 and the jet-to-plate spacing ratio at 1.4 yielded sharp size cuts with a maximum collection efficiency of 92% and a cut-size (d_{50}) of 0.05 μ m.

Keywords: virtual impactor, PTI, volatile metals, gas quenching probe, fly ash.

1. INTRODUCTION

The gas quenching (GQ) probe technique has been further developed for measurement of gas species in fluidized bed combustion (FBC) conditions [1-4]. In a GQ probe sampling system a trapper solution is directly injected into the hot probe tip in order to absorb and quench the extracted hot gases. The trapper solution is then circulated back to the reservoir by a vacuum pump. The latest modification of the probe tip is presented in Fig. 1. A quartz tube holding the sintered quartz filter is added to eliminate the effects of the probe cooling water on the filter temperature and the potential losses of sampled species. The technique is however still subject to uncertainties potentially caused by the fly ashes accumulated on the filter during sampling [4]. It is therefore useful to separate the solid particulates from the extracted gas in such a manner that further contacts between the collected particles and the gas stream are minimized. This paper presents the results from the study into the design and test of a novel virtual impactor developed based on the Particle Trap Impactor (PTI) concept [5, 6], which can incorporate with the GQ probe for sampling of gas species in hot combustion gases in FBC conditions.

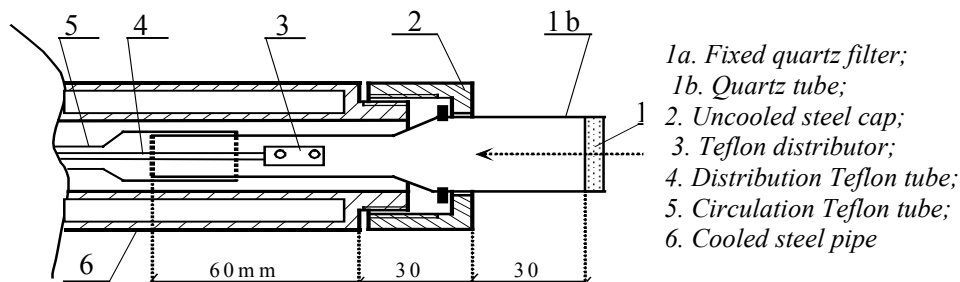


Fig. 1 The new modified GQ probe with detachable quartz module

2. EXPERIMENTAL

2.1. Description of the impactor incorporated with the GQ probe.

General features of the quenching and trap (QT) impactor used in this study are shown in Fig.2. The impactor, made of stainless steel, consists of three major components: an impactor

house, a flat separating plate and an end cap. A sintered quartz filter can be added in the impactor. The impactor house is cylindrically shaped and built with a round nozzle and an impactor cavity. An orifice aligned with the nozzle is formed chiefly by a truncated hole located on the edge of the separating plate and partly by the side wall of the impactor house as can be seen in the figure.

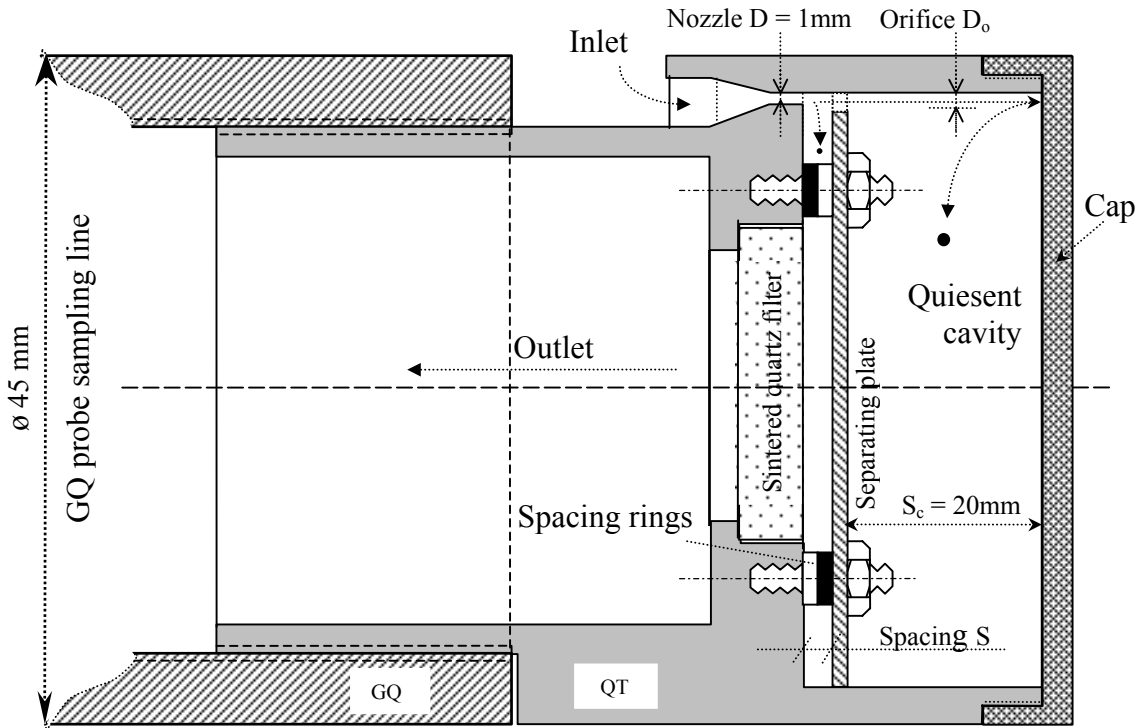


Fig. 2 Particle Trap Impactor incorporated with the GQ probe

The choices of the nozzle diameter ($D = 1\text{mm}$), the orifice diameter ($D_o = 1.4, 1.5$ and 1.6), the jet-to-plate spacing ($S = 0.5, 1.0, 1.5$ and 2.0), the cavity depth ($S_c = 20\text{mm}$) and the geometry of cavity are connected to the studies on the PTI [6] and virtual impactors [7]. On operation, the nozzle and the orifice are on the top side of the impactor as shown in the figure.

2.2. Experimental setup

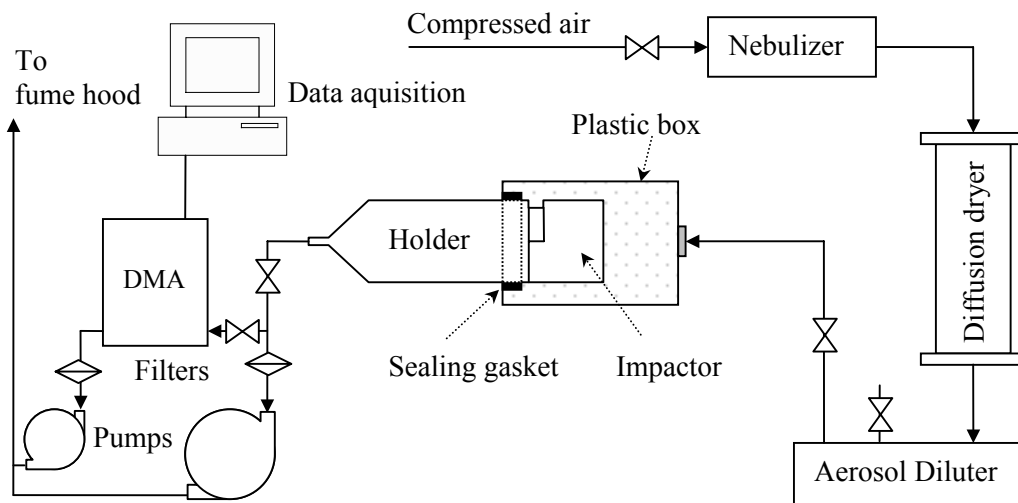


Fig. 3 Schematic diagram of the experimental setup

The experimental setup is schematically shown in Fig. 3. The impactor assembly consists of an impactor holder, the impactor and a sealed transparent plastic box. The impactor is mounted to the holder and inserted into the plastic box, which is connected to an aerosol source. The impactor holder is connected to a particle differential mobility analyzer (DMA). Aerosol particulates are produced from KCl aqueous solution by means of the TSI Constant Output Atomizer Model 3075. Two vacuum pumps were used. The smaller is located after the DMA in order to extract a small portion (1 L/min) of the total aerosol flow passing the impactor assembly (11 L/min), through the DMA. The bigger is located between the impactor assembly and the DMA, from which a gas flow rate of 10 L/min was produced.

3. RESULTS AND DISCUSSION

3.1. Optimization of the D_o/D ratio

For the chosen parameters, the value of D_o/D , the orifice to jet diameter ratio was 1.4, 1.5 and 1.6, respectively. The ratio of jet-to-plate spacing to the jet diameter, S/D , was set at 1.0 for experiments to find the optimal D_o/D , among the three values. The collection efficiency of the impactor, defined as the percentage of the collected particle number over the total number of the particle enter the impactor, is computed and presented in Fig. 4. As can be seen in the figure, the collection efficiency of the impactor slightly decreased when the ratio D_o/D was increased. The maximum collection efficiency in each case is about 92%. The three data series are quite similar with a similar cut-size (d_{50}) of about 50 nm. The D_o/D value of 1.6 yielded lowest collection efficiency and the data was a little bit scattered compared to the other two. Even though, the best collection efficiency was obtained from the D_o/D value of 1.4. This ratio was used in subsequent experiments.

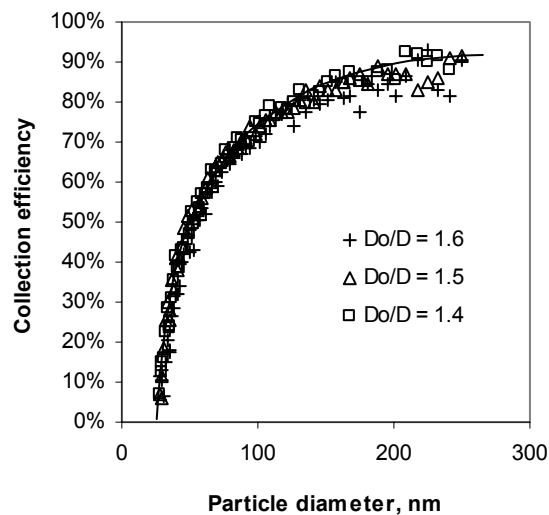


Fig. 4 Effect of the orifice to jet diameter ratio on the impactor efficiency.

3.2. Optimization of the S/D ratio

Fig. 5 presents the results of experiments which were performed to determine the optimal value of the ratio of jet-to-plate spacing to the jet diameter, S/D , while the D_o/D ratio was held constant at 1.4. The collection efficiency of the impactor slightly increased as the S/D ratio was increased from 0.5 to 1.0 and 1.5, but started to drop when the ratio was increased further to 2.0. The data from the last experiment was scattered especially for the fraction of courser

particles. The maximum collection efficiencies in the first three cases were quite similar and about 92%, but the data from the experiment for the S/D ratio of 1.5 yielded a much sharper size-cut and a smaller d_{50} value well as, about 40nm. It suggests that, in combination with the chosen parameters, the ratio of jet-to-plate spacing to the jet diameter at 1.5 is optimal.

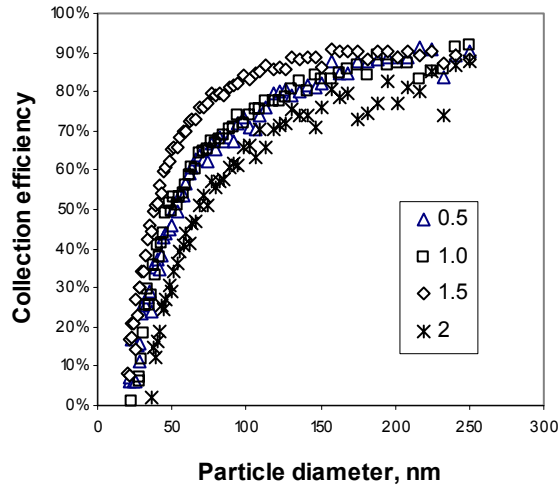


Figure 5. Effect of the jet-to-plate spacing to jet diameter ratio on the impactor efficiency.

3.3. Comparison with sintered quartz filter

In these experiments, a sintered quartz filter used by Tran et al. [4] was added in the QT impactor as shown in Fig. 2. The filter has a diameter of 20mm, a thickness of 3mm and a porosity of 20-40 μ m. The collection efficiency of the impactor with the filter was compared with the impactor without filter in the same conditions. The jet-to-plate spacing to the jet diameter ratio was 1.5. The results of the experiments presented in Fig. 6 show that the impactor did not collect the particles with a diameter smaller than 20nm, while the impactor with the filter did and the overall collection efficiency increased as the particle diameter decreased from 20nm. However, no apparent advantage to the filter addition was observed in collection of the particles with a diameter larger than 20nm.

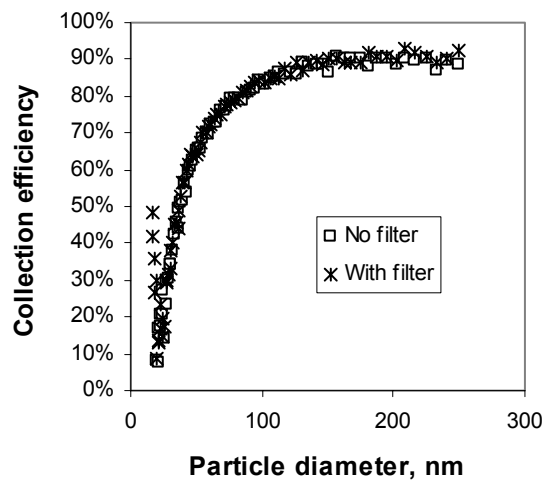


Figure 6. Collection efficiency of the impactor without and with the filter

The increase in the collection efficiency of the impactor with the filter as the particle diameter decreased can be explained by the filtration theory [7]. For the submicron particles with a

diameter smaller than 100nm, according to this theory, the filter efficiency is governed by diffusion regime and, therefore, increases with as the particle diameter decreases.

4. Summary and conclusions

The QT impactor designed based on the PTI concept has been constructed and tested at room temperature. With the nozzle diameter of 1 mm in combination with the ratio of D_0/D at 1.4 and S/D at 1.5 the impactor yielded very sharp size cuts with a maximum collection efficiency of 92% and a d_{50} of 50nm. Compared with the sintered filter quartz, the impactor collection efficiency is very similar. Only small difference comes from the particles smaller than 20nm in diameter. This difference is however believed to be negligible since the particles smaller than 20nm account for a very small mass portion of the total mass of fly ashes in FBC boilers [8, 9]. The results indicate that the QT impactor can be useful in combination with the GQ probe for measurement of the volatile metal species of hot flue gas, both in gas and solid phases. Further tests with the GQ probe in forms of field measurement are needed.

ACKNOWLEDGEMENT

This research has been supported by the Swedish Energy Administration Board, which is gratefully acknowledged.

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Passive Measurements of Time-variable Signals of Pressure During FB Combustion of Liquid Fuels

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INTRODUCTION

The mechanism of liquid fuel combustion in fluidized bed includes stages of atomization, vaporization, pyrolysis, mixing and oxidation, which occur in an ideal sequence moving from the fuel inlet port to the bed exit, provided that the residence time in the bed is long enough [1]. Otherwise, diffusive flames occur above the bed as soon as fuel-rich sockets are released and ignited [2]. These flame have a transient behavior and in some cases could degenerate in micro-explosions. In addition, the periodic eruption of air bubble at the bed surface represents another perturbation because induces pressure fluctuations and makes fresh air available for combustion. Therefore, the properties of the system are dramatically time-dependent because a number of dynamic phenomena overlap contributing to the establishment of a complex scenario.

Passive measurements of pressure signals could provide useful information about the phenomena occurring inside the reactor. The application of pressure or acoustic probes to fluidized beds is a well-established technique for studying and characterizing bed fluid-dynamic under non-reactive conditions [3]. Acoustic signals generated during premixed FB combustion of gaseous hydrocarbons were only recently taken into consideration by Zukowsky [4]. The analysis of his results demonstrated that the combustor exhibits an explosive behavior in a large temperature range; this finding is attributed to the difficulty to ignite and burn the mixture inside the bed. In a similar way, the acquisition of pressure signals during the combustion of liquid fuels is here applied for a more complex burning mechanism with respect to premixed combustion. The elaboration of time-variable signals by using standard and/or purposely developed mathematical tools provides quantitative estimation of characteristic frequencies of the observed phenomena, which is the major argument, the present paper relays on.

EXPERIMENTAL APPARATUS AND TECHNIQUE

An atmospheric bubbling fluidized bed reactor (see Fig. 1) is used for experiments of steady state combustion. The fluidization column is made by two stainless steel tubes with an internal diameter of 140 mm and 200 mm and a total height of about 3 m. The reactor can work at operating temperatures up to 900°C thanks to electrical heating that is supplied by radiant shells installed along the fluidization column for a total height of 2 m. The fluidization gas can be pre-heated before the air distributor. The latter is formed by a reversed cone filled with 3/8" AISI 304 spheres.

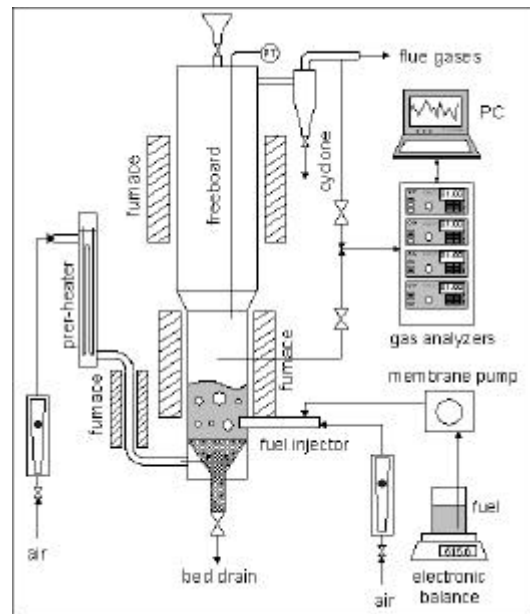


Fig. 1: scheme of the FBR140 experimental facility

Gasoil (diesel fuel) for automotive application has been used during experiments. It was metered by means of a membrane pump (KNF Stepdos type). A horizontal water-cooled fuel injector is located at an elevation of 130 mm above the air distributor. It provides fuel injection into the reactor through a 2 mm nozzle with the assistance of a dispersion air flow rate. The gasoil vessel is mounted on a digital balance in order to determine the mass flow rate with good accuracy.

Two air streams, measured by rotameters, were used for bed fluidization and fuel atomization. Flue gases at the exit of the fluidization column are passed to a cyclone and then to the stack. At the height of 430 mm above the distributor a cooled probe samples gas from the splashing zone. Alternatively, the sampling is accomplished at the stack. The sampled gas passes in sequence through a filter, a heated tube, a cooling unit, a pump and, finally, a battery of gas analyzers for O₂, CO₂, CO, N₂O, NO_x and CH₄. A pressure transducer (Druck PTX type, 0-100 mbar range, 2 kHz sampling rate) monitors dynamic changes of pressure inside the reactor. It is connected to the freeboard by means of a wave-guide made by a 6 mm ID stainless steel tube, which allows pressure to be measured on the reactor axis at an elevation of 1.0 m above the air distributor.

Silica sand (0.20-0.40 mm size range) was used as bed material. The bed mass was 7 kg corresponding to a static bed height of 300 mm above the distributor and to a bed shape ratio $H_{mf}/d_t > 2$. The oxygen concentration in the flue gas was set at 5% in all tests. After the reactor reaches 500 °C thank to electrical heating, gasoil is continuously fed into the reactor. Temperatures, pressures, freeboard and flue gas concentrations are on-line monitored and recorded by a data acquisition system supervised by a personal computer. Typically, in a steady-state combustion test all measured variables are kept at a constant value for at least 30 min.

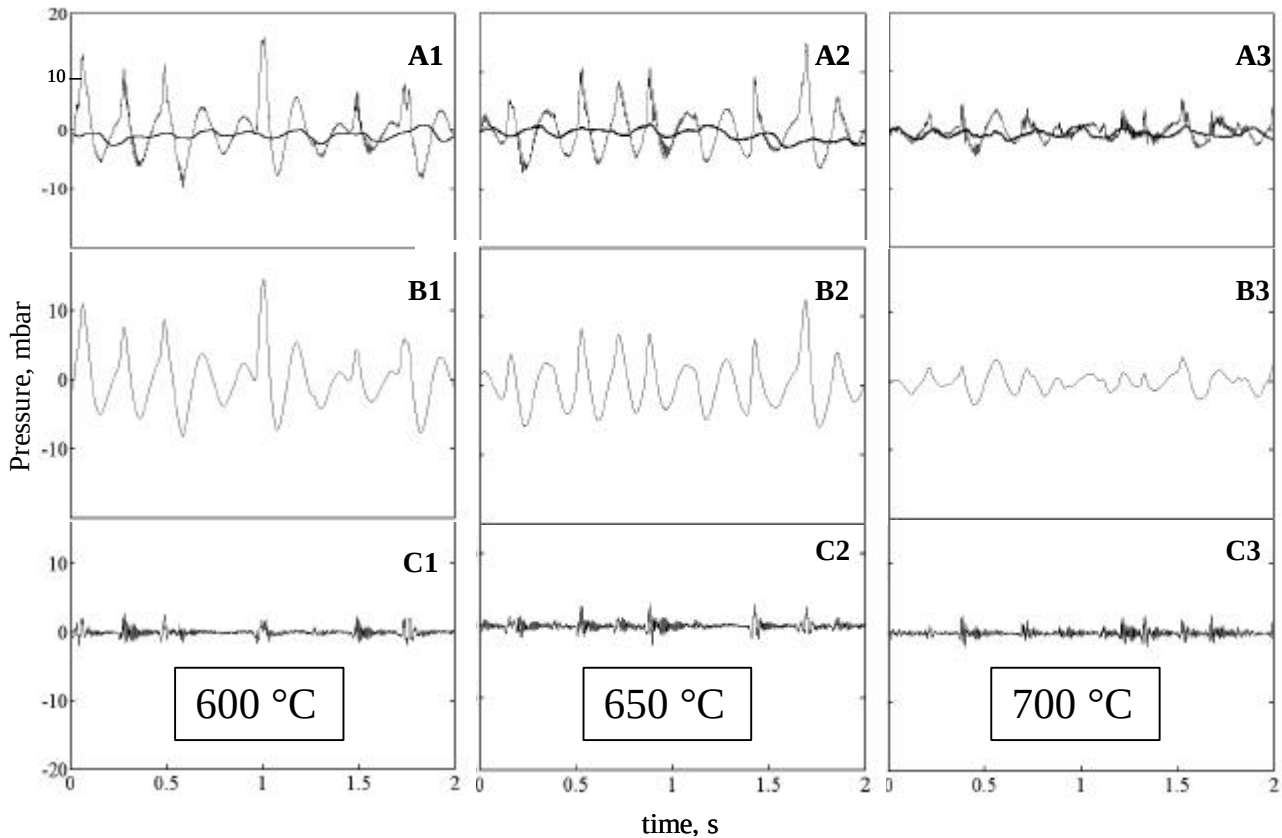


Fig. 2: pressure profiles taken in the freeboard (A), low-frequency curve (B) and high-frequency curve (C) at different temperature

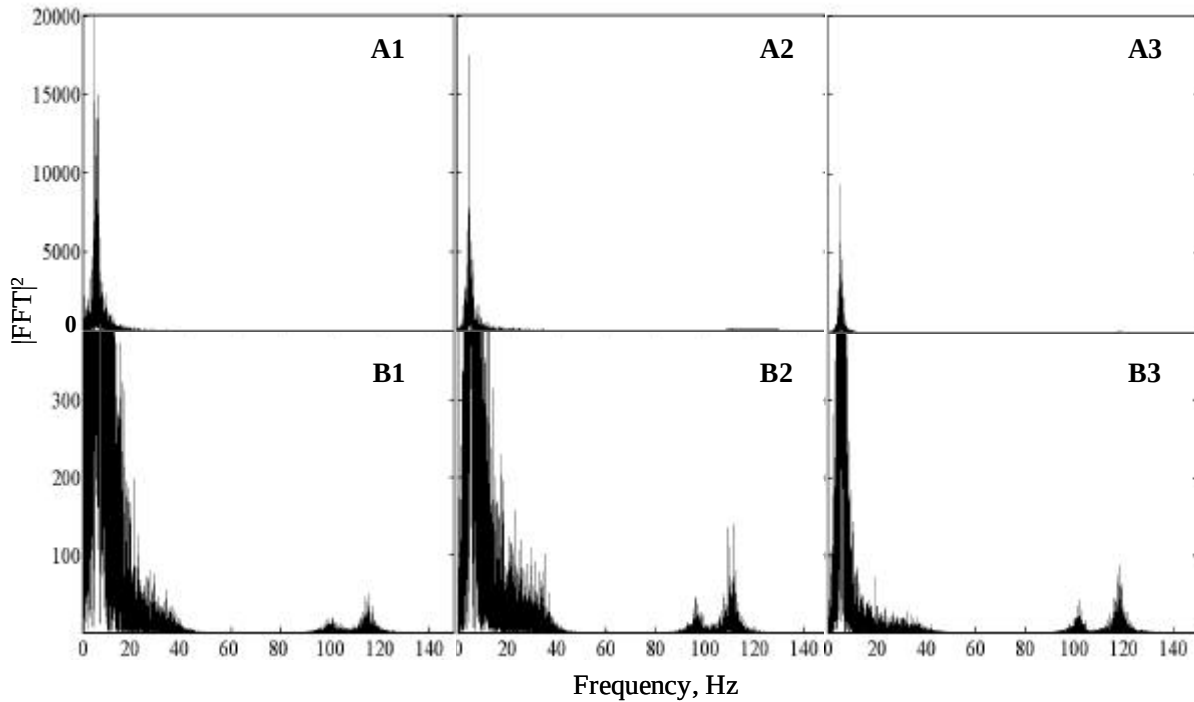


Fig.3: Power spectra from the FFT analysis of pressure signals during gasoil combustion at different temperatures

EXPERIMENTAL RESULTS

Time profiles of the freeboard pressure obtained during gasoil combustion at three different bed temperatures ($T=600, 650$ and 700 °C) are reported in Figs. 2-A1, 2-A2, 2-A3. Data have been always sampled at a frequency of 2 kHz. It appears that the pressure is fluctuating and oscillations are very large with respect to the average value. For comparison, in each diagram another curve is plotted for a test carried out under the same conditions, but in absence of combustion. This latter curve will be referred to as “fluid-dynamic” curve and exhibits a characteristic oscillating frequency of the order 4-5 Hz.

Pressure fluctuations are largely increased as a consequence of the combustion at lower temperature, but are significantly smoothed when the temperature is raised to 700 °C. Analysis of results also shows that there is a combination of phenomena having different characteristic frequencies. In particular, an oscillation with a larger frequency sometimes appears in the pressure profile. Therefore, pressure signals were subjected to a simple filtering procedure in order to distinguish between contributions of low and relatively high frequencies of the oscillating phenomena. The filtering technique is based on the local averaging of the original signal over an interval of N points centered with respect to the current point. The procedure is iterated for each point of the original signal producing the data series, which will be referred to as “low-frequency curve” (see Figs. 2-B1, 2-B2, 2-B3). Then the so-called “high-frequency curve” is obtained by subtracting the low-frequency one from the original signal at each time (see Figs. 2-C1, 2-C2, 2-C3). The fluctuations of the low-frequency curves well resemble the original signal. They present a characteristic frequency in the range $f = 5-7$ Hz, as can be easily revealed by an immediate analysis of the curves in Figs. 2-B1, 2-B2, 2-B3. Profiles reported in Figs 2-C suggest that the high frequency fluctuations are started in an irregular way and rapidly smoothed. One can make a rough estimation of their occurrence by simply counting them in Fig. 2-C1, 2-C2, 2-C3; a characteristic frequency turns out in the range 3-5 Hz. The high frequency fluctuations can be reasonably attributed to the acoustic effects associated to special combustion-related events (such as flame ignition, micro-explosion, etc.), which are known to occur during FB combustion of liquid or gaseous fuels [2, 5, 6].

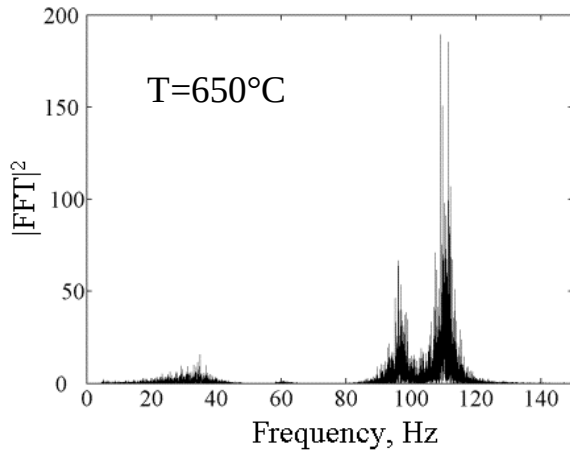


Fig.4: Power spectrum from the FFT analysis of pressure signal in Fig. 2-C2

The standard FFT analysis of the pressure signals was carried out in order to determine the span and the relative importance of the observed frequencies. The FFT power spectra of the freeboard pressure obtained during gasoil combustion at the above mentioned bed temperatures are reported in Figs. 3-A1, 3-A2, 3-A3. A cluster of peaks occurring in all three figures at about $f_p = 10$ Hz clearly indicates that this latter frequency is by far the predominant one. However, the FFT analysis revealed other peaks that do not appear in Figs. 3-A. Re-plotting the same power spectra with an expanded y-axis scale clearly points out the existence of other characteristic frequencies (see Figs. 3-B1, 3-

B2, 3-B3). First, the peak at $f_p \approx 10$ Hz appears to be followed by a “tail” of frequencies up to about 50 Hz; most importantly, two smaller clusters of frequencies are revealed at $f_{H1} = 100$ Hz and $f_{H2} = 115$ Hz, respectively, for all of the three bed temperatures; further, the above two peaks move slightly toward higher frequencies as the bed temperature is increased.

In order to crosscheck the above-mentioned filtering procedure, the FFT analysis was extended to the “high-frequency curve” data (see Fig. 2-C2 for 650°C bed temperature). The resulting power spectrum is reported in Fig. 4. Again, two clusters of frequencies are revealed at $f_{H1} = 95$ Hz and $f_{H2} = 110$ Hz. This confirms that the adopted filtering procedure did not alter the information contained in the original data series for the high-frequency range.

In order to attempt an interpretation of the above values, the acoustic resonance frequency, f_{ar} , of the experimental combustor was calculated. The eq. $f_{ar} = c/(nL)$ was simply used where c is the sound speed at the given temperature, L the combustor length, $n=2$ or $n=4$ for closed-end or semi-open tube, respectively. With reference to a bed temperature of 650°C, the above eq. yielded $f_{ar}=109$ Hz for the closed tube, $f_{ar}=151$ Hz and $f_{ar}=85$ Hz for semi-open tubes having the length of the lower and upper combustor section, respectively. The above frequencies define a range that reasonably well includes f_{H1} and f_{H2} provided by FFT analysis.

The following final remarks can be singled out: i) the dominant frequency $f = 10$ Hz at which the largest cluster of peaks occurs is exactly of the same order of magnitude of both the “fluid-dynamic” and the “low-frequency” fluctuations; ii) the frequencies $f_{H1} = 100$ Hz and $f_{H2} = 115$ Hz appear related to the acoustic resonance frequency of the combustor; iii) the occurrence of random or externally-driven disturbances to the sampled signal is to be considered unlikely in the experimental set-up, but is presently in course of ascertainment.

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Testing a novel instrument for Hg^0 and Hg^{++} monitoring in flue gas

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ABSTRACT

ENEL is involved in the development of a on-line monitoring system for elemental and ionic mercury. In a previous paper a novel instrument general scheme and the first results were presented. The present paper shows the results of the lab and field validation of a more compact and suitable instrument version. The interference of various gas on different Hg species was evaluated.

INTRODUCTION

In order to meet the new regulation limits it is necessary to reduce the mercury emissions. This is achieved by using very efficient precipitators and scrubbers or by injection of sorbents in flue gas. The efficiency of such devices depend on the oxidation state of mercury and a key aspect of this work is the ability to accurately measure Hg in all its forms by a on-line systems. Some continuous mercury monitor devices are being developed, however tests are still in progress. The main efforts are focused to improve the sampling system and to evaluate the monitor accuracy and reliability over extended periods [1].

ENEL project is focused to the development of a on-line monitoring system for elemental and ionic mercury, in order to reduce sampling and analysis times with respect to off-line analysis.

The ideal solution is a on-line system for mercury measurement that can operate continuously and that allows to detect both elemental and ionic mercury (vapor phase) at different flue gas conditions (gas temperature up to 350°C, dust load up to 15 g/Nm³). In a previous paper [2] the instrument general scheme and the first results were presented. A recent paper examined the problems connected to the sampling of mercury when the speciation is required [3]. The present paper shows the results of the lab and field validation of a more compact and suitable instrument version.

DESCRIPTION OF THE MERCURY ANALYZER

As described elsewhere [2], the system is composed by two parts, the commercial instrument (Flow Injection Mercury System, FIMS 400, Perkin Elmer) for the mercury determination by Cold-Vapor Atomic Absorption Spectroscopy (CV AAS) in liquids, and a device that captures the vapor phase mercury through the absorption in a solution (Figure 1).

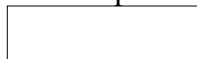


Fig. 1 Apparatus general scheme

The basic principle is derived from the Ontario Hydro Method where the absorbing impingers containing solutions of KCl and KMnO_4 are substituted by two absorption loops.

The FIMS was modified in order to allow the sampling and the analysis of the two different solutions (KCl and KMnO_4) every 20 seconds; while a loop is filled with the first solution, the other loop sends the second one to the flow injection cell. The mercury is reduced by NaBH_4 and transported to the atomic absorption cell by a carrier gas (nitrogen).

The sampling train consists of a steel supported PTFE probe equipped with an Alundum filter (Figure 2) in order to remove the particulate prior to the flue gas entrance in the analytic device.

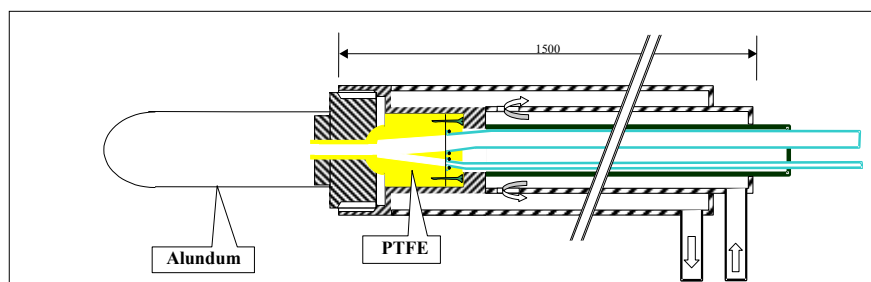


Fig. 2 Cooled probe scheme

The particulate-free gas is quenched with the KCl solution at the head of the probe, which is cooled by air when the gas temperature is higher than 100°C in order to avoid any solution loss. The KCl solution, containing ionic mercury, after a gas-liquid separator is analyzed, while the gas containing the elemental Hg goes to the second quenching loop where KMnO_4 is used in order to oxidize and capture mercury. A second gas-liquid separator allows to part the solution from the gas.

LABORATORY VALIDATION

In order to assess the mercury monitoring system accuracy and reliability some laboratory tests were carried out generating a synthetic gas at different concentrations of elemental and ionic mercury. The collection efficiency of KCl and KMnO_4 absorbing solutions was measured. Moreover the possibility of introducing artifacts with the sampling system (filter) was evaluated.

Mercury generation system

A generation device was developed in order to produce a constant flow of mercury vapors, where the elemental mercury or a mercury salts are vaporized in an oven.

The mercury vapor in a nitrogen flow was conveyed to the absorption system by a heated line at 150°C . The concentration of mercury in the gas depends both on the oven temperature and on the gas carrier flow rate (3 l/min).

FIMS calibration

A first instrumental calibration is made using some standard of known concentration in mercury. In the actual arrangement with gas flow of 3 l/min and liquid flow (for the absorption solutions) of 3 ml/min, the system has a linear response up to $25 \mu\text{g}/\text{Nm}^3$. The system detection limit has been estimated in $<10\text{ng}/\text{Nm}^3$ of sampled gas.

Laboratory test results

An important stage of the laboratory work was the evaluation of the selectivity and efficiency for the two solutions respect to all the species that can be present in flue gases (Hg^0 and Hg^{2+}).

We choose three mercury salts (HgCl_2 , HgO and HgSO_4), and elemental mercury (Thermodynamic properties in Table 1). HgSO_4 decomposes to elemental Hg, for this reason this salt was discarded.

Table 2 summarizes the mercury generator set-up during the selectivity tests carried out in nitrogen. The results show that the elemental mercury is retained by the oxidant solution (3,5% of Hg^0

absorbed by KCl solution), mercury chloride (about 100%) is retained by the KCl solution. The mercury oxide, although it is an ionic salt, is absorbed by the oxidant solution, probably due to the decomposition of HgO in Hg during the salt warming.

	Melting Point (°C)	Vapor Pressure (mmHg)	Boiling Point (°C)
HgCl ₂	277	1 (136.2°C)	302
HgO	500 d	N.A.	N.A.
HgSO ₄	d	N.A.	N.A.
Hg	-38.87	2x10 ⁻³ (25°C)	356.72

Table 1 Thermodynamics properties of some mercury salts

Mercury Specie	Mercury form	Generation T(°C)	Abs. Solution
Hg	Hg ⁰	50	KMnO ₄
HgCl ₂	Hg ²⁺	80	KCl
HgO	Hg ²⁺	80	KMnO ₄

Table 2: Absorption of mercury species (N₂ carrier) - test matrix

As the analytical system requires a particulate-free gas we tested different filters to be used. As far as the gas sampling is concerned the best set-up found include a ceramic (alundum) filter thermally treated. Some tests were performed in order to test the possible interference of the gas contained in combustion gases. The test matrix is summarized in table 3.

	Hg ⁰	HgCl ₂	HgO
SO ₂	1200-800-400 ppm	800 ppm	800 ppm
O ₂	5%	5%	5%
SO ₂ +O ₂	800ppm (SO ₂) 5% (O ₂)	800ppm (SO ₂) 5% (O ₂)	800ppm (SO ₂) 5% (O ₂)
NO ₂ +NO	100-200-300ppm (NO)	100-200-300ppm (NO)	100-200-300ppm (NO)
	10-20-30 ppm (NO ₂)	10-20-30 ppm (NO ₂)	10-20-30 ppm (NO ₂)

Table 3: Effect of gas composition - test matrix

Fig. 3 shows that the presence of 800 ppm of SO₂ produces no change Hg²⁺, a moderate decrease of Hg⁰ signal and an increase of 40% for HgO signal.

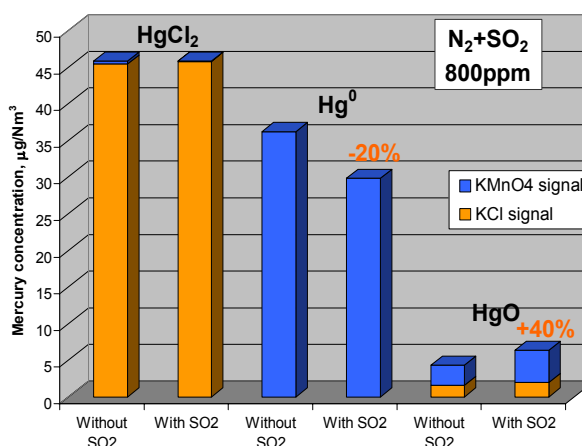


Fig. 3 Effect of 800 ppm of SO₂ on the instrumental response

The decrease for elemental Hg is dependent on the SO₂ concentration (Fig 4), perhaps the oxidation of SO₂ competes with mercury oxidation and capture by KMnO₄.

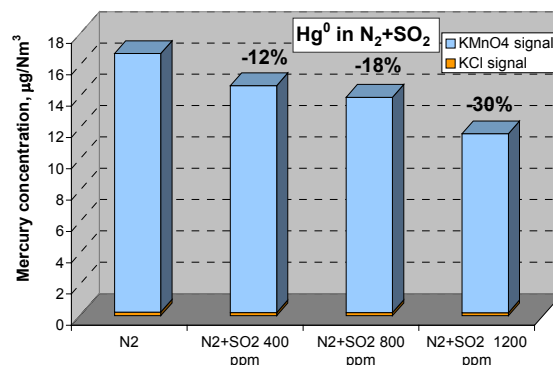


Fig 4 Effect of different concentration of SO₂ on the elemental mercury response

No signal variation is observed adding O₂ (Fig. 5), .

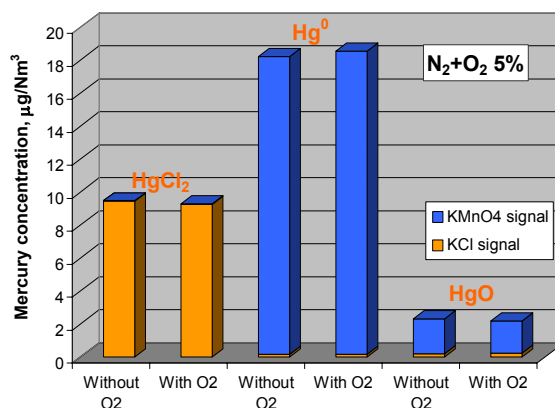


Fig 5 Effect of Oxygen on the instrumental response

CONCLUSIONS AND FUTURE WORK

The future work will be focused to reduce the SO₂ interference optimizing the absorption loop and to study the effect of other gas components as H₂O and HCl. The instrument was used successfully to evaluate the oxidation of mercury in an SCR end other applications are planned in order to optimize the flue gas purification devices during coal combustion.

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Two-Dimensional Temperature Measurements in Flames using Filtered Rayleigh Scattering at 254 nm

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ABSTRACT

Two-dimensional temperature measurements using filtered Rayleigh scattering (FRS) have been demonstrated. A tunable single-longitudinal-mode alexandrite laser was employed to provide the tunable narrow-line-width ultraviolet laser beam at 254 nm. Isotopic-enhanced mercury was utilized as an ultraviolet atomic filter. The strong absorption of the filter enabled effective suppression of the elastic background. The transmission curve of the mercury filter was characterized by combining experimental measurements and proper modeling. The Rayleigh-Brillouin spectral profiles were calculated employing the kinetic model. Quantitative interpretations of the two-dimensional FRS signals were performed in flames. The temperatures values obtained were in reasonable agreement with adiabatic calculations.

INTRODUCTION

Non-intrusive temperature measurements provide crucial information to the understanding of combustion processes. Many laser-based non-intrusive optical techniques have been developed for combustion temperature measurements with high temporal and spatial resolution. Most of the techniques are based on local-thermal-equilibrium and by probing the thermal populations of molecular ground ro-vibrational levels, such as laser-induced fluorescence (LIF) [1, 2], multiplex polarization-spectroscopy [3], multiplex degenerate-four-wave-mixing [4] and coherent anti-Stokes Raman scattering (CARS) [5].

CARS thermometry is a fully developed technique and provides probably the most accurate temperature measurements [6], however it is inherently not amendable to two-dimensional (2D) measurements. The recently developed two-line atomic fluorescence (TLAF) [7, 8] methods can provide 2D temperature information and have been applied successfully in an SI engine [9]. However, this technique suffers from the need of atoms seeded into the flame, which can be impractical and oxidization of the seeding species cause problems for applications in lean environments. Besides, as two tunable laser systems and two independent ICCD detection systems are required, the broad applications of this methodology are limited by the expensive and sophisticated experimental setup.

Laser-induced Rayleigh scattering (LRS) is an outstanding diagnostic tool for the study of gases in combustion environments [10, 11], for its simplicity and ease of implementation. Due to the relatively strong scattering cross-section of Rayleigh scattering (which is generally 1000 times stronger than Raman scattering), LRS has shown its utility in quantitative 2D gas density or temperature measurements. Temperature measurements in two-dimensions with LRS have been performed in turbulent flames [12, 13] and swirl combustors [14, 15]. LRS signal is linearly dependent on the gas number density and excitation laser power. As a non-resonant process, LRS is also unaffected by quenching and saturation. However, for the elastic nature of Rayleigh scattering, it is often difficult to decouple LRS from any spurious elastic background like Mie scattering from particles and multi-scattering from optical windows. All the above mentioned LRS measurements have been performed with judicious

design of the experimental setups to prevent the strong scattering light from particles and surfaces. This hinders greatly the broad applications of LRS thermometry.

Fortunately, due to the Doppler broadening and collision broadening, Rayleigh scattering from molecules are spectrally distinguishable from the spurious background scatterings introduced by slowly moving particles and surfaces. Atomic or molecular filters, made of an optical cell filled with atomic or molecular gas, provides ultra narrow and strong absorption lines, which can be used to spectrally separate the un-broadened spurious light from part of thermally broadened molecular Rayleigh scattering. This technique named filtered Rayleigh scattering (FRS) was applied by Miles et al. in 1992 [16] in their study of a supersonic flow. For the broadly available of injection seeded Nd:YAG lasers and the easy handling of I_2 molecules, two dimensional FRS temperature measurements have been performed by a few groups combining the 532 nm laser and molecular I_2 filter. With this technique, Hoffman et al. [17] performed two dimensional temperature images in a lightly sooty CH_4 /air flame. Simultaneously 2D FRS temperature imaging and particle image velocimetry velocity measurement was performed by Elliott et al. [18] in a methane/air stagnation-flow flame and by Most et al. [19] in a turbulent flame. Using the strong mercury 254 nm line, atomic mercury filter was utilized together with a narrow line width Ti:sapphire laser system in FRS temperature measurements by Yalin et al. [20, 21].

In the present work, the ultraviolet FRS thermometry for 2D temperature imaging has been investigated by combining a single-longitudinal-mode (SLM) alexandrite laser with an atomic mercury filter.

FRS METHODOLOGY

The basic idea of the Filtered Rayleigh Scattering (FRS) is shown in Figure 1. By using a narrow filter, the strong elastically scattered light from slow moving particles, optical windows and other surfaces are blocked while part of the broadened molecular Rayleigh scattering is transmitted. There are two critical points in doing FRS. The first is the need of a

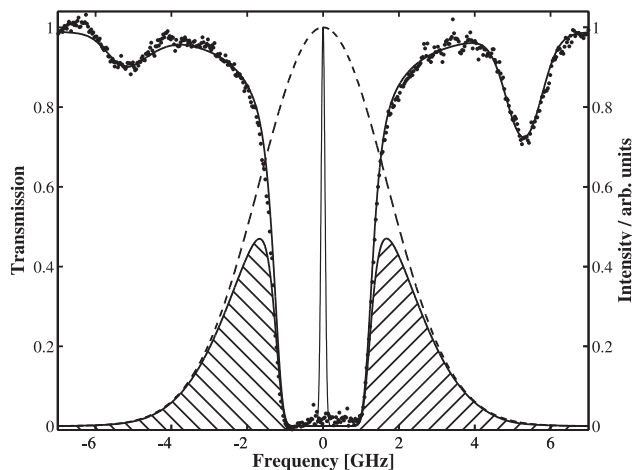


Figure 1. The molecular Rayleigh scattering line profile at 500 K, indicated by the dashed line, overlaps with the mercury absorption notch generating the marked area, the transmission profile through the filter. The dots represent the experimental data of the mercury absorption notch. The narrow profile in the middle is the elastic scattering from surfaces and particles which has a linewidth as the irradiated laser.

narrow filter with a steep slope in its transmission curve, which can efficiently block the un-shifted scattered light while transmitting part of the broadened scattered light. The other is a suitable laser system, which needs to have a linewidth much narrower than the Doppler broadening and the possibility to be positioned to the filter absorption frequency. It is clearly shown in Figure 1 that a quantitative FRS measurement will rely on the calibration of the mercury filter transmission curve and the proper modeling of the Rayleigh scattering line shape.

In the present experiments, a quartz cell filled with single isotope atomic mercury Hg202 was used as a filter. The strong resonance absorption line of mercury atoms at 254 nm formed the absorption notch to sufficiently block the un-

broadened scattering. The use of isotope-enhanced mercury simplifies the absorption profile of the filter to a single hyperfine-structure line. This simplification improves the transmission

of molecular Rayleigh scattering and facilitates the notch filter modeling. The transmission curve of the starved and isotope-enhanced mercury filter was measured with the experimental setup shown in Figure 2.

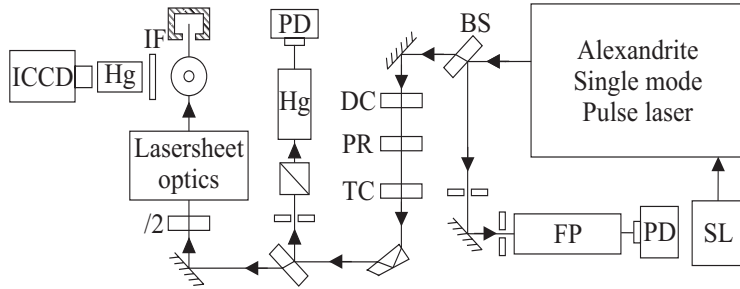


Figure 2. Experimental setup for FRS measurements. BS: beam splitter; DC: doubling crystal; PR: polarization rotator; TC: tripling crystal; PD: photodiode; IF: interference filter; FP: Fabry-Perot etalon; SL: seeder laser.

The fundamental output from a SLM alexandrite laser system (see Ref. [22] for technical details of the laser system) was frequency tripled to obtain the required 254 nm with a linewidth less than 100 MHz, pulse energy 20-30 mJ and pulse duration about 90 ns. To characterize the mercury cell the laser frequency was then scanned over the spectral region of the notch.

In order to test the feasibility of the mercury filter, the images of laser Rayleigh scattering

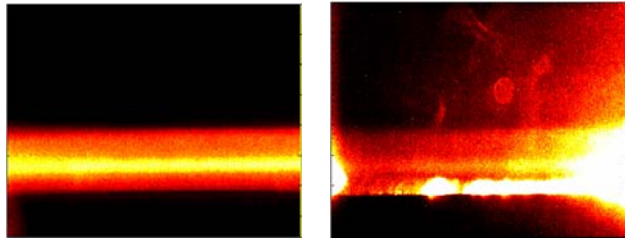


Figure 3. Laser Rayleigh scattering images. The laser sheet is brushing a metal surface; to the left the mercury filter is used to filter away the scattered light; to the right no filter was used.

were taken perpendicular to the laser sheet above a metal surface, with the setup as shown in Figure 2. With the SLM laser fine tuned to the middle of the mercury absorption notch, the strong elastic scattering (Figure 3, right) can be effectively blocked and a 'clean' molecular Rayleigh scattering image (Figure 3, left) can be obtained.

2D TEMPERATURE MEASUREMENTS

Open air acetylene flames of different air/fuel ratios, ϕ , have been studied using the FRS method with the experimental setup shown in Figure 2. The vertically polarized 254 nm laser beam was focused to a vertical laser sheet through the flame of a Bunsen burner. Perpendicular to the laser sheet, an ICCD camera was utilized to image the laser sheet/flame intersection through the mercury filter.

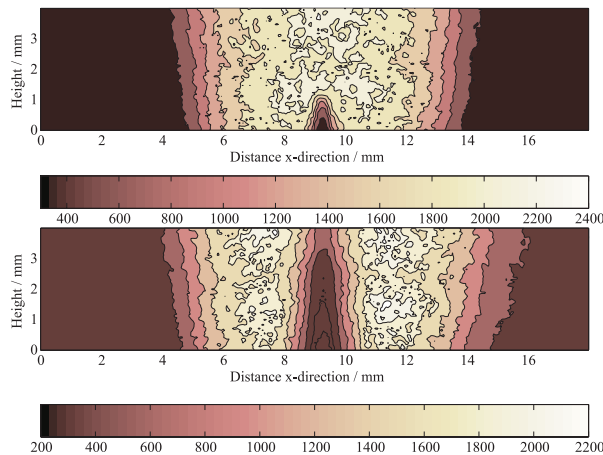


Figure 4. FRS 2D temperature distribution in acetylene/air premixed flames. The upper picture at $\phi = 1.6$ and the lower at $\phi = 2.4$.

The Rayleigh scattering line profiles were calculated with Tenti's code [23]. In order to take care of the Rayleigh cross section of different gases [24], the mole fractions of the most abundant species in the burned gas region was estimated with an adiabatic flame calculation program using the Olikara and Borman equilibrium routines.

Shown in Figure 4 are the 2D FRS temperature distributions in acetylene/air premixed flames from a Bunsen-type burner with different mixing ratio. The measured temperatures were consistent with adiabatic flame temperatures calculated using the Olikara and Borman equilibrium routines.

For $f_i = 2.4 \Rightarrow 2298$ K (adiabatic flame temp)

For $f_i = 1.6 \Rightarrow 2551$ K (adiabatic flame temp)

RESULTS AND DISCUSSIONS

In summary, the FRS method used in the present work has the following merits. Firstly, mercury is an ideal choice for an atomic filter and provide very high extinction ratio even at room temperature ($\sim 10^{-10}$ for a 10 cm long cell at 300 K). Secondly, as the Rayleigh scattering cross section is proportional to $1/\lambda^4$, the UV light is much in favor for the Rayleigh signal. The present investigation has indicated that this method can be readily applied to 'dirty' environments or close to surfaces combustion studies.

We have demonstrated 2D temperature imaging using FRS by combining a tunable SLM laser and a mercury filter. It was found that FRS as a comprehensive complement to other existing spectroscopic methods for temperature measurements was especially useful in measurements close to surface or in particle laden environments. Instantaneous two dimensional temperatures can be obtained providing knowledge of the major species concentration and the pressure. We anticipate the application of FRS 2D temperature imaging in high pressure environments, for instance in engines, as the FRS signal depends linearly on the pressure. FRS 2D temperature imaging technique is a complementary to other existing techniques. It can be for example used in lean flames, where TLAf can hardly be applied.

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EXPERIMENTAL ANALYSIS OF RECIRCULATION PHENOMENA IN A NATURAL GAS SWIRL COMBUSTOR

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Introduction and experimental set-up

This paper deals with the experimental characterization of a natural gas swirl combustor, analysing by different techniques both the flame front behaviour and the recirculating regions induced by the swirl inside the combustion chamber. Swirl effect is often used in combustion devices in order to improve flame stability and enhance mixing process [1]. The present analysis has been carried out in order to quantify the degree of mixing between hot products and cold reactants which is generated by the swirling air motion, both inside and outside the flame region, suggesting improvement to the burner design, by promoting or hindering the development of these phenomena. Fig. 1 reports a schematic view of the investigated burner (for more details, see [2]). As it can be seen, the burner is equipped with an axial+tangential swirl generator and with a fuel injector coaxial to the air stream: it is a configuration quite similar to those used for typical industrial appliances (diffusive atmospheric pressure burners). A cylindrical quartz combustion chamber (internal diameter=192 mm) has been used for flame confinement, making possible flame visualization and measurements by laser anemometry.

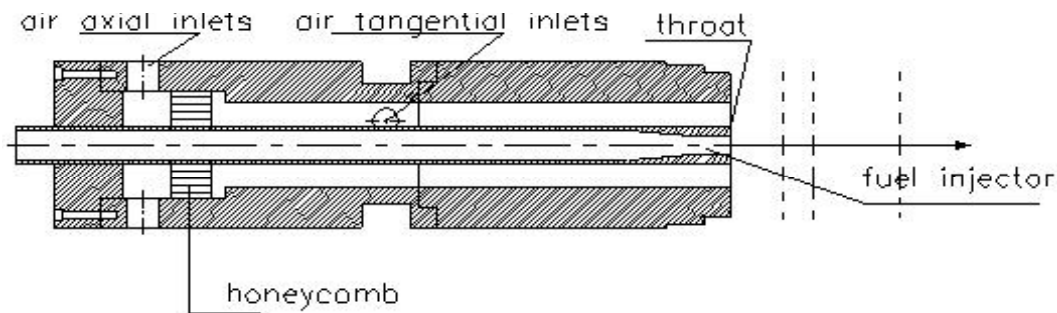


Fig. 1: schematic view of the investigated burner.

Tab. 1 reports the main operating conditions used for the experimental measurements described in this paper.

Air flow rate [g/s]	8.8
Reynolds number of air jet	20700
Natural gas flow rate [g/s]	0.35
Reynolds number of natural gas jet	5600
Input thermal power [kW]	17
Air swirl number S	0.82
Fuel/Air Momentum ratio MR	0.91
Fuel/Air Equivalence ratio Φ	0.69

Tab. 1: main operating conditions of the investigated burner.

Fig. 2 shows a typical image of the investigated flame, with the indication of two measurement traverses h/R_b (R_b = radius of the air efflux = 18 mm). It can be observed the typical calyx-shaped flame, due to swirl effect and low equivalence ratio. Fig. 3 reports the position of zero axial velocity line and stoichiometric composition deduced from measurements in isothermal conditions

performed by LDV, PIV and 2-D visualizations: the morphology of the line puts into evidence the penetration of the central fuel jet, which is important for flame stabilization and corresponds quite strictly to the flame image. In fact, the structure of the near field is almost un-influenced by combustion development, so that isothermal results can be extended to reactive conditions.

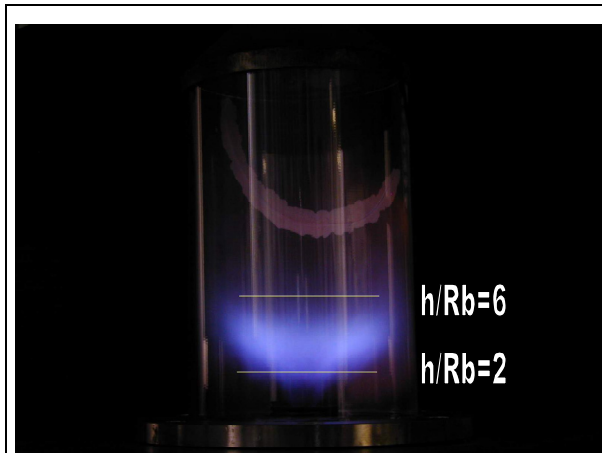


Fig. 2: typical image of the analysed swirling flame

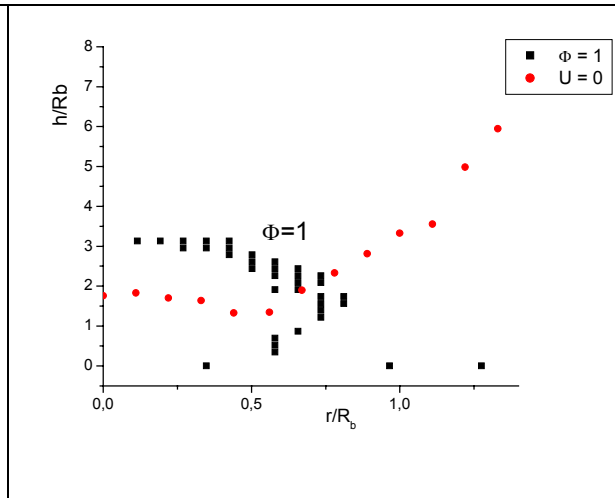


Fig. 3: zero axial velocity and stoichiometric lines deduced from isothermal measurements.

Owing to the high complexity of the flow inside the combustion chamber (due to the high swirl intensity imparted to the air stream), the experimental characterization has been carried out through different techniques. Measurement by LDV of the reactive flow field has been performed at increasing distances h/R_b from the efflux, in order to analyse the formation of the recirculating regions and their possible influence upon flame development. Mean temperature was measured using a Pt/Pt-13% Rh bare wire thermocouple with 0.3 mm diameter bead. A correction was made for the radiation error, using the measured velocity values for the evaluation of convective heat transfer coefficient.

Experimental results

Fig. 4 a, b, c reports the results relative to the radial semi-profiles of mean axial velocity and temperature (already corrected for radiative losses) at increasing distances h/R_b from the efflux. The radial coordinate has been normalised to the radius R of the cylindrical combustion chamber. From the analysis of the profiles, different regions (progressively interacting) can be distinguished:

- at $h/R_b=0.66$, it was observed a central relatively “cold” region characterised by a velocity peak (2.5 m/s) which can be attributed to the natural gas jet, already decelerated by the formation of the central toroidal recirculation region, induced by swirl. The two parallel streams are separated by the incipient formation of the central recirculation region induced by swirl effect. The central recirculating hot products oppose to the fuel jet (decelerating it, as previously noticed) and mix to develop combustion and stabilise the flame close to the burner exit. Fuel/air momentum ratio is the controlling parameter of this process, together with the swirl motion. A recirculation region, characterised by a quasi uniform temperature value (about 900 °C, progressively cooling towards the quartz walls), is present at the region between the outflowing reactants and the chamber walls. This reverse flow is induced by a corner recirculation due to the air stream radial expansion and the wall confinement. The high temperatures measured in this zone indicate the presence of a large fraction of already burned gases which are entrained by the reactant flow. At this short distance from the burner exit, the external recirculating flow is hotter than the inner reverse stream and produces a fast pre-heating of the incoming air jet.

- at $h/R_b=2$, the central fuel jet completely disappears in the central recirculation region, indicating complete mixing with the coaxial air stream and counter-propagating burned gases. Observing Fig. 3, it can be noticed that in isothermal condition at this traverse, ends the penetration of the central jet with the onset of stoichiometric equivalence ratio at the boundary with the coaxial air stream. The consequent development of combustion reactions is clearly visible also by the temperature increase (up to 1200°C) in the correspondence of the burner axis (see also the flame visualization in Fig. 2).
- the profiles result more uniform at $h/R_b=4$, where it can be noticed the weakening of the recirculating regions, both central and peripheral: combustion reactions should be almost completed, as indicated by the uniform temperature profile.

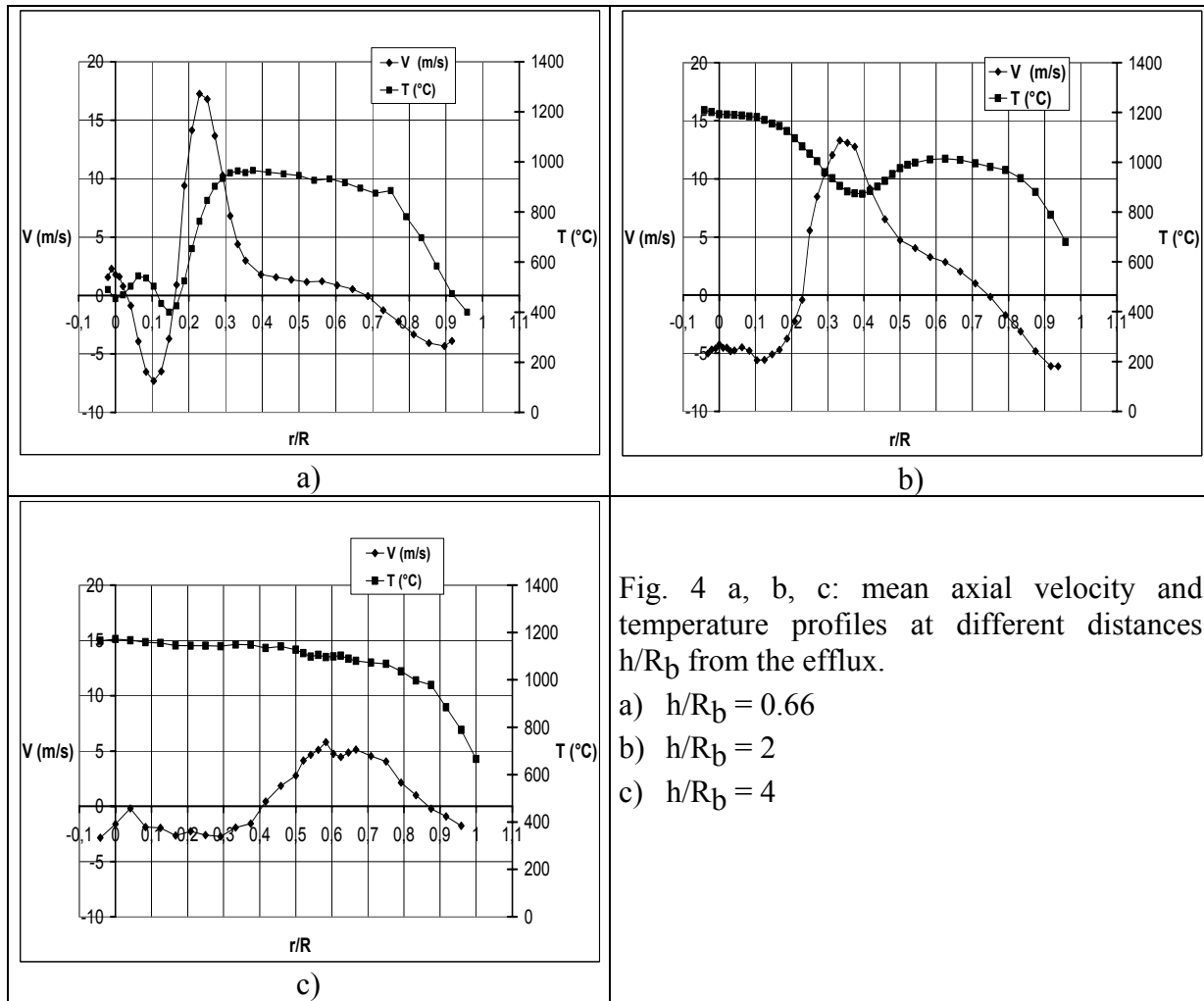


Fig. 4 a, b, c: mean axial velocity and temperature profiles at different distances h/R_b from the efflux.

- a) $h/R_b = 0.66$
 b) $h/R_b = 2$
 c) $h/R_b = 4$

Moreover, a quantitative analysis of the recirculating phenomena was obtained by integration of the mean velocity radial profiles in the different regions (previously described). Thus, it was possible to estimate the flow rate corresponding to every distinct stream: reactants (ascending flow) or products (reverse flow). Fig. 5 reports the behaviour of the recirculated flow rates as a function of h/R_b : the values have been normalised to M_0 , that is the injected mass flow rate through the burner. M_{re} represents the flow rate corresponding to the positive velocity part of the radial profile, M_{ir} is the central recirculating flow rate and M_{cr} is the result of integration of the peripheral recirculation zone. There is a progressive mixing of reactants with recirculating hot products and thus the ascending (positive) mass flow rate initially increases. It can be observed that the contribution of the central recirculation region is very low, while the corner recirculating flow rate (and, consequently, the positive flow) is maximum (about 1.5 times the total injected flow rate) in

the correspondence of $h/R_b \approx 2$, that is just the crucial traverse for combustion reactions development. Therefore, it is evident the possibility of a strict interaction between the flame and the surrounding recirculating flow, which can contribute to local pre-heating and leaning of the reactant mixture with respect to feeding conditions (so that the value of the equivalence ratio $\phi=0.69$ fed to the burner is purely indicative).

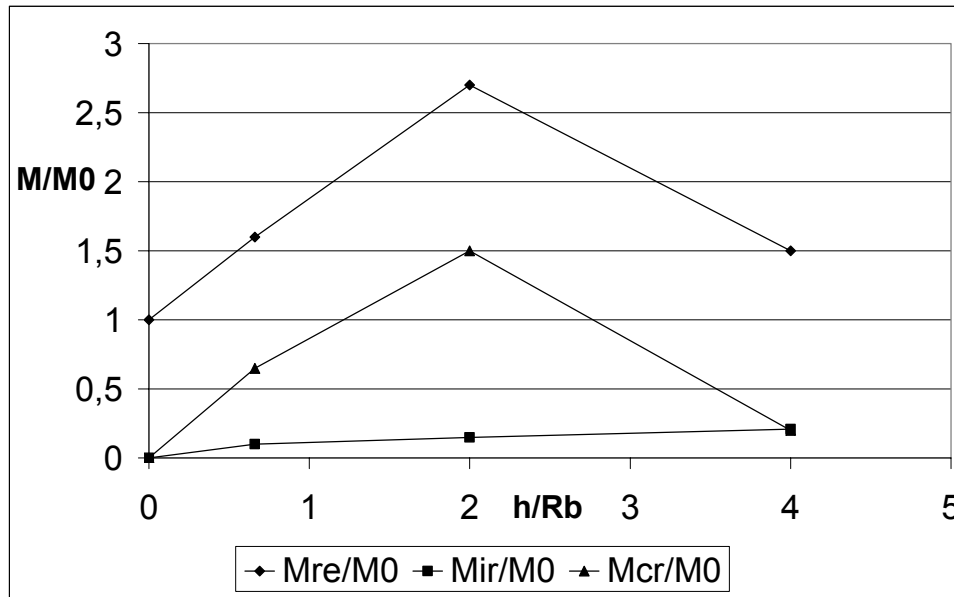


Fig. 5: recirculating flow rates evaluated by the measured axial velocity profiles as a function of h/R_b

Conclusions

The recirculation phenomena inside a swirl natural gas combustor have been analysed by means of different experimental techniques. The results obtained put into evidence that the onset of different recirculation regions, connected to swirl strength, can strictly influence the main combustion features. In fact, while the toroidal central recirculation region is important for reactants mixing and flame stabilization, the corner recirculating zone (close to the combustion chamber walls) induces entrainment of a large amount of hot burned gases into the outflowing reactant mixture. The observed large amount of internal exhaust gas recirculation suggests the possibility of using this mechanism, depending on swirl intensity and chamber diameter, to control flame dilution and abatement of thermal NO_x .

Acknowledgements

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Detection of formaldehyde in combustion environments

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ABSTRACTS

We report here on the investigation of the spectroscopic properties of formaldehyde in the $\tilde{A}^1A_2 \leftarrow \tilde{X}^1A_1$ band system at elevated temperatures (295 – 770 K) and pressures (up to 10 bar). The quantum yield of laser-induced fluorescence excited with 355 nm Nd:YAG laser was studied from fluorescence-lifetime measurements. Simultaneous imaging of OH and formaldehyde has been performed both in a laboratory flame.

INTRODUCTION

Formaldehyde is one of the most important combustion intermediate species, which are formed in the preheating phase of hydrocarbon combustion. Since the formaldehyde is completely consumed in the reaction zone, it is well-suited as a tracer species of cool-flame regions. Heat release rate might also be measured with the product of the densities of formaldehyde and OH [1].

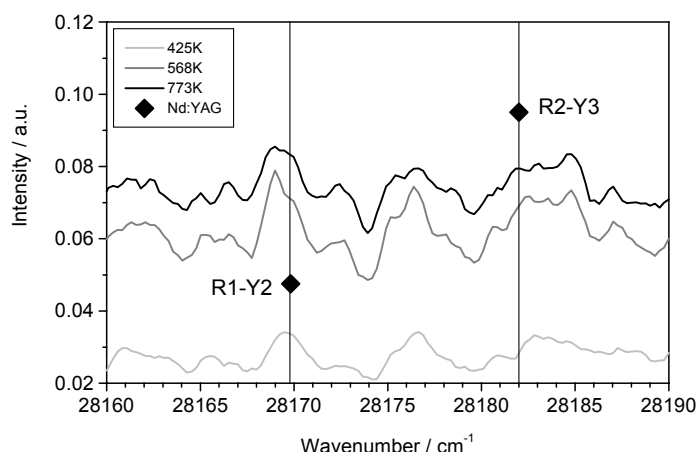
Laser-induced-fluorescence (LIF) is often a sensitive technique for measuring low concentration of species. However, for concentration measurements, quantities such as the absorption coefficient and the fluorescence quantum yield have to be known in most cases. This work reports results obtained from measurements of the spectral absorption of gas-phase formaldehyde at temperatures between 420 K and 750 K and pressures from below atmospheric pressure up to 1 MPa, with a particular address to tripled Nd:YAG laser-based diagnostics for quantitative measurements of concentrations [2]. The conditions should approach those valid for the pre-ignition conditions of temperature and pressure for IC engines. The aim of the work was to combine experiments with theoretical modelling of the absorption and fluorescence properties to enable quantitative measurements of concentration at varying combustion conditions. An initial part of the theoretical treatment of spectra is presented. The work presented in this paper show also results on the time-resolved fluorescence properties under the same experimental conditions [3]. In particular the dependence of the lifetime to temperature and pressure are investigated. In addition the spectral properties of the fluorescence at different conditions have been studied with time-gated intensified detectors.

Planar Laser-Induced Fluorescence (PLIF) of OH and formadehyde was performed simultaneously in a laboratory flame [4].

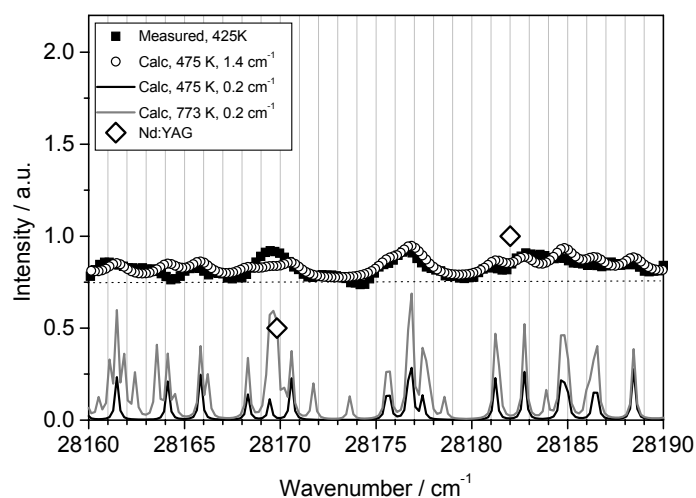
SPECTROSCOPIC STUDIES

Gas phase formaldehyde was prepared from formalin (Merck, KgaA, aqueous solution of ~37% formaldehyde and ~10% methanol). Formalin was stored in a reservoir, which was heated between 343 K and 353 K. To minimize formaldehyde polymerisation, ducts between the reservoir and the cell were maintained at 400 K. The cell temperature could be changed between room temperature and 820 K. The cell was evacuated to pressures below 100 Pa

before formaldehyde was introduced into the cell. After having introduced the sample, N_2 could be inserted to the desired pressure up to 1 MPa. The temporal evolution of the fluorescence was recorded time-resolved using a fast photomultiplier tube and an oscilloscope. Temporal profiles were recorded for broadband emission. Several interference filters were also used in some occasions to study the dependence of the fluorescence lifetime on the emission wavelength.



(a)



(b)

Figure 1. Partially rotationally-resolved absorption of formaldehyde: a) Experimental spectra at different pressures close to the 3rd order of the strongest transition for Nd:YAG, R2-Y3; b) Comparison between measurements and calculations using the software AsyrotWin [5] and known rotational constants from literature.

The broadband UV absorption spectral profiles showed sensitivity to temperature but not to pressure, whereas the partially rotationally resolved spectral profiles showed sensitivity to both temperature and pressure. An increase in pressure resulted in broadening of the line structure. Figure 1 shows examples of measured and calculated subatmospheric-pressure

spectra. At low temperature the profiles were reproduced reasonably well by calculations based on an asymmetric rotator model [5]. The spectral profiles of the fluorescence from formaldehyde (350 nm - 600 nm) changed with temperature whereas changes in pressure did not seem to have any considerable effect. However, the fluorescence lifetimes showed considerable sensitivity to both temperature and pressure. Results are shown in Fig.2. An increase in pressure or temperature caused a decrease of the lifetime, although in different ways.

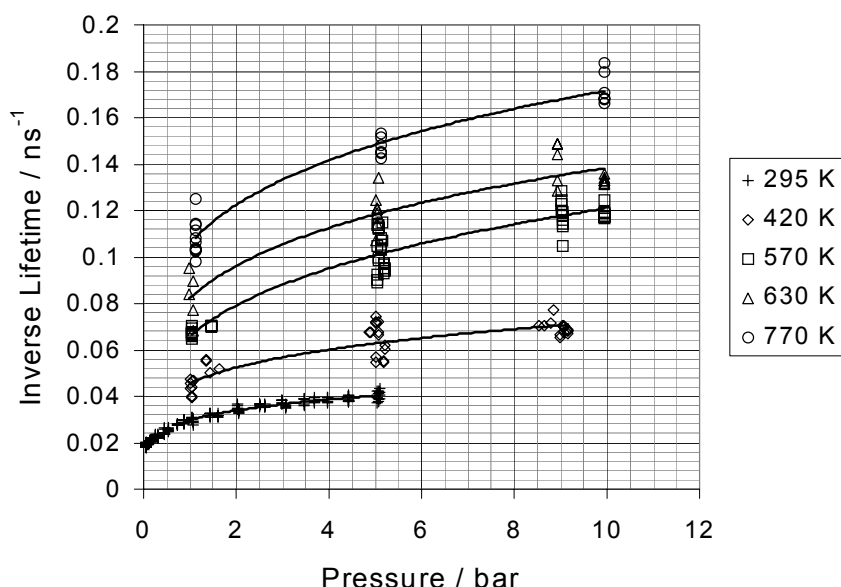


Figure 2 Stern-Volmer plots of the decay rates (inverse lifetimes) observed for various pressures. The lines fitted to the data represent exponential functions.

SIMULTANEOUS MEASUREMENTS OF PLIF FROM OH AND FORMALDEHYDE

Simultaneous measurements of PLIF of OH and formaldehyde was performed by using a Nd:YAG-pumped-OPO laser system. A small portion of the 355 nm laser radiation from the 3rd harmonic of the Nd:YAG laser was split out to excite formaldehyde. A formaldehyde emission spectrum as shown in Figure 3 was obtained by collecting the LIF with a spectrometer equipped with an ICCD camera after a GG395 filter. The major part of the 355 nm laser was used to pump the OPO laser to provide a tunable laser radiation. The OH radical in the flame was excited using the $Q_1(8)$ transition around 283 nm in $v''=0, v'=1$ band of the $A^2\Sigma^+ - X^2\Pi^+$ system. The fluorescence from the decay of the excited OH molecules was detected in the (1,1) and (0,0) bands near 309 nm.

The two UV laser beams were spatially overlapped. A two-color laser sheet, formed through an optical system, crossed a premixed DME/air flame vertically at the middle. The LIF signal from the two species was collected with an ICCD camera equipped with a stereoscope, perpendicular to the excitation beam. The stereoscope provided two optical channels by splitting the image into two images at the ICCD focal plane. Different optical filters; GG395 for formaldehyde; and a narrow band interference filter for OH were used. They were placed at the two optical channels to single out the pure LIF images. Figure 4 shows a simultaneous PLIF image of OH and formaldehyde collected with the same ICCD camera.

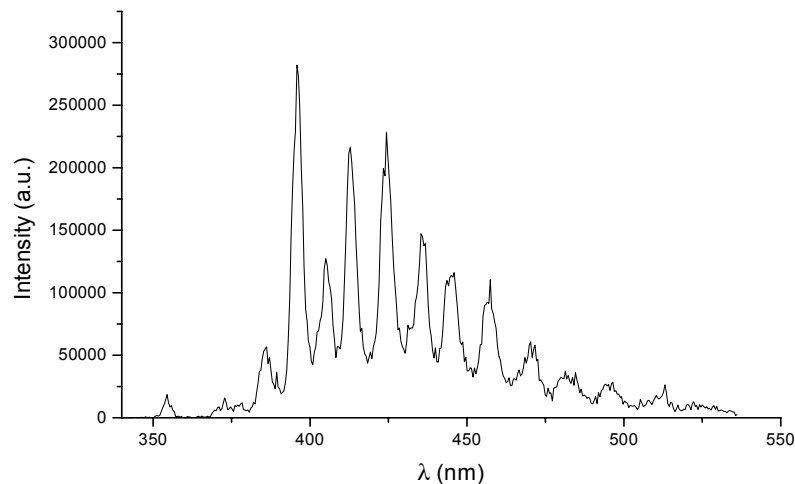


Figure 3. LIF emission spectrum of formaldehyde follow the excitation with 355 nm laser.

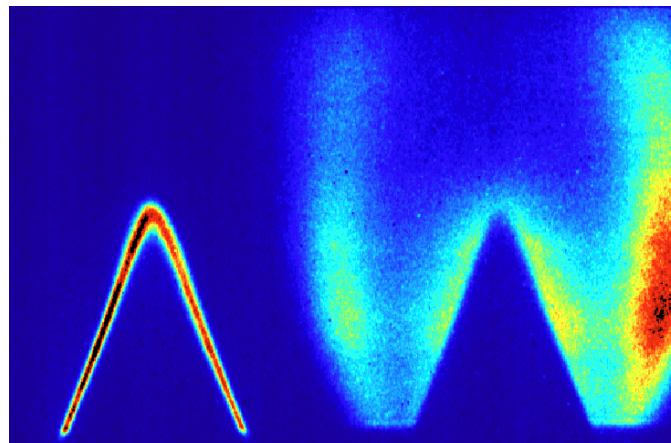


Figure 4. Simultaneous PLIF of formaldehyde (left) and OH (right) of a DEM/air premixed flame from a Bunsen-type burner.

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Temperature measurements using thermographic phosphors applied to combustion diagnostics.

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ABSTRACT

In recent years, thermographic phosphors used for surface temperature measurements have been developed to suit combustion applications. Pulsed ultraviolet laser radiation at 266 nm and 7 ns duration was used to excite a thermographic phosphor, $\text{Mg}_4\text{FGeO}_6\text{:Mn}$, which was adapted to the surface of the investigated material. The laser-induced emission from the phosphor was recorded. The techniques were successfully used in a flame spread scenario for two-dimensional measurements of surface temperature on a low-density fibre board. The technique was also applied to temperature measurements of decomposing materials in a pyrolysis oven. The material investigated was birch particles. Recent development of the technique has allowed other applications, e.g., to such as engine valve and droplets temperature measurements.

Keywords: Laser diagnostics, Combustion Diagnostics, Temperature Measurements.

INTRODUCTION

In recent years a new technique has been developed for remote measurements of surface temperature. It is used in scientific and industrial applications of surface thermometry to complicated geometries, e.g., rotor engines [1], turbine engines [2], and also in medicine. Other quantities such as heat flux through a surface have been investigated, because of its high importance to science and engineering community.

During the last years, as the applications of thermographic phosphors have expanded, some attempts have been made in combustion environment [3]-[6]. A useful review article [7] could be a good assistance as an introduction to the subject of phosphor thermometry.

A phosphor becomes highly fluorescent or phosphorescent when it is excited by an appropriate source, e.g. an electron beam or ultraviolet radiation. Typically the emission is in the visible region and has a lifetime of the order 10^{-3} s. The phosphor consists of a host material and a doping agent, from which the light is emitted. A large number of different phosphors are produced today covering a large band of temperatures from cryogenic temperatures up to 1673-1873 K or higher, making them suitable to many applications. Each selected phosphor is very sensitive in a specific range of temperatures exhibiting an accuracy of the order 1-5 K.

Thermographic phosphors (TP) have normally been used for hard non-combustible materials such as steel or concrete. For those surfaces the phosphor can be applied to the surface and only a very thin layer is required ensuring that the phosphor layer does not influence the flow.

TWO-DIMENSIONAL TEMPERATURE MEASUREMENTS

Laser-induced phosphorescence from a thermographic phosphor material applied to a surface of investigation was measured with a fast framing camera. The phosphor was excited by the

fourth harmonic of an Nd: YAG laser at 266 nm. The phosphorescence images were obtained by eight consecutively gated CCD detectors enable pixel by pixel-lifetime evaluation of the phosphorescence by interpolating an exponential-decay curve to the counts of the corresponding pixel positions of the sequential CCD images. The temperature at each pixel position was evaluated using a previous calibration procedure of temperature against lifetime. The 2D-temperature imaging technique was tested on a low-density fiber board (5 cm wide, 12 cm high, 1 cm thick) in a small flame spread scenario. Laser radiation with energy of 24 mJ / pulse was expanded by a spherical quartz lens to 100 cm² at the target yielding a fluency of the order 0.25 mJ/cm². The phosphorescence from the surface of the combustible board was recorded with the framing camera. The detectors inside the camera were sequentially gated with an individual exposure time of 100 μ s so that immediately as one detector was deactivated the following detector was activated.

Two-dimensional measurement during Flamespread

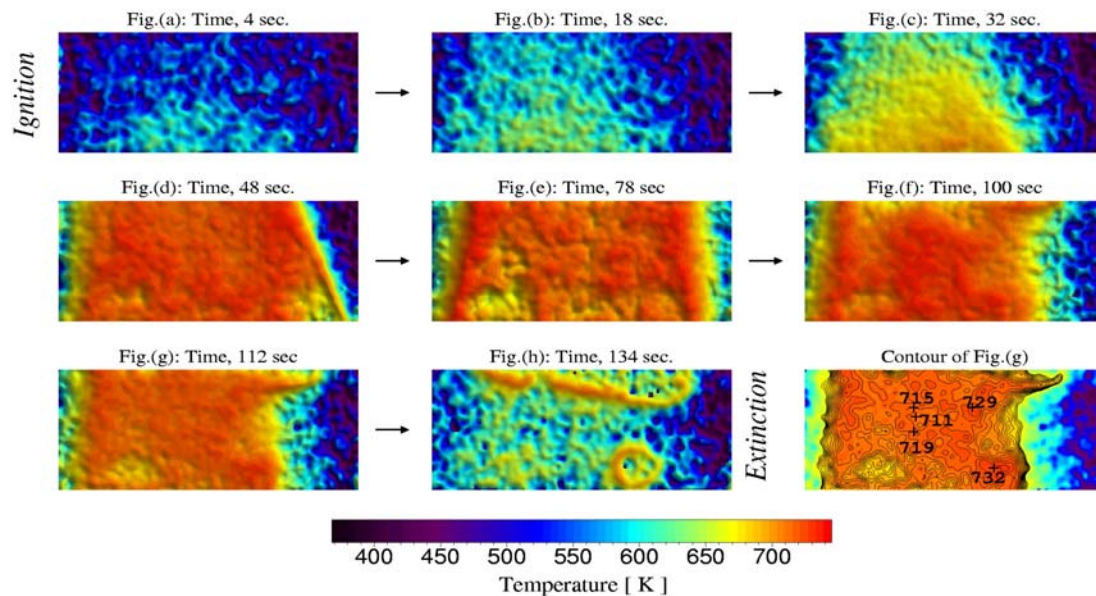


Fig. 1 Temperature during flame-spread: Two-dimensional surface temperature of a low-density fiber board in a flame-spread scenario. Time shown below each image is time after pool ignition

Figure 1 shows the surface temperature at the higher part of the board during different moments of an upward spreading flame. Figures 1a and 1b give the temperature soon after (4 seconds and 18 seconds, respectively) the time of ignition of the alcohol before any strong temperature changes were observed in the upper region. Later, 32 seconds after ignition, the flames had reached the investigated region and regions of hot temperature are seen in Fig. 1c. The flame spread increased faster until it reached maximum temperature as shown in Fig. 1d, corresponding to 48 seconds after ignition. A maximum temperature of 673-773 K and strong gradients of temperature are observed in the figure. Thirty seconds after, Fig. 1e, the flame started to decrease in intensity and local flame extinction started to appear some tens of seconds later as shown in Figs. 1f and 1g. Finally flames were only observed at the upper edges of the board and in Fig. 1h flames do not appear any longer. Just some local areas continued to react, most probably by pyrolysis. In the lower right figure, contour plots of temperatures (from Fig. 1g) are presented with a temperature resolution of 5 K so that gradients can be more clearly seen.

TEMPERATURE MEASUREMENTS OF DECOMPOSING MATERIALS

Surface temperatures of decomposing materials during a pyrolysis phase are presented. The surface temperature of individual particles was measured inside a high temperature reactor using thermographic phosphors which allowed remote, instantaneous measurements.

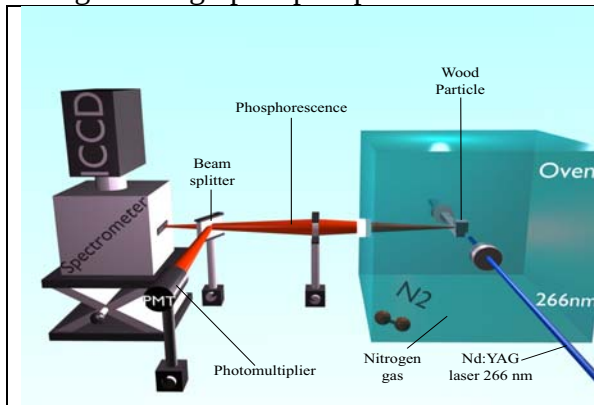


Fig. 2. A reactor filled with nitrogen gas was used to study the pyrolysis of wood particles. After the excitation with 266 nm, the phosphorescence emission, from the wood particles, was collected by a spectrograph and a photomultiplier.

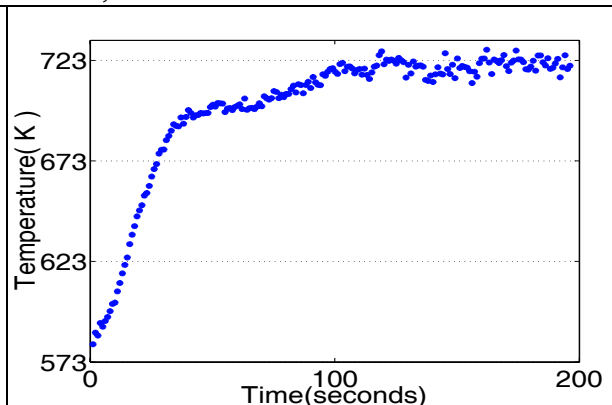


Fig. 3 Using the ratio technique, the surface temperature during pyrolysis was measured. The bump seen in the figure was believed to originate from the drying phase (water evaporation). After 100 seconds, the surface temperature was seen to converge to the reactor temperature.

An ultraviolet laser beam was used to excite the phosphor particles deposited on the investigated materials see Fig. 2. The emission from the thin coating of phosphor powder was spectrally resolved. In Fig. 3, results from these measurements were presented. The measured surface temperature increased to reach a temperature slightly lower than 733 K. It was noticed at a time duration between 50-100 seconds after the introduction of the particle in the reactor, that it occurred an evaporation phase of the water contained inside the particles. This evaporation phase decrease the surface temperature and thus could alter the pyrolysis rate.

INTERNAL COMBUSTION ENGINE VALVE TEMPERATURE MEASUREMENTS

The thermographic phosphor was also used for temperature measurement of internal components inside an optical laboratory engine. The components investigated recently in our laboratory were intake and exhaust valves temperatures. The technique allowed remote measurements of valves temperatures inside the combustion chamber. Previous measurements were mostly based on thermocouples placed on the back of the valves in the intake and exhaust ports (see Refs. [8]-[10]).

The engine was operated with gasoline fuel at around 1200 rpm. Changing the fuel from gasoline to iso-octane improved the signal to background ratio. Nevertheless sufficient signal was recorded using gasoline.

The phosphor particles were coated on the polished surface of the investigated valves. The coating was made using a commercial ceramic binder which was mixed with the phosphors particles and applied on the surface of interest.

The thermographic phosphor was excited by the fourth harmonic of an Nd: YAG laser (266 nm), the subsequent phosphorescence emission was transmitted to a photomultiplier through quartz fibres. The signal was digitized by a fast oscilloscope (TDS620) and then stored through a GPIB interface.

Results from these measurements are shown in Fig. 4 and Fig. 5. The temperature of the intake valve was lower than that of the exhaust valve. That is due to the fresh gas entering the combustion chamber through the concerned valve. Measuring surface temperature of the intake valve could increase the understanding of the evaporation process of the fuel when in contact with high temperature surfaces. Further investigations are being carried out to characterize the temperature of the valves and piston two dimensionally.

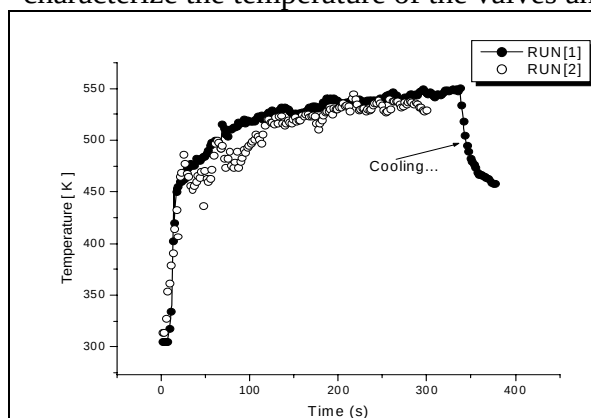


Fig. 4 Intake valve temperature of an engine operated with gasoline fuel.

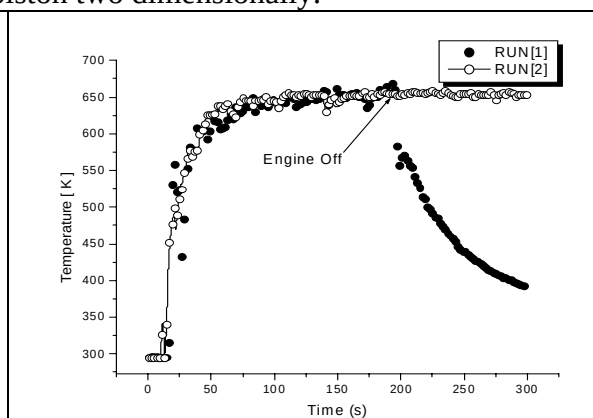


Fig. 5 Exhaust valve temperature of an engine operated with gasoline.

CONCLUSIONS

Thermographic phosphors were successfully used for temperature measurements of reactive and non-reactive surfaces. Special interests towards the exploitation of the technique for temperature measurement of internal combustion engines components, gas phase and the liquid phase e.g. droplets, and sprays are driving the investigation further.

ACKNOWLEDGMENTS

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GAS-MIXING IN THE SPLASH REGION OF A BUBBLING FLUIDIZED BED: FLOW STRUCTURES ASSOCIATED WITH A SINGLE BUBBLE BURSTING AT THE BED SURFACE

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INTRODUCTION

The increasing interest in clean conversion processes of unconventional energy sources provides the driving force toward exploitation of non-fossil solid fuels. Under this respect, fluidized bed (FB) reactors have gained consideration as a viable and attractive option. Despite the growing interest [1], fundamental processes associated with high-volatile solid fuels burning in a FB combustor often remain obscure and call for additional investigation.

Thermal conversion of high-volatile solid fuels in FB combustors (FBCs) is mainly affected by: i) mixing/segregation phenomena with respect to fluidizing gas and bed inert solids; ii) the extent of mixing between segregated gaseous pockets/streams in the splashing zone or in the upper freeboard [2]. Solimene [3] reviewing the role of both issues highlighted that under stratified conversion conditions, typically occurring in FBC, volatile matter burn-out in the splash zone is mainly governed by the combustion between relatively large oxygen pockets - totally or partly segregated - generated by bubbles bursting at the bed surface and a volatile-rich environment.

The hydrodynamic patterns associated with bubbles bursting at the bed surface is particularly relevant since it is believed that the effectiveness of gas mixing in the splash zone is largely determined by the flow structures left behind by bubble eruption.

Phenomena related to bubble bursting at the bed surface have been mainly analyzed in the light of two theories: i) the “Pulsed Jet” model [4-5]; ii) the “Ghost Bubbles” theory [6]. Nevertheless, experimental investigations aiming at the comprehension of hydrodynamic patterns associated to single bubble bursting at the bed surface show departures from either theory [7-9]. The formation of flow structures similar to a downward vortex ring - not in agreement with both theories - has been highlighted.

The present paper reports on the assessment of the hydrodynamic patterns associated with bubble bursting by means of a laser-assisted flow visualization technique. The macroscopic and microscopic features of the flow structures generated upon bubble bursting are investigated by image analysis with the aid of scaling concepts borrowed by fractal geometry.

EXPERIMENTAL

The experimental apparatus, extensively described in Solimene [3], consisted of a fluidization column, a single bubble injector, a set of pressure transducers and a laser sheet source synchronized with a video camera recording system (Fig. 1). The fluidization column (0.35 m ID Perspex tube, 2 m high) was equipped with pressure taps and with three flat glass windows fitted to the wall of the column for optical access (inset of Fig. 1). The single-bubble injection system consisted of a pressurized vessel, a gas-seeding device and an injection nozzle (10 mm ID tube flushing the gas distributor and located at the column centreline).

The diagnostic system was a planar laser light scattering (PLLS) set-up. The second harmonic of a Nd:YAG pulsed laser (532 nm) was used. The laser beam was shaped into a 1 mm thick light sheet by means of a set of cylindrical lenses. The light sheet crosses the fluidization column passing through the W1 and W2 glass windows (Fig. 1 inset) illuminating a rectangular area of about 0.35x0.30m in the splash zone just above the fluidized bed surface

and intersecting the column axis. The video recording system (a progressive scan CCD video camera synchronized to the laser pulses) was able to record frame-by-frame a window of investigation 0.35m wide and 0.26m high at a maximum sampling rate of 30 f.p.s..

Glass beads used as bed material (density 2540 kg/m³, Sauter diameter 277 μm) belong to Group B of Geldart classification of powders. A 0.30 m settled bed (aspect ratio $\cong 1$) was fluidized with technical air at atmospheric pressure and room temperature (minimum fluidization velocity of bed solids, U_{mf} , is 0.05 m/s). The adopted gas seeding material was such that particles behaved as a non-diffusive tracer [3].

Experiments consisted of the injection of a single bubble in an incipiently fluidized bed. Data logging started immediately before the bubble was injected and lasted for a few seconds. The injected bubble diameter, estimated following the procedure reported in Solimene [3], was varied between 10 and 20 cm. An *ad hoc* LabVIEW[®] procedure was developed for the frame-to-frame analysis of acquired images based on the recognition of connected planar domains representing pockets of seeded gas. Domains were characterized in terms of area, center-of-gravity, axial and radial average velocity and angular velocity. A box-counting technique has been applied to digitized frames to characterize the scaling features of the objects corresponding to the seeded gas regions in each snapshot, according to algorithms borrowed from percolation theory [10].

RESULTS

Phenomenologies associated with bubble bursting at the fluidized bed surface have been analyzed with reference to the eruption of an isolated bubble along the centerline of the fluidization column. The time at which the bubble approached the bed surface, identified by the incipient formation of a “dome” of bed solids, was taken as the time scale origin ($t=0$).

Characterization of flow structures: Macroscopic features.

Figure 2 reports a typical sequence of frames recorded immediately after the injection of a single bubble (calculated bubble diameter 0.09 m). As the bubble approaches the bed surface, a “dome” of bed solids is first raised. A pocket of seeded gas (“nose” pocket) becomes apparent above the dome due to some throughflow of seeded gas. As the dome collapses, two heavily seeded areas become apparent, presumably two lobes of a “toroidal” pocket of seeded gas formed as the collapsing solids squeeze the seeded gas out. The left lobe rotates clockwise, the right lobe counterclockwise. The toroidal vortex ring rises, keeping its angular momentum relatively constant. Seeded gas regions become apparent also behind the vortex ring, eventually strained and stretched by the rotation of the toroidal vortex ring. The nose pocket is progressively drawn towards either of the lobes, eventually merging with it. Rotation of the toroidal pocket induces strain and nonuniformities appear within the pocket itself, with alternating seeded and non seeded regions wrapped one on the other. Secondary vortices are eventually shed out of the toroidal pocket, whose rotation is opposite to that of the main vortex. Vortex shedding significantly enhances gas entrainment from the

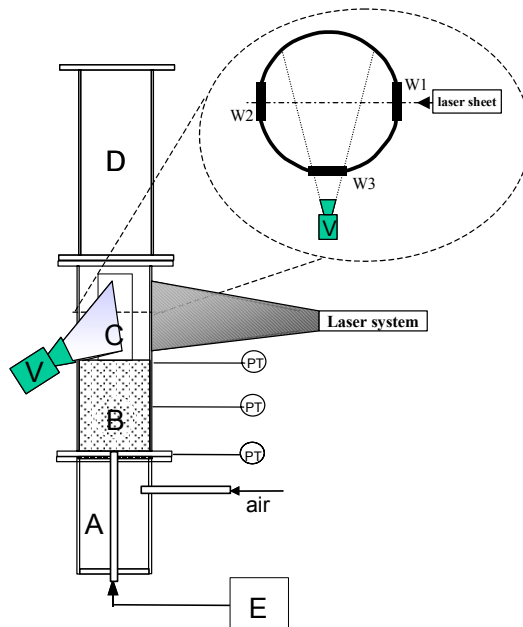


Fig. 1 The experimental apparatus. A) windbox; B) fluidized bed; C) splash zone; D) freeboard; E) single bubble injection device; V) video camera; PT: pressure transducer. In the inset: a cross section of the fluidization column at the glass windows (W1, W2 and W3) level.

mainstream. Altogether, the phenomenology agrees with previous findings reported in the literature [7-9].

Figure 3 reports the axial displacement of the center-of-gravity of both lobes of the toroidal vortex ring. The toroidal region rises at a fairly constant velocity of about $v_p=0.12$ m/s. The mainstream gas superficial velocity (U_g) was about 0.05 m/s. Analysis of the early frames of the videorecording, just after bubble injection, suggested that the axial displacement of the dome as the bubble approaches the bed surface occurs at a velocity of about 0.75 m/s. This figure is fairly consistent with the theoretical bubble uprise velocity which is in the order of 0.68 m/s. That is, the uprise of the toroidal region occurs at a velocity which is intermediate between the velocity of the erupting bubble and U_g .

Figure 3 reports the volume of the toroidal region V_p as a function of the elapsed time, computed from the area of the lobes under the assumption of axi-symmetric shape of the vortex ring. Despite some uncertainty associated with the assessment of the lobe area immediately after bubble bursting, V_p is reasonably close to the volume of the injected bubble, supporting the view that the vortex ring is the remnant of the injected bubble. V_p increases steadily with time at a growth rate of about $\dot{V} = 3.2 \cdot 10^{-3} \text{ m}^3/\text{s}$.

Characterization of flow structures: Microscopic features.

The microscopic features of the flow structures generated by bubble bursting have been characterized by image analysis of individual snapshots similar to those reported in Fig. 2. The key parameter was the specific intermaterial surface area (S_v), computed as the ratio between the perimeter of the seeded region (i.e. the length of the interface between seeded and non-seeded regions) and its area. In order to probe the detailed structure of objects generated by free-shear straining/stretching of seeded gas regions, the scaling concept of geometrical properties of fractal objects has been invoked. To this end S_v has been measured as a function of a “yardstick” by means of a box-counting technique (Fig. 4). The lateral box size l_{box} was varied in the range 1 to 70 mm.

Figure 4 reports the scaling plots of S_v vs l_{box}

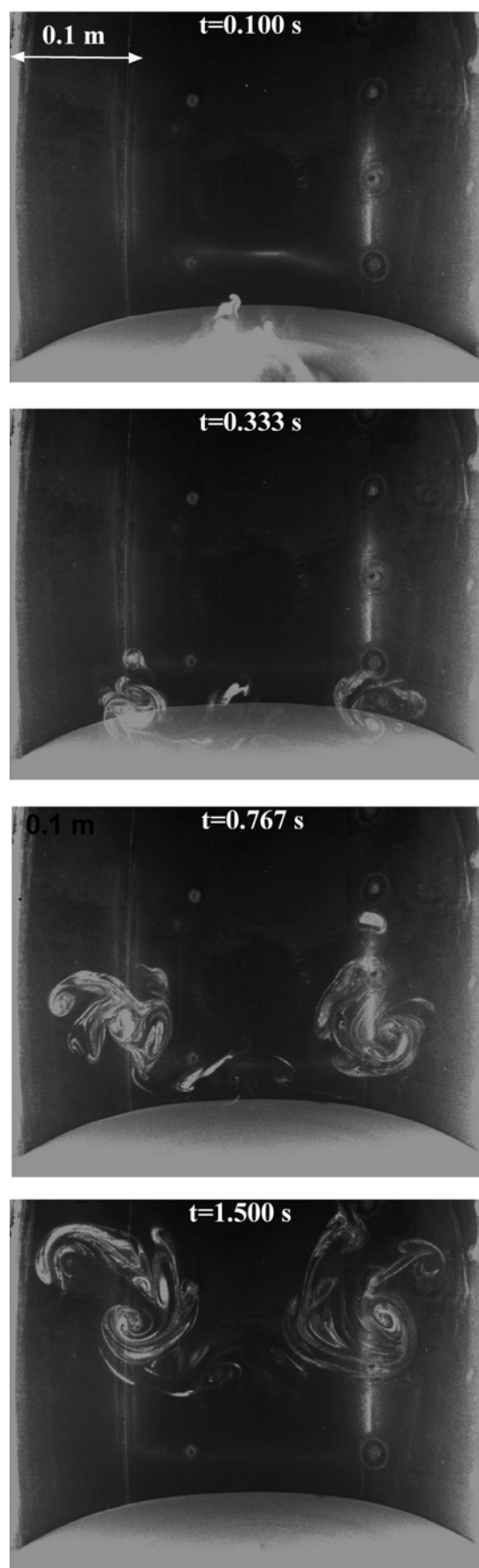


Fig.2 Sequence of frames after a single bubble injection into a fluidized bed

for single bubble eruption. Value of S_v for the smallest l_{box} is about 0.4 mm^{-1} . At large value of l_{box} fractal behaviour is observed, $S_v \propto l_{\text{box}}^{-n}$, with $n=0.52$ [an euclidean object in 2D would be characterized by $n=0$]. For small values of l_{box} , values of S_v become less dependent on the “yardstick” size.

Analysis of S_v corresponding to the minimum box size ($l_{\text{box}} \cong 1 \text{ mm}$) - compatible with the space-resolution of the experiment - as a function of the time elapsed suggests that a limited increase of S_v is observed under operating conditions tested. A rather fine microstructure, characterized by $S_v \cong 0.5 \text{ mm}^{-1}$, appears to be established since the very early stage of bubble eruption.

Relevance to gas mixing

The reported observation suggests that bubble bursting gives rise to well identified coherent gas pockets behaving as toroidal vortex rings. Gas mixing between each pocket and the mainstream depends on: a) macromixing associated with entrainment of mainstream gas (occurring at the rate $\dot{V}$) into the pocket volume (V_p); b) micromixing due to diffusion of species towards the intermaterial surface developing within the pocket. With reference to data obtained in the present work, the macromixing time-scale would be in the order of $t_M = V_p / \dot{V} \approx 1 \text{ s}$. The micromixing time-scale, on the other hand, would be in the order of $t_\mu = 1 / (D \cdot S_v^2) \approx 0.04 - 0.4 \text{ s}$, if $S_v \cong 0.5 \text{ mm}^{-1}$ and a diffusivity variable in the range $D \cong 10^{-5} - 10^{-4} \text{ m}^2/\text{s}$ are assumed. Accordingly, it is inferred that macromixing would be the rate-limiting process in gas mixing as far as isolated flow structures generated by single bubble eruption are concerned.

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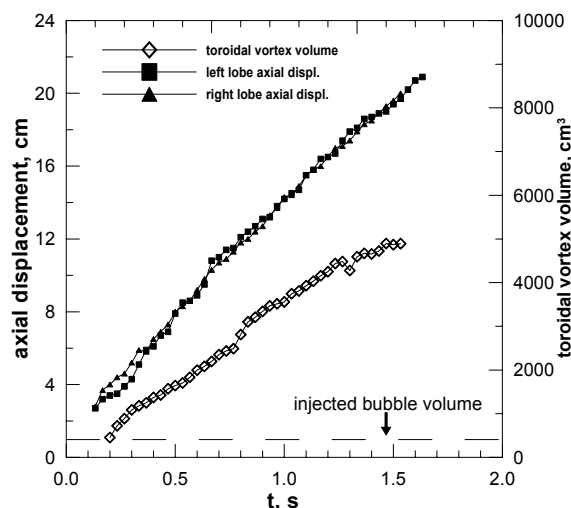


Fig. 3 Axial displacement of left and right lobe and volume of toroidal vortex vs. time [$t=0$ corresponds to dome incipient formation]. Dashed line represents the calculated volume of the injected bubble

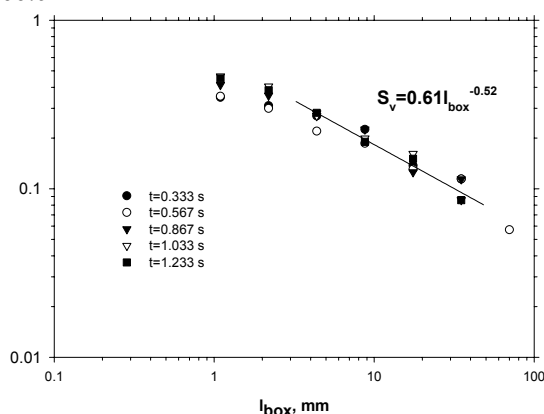


Fig. 4 The specific intermaterial surface area S_v as a function of the lateral box size l_{box} .

Soot Diagnostics for Non-Premixed and Partial Premixed Flames

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Measurements of soot concentrations in flames are conducted by applying an optical light extinction technique. Coannular ethylene/air nonpremixed flames are established to investigate soot formation. Light extinction (LE) is a non-intrusive method that allows measurements of the soot field without changing the flame properties or intruding into the flame medium. We use a coherent light source, namely, a He-Ne laser, to measure the soot volume fraction field. As incident light travels through the soot-containing region within the flame, light is absorbed and scattered, which results in the attenuation of the transmitted light intensity. Abel inversion is subsequently used to obtain the soot volume fraction field distribution once its measured projection distribution is known in an axisymmetric field. As expected, smaller amounts of soot are found in partially premixed flames as compared to nonpremixed flames. In partially premixed flames, the soot producing region is in the annular outer ring along the lower region of the flame. However, soot is observed in the central regions of the flames farther downstream. Results are validated with published results for a nonpremixed flame.

Introduction

The exact formation of soot and the response of soot production to various flame conditions are not well characterized. Therefore, there is a need to understand the mechanism of soot formation and oxidation and to obtain accurate measurements of soot concentrations under a variety of conditions. The measurements should be useful for the development and validation of evolving numerical models for soot formation, growth, oxidation and transport [1].

The light extinction (LE) method is non-intrusive method that allows measurements of the soot field without changing the flame properties or intruding into the flame medium. As the incident light travels through the soot-containing region within a flame, light is absorbed, scattered or transmitted, which results in the attenuation of the light intensity. The ratio of the transmitted to incident light intensity can be used to obtain the soot volume fraction by employing Bouguer's law, which relates the ratio of the transmitted and incident light

intensities to the soot concentration [2]. An Abel inversion can be used to obtain the field distribution of soot volume fraction once its measured projection value distribution is known in an axisymmetric field. Santoro et al. first employed the light extinction method at various points in a soot field to measure the soot distribution in a nonpremixed co-flow ethylene-air flame [2]. Greenberg and Ku [3] and Quay et al. [4] compared the results obtained with the full field technique with those obtained by Santoro et al. and found good agreement. Mitrovic and Lee measured the soot volume fractions in partially premixed ethylene flames using laser-induced incandescence (LII) [5].

Experimental Procedure

Steady laminar partially premixed flames burning ethylene (99.5%) in laboratory air were established on co-annular axisymmetric burner. The fuel flow-rate was maintained at $3.85\text{cm}^3/\text{s}$ and additional air to partially premix it was

varied between 5.65-1.88 cm³/s (corresponding to equivalence ratios between 10 and 27). The outer airflow was maintained at 999cm³/s. A higher outer air velocity reduces the pulsing global instability in the flames, but reduces the visible flame height [8]. The light source is a 30 mW He-Ne laser operating at a wavelength of 632.8 nm. The laser beam passes through a neutral density filter, a beam expander and a set of diffusers. The beam through the diffusers is collected by a condenser lens and directed through a collimator before it encounters the soot-laden flame region. The light beam then passes through a relay lens, and band-pass and neutral density filters. A second neutral density filter is placed after the band-pass filter to further diminish any influence of the flame intensity. Finally, the light is decollimated on to the CCD camera. The image is digitized and processed by a computer.

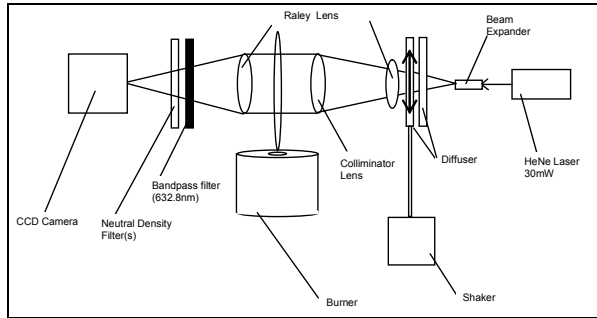


Figure 1 Experimental set up

Theoretical Background

The attenuated light intensity I_{at} is compared to the intensity of the original light beam I_o and the line of sight fractional absorption is calculated after making two corrections. The first involves the flame intensity by acquiring an image of the flame with the light source turned off I_f . The second is due to the background and is corrected for by considering an image obtained in the absence of both the flame and light source I_{as} . The light transmittance

$$T = I/I_o, \text{ where} \quad (1)$$

$$I = I_{at} - I_f, \text{ and} \quad (2)$$

$$I_o = I_b - I_{as}. \quad (3)$$

The transmittance depends on the soot volume fraction f_v in the path of a ray and the light wavelength λ . This relationship is described through Bouguer's law, i.e.,

$$\ln T = -\frac{K_e}{\lambda} \int_{-R}^R f_v ds,$$

where, K_e denotes the dimensionless extinction coefficient, and R the radius of the flame at the axial location above the burner. Thus, the integrated soot volume fraction

$$\int_{-R}^R f_v ds = -\frac{\lambda}{K_e} \ln T. \quad (5)$$

The dimensionless extinction coefficient

$$K_e = K_a(1 + \alpha_a) \quad (6)$$

can be calculated by applying Mie's theory provided the soot particles have a small optical dimension so that

$$K_a = \frac{36\pi \lambda k_\lambda}{(n_\lambda^2 - k_\lambda^2 + 2)^2 + 4n_\lambda^2 k_\lambda^2}. \quad (7)$$

In Eq. (7), n_λ and k_λ denote the real and imaginary parts of the complex refractive index of the particle's material. Choi et al. have provided experimentally measured values of the dimensionless extinction coefficient [6]. They report that a value of $K_e = 8.6 \pm 1.5$ is appropriate for hydrocarbon fuels at a light wavelength of 632nm. We have chosen the lower limit of this value (7.1) in our analysis by comparing our transmittance and soot volume fraction results with those of Santoro and coworkers [4].

Abel Inversion

An inversion method must be applied to reconstruct the non-uniform spatial soot distribution from the path integrated data. The projection distribution $P(x)$ represents the projection value distribution that is recorded by the line of sight optical measurement. The hypothetical distribution $F(r)$ is the distribution of the region of interest. Both distributions, P and F contain the same information regarding the physical data in the region. The objective is to obtain the field distribution F given only the

projection distribution P and the assumption that F is axisymmetric.

$$P(x) = 2 \int_{y=0}^{\infty} F(r) dy = 2 \int_{r=x}^{\infty} \frac{rF(r)dr}{\sqrt{x^2 - y^2}}. \quad (8)$$

Recognizing that r represents a dummy integration variable, (that is $r=x$ is the radius of the line of sight measurement), by change of variables the Abel transform of the field $F(r)$ can be obtained as

$$P(x) = \int_{m=x}^{\infty} \frac{mF(m)dm}{\sqrt{m^2 - x^2}} = P(r) = \int_{m=r}^{\infty} \frac{mF(m)dm}{\sqrt{m^2 - r^2}}. \quad (9)$$

The analytical inversion is

$$F(r) = -\frac{1}{\pi} \int_{m=r}^{\infty} \frac{dp/dm}{\sqrt{m^2 - r^2}} dm. \quad (10)$$

Equation 10 allows one to calculate the distribution $F(r)$ if $P(x)$ is known.

The Abel inversion algorithm is very sensitive to small local changes in areas of low signal to noise ratio. The Fourier transform approach is an effective means to filter noise from optical measurements in flames [2]. This method is applied to our data prior to a polynomial high order curve fitting function.

Results and discussion

Figure 2 presents the soot distribution in a nonpremixed ethylene flame. The outer radial regions of the flame contain the largest amounts of soot. These results are in good agreement with Greenberg and Ku [5]. There is a slight discrepancy at the centerline, especially at a 50 mm axial displacement, where a fictitious peak can be observed. This occurs, since the noise cannot be filtered completely without losing resolution. The noise creates gradients that significantly influence the Abel inversion algorithm. The deviation of the measurements increases in the regions further than 50 mm downstream of the burner. This is due to the loss of parallel rays collimation. The nonparallel light rays brighten up attenuated areas of the image, which should have appeared as dark regions.

Soot volume fractions were obtained for partially premixed flames established at

equivalence ratios ranging from 5-24 at heights of 20 mm to 70 mm above the burner. Figures 3-7 present the soot volume fraction as a function of the radial distance from the burner axis for different axial displacements. The soot volume fraction increases when small amounts of air are added to the mixture. This is true for equivalence ratios greater than twenty-four at which soot volume fraction reaches its maximum value. The soot-producing region is the annular outer ring in the lower region of the flame, but the presence of soot is observed in the central regions of flame farther downstream.

For equivalence ratios below twenty-four and larger than ten, soot volume fraction slightly decreases. A drastic reduction in soot production can be observed when the equivalence ratio falls below ten. The same trend is observed at different heights within the flame region at the same equivalence ratio. Hura and Glassman [7] suggested that the initial increase in the soot volume fraction for equivalence ratios greater than 20 is due to the chemistry of intermediate carbons that are significantly altered by the partial premixing. Here, the increase in soot production results from oxygen addition, which enhances the local radical pool and alters the hydrocarbon chemistry.

The flame height follows the same trend as the soot volume fraction. It first increases ($\Phi > 24$) and then decreases ($\Phi < 24$). As more air is added to the mixture, the flame becomes shorter and more rounded.

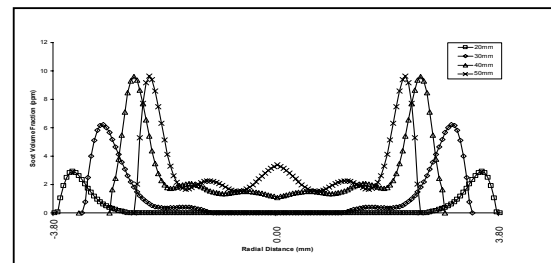


Fig 2: Soot Volume Fraction of a laminar

Conclusions

A full-field light extinction measurement was successfully applied to measure soot volume

fraction of partially premixed ethylene flames. The light extinction method is a relatively inexpensive method to measure the soot volume fraction in flames. Our results show that soot volume fraction is higher at outer radii as compared to the centerline. The soot volume fraction decreases with decreasing equivalent ratios. As more air is added to the mixture, the concentration of soot and the height of the flame tend to decrease.

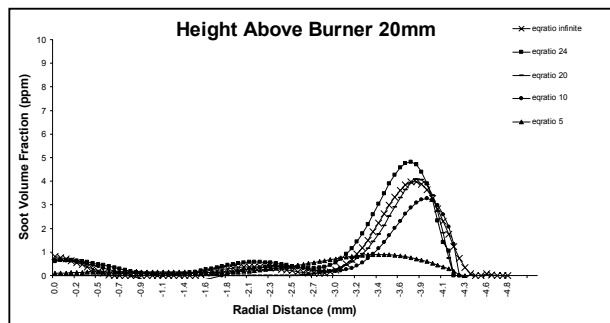


Fig 3: Soot Volume Fraction $\Phi=\infty, 24, 20, 10, 5$

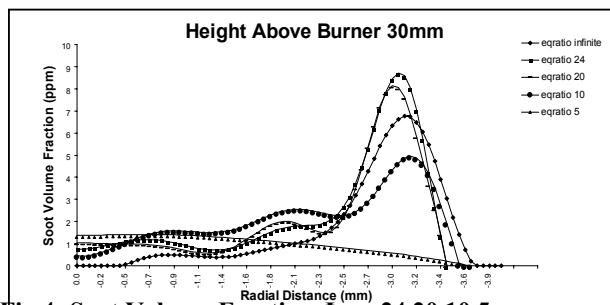


Fig 4: Soot Volume Fraction $\Phi=\infty, 24, 20, 10, 5$

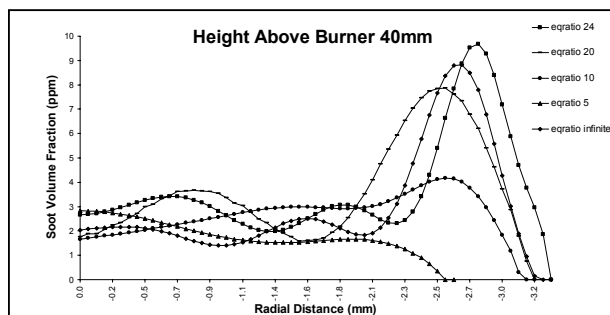


Fig 5: Soot Volume Fraction $\Phi=\infty, 24, 20, 10, 5$

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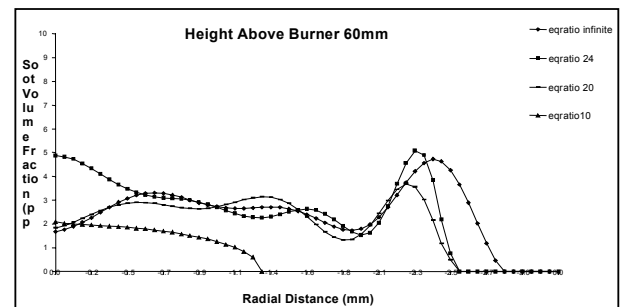


Fig 6: Soot Volume Fraction $\Phi=\infty, 24, 20, 10$

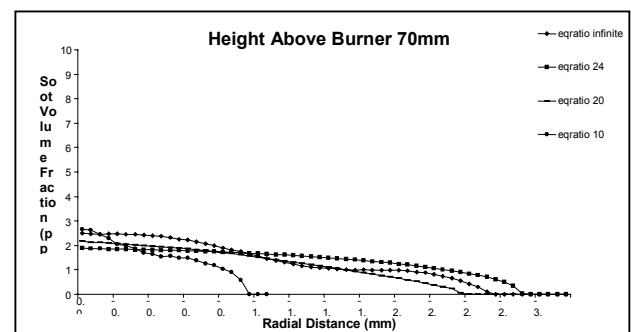


Fig 7: Soot Volume Fraction $\Phi=\infty, 24, 20, 10$

The Catalytic combustion of soot: mechanisms and models

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Diesel soot emissions from stationary or mobile sources will soon be reduced by the use of traps periodically regenerated by catalytic means. These traps control particulate emissions by physically trapping the particles in their porous structure. Regeneration is required to avoid excessive pressure drop and consequent fuel penalty. Two regeneration means, both based on trap heating by catalytic combustion of post-injected hydrocarbons, are considered and analysed by either experimental and modeling tools. A multifunctional wall-flow trap concept, coupling both soot and fuel combustion catalysts at opposite side of the permeable channel walls, shows promise compared to a conventional two bricks solution (decoupled fuel converted + catalytic trap) in terms of space and post-injected fuel savings.

INTRODUCTION

Diesel particulate emissions, due to their chemical composition and extremely small size ($<1\mu\text{m}$) are a matter of health and environmental concern. They can be controlled either at their source, through engine design and a proper control of the combustion process (e.g. common-rail system) or via exhaust gas aftertreatment by using particulate filters [1]. The most promising of such protocols exploits one of the peculiar features of last-generation Common Rail diesel engines: the possibility to post-inject on purpose some fuel that gets burned in a specific honeycomb oxidation catalyst placed upstream the trap. The consequent temperature rise of the exhaust gases helps to ignite the catalytic combustion of the soot trapped, eventually leading to the combustion of most of the trapped soot and to the consequent decrease of the trap pressure drop and the related fuel penalty (see Fig. 1a).

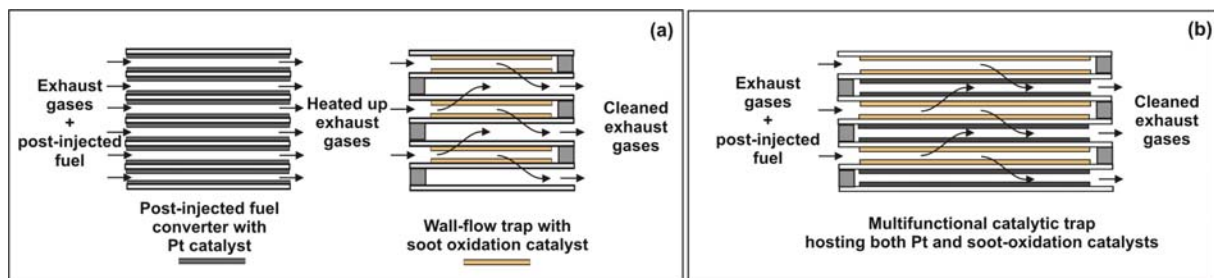


Fig. 1. Conventional (“two bricks”) and innovative means for the regeneration of diesel oxidation catalytic traps by catalytic combustion of post-injected fuel.

The next frontier for further progress in the field will be to find the technological means to reduce or even eliminate this fuel penalty. In this context, our group plans to investigate multifunctional traps hosting both post-injected-HC and soot combustion catalysts as those depicted in Fig. 1.b. This should lead to a more compact system also entailing potential fuel saving, as later on explained.

This paper deals with the development and bench testing of a new catalytic trap based the CeO_2 -promoted PrCrO_3 perovskite for the de-coupled or “two bricks” solution (Fig. 1a). Early modelling results on the innovative multifunctional trap concept (Fig. 1b) are then presented and discussed.

EXPERIMENTAL PROCEDURES

A simultaneous synthesis and deposition of the CeO_2 -promoted PrCrO_3 catalyst was obtained by *in-situ combustion synthesis* directly inside the wall-flow filter. The ceramic support was dipped in the aqueous solution with precursors and then placed into an oven at 600 °C. The aqueous phase was rapidly brought to the boiling point, then the mixture ignited and the main reaction took place *in situ*. The cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$) wall-flow monoliths developed by Corning were selected as supports (cell structure = 14/200, diameter 300 mm, length = 6 – 12”; pore diameter of channel walls = 9 μm , porosity of channel walls = 42 %). A good chemical compatibility between catalysts and ceramic materials was in fact assessed by means of XRD analysis after a suitable high temperature treatment (2h at 900°C) performed on intimate catalyst-trap powder mixtures.

The developed traps were tested in a pilot plant on real Diesel exhaust gases (Kubota 1000 cc IDI engine, capable of up to 23 hp at 3000 rpm), where the temperature and gas composition before and after the trap could be controlled and monitored as well as the filtration efficiency and the evolution of the pressure drop through the trap (a sign of soot accumulation therein). A detailed description of the pilot plant and of the procedure adopted was provided in [2]. Basically, the trap is laden under steady state idle conditions and then regeneration is induced by post-injecting a given flow rate of fuel in a two bricks set up (Fig. 1a). A parallel run on a non-catalytic trap was carried out so as to draw a comparison.

MULTIFUNCTIONAL CATALYTIC TRAP MODELLING

The schematic front view of an honeycomb wall-flow diesel particulate trap is shown in Fig. 1a. As evident from Fig. 2b, 2c and 1a, adjacent channels are plugged at alternate ends. The exhaust enters an inlet channel, flows through the porous wall and exits the trap from an adjacent exit channel. The porous inlet channel walls act as the filtering media. The particulate matter, retained by the porous walls, increases the pressure drops and has thus to be eliminated by periodic regeneration. It can be clearly noticed from the frontal view monolith's (fig 2a), that the filter has many symmetric plans. As a consequence, it was easy to divide the all filter in many simple elementary volumes (Figs. 2b and 2c) for the sake of reducing the computational domain and time, without losing any interesting information. As depicted in Fig. 2c, the selected volume includes an inlet section, an outlet section and a portion of the filtering channel wall.

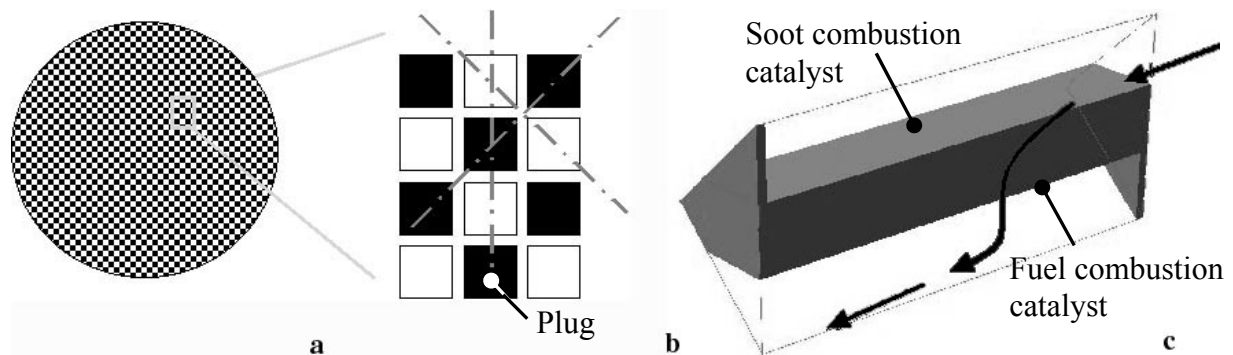


Fig. 2. Discretisation scheme adopted for the multifunctional trap modeling.

The governing mass, heat and momentum balance equations adopted over this volume are those provided in the software package CFD-ACE+. Heat transfer in the porous channel wall was calculated as a combination of conduction, convection and radiation provided by the same software tool by assuming the following values for some constitutive parameters of the cordierite trap: solid density = 3200 kg/m³; solid heat conductivity = 55 W/m/K; channel wall porosity = 48%. As a basic assumption the thickness of the catalyst layers was considered insignificant and the conversion of post injected fuel (C16) complete. Preliminary simulations were carried out within these constraints so as to assess the steady state temperature patterns obtained within the multifunctional traps as a function of different post-injected fuel amounts.

RESULTS AND DISCUSSION

Experimental results on the “two-bricks” regeneration system

Fig. 3 compares the results of the induced-regeneration runs obtained with a non-catalytic (a) and the CeO₂-PrCrO₃ catalysed (b) cordierite wall-flow monoliths with different specific flow rates of post-injected fuel. After a loading of the trap up to about 250-300 mbar pressure drop is reached, the regeneration is forced by post-injecting fuel which gets burned over the oxidising converter placed upstream the trap.

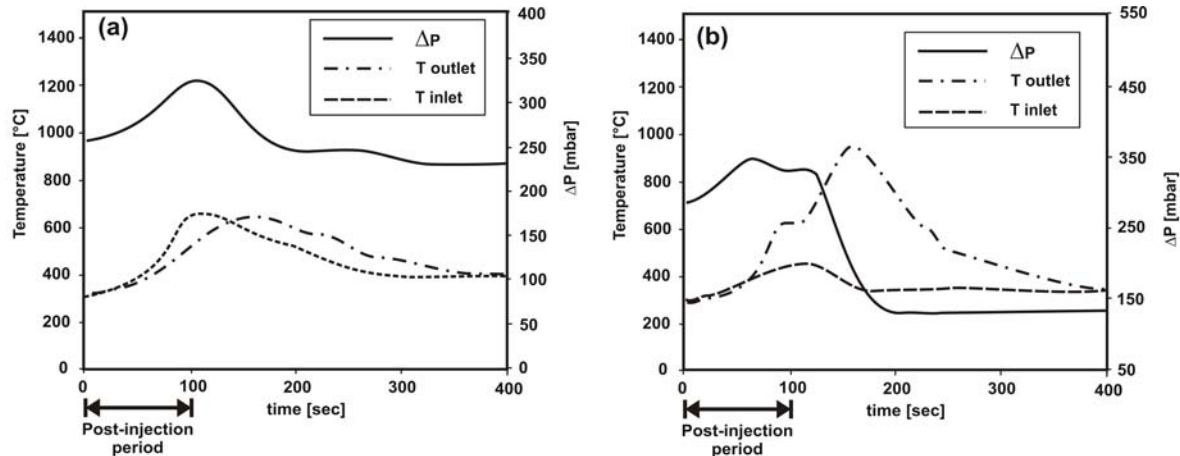


Fig. 3. Regeneration cycle for the non-catalytic (a) and the catalytic (CeO₂-promoted PrCrO₃) (b) wall-flow traps; superficial gas velocity = 0.205 m/s (Cordierite wall-flow monolith by Corning). Post injected fuel (kg/kg of exhaust gases): (a) = 0.0125 (additional fuel consumption during post-injection: 24%); (b) = 0.005 (additional fuel consumption during post-injection: 10%).

A major difference between the two traps lies in the degree of completeness of the regeneration process. Despite the higher flow rate employed, the non-catalytic trap does not regenerate completely during the test. Conversely, the soot accumulated in the catalytic trap underwent a significant conversion during regeneration, thanks to the promoting effect of the catalyst placed therein. In this latter case, the pressure drop gets in fact reduced from just above 300 mbar down to less than 150 mbar at equal superficial gas velocity. A further index of the high combustion rate induced by the catalyst is the remarkable difference between the upstream (lower) and the downstream (higher) temperatures, a direct consequence of the heat of combustion released. It is even more important that regeneration is induced for the catalytic trap by post injecting a comparatively low fuel flow rate (corresponding to 10% of the fuel burned out in the engine itself) which heats up the exhaust gases to just slightly more than 400°C. Conversely, as above underlined, the non-catalytic wall-flow shows only limited regeneration (the pressure drop is reduced by just a few tens of mbars) even is a much higher

specific amount of fuel has been post-injected (corresponding to 24% of the fuel burned out in the engine itself) and the gas temperature at the trap inlet reaches more or less 650°C.

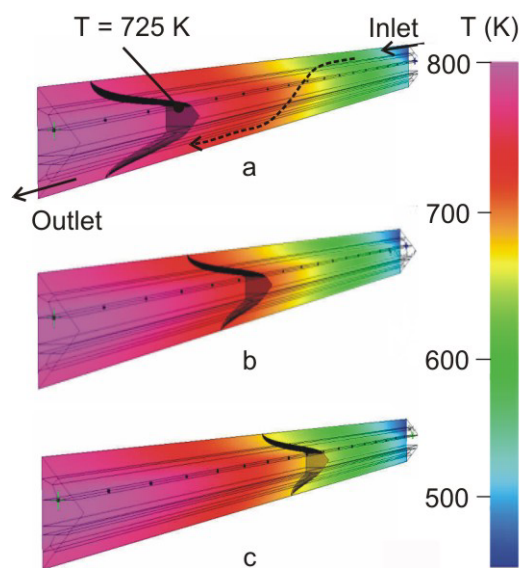


Fig.4. Steady-state temperature patterns in the multifunctional trap when post-injecting different fuel amounts ($a = 0.8 \% \text{ w/w}$; $b = 1 \% \text{ w/w}$; $c = 1.2 \% \text{ w/w}$). Inlet conditions: $v = 4 \text{ m/s}$; $T = 450 \text{ K}$; $\text{O}_2 \text{ conc.} = 9 \text{ vol}\%$.

Model calculations on the multifunctional trap

The results of model calculations over the multifunctional trap are shown in Fig. 4. The prevalent goal of the calculations was to assess how the multifunctional monolith gets heated by localised combustion of post-injected hydrocarbons. As shown aside, the hottest parts of the trap are those facing the downstream exhaust line. The higher is the flow rate of post-injected fuel, the wider is the zone of the trap than gets heated up to temperatures ($>725\text{K}$) at which the catalytically-promoted combustion of soot is fast. This is a major difference with the two-bricks system, in which all the exhaust gases are pre-heated before entering the trap, which is progressively and rather homogeneously brought to high temperatures.

The particular heat-up behaviour of the single-brick solution seems to have pros:

- the heating is preferentially localised in the downstream part of the trap where most of the soot is known to be trapped;
- the catalyst distribution along the channel

length might keep this into account by having more catalyst deposited in that location for the sake of igniting soot combustion as soon as possible thus reducing the fuel penalty.

Some concerns arise for the regeneration of the inlet trap section, as it seems to remain relatively close to the gas inlet temperature. However, it is likely that, once ignited, soot combustion can propagate somehow backward towards the upstream part of the monolith.

Both experimental and modelling studies are in progress to check this occurrence and to evaluate the overall performance of the multifunctional trap.

CONCLUSIONS

The aim of this work was to check the potential of two Diesel particulate trap concepts, one conventional (two-bricks), one highly innovative (single-brick), both control suitable for regeneration via catalytic combustion of post-injected fuel periodically obtained by use of the Common-Rail feed system. By developing a very active CeO_2 -promoted PrCrO_3 catalyst, fast and rather complete trap regeneration could be achieved with just 10% fuel consumption increase during regeneration (a regeneration cycle is expected each 300-500 km). A multifunctional wall-flow trap concept, coupling both soot and fuel combustion catalysts at opposite side of the permeable channel walls, shows promise in terms of space saving and further reduction of post-injected fuel requirements per regeneration cycle.

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Modeling of PAH and Soot Formation in Laminar Premixed Flames

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INTRODUCTION

Combustion is a major source of airborne species of health concern such as particulate matter and polycyclic aromatic hydrocarbons (PAH). On the other side, controlled fuel-rich combustion is a largely used process for carbon black synthesis [1] and it was found to be suitable for the synthesis of fullerenes [2] and nanotubes [3]. PAH are thought to be key intermediates in soot and fullerene formation [2] and kinetic models of increasing complexity have been developed in order to approach a quantitative assessment of fuel-rich combustion [4, 5]. In the present work, a semi-detailed kinetic model for the oxidation and pyrolysis of several fuels [6] was extended to describe soot particle formation using the sectional technique proposed by Pope and Howard [7] and further developed [8-10]. Classes of particles with increasing molecular mass were defined and numbers of carbon and hydrogen atoms corresponding to the average mass of each class were assigned. According to experimental data, H/C ratios decrease with increasing particle size. Particles up to about 70 nm diameter are included. Kinetic parameters describing growth reactions have been chosen based on published data, taking into account the increase of the collision cross sections with particle size. Model predictions of PAH and soot concentration are compared with experimental data of a fuel-rich premixed atmospheric benzene/air flame [11]. In recent work [12, 13], the same approach for soot formation was used to extend a different kinetic scheme [14] to model a low pressure benzene flame with encouraging results.

THE DISCRETE SECTIONAL APPROACH

The complete description of the formation of very large molecules within a detailed kinetic model is limited by the quick increase of the number of species of similar mass and of isomers of identical formula. Therefore, the investigated range of very large PAH and particles has been divided in classes (BINs) covering certain mass ranges and defined by the average molecular masses, while given numbers of carbon and hydrogen atoms are assigned. Soot formation is described in the form of usual gas phase kinetics. Stoichiometric coefficients are calculated in order to respect the mass and elemental balances of all individual reactions. The first BIN is equal to coronene. It has an average molecular mass of 300 a.m.u., covers the mass range 201-400 a.m.u. and has the nominal composition $C_{24}H_{12}$. The next BIN has double average mass and mass range than the previous one, i.e., BIN2 has an average mass of 600 a.m.u. and covers the range 401-800 a.m.u. The largest BIN, BIN20 has the nominal composition $C_{12972032}H_{1622016}$ and a H/C ratio of 0.125, corresponding to an average mass of 157,286,400 a.m.u. Diameters have been determined based on the assumption of spherical structures with a density of 1.8 g/cm^3 [1].

Figure 1 shows the hydrogen mole fraction of different hydrocarbons and soot vs. molecular mass. Filled symbols are taken from Wagner [15], empty symbols represent the BINs. The H/C ratio decreases with increasing molecular mass, in agreement with the findings of Wagner and

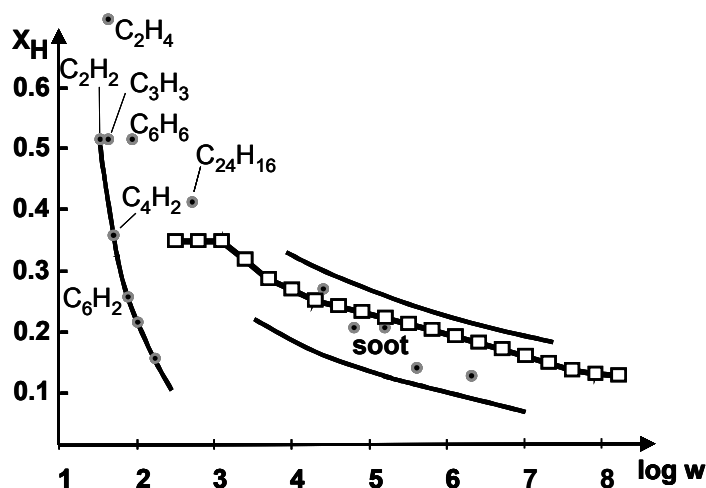


Fig. 1 Hydrogen mole fractions of different hydrocarbons (filled symbols, [18]) and soot (open symbols) vs. molecular mass.

also of Furutani et al. [16]. Previously, the maxima of experimental particle diameter distributions determined in one-dimensional premixed low-pressure C_2H_2 flames [17] have been correlated with H/C ratios measured under similar conditions [18]. The decrease of the H/C ratio is thought to correspond both to an increasing number of condensed rings and to an increase of curvature induced by the presence of five-membered ring species. Curvature is expected to determine, in a large extent, properties of soot material, therefore, the importance of its correct

assessment in model predictions is significant. Future work should include the definition of several BINs within the same range of molecular masses but with different H/C ratios.

REACTION CLASSES FOR THE SOOT MODEL

The reactions describing nucleation and coagulation of the BINs, their oxidation and growth by addition of gas-phase species are summarized in table 1. Nascent soot particles are formed via reactions between PAH radicals or between stable PAH and their radicals. The kinetic rates are evaluated on the basis of the reaction phenyl + benzene and the recombination of phenyl. Frequency factors have been scaled based on the change in collision frequencies relative to those of benzene + phenyl or phenyl recombination. These reactions are treated as irreversible. BIN radicals are formed via hydrogen abstraction with H and OH radicals, both forward and reverse reactions have been taken into account. Also, unimolecular hydrogen loss from parent BINs and the corresponding reverse reaction, have been included in the model. Reactions of benzene and phenyl have been used as reference for all reactions involved in the formation of BIN radicals. OH was found to be the dominant oxidizing species in flames, for soot particles under conditions typical of a premixed flame with collision efficiencies in a range from 0.13 to 0.27 [19]. Oxidation of PAH and therefore of small BINs is thought to be significantly slower,

Nucleation	$PAH^* + PAH^* \Rightarrow \alpha BIN_{1,2} + \beta H_2 + 2H$
	$PAH^* + PAH \Rightarrow \alpha BIN_{1,2} + \beta H_2 + H$
H Abstr.	$H + BIN = H_2 + BIN^*$
	$OH + BIN = H_2O + BIN^*$
Unim. H loss	$BIN = H + BIN^*$
Oxidation	$BIN_i + OH \Rightarrow \alpha BIN_{i-1} + \beta BIN_i + CO + \gamma H$
Surf. Growth	$C_2H_2 + BIN_i^* \Rightarrow \alpha BIN_i + \beta BIN_{i+1} + \gamma H_2 + H$
	$PAH^* + BIN_i^* \Rightarrow \alpha BIN_i + \beta BIN_{i+1} + \gamma H_2 + 2H$
	$PAH + BIN_i^* \Rightarrow \alpha BIN_i + \beta BIN_{i+1} + \gamma H_2 + H$
	$PAH^* + BIN_i \Rightarrow \alpha BIN_i + \beta BIN_{i+1} + \gamma H_2 + H$
Coagulation ($j \leq i$)	$BIN_j^* + BIN_i^* \Rightarrow \alpha BIN_i + \beta BIN_{i+1} + \gamma H_2 + 2H$
	$BIN_j + BIN_i^* \Rightarrow \alpha BIN_i + \beta BIN_{i+1} + \gamma H_2 + H$
	$BIN_j + BIN_i \Rightarrow \alpha BIN_i + \beta BIN_{i+1} + \gamma H_2 + H$ ($j, i \geq 5$)

Table 1 Classes of reactions for BINs

rate constants similar to those describing oxidation of single-ring aromatics have been used [4, 5]. Surface growth occurs via reaction with acetylene, PAH and PAH radicals to soot nuclei activated by H abstraction, as well as of PAH radicals to parent BINs. Particle coagulation by reactions between BINs and BIN radicals, between BIN radicals as well as between stable BINs beyond BIN4 are included in the model.

COMPARISON WITH EXPERIMENTAL DATA

The simulation results obtained with the model are compared with experimental measurements of a fuel-rich premixed atmospheric benzene/air flame ($C/O = 0.72$, $v = 4 \text{ cm s}^{-1}$ at 298 K) [11]. The computational model is a modified version of the code PREMIX [20]. These modifications allow to use H abstraction reactions described in a simplified form (which assumes analogy and similarity rules for the estimation of the kinetic parameters) and they also allow flexibility with respect to equivalent or lumped reactions with several products.

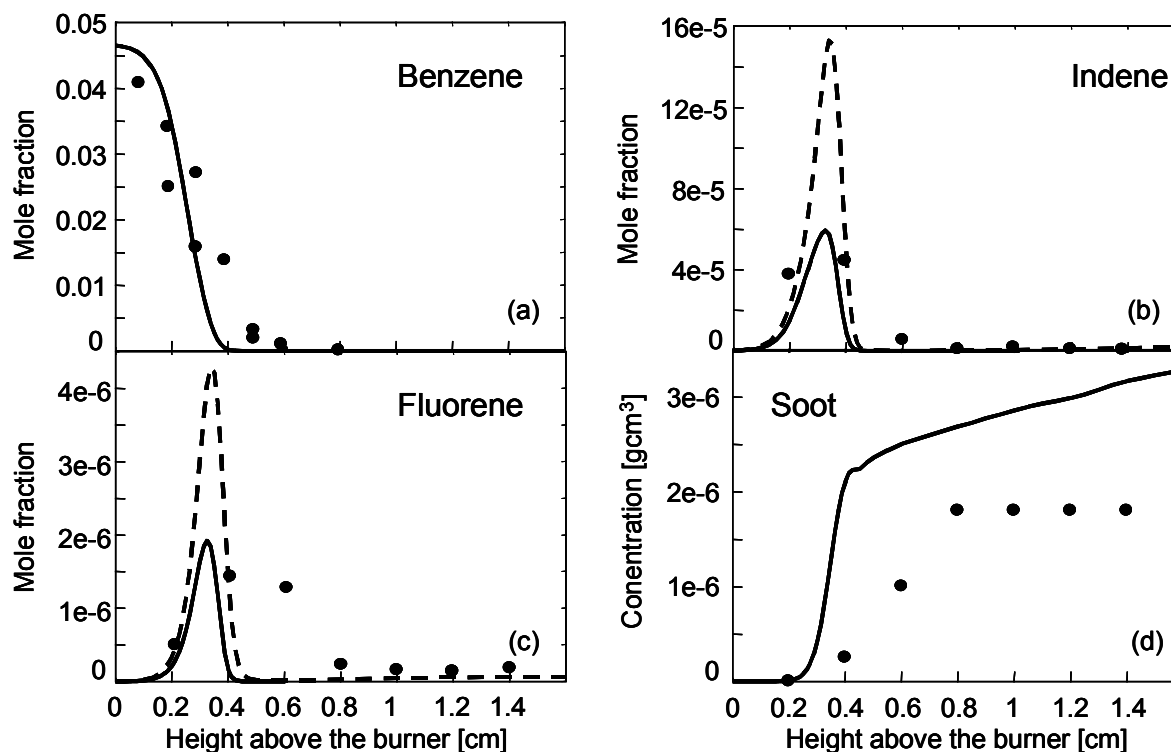


Fig. 2 Comparison between model predictions (lines) and experimental measurements (symbols) of a premixed atmospheric benzene/air flame [13]. Solid lines: full model with soot; dashed lines: model without soot.

Figure 2 shows the concentration profiles of selected species and soot. Panel (a) shows that the conversion of the fuel is correctly predicted. Panel (b) and (c) also show the comparison with simulation results of a previous model without the extension to soot. Different from the low pressure benzene flame [12, 13], maxima of predicted PAH profiles, indene and fluorene in this example, decrease significantly with the introduction of the soot portion, reaching better agreements with experimental data. Panel (d) shows the concentration of soot. The model slightly overestimates the experimental data, but this preliminary agreement is still satisfactory. In fact these measures are quite difficult and it was found that uncertainties of soot data are non negligible [12, 13]. Figure 3 shows the mole fractions of soot, starting from BIN4, against the particle diameter at fixed height above the burner. These profiles show a bimodal behavior, in qualitative agreement with recent experimental measurements [21, 22]. The minimum of the distribution and the mole fractions of smaller BINs decrease with

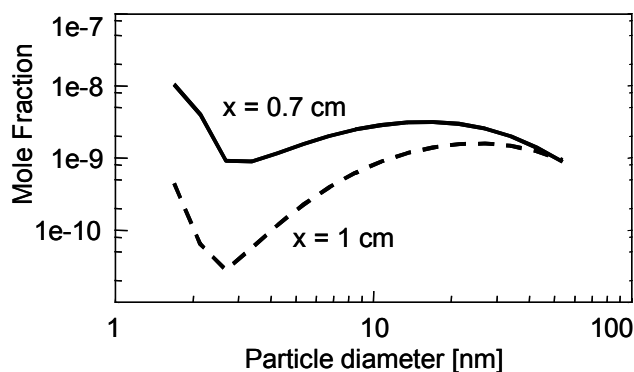


Fig. 3 Mole fraction of BINs vs. Particle diameter at different height above the burner

increasing height above the burner, while the second maximum moves to larger diameters, keeping the total concentration of soot almost constant, as shown in Fig. 2.

CONCLUSION

An existing semi-detailed kinetic model was extended to soot particles using the discrete sectional approach. The comparison with experimental measurements of a benzene/air premixed flame shows encouraging results. The bimodal distribution of particle diameters is in qualitative agreement with experimental data. More work is needed to validate the model against experimental data of different fuels and in different operating conditions.

ACKNOWLEDGEMENTS

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Sulfation and Reactivation of Three Limestones in a Dry Desulfurization Process

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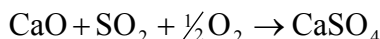
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INTRODUCTION

Dry desulfurization by direct injection of sorbents into a fossil-fuel boiler or a coal-fired burner offers a potential cost-effective alternative to more expensive SO₂ removal technologies, such as semidry or wet flue gas desulfurization.

To achieve compliance with environmental quality standards on sulfur emissions, this simple technology typically uses commercial limestone as dry powdered sorbent, which reacts at high temperature (800-900°C) with the flue gas. It is a widespread opinion that, in the high temperature region, the sulfur capture by limestone is accomplished by two reaction steps: (1) fast calcination (decomposition) of CaCO₃ to produce high surface area and high porosity calcium oxide and (2) sulfation of the obtained CaO, in the presence of O₂, to form both CaSO₄ and CaSO₃ [1].



Despite several studies [2-3] related to the system limestone/SO₂ have been proposed, it is still difficult to predict the behavior of these sorbents in sulfur dioxide removal processes, not only in real-size applications but also in laboratory-scale tests.

Therefore, the first aim of this work has been to evaluate the sulfur adsorption efficiency of three different commercial limestones in a laboratory-scale equipment. Moreover, the solid CaCO₃ usually exhibits a partial conversion to calcium sulfate and sulfite [4]. Since a large amount of the sorbent goes unreacted through the process, a regeneration treatment to restore the spent sorbent reactivity has been also investigated.

EXPERIMENTAL APPARATUS

Experimental tests were carried out in a well-mixed recycle reactor, located in an electrical tubular oven. As shown in figure 1, the cylindrical quartz-made reactor was constituted by two sections: the pre-heating zone (A), 900 mm height and 32 mm i.d., partially filled with alumina pellets in order to heat quickly the reactants up to the reaction temperature, and the reaction section (B), 400 mm height and 27 mm i.d., provided by a porous sample holder and an internal cooling jacket. During the experiments, the upper part of the reactor was kept inside the oven, while the reaction section was rapidly inserted into the pre-heating tube when the gaseous stream reached stationary conditions at 850°C.

The limestone amount (size-fraction: 0,4-0,6 mm) for the experiments was approximately 0,7 g; it was set on the sample holder prior to insert the reaction section inside the oven. This test procedure allows to simulate the direct limestone injection that occurs in real-size applications, studying also the initial simultaneous sorbent calcination and sulfation of the

obtained CaO. Before leaving the reactor the flue gas was quickly quenched by contacting it with the internal cooling jacket.

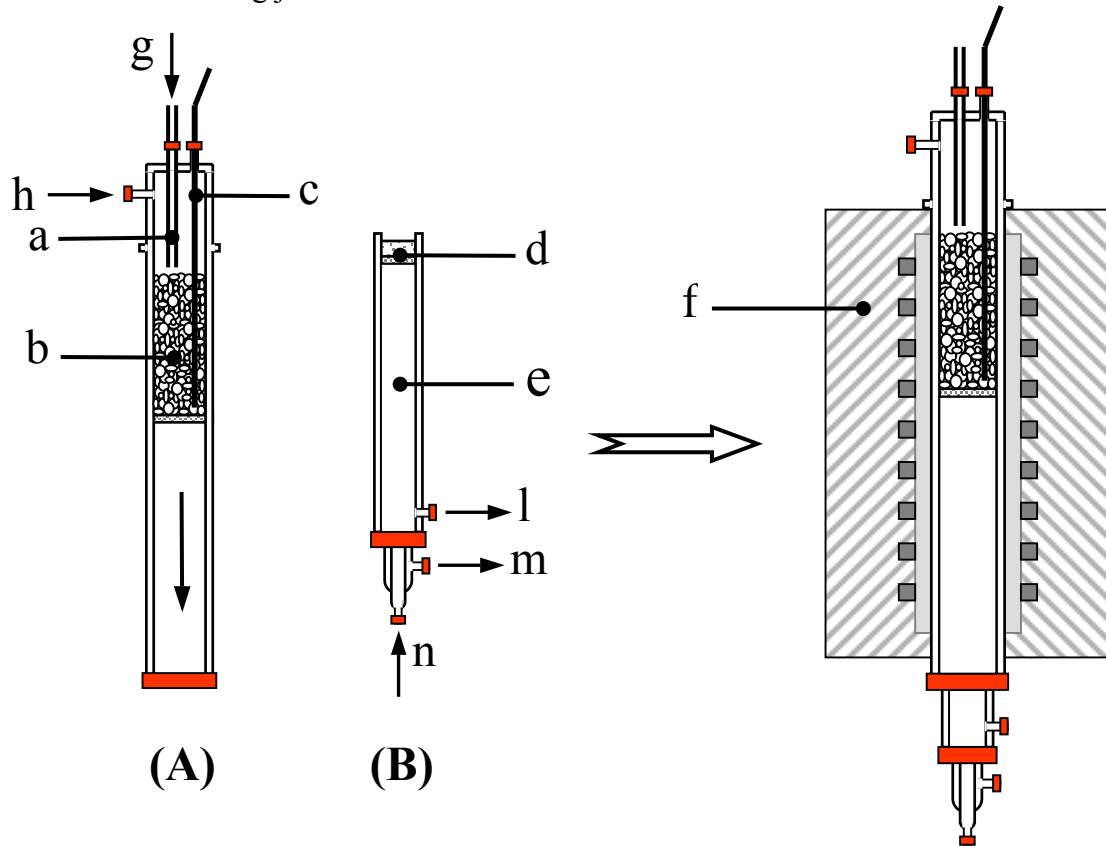


Fig. 1 Recycle reactor layout. (A) pre-heating zone: a, alumina pipe; b, alumina pellets; c, thermocouple; g, inlet water; h, inlet gas; (B) reaction section: d, sample holder; e, cooling jacket; l, outlet gas; m, outlet cooling water; n, inlet cooling water; f, tubular electrical oven.

The reactor was provided by an alumina pipe, used in the reactivation stage for feeding water inside the pre-heating zone to produce steam, and by an external recycle loop, with a gas recirculation pump, in order to obtain high linear velocities in the reactor, thus reducing the mass transfer resistance toward the sorbent particles.

The laboratory equipment was fed with a synthetic flue gas, containing SO₂, CO₂, air and N₂. The total flow rate of the pre-mixed gas has been set to 2,15 NI/min with a partial pressure of 1300 ppm SO₂, while a flow rate in the range 45-55 NI/min has been measured downstream the recirculation pump. Gas sampling and analysis has been performed through a continuous gas analyzer (Horiba PG-250), provided by IR detector, to monitor the outlet gas concentrations; moreover, after each experimental run, the inlet SO₂ concentration in the flue gas has been measured by-passing the reactor for a few minutes.

Consequently, the on-line results were obtained in the form of outlet SO₂ and CO₂ concentrations as a function of time, allowing the determination of the characteristic sulfation and calcination curves. The typical trends evidenced experimentally are shown, for the sake of example, in figures 2-a for SO₂ and 2-b for CO₂. The sulfur fixed on the sorbent, as well as the amount of CO₂ produced by CaCO₃ decomposition, were evaluated from these data by integration with respect to time of the area bounded between the curves obtained with and without limestone inside the reactor. Sorbent conversion (S/Ca) is computed as follows:

$$\frac{S}{Ca} = \frac{\text{SO}_2 \text{ moles adsorbed}}{\text{initial moles of Ca(OH)}_2} \quad (3)$$

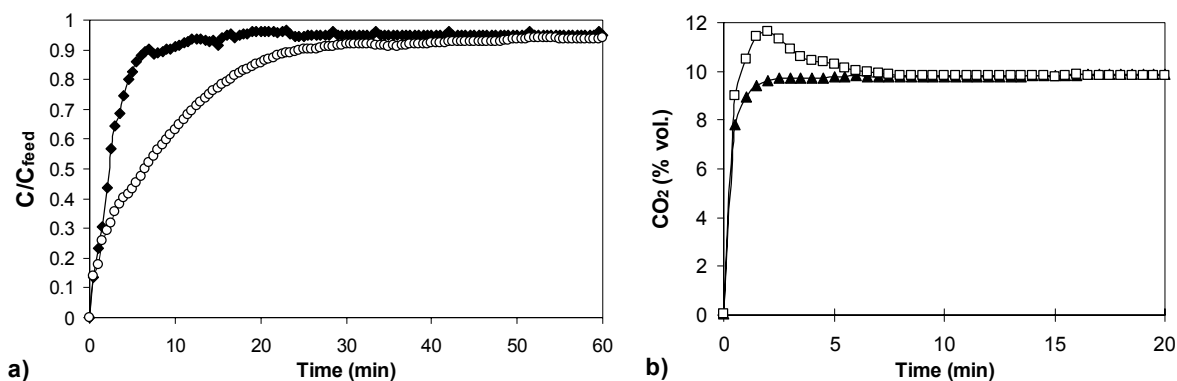


Fig. 2 Examples of the experimental curves: a) SO_2 measured trends with (○) and without (◇) limestone; b) CO_2 desorption curves with (□) and without (▲) limestone.

The calcium utilization has been also evaluated by means of chemical analyses performed with inductively coupled plasma - optical emission spectrometry (ICP-OES, Perkin-Elmer Optima 2000 DV) on the spent sorbents. ICP analyses provide informations about the unreacted CaO , theoretically available for a new desulfurization test, and an independent way to measure the overall ($\text{CaSO}_3 + \text{CaSO}_4$) sulfur amount fixed on limestone.

RESULTS AND DISCUSSION

Several preliminary desulfurization tests were performed with ground marble (high purity CaCO_3) to verify the reliability of the experimental procedure, which has been found to be satisfactory; the measured conversion values were all in the range 21-26%. Then, it was investigated the influence of three different commercial limestones on SO_2 removal; in particular, the degree of sulfation of the three samples was calculated to be 25-28% for Limestone A, 24-29% for B and 26-30% for C. These S/Ca values are very close to each other, showing that the three sorbents had similar SO_2 removal efficiency. These results underlined that the main problem of the process is related to the partial conversion of the solid CaCO_3 , with consequent high disposal costs.

As reported in figures 2-a and 2-b, the process initially involves simultaneous calcination and sulfation, then only sulfation of the calcinated sorbent was observed. As mentioned before, the decomposition of CaCO_3 at high temperature, through a reduction of the solid volume, produces a porous CaO , which begins to quickly react with SO_2 to form calcium sulfate and sulfite. Sulfation products are usually formed close to the surface of the sorbent particles and its larger molar volume causes pores plugging, which reduces the diffusion of SO_2 through the product layer, preventing full calcium utilization.

Reactivation of the partially utilized limestone by steam hydration [5-6] has been performed, foreseeing the possibility to recycle back the hydrated products to a new desulfurization stage, so as to enhance the overall sulfur uptake of the sorbent.

In situ steam reactivation were carried out at 250°C for 30 minutes, by pumping 0,4 ml/min of water inside the pre-heating zone of the reactor; the reactor was also flushed with nitrogen, 1,5 Nl/min, to improve the contact between steam and the spent sorbents. Steam hydration leads to the formation of $\text{Ca}(\text{OH})_2$, which has a molar volume larger than the unreacted CaO ; therefore, the reactivation breaks the sulfate/sulfite shell formed during the desulfurization step allowing, respectively, the exposure of fresh material for a further sulfation run and a better diffusion of SO_2 toward the solid sorbent. As reported in table I, all the samples were restorable with steam and it was possible to reach an high sorbent conversion resulfating the hydrated products.

Sorbent	Run Number					Overall S/Ca %
	I	II	III	IV	V	
Limestone A	28%	11%	18%	7%	6%	70%
Limestone B	24%	21%	11%	6%	5%	67%
Limestone C	30%	24%	18%	7%	8%	87%

Tab. I Limestones utilization in a cycle of sulfation and reactivation tests.

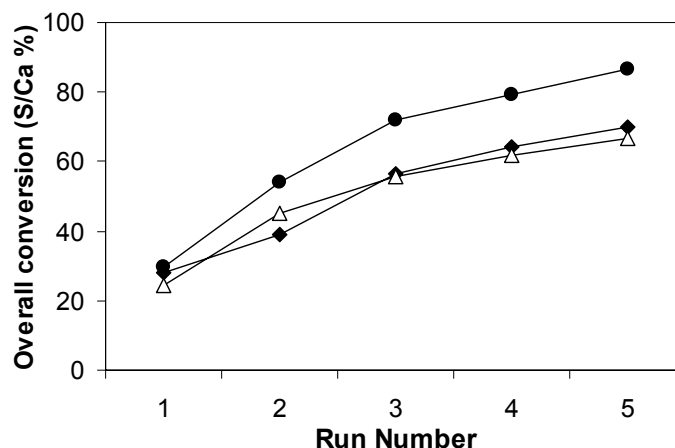


Fig. 3 Effect of sequencing reactivations on the overall sorbent conversion: 10,7% CO₂; 3,8% O₂; 1300 ppm SO₂; (♦) Limestone A; (Δ) Limestone B; (●) Limestone C.

One of the investigated sorbents, Limestone C, was more reactive than other ones, while Limestones A and B had a similar behavior (figure 3). Moreover, experimental outcomes have shown that spent sorbents could be reused in several cycles of sulfation and reactivation increasing the total sorbent utilization up to 87%. After a sequence of desulfurization tests, a uniform sulfation has been reached inside the sorbent particles; the degree of sulfation decreases after each test and, in particular, it has been found a negligible increase after four experimental runs.

It should be noted that the overall solid utilization has been greatly increased since the reactivation can be carried out several times on the same sorbents; a good recovery in the spent sorbents reactivity it was observed mainly in second and third reactivation step.

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Numerical modeling of NO_x emission in a highly diluted laminar premixed flame

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ABSTRACT

The continued effort to find both high-efficiency and low-emission power cycles makes different mixtures attractive to use in a gas turbine power plant. Wet cycles, CO₂ separation/capture and biogas combustion are processes that involve high concentrations of the inert gases H₂O, CO₂ and N₂ [1]. It has been shown earlier that combustion in humidified air lowers the NO_x formation, both in premixed and diffusion flames [1,2,3]. Decrease in combustion temperature, dilution effects and chemical effects may all be reasons for the NO_x reduction. Here, the latter two effects were investigated for a laminar premixed natural gas flame diluted with H₂O, CO₂, N₂ and Ar, operated at a constant combustion temperature of 2000K. The result showed that the NO reaction rate is only dependent on O₂ concentration at constant combustion temperature. O and O₂ are at chemical equilibrium in the post-flame zone.

INTRODUCTION

New high-efficiency power cycles and environmentally friendly cycles have introduced combustion atmospheres that differ from the traditional hydrocarbons/air mixtures. These new combustion atmospheres have attracted greater attention toward understanding why the NO_x emission in a flame is reduced. Although it is generally accepted that thermal NO_x increases with O-atom concentration, several reasons for the decrease in O atoms have been suggested as an explanation [3]: dilution effects, equivalence ratio change and O-atom suppression. These different effects have a reduction in O atom concentration in common, and reduction in O atoms will undoubtedly suppress the production of thermal NO_x. If the flame is diluted, while maintaining the same equivalence ratio, the combustion temperature is decreased, which reduces the NO_x. To maintain the same combustion temperature, the flame has to be operated under richer conditions. Thus, less oxygen will be present in the post-flame zone, if chemical equilibrium exists between the O-atoms and the O₂ molecules, the concentration of the O atoms will also be reduced. Finally, it is suggested [3] that the reaction $O + H_2O \rightarrow 2OH$, promoted by H₂O, suppresses the O atom concentration.

THEORY [4]

The thermal NO_x mechanism consists of three elementary reactions. These are usually referred to as the extended Zeldovich mechanism.



In a fuel-lean flame, the reactions can be separated into the fuel reaction zone and the post-flame zone. In the fuel reaction zone, in which the radical pool is significant, the third Zeldovich reaction occurs. In a practical combustor, its contribution to the total NO_x production is very small. The first and second Zeldovich reactions generate NO in the post-flame zone as long as the temperature is sufficiently high ($>1800\text{K}$). Since the first reaction is much slower than the second it will govern the reaction rate of NO. The process is known to be exponential in combustion temperature. If one invokes all forward and backward reactions for the three Zeldovich reactions, the reaction rate for the NO can be expressed by the species concentration. By introducing some assumptions, the expression can be simplified to be dependent on only combustion temperature, nitrogen concentration and the oxygen concentration in the post-flame zone.

$$\frac{d[\text{NO}]}{dt} = k_{1,f}[\text{O}][\text{N}_2] - k_{1,b}[\text{NO}][\text{N}] + k_{2,f}[\text{N}][\text{O}_2] - k_{2,b}[\text{NO}][\text{O}] + k_{3,f}[\text{N}][\text{OH}] - k_{3,b}[\text{NO}][\text{H}]$$

In the post-flame zone, the relevant time scales are sufficiently long for the O_2 and O to be assumed to reach their equilibrium values. The O atom concentration can be related to the concentration of O_2 through the concentration equilibrium constant:

$$K_{\text{O,Teq}} = \frac{[\text{O}]_{\text{eq}}}{[\text{O}_2]_{\text{eq}}^{1/2}}$$

Since the first reaction is rate-limiting, all N atoms that are formed in the first reaction are immediately consumed by the second reaction. By this, one can assume that the N atoms have reached the steady state.

$$\frac{d[\text{N}]}{dt} = k_{1,f}[\text{O}][\text{N}_2] - k_{2,f}[\text{N}][\text{O}_2]$$

As the NO is not likely to reach chemical equilibrium within the available time-scale, the reverse reactions can be neglected. Under these assumptions, the simplified expression for the NO reaction rate in the post-flame zone is formulated:

$$\frac{d[\text{NO}]}{dt} = 2k_{1,f}[\text{O}]_{\text{eq}}[\text{N}_2]_{\text{eq}} = 2k_{1,f}[\text{O}_2]_{\text{eq}}^{1/2}[\text{N}_2]_{\text{eq}}$$

Accordingly, the NO production rate is dependent on combustion temperature and air-to-fuel equivalence ratio. The combustion temperature and the air-to-fuel equivalence ratio are coupled through the fuel and air composition. When a flame is diluted with a non-reacting or quasi-reacting species, the flame temperature decreases due to the increased specific heat capacity. At a larger degree of dilution, the flame has to be operated under richer conditions in order to maintain the same combustion temperature.

MODELING

To model the flame, a one-dimensional flame code with a detailed chemistry was used. The flame code was developed by F. Mauss et al.¹ and solves the combustion evolution for a one-dimensional laminar and premixed flame. A detailed chemistry, developed by Warnatz [5] and improved by Zeuch [6], was used to model the chemical kinetics. The NO_x production was described by a NO_x mechanism [7], including thermal, prompt and N_2O -intermediate. Altogether, the mechanisms consist of 116 species and 1389 reactions. However, at temperature above 1800K, the thermal NO_x is dominating.

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Four different diluents, argon, carbon dioxide, water and nitrogen, were mixed one at a time with the synthetic air (20.95 mole % oxygen and 79.05 mole % nitrogen). All cases were investigated at atmospheric pressure and with a maximum combustion temperature of $2000\text{K} \pm 0.4\text{K}$. The fuel was natural gas and the inlet temperature for the fuel-air-diluent mixture was 800K . The equivalence air-to-fuel ratio, ϕ , is based on non-diluted air mixtures. The degree of dilution, Ω_{mass} , was increased from 0% to 33%, based on mass of diluent over mass of non-diluted synthetic air. All combustion properties were collected at a point at which NO had reached a constant gradient. The gradient, $d[\text{NO}]/dx$, for the NO was calculated using a second-order difference method. The production rate of NO was obtained by multiplying the local gas velocity, S_{LOC} , in the 1D flame by the gradient for NO.

$$\frac{d[\text{NO}]}{dt} = S_{\text{LOC}} \frac{d[\text{NO}]}{dx}$$

RESULTS

The flame profile consists of a fuel combustion zone and a post-flame zone. Besides the NO reactions, most of the reactions occur in the combustion zone. In Figure 1, the $[\text{NO}]$ and the ratio between $[\text{O}]$ and $[\text{O}_2]^{1/2}$ are plotted for the dry condition and for diluted conditions. At the start of the flame profile, the NO gradient is large but immediately approaches a constant value. For diluted conditions, the NO concentrations are lower. Furthermore, the ratio between $[\text{O}]$ and $[\text{O}_2]^{1/2}$ approaches a constant value at the same time, independently of diluent and the degree of dilution. Equilibrium between O and O_2 seems to appear as soon as the fast reactions are over. In Figure 2, the laminar flame speed is shown as a function of dilution. The flame speed decreases with increased dilution, especially for H_2O and CO_2 . The specific heat capacity for the diluents can be arranged Ar, N_2 , CO_2 and H_2O in order of size. This is reflected by larger equivalence ratio for diluents with higher heat capacity.

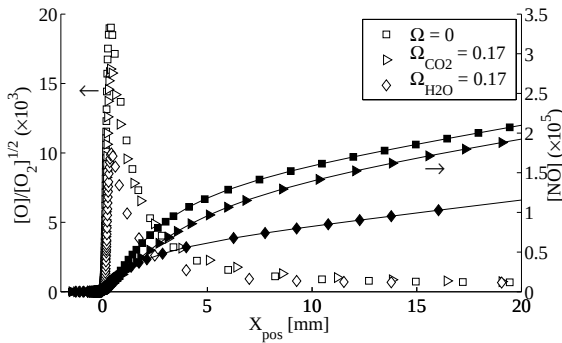


Figure 1. The laminar flame profile demonstrates how O/O_2 reaches equilibrium. In the post-flame zone, NO reached a constant gradient, but not equilibrium.

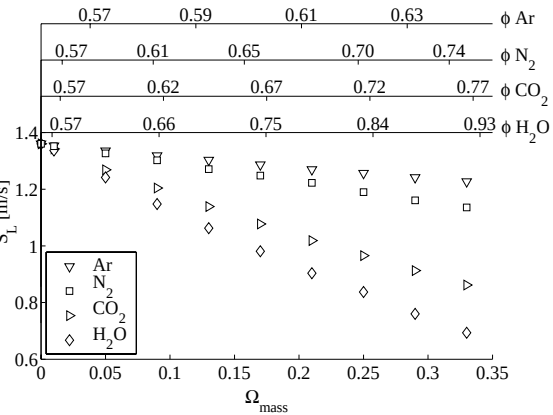


Figure 2. The laminar flame speed (S_L) as a function of the degree of dilution. For each diluent, the corresponding equivalence ratio is shown at the top.

The rate of formation of NO decreases with increased dilution. In Figure 3, it can be seen that flames diluted with H_2O have a strong reduction in reaction rate. This reduction is less strong with CO_2 , and for N_2 and Ar rate of formation of NO behaves similarly. Figure 4 shows that a proportional dependency exists between both $[\text{O}_2]^{1/2}[\text{N}_2]$ and $[\text{O}][\text{N}_2]$. The proportionality constant is independent of the kind of dilution.

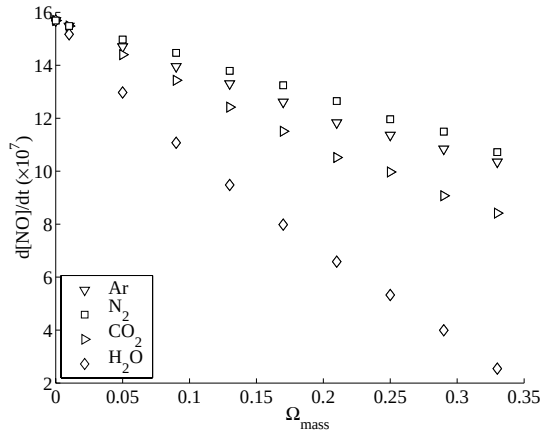


Figure 3. The rate of formation of NO as a function of degree of dilution.

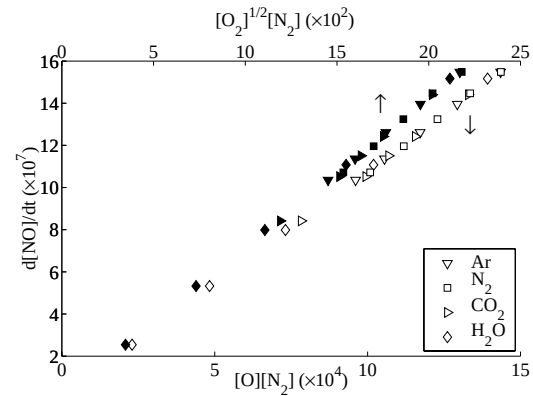


Figure 4. The rate of formation of NO as a function of O/N_2 , bottom scale, and O_2/N_2 , top scale.

CONCLUSIONS

- The rate of formation of NO is strongly reduced by addition of any diluents at constant combustion temperature. For nitrogen and argon, the reduction is about 35% - 45% at 33% dilution. For water, it is as good as 85%.
- Since equilibrium exists between O and O_2 , the reduction of the rate of formation for NO is only a result of reduced O_2 concentration in the post-flame zone. This means that if the diluent has high specific heat capacity, the combustion must use a richer flame to maintain the same combustion temperature. Richer combustion leads to less O_2 in the post-flame zone, which reduces the rate of formation of NO.

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Nano-sized Organic Carbon Emissions of an in-use Vehicle Powered with a 'Common Rail' Diesel Engine

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Keywords: particle sizing, UV extinction/scattering spectroscopy, diesel exhaust

FOREWORD

In the last years, a large amount of work has been devoted to qualify and to quantify the carbonaceous condensed by-products of combustion in a variety of systems : flames, burners and i.c. engines. As technological advancements leads to substantial improvements both in enhancing performances and in reducing emissions, the need arises of updating the available data base of physical, chemical and optical properties of those species, as well as of their emission rates. One of the recent and most striking improvements in engines technology is the introduction on large-scale markets of the very-high-pressure injection, compression-ignited engines, also referred to as "common rail" diesel engines. This paper provides work-in-progress new data on this topic.

TESTS AND PROCEDURES

We present results of measurements taken on the exhausts of an in-use, last generation (2003) vehicle, equipped with a "common rail" diesel engine. The vehicle was run at the chassis dynamometer on a standard ECE + EUDC cycle, corresponding to four repeated urban drive cycles (4,08 km) and one extra-urban drive cycle (6,81 km), for an overall covered distance of 10,89 km.

Measurements on air-diluted exhausts

Standard measurement methods were used to characterize both regulated and some unregulated emissions in air-diluted exhausts. The Constant Volume Sampling (CVS) procedure yielded both time-resolved (10 points/s) and time-integrated values of mass flow rates of O₂, CO₂, CO, NO_x and THC (total hydrocarbons).

The same air-diluted exhausts have been flown in a 20-m long tube and explored on-line by means of broadband UV extinction spectroscopy, spectrally resolved in the 200-400 nm band. The resulting extinction spectra have been inverted in terms of gaseous components (NO and NO₂) and particulate matter (organic carbon, OC, and elemental carbon, EC), as functions of the cycle time, with a 1 s time resolution.

Measurements on water-trapped species

Furthermore, undiluted exhausts have been flown and cooled in a heat exchanger, in order to condense and to collect the water produced in combustion, along with any hydrophilic matter trapped in the liquid phase, for off-line analysis. To this purpose, each drive cycle was repeated twice, with and without the cooling, respectively, in order to compare the effects of the condensation process.

The collected samples, in the form of aqueous suspensions/solutions. have been then characterized off-line with a number of optical, physical and chemical analysis.

Firstly, extinction and scattering spectroscopy were applied, leading to the retrieval of

volume-averaged size (d_{63}) and of number concentrations of hydrosols, as well as of the complex refractive index in the spectral band 200-400 nm.

Next, electrospray-high resolution nano-differential mobility analysis (ES-nDMA) and dynamic light scattering (DLS) were carried out, in order to retrieve the size distribution function of the hydrosols. Finally, a TOC (Total Organic Carbon) analysis has provided quantitative measurements of the carbon content of the aqueous suspension.

RESULTS AND DISCUSSION

CVS data confirmed the compliance of the vehicle under test with the EURO III limits (Table I).

As a preliminary outcome, we highlight here the possibility to retrieve quickly and easily the overall efficiency of chemical-to-mechanical energy conversion in a real vehicle, exploiting the data of CO_2 emissions, indicative of the chemical energy, and the corresponding dynamic regimes of the vehicle during the drive cycles, accounting for the mechanical work.

Time-resolved extinction spectra on air-diluted exhausts revealed the existence of two different classes of absorbing condensed matter, the former identified as ‘soot-like’ particles, the latter attributed to organic carbon with aromatic functionalities. Both show strong increases at higher vehicle’s speeds and loads.

Comparison of values of organic carbon flow rates with and without cooling and water condensation, both from CVS data and uv extinction spectra, reveals that a large fraction of uv-absorbing species is removed from the exhausts and is trapped into the condensed water.

The aqueous samples have been analysed by means of Optical Ultraviolet Extinction and Scattering Spectroscopy, nano-Differential Mobility Analysis and Total Organic Compound (TOC) Analysis.

The extinction spectrum, reported in Fig.1, shows a strong absorption band for $\lambda < 250$ nm, with a peak value as high as 120 cm^{-1} at $\lambda = 200$ nm, whereas the samples are nearly transparent above. The observed peak values are comparable or even higher than those measured in condensed samples obtained from gasoline and older diesel engines in previous investigations [1].

The scattering spectrum of the aqueous suspension exceeds that of the ‘reference’ distilled water, and the resulting “excess” scattering vanishes at $\lambda \approx 240$ nm, implying that the real refractive index of hydrosols equals that of the water $n_w(240 \text{ nm}) = 1,37$.

Ratioing the scattering intensity, shown in Fig.2, which scales as the sixth power of the particle size, to the spectral extinction coefficient, whose intensity is a linear function of the particles volume fraction, allowed us to retrieve the volume-averaged particle size, with values d_{63} in the range 8-10 nm. These averaged values are strongly biased by the larger particles, even though their number concentration is vanishingly low.

Electro-spray nano-DMA analysis of the aqueous samples, size-resolved in the range 1-10 nm, gave as a result the size distribution function shown in Fig.3, which peaks at nearly 3 nm and spreads out between 2 and 6 nm. These data confirm and detail the optical data, in terms discussed above.

TOC analysis gave quantitative results of carbon content, in good agreement with those estimated from optical extinction of water samples without soot, whereas the corresponding values for soot-containing samples turned out to be much higher than those retrieved optically.

CONCLUSION

The reported experimental results show that the tested vehicle, powered by a “common rail”

diesel engine, although complying with current emissions limits, yet releases amounts of nano-sized organic carbon comparable to those of previous-technology i.c. engines. Due to the fastly increasing diffusion of such new generation vehicles, it is worthwhile to keep on studying and detailing their operating specifications, at least from the viewpoint of environmental impact, which is an issue far from being fully assessed.

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Table I - Emissions and Fuel Consumption

Species	Values of the Test					Fuel Consumption		Particulate
	CO	HC	NOx	HC+NOx	CO2	L/100km	g/km	
Units	g/km	g/km	g/km	g/km	g/km	L/100km	g/km	mg/km
NEDC	0.222	0.022	0.516	0.538	163.8	6.198	51.75	24.37
EUDC	0.002	0.004	0.371	0.375	144.0	5.434	45.37	44.43
Total EDC	0.085	0.011	0.425	0.436	151.4	5.720	47.76	36.92
EURO III Limits	0.640	-	0.500	0.560	-	-	-	50.00

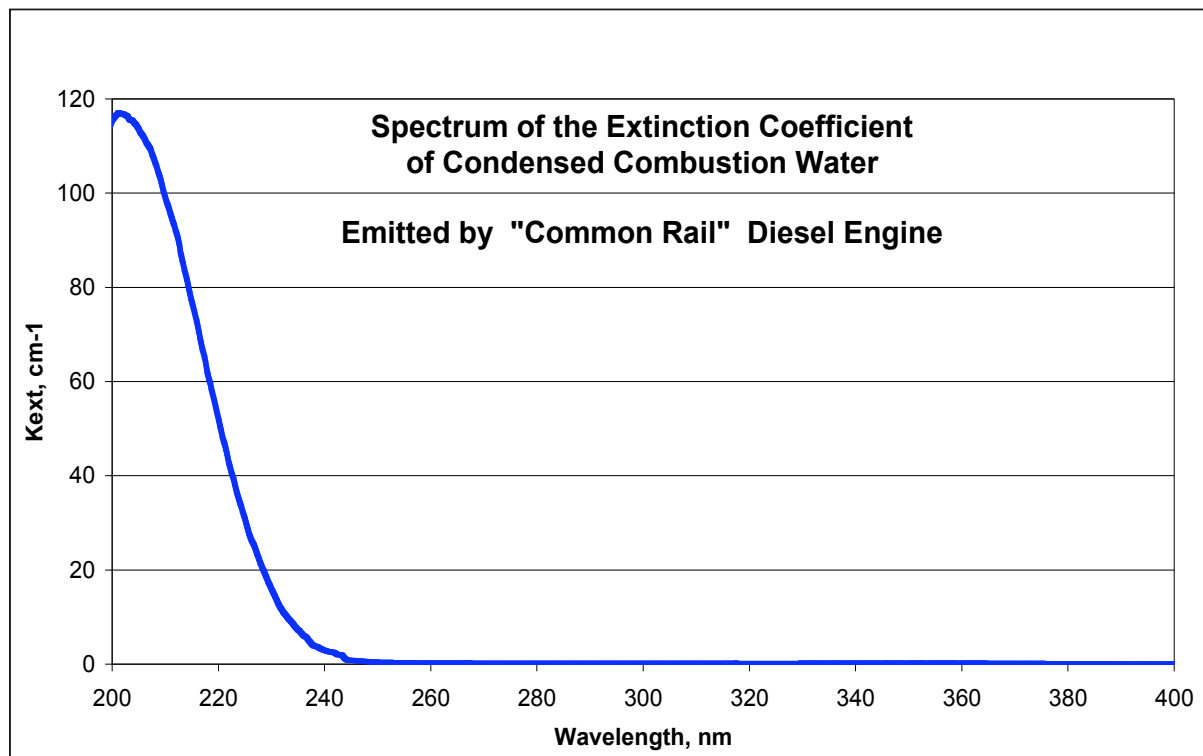


Figure 1 - Extinction Spectrum

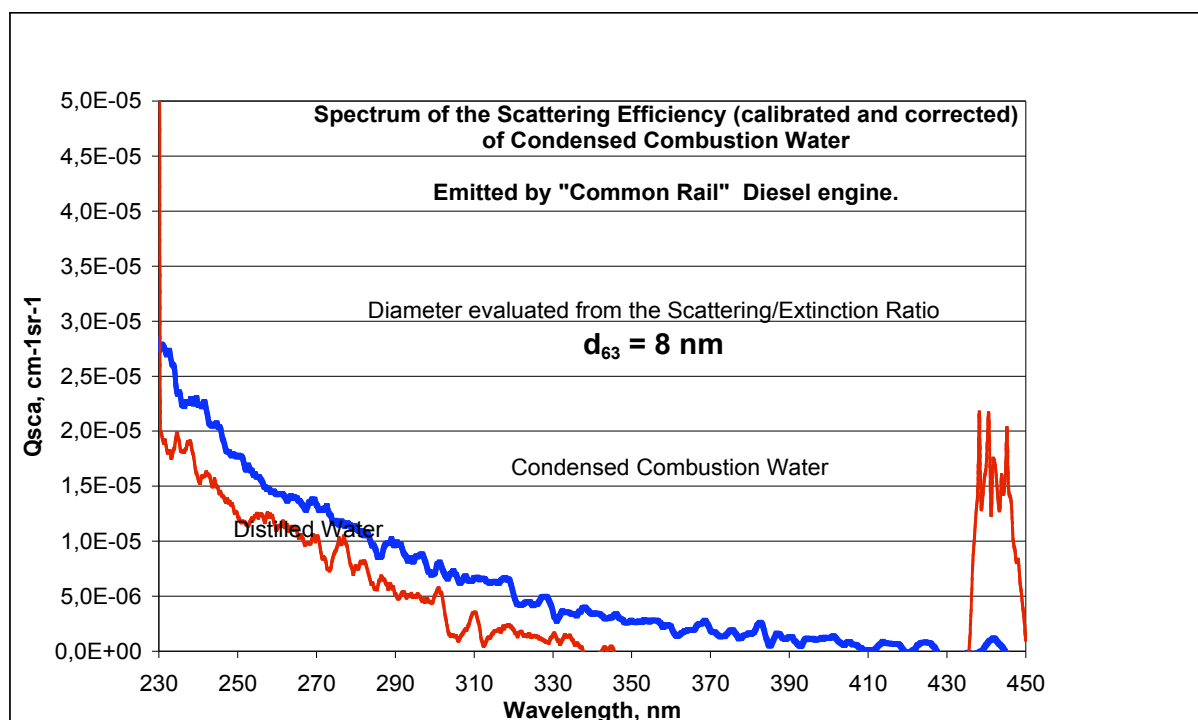


Figure 2 - scattering spectrum

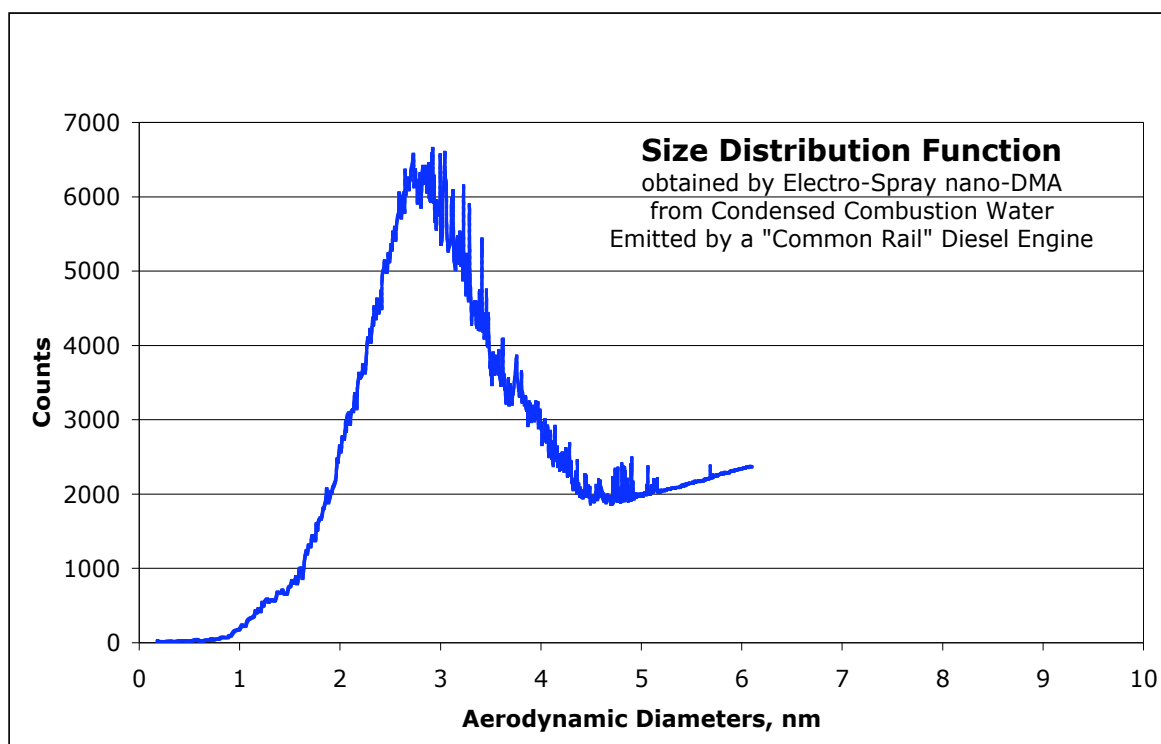


Figure 3 - nDMA size spectrum

Characterization of atmospheric particulate matter by thermal analysis

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INTRODUCTION

One of the most important problems for air quality management is the pollution from fine particulate matter, PM₁₀ and PM_{2.5}. Particulate Matter (P.M.) is one the most important pollutant monitored for the air quality assessment and in particular PM₁₀/PM_{2.5} have direct effects on human health. This pollutant deals with a wide range of sources either anthropogenic, natural or “secondary”, as well as with climatological and meteorological phenomena [Schnelle-Kreis 2001, Lunz 2001]. Many research studies have shown that the composition of the PM_{10/2.5} is very different, depending on the monitoring site [Paoletti 2001]. The complex mixture of inorganic and organic compound dealing with the particulate matter composition is one of the main aspects either for their characterization or for the sources emissions apportionment. Carbonaceous materials make up a large fraction, sometime dominant, of ambient particles and depending on their nature it is possible to distinguish the emitting sources, either primary or secondary ones. The carbonaceous fraction is composed of elemental carbon (EC) also called Black Carbon (BC) (graphitic carbon mostly emitted by combustion processes) and organic carbon (OC) (a mixture of hydrocarbons and oxygenates compounds) can be emitted either directly from sources (primary OC) or formed in ambient air. The long range transport phenomena and the consequential interaction of the aerosols with the atmospheric chemistry is, at the present time, one of the main research topics. The emitted soot particles (EC) through coagulation, condensation of aerosol organic compounds and cloud processing change their chemical composition. The complex mixture of OC carbon is constituted of hundreds of organic compounds of different types (aliphatic, PAH etc.) and they also interact with the organic atmospheric chemistry. The researchers were trying to identify the main constituents of this pollutant and the biggest work is now focusing on the identification of molecular constituents and potential tracers that will possibly explain the various sources contributions.

Many techniques are implemented to analyze the collected particles either for the identification of the amount of carbonaceous constituents or for the speciation of the organic components [Fraser et al. 2002, Chow et al. 1993]. Some techniques for the determination of elemental and organic carbon are accepted by the USEPA but the results of recent round robin tests show very high uncertainty in the experimental results [Puxbaum et al. 2001].

The first tests of the characterization of the PM by thermogravimetric balance (TGA), coupled with FTIR, are presented. The aim of this activities is to developed a method to characterize either the ambient air particles or the directly emitted ones, in particular from combustion processes.

PARTICULATE MATTER INVESTIGATION

The complex research work of studying the particulate matter nature, either for air quality monitoring or for the emission characterization, in particular referring to the combustion processes, needs a detailed and methodological approach. In figure 1 all the steps are shown: in our research activities we focused on six main topics: the sampling, the analysis, the

evaluation and elaboration of the air quality data, the meteorological characterization, the emission inventory and the dispersion models. All these phases are strictly correlated one to each other. Firstly, starting from the monitoring of the air quality and the acquisition of meteorological parameters that after appropriate elaboration can well describe the type of pollution of the interesting site.

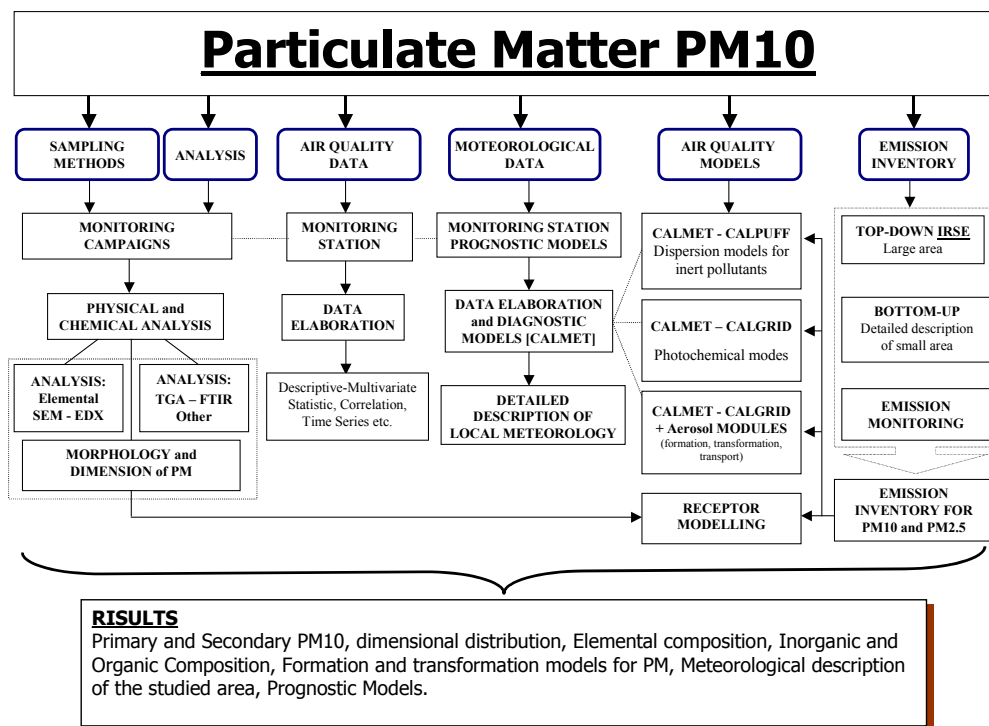


Figure 1 Methodological approach to the study of particulate matter.

Secondly, the emission inventory estimation is one of the main steps for air quality management due to the apportionment of source contribution; for this purpose it is important to use new and detailed emission factor. Then, the sampling and analysis of the PM₁₀ are necessary to characterize the particles by chemical and physical points of view. The last phase is the modeling one, used to estimate how the emission scenarios together with meteorological condition, deal with the pollutant concentration in air.

EXPERIMENTAL

Sampling

Sampling techniques used for characterization of PM are very different concerning to the type of the chemical and physical analysis that should be done. We used either high volume sampler (HVS), Andersen GMW Instruments, with operating flow rate of 1.13 m³/min and low volume sampler (LVS), Tecora TCR, with sampling head USEPA-cfr part.50 for PM₁₀ and USEPA Wins impactor for PM_{2.5}, with operating flow rate of 16.7 liter/min.

For collecting the aerosols samples we used quartz fiber filters Ø47 mm diameter and 210x240 mm quartz filter paper used with the two different particulate matter samplers. We also used POLICARBONAT PC40 AOX filter Ø47 mm, Ø0.4 µm pore diameters with the LVS. These two types of filter media were used for chemical speciation of the particulate matter: the quartz fiber filters were used, due to their inert behavior, for thermal analysis and the polycarbonate filters for the morphological and dimension analysis. With the HVS sampler we performed 24 hr a day and of 27 m³ of air sampling and with the LVS we

collected the particles for 15 minutes every 2 hr during 24 hr for a total amount of 2 m³ of air.

Analysis

The polycarbonate filters were analyzed with scanning electron microscope SEM-EDX, Jeol 6100, equipped with Oxford ISIS EDX System. This technique allows to analyze the particulate matter with various magnification x100 to x50.000, with very high resolution and to store digitalized images. Those images are then elaborated with an image analysis software, Image-Pro® Plus, for the dimensional and morphological analysis. This software allows to identify up to 20.000 particles on each samples [100µm²] and measured for their dimensions and shapes characteristics. By the EDX system, X-ray mapping of the following elements were possibly detected on the polycarbonate filters: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Fe, Ni, Cu, Zn, Br and Pb. Post processing of image analysis was performed to correlate chemical and dimension results.

Thermogravimetric (TG) data are obtained using a Netzsch STA 409/C thermoanalyzer. Typical sample weights of 15 mg to 30 mg are employed, depending on the pollutant concentration in air the PM weights varies from 3 mg to 0.4 mg. Experimental runs are carried out using a purge gas flow (60 ml/min) either of air or nitrogen. FTIR measurements are carried out using a Bruker Equinox 55 spectrometer equipped with DTGS and MCT detectors. TG-FTIR simultaneous measurements for the on-line analysis of volatile compounds formed during TG runs are carried out coupling the FTIR spectrometer to the Netzsch TG. FTIR measurements are carried out with a MCT detector in a specifically developed low volume gas cell (8.7 ml) with a 123 mm path-length, heated at a constant temperature of 250°C. A new thermoanalyzer, TA instruments 500, was utilized for the test run. This new analyzer allows to carry out more sensible measurement due to the low values of the weight loss that should be done (10¹ µg - 10³ µg).

RESULTS AND DISCUSSION

The particulate matter samples used for this investigation were collected in Pisa in two different monitoring sites, an urban station and a rural station. The sampling was performed during two weeks one in February 2003 and the other in March 2003. The sampling were done for 24 hr per day and for seven days per week. In figure 2 an image is shown of the PM10 collected with the LVS and used for the elemental and morphological analysis.

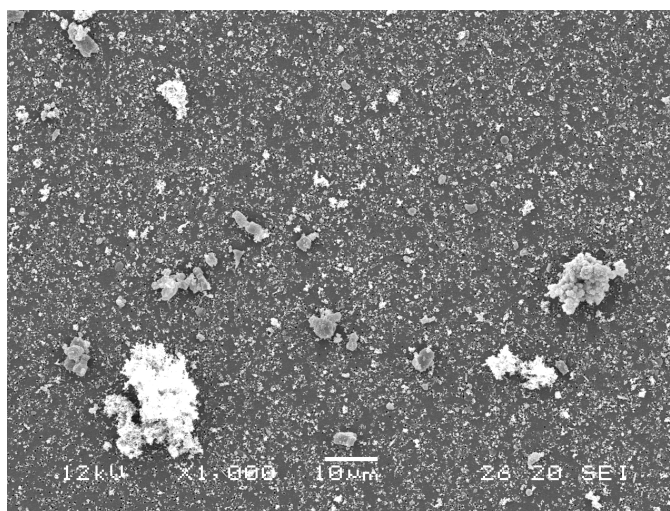


Figure 2 Particulate matter PM10 on polycarbonate filter by SEM analysis.

In table 1 preliminary results of the thermal characterization of the PM10 were reported. The main differences in the weight loss changes were related to the evolution of the organic matter present in the particles. The first step is due to the presence of moisture and then the light and heavy organic compound up to the soot particles. These results allow to identify the OC and EC fraction of the analyzed samples that were important components used for the source apportionment of the emissions, as previously said. The scanning tests were performed in air with an heating rate of 10°C/min up to 960°C followed by 20 minutes of isotherm.

Sample N°	PM10 concentration [$\mu\text{g}/\text{m}^3$]	Weight loss PM10 [wt %]				
		100°C	450°C	750°C	n.d.	Total
10SC	90	5.2	47.5	14.3	33	70.2
2SC	91	4.1	40.3	10.7	44.9	66.6
1SB	47	6.4	49.3	5.3	46.5	69.6

Table 1 Results of the thermal characterization of the PM10

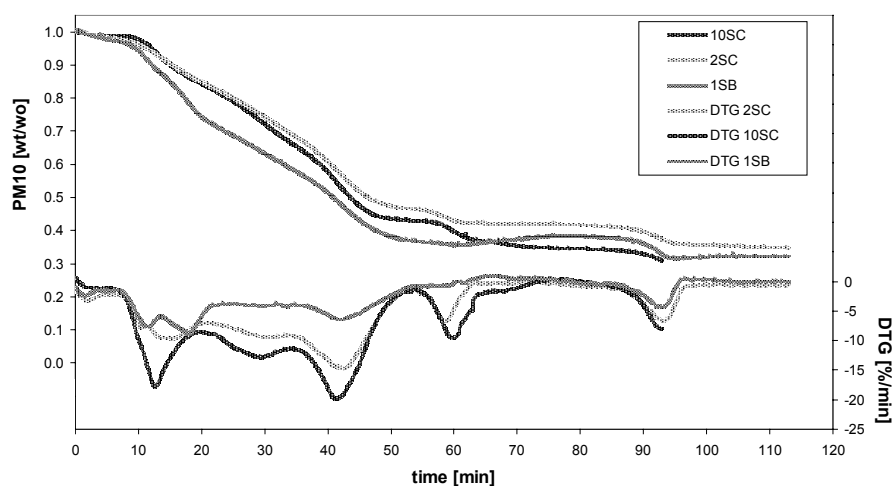


Figure 3 PM10 analyzed with TGA [HR: 10°C/min time: 960°C + isothermal run 20 min]

So far the behaviors shown in figure 3 have been detected. Studying the DTG several peaks during the weight loss tests were identified. Those peaks can be correlated firstly to the moisture release (100°C) and then to the various steps (450°C-500°C, 750°C-800°C) for volatile materials and combustion processes. The main steps to compute the organic and elemental carbon as far as their operative definitions are 450°C and 750°C. Different tests with inert gas and heating programming are now studied to upgrade the tests performances.

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The Chemical Structure of a n-Hexane Premixed Laminar Flame

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INTRODUCTION

The study of the combustion of hydrocarbons in simple combustion systems, i.e. premixed laminar flat flames, permits to obtain information on the chemical reactions through which the fuel oxidize and pyrolyze forming gaseous pollutants and particulate species.

In this paper the structure of atmospheric-pressure, fuel-rich ($C/O=0.8$), premixed n-hexane/oxygen/60%nitrogen flame was analyzed by measuring flame temperature and composition along the flame axis. Profiles of temperature, extinction and concentrations of stable combustion products including pyrolytic species, such as acetylene, benzene, polycyclic aromatic compounds (PAHs) and soot were measured.

Previous work [1], comparing ethylene and benzene flames, showed that in the ethylene flames the oxidation and pyrolytic regions were well separated whereas in the benzene flame there was a large overlapping of these two regions. In order to study the oxidation and the pyrolytic routes through which an aliphatic and an aromatic hydrocarbon with the same atom carbon number are consumed, the n-hexane flame was compared with a benzene-air premixed flame of similar flame temperature and C/O ratio ($C/O=0.77$) [2].

Moreover some considerations about the influence of the aliphatic and aromatic character of the hydrocarbon fuel on the PAH and soot formation process were done.

EXPERIMENTAL

The atmospheric-pressure-rich-premixed n-hexane/oxygen/60%nitrogen flame was produced on a water cooled sintered bronze burner (Mc Kenna, Holthuis & Associates) at C/O ratio = 0.8 and cold gas velocity = 4 cm/s.

Soot, condensible species and gaseous combustion products were isokinetically sampled by means of a stainless steel water-cooled probe (i.d.=2 mm).

Temperature measurements were performed by a fast-response silica-coated 25 μ m Pt/Pt-13%Rh thermocouple with a bead size of about 50 μ m. A fast-insertion procedure was used to avoid massive soot deposition on the thermocouple bead.

On-line gas chromatography with flame ionization detection and thermal conductivity detector were used for the analysis of light hydrocarbons (C_1 - C_6) and CO, CO₂, H₂, O₂, respectively.

Soot and condensible species were collected in a cold trap and on a teflon filter and then extracted by dichloromethane. Polycyclic aromatic hydrocarbons with molecular masses up to 300u were analyzed in the condensed species by gaschromatography-mass spectrometry (GC-MS) on a HP5890 gas chromatograph coupled with a HP5970 mass spectrometer. More detail on the experimental apparatus are given in previous work [3].

Extinction measurements were performed at $\lambda = 632.8$ nm using an Helium-Neon gas laser.

RESULTS AND DISCUSSION

Fig. 1 reports the overall structure of n-hexane flame in terms of profiles of temperature, concentration of reactant, concentrations of main carbon containing gases (CO , CO_2) and

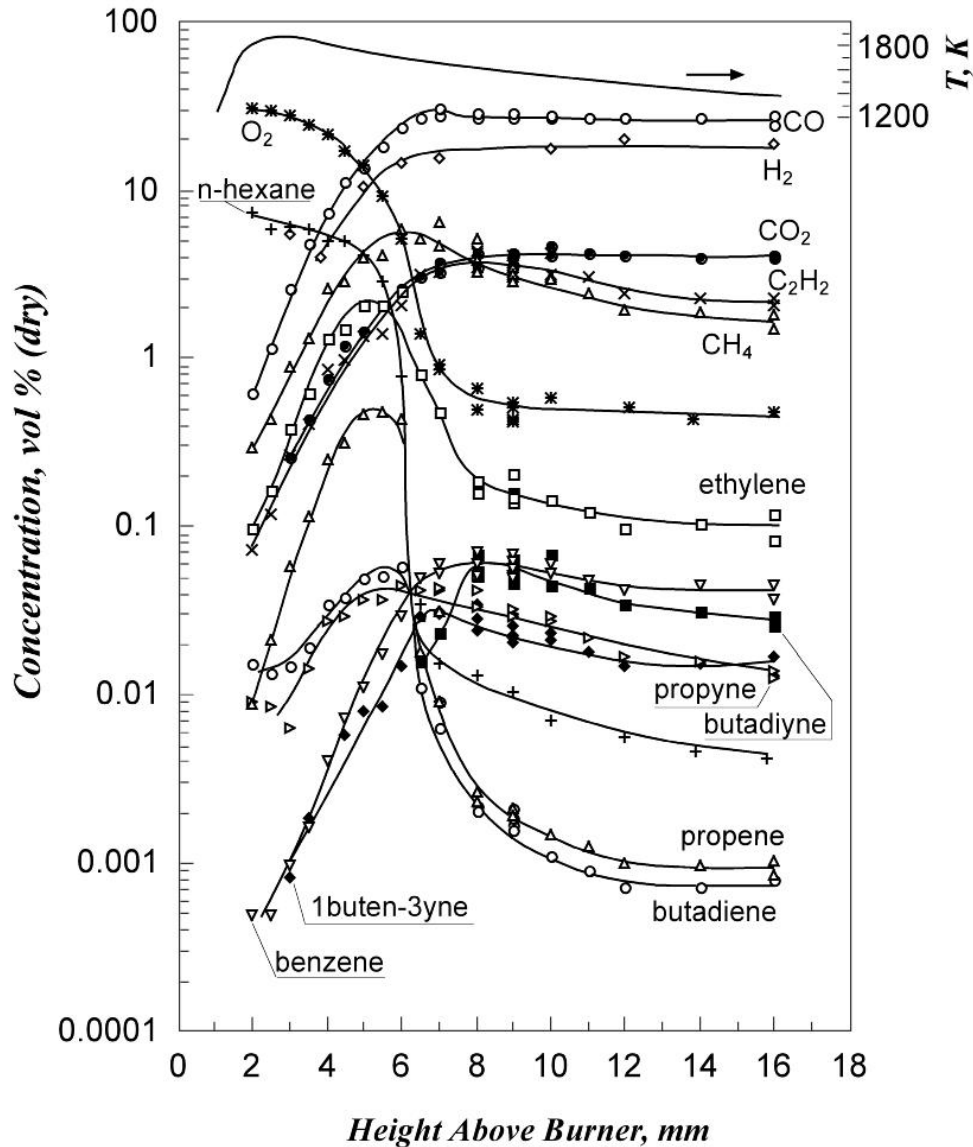


Fig. 1 Temperature and concentration profiles of reactants, CO , CO_2 and light hydrocarbons in the n-hexane flame ($\text{C/O}=0.8$, $v_o=4\text{cm/s}$).

pyrolytic hydrocarbons up to benzene.

The observation of the temperature peak position and CO concentration maximum shows that the concentration profiles are shifted about 3mm downstream the flame respect the temperature profile, due to the sampling probe effect.

Acetylene and methane are the most abundant light hydrocarbons products. The maximum concentration of methane is higher, whereas the final concentration of acetylene and methane are almost the same. Ethylene, propene and butadiene show a rise-decay concentration profile.

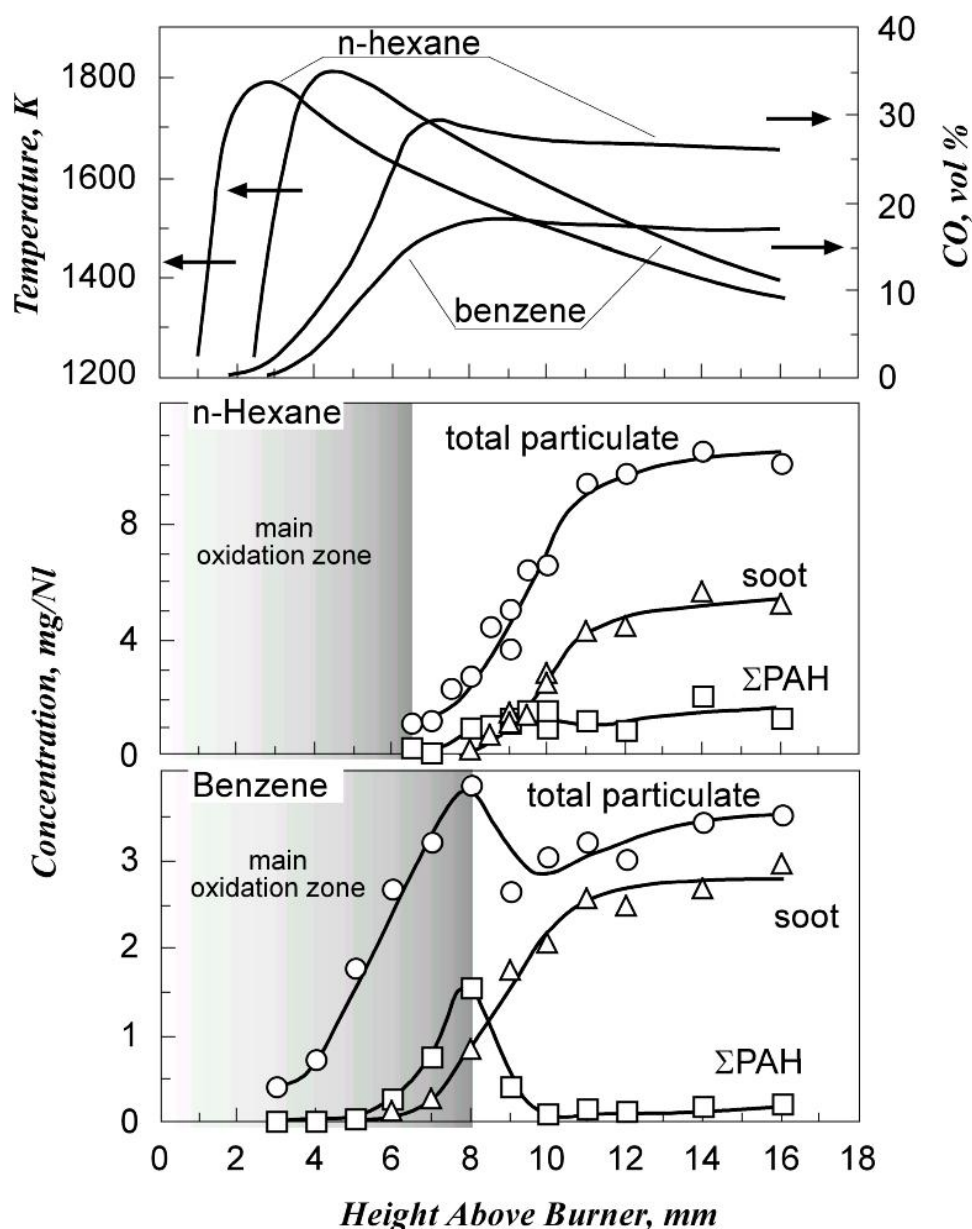


Fig. 2 Temperature and concentration profiles of PAHs, soot and total particulate in the n-hexane and benzene flames.

In the upper part of Fig.2 are reported the temperature and CO concentration profiles of the n-hexane and benzene flames. The values of the temperature at the maxima are almost the same (≈ 1800 K) and the CO maxima position show the shift of about 3 mm between the temperature and concentration measurements. In the lower part of Fig.2 are reported the concentration profiles of PAHs, soot and total particulates generated in the n-hexane and benzene flames. To correctly compare the concentrations in the studied flames it is necessary to use a multiplier of 1.5 for the concentrations in the benzene flame due to the different dilution. The maximum concentration of PAH species is almost the same for both flames, but in the benzene flames the final concentration is lower. The final concentrations of are not so different, but in the n-hexane flame the concentration of total particulate is much more higher. It is well evident the different combustion behaviour of the two fuels. In the n-hexane flame the main oxidation zone is clearly separated from the pyrolytic region, so the heavy pyrolytic species are produced downstream the oxidation zone, on the contrary in the benzene flame

there is an overlapping of the oxidation and pyrolysis processes and the particulate and the PAHs produced reach their concentration maxima at the end of the main oxidation zone.

In Fig.3 are reported the extinction profiles measured at $\lambda=632.8$ nm in the benzene and n-hexane flame. Extinction measurements in the n-hexane flame show the formation of absorbing species (i.e. heavy pyrolytic species) just downstream the oxidation zone, whereas

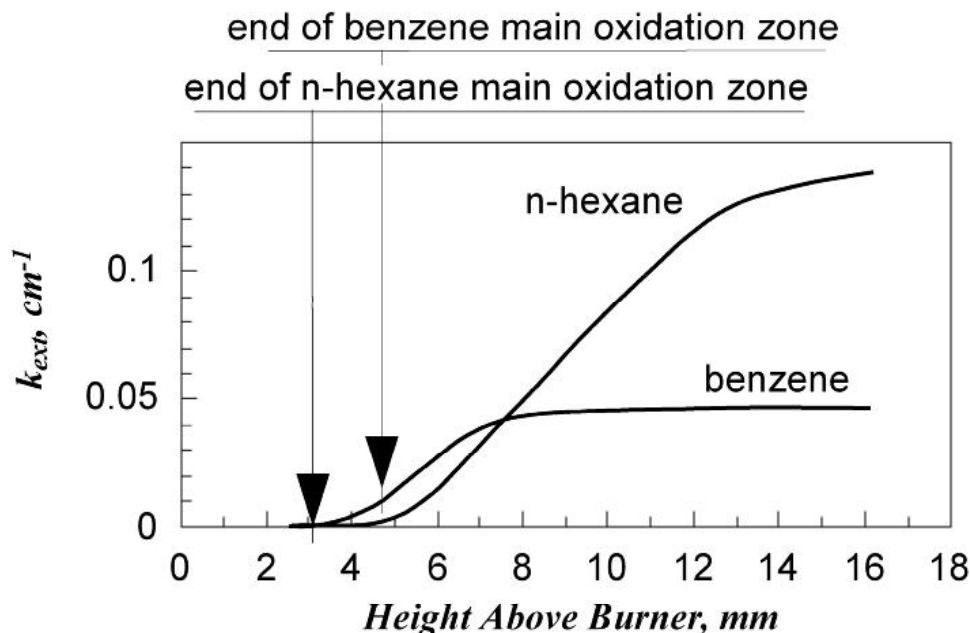


Fig. 3 Extinction profiles at $\lambda=632.8$ nm in the n-hexane and benzene flames.

in the benzene flame the extinction profile already arise in the oxidation zone.

The final values of the extinction measured in the two flames do not agree with the gravimetrically measured soot concentration (Fig. 2). This discrepancy may be due both to the absorption at flame temperature of the particulate species different from soot and to the different characteristics of the soot produced from the two different fuels [4].

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MALDI-TOF Mass Spectrometry and Size Exclusion Chromatography (SEC) approaches for molecular weight evaluation of combustion products

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INTRODUCTION AND EXPERIMENTAL APPROACH

The evaluation of molecular weight (MW) distributions of combustion products obtained burning a fuel under fuel-rich conditions is relevant in determining the mechanism of soot formation. In this work two approaches have been used to this aim: Matrix-Assisted Laser Desorption/Ionization Time-of-Flight (MALDI-TOF) Mass Spectrometry and Size exclusion Chromatography (SEC). The two techniques present complementary advantages and shortcomings: MALDI does not need standard molecules with similar chemical structures whereas this is necessary for the attribution of MW by SEC, but the preparation of samples and the choice of operative parameters are much more difficult for MALDI than for SEC analysis.

In this work the coupling of MALDI and SEC analysis allowed to obtain interesting insights on the chemical structure of the high molecular species extracted from soot.

Carbonaceous particulate was sampled in a rich premixed laminar ethylene/oxygen flame, produced on a commercial McKenna burner. The burner and the sampling system have been described in detail in previous work [1]. The particulate was washed with dichloromethane in order to extract the organic species adsorbed on it (named soot extract in the following of the work). Polycyclic aromatic hydrocarbons up to 300 u, named GC-PAH, were analyzed in the soot extract by gas chromatography-mass spectrometry (GC-MS). Soot extract, dried and weighed, was sonicated in N-methyl-2-pyrrolidinone (NMP) solvent for the following examination by SEC and MALDI.

The SEC analysis has been carried out on an individual pore PL-gel styrene-divinylbenzene column where the column particle sizes are of 5 μm and the pore dimensions are of 50 nm. This column is able to separate polystyrene standards in the 100-100,000 atomic mass units range.

A Bruker Daltonics Reflex IV MALDI-TOF mass spectrometer instrument was used in reflector mode. The instrument features the 337 nm wavelength of a nitrogen laser with a pulse length of 3 nanoseconds and an acquisition, automation and data processing software package.

RESULTS AND DISCUSSION

In previous works [2-4] Size Exclusion Chromatography (SEC) has shown to be a useful technique for determining MW of flame-formed particulates in ranges well above the limits of other conventional techniques. However, the need of suitable standards for the calibration of the system constitutes the main limitation of this technique. Indeed the effective use of the calibration method would require calibrants and solutes to be of similar structures. SEC

technique is commonly used for synthetic and biological polymers like proteins for which suitable standards are available. By contrast, complex carbon systems like combustion-formed carbonaceous materials, include unidentified molecular structures beyond the range detectable by GC-MS and consequently, suitable calibrant molecules cannot be easily defined. As observed in previous work [2-4] the use of N-methyl-2-pyrrolidone as eluent allowed to overcome these limitations and a calibration curve based on polystyrene standards has been considered reliable for the MW attribution of flame-formed samples. Nevertheless, the validation of SEC results by means of a comparison with another technique not requiring a calibration is desirable. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) seems to be suitable to this purpose since it gives directly a response in term of molecular weight without a comparison with a standard molecule. MALDI-TOF MS was introduced by Karas and Hillenkamp in 1988 [5]. This soft ionization method was soon established for the determination of high molecular weight biomolecules in a mass range even above 100,000 u. However, up to now, the MALDI technique has been mainly applied to synthetic polymers, as summarized by Nielen in a recent review [6] and only a few work has been done on carbon materials as coal, coal-derived samples [7- 8], soot extract [9]. The practical limitation of a linear TOF spectrometer is the relatively low mass resolution achievable because of the energy spread of the generated ion packet and other experimental factors such as delayed ion formation and space charge effects. The resolution can be remarkably improved by adding an ion mirror, or reflector to the time-of-flight mass spectrometer, but this limits the high MW range detectable that arrives just up to 20,000 u. Another limitation, which is particularly important when complex and unknown structure samples are analyzed, regards the choice of a suitable matrix and the modality of sample preparation and deposition onto the MALDI target. Anyway, the match of SEC and MALDI techniques can give interesting findings in soot extract analysis and this has been attempted in the present work.

A typical SEC chromatogram of a soot extract collected in the soot formation region is reported in Fig.1.

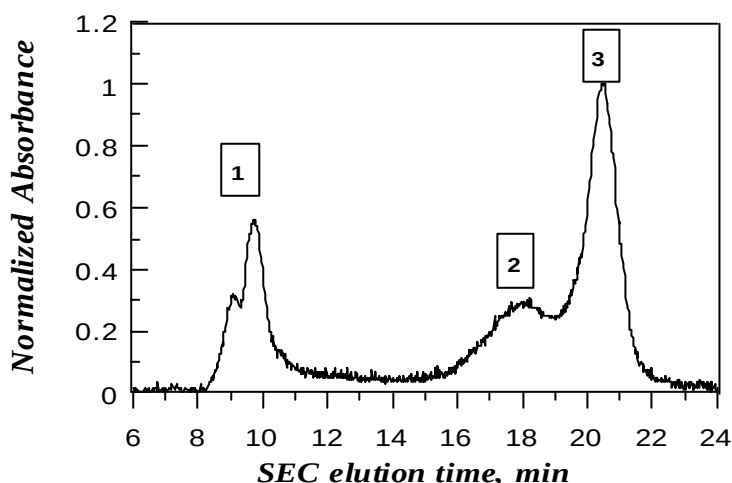


Fig. 1 Height normalized chromatogram of soot extract at $\lambda = 450$ nm.

Three different MW ranges are observable, labeled in figure with progressive numbers: in the MW region (1) the peak presents a very large distribution with two different maxima corresponding to MW very near to the exclusion limit of the column (100,000 and 200,000 u); the second region (2) corresponds to a MW just above the GC-MS threshold (800-2000u);

the third (3) and the most prominent peak is due to GC-MS PAH (200-400 u). As reported in a previous work [9] the MALDI analysis of a soot extract using sinapinic acid as a matrix showed just the presence of GC-MS PAH, i. e. (3) peak. By deflecting all the masses up to 400 u (by means of metallic plates that avoid the arrival of these masses on the detector) it has been possible to put in evidence a peak with a maximum at about 1000 u (corresponding to (2) peak in the SEC chromatogram). No masses above 2000 u have been observed, even if the MW limit in linear mode is 200,000 u, in agreement with the absence of SEC peaks in the 2,500 – 100,000 u region. The high mass SEC peak (1) was not detected by MALDI as having a MW just in correspondence of MALDI limit (200,000 u), therefore confirming the SEC MW attribution on PS basis. A deeper analysis of (2) peak is important since it constitutes the first MW range above the GC-MS limits and it can give information on the growth mechanism of small PAH. In the present work this analysis has been performed separating and collecting the (2) peak by SEC for the further MALDI analysis since it is well known that MALDI resolution can be improved if the polydispersity of the sample is reduced [6]. The matrix used as a first trial was sinapinic acid, which should be the best matrix for complex carbonaceous materials [7].

The spectrum obtained analyzing the SEC fraction in the MW range of 800 - 2000 u (not shown here) presented a peak in the same range of the whole sample spectrum [9] with a maximum at about 900 u. A further attempt has been done by using the sample at very high concentrations (≈ 3000 mg/l) and without using matrix. Unexpectedly, the spectrum acquired in reflector mode presented signals up to 3000 u with an excellent resolution in the range of interest ($M/\Delta M \geq 3000$ u, which allowed separation of signals of large PAH differing in mass by 1 u up to 3000 u). In literature [5] is reported that there is an upper mass limit of molecules, approximately 1000 u, which can be desorbed as intact ions when direct laser desorption is used (i. e. without matrix). The high resolution obtained allows to individuate a sequence of species with mass increment of 24 u between 532 and 2800 u, with a maximum at 724 u, as shown in the left part of Fig. 2 and in better evidence in the right part of Fig. 2 and its inset, which are zooms of the whole mass spectrum.

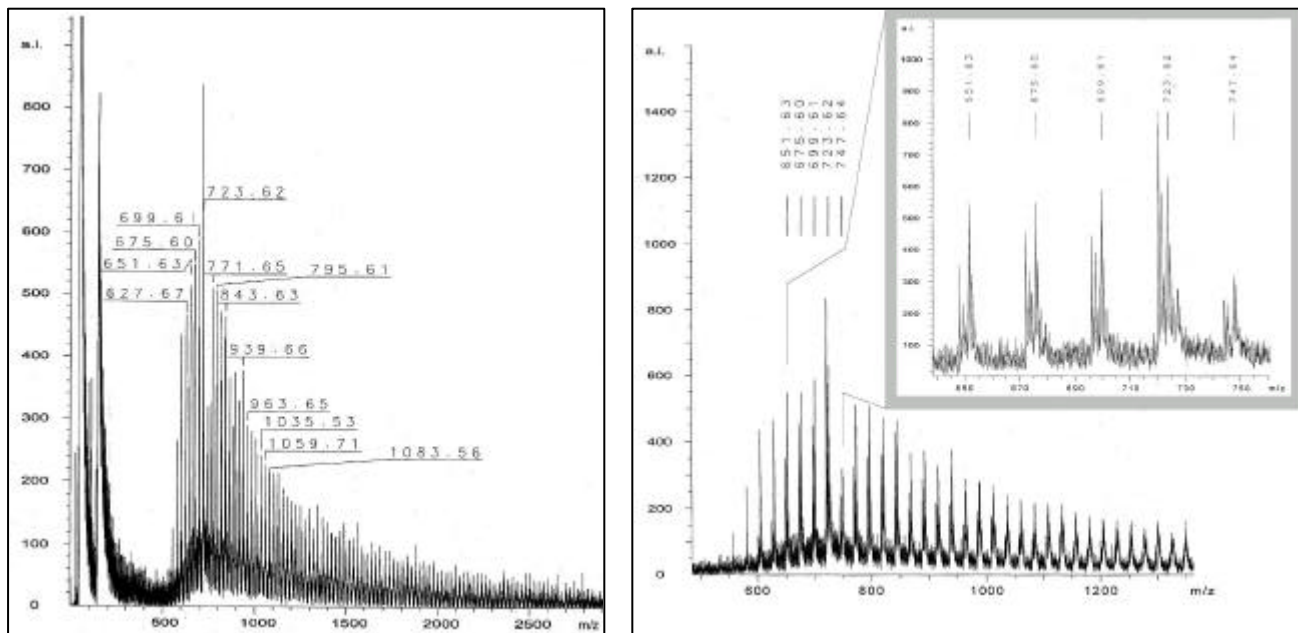


Fig. 2 LDI-TOF mass spectrum of 2 fraction of soot extract separated by SEC (a) and its zoom in the range 500-1500u. Reflecter mode.

This increment suggests that the growth of PAH occurs by addition of acetylene, as proposed by Frenklach [10]. Experimentally, by using different kinds of mass spectrometric techniques other authors [11, 12] have found sequences of heavy PAH with mass increment of 24 u confirming Frenklach's mechanism and have proposed PAH structures on the basis of a stabilomer grid [13] or a molecular map [12]. In the present work the sequence of heavy PAH has been further extended with respect to those found by Dobbins (520 u) [11] and Lafleur (1792 u) [12], arriving up to masses comparable in size to nanoparticles of soot (2700 u $\cong$ 2 nm, assuming a spherical shape and a density of 1.8 g/l). However, the MW found here are not consistent with the structure proposed in refs. 11 and 12 as corresponding to the most stable PAH. Further work is necessary in order to have more insight on the structure of these class of species, for example the coupling of LDI analysis with TOF-MS operating in linear mode. In fact the comparison between spectra obtained in reflector and in linear mode can allow to understand if the detected species are molecules really present in our sample or just fragments of bigger structures. To this purpose it will be necessary to set-up the MALDI or LDI operative parameters for obtaining a spectrum in linear mode with a resolution comparable with that obtained here in reflector mode.

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Aromaticity of Carbonaceous Particulates by Means of Spectroscopic Analysis

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INTRODUCTION

UV-visible spectroscopy can be used to investigate the structure of high molecular weight aromatic materials in tarry and/or solid phase, however carbonaceous solid materials are hardly dissolved in solvents and experimental data available are generally limited to uv-visible spectroscopy of solvent extracts that can not be considered representative of the whole carbon material [1]. Recently N-methyl-pyrrolidinone (NMP) and ultrasonic agitation have been used to obtain stable suspensions and/or solutions of solid carbon materials, prone to be analyzed by UV-visible spectroscopy and other analytical techniques [2, 3].

In the present work UV-visible spectroscopic features as the absorption coefficient and the spectral shape of tarry and solid carbon products collected in fuel-rich ethylene and benzene premixed flames have been measured and compared to the spectra of reference materials like polycyclic aromatic hydrocarbons mixtures, naphthalene pitch, asphaltenes, carbon black, etc., in order to get information about the aromatic moieties and aromatization process involved in the mechanism of soot inception and growth.

EXPERIMENTAL SET UP

The combustion products were sampled in an premixed laminar ethylene/oxygen flame (equivalence ratio $\Phi = 3.03$), and in a benzene/air flame ($\Phi = 2$) produced on a commercial McKenna burner at atmospheric pressure. Solid and tarry materials collected on the probe walls, on the teflon filter (0.5 microns) and in an ice-cooled trap placed along the sampling line were extracted by dichloromethane (DCM) to separate the DCM soluble material, from the solid carbonaceous material, denoted soot, insoluble in DCM. The experimental apparatus and the extraction procedure details were described in previous works ([4, 5]). Samples for the spectroscopic analysis were prepared by ultrasonic agitation for about 30 min in NMP. Absorption spectra were recorded on a HP 84523 Diode Array spectrophotometer in the wavelength region of 260-800 nm using 1-cm quartz cuvette.

Detailed description and sources of commercial carbonaceous materials are reported elsewhere [6, 7].

RESULTS AND DISCUSSION

In the present work absorption coefficients of high molecular weight species and soot sampled in two different premixed fuel-rich flames have been measured in the UV-visible region and compared with UV-visible coefficients of carbon-rich materials commercially available by dissolving known amounts of the samples in NMP. Usually the absorption coefficients are relative to the molar specific absorption coefficients, but in this work they have been evaluated on weight basis (grams of sample/liter of solution) since the molecular mass of the flame samples and of most of the materials used as reference is unknown.

Figure 1 reports the absorption coefficients at selected wavelengths of some individual polycyclic aromatic hydrocarbons (PAH), PAH mixtures as naphthalene (NAO) and phenanthrene aromatic oil (PAO) and carbon materials like fuel oil asphaltenes (separated by

ASTM D2007/80 and IP143/78 procedures) naphthalene pitch, carbon nanotubes, carbon black (N110 and N330).

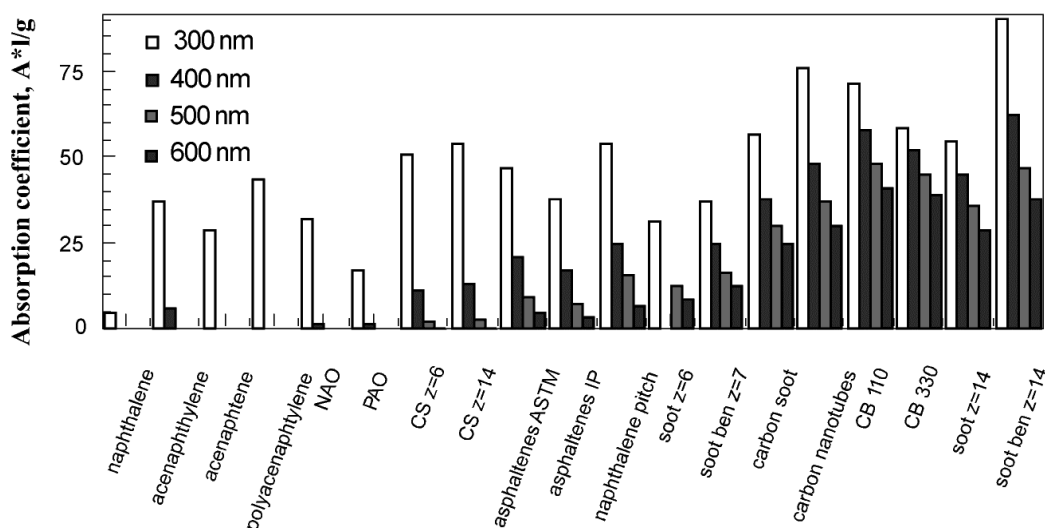


Fig. 1 Absorption coefficients at selected wavelengths of commercial carbonaceous materials and combustion products (soot-CS) sampled from ethylene and benzene flame.

In the same figure the coefficients of tarry condensed species (CS) and of relative dry soot are also reported for the ethylene flame. The absorptions coefficients of CS and soot are referred to samples collected at the limits of the soot formation region, i.e. in the soot inception region ($z=6$ mm of the ethylene flame) and downstream of the flame ($z=14$ mm). The absorption value of CS sampled in the benzene flame was found to be very low probably due to the large mass contribution of phenolic species in the CS and for this reason the absorptivity coefficients of the CS of the benzene flame are not reported in figure.

The uv (300 nm) absorption coefficients of CS sampled in the ethylene flame are quite similar to those of naphthalene and phenanthrene aromatic oils due to the predominance in the uv region of the absorption of two-, three- ring PAH very abundant in the CS sampled in the ethylene flame. Light PAH do not absorb in the visible (400, 500 and 600 nm), by consequence the significant absorption of CS spectra at 400 and 500 nm has to be due to larger aromatic structures that could have a polymeric nature. The absorption in the visible is completely absent in a simple PAH polymer like polyacenaphthylene where the aromatic rings are not conjugated, whereas the visible absorption clearly appears in more largely conjugated aromatic polymeric structures as naphthalene pitch and asphaltene where large and strongly condensed aromatic units are postulated to exist. Moreover it is well known that the absorption of aromatics shifts toward the visible as the number of condensed rings increase [8]. Thus, it can be argued that the CS visible absorption is due to an unidentified portion of aromatic species larger and strongly condensed than the PAH.

The spectral shape of naphthalene pitch and asphaltene and in particular the high absorption coefficient in the visible are very similar to those of the *young soot* collected at the inception testifying that larger condensed aromatic species, typically contained in the naphthalene pitch and in asphaltene, are the predominant contributors to the soot structure. The absorption coefficients of *mature soot* sampled at the end of the soot formation region (14 mm height of the flame), is very high both in the uv and visible regions and these coefficients are more similar to those of carbon materials coming from pyrolytic processes like carbon black, carbon soot and carbon nanotubes.

It is worth noting that *mature* soot formed in the benzene flame appears much more absorbing than ethylene soot and very similar to the carbon soot and carbon nanotubes that are soot produced in the graphite vaporization in an electric arc, typically containing fullerenic structures as reported by many authors [9].

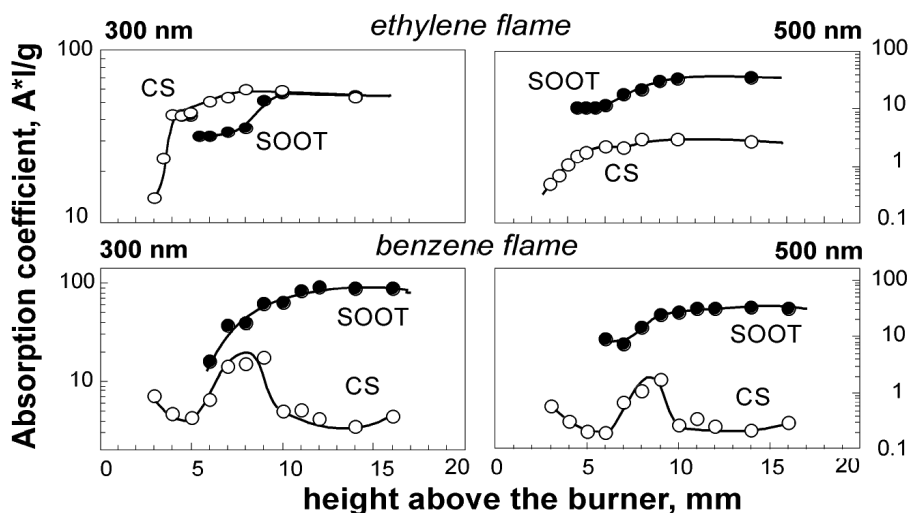


Fig. 2 Soot and CS absorption from ethylene and benzene flame at discrete wavelengths.

The evolution of the aromatisation process occurring along the flame and regarding both tarry condensed species and soot is clearly shown in figure 2 where the axial profiles of the absorption coefficients at fixed wavelengths in the uv (300nm) and in the visible (500nm) of ethylene and benzene soot are reported in comparison with the condensed species. Both in the UV and in the visible region soot absorption coefficients increase along the flame axis for both flames reaching a constant value at about 10 mm of flame height. It is interesting to note that the specific absorbance of benzene soot is much higher in the UV region with respect to the ethylene soot, meanwhile in the visible region they exhibit similar values. This indicates a different structure of aromatic moieties, i.e. different structure of benzene and ethylene soot. This is in agreement with recent results obtained by analyzing differences in the molecular weight ranges of soot formed in ethylene and benzene flame inferred by size exclusion chromatography (SEC) [10].

The specific absorption of condensed species increases along the ethylene flame and the maximum value is almost coincident with the maximum value of soot. Moreover, it has to be noted that the specific absorption of CS in the visible is very low with respect to that of soot and it shows a rise-decay profile in the region of maximum soot formation.

As mentioned before the specific absorption of CS in the benzene flame is very low since it is affected by the large presence of phenolic species which largely contribute to the total mass of CS, but do not contribute to the absorption in the uv and even less in the visible.

Overall it can be stated that the evaluation of specific absorption coefficients of soot and CS along the axis of a soot-forming flame is a good indicator of the occurrence of structural changes that CS and even more soot particles undergo along the flame.

The increase of the absorption coefficient in both uv and visible region could be generally related to the increase of aromaticity degree of soot texture. Moreover, it has to be observed that the rise of the absorption in the visible is much steeper and testifies the increase of the number of condensed rings constituting the aromatic moieties of soot structure. This corresponds in some way also to the increase of the molecular weight, i.e. the size of the particles. The rapid increase of the visible absorption of soot is better shown in Figure 3 by reporting the absorption spectra of soot normalized on the maximum at 260 nm. On the left of

the figure are reported the spectra of soot collected in the ethylene flame and on the right those relative to soot collected in the benzene flame at different heights above the burner. This representation allows to put in evidence the progressive change of spectral slopes in the direction of a higher aromatic condensation going downstream of the flame. It can be also observed that in the ethylene flame the absorption rise in the visible is much more gradual along the flame and extended in a larger region of absorption intensity. This is indicative of a much more progressive growth of aromaticity in soot particles starting from smaller and less aromatic structures and arriving to larger and more aromatic particles.

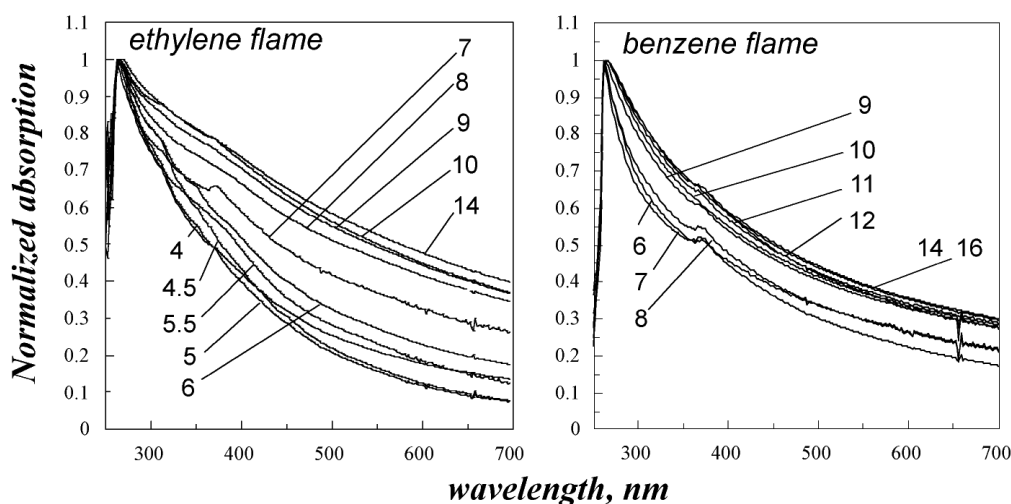


Fig. 3 Height normalized UV-visible absorption spectra of and ethylene and benzene soot collected at different height above the burner.

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The perspective of TOF Mass Spectrometry application for on-line analysis of light hydrocarbons, PAH and particulates from combustion processes

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INTRODUCTION

Improving understanding of mechanisms of soot formation in flames is of practical importance because of the associated implications in environmental pollution caused by exhaust emissions from power-generation plants and internal combustion engines. The mechanisms are so complex that current knowledge about them is still incomplete, even though numerous efforts have led to a rich literature on soot formation (reviewed in Haynes and Wagner, [1]; Haynes, [2]). In particular, the growth process that leads from small polycyclic aromatic hydrocarbons up to soot particles is unknown as the species with an intermediate molecular weight (MW), which can constitute the soot precursors, are not yet characterized.

From the experimental point of view a large array of methods has been applied for detecting soot precursors and for determining molecular weight and size of first soot particles but without reaching a complete success. In particular the most recent papers regard the use of transmission electron microscopy (TEM) [3], laser microprobe mass spectrometry (LMMS) [4], Real-Time Aerosol Mass Spectrometry [5]. These techniques lack in determining size lower than 10 nm and for soot precursors and first soot particles they can only evaluate low molecular mass fragments (up to 300 u) that can give useful information about their chemical structures but not about their MW.

By contrast techniques generally used for detecting PAH such as gas chromatography-mass spectrometry, can detect species just up to some hundreds of units. Therefore, a gap in the experimental detection between PAH MW (400-500 u) and soot particles MW (10 nm, i.e. 500,000 u) remains not filled yet.

In this work the project of an improved instrument based on time of flight mass spectrometry was proposed for the on-line analysis of PAH and soot precursors from combustion systems.

In the following paragraphs the state of art about TOF-MS instrumentations applied in combustion has been briefly described and analyzed in order to design and set-up an on-line TOF-MS apparatus for the analysis of nanometer-size particulates.

STATE OF ART

Time-of-flight mass spectrometry (TOF-MS) is very simple in concept: a packet of ions given the same kinetic energy fly down an evacuated, field-free tube and arrive at an ion detector in the order of their mass-to-charge (m/z) values. The detector output current, measured as a function of time, can easily be converted into a mass spectrum [6]. Moreover, TOF-MS has no fundamental limit on the range of m/z values analyzable and the m/z scale

can be accurately calibrated on the basis of only two points.

Notwithstanding all these advantages, TOF-MS is not yet established as a diagnostic technique for the “on-line” analysis of large masses.

TOF-MS instruments are commonly used in MALDI (Matrix Assisted Laser Desorption Ionization) configuration to analyze proteins and synthetic polymers with masses up to hundreds of thousand of units, even if their application to different kind of materials (coal derived samples, soot extracts) is still pionieristic [7, 8].

On the contrary, the “on-line” TOF-MS approach, without the presence of a matrix and with a sampling in an hostile ambient, such as a combustion system, presents shortcomings that have limited up to now the detection at some hundreds of units.

In tab. 1 the main research groups that used mass spectrometry for the analysis of PAH and soot precursors with some details of their approach and the mass range detected are summarized. It can be observed that the MW measured do not exceed some hundreds of units and only when applied to species already present in flame as ions the detection can arrive up to 5,000 u [9]. However, in this case it is necessary to have an equilibrium between ions and their corresponding neutral components in order to assume ions species representative of the neutral ones, but it is not always verified, particularly for high MW [9].

Table 1

Research group&Instrument Acronim	Source	Sizing method	Ionization method	Mass spectrometer	Mass range observed
McEnally-Pfefferle (PTMS) [10]	Atmospheric pressure coflowing non-premixed flame	none	Laser Desorption Ionization (LDI)	On-line single photon photoionization TOF-MS	PAH MW ≤ 202u
Bittner-Howard [11]	Low-pressure premixed flame	none	Electron impact	Molecular-beam quadrupole mass spectrometer	PAH MW ≤ 700u
Lafleur-Howard [12]	Jet-stirred PFR	none	Chemical ionization	API-MS DLI-MS	PAH MW ≤ 448u 400 < MW ≤ 2000u
Homann (TOF-MS) [9]	Low-pressure premixed flame	none	none	On-line reflectron TOF-MS	PAH ions MW ≤ 5000u
Dobbins (LMMS) [4]	Atmospheric pressure laminar diffusion flame	none	Laser Desorption Ionization (LDI)	Off-line microprobe MS	PAH MW ≤ 620u
Hepp-Siegmann (TOF-MS) [13]	Atmospheric pressure diffusion flame	none	Laser Desorption Ionization (LDI)	On-line Reflectron TOF-MS	PAH MW ≤ 400u Fullerene clusters ≤ 6000u
Reilly, Ramsey, Whetten (ITMS) [5]	Diffusion flames, aerosol source	Aerodynamic sizing (particle levitation or photomultiplier tubes)	Laser Desorption Ionization (LDI)	On-line Ion Trap MS	Particles (0.2 – 1 µm) Organic species desorbed from particles MW ≤ 350 u
Prather (ATOFMS) [14]	aerosol source	Aerodynamic sizing (photomultiplier tubes)	Laser Desorption Ionization (LDI)	On-line Reflectron TOF-MS	Particles (0.3 – 10 µm) Organic species desorbed from particles MW ≤ 800 u

It can also noted that only coupling an aerodynamic sizing method with TOF-MS it is possible to extend the detection to soot particles, but jumping all the MW range between small PAH molecules and micrometric particles.

The main problems causing low MW detection limits of TOF-MS are connected with the ionization system and the source.

As regard the ionization, the largest used method is the laser ionization since the characteristic short pulses of high-intensity light of a laser are ideal for the coupling with time

of flight detection. Because the ionization potential of PAH (depending on PAH; generally $> 7\text{eV}$) and soot (depending on the hydrogen content and the internal structure of the particles, but for sure $>$ of the graphite value 4.4 eV) is larger than the energy of one photon from any laser used, two photons are necessary for ionization of these species. However, by using multiphoton laser ionization a strong fragmentation both of PAH and soot have been observed, in different amount on the basis of the wavelength, i.e. the energy, of the lasers used.

As regard the source, meaning with “source” the set-up for transferring the combustion byproducts to TOF-MS, the shortcomings are connected with the passage from atmospheric pressure to the high vacuum of a mass spectrometer, the intrusivity of the sampling in a combustion system and the difficulty for large molecules to arrive intact to the detector.

CHARACTERISTICS OF A TOF-MS SYSTEM FOR THE ON-LINE ANALYSIS OF NANOMETRIC-SIZE PARTICULATES

The problems of sampling and ionization are strictly linked. In fact conceptually, of course, it is straightforward to analyze the “natural” ions formed in the combustion process, as realized by Homann et al. [9]. Practically, it requires a probing technique that immediately quenches collisions by means of a molecular beam. Probes for this purpose have a significant opening angle. It restricts this method to one-dimensional sampling of flames where the influence of the probe does not disturb the processes in the flame. It is technically demanding to run a molecular beam behind an orifice large enough to avoid the instantaneous clogging by tar and soot deposition. This problem has confined the method application to flames that burn at reduced pressure (20-30mbar).

It has been planned to use an atmospheric flame as combustion system, since it is the condition generally occurring in practical systems. In a preliminary phase of the work, sampling will be performed in non-sooting flames, in order to reduce clogging problems without the need of using too large orifices that can perturb the flame. Moreover, the chosen system will be a laminar premixed flame as it can be considered a one-dimensional system. In fact, premixing the fuel and oxidant reduces the influence of transport phenomena on the combustion process, thereby enabling chemical processes to become a dominant factor in determining the flame structure. In a premixed flame the radial concentration profile of all the species is constant and therefore the location of the sampling point (along the axis or the border of the flame) is not crucial. The burner will be equipped with a micrometric screw in order to change the sampling height along a spatial dimension that can be converted, through the velocity profile, in a temporal coordinate (reaction time).

In order to reduce the intrusivity of the probe the tip can be designed with a conic shape regulating the suction pressure for obtaining an isokinetic sampling. Behind the probe the combustion gases can be immediately diluted and cooled by an inert gas stream that mixes turbulently with the flame gases. The dilution ratio can be optimized in order to have detectable concentration of species but limiting the fouling of the detectors.

After the dilution, a conical skimmer leads the gases into a second high vacuum pumping stage, in which the pressure is 10^{-6} mbar. Finally, the molecular beam is collimated in a small diameter orifice leading into the third stage where the pressure is 10^{-9} mbar.

The described system can allow also the detection of “natural” ions in flame and it will be performed as a first trial. After that, ionization systems alternative to the lasers commonly used with nanoseconds pulses will be realized, for example the chemical ionization with selected ions with suitable energies or lasers with picoseconds or femtoseconds pulses, which are more expensive, but can reduce the fragmentation problems.

The sampling system will be coupled with a commercial reflectron TOF-MS, whose sketch is reported in Fig. 1. This TOF-MS will be modified for extending the detection limits up to

hundreds of thousand of units. The main modification will regard the acceleration voltage to be applied for accelerating the molecular beam, after its ionization. In order to allow that also very large molecules could fly up to the detector through a field-free tube the acceleration voltage has to reach very high values (25, 30 keV) and this requires a great effort for adapting the electronics of the instrument. Therefore, the increasing of acceleration voltage will be performed gradually, testing continuously the new detection limits reached.

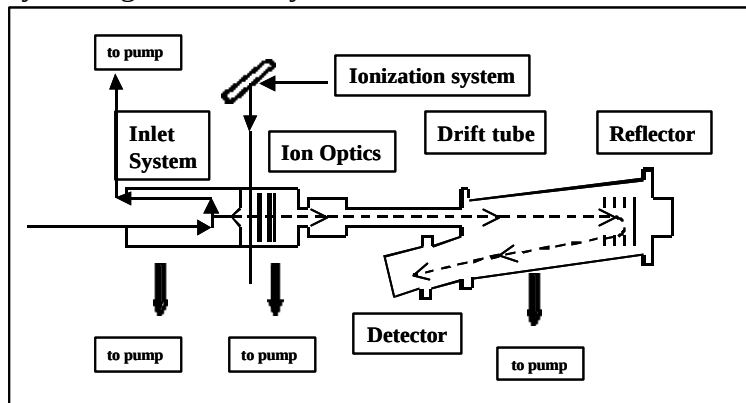


Fig. 1 Time-of-flight mass spectrometer system.

After setting-up all the system, concentration profiles of combustion byproducts from light hydrocarbons up to soot precursor species will be evaluated acquiring on-line MS spectra at different sampling height above the burner. The comparison with concentration profiles evaluated from sampling and off-line analysis, at least for the species up to 300u, will allow to test the reliability of the system.

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MODELING OF NANOPARTICLE AND SOOT FORMATION IN A CO-FLOWING DIFFUSION FLAME

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Introduction

Combustion-generated aerosols pose significant health and environmental problems. Epidemiological observations consistently find that increased particle concentration is correlated with a variety of detrimental health effects including increased mortality. At the same time, anthropogenic aerosols affect the Earth's radiation balance directly by backscattering or by absorbing radiation, and indirectly by increasing cloud condensation and thus. A quantitative understanding of particulate formation mechanisms and the ability to accurately model these processes is critical for the goal of zero-emission combustion systems.

In this communication a model of hydrocarbon oxidation and pyrolysis is applied to predict concentration profiles of the particulate (soot and high molecular mass compounds) in a co-flowing diffusion flames of diluted ethylene and air. Predictions are compared with particle volume fraction and sizes measured by classical optical extinction/scattering methods.

Flame Conditions

An atmospheric pressure, axisymmetric, laminar diffusion flame is modelled. The flame is stabilized on a co-flowing burner having a 12 mm diameter uncooled vertical tube for the fuel mixture and a concentric tube (108 mm diam.) for air. The air-annulus is reduced at the burner lip by a ring (i.d. 55 mm) to stabilize the flame. The fuel is a mixture 30.5% (vol) ethylene and 69.5% nitrogen with a total flow rate of 770 cm³/min while the air flow rate is 44,000 cm³/min.

This flame has been studied experimentally by McEnally and Pfefferle [1] and lately, with probe measurements and optical diagnostics by Rolando [2]. Temperature measurements, particulate volume fractions and mean sizes have been obtained for a range of radii at several axial heights.

Modeling

Gas-phase chemistry and aromatic growth

A detailed kinetic mechanism of hydrocarbon oxidation and pyrolysis is used [3-6]. The gas-phase mechanism includes the pyrolysis and oxidation of C1 and C2 species, the formation of benzene and reactions leading to the formation of larger aromatic compounds. The complete detailed reaction mechanism for the initial formation of aromatics consists of 279 reactions and 60 chemical species. Details of the mechanism and rate constants have been reported previously [5,6].

The process of aromatic growth to form higher molecular mass aromatic compounds is modeled by a radical-molecule sequence of reactions involving five-membered ring PAHs. The sequence begins with the H-abstraction from aromatic compounds to produce the corresponding radical. Iteration of this mechanism followed by rearrangement of the carbon framework ultimately leads to the formation of high-molecular-mass compounds. Details on the kinetic mechanism of aromatic growth and on the kinetic constants are reported elsewhere [7].

Collision and subsequent coagulation of the high-molecular-mass compounds is accounted for through the sticking probability, i.e. the probability of coagulation upon collision, which can be related to interactions between molecules, i.e. Van der Waals forces. Particles with sizes around 1-2 nm have a coagulation rate three orders of magnitude lower than the gas kinetic limit; as particle size increases the coagulation rate also increases and even approaches the gas kinetic limit for particles having high polarizability (graphitic-like). The change of the size distribution function of particles due to coagulation has been described by computing the population balance equation described by the Smoluchowsky equation. The size dependent coagulation rate is computed by multiplying the coagulation rate obtained from kinetic theory and the sticking probability evaluated from the interaction potential between particles.

The forming clusters are assumed to be solid particles which add and lose mass by surface reactions after activation of the surface by H atom abstraction. Acetylene is the major species through which mass is added whereas oxygen is the main oxidizing species. A steady-state approximation is adopted for fast reacting intermediates which implies that the number of radical sites is independent of particle size and the rate is determined only by the gas-phase environment [8].

In order to include the aromatic growth mechanism in the diffusion-flame model, the method of moments [9] is used. Three moments of carbon number per mole concentration are modelled; the zeroth moment M_0 is mole concentration, the first moment M_1 leads to mass concentration and the second moment M_2 gives the variance of the particle size distribution function. Mean particle size (C/molecule) is the ratio M_1/M_0 . An assumed probability density function (pdf) is needed and here a lognormal size distribution function is assumed. The geometric mean and variance of the lognormal pdf is matched to the arithmetic mean and variance obtained from the independent transport equations for M_0 , M_1 and M_2 . The pdf affects those reactions whose rates are dependent on particle size. A log-normal size distribution function is used in the calculation. Changes in the shape of the size distribution function do not alter model previsions.

Computations are performed by an axisymmetric steady-state solver for continuity, axial and radial momentum, species mass fraction, enthalpy and statistical moments.

Results and Discussion

Flame structure has been successfully modelled in terms of temperature, stable species and trace compounds. The predicted flame is shortened in the present work because the particulates do not burn out completely. In this paper, we examine the process of aromatic growth and particle inception giving attention to particulate volume fractions and particle sizes.

Figures 1 and 2 report the comparison between modelled and measured volume fractions (right) and particle sizes (left) of the high-molecular-mass compounds as a function of the radial coordinate at two axial locations, namely 30 and 60 mm., i.e. at the beginning of the flame (30 mm) and around its maximum temperature (60 mm)

Measured volume fractions and particle diameters are from classical light scattering – extinction techniques [10]. Extinction measurements have been performed both in the ultraviolet and in the

visible range; in this way soot particles as well as their precursors can be measured. Light scattering at one wavelength cannot distinguish between soot and its precursor nanoparticles since it only provides the sixth moment of the size distribution function and the presence of smaller particles is obscured by the larger soot particles.

The model results agree quite well with the measured data. At 30mm, the simulation of the particulate volume fraction in the wing region follows reasonably well the experimental data. The agreement is even better at 60mm.

Particle diameter is reproduced at both axial positions to within a factor of two. It should be remembered that the comparison is made between modelled mean size and the measured 6/3 moment of the size distribution, the latter being weighed by the larger particles.

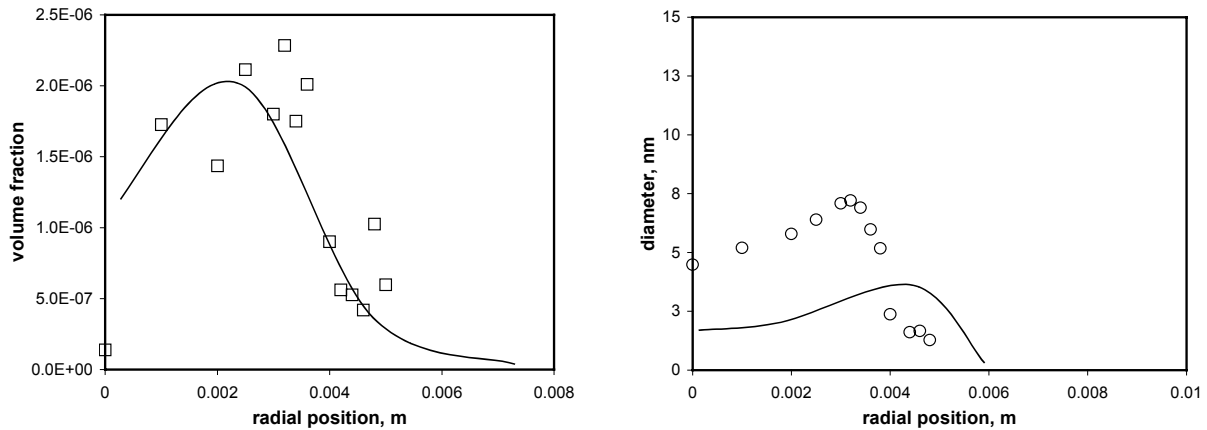


Fig.1 Comparison between modelled and measured volume fraction (right) and particle diameter (left) as a function of the radial coordinate at 30mm above the burner exit

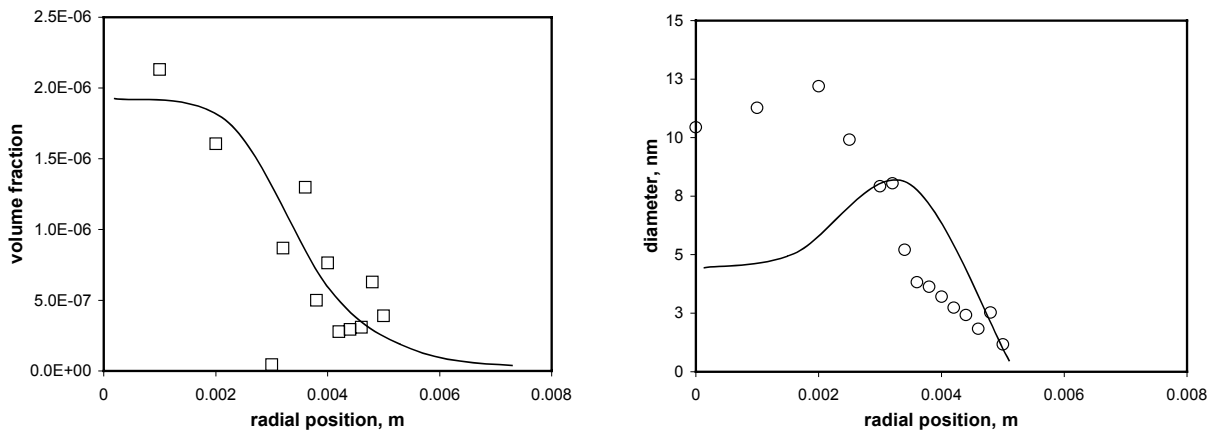


Fig.2 comparison between modelled and measured volume fraction (right) and particle diameter (left) as a function of the radial coordinate at 60mm above the burner exit.

At low axial locations (30mm), very small particles with sizes of the order of few nanometer are predicted by the model. These particles, which have a size typical of high-molecular-mass compounds, are formed in the fuel side of the flame and grow up to soot precursor particles in the flame wings. Moving to higher flame heights particles with sizes typical of the primary soot particles (about 20nm) are formed also on the flame centreline. Analysis of the predictions reveals that surface growth is the controlling parameter in the process of soot loading whereas the radical-molecule combination mechanism controls the formation of soot precursors.

Conclusions

A detailed kinetic mechanism is used to simulate the formation of particulate in a co-flowing diffusion flame of ethylene. The model includes hydrocarbon oxidation and pyrolysis, particle inception and coagulation, and finally surface growth and oxidation.

The model predicts with a good level of accuracy the volume fraction of total particulate, in comparison with optical measurements in different flame locations and particularly in the wings of the flame. The model also simulates the mean size of particle diameter in the different regions of the flame showing the formation of nano-sized precursor particles in diffusion flames.

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Carbonaceous Nanoparticles Formed in a co-Flowing Diffusion Flame

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INTRODUCTION

Carbon nanoparticles smaller than 5nm and different from soot particles are formed in fuel rich combustion systems. The experimental evidence of the presence of these carbonaceous structures come from the excess of light scattering in flame respect to the background due to gas phase compounds and from UV absorption [1]. Different studies have detected these nanoparticles in laminar premixed flames [1-3]. In this communication, the volume fractions and the mean sizes of nanoparticles and soot are measured in a laminar co-flowing diffusion flame of ethylene and air by means of broadband UV-visible extinction measurements from 200nm to 500nm and laser light scattering. The results are compared with measurements performed with a fine-wire thermocouple used to determine the volume fractions and emissivity of the carbonaceous particles and with Atomic Force Microscopy used to determine particle size distributions.

TECHNIQUES AND EXPERIMENTAL APPARATUS

The burner is a 12 mm diameter uncooled vertical tube for the fuel mixture and a concentric tube (108 mm diam.) for air. The fuel is a mixture 32% (volume) ethylene and 68% nitrogen. Burner average velocities are 35cm/s for both fuel and air.

By performing absorption/scattering measurements, the volume fractions and mean diameters of particles are evaluated at different positions in flame. For the determination of the UV-visible absorption spectra, the laser beam ($\lambda=1064$ nm of a Nd:Yag pulsed laser source) is condensed into air with a short focal lens, which induces a high temperature plasma accompanied by a high intensity light source, suitable for absorption measurements in the UV-visible spectral range (200 – 500nm) [4]. The light scattering measurements are performed using the forth harmonic of the laser ($\lambda=266$ nm), the laser beam and the detected scattering signals are both vertically polarized. The detection system consists of a spectrometer coupled to an intensified and gated CCD camera, which acquires and records the signal on a single shot basis.

Volume fractions and particles emissivity are measured with a Pt/13%Rh-Pt thermocouple. Particles are driven by thermophoretic forces on the thermocouple junction, which induces a decay in the temporal signal of the temperature. From the temperature decay it is possible to evaluate the volume fraction and the emissivity of the particles [3]. The thermocouple filaments diameter are 100 μ m and the junction diameter is 330 μ m.

Carbonaceous particles are collected on a mica grid for Atomic Force Microscopy by thermophoretic deposition at various heights in the flame. A special-purpose holder, mounted over the piston extension of a double acting pneumatic cylinder, permits to collect samples on mica substrates with a very low residence time in the flame (about 20 ms). Tapping Mode

Atomic Force Microscopy (TM-AFM) is used for the determination of the particle size distribution of the collected particles. The results are compared with those obtained with scattering measurements.

LIGHT ABSORPTION MEASUREMENTS

Absorption spectra recorded at 20mm above the burner are reported at various chords in Fig.1.

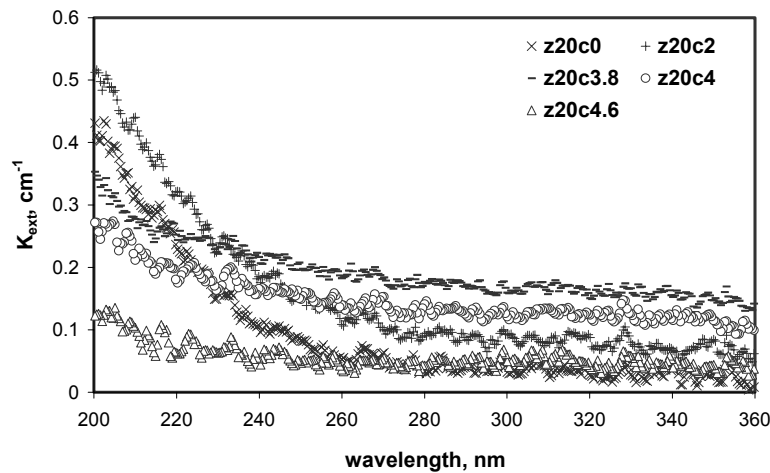


Fig. 1 Absorption spectra measured at 20mm above the burner

At central chords the K_{ext} spectrum shows very high values from 200 to 280nm. At higher chords the strong absorption in the 200-280nm region is reduced, but the values at 280nm are much higher.

All the measured spectra are Abel inverted and are cleaned from the contribution of gaseous compounds, such as CO_2 , H_2O and O_2 , which are known to strongly absorb light in the UV region at flame temperatures [4]. The gaseous concentrations are estimated by numerical modelling of the flame structure [5].

From the Abel inverted spectra the volume fractions of both classes of detected particles are determined. Each spectrum measured may be considered as due to two components: nanoparticles, which absorb light in the UV region up to 280nm but are completely transparent in the visible, and soot particles, which show strong absorption both in the UV and visible range, whose spectral shape is assumed constant. Thus, both the volume fractions, f_v^{npart} and f_v^{soot} , can be determined when the volume attenuation coefficients, *specific cross sections*, $C_{abs}/V = K_{abs}/f_v$ for the two different materials are known. In the Rayleigh regime this quantity is a function of the refractive index of the particles. At 266 nm, the volume attenuation coefficients of nanoparticles and soot are $3E4 \text{ cm}^{-1}$ and $2.8E5 \text{ cm}^{-1}$, respectively, assuming the refractive index equal to $m_{npart}=1.4-0.08i$ and $m_{soot}=1.4-0.75i$ [6], while at 532nm $m_{soot}=1.56-0.6i$ and $m_{npart}=0$.

In Fig.2, the volume fractions of soot and nanoparticles are reported versus radius for two heights above the burner, namely 20 and 70mm. At lower heights soot particles are confined in the wing of the flame, while at higher heights they are present also in the centerline of the flame. Nanoparticles volume fractions are reduced from a maximum value of $2E-6$ to $5E-7$ passing from 20mm to 70mm.

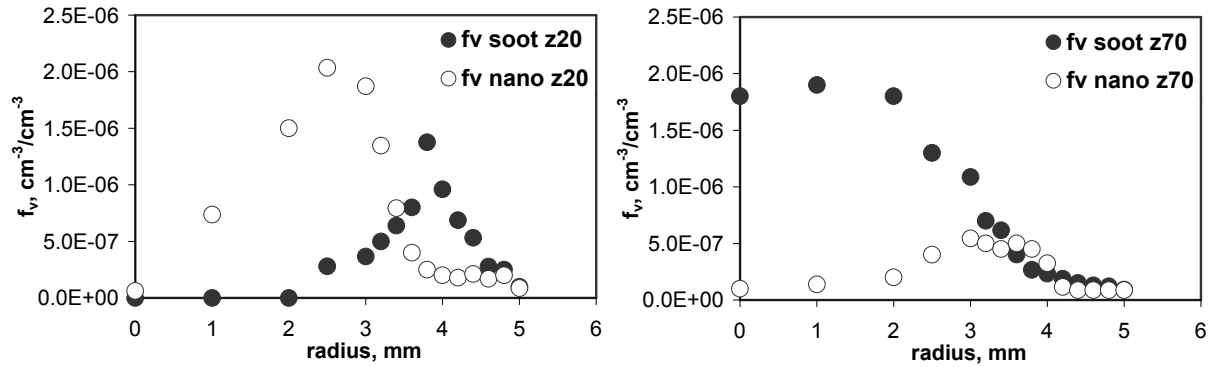


Fig. 2 Volume fractions of soot and nanoparticles versus radius at 20mm and 70mm above the burner

THERMOCOUPLE MEASUREMENTS

Transient thermocouple technique has recently been used to determine volume fractions and emissivity of particles in a laminar premixed flame [3]. The technique presents many advantages as low cost and easy realization, and it is a point measurement.

Fig.3 shows the emissivity of the particles versus radius at 20mm and 70mm above the burner. At lower heights and central radius emissivity values are of the order 0.5-0.6. In this region of the flame only nanoparticles are present. Soot particles are present only in the wing region at lower heights (emissivity ≥ 1), while at higher heights soot extends from the wing to the centreline as shown by the emissivity measurements (constant value of about 1 along the radius).

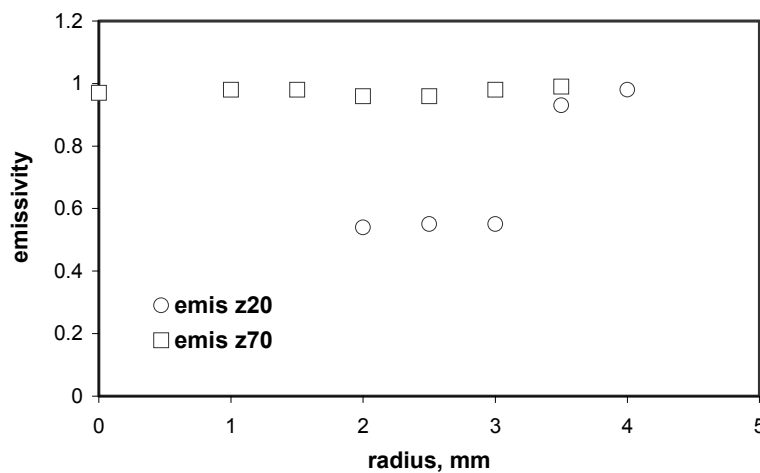


Fig. Emissivity of particulate at 20 and 70mm above the burner

SCATTERING AND AFM MEASUREMENTS

Scattering and AFM measurements are performed for evaluating mean diameters of particulate. Mica substrate is a 10mm diameter circle, like the inner tube of the burner, consequently the particles detected are all those present at a specific height. Scattering measurements are point ones, and for each height they give diameter values versus radius.

The two techniques are compared at 20 and 70mm above the burner in Fig.4. At 20mm AFM data find the presence of many particles of sizes between 2-5nm, and some particles much larger. Scattering measurements along the radius furnish a mean diameter between 4 and 8nm. This means that only few soot particles are formed. At 70mm a large amount of soot particles are present and scattering measurements confirm this data.

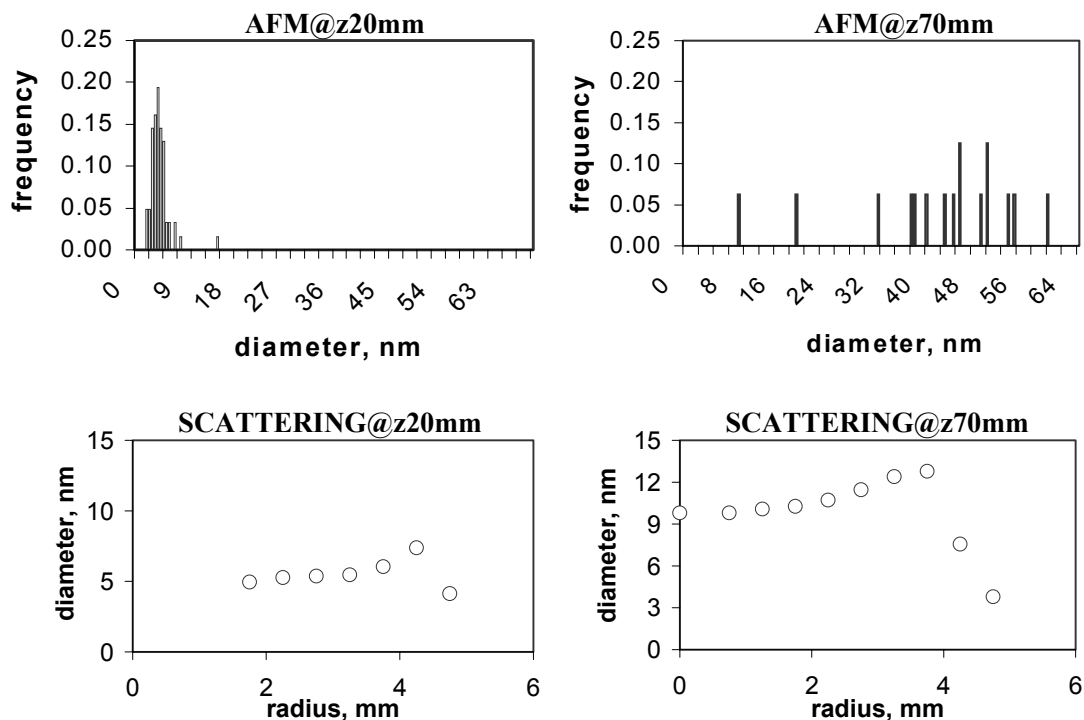


Fig. 4 Comparison between AFM and scattering data at 20 and 70mm above the burner

CONCLUSION

Visible transparent nano-particles and soot present in a laminar co-flowing diffusion flame was characterized by different “in-situ” and “ex-situ” measurements. With thermocouple measurements we have measured particle emissivity. Particle volume fractions were estimated by broadband absorption measurements. Particles diameters were estimated by light scattering measurements. Moreover, microscopy measurements were used as a complement of the optical measurements and furnished the size distribution function of the particulate.

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Numerical Investigation of the Primary Particle Shape of Soot Aggregates in Premixed Laminar Flames

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ABSTRACT

Transition from coalescent to aggregate growth of soot particles in laminar premixed flames was investigated using detailed numerical simulations based on a recently developed method-of-moments model for particle aggregation coupled with a detailed chemical kinetic mechanism of soot formation. The combined model was applied to ensemble-averaged simulations of a number of burner-stabilized premixed laminar flames and compared to measurements and a previously developed model of soot particle aggregation. The averaged simulations were supplemented with detailed single particle Monte-Carlo simulation of soot particle dynamics in the same environment. Aggregation behavior of soot particles and, in particular, the evolution of primary particle shapes is investigated.

INTRODUCTION

Soot particles formed in combustion processes typically exhibit a complex aggregated structure, (see [1-5] and references therein). TEM images reveal that particles are comprised of randomly arranged roughly spherical primary particles characterized by a high degree of overlapping. While the experimental characterization of the morphology of aggregated soot particles has received considerable attention, models of soot formation often assume the growth of particles as completely coalescent [6]. Kazakov and Frenklach [7] were the first to include particle aggregation into a detailed soot model based on the method of moments and to apply it to model soot formation and aggregation in high pressure premixed flames. Particle aggregation was however modeled in an ad-hoc manner as the diameter of primary particles and thus the location at which transition from coalescent to aggregate growth occurs has to be known a priori. Recently Mitchell and Frenklach [8,9] conducted detailed Monte-Carlo studies of the time evolution of single soot particles subject to coagulation and simultaneous surface growth. It was shown that the spherical appearance of primary particles could be explained based on geometric reasoning using a ballistic model of soot growth. On that basis, a physical model for the transition from coalescent to aggregate growth was developed. Due to its complexity, an extension of that method to investigate transition characteristics of an entire ensemble of particles in flames is however not feasible at present.

In this study the model developed by Mitchell and Frenklach is included into the method of moments describing the dynamics of the soot particle ensemble without prescribing any functional form for its size distribution. Combined with a detailed chemistry and soot model [10,11,13], the extended model is applied to simulate aggregate growth of soot particles in an ensemble-averaged manner.

MODELLING

The approach developed in this study is based on detailed Monte-Carlo simulations of the growth of single particles in high-pressure flame environments conducted by Mitchell and Frenklach [8, 9]. The results from the Monte-Carlo study indicated that the shape of aggregated particles is well described by parameter d_i , which relates its normalized volume to

its normalized surface:

$$(S_i / S_0) = (V_i / V_0)^{d_i}, \text{ with } d_i \in [2/3, 1], \quad (1)$$

where d_i is shape descriptor of particle of size i ; V_i , V_0 , S_i and S_0 are the volume and surface of particles of size i and of the smallest particle, respectively.

To obtain the shape descriptor d for the whole ensemble of particles, an equation for total surface was developed and added to the previously developed method of moments with interpolative closure (MOMIC) [13]. The new aggregation model calculates the evolution of total volume and total surface of a particle ensemble. The resulting normalized surface to volume ratio, or d , provides information about the shape of particles or the degree of aggregation. A premixed laminar flames also investigated in [7] was studied. Measurements of soot volume fractions and temperature for this flame were taken from literature [12]. A detailed mechanism, developed by Frenklach, Wang and coworkers [10, 11], was used to describe reactions in the gas phase. The mechanism for surface reactions was identical to that in Ref. [10]. The new model for particle aggregation was integrated into a modified version of the Sandia burner code [14] including transport equations for the soot moments [15].

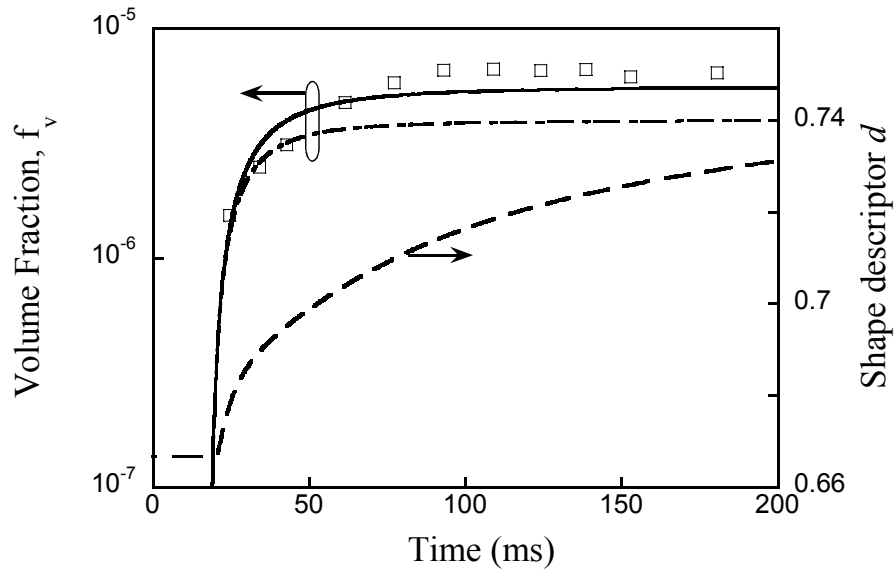


Fig 1: Soot Volume Fraction calculated with the coalescence only (dashed-dotted line) and the new aggregation model (line) compared to measured data (symbols) [12]. Also shown is the evolution of the shape descriptor d .

RESULTS AND DISCUSSION

Figure 1 shows soot volume fraction obtained with both the coalescence only and the aggregation model along with measured data [12]. It can be seen that including aggregation increases the final soot volume fraction. This is due to an increase in surface area, which is caused by the fractal shape of aggregates. This result differs from the findings obtained with the previously developed aggregation model [7], where particle aggregation had only a moderate effect on final soot volume fraction. This can be explained by determining when transition from coalescent to aggregate growth occurs. For this purpose the evolution of the shape descriptor d , also shown in Fig. 1, was investigated. The new aggregation model predicts a smooth transition, which commences when $d > 2/3$, while the previous model assumed an instantaneous transition when the mean particle diameter reached a critical size. The present model predicts that particles deviate on average from spherical shape earlier in

the flame, in a region of the flame where surface growth is still active.

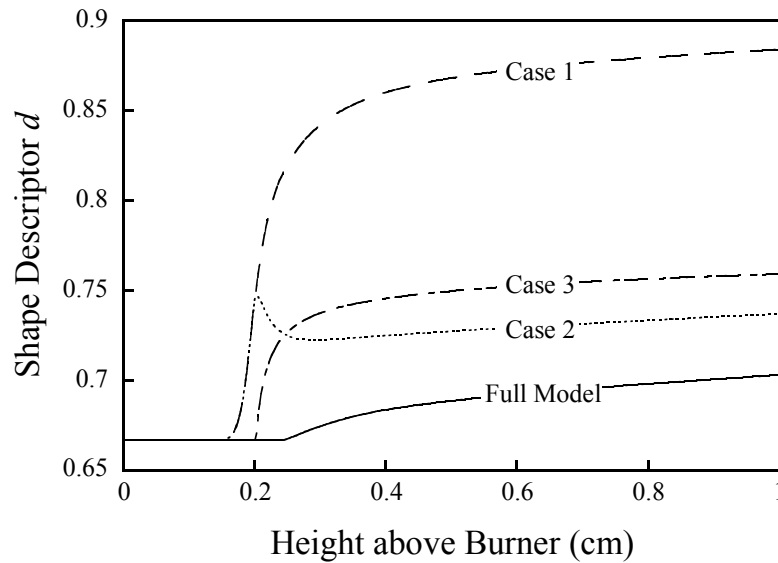


Fig 2: Evolution of shape descriptor d with respect to height above burner obtained with: (a) the full model, (b) surface reactions artificially switched off (Case 1), (c) surface reactions artificially switched off until the maximum of nucleation (Case 2) and (d) nucleation artificially switched off after the maximum of nucleation (Case 3).

To investigate the effect of the different processes involved in soot formation three test cases, shown in Fig. 2, were calculated. In Case 1, surface growth was completely switched off. In the absence of surface growth particles start to form aggregates as soon as coagulation sets in and the final value of the shape descriptor d increases markedly as compared to the simulation with the full model, referred to as base case. The results from Case 1 indicate that surface growth is indeed responsible for the time gap between the start of coagulation and the formation of aggregates. To verify this assumption, surface growth was artificially switched off until the point of maximum nucleation in Case 2. Here particles start to form aggregates as soon as coagulation sets in, documented by a sharp increase in the shape descriptor d identical to that observed in Case 1. At the point in the flame where surface growth is switched on, the shape descriptor d decreases. Surface growth covers the initially formed aggregates and increases their sphericity. As soon as surface growth has dropped off and particle nucleation ceased, coagulation dominates and the degree of aggregation increases again.

Finally, the effect of particle inception on the formation of aggregates was investigated in Case 3. This was accomplished by switching off nucleation artificially after its maximum value is reached. Particles start to deviate in average from spherical shape immediately after nucleation is switched off which is later than in Case 1 but earlier than in the base case. Also, the final value of d is markedly increased. This shows that nucleation plays an important role in determining the onset of aggregate formation as well as particles' final degree of aggregation. The reason for the influence of nucleation on the particle shape is twofold. Firstly, since incepted particles are assumed to be spherical, nucleation is a strong source of spherical particles. Secondly, the shape of particles is affected by the size dependence of coagulation. Initially, the newly incepted particles coagulate leading to larger particles. These particles being larger than the incepted particles coagulate more rapidly with smaller particles than other large particles. Small particles are available as long as nucleation is strong. This leads to aggregates consisting of small particles, which in turn are readily covered by surface growth. Once nucleation stops, larger particles rapidly scavenge the remaining small particles and start to coagulate among themselves. This results in aggregates consisting of large primary particles with gaps that cannot be filled easily by surface growth. While surface

growth is not strong enough to cover the large aggregates, it might still increase the sphericity of their primary particles.

CONCLUSION

A new model of soot particle aggregation is developed in the present study and included into the previously developed method of moments describing the dynamics of the soot particle ensemble. The new approach describes the aggregate nature of particles by their normalized surface to volume ratio. This is motivated by the fact that soot aggregates are usually comprised of primary particles exhibiting a high degree of overlapping caused by simultaneous coagulation and surface growth. The new model is based on results from detailed Monte Carlo simulations of the dynamics of single soot particles and improves a previously developed model of particle aggregation, as the location of transition from coalescent to aggregate growth does not have to be known a priori.

A burner stabilized premixed laminar flames is calculated to investigate the aggregate growth of particles. The simulations show that the degree of aggregation and the location at which transition from coalescent to aggregate growth occurs is governed by a complex interaction of nucleation, coagulation and surface growth. Nucleation appears to be the dominant process controlling the shape and the transition time since it determines the number of small particles. The presence of small particles leads to the formation of aggregates that are more readily covered by surface growth and depending on the strength of surface growth exhibit a more spherical shape. Thus, with the provision of simultaneous surface growth, the strength of nucleation is found to control the transition from coalescent to aggregate growth.

ACKNOWLEDGEMENTS

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CHARACTERIZATION OF POLLUTANT EMISSIONS IN A RADIANT TUBE NATURAL GAS BURNER

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Abstract

The aim of this work is the characterization of pollutant emissions at the exhaust of a radiant tube natural gas burner, equipped with a screw-type swirl generator to impart a rotational motion to the air stream. In this burner typology the flame is confined inside a long tube ($L/D \approx 15$) which is used as a radiant heater for steel industrial ovens. The analysis of pollutant emissions (nitric oxides by chemiluminescence, CO by infrared system) has been carried out for different operating conditions of the burner, similar to industrial appliances: input thermal powers from 12.8 up to 18 kW and equivalence ratio from 0.5 (very lean flame) to 0.95 (quasi-stoichiometric condition). Moreover, pollutant emissions sensitivity to burnt gas external recirculation has been analyzed. The influence of the different parameters upon pollutant emissions has been clearly identified, determining the optimal operating range of the device and suggesting possible solutions for the design of new burners of similar typology.

Introduction

This work analyses the influence of operating conditions on flame morphology and pollutant emissions of an industrial natural gas – air swirl burner characterized by a rotational motion imparted to the air with the fuel injected coaxially to the air stream. The aim of swirl motion is usually to enhance the mixing process between the reactants increasing flame stabilization [1], contributing also to a reduction of pollutant emissions such as NO_x and CO.

The external exhaust gas recirculation (external EGR) has been used to reduce the nitric oxide emissions, by reducing the overall temperature in the combustion region. In fact the high temperature in the reactive zone is known as the main factor influencing Thermal NO_x formation [2], while temperature reduction may influence the overall combustion performance carrying to higher CO emissions. The flame was investigated through direct imaging and pollutant emissions measurements at the exhaust.

Experimental set-up

In figure 1 it is showed the analysed burner, which is used in the steel industry for surface treatment. Because of the presence of a strict composition atmosphere in the treatment oven the flame has to be confined inside two coaxial tubes: in the inner one ($D_{\text{tube}}/D_{\text{efflux}} = 1.2$, $L_{\text{tube}}/D_{\text{tube}} \approx 15$) the combustion reaction is carried out, while the annular enclosure between the inner and outer tubes is used to carry the combustion products out and to heat up the incoming air stream.

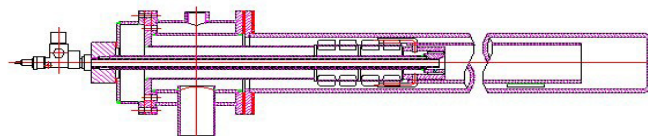


Figure 1: the burner geometry.

This burner is characterised by air swirl motion produced by a screw type swirl generator; the natural gas is injected through an annular section coaxial with the air flow. Centrally to the burner, there is a premixed pilot flame used to ignite the mixture and to prevent burnout. The analysed operating conditions of the burner are listed in Table 1.

	Air	Methane
Nominal Flow Rate [NL/min]	240	21.3
Nominal Reynolds Number	$\cong 8000$	$\cong 500$
Swirl Number S	0.85	0
Pilot Burner Flow Rate [NL/min]	23.8	2.5
Analized equivalence ratio Φ of the main burner	$0.5 \div 0.95$	

Table 1: burner operating conditions.

Flame direct imaging and pollutant emissions measurements have been performed for different input thermal powers (from 10 kW to 18 kW) and equivalence ratio (from 0.5 to 0.95). Swirl number of the air flow, defined in [1], has been estimated by integration of axial and tangential velocity radial profiles, measured by LDV in isothermal conditions along a diameter at the minimum available axial distance from the burner exit (3.5 mm), and resulted equal to 0.85. The flame imaging has been carried out by means of a digital camera and the tube used to confine the flame has been replaced by a quartz transparent tube (tube length=1000 mm). The external gas recirculation has been obtained by means of an ejector system put on the air feeding line. This ejector creates a pressure difference between the exhaust duct and the air inlet driving to entrainment of combustion products into the main air stream.

Pollutant emissions measurements have been performed by means of a conventional apparatus. Measurement techniques are based on chemiluminescence for NO_x analysis, infrared techniques for CO and CO_2 , and paramagnetic properties for O_2 .

Experimental results

By the imaging it was possible to determine the combustion behavior for different operating conditions in terms of flame length and color. Figure 2 reports the flame length as a function of the air inlet Reynolds number (increase of inlet Reynolds number corresponds to lower value of equivalence ratio).

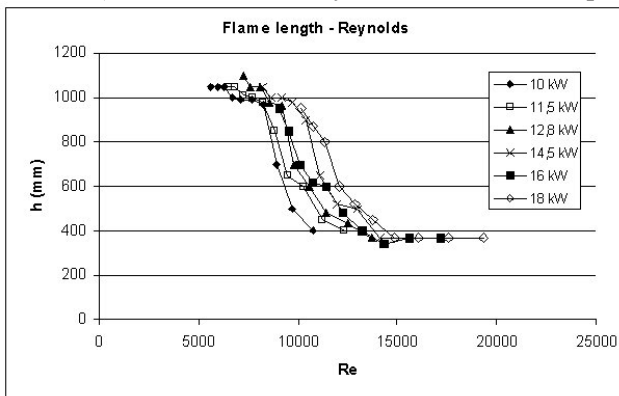
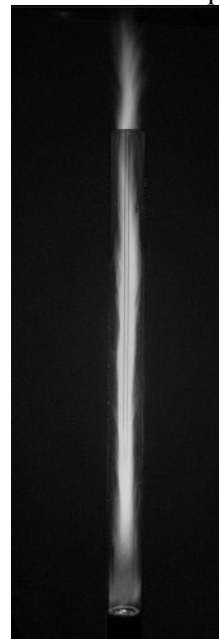


Figure 2: flame length as a function of the air inlet Reynolds number for different thermal powers.



$Re = 8076; \phi = 0.9.$



$Re = 13729; \phi = 0.65.$

Figure 3 : flame images for same input thermal power = 12.8 kW.

It has to be noticed that the flame length reduces increasing Re and this behavior is the same for different input thermal powers, the only difference being that the curves are shifted toward higher Re increasing the input thermal power, in accordance with [3].

Moreover it has to be mentioned as increasing the air inlet Re the color flame changed from a yellow color to a blue color. In the first case the flame is similar to a typical diffusion flame with a fuel jet surrounded by a coaxial air jet, with long reaction time due to the low mixing efficiency between the reactants. In the second case the flame is more similar to a quasi premixed flame with fast mixing and an intense blue color. Figure 3 reports two flame images for two different Re and same input thermal power.

The pollutant emissions measurements have been carried out for the same thermal powers and equivalence ratios of the previous images. The results are reported in figures 4 and 5 as E_{NOx} and E_{CO} index [4].

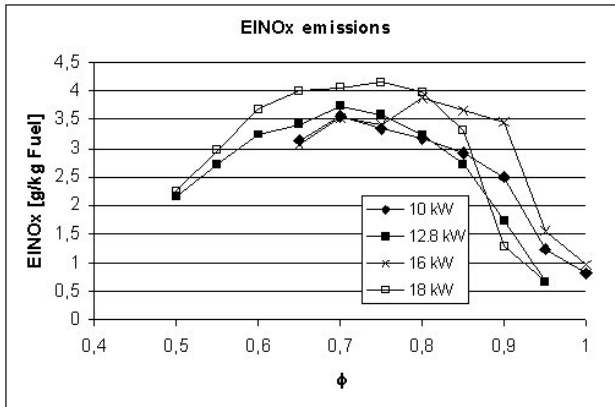


Figure 4: NO_x emissions for different input thermal power and equivalence ratio.

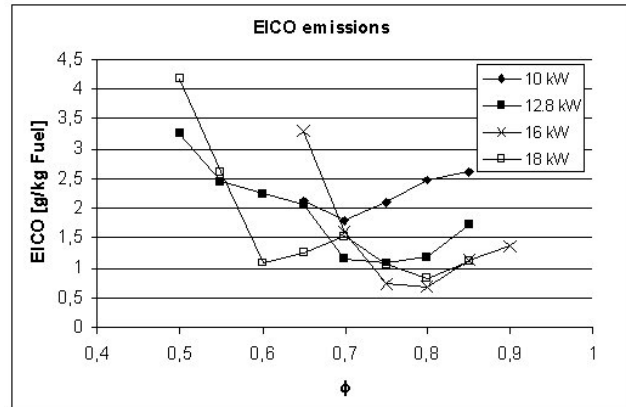


Figure 5: CO emissions for different input thermal power and equivalence ratio.

From figure 4 it is possible to notice as the NO_x emission increases with the equivalence ratio and after a value of 0.85 it begins to reduce strongly. In the lower equivalence ratio zone the flame is shorter (low equivalence ratio means higher Re) and the reduction in NO_x emissions is due to the lower flame temperatures or shorter residence time.

CO emission has been reported for equivalence ratio lower than 0.85 because beyond this value it increases rapidly, due to the bad reactants mixing and the very long flame: in fact in this case the reacting flow impacts to the end of the radiant tube and the reactions are quenched carrying to high CO values.

Figs. 6 and 7 report NO_x and CO emissions at the same input thermal power (12.8 kW), with and without the external gas recirculation. Figs. 8 and 9 are referred to the 18 kW input thermal power operating condition.

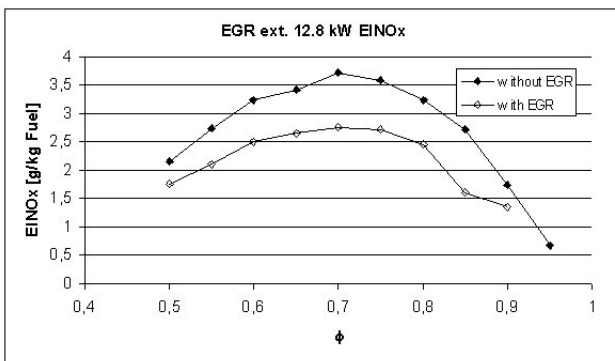


Figure 6: comparison of NO_x emissions for 12.8 kW input thermal power with and without external gas recirculation.

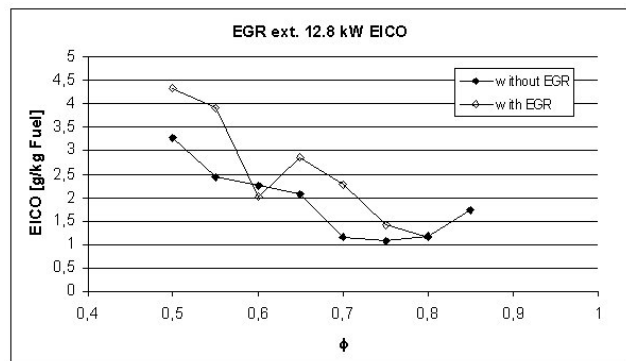


Figure 7: comparison of CO emissions for 12.8 kW input thermal power with and without external gas recirculation.

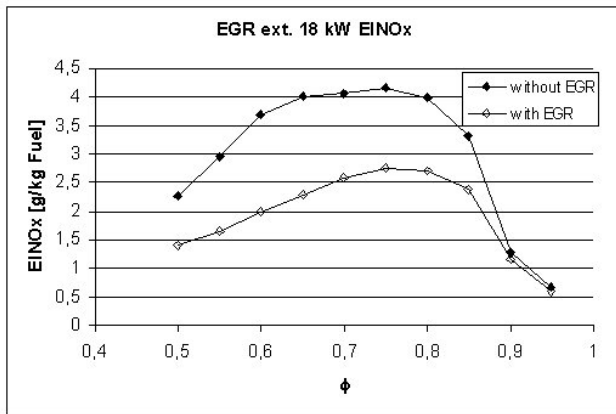


Figure 8: comparison of NOx emissions for 18 kW input thermal power with and without external gas recirculation.

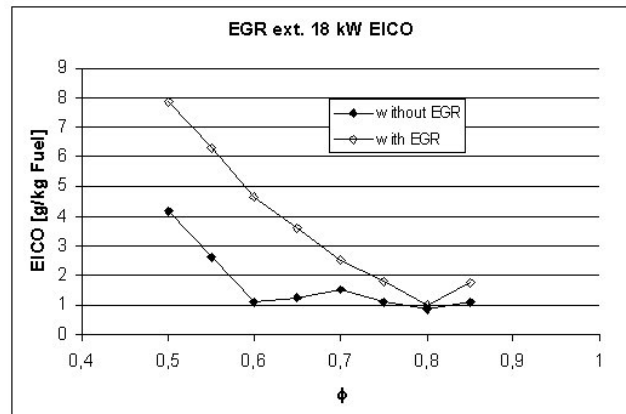


Figure 9: comparison of CO emissions for 18 kW input thermal power with and without external gas recirculation.

The mass amount of recirculating combustion products ranges from 30 to 35 % of the air mass flow inlet. For equivalence ratio close to the stoichiometric value the EINOx is similar with and without EGR. In this case it has to be reminded as in this region the reactants mixing is not good and the fluid dynamic plays the main role in the combustion process. At the contrary, the emission level is lower moving toward lean equivalence ratio because of a good mixing and the lower mean combustion temperature reached through the addition of cooler combustion products. Because of the lower mean combustion temperature the CO level is higher as it is highlighted in figures 7 and 9 moving toward lower equivalence ratio. This fact reduces the optimal operating field of the burner, in the presence of EGR.

It has to be underlined that the more stringent emission limit for this burner typology is 2.7 and 1 for EINOx and EICO respectively. By the external exhaust gas recirculation it is possible to reach the limit for EINOx but for EICO it is not satisfied.

Conclusions

In this work it has been highlighted as the combustion regime for a confined flame is strongly dependent on the fluid dynamic, the Reynolds number being the governing factor.

Moreover it has been showed as the external exhaust gas recirculation can reduce the NOx emissions only when the combustion regime is characterized by good reactants mixing, affecting also CO formation.

The future work will continue improving the fuel – air mixing and investigating the use of the internal exhaust gas recirculation to reduce the CO emission, by a change of efflux geometry.

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Passive control of methane premixed industrial burner

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ABSTRACT

In this work we analyze experimentally the flow topology of a methane–air premixed bluff-body burner at atmospheric pressure; reactants are not preheated before entering into the burner. We analyzed the flame at Reynolds number (Re) 8000 and equivalence ratio (ϕ) 0.75. On the actual burner, at the same operating conditions, we tested also a passive control strategy consisting in injecting air from small holes located on a ring surrounding the head of the burner. Pointwise velocity and temperature are measured by means of Laser Anemometry Doppler (LDA) technique and thermocouples respectively. Pollutants are determined by means of a combustion analyzer while noise emissions are measured by microphones placed at the combustion chamber wall.

INTRODUCTION

Premixed industrial burners are very important components in both aeronautical and mechanical applications. The main drawback of these systems is the rising of instability, which can be limited by a recirculation of hot products, achieved by means of a bluff-body placed at the exit section. As shown in [1] and [2], the recirculation zone acts like a heat source since fresh mixture is preheated in the shear layer. The bluff-body recirculation zone results in a toroidal vortex that 1) mixes the fresh mixture with hot products; 2) increases the residence time of the reactant mixture in high temperature regions; 3) increases the heat transfer between hot and cold regions.

In order to reduce further the fluid dynamic instabilities and the amount of pollutants, often correlated to noise, a passive control strategy on the actual burner has been tested. The control methodology consists in perturbing the flame by means of air jets exhausting from holes located on a ring surrounding the burner exit section. Such a method has been designed and numerically simulated by Giacomazzi and Bruno [3] for the active control of a nonpremixed flame: they obtained good results in terms of flame stability and pollutant emissions by pulsating the auxiliary air jets.

Experimental results of our analysis represent a basis for developing passive/active control strategies for turbulent flames, a task which is presently underway by the authors.

EXPERIMENTAL SET-UP

Experiments have been performed at the Combustion Fluid Dynamic Laboratory of C.R. Casaccia of ENEA (Italian Agency for Energy and Environment). The burner, sketched in Fig. 1, is formed by two parts, the base (premixing zone) and the top (outlet zone). The base consists of a Bunsen burner modified for the forced inletting air. The top of the burner (quarl) is formed by three parts: an external pipe with a diameter D of 25 mm, an inner conical bluff

body with a diameter d of 15 mm [4] and a ring with 11 holes, used for the control. An alumina particles (5 μm mean diameter) seeder system is used to seed the fluid dynamic field.

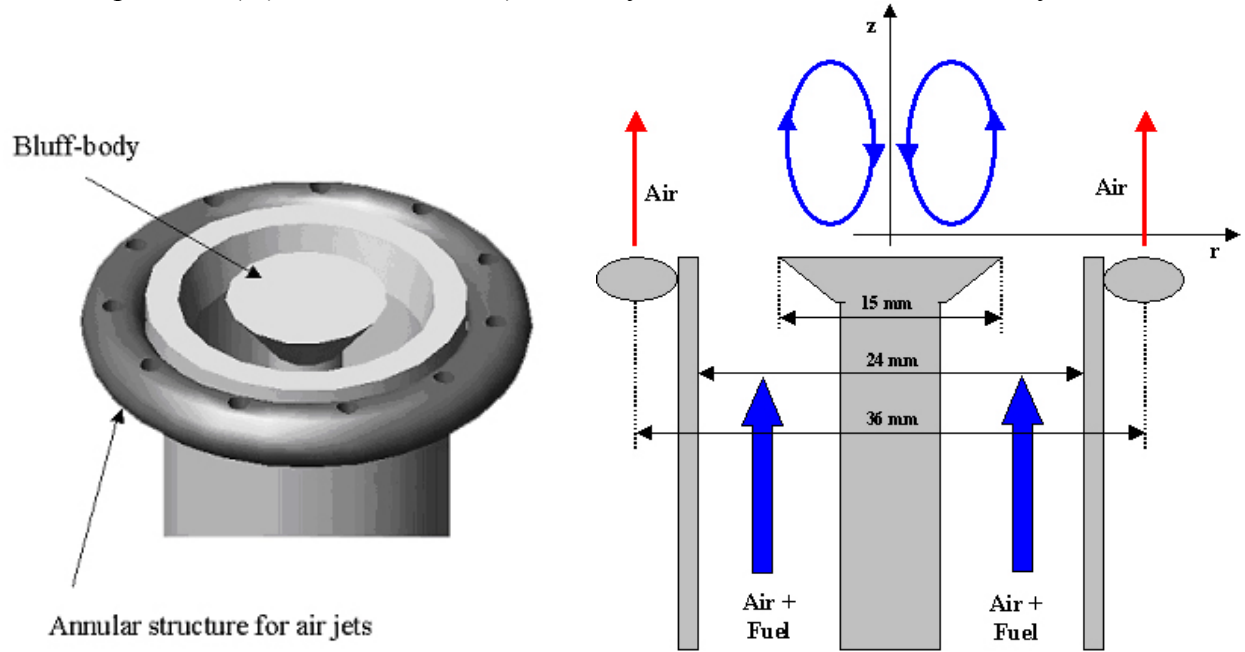


Fig. 1 The annular burner DG-25-15-CON.

Combustion regimes and flow conditions are characterized by means of two global nondimensional parameters, the equivalence ratio (Φ and Φ') and the Reynolds number (Re):

$$Re = \frac{U \cdot D_{equ.}}{\nu}$$

$$\Phi = \frac{\left(\frac{\dot{m}_{fuel}}{\dot{m}_{air_princ}} \right)}{\left(\frac{\dot{m}_{fuel}}{\dot{m}_{air_princ}} \right)_{st}}$$

$$\Phi' = \frac{\left(\frac{\dot{m}_{fuel}}{\dot{m}_{air_princ} + \dot{m}_{air_in}} \right)}{\left(\frac{\dot{m}_{fuel}}{\dot{m}_{air_princ}} \right)_{st}}$$

where U is the flow velocity at the exit burner, $D_{equ.} = \sqrt{D^2 - d^2}$ is the equivalent diameter of the burner, ν is the kinematic viscosity, $\dot{m}_{fuel}$ is the fuel mass flow rate, $\dot{m}_{air_princ}$ is the mass flow rate of the main stream, $\dot{m}_{air_in}$ is the mass flow rate of the control air flow. Operating conditions analyzed in this work are summarized in Tab.1.

No Control	Control
$\dot{m}_{air_main} = 2.19 \cdot 10^{-3} \text{ kg/s}$	$\dot{m}_{air_main} = 2.19 \cdot 10^{-3} \text{ kg/s}$
$\dot{m}_{fuel} = 9.55 \cdot 10^{-5} \text{ kg/s}$	$\dot{m}_{fuel} = 9.55 \cdot 10^{-5} \text{ kg/s}$
$\dot{m}_{air_control} = 0$	$\dot{m}_{air_control} = 3.93 \cdot 10^{-4} \text{ kg/s}$
$Re = 8000$	$Re = 8000$
$\Phi = 0.75$	$\Phi = 0.75$ and $\Phi' = 0.65$

Tab. 1 Exnerimental test- matrix and burning conditions.

EXPERIMENTAL RESULTS

Comparing the averaged velocity fields with and without control (Fig. 2) we note that the surrounding control air jets induces a flame stretch. The average temperature at $z=45\text{ mm}$ reported in Fig.3, also shows that the mixing of the control fresh air with the hot gases outside the recirculation zone, leads the mean temperature to decrease significantly.

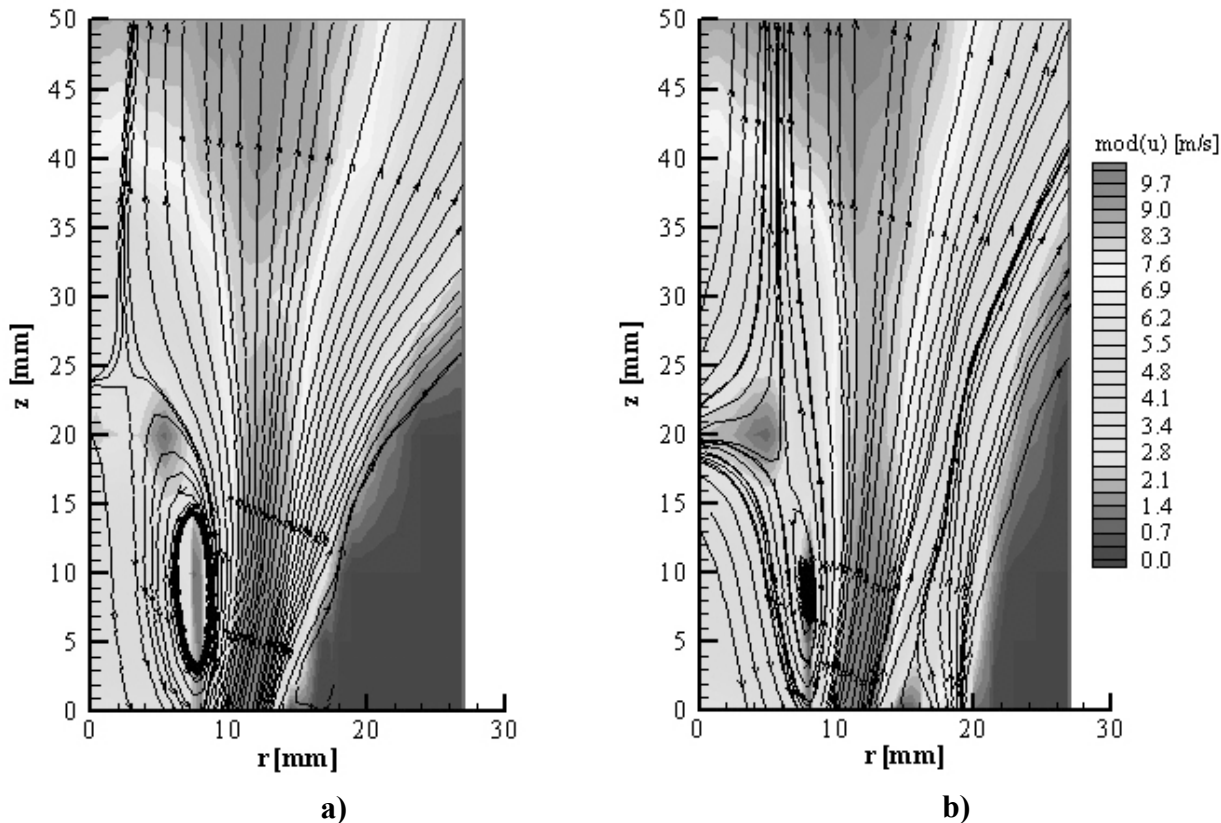


Fig. 2 Averaged velocity fields without (a) and with the control (b).

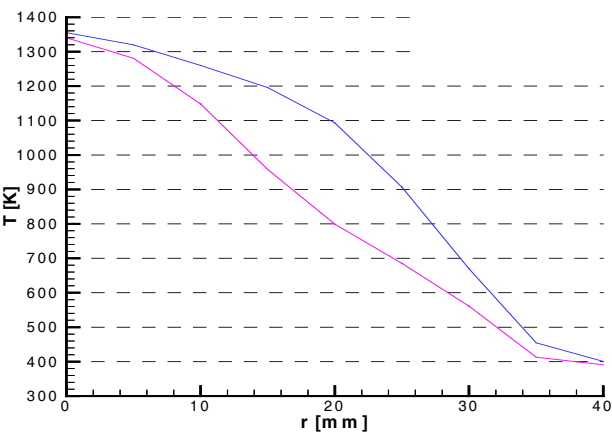


Fig. 3 The mean temperature at $z=45\text{ mm}$ ($z/D=2.2$) (magenta is with the control and blue is without).

Pollutant emissions	
CO	3.5
NO _x	0.54
C _x H _y	1.6

Tab. 2 Pollutants Emission Index ratio $[EI_i]_{\text{with}}/[EI_i]_{\text{without}}$.

The *Emission index* [5] $EI_i = \frac{\dot{m}_i}{\dot{m}_{f,burnt}}$, where $\dot{m}_{f,burnt}$ is the burnt fuel mass flow rate and $\dot{m}_i$

is the pollutant mass flow rate is reported in (Tab.2). The passive control increases CO largely, C_xH_y slightly, and decreases NO_x (Tab.2).

The decreasing of the temperature freezes the reaction of CO oxidation and prevents NO_x production (we have just considered the *thermal* NO_x).

Overall noise emissions are determined by the *Sound Pressure Level* defined as

$$SPL = 20 \log_{10} \left(\frac{p_e}{p_0} \right) \quad \text{where } p_e \text{ is the}$$

pressure standard deviation and p_0 is the reference pressure (20 μPa). The passive control reduces noise emission since:

$$SPL_{without} - SPL_{with} = 8 \text{ dB}$$

The acoustic spectra are shown in Fig. 4 showing that a reduction of pressure energy is achieved over the whole frequency range.

Further studies are underway in order for control performances in terms of pollutant emissions to be improved also by mean of an active fed-back control of the auxiliary jets flow.

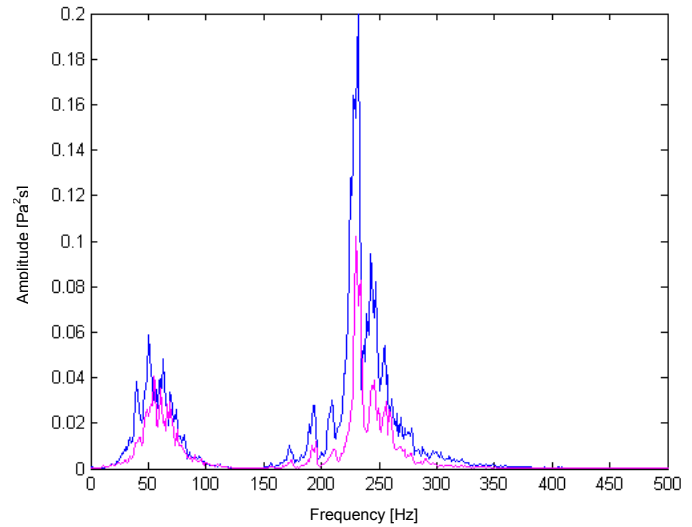


Fig. 4 Power Spectral Density at 40 cm from the flame (magenta is with the control and blue is without).

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Soft-sensors design for unsteady-state VOC afterburners

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Abstract

The catalytic reverse-flow reactor is efficient for autothermal treatment of lean mixtures. When the inlet concentration and composition are variable it is important to avoid catalyst overheating or reaction extinction; as on-line measurements may be extremely difficult and expensive, a soft-sensor, derived from non-linear high gain techniques, has been developed to estimate the inlet concentration and the reactor conversion from three temperatures measured. This observer has been demonstrated to give correct prediction both when extinction occurs and when various unknown pollutants are fed.

Introduction

Forced unsteady-state gas-solid catalytic reactors have been deeply investigated in the past, as it has been demonstrated that temperature and composition distributions, which cannot be obtained in any steady-state regime, can be obtained by means of forced variations of inlet parameters, as it has been showed by Matros and Bunimovich (1996), thus improving both conversion and selectivity in a number of chemical processes. A simple technical solution to obtain forced unsteady-state conditions is the periodic reversal of the flow direction; this device is particularly efficient for the treatment of lean mixtures of waste gases as the reversal of the flow keeps the heat of reaction inside the bed and allows autothermal operation even when cold and lean mixtures are fed, thus reducing strongly the need for auxiliary fuel, except for start up (Matros and Bunimovich 1996; Eigenberger, 1992).

In addition to the intrinsically dynamic behaviour of the reverse-flow reactor (RFR), one must deal with unexpected external perturbations (feed concentration, composition and temperature) which may lead to reactor extinction (and thus pollutants emissions) or catalyst overheating (and thus subsequent deactivation). In order to avoid these problems it is necessary to implement some closed-loop control strategies based on the measurement of the inlet concentration (and composition) and the outlet conversion. The aim of this paper is to describe a model-based soft-sensor (observer) that quickly and reliably estimates the feed composition from some temperature measurements in the reactor, thus avoiding expensive hardware sensors and time consuming on-line measurements. The observer combines the knowledge of the physical system (model) with experimental data (some on-line measures) to provide on-line estimates of the sought states and/or parameters.

The model

A medium-scale RFR, as schematically shown in Figure 1 (Ramdani et al., 2001), has been considered: the monolith is catalytically active in the core region, while is inert in both ending sections; an electric heater is installed in the middle region to maintain ignition, while fresh air is employed as an effective means of lowering the temperature in the catalytic section. Fast flow reversal is needed to keep high the temperature in the catalytic region. The wide square cross-section of the monoliths prevents heat losses over their whole length, while

heat losses through the reactor wall can occur in the central region. The combustion of xylene over a $\text{Pt}/\text{Al}_2\text{O}_3$ has been considered.

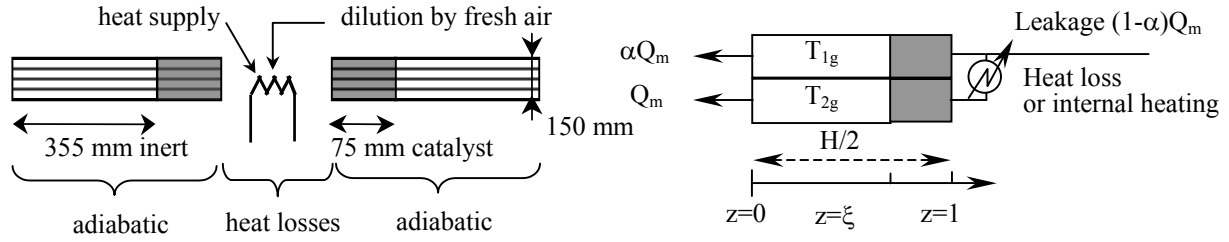


Figure 1. Left: main geometrical characteristics of the RFR. Right: the countercurrent model

Deriving an observer from a detailed model accounting for heat losses through the reactor wall, finite flow reversal frequency, reaction kinetics is an overwhelming task; as a consequence a simplified model has been developed. By taking advantage of the high frequency of flow reversal, the analogy with the countercurrent reactor has been considered (Nieken and al., 1995); the method described by Balakotaiah and Dommeti (1999) has been used to derive the following pseudo-homogeneous energy balance equation:

$$\left(\frac{1}{P_{ax}} + \frac{1+\alpha^2}{2P} \right) \frac{\partial^2 T_s}{\partial x^2} + \frac{1-\alpha}{2} \frac{\partial T_s}{\partial x} + P \Delta T_{ad} \psi(x) = \tau \frac{\partial T_s}{\partial t} \quad \text{where:}$$

$$P = \frac{h a_c H}{2 \rho_g u_0 c_{p,g}}, \quad \frac{1}{P_{ax}} = \frac{2 \lambda_{ax}^s}{H \rho_g u_0 c_{p,g}}, \quad \Delta T_{ad} = \frac{-\Delta H}{M c_{p,g}} w_{10}, \quad \psi(x) = \frac{\omega_1(x) + \omega_2(x)}{2 \omega_{10}}, \quad \tau = \frac{(1-\varepsilon) \rho_s c_{p,s} H}{2 \rho_g u_0 c_{p,g}}$$

The mass fractions (ω) on the solid surface are evaluated by means of the mass balance equations for the gas and the solid, assuming first order kinetics and pseudo-steady state conditions for the catalyst. The correction for finite flow reversal frequency of Edouard et al. (2003) has been adopted. Figure 2 shows a comparison between the measured temperatures and the predictions obtained by means of a detailed (two phase) model and of a simplified homogeneous countercurrent model with and without correction for the finite frequency.

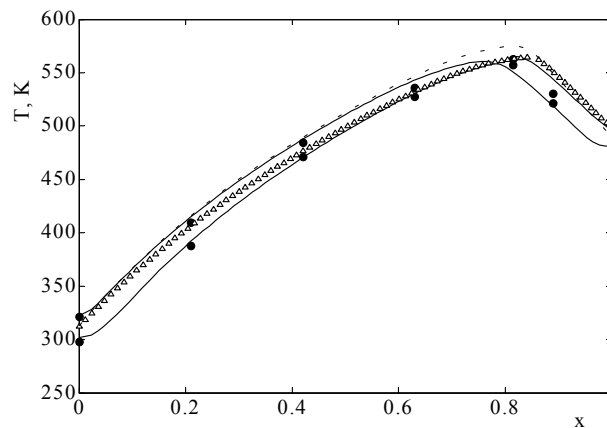


Figure 2. Comparison between an experiment (●) and the results of simulations with detailed model (upstream and downstream monoliths, —) and simplified homogeneous model with (Δ) and without (---) correction for the finite frequency.

$P = 73.9$, $\Delta T_{ad} = 25$ K, $\tau = 143$ s, switching period = 16 s.

The model equations have been discretised according to a finite difference scheme, thus

leading to the following system:

$$\dot{x}(t) = A(\alpha(t))x(t) + G(x, z), \quad x(t) = [x_1(t) \quad \dots \quad x_n(t)]^T, \quad x_i(t) = T_s(x_i), \quad z = \begin{bmatrix} k_0/k_D \\ \Delta T_{ad} \end{bmatrix}$$

The observer which has been designed is able to estimate both the inlet concentration (ΔT_{ad}) and k_0/k_D , in order to take into account both variations of the inlet concentration and changes in the feed composition (and subsequent variation of the kinetic parameters). An high gain observer has been employed as it does not require the solution of any differential equation and its calibration is very simple, thus allowing to overcome the numerical difficulties in solving the dynamic Riccati equations in the Kalman filter based observers. The general equation of the observer is:

$$\dot{\hat{x}}(t) = A(\alpha(t))\hat{x}(t) + G(\hat{x}, z) + K(\hat{x} - x_{measured})$$

The measured variables are the temperature at the inlet of the inert and of the reactive monoliths and the temperature at the outlet of the upstream reactive monolith. The first and the last temperature are used to update the estimate of the temperatures in the upstream and in the downstream monolith.

When the estimated conversion is equal to unit the reaction is under diffusive control and the system becomes linear. Thus a linear observer is used to estimate the inlet concentration from the second measured temperature; the gain K is evaluated according to Edouard et al. (2003) and Farza et al. (1998). When the conversion starts decreasing the reaction becomes under kinetic control and a non-linear observer has been implemented (Hammouri and Farza, 2003) in order to evaluate the inlet concentration and the kinetic parameters.

Results.

The proposed observer has been validated by means of simulations; the complete model has been considered as a source of experimental data. Figure 3 (left) shows a comparison between the prediction of the observer and the simulated values of inlet concentration and outlet conversion in the case of xylene combustion; fast and accurate reponse without overshoot are obtained for both variables even when steep changes are considered. The prediction are reliable both when the conversion is equal to 1 and when the reaction is extinguishing; it is important to point out that when the reaction is extinguished the temperatures quickly moves down to the ambient value and the system is no longer

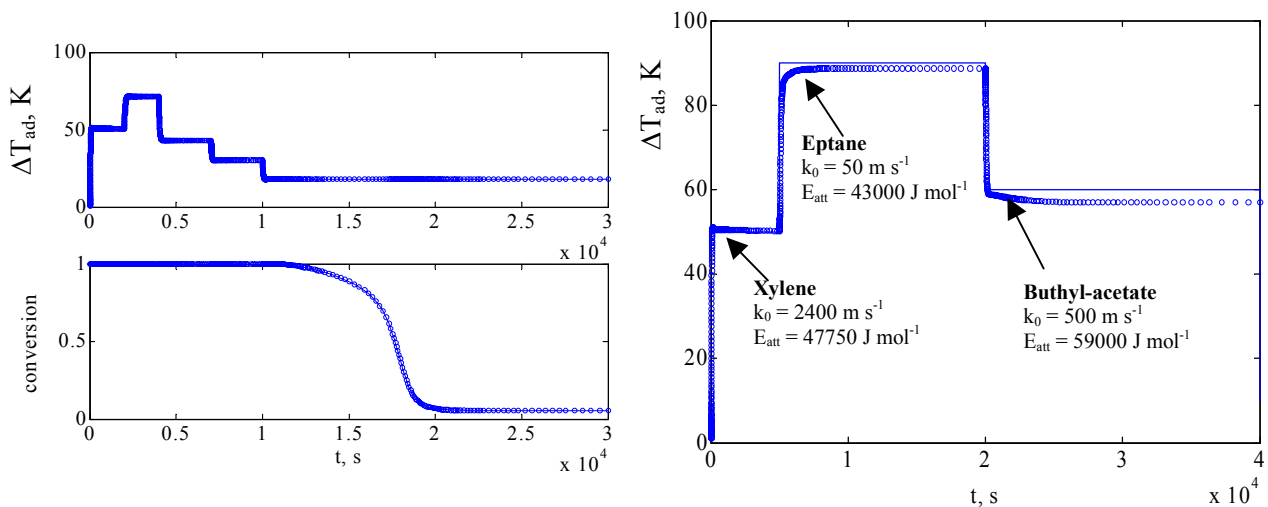


Figure 3. Comparison between the prediction of the observer and the simulated values of inlet concentration and conversion when xylene (left) and when different pollutants (right) are fed.

observable. The same accuracy is obtained when different pollutants (with different concentration) are considered to be fed to the reactor as it is shown in Figure 3 (right). A further test has been accomplished considering random changes in the frequency factor, activation energy and inlet composition of the reactor feed; this may simulate the change of the kinetic parameter due to catalyst fouling or deactivation. Also in this situation the estimations of the observer are closed to the correct values.

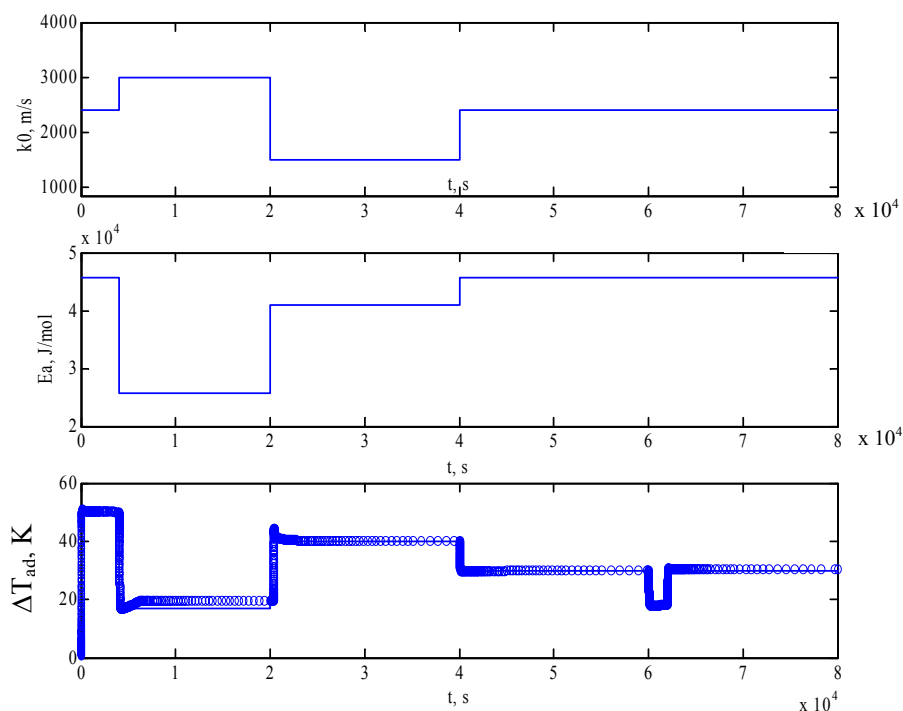


Figure 4. Comparison between the prediction of the observer and the simulated values of inlet concentration when the kinetic parameters of the pollutant changes.

Conclusions.

A non-linear high gain observer has been proposed to estimate the inlet concentration in a RFR. The observer is based on a simplified pseudo-homogeneous countercurrent model of the reactor and on three temperature measurements. Correct predictions of the inlet concentration and of the outlet conversion are obtained both when the reactor is fully ignited and when conversion decreases place and when the composition of the feed changes, thus avoiding expensive physical sensors and time consuming on-line measurements for control purposes.

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Some Remarks about the Combustion Phenomena in Hybrid Rockets

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INTRODUCTION

One of the most interesting kinds of combustion for engineering applications is that between a solid fuel and a gaseous oxidizer. This combustion process, that is the nature's way of burning fuels and oxidizer like a candle or coal with air, is typical of hybrid rockets and solid fuel ram/scramjets. In any case, such a combustion mechanism is very complex. The solid fuel regression rate is the main parameter for a thorough characterization of the hybrid internal ballistic, so the research key objective is the formulation of a suitable model capable of predicting the fuel consumption rate as function of the thermo-fluid-dynamic characteristics. It was demonstrated, by both theoretical and experimental works¹, that the regression rate depends primarily on the convective heat transfer from the flame to the fuel surface. The mass flux in the port is, then, a fundamental operating parameter governing the fuel consumption rate. Pressure was also found to influence the regression rate by several investigators who attributed this effect to either the wall heterogeneous reactions with the oxidizer² or the finite-rate gas phase chemical kinetics³. Furthermore, the oxidizer injection characteristics have a considerable weight. The whole combustion process will be affected severely by the incoming oxidizer flow pattern. Many tests were performed on the hybrid rocket developed at the University of Naples in order to investigate the regression rate behaviour.

EXPERIMENTAL SET-UP AND DATA REDUCTION

A schematic of the axisymmetric combustion chamber used for experimental tests is shown in Fig. 1. Simple cylindrical one-port high density polyethylene fuel grains, 570 mm long, were tested. The port initial diameter, D_0 , was chosen equal to 16, 25, 50 and 75 mm, in order to achieve a wide range of mass fluxes and observe the influence of the oxygen impingement on the grain's surface. Before and after the grain, a pre-chamber and a mixing chamber were added respectively, the former to shift the strong recirculation region caused by the oxygen injection so increasing the regression rates; the latter to improve the combustion efficiency.

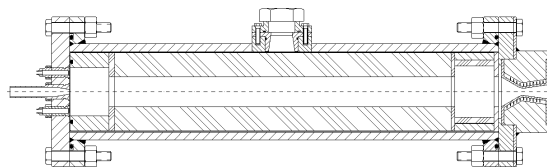


Fig. 1 Hybrid rocket engine scheme

A water cooled nozzle was used to insure constant chamber pressure during the run. Chamber pressure and motor thrust were measured by capacitive transducers and load cells respectively. All the signals were acquired by a National Instrument[®] DAQ device, recorded and processed by the LabView[®] software that controls the system. Time and space-averaged regression rates were computed by the fuel mass loss while the instantaneous regression rate was measured by means of the ultrasound pulse-echo technique. One ultrasonic transducer

was employed in order to obtain the time evolution of the local grain's thickness and, in turn, the regression rate in that point (see the top of Fig. 1). A detailed analysis of the accuracy of the ultrasound experimental measurements was conducted⁴. The principal result is that the measurement error caused by the change of speed of sound in the fuel in the steady state are less than 5% in all the experimented conditions. The thickness data were filtered by applying a low-pass digital filter. For the calculation of the regression rate a central formula was applied to take the thickness derivative. The instantaneous local oxygen mass flux was computed applying a running average to the mass flow rate signal and assuming that the fuel consumption is axisymmetric.

RESULTS AND DISCUSSION

In Fig. 2 the time- and spatially averaged regression rates are reported as function of the oxidizer mass flux with the data in Ref. 5, 6, 7 for comparison. In the experimental conditions the oxygen mass flow rate as well as the chamber pressure and the motor thrust are constant so that the mass flux variation during a single test is only due to the port area change.

At the same oxidizer mass flux level and pressure range, the current regression rates are up to 2.5 times faster than those in references, and show lower influence of the mass flux as demonstrated by the exponent of the power law, substantially less than 0.8 expected from a fully developed turbulent boundary layer correlation.

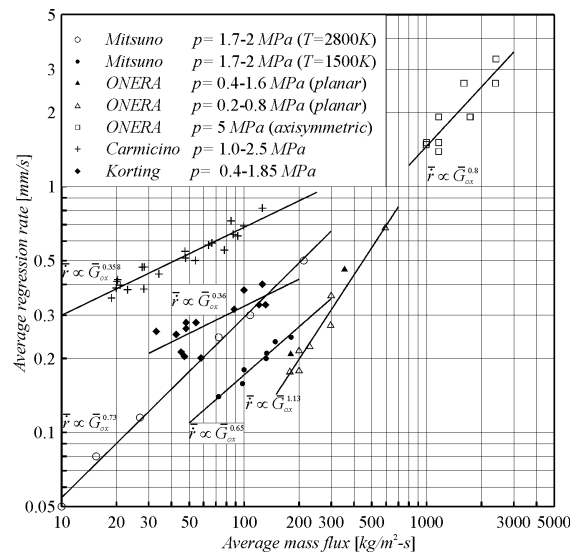


Fig. 2 Comparison of average regression rates

This is a consequence of the different flowfield. In fact, in this condition the oxygen injection, generating a flow recirculation zone, leads to a non uniform convective heat transfer distribution in which the wall heat flux and the regression rate increase from a low value just downstream the pre-chamber to a maximum at the jet impingement region, and, further downstream, decrease gradually along the combustor axis.

The port diameter profiles after the test, D_2 , have a shape consistent with what described above (Fig. 3). All the curves in the first diagram of Fig. 3 ($D_0 = 50$ mm) display a maximum, whose location moves downstream as the fuel consumption increases. The same behaviour is verified for 75 mm port initial diameter grains. Different profiles, instead, are exhibited in the second diagram ($D_0 = 25$ mm) by the curves relative to tests 1, 10 and 19 and are consistent with those of 16 mm port initial diameter case. In Fig. 3 the approximate jet diameter is plotted by assuming a divergence angle varying between 6° and 8°. The comparison between the jet pattern and the diameter profiles suggests that the maximum regression rate occurs in

the region where the oxygen jet impinges on the grain's surface coherently with the maximum convective heat transfer expected in this zone. For 25 mm and 16 mm initial diameter grains this behaviour is not so evident maybe because of the restricted region interested by the jet impingement.

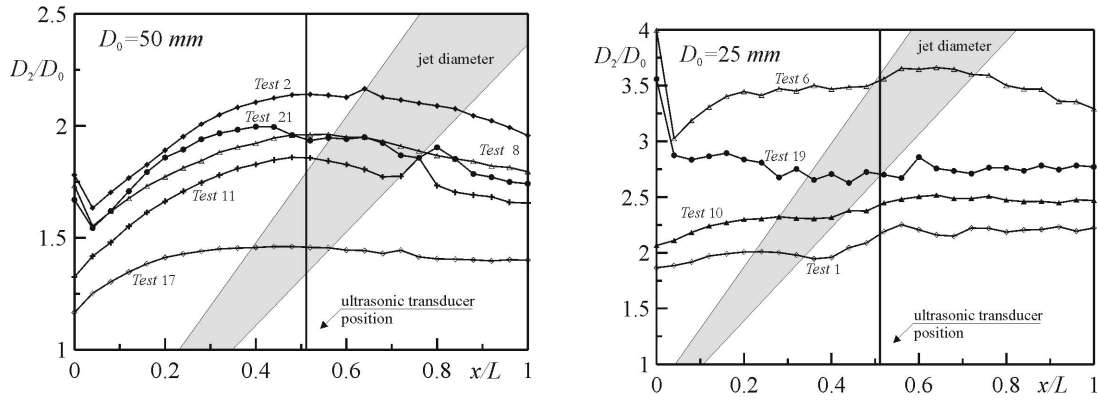


Fig. 3 After burning port diameter profile

Looking at the instantaneous regression rate curves plotted versus the local instantaneous grain diameter D (Fig. 4) support this hypothesis. Indeed, qualitatively matching the data in Fig. 3 and Fig. 4, we can see that, for $D_0 = 50$ mm, during the run, the oxygen impacts on the grain at the transducer location and so the regression rate appears increasing or approximately constant.

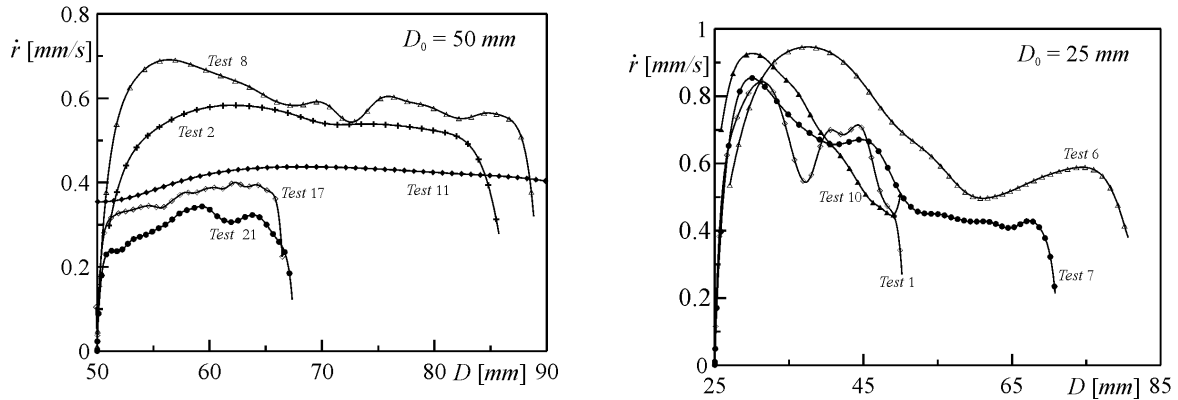


Fig. 4 Local regression rates versus the local port diameter

Actually, it is possible to make an analogy with the flowfield in solid fuel ramjets with a facing rearward step at the air inlet. Following the results found in literature^{8,9}, an empirical correlation was developed to describe the average regression rate, $\bar{r}$, in the form of power law of mass flux and pressure:

$$\bar{r} = 0.0745 \bar{G}_{ox}^{0.338} p^{0.233} \quad R^2 = 0.965 \quad (1)$$

In Eq. (1), the regression rate is expressed in mm/s, the average oxygen mass flux, $\bar{G}_{ox}$, in kg/m²s and the pressure, p , in atm. The exponents in Eq. (1) are completely comparable with those mentioned in literature further demonstrating that the actual flowfield in the hybrid rocket experimented here is similar to that in solid fuel ramjets.

On the other hand, an accurate theoretical analysis¹⁰ shows that a dominant role is played by the average port diameter and that this is equivalent to the verified pressure effect, yielding

the following correlation:

$$\bar{r} = 0.00936 \bar{G}_{ox}^{-0.555} \bar{D}^{0.462} \quad R^2 = 0.964 \quad (2)$$

Here the average diameter is in millimeters.

Finally, the same analysis demonstrates that better accuracy can be achieved by taking into account the influence of oxidizer to fuel ratio O/F :

$$\frac{r_f \bar{r}}{\bar{G}_{ox}} = 0.378 Re_D^{-0.4} \left(\frac{d}{\bar{D}} \right)^{-0.67} \left(\frac{O/F - 0.58}{(O/F)^2} \right)^{0.71} \quad R^2 = 0.980 \quad (3)$$

where r_f and d are the fuel density and the injector diameter. The predicted regression rates in Eq. (3) agree with the experimental ones with a maximum deviation of $\pm 10\%$.

CONCLUSIONS

The experimental tests performed on the hybrid rocket showed regression rates higher than those in literature. The non uniform port diameter profile after burn, showing a region of maximum consumption, suggested that a strong oxygen injection effect must influence the heat transfer mechanism, as in solid fuel ramjets. The ultrasound pulse-echo technique was used in order to gain extra information on the local regression rate behaviour during the run. Several correlation were developed in order to predict the regression rate as function of different control parameters. In conclusion this tests campaign demonstrated the fundamental role of the injection characteristics in determining the regression rates in hybrid rockets as well as the geometry and the chamber pressure.

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CFD Simulation of Layered Fuel-Air Explosions

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INTRODUCTION

The explosions involving layered fuel-air mixtures are of interest both for safety and technical applications. This paper deals with the analysis of flame propagation in large-scale layered mixtures, aiming at the prediction of consequences of explosions when flammable clouds are formed from accidental liquid spills or gas leaks in closed or partially confined environment [1-8]. Infact, following the initial dispersion of lighter than air gases or vapors, it is very likely that a layered mixture is formed, being a large portion rich or lean or even outside the flammability limits. A common over-conservative assumption is that the whole amount of the escaped flammable gas forms an homogenous stoichiometric mixture and participates in the explosion. To this regard, the mitigation devices are more expensive.

The flame propagation process in layered mixtures experimentally was first observed by Phillips [1]. The contemporary presence of three modes of combustion is characteristic: a laminar premixed combustion front travels across the layer of fuel-air mixture initially within the upper (UFL) and lower (LFL) flammability limits, strictly followed by a diffusive combustion front, which forms in correspondence of the stoichiometric line, between the excess of fuel in the rich layer and the excess of air in the poor layer. Finally, if a rich layer is initially present, a convective flame is established, after a certain distance, due to the convective mixing of the unburnt fuel with the air determined by the hot products of the previous combustion modes.

So far, few models for this type of flame propagation have been developed and presented in the literature [2-5,8]. On the other side, for engineering purposes, there is the need to reproduce this complex phenomenon for real environments and not for small laboratory scales. However, this is a formidable task due to the very large scale disparity: in space between the laminar premixed front thickness and the typical dimension of the devices involved; in time between the chemical reaction rate or the pressure wave velocity and the time of flame propagation across the domain.

A CFD approach to reproduce the laminar flame propagation in layered methane-air mixtures, adopting a grid size suitable for evaluating large-scale gas explosions, is proposed by implementing a new combustion model as user subroutine of a commercial solver named CFD-ACE+, developed by CFD Research Corporation, USA. At the moment, only the first premixed laminar combustion model has been implemented. The results are validated over experimental test cases where the layered fuel air mixture allows for the presence of this mechanism alone [3].

THE MODEL

A sub-grid model is determined, thus avoiding to solve of the smallest scale, the laminar flame thickness. It is based on two main elements: a criterion to determine the flame location and a model for the burning rate. Let us consider the determination of the flame location in a given cell. In a control volume approach the state variables resolved by the code represent cell average values.

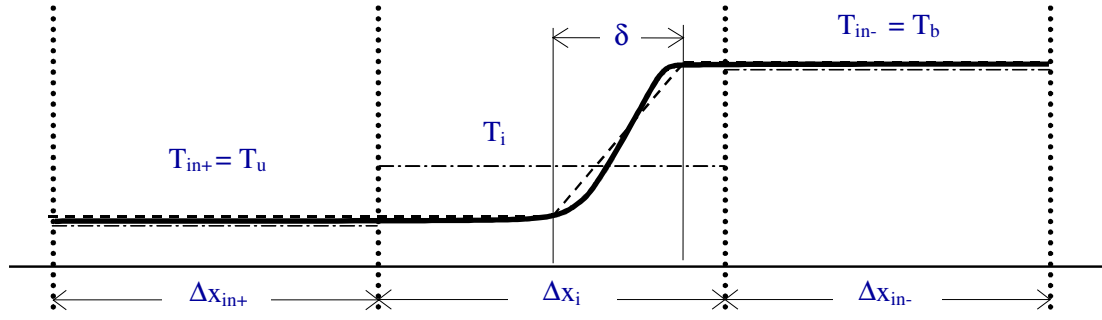


Figure 1. Temperature profiles in the direction normal to the flame front in the instant when a full flame thickness δ is entered in cell i . Three cells are represented. Solid line, real temperature profile; dot-dashed line, average temperature value; dashed line, reconstructed temperature profile.

The knowledge of the average value in this cell and in all the surrounding cells, coupled with the knowledge of a typical profile of the variables while crossing the flame front, allows the determination of the flame in-cell reconstruction (see Fig. 1). At the instant when the flame has just fully entered the cell, occupying a portion equal to δ , the “temperature of flame entering” T_{fe} is:

$$T_{fe} = \frac{1}{\Delta x_i} \left[T_u (\Delta x_i - \delta) + \frac{(T_u + T_b)}{2} \delta \right] \quad (1)$$

where T_u and T_b , are given by the average temperature values computed by the code in cells i_{n+} and i_{n-} respectively, δ can be computed as function of the unburnt mixture in cell i_{n+} and Δx_i is the cell size. T_{fe} depends only on fully burnt and unburnt conditions. The flame will be assumed to have entered the cell i , the first time it results,

$$T_i \geq T_{fe} \quad (2)$$

where T_i is the average temperature of the cell i . The flame will not be allowed to enter all the cells having equivalent ratio ϕ_i outside the flammability limits, even if condition (2) occurs. Regarding the burning rate model, a direct description of the fast chemical kinetic would require very small time steps compared to the time steps adequate to describe the flame propagation. To avoid this stiffness, a simple constant burning rate R_i in cell i could be determined as a linear function of the laminar flame velocity S_L :

$$R_i = \rho_{in+} Y_{in+} A_f S_L (\phi_{in+}) \quad (3)$$

This value is computed at the time of flame entering in cell i and it does not change until the flame enter in the next cell.

Direct coupling of the capturing criteria (2) with the burning rate (3) will give inaccurate results. It is based on the assumption that average values in the cell well approximate local values. Instead, in cells where the flow experience large variations, average values greatly differ from local point values. If the flame structure is much smaller than the cell size, heat fluxes on the boundaries should be zero for most of the time the flame travels in the cell. Conversely, numerical evaluation of the fluxes adopting average values of the temperature in the cells leads to non-null fluxes for all the time the flame travels into the cell. As a consequence, a loss of heat is computed from the already burnt cell, which could not reach the nominal temperature of the burnt mixture, and towards the unburnt cell. This is a common problem, also reported in computations of turbulent flame propagations and often referred to as the occurrence of a numerical instability. Some remedies have also been indicated [10].

To remain coherent to the reconstruction principium, we propose two correction terms. With reference to the flame located in cell i , the first consists of replacing T_i in the (2) with the temperature T_{chk} computed as:

$$T_{chk} = T_i + (T_{in+} - T_0) - b_{in-} (T_{ad,in-} - T_{in-}) \quad (4)$$

where T_0 is the value of the ambient temperature before the ignition and $T_{ad,in-}$ is the adiabatic flame temperature computed as a function of the equivalence ratio of cell i_{n-} at the instant when the flame enter in cell i_{n-} . The second correction affects the burning rate (3). This correction is required to ensure the correct value of the integral burning rate over the whole domain. It is obtained by multiplying Eq. (3) by a function of the progress variable:

$$R_c = R \cdot c^2(1 - c) \quad (5)$$

RESULTS AND CONCLUSIONS

The experimental set-up of Feng et al. [3] has been considered for model validation. A Plexiglas chamber forms the equipment, 2.13 m long and 0.419 m high, with a transverse dimension of 0.076 m, separate by two mobile planes. A first separator, at a fixed distance h of 0.01905 m from the roof, forms the upper vane, which is filled by a homogeneous flammable mixture of methane and air. It is removed just prior to the ignition. A second separator can be freely located along the axis y to determine the total height H of the room, thus providing values of the parameter $m = H/h$ varying from 1 to 22. Three different values of m have been simulated:

- $m = 1$; in this case only a single flammable layer exists; the flame experiences the maximum acceleration and no effect due to the layering are included;
- $m = 2$; in this case the flammable layer occupies the upper half part of the room; the flame experiences a lower acceleration;
- $m = 22$; in this case the flammable layer occupies only a small part of the entire volume; it is almost equivalent to the flame propagation in a flammable layer located at the top of a channel of infinite height, giving, apart from a small initial transient, a steady propagation.

Variation of the parameter m allows appreciating the ability of the model to catch different flame dynamics without the need to tune any model constant.

The problem has been simulated as two-dimensional. For all cases the flammable layer has been discretised with only 4 cells along y , each having a dimension $\Delta x = 0.0106$ m and $\Delta y = 0.0085$ m for a total of 800 cells. A constant time step of 0.0001 s has been used for all computations. Ignition of the mixture is given by assigning a prescribed burning rate in a single cell located on the left side of the flammable layer. The flame shape is well reproduced, particularly the increasing of the flame front surface with respect to the height of the flammable layer. Part of the fuel appears not burned in the front, in consequence of the dilution with air to a value outside the LFL, prior to the flame arrival. Results on the flame acceleration obtained for all the three values of m simulated are reported in Fig. 2, together with the corresponding experimental results. Satisfactory agreement between experimental and computed results is obtained.

Results have shown the ability of the model to reproduce the flame speed and acceleration in a layered methane-air mixture, by varying the filling ratio along the height of a combustion chamber, even adopting very coarse grid.

Increasing the ratio between the laminar flame thickness and the characteristic dimension of the flammable layer better satisfies the model assumptions. Therefore the model is expected to perform satisfactory well also in the case of very large configurations. The extension to

other fuels is very simple, requiring only the knowledge of fundamental properties of the mixture, as the flammability limits, the laminar flame speed and adiabatic temperature as function of the equivalence ratio of the mixture in unburnt conditions.

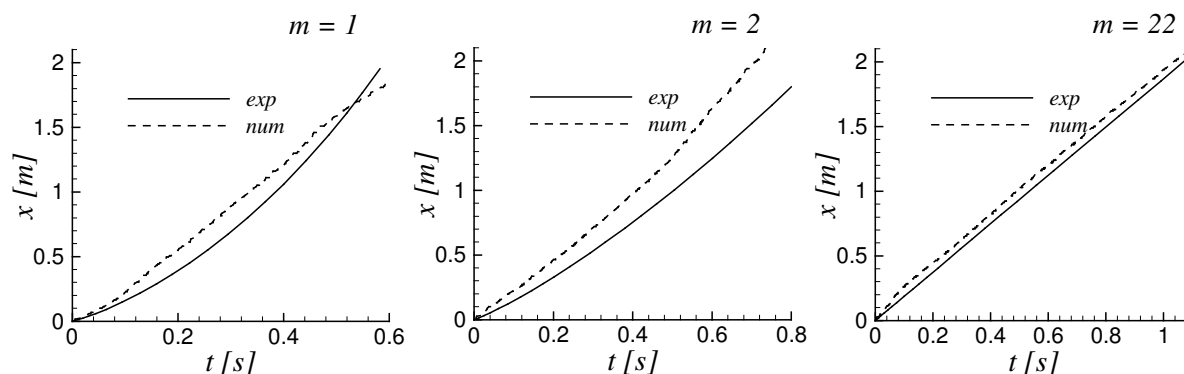


Figure 2. Comparison of the flame front position vs. time, as obtained in the experiments (solid line) and as obtained by present simulations (dashed line).

This model can be easily incorporated in existing codes, having the possibility to modify the expression of the source terms. The quantities required can be easily computed on a point-by-point basis, so that the computational overload is not too large and parallel implementations can be preserved. No adjustable parameters appear in the model.

Further validation is still required. This will be the object of the forthcoming research activity.

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Effects of fuel temperature and flame locations on combustion behaviors of LPG with high temperature air

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INTRODUCTION

Combustion in condition of diluted air and fuel with high temperature holds the potential to overcome the limitations of conventional combustion and achieve maximize energy efficiency, and minimize pollution (reduce emissions of CO₂, CO and nitric oxide). This technology is referred to as High-temperature air combustion (HiTAC), or Flameless Oxidization.

The objective of this study is to understand the effects of fuel temperature and flame locations on combustion characteristics of LPG with high temperature air. The numerical studies of combustion in a semi-industrial scale test furnace equipped with two sets of two-flame High-cycle Regenerative System (HRS) have been performed.

TEST FURNACE CONFIGURATION AND NUMERICAL MODELS

The HiTAC test furnace at the Royal Institute of Technology (KTH) Sweden used in this study has an internal dimensions of 2.9×1.6×1.6 m. Four tubes with an external diameter of 0.11 m each and cooled with air have been installed horizontally in each corner of the furnace to remove heat from the combustion chamber.

Figure 1(a) represents the computational domain of the HiTAC test furnace at KTH. The furnace is equipped with four high-cycle regenerative burners with capacity of 100 kW each. The burners (four burners marked A, B, C, D) are placed on the sidewalls of the furnace as it is shown in Figure 1(a).

The used fuel was gasol, the main (mass%) are: CH₄=0.02%, C₂H₆=0.95%, C₃H₈=98.35%, C₄H₁₀=0.67%. For the studies case, the fluxes of fuel were 7.7 Nm³/h, and the air flowrates were 214 Nm³/h. The temperature of air after preheated (regenerator) was 1311K obtained by measurement.

The model for combustion was employed including eddy dissipation concept (EDC) with a two-step mechanism to describe the chemical reaction. The turbulence was modeled by using the standard $k-\varepsilon$ turbulence model and radiation was handled using discrete transfer method.

DISCUSSION OF CALCULATING RESULTS

The numerical simulation on this semi-industrial-furnace equipped with two sets of two-flame High-cycle Regenerative System (HRS) have been validated in our previous study [1-2] by comparing with experimental results including in-furnace species and temperature. The agreement of predicted and measured species is good with the experimental error except the small zone near the burner. The effects of fuel temperature and flame locations on emission of

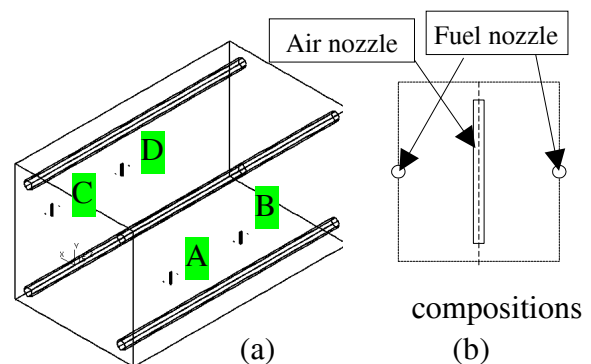


Figure 1 Configuration of the HiTAC test furnace
(a) Furnace (b) Burner

NO have also been reported in our work [2]. In this present, we focus on the influences of fuel temperature and flame locations on the characteristics of combustion and flame structure.

Effect of flame location

In order to understand the effect of flame locations on the behaviors of combustion and flame structure, the three basic flame configurations named as single side (firing by combining of burner A and B or Burner C and D), Counter (firing by combining of burner A and C or Burner B and D) and Stagger (firing by combining of burner A and D or Burner B and C) were investigated.

Figure 2 depicts the temperature distributions on the horizontal plane, including the central plane, of injection ports of combustion air for different flame locations which used in this study are Counter mode, fired by combining of burner B and D, Single-side mode, fired by combining of burner C and D and Stagger mode, fired by combining of burner A and D.

The peak temperatures of the gases are 1856, 1821 and 1900 K for combustion modes of counter, single-side and stagger, respectively.

The maximum flame temperature occurs at the case of stagger mode. This is the fact that the recirculation formed by burner's locations for stagger mode decreases the heat transfer from flame. Again, the highest temperature zones are found to occur in the middle of the combustion chamber at the burner level, farther away from the burner face. The counter mode gives the longest distance from burner face which the maximum temperature appears, while the stagger mode gives the shortest.

To describe the flame shape and size under HiTAC, the oxidation mixture ratio [3] was used in this work. The oxidation mixture ratio is calculated as mass fraction of oxygen to mass fraction of oxygen and the sum of oxygen needed to complete combustion as follows:

$$R_o = \frac{m_o}{m_o + \sum_c s_c m_{F,c}} \quad (1)$$

where $s = n_o M_o / n_F M_F$. $R_o = 0.99$ is assumed to indicate a flame border. Thus the flame volume can be approximately defined when $0 \leq R_o \leq 0.99$ [3].

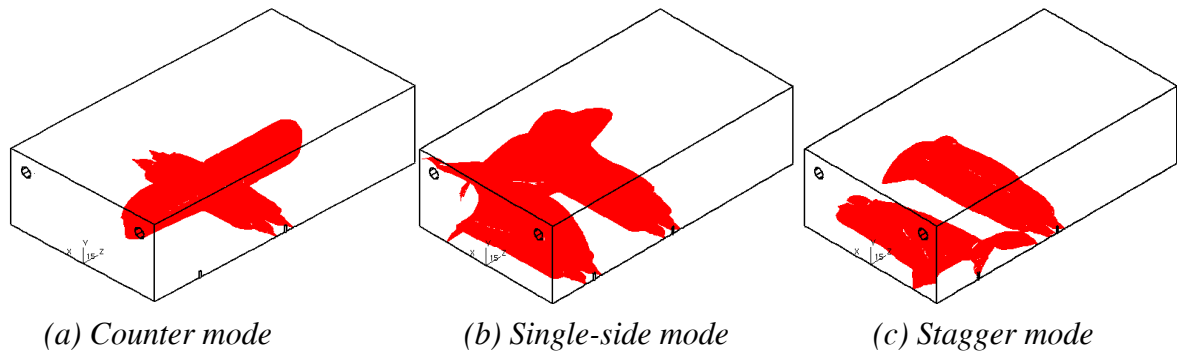


Figure 2 Temperature profiles (K) at various combustion modes

(a) Counter mode (b) Single-side (c) Stagger mode

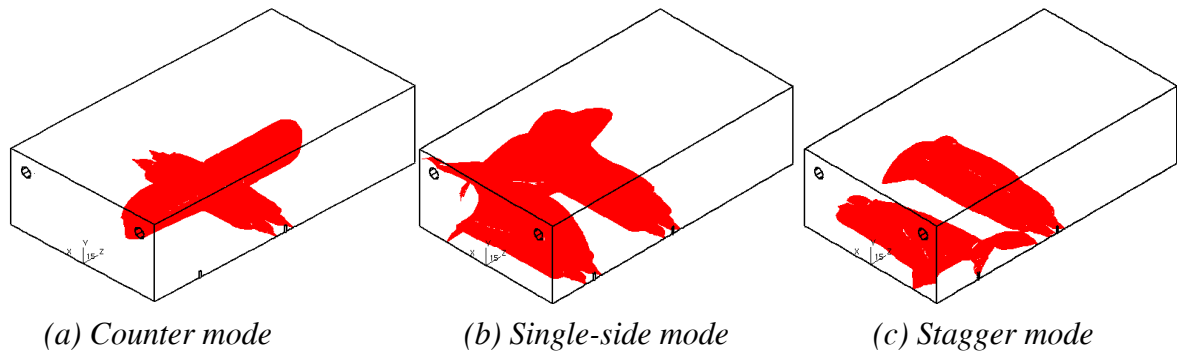


Figure 3 Flame shape for difference firing modes

Figure 3 shows the influences of flame locations on the variations of flame volume which was

figured out by the oxidation mixture ratio. Because of difference of burner's locations, the flame shape and size are different. The Counter flame occupies the smallest flame volume and the Single-side firing configuration flame occupies the biggest fraction of the furnace volume. Consistent with this conclusion, the Counter mode has maximum local peak firing rate ($5.1 \times 10^5 \text{ kW/m}^3$) and maximum flame combustion intensity (681.6 kW/m^3). The Single-side mode has the smallest local peak firing rate ($8.55 \times 10^4 \text{ kW/m}^3$) and the smallest flame combustion intensity (349.3 kW/m^3).

Effect of elevated fuel temperature

Simulations were performed for fuel temperature from room temperature to 1273K at the stagger mode. At this stage of the study the thermal decomposition of propane at elevated temperature before outlet from the gas nozzle was not considered. For all of the simulations, the excess air ratio and fuel thermal input to the burners was kept at constant value. The fuel injection velocities were varied by changing the fuel temperature. Other boundary conditions were also kept unchanged during the simulations.

The temperatures of fuel studied numerically were at the cases of 293, 573, 773, 873 and 1273 K. The peak temperatures for above cases were 1900, 1844, 1815, 1807 and 1795 K, respectively. It is obvious that the flame temperature decreases as the preheated fuel temperature increased, and the temperature distribution tends to more uniform. The explanation for this phenomenon is the effect of fuel injection at a higher temperature, thus a higher velocity limits the mixing of the fuel with the combustion air in the primary combustion region.

The variation of the flame volume with fuel temperature can be described using the Furnace Flame Occupation Coefficient, which is defined as the ratio between the flame and furnace volume. The fuel temperature has a strong effect on the flame volume. When the temperatures of fuel were at the cases of 293, 573, 773 and 873 K for stagger mode, the Furnace Flame Occupation Coefficient were 6.2%, 9.7%, 18.7% and 24.6%, respectively. It creates more uniform distribution of reactants inside the flame and larger flame volume with elevated fuel temperature.

Flame entrainment ratio

The flame entrainment ratio (R_{fe}) is defined as the ratio of the mass flow rates through the cross section of the flame and the initial total mass flow rates.

Figure 4 shows the flame entrainment ratio at stagger mode is function of the normalized distance, which is defined by the ratio of flame length to burner diameter. The entrainment increases with increasing of flame length for Stagger mode. The maximum entrainment ratio appears closing to the flue gas outlet. This trend increases when the fuel temperature is elevated since the velocity of fuel is increased.

The counter mode offers a symmetrical profile of flame entrainment ratio since the flows of two firing burners are impeded. The entrainment of flame became very small at the middle of two firing burners. This is the fact that the flow direction of flue gas in flame is changed from vertical burner face to single-side burner face.

OPTIMAL DESIGN OF HITAC FURNACE

Figure 5 shows the scheme of the flame zone and the flue gas recirculation zone. In this study, it is assumed that all the positive velocities across the cross section of the furnace are included in the flame section. This assumption has enough precision at least in the partly furnace from the burner face to the maximum flame cross.

The mass conservation for the study part of the chamber is as following:

$$m_0 + m_r = m_f \quad (2)$$

where, m_f is the mass flux through the flame cross section, and m_r is the mass of the flue gas recirculation.

According the definition of the flame entrainment ratio:

$$R_{fe} = \frac{m_f}{m_o} \quad (3)$$

The area of flue gas recirculation can be expressed as:

$$A_r = \frac{m_o (R_{fe} - 1)}{\rho_r v_r} \quad (4)$$

Here, ρ , v , A are density, velocity and fluid flow area respectively, r denotes the recirculation flue gas.

The minimum cross section of the flue gas recirculation flowing could be existed at the section where the maximum flame diameter appears (i.e. maximum R_{fe}).

If the studied burner is equipped to a furnace with cylinder combustion chamber, according to the previous calculation, the minimum diameter of combustion chamber will be 0.5m. This is approximately 2.7 times of the burner diameter.

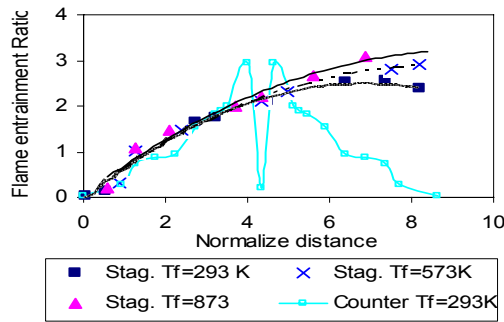


Figure 4 Effect of fuel temperature and flame locations on flame entrainment ratio

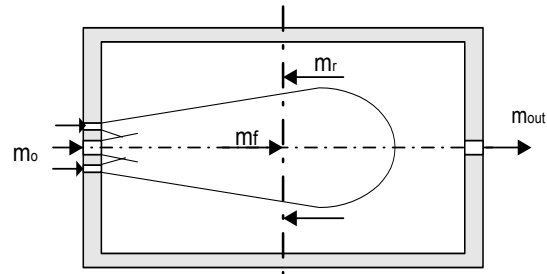


Figure 5 The scheme of structure of the flame zone and recirculation in an enclosed combustion chamber

CONCLUSIONS

- Flame locations have influences on the combustion and flame properties. The Single-side mode has a higher volume and a smaller combustion intensity of flame, and Counter leads to smaller flame volume and larger flame combustion intensity.
- Elevated fuel inlet temperature results in a lower maximum flame temperature and a larger flame volume, thus more uniform temperature distribution.
- The flame entrainment ratio is proposed as a criteria parameter to optimum design of HiTAC furnace.

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Flame Length above a Coaxial Burner with Oxygen Enrichment.

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INTRODUCTION

Oxy-fuel combustion has experienced a growing interest in the furnace industry over the last years because of its numerous advantages in terms of reacting properties with regard to conventional air fed combustion [1]. Thanks to its high burning velocity and wide flammability range, pure oxygen combustion does not require aerodynamic assistance for stabilisation which yields simple designed industrial burners. Power generation with CO₂ capture is now a new application for the use of oxy-fuel solution where pure oxygen is injected in the combustor. Carbon dioxide is the working fluid for the gas turbine cycle and is used to dilute the gases inside the combustor to avoid extreme temperatures. Knowledge of the interaction between mixing and combustion is therefore of prime importance for the design of burners and combustors.

The aim of the presented results is to investigate the effect of varying the oxygen mass flow on the length of a methane jet flame above a coaxial burner. The flames studied range from the laminar to the turbulence transition regime. The flame length in the laminar regime is a good indicator to evaluate the effect of the near field oxy-combustion on the total flame.

EXPERIMENTAL SET-UP RESULTS AND DISCUSSION

The experimental set-up is composed of a coaxial burner. Methane flows through the central tube of 2.33 mm diameter and pure oxygen is supplied through the annulus of 3.01 mm and 6.97 mm internal and external diameter respectively. The flow rates are controlled by mass flow regulators with an uncertainty of +/- 0.1 Nl/min for methane and +/- 0.15 Nl/min for oxygen. The range of mass flow rates, volumetric exit velocities and Reynolds number are gathered in table 1. The flame length is taken to be the last visible luminous point from instantaneous picture. Several shots are taken to give an average value.

It must be noted that for certain cases with low oxygen flow, above a certain distance it is not pure oxygen combustion any longer because the jets develop in open air. However, these cases are not irrelevant to confined configuration, as the ambient fluid would be composed of product gases. Indeed, measurements of species concentrations in a confined oxy-fuel flames [2] showed that at an axial location greater than 25 diameters, the annular oxygen stream cannot be perceived from the radial profiles.

	FLOW RATE (Nl/min)	Re	GAS VELOCITY (m/s)
methane central stream	0 – 9.6	0 – 5704	0 – 40.4
oxygen annular stream	0 – 15.2	0 – 3903	0 – 8.8

Table 1. Experimental conditions.

RESULTS AND DISCUSSION

Figure 1 shows the evolution of the flame length L_f as a function of the methane velocity for different oxygen flow rate (expressed as flow velocity). One recognizes the well-established trends as the fuel flow rate increases, namely: the laminar, intermediate (or transitional) and turbulent regimes. The annular oxygen stream has an influence for both the laminar and transitional regimes. In the former, the presence of oxygen reduces the flame length as a consequence of increased stoichiometric mixture fraction and wider flammability range in the near field, while in the latter it delays the turbulent regime to higher Reynolds number due to the increase in temperature hence viscosity. For annular flow velocities greater than 2 m/s, the oxygen stream has no further influence on the flame length.

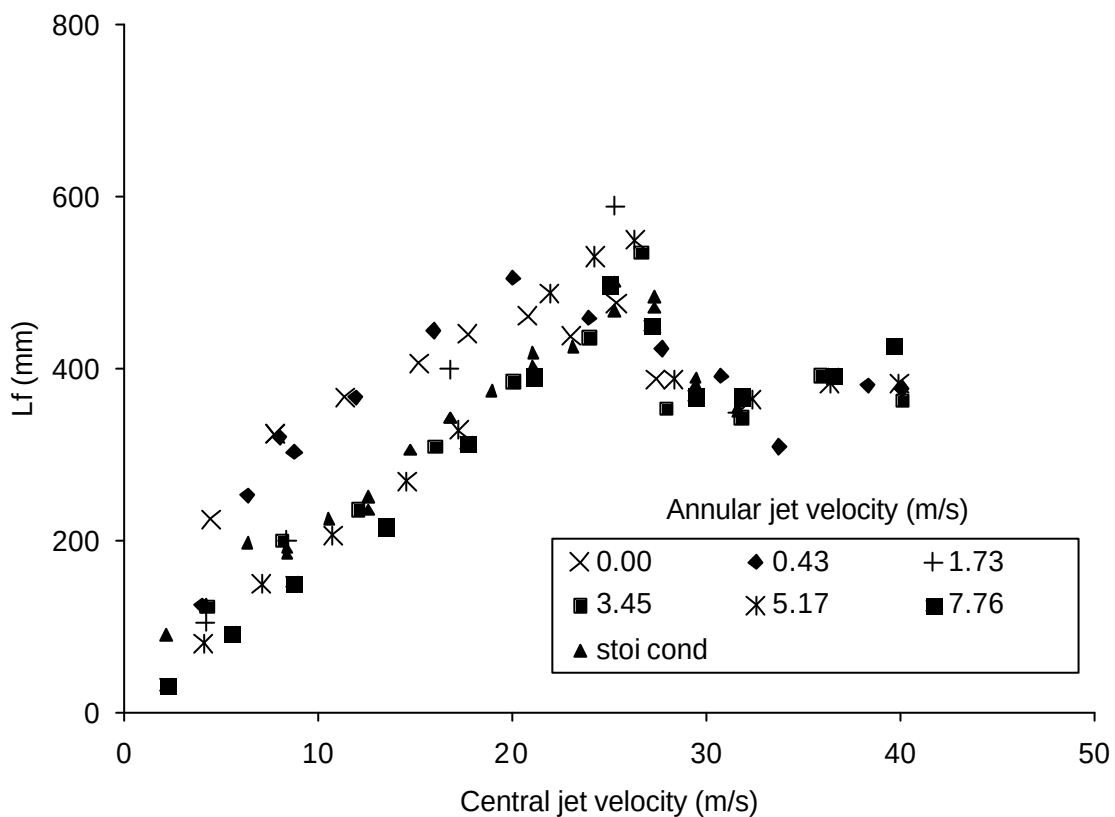


Fig. 1 Flame length as a function of central jet velocity at constant annular jet velocity.

Figure 2 shows a set of results obtained by keeping the fuel rate constant while increasing the oxygen flow rate in the annular stream.

Central jet laminar case ($Re_j < 3000$)

Three stages can be seen as the oxygen flow rate increases:

1. At low rates ($U_a < 1\text{ m/s}$), there is no noticeable effect as the oxygen is merely entrained and only aids in stabilising the flame to the burner.
2. At intermediate oxygen rates ($U_a < 2\text{ m/s}$), the flame length undergoes a sharp decrease because of the active interaction between the two coaxial streams in the near field.

3. Finally at higher flow rates L_f decreases very slowly because the annular flow completely controls the combined jet.

It is believed that the second stage is directly related to the potential core and turbulent transition of the annular oxygen stream. Indeed, for a constant fuel rate when the oxygen velocity increases, so does the length of the potential core until the annular jet becomes turbulent which lengthens the mixing layer, hence increases the surface of pure oxygen combustion. Above this distance, the annular stream is composed of oxygen, entrained air as well as high CO and intermediate species produced in the near field. A visual observation of the flames reveals that the decrease in oxygen annular flow leads to more yellow radiating flame which is characteristic of high CO and unburned species levels. The case at $U_j = 4.2$ m/s represents a direct transition to the third stage due to the very low central jet Reynolds number.

Central jet transition to turbulent case ($Re_j = 3568-4462$)

One can notice a discontinuity when the flow rate of oxygen increases above a threshold of 1.2 Nl/min. This is clearly the laminarization effect induced by the oxy-fuel combustion: when little or no oxygen flows the methane jet flame is in a turbulent regime (constant flame length), but above the threshold the high viscosity reacting layer at the nozzle exit cancels out the turbulent controlled mixing and turns the flame back to a laminar regime. The flame length is hence lengthened abruptly and further increase in oxygen leads to the slow decrease in length as discussed previously for the laminar case. As the methane jet Reynolds number increases towards the turbulent regime, there is no influence of an increase in oxygen rate as shown for $U_j = 31.61$ m/s.

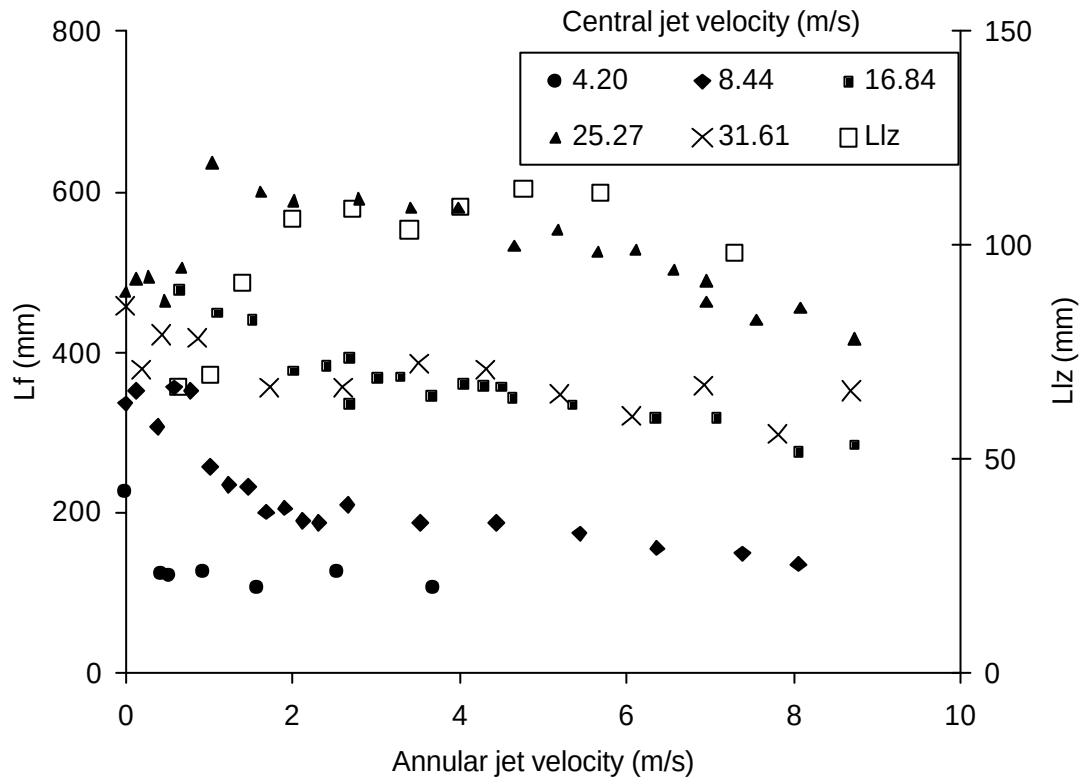


Fig. 2 Flame length as a function of annular jet velocity at constant central jet velocity.

An attempt has been made to visually determine the axial distance above the nozzle where the flame turns to turbulent. Although this transition length is not defined accurately because of the lack of accuracy in the method, it is clearly observed where the flame suddenly expands and exhibits strong and large turbulent structures. This laminar length is noted L_z and plotted on figure 2 for a fuel velocity $U_j = 27.9$ m/s. The plot follows the interpretation of a growing oxygen stream laminarizing the turbulent central jet (therefore increasing the flame length), up to the point where the annular potential core does not grow any longer. Once the laminar length has reached a threshold, increasing the oxygen rate reduces the flame length because of enhanced mixing.

CONCLUSION AND PERSPECTIVES

It has been seen that the strong influence of oxygen enrichment on combustion above a coaxial burner is linked to the own development of the annular and central jet. Further measurements must be done in order to refine the evaluation of the jet characteristics as length of the central and annular jets potential core and intensity of mixing in the shear layer. These parameters should be related to the length of the flame considering that the flame ends near the point where the stoichiometric mixture fraction is reached on the centreline.

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RANS and LES Modeling of Premixed Combustion for an Industrial Gas Turbine Combustor

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Turbulent premixed flames in industrial combustors are characterized by large turbulent Reynolds number $Re_t \sim 10^2 - 10^3$ and moderately large Damkohler number $Da \sim 10$; at these conditions instantaneous reaction zones are not laminar but thickened by micro-turbulence. Instantaneous combustion takes place in thin, in comparison with integral turbulence scale, and strongly wrinkled flamelet sheets with developed small-scale structure that fundamentally cannot be unresolved by combustion model balance equations. In the presented simulations we used our TFC turbulent premixed combustion model [1-3], where this problem is solved in context of Kolmogorov hypothesis of statistically hydrodynamic equilibrium of the small-scale instantaneous reaction zones. It allows to express the averaged combustion rates (the source term in the model equation) in terms of large-scale turbulent parameters and the characteristic chemical time. This gave the opportunity to reach a good agreement between the model prediction and the standard experimental data at turbulence level typical for gas turbines. Reasonable prediction, through simulations, of the dependence of the turbulent speed on turbulence and chemistry against the spherical bomb data (Institute of Chemistry Physics, Russia) are presented in [2, 4], the correct prediction of the flame width and profile parameters against the high velocity combustion data in the channel (ONERA, France) was demonstrated in [5, 6], see also the review paper [7].

From the methodological point of view, the combustion model is closed to the " $k - \varepsilon$ " turbulence model: both models are based on the ideas of small-scale equilibrium and are valid at intensive turbulence, in our simulations they are used together. Very significant that both models are consistent in spite of the counter-gradient transport phenomenon typical in premixed flames (that also could be described in the context of the TFC model [6]) as the " $k - \varepsilon$ " turbulence model is used only for estimation of the gradient turbulent diffusion component of the transport [6].

Another problem connected with the combustion prediction in real combustors is that averaged stationary picture, obtained by RANS simulations, are not sufficient for engineering estimation of instability process. The resolution of instantaneous non-stationary eddies structure of the reacting flow are necessary, in particular in connection with existence at certain conditions of undesirable unsteady combustion phenomenon that drives large pressure pulsations. The Large Eddy Simulation (LES) is one of the promising approaches to this problem. We have developed an original joint RANS/LES approach that is based not on performing LES instead of RANS but together with it [8]. The first step is the RANS simulation with a finest grid for description of the combustion process including preliminary air and gas fuel mixing, wall cooling air jets and so on; the second step is LES with more

rough grid but using some results of RANS for prediction the LES model the combustion rates and used Kolmogorov subgrid viscosity.

The combustion analysis was performed in the terms of progress variable c ($c = 0$ in reactants and $c = 1$ in products). The unclosed equation is the following:

$$\partial \bar{\rho} \tilde{c} / \partial t + \nabla \cdot \bar{\rho} \tilde{u} \tilde{c} = - \nabla \cdot \bar{\rho} \tilde{u}'' c'' + \bar{\rho} \tilde{W} \quad (1)$$

A difficulty arises designing the model equation using as a base eq. (1), connected with the fact that the transport $\bar{\rho} \tilde{u}'' c''$ is controlled not only by the turbulent diffusion but also by the pressure driven different acceleration of cold reactants and hot products. It yields the counter-gradient transport phenomenon so the " $k - \varepsilon$ " cannot be used directly, even for qualitative description of the transport. We resolve this problem but only for the transient combustion regime when flames have increasing brush width controlled by the flow turbulence and at the same time nearly constant flame speed U_t [6]. In 50th A.G. Prudnikov in Russia was the first who experimentally discovered in 50th this transient regime of combustion as the dominant regime in high turbulence combustors.

We present the transport as a sum of turbulent diffusion and pressure driven fluxes $\bar{\rho} \tilde{u}'' c'' = (\bar{\rho} \tilde{u}'' c'')_{t.d.} + (\bar{\rho} \tilde{u}'' c'')_{p.d.}$ and approximate the turbulent diffusion component in the context of the " $k - \varepsilon$ " turbulence model $(\bar{\rho} \tilde{u}'' c'')_{t.d.} = - \bar{\rho} D_t \nabla \tilde{c}$ ($D_t = C_D k / \varepsilon$). At the same time the summand $\nabla \cdot (\bar{\rho} \tilde{u}'' c'')_{p.d.}$ was included in the model source term that, for the flame as a running wave, is equal to $\rho_u U_t |\nabla \tilde{c}|$, where the flame speed $U_t = U_f (\bar{S} / S_0)$ is controlled by the speed U_f of the thickened flamelet and by the dimensionless area of the flamelet sheet $(\bar{S} / S_0)$. Assumption of the small-scale equilibrium permitted to express them in term of the chemical time and large scale turbulence parameters: $U_f \approx u' \cdot Da^{-1/2}$, $(\bar{S} / S_0) \approx (Da)^{3/4}$ where $Da = \tau_t / \tau_{ch}$ is the Damköhler number ($\tau_t = L / u'$ and $\tau_{ch} = \chi / U_l^2$, χ is the molecular heat transfer coefficient, U_l is the laminar flame speed) and hence $U_t = U_f (\bar{S} / S_0) = A \cdot u' \cdot Da^{1/4} = A \cdot u'^{3/4} U_l^{1/2} \chi^{-1/4} L^{1/4} = A' k^{3/4} \varepsilon^{-1/4} \chi^{-1/4} U_l^{1/2}$. Finally the model equations was the following

$$\partial \bar{\rho} \tilde{c} / \partial t + \nabla \cdot \bar{\rho} \tilde{u} \tilde{c} = \nabla \cdot (\bar{\rho} D_t \nabla \tilde{c}) + A' \rho_u k^{3/4} \varepsilon^{-1/4} \chi^{-1/4} U_l^{1/2} |\nabla \tilde{c}| \quad (2)$$

that simulated with the CFD equations and the " $k - \varepsilon$ " turbulence model gives the fields of the temperature and the main concentrations presented in reactants and products. For LES approach (using the fields of k and ε from RANS) the same eq. (2) was used but with the subgrid Richardson diffusion coefficient $D_{sg} = B \varepsilon^{1/3} \Delta^{4/3}$ (instead of D_t) following directly from the Kolmogorov spectrum $E(k) \sim \varepsilon^{2/3} k^{-5/3}$, where Δ is LES mesh size. The source term as a first approximation was used the same from an estimation the most part of small-scale wrinkles, giving the main contribution in the flamelet sheet area, fall inside the mesh.

In figures 1 and 2, we present as an example some results of a commercial gas turbine combustor GE10 numerical simulation. We performed detailed CFD analysis of the mixing channel and the analysis of the combustion chamber taking into account the pilot fuel and the effect of cooling air jets. In fig.1, we show contour plots of temperature and turbulent pulsation for the combustion section. In fig.2, we show the fuel concentration in the terminal part of the mixing channel. We performed a LES simulation for a simplified geometry of the same

combustor using the hybrid model RANS/LES [8]; LES is able to show the effects of large scale vortex on flame front (fig. 3)

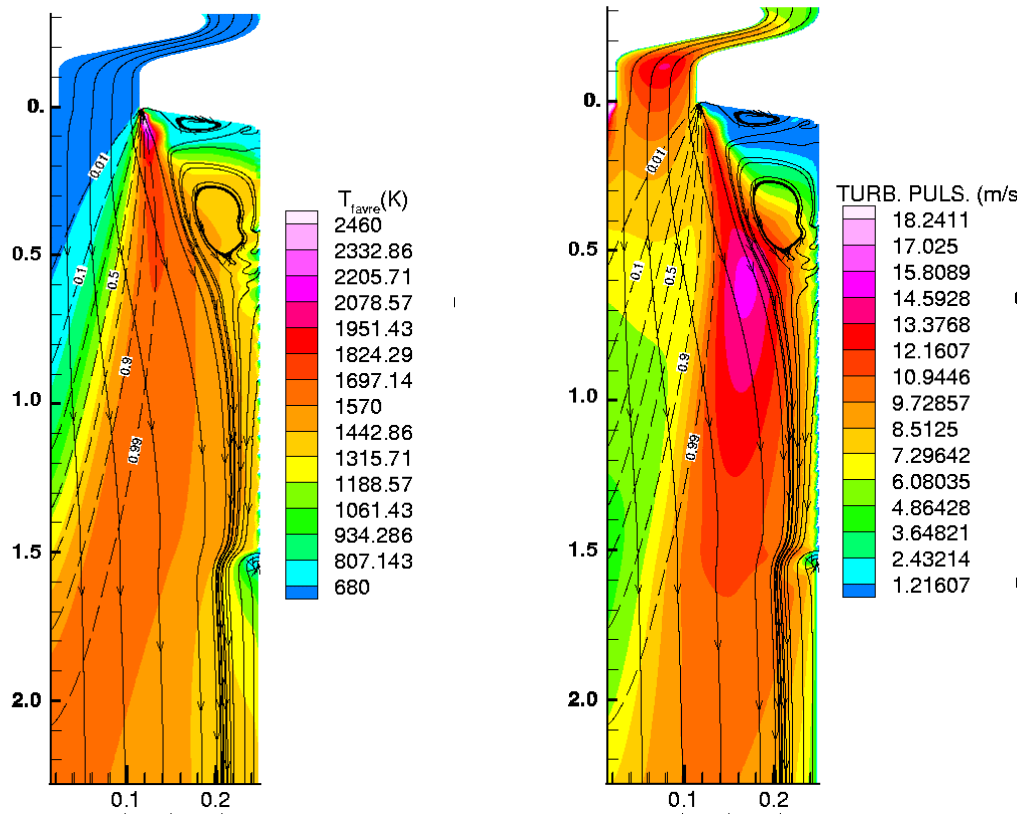


Fig1: Combustion chamber simulation (2D axial-symmetrical). Contour of temperature (left) and turbulent pulsation (right) with isolines of progress variable (dashed lines) and streamline

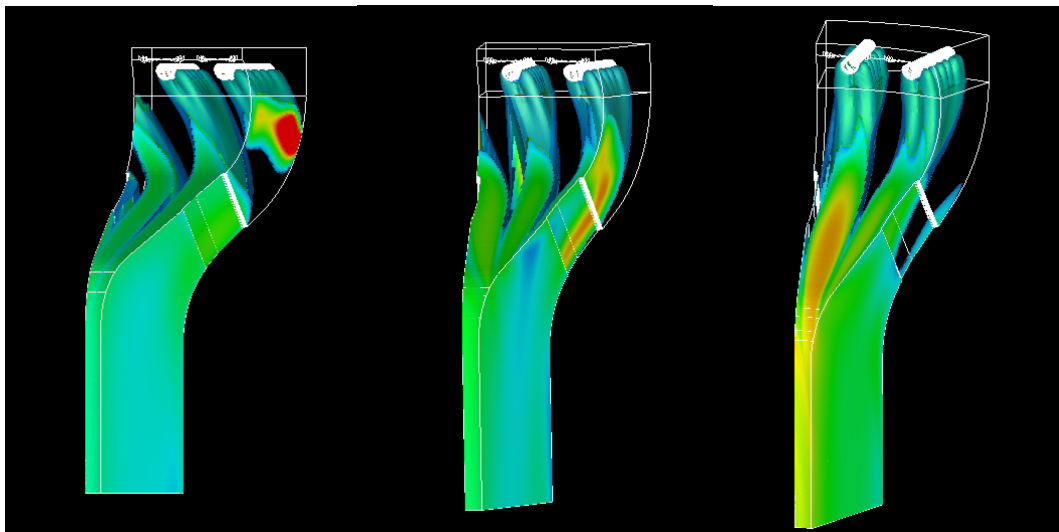


Fig.2: Fuel Concentration (red higher, green intermediate, blue low) in the terminal part of mixing channel (30 degree sector). Depending on the upstream air flow controller setting, a strong (left), medium (center) or null (right) air swirl component is impacting the fuel nozzles (on top). It is anyway strongly damped afterward by the

winglets used in the combustor.

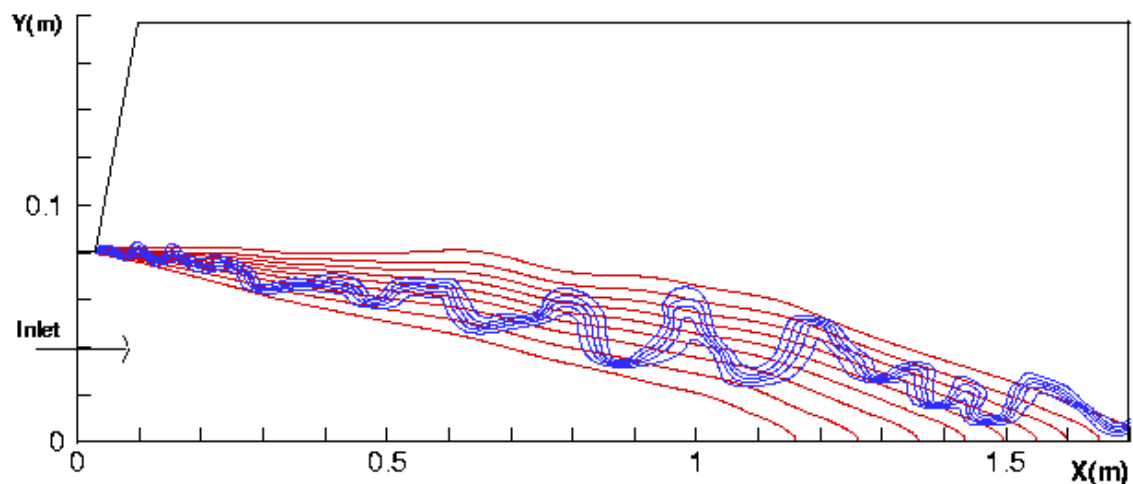


Fig 3: Simplified combustion chamber. Section of a 30 degrees sector 3D simulation. Contour-lines of progress variable for RANS (red: from 0.1 to 0.9 step 0.1) and instantaneous LES (blue: from 0.1 to 0.9 step 0.2).

Conclusions following from our experience on modeling of gas turbine combustors:

1. The thickened flamelet combustion mechanism seems adequate for description of industrial premixed combustion at strong turbulence;
2. Applying the Kolmogorov ideas of small-scale equilibrium to the concept of the thickened flamelet mechanism yields the combustion model with minimal number of empirical coefficients describing main controlling processes;
3. Using joint RANS/LES simulations of the TFC combustion model could be fruitful tool for analysis and preliminary designing of industrial combustors. It gives an opportunity to describe both averaged fields using RANS simulation and some fits of unsteady characteristics using LES based on information from RANS simulation.. We hope that developing of this approach could be useful in future for prediction of the unsteady combustion regimes.

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Mild combustion for fuel-NO_x reduction

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INTRODUCTION

One source of pollution in the combustion of fossil fuels is the formation of nitrogen oxides. While using “clean” (that is nitrogen-free) fuels the main source for nitrogen oxides is the thermal mechanism, in the case of nitrogen-containing fuels NO_x are also produced through the fuel mechanism. The aim of this paper was to investigate the possibility to use mild combustion (De Joannon M. et al., 2000; Wüning J.A and Wüning J.G., 1997) to reduce the formation of NO_x through the fuel mechanism. This can be done because this technology provides a relatively high content of hydrocarbon radicals all over the combustion chamber leading to a reburning-like situation. Moreover, in order to achieve a higher pollution control it was investigated also the possibility of coupling mild combustion with the Selective Non-Catalytic Reduction process by injecting ammonia directly into the combustion chamber.

MATERIALS AND METHODS

The laboratory-scale burner, its working and the start – up procedure to achieve mild combustion operative conditions, have been already described in detail elsewhere (Cavigiolo et al., 2003). Previous experiments already demonstrated the ability of mild combustion to strongly reduce thermal NO_x formation when using methane and ethane as fuels. However, these are nitrogen-free fuels and consequently no information can be deduced from such experiments on the abatement of fuel-NO_x. In order to simulate nitrogen oxides formation via this mechanism without renouncing to the use of those gaseous fuels, we introduced NO (or NH₃ or HCN) directly into the combustion chamber. Since preliminary experiments showed no significant differences when injecting the same amount of NO or NH₃ into the combustion chamber, all the experiments discussed in this paper were performed injecting NO, thus simulating the presence of various N – containing fuels. Considered that the volumetric combustion caused by the high internal recycle into the chamber makes the fuel radicals available for NO_x reduction even to zones far from the injecting nozzle, the mild combustion chamber can be thought as to be composed by a combustion region in which a reburning processes is always present. Experimental runs have been carried out injecting into the combustion chamber a known amount of NO so as to have a concentration of NO in the inlet stream equal to 600 ppm once mild combustion was established. The influence of the average temperature in the combustion chamber has been investigated, as well as that of the oxygen excess concentration with respect to the stoichiometric value.

A typical thermal DeNO_x process involves the injection of ammonia downstream the combustion region. In the presence of oxygen, ammonia produces NH₂ radicals that can react with NO leading to N₂. However, NH₂ can be also oxidized to NO, therefore this process is efficient only in a narrow range of temperatures, from about 870 to about 950°C. In mild combustion burners the combustion chamber temperature can be set within this range thanks to the high thermal homogenization. Therefore, ammonia can be injected directly into the combustion chamber.

Experimental results have been discussed using two detailed kinetic models, namely that proposed by Miller and Bowman (1989) (in the following referred to as the MB mechanism) and that of Faravelli et al. (2003) (FFR model).

RESULTS AND DISCUSSION

Reburning-like experiments have been carried out injecting 600 ppm of NO in the combustion chamber when operating the burner in mild conditions with an oxygen excess of 1% respect to the stoichiometric value. As it is shown in figure 1A, in the temperature range explored, fuel-NO_x emissions are nearly constant, leading to an abatement of about 40-45%. It is noteworthy that NO and NO_x emissions were always the same, indicating that no conversion of NO to NO₂ proceeds. Computations, carried out using a Perfectly Stirred Reactor (PSR) model (Glaborg P. et al., 1990; Kee R.J et al. 1994), also predict an almost constant emission with temperature (see Figure 1A). FFR mechanism is slightly more reactive than MB, leading to a larger NO abatement in the whole temperature range.

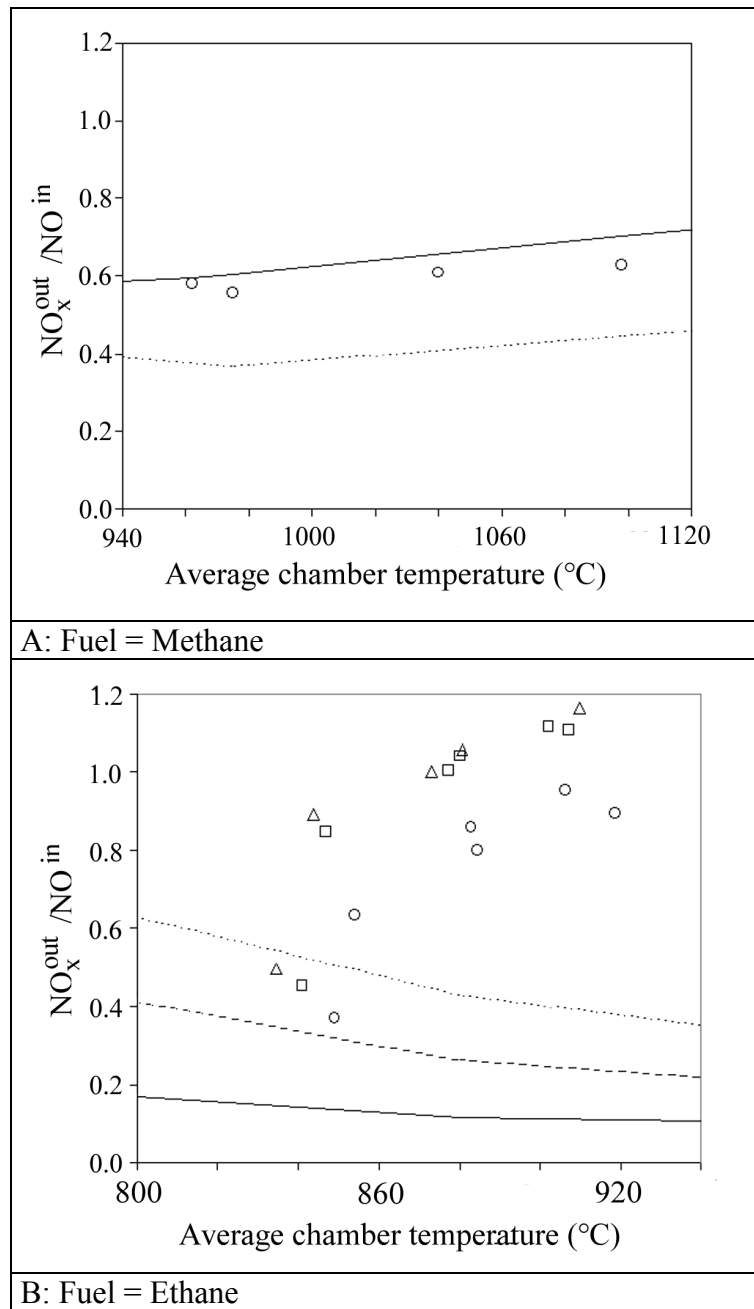


Figure 1: Reburning **A**) (○) 1% O₂ excess; (—) PSR model with MB mechanism and (...) PSR model with FFR mechanism **B**) (○) 1%, (□) 3% and (Δ) 5% O₂ excess. PSR with MB mechanism at (—) 1%, (---) 3% and (...) 5% O₂ excess.

In the case of ethane, we also investigated the dependence of NO_x abatement on the oxidant availability. The experimental runs were conducted with an oxygen excess with respect to stoichiometry of 1%, 3% and 5%. As Figure 1B shows, at a given oxidant excess, NO_x emissions strongly increase with temperature. The temperature range investigated is shifted toward lower values with respect to methane because, for this fuel, mild oxidation requires lower combustion chamber temperatures (Cavigiolo et al., 2003). As expected, the higher the oxidant availability, the higher the fuel-NO_x emission. Moreover, over 870°C and for oxygen excesses larger than 3% the reduction becomes net production, thus limiting to this temperature the applicability window of this technology with ethane. This behavior can be explained by the presence of hot spots in the combustion chamber arising from the more reactive nature of ethane with respect to methane. Figure 1B also shows the comparison between the experimental data and the PSR model results obtained using the MB kinetic mechanism. The model a decrease for fuel-NO_x emissions as the temperature increases, in evident contradiction with our experimental data. Similar results can be obtained using the FFR kinetic mechanism. This confirms that the PSR approximation is not correct for ethane mild combustion in the conditions investigated. Probably, the most part of NO_x production for ethane combustion is located near the inlet region of the burner, where a bad mixed zone is evidenced, with the presence of hot spots at high temperatures. This behavior is due, probably, to the higher ignition tendency of this fuel if compared with methane. However, it should be noted that, by choosing a convenient temperature window where mixing is fast enough with respect to chemical kinetics, it is possible to reduce more than one half of the fuel-NO_x. A better schematization of the burning chamber would require a different description of the mixing in the proximity of the nozzle tip.

The results obtained coupling mild combustion and thermal DeNO_x process for methane are shown in figure 2.

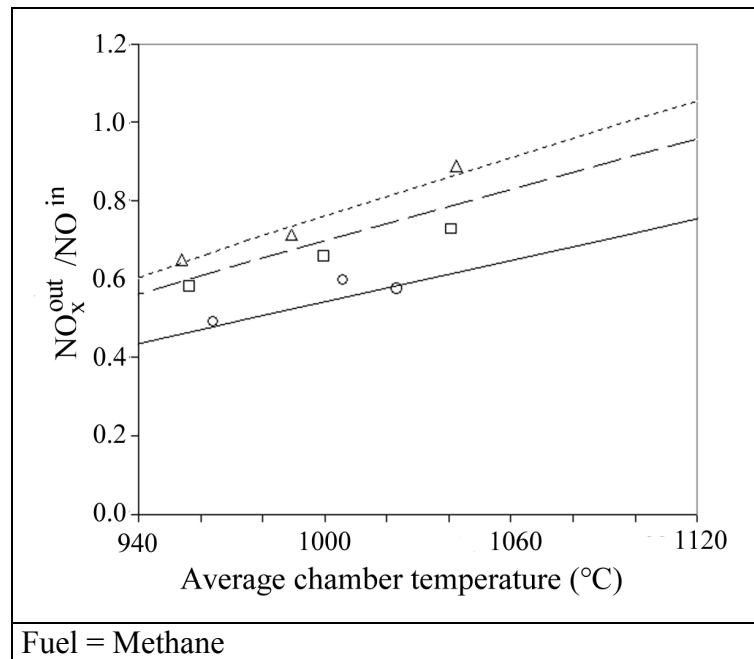


Figure 2: Thermal DeNO_x: (○) 1%, (□) 3% and (Δ) 5% O₂ excess. PSR with MB mechanism at (—) 1%, (---) 3% and (...) 5% O₂ excess. ($\beta = \text{NH}_3/\text{NO}^{\text{in}} = 1$)

We can see that also in this case, fixed the inlet ratio of NH₃ to NO, the concentration of nitrogen oxides depends on the oxygen excess and the mean chamber temperature. In particular, increasing the oxygen availability decreases the NO_x abatement, while a decrease in temperature (in the range

investigated) leads to a better NO_x removal. The same figure also shows the PSR model predictions obtained using the MB kinetic mechanism.

CONCLUSIONS

The main result of this work is that mild combustion can also reduce fuel-NO_x produced by the oxidation of nitrogen-rich fuels. The NO_x reduction achievable strongly depends on the oxygen excess: the lower the amount of oxygen in the combustion chamber, the larger the NO_x abatement. On the whole, mild combustion has been able to reduce fuel-NO_x up to about 40% for methane experiments, and up to about 60% in the ethane experiments.

Ammonia injection in the combustion chamber has no effect for “high” temperature mild combustion (in the range 950-1100°C) with a low oxygen excess, while it is detrimental when the oxygen excess is high. The opposite is true for “low” temperature mild combustion, where ammonia injection can increase significantly the NO_x abatement.

In conclusion, mild combustion can always reduce significantly fuel-NO_x provided that a low oxygen excess is present in combustion chamber. Depending on the fuel, and consequently on the combustion chamber temperature, the injection of ammonia can significantly increase the NO_x reduction.

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The Role of Interparticle Forces in Fluidized Bed Reactors

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Pressure drops and bed expansion curves have been obtained to establish the influence of temperature on minimum fluidization velocity, terminal velocity, Richardson and Zaki exponent and size of fluidized particles for a Groups A material of Geldart classification. Experiments have been carried out by means of a laboratory scale fluidized bed operated with and without the application of acoustic fields having different intensities and frequencies, at temperatures varying from ambient temperature up to 600°C. The experimental results have been interpreted on the basis of a simple model predicting the effectiveness of sound assisted fluidization in reducing interparticle forces.

INTRODUCTION

The interest in handling relatively fine particles in various industrial processes carried out at thermal levels above ambient conditions raises the question of the caution in scaling up cold models not only in the case of cohesive particles, which belong to Geldart's C powders but also of powders classified as A (1). Very few indications are reported in literature on the effect of temperature on fluidization quality. Yates (2) found that the correlations obtained at ambient temperature can still be used at high temperatures when variations of density and viscosity of gas and a correct value of the minimum fluidization voidage are used. However it is not clear how temperature influences the minimum fluidization bed voidage. Botterill et al. (3), found that it depends on both temperature and particle size. Raso et al. (4) and Formisani et al. (5) found a moderate increase in minimum fluidization voidage with temperature.

A systematic approach to characterize the effect of temperature on the fluidization of a Group A powder of Geldart classification, has been carried out in this work. Pressure drops and bed expansion curves have been obtained to establish the influence of temperature on minimum fluidization velocity, terminal velocity, Richardson and Zaki exponent and size of fluidized particles. The relevance of interparticle forces on fluidization has been highlighted by carrying out experiments under sound assisted conditions. A simple model has been developed to account for the role played by van der Waals forces on the size of fluidized particles for a multi-sizes Group A powder.

EXPERIMENTAL APPARATUS AND TECHNIQUE

The experimental apparatus used is shown in Fig.1. Details of the apparatus is reported elsewhere (6). Tests were carried out with or without application of acoustic field with intensity of 150 dB and frequency varying between 50 and 300Hz. Tests were carried out at a temperature ranging from ambient temperature up to 600°C and using nitrogen from cylinders as fluidizing gas. The properties of the material tested are reported in Table I. Experiments aimed at characterizing the effect of temperature on: minimum fluidization and terminal velocities, Richardson and Zaki

Table I. Properties of material

	Silica sand
Particle size, (mm)	6-146
Sauter diameter, (mm)	60
Apparent density, (kg/m ³)	2600
Sphericity factor	0.73
Gerdart Classification	A

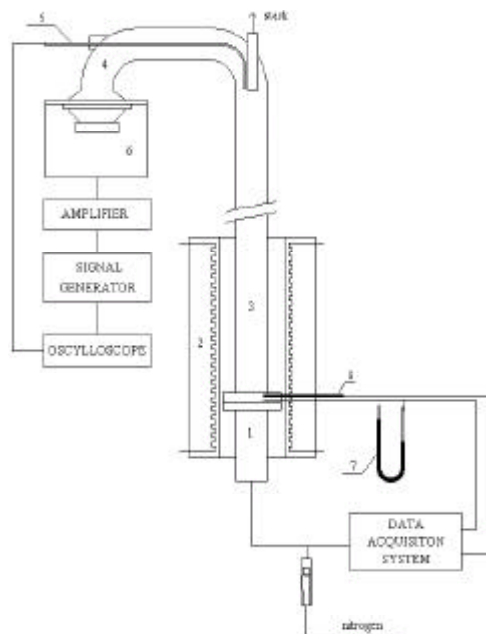


Figure 1. Experimental Apparatus: 1) pre-heater; 2) electric heaters; 3) 40mm ID fluidization column; 4) sound guide; 5) microphone; 6) loudspeaker; 7) monometer; 8) thermocouple.

low frequencies ($f < 1\text{Hz}$) as well as relatively high frequencies ($f > 10^4\text{ Hz}$) are not able to promote a relative motion of particles. For frequencies larger than 10Hz, coarse particles are fixed in the space ($A_{ds}/A_g = 0$) and fine particles oscillate ($0 < A_{df}/A_g \leq 1$).

Cohesive forces between particles counteract the relative displacement of the particles. Coarse/fine particle detachment occurs when the disaggregating force due to particles relative motion overcomes the cohesive forces acting at contact points. According to Russo et al. (7), it is $F_{c, \text{cohesive}} = nmF_{cw}$, with n number of contact points between particles, μ static friction coefficient and F_{cw} van der Waals force between particles (8). $\mu = 0.5$ (9) and $n = 3$ have been used in calculations. The effects of temperature has been accounted for considering that: i) gas viscosity and density are temperature dependent (10): $\rho_g = 12 \times (293/T)$ and $\mu_g = 146 \times 10^{-6} T^{1.504} / (T + 120)$; ii) temperature does not affect the density of the solid particles; iii) two alternative considerations have been made on van der Waals forces: (A case) $F_{cw} = \text{const}$, or (B Case) $F_{cw} = F_{cw}(T)$ as increasing Hamaker constant (11).

Figure 2B gives the highest value of the disaggregating forces due to the application of a 150dB sound field acting on a 80 μm /10 μm particles aggregate as a function of frequency at

exponent, relevance of interparticle forces.

THEORY

A simplified model was used to predict the influence of temperature on the size of fluidized particles. It assumes that a small particle adheres on a larger one if its weight is smaller than van der Waals forces active at contact points between particles. Accordingly, particles of different sizes stay alone or as aggregates depending on the magnitude of cohesive and gravitational forces. The application of an acoustic field may produce the break up of the aggregate, when inertial and drag forces applied to the aggregate particles overcome its cohesion. Coarse and fine particles follow gas oscillations with an amplitude that depends on their size and on intensity and frequency of the acoustic field. Details of the model are reported elsewhere (6). Figure 2A gives the relative displacements of particles of different size vs. gas particles, A_{di}/A_g . $A_{di}/A_g = 1$ means that particles oscillate as gas does, $A_{di}/A_g = 0$ means that particles are stationary in the space. For the particles size considered, relatively

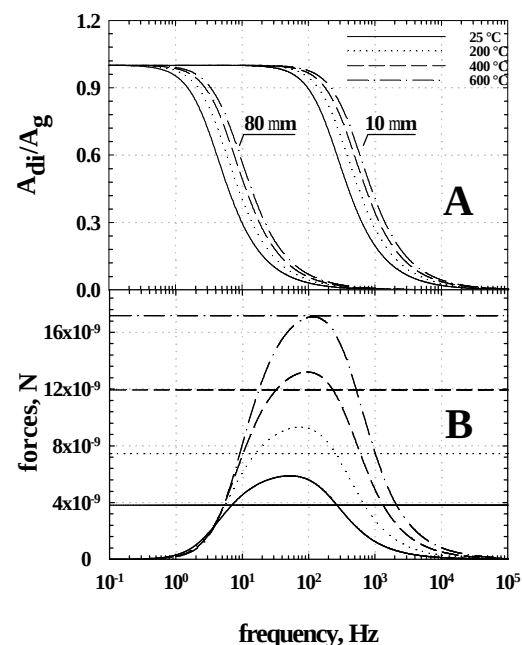


Fig 2. A) Relative displacements of particles toward gas displacement: A_{di}/A_g and B) maximum disaggregating forces and cohesive forces on a 80mm/10mm particles aggregate as a function of sound frequency.

different temperatures. In the figure the cohesive forces active between the small and the coarse particles are also reported as horizontal lines. Disaggregating forces, negligible for frequencies $<1\text{Hz}$, first increase reaching a maximum value and then decrease becoming negligible for frequencies $>10^4\text{Hz}$. The increase in temperature results in an increase of the maximum disaggregating forces of a factor of 3 and also in a moderate increase of the optimal frequency of sound. The sound will be able to separate the aggregated particles when disaggregating forces are larger than cohesive forces (horizontal lines). With reference to ambient conditions (solid lines), a frequency in the range 7-300Hz is required when an acoustic field of 150dB is applied. With reference to A case, the disaggregating forces increase with temperature, while cohesive forces remain the same (solid horizontal line). This results in a larger range of operative frequencies. However, this conclusion is not fulfilled by comparing the curves of disaggregating forces with those of cohesive forces when the latter are assumed to be temperature dependent (B Case). In this case an increase of temperature results in a decrease of the range of operability frequencies and at 600°C an acoustic field of 150 dB is not able to separate the particles whatever the frequency used (dash-dot lines).

EXPERIMENTAL RESULTS

Minimum fluidization velocity, minimum fluidization bed voidage, terminal velocity, Richardson-Zaki exponent and average size of fluidized particles calculated by working out minimum fluidization (12) or terminal (13) velocities are reported in Fig. 3 as a function of bed temperature. Data are obtained in tests carried out without the use of an acoustic field (solid symbols) and under sound assisted conditions (open symbols) with acoustic fields intensity of 150 dB and frequencies of 50, 120, 300 Hz.

All the variables increase with temperature. This behaviour is not expected on the bases of purely hydrodynamic considerations on the effect of temperature on gas viscosity and density. The comparison among tests carried out with and without the application of acoustic fields shows that at ambient conditions the application of sound involves a remarkable reduction of all considered variables. Increasing temperature, there is lower and lower influence of sound application that eventually vanishes for bed temperature of 600°C . The

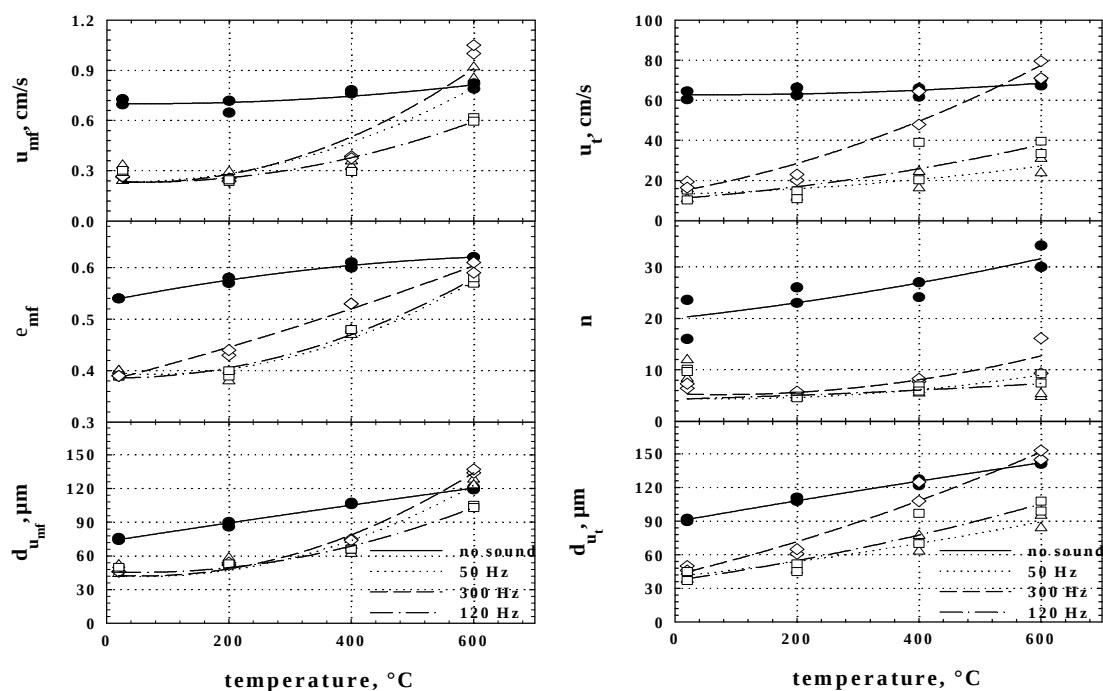


Fig. 3. Minimum fluidization velocity, bed voidage, terminal velocity, Richardson-Zaki exponent and average sizes of fluidized particles as a function of temperature.

frequency of the acoustic field shows a non monotonous trend: 120Hz is the most effective frequency. The value of Richardson and Zaki exponent at ambient conditions without sound, $n=20$, is relatively high and it increases up to $n=30$ as temperature increases up to 600°C. Such high values of n are representative of high degrees of cohesiveness of the material (14) and its increase with temperature indicates an increased role of cohesive forces. The application of an acoustic field reduces n by a factor of 3, $5 \leq n \leq 10$. The comparison among average sizes of fluidized particles calculated working out minimum fluidization or terminal velocities shows that, whatever the procedure used the average sizes of fluidized particles obtained without sound are larger than the average size of the material, 60 μ m. The application of sound generally reduces the size of fluidized particles even if the effect decreases as temperature increases and vanishes at temperature of 600°C.

With reference to the simple model presented in Theory section it must be noted that predictions are in agreement with experimental findings even if the effect of an increase of temperature can be only partially justified by theory when an increase of cohesiveness of the material with temperature is assumed (B Case).

Experimental values of minimum fluidization velocity, terminal velocity and Richardson-Zaki exponent were compared with values predicted by Ergun (12), Stokes (13) and Richardson and Zaki (15) correlation. Deviation are smaller if data from sound assisted fluidization experiments are considered. The reduction of interparticles forces increases the predictivity of the correlations.

CONCLUSIONS

- The influence of temperature on fluidization has been investigated for a Groups A material of Geldart classification. The powder shows unexpected behaviour based on purely hydrodynamic considerations on the effect of temperature on gas viscosity and density.
- Comparing experimental findings in ordinary and sound assisted fluidization has highlighted the role played by interparticle forces on fluidization behaviour.
- Deviations of literature correlations for Group A material are relatively high and increase with temperature. These decrease when cohesive forces diminish.
- A simple model has been presented to account for the role played by van der Waals forces on the size of fluidized particles. The model can account for temperature effects on both hydrodynamic and cohesive forces.

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Fullerenes Formation in Atmospheric Pressure Opposed Flow Oxy-Flames

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INTRODUCTION

Fullerenes, remarkable allotropic form of carbon, have an unique structure consisting of carbon hexagons and pentagons that form a spherical shell composed only of carbon atoms. Their unique structure, resulting in special physical and chemical properties, has stimulated the imagination of many scientists and engineers. Today, the potential applications of fullerenic materials include superconductors, catalysts, optical and electronic devices, polymer composites, biological and medical materials. First discovered in graphite vaporization [1], fullerenes are proved to be formed in flames and can be extracted in macroscopic quantities [2,3]. Much of the research on fullerene formation in flames has been done under low-pressure conditions. Premixed flames of benzene and oxygen with and without inert diluent were studied by Howard and co-workers [2]. Hebgren et al. [3] found that fullerenes are formed in low-pressure benzene/oxygen diffusion flames with local yields as large as those seen in premixed flames. The formation of fullerenes is often accompanied by formation of other fullerenic materials that include carbon nanotubes, multishell carbon onions, nanopolyhedrals and fullerenic soot characterized by the presence of well-defined curved carbon layers. In this work the formation of fullerenes is studied for the practically important case of atmospheric pressure flame using well-defined opposed flow geometry.

EXPERIMENTAL SETUP

Figure 1 shows the experimental setup used in the present study. A counter-flow burner forms two opposite streams of gases; the fuel (methane seeded with acetylene) is supplied from the top nozzle and the oxidizer (oxygen enriched air) is introduced from the bottom nozzle. The fuel and oxidizer flows impinge against each other forming a stable stagnation plane, with a diffusion flame established from the oxidizer side. The introduction of co-flowing nitrogen through a cylindrical annular duct extinguishes the flame near the outer jacket. A detailed description of the burner is given by Beltrame et al. [4]. The experiments were conducted varying fuel and oxidizer velocities, acetylene concentration in the fuel stream, and oxygen content of the oxidizer.

A quartz microprobe with an inserted filter was used to collect carbon material from the flame. The conical tip of the quartz tube had an orifice of 0.5 mm. The filter was made of an aluminum foil packed with fine quartz wool. Typical sampling time was close to three minutes but in some cases was reduced due to the blockage of the probe tip by carbon materials. The filters were removed from the probe and dried out in a desiccator to remove water. The total mass of condensable material was then obtained by measuring the mass of the filter before and after the sampling. Further sample preparation involved sonication in toluene and filtering [3]. Fullerene analysis was conducted using a high-pressure liquid chromatograph (Agilent 1100 Series, Palo Alto, USA) equipped with an analytical Cosmosil Buckyprep column (Nacalai Tesque, Kyoto, Japan). A variable wavelength UV-vis detector

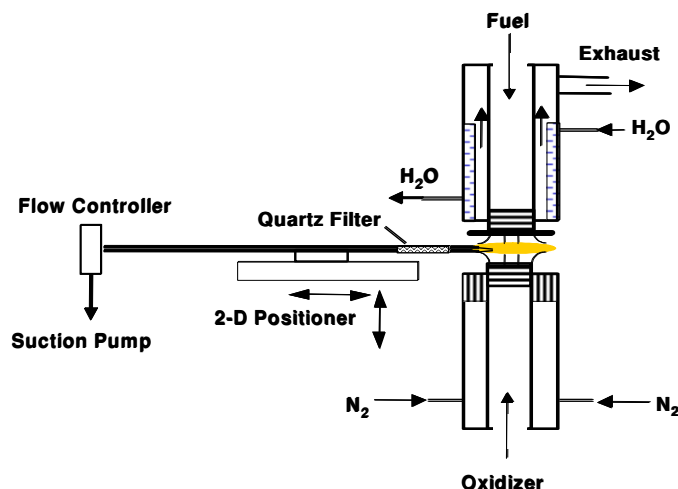


Fig. 1. Schematic of the experimental setup.

was used at 330 nm. The instrument has been calibrated by means of C60 and C70 standards. Additionally, samples of collected material were analyzed by transmission electron microscopy (TEM) using a JEOL JEM-3010 electron microscope.

NUMERICAL MODEL

In the present work a reaction mechanism developed by Pope et al. [5] and later completed and tested in premixed low-pressure benzene flames has been adopted [6]. This mechanism considers two main formation pathways. The first is called direct pathway, in which all carbon is added by hydrogen-abstraction/acetylene-addition sequences to the growing curved PAH. The second is called the coagulation pathway, since it involves reactive coagulation or C-C bonding between two PAHs of C_{5v} symmetry. It was also reported [5] that intramolecular rearrangements play an important role in C60 and C70 formation. In premixed flames virtually all the fullerenes are formed via the direct pathway [6], therefore in this work the coagulation pathway has been neglected to limit computational time. Simulations were done using the OPPDIF code [7]. The radiation losses, typically leading to temperature correction by less than 50 K [4], were neglected.

RESULTS AND DISCUSSION

The presence of fullerenes in the sampled material was independently verified by high-pressure liquid chromatography (HPLC) and by high-resolution TEM analysis. TEM imaging, performed on a drop of filtered toluene solution transferred to a TEM grid, revealed presence of characteristic fringes produced by hexagonal arrangement of fullerenes on the grid surface. The results of HPLC analysis are shown in Fig. 2. Fullerenes are detected in the 4 mm range adjacent to the stagnation plane. Even though no probe disturbance of the flame was visually observed, it is very probable that used sampling method has limited space resolution averaging the measured concentrations. The overall concentration of fullerenes in the sampled gas is relatively high, reaching 1 µg/l. Figure 2(b) represents the molar ratio of C60 and C70 as a function of axial position. It is observed that this ratio is nearly constant along the flame axis and close to three showing relative abundance of C60.

Numerical results were obtained changing the acetylene content in the fuel from 0 to 4%, the oxygen content in the oxidizer from 21 to 50%, and the effective strain rate from 20 to 40 s⁻¹. The maximum mole fractions of C60 and C70 were found just at the beginning of the oxidation zone in the vicinity of the stagnation plane (Fig. 3). This region is characterized by

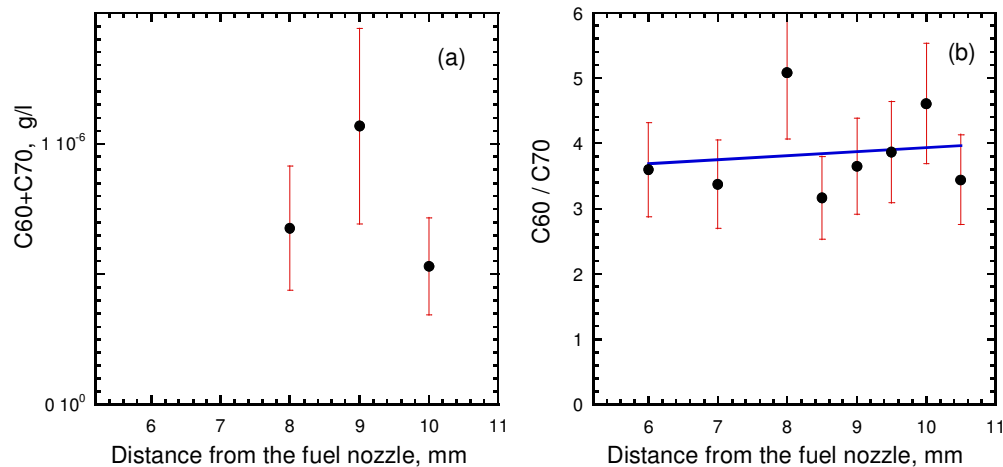


Fig. 2. The results of HPLC analysis: (a) concentration of fullerenes in the sampled gas, (b) C60/C70 molar ratio: fuel - 96%CH₄+4%C₂H₂, oxidizer - 50%N₂+50%O₂, strain rate 20 s⁻¹.

high concentration of fullerene precursors, like fluoranthene (C₁₆H₁₀) and corannulene (C₂₀H₁₀), and high concentrations of H and C₂H₂. Closer to the flame front acetylene and fullerene precursors are consumed by oxidation. The peak of fullerene concentration is shifted to the high-temperature zone relatively to the maximums of C₁₆H₁₀ and C₂₀H₁₀.

Pope et al. [5] stated that fullerene formation is accelerated dramatically by increasing of C₂H₂ and decreasing of H₂ concentrations and to a lesser extent by increasing of H concentration. Numerical modeling shows that acetylene and fullerene precursors are positively affected by an increase of the inlet concentration of C₂H₂, while H and H₂ distributions remain almost constant, consistent with thermodynamic driving force leading to species of increasing size. It is found that an increase of oxygen content in the oxidizer contributes to the shift of the C60 and C70 peaks toward the fuel nozzle. The concentrations of fullerenes are slightly affected by the oxygen content; in fact, an increase of C₂H₂ and H at the position of maximum fullerenes formation is offset by a decrease of fullerene precursors and an increase of H₂. The extent of C60 and C70 formation decreases with increasing strain rate, mainly due to a decrease of the fullerene precursors.

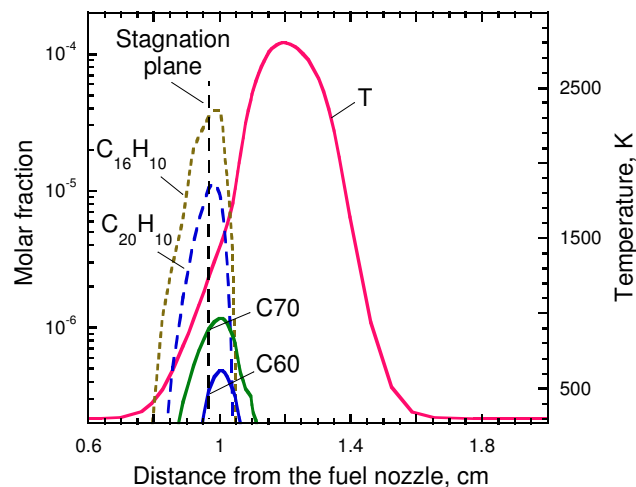


Fig. 3. Predicted mole fractions of C60, C70, C₁₆H₁₀, and C₂₀H₁₀ and temperature distribution: fuel - 96%CH₄+4%C₂H₂, oxidizer - 50%N₂+50%O₂, strain rate 20 s⁻¹.

The C60/C70 ratio is found to be between 0.4 and 0.7 in all conducted simulations, due to the different reaction rates at the branching of the direct formation pathways for C60 and C70 [5]. The strong reverse reaction of the intramolecular rearrangement at the beginning of the cage-closing sequence for C60 slows C60 formation relative to C70 formation. The higher value of C70 with respect to C60 is in disagree with the experimental data, that show higher concentrations of C60 at every position of the probe along the flame axis. Considering the branching of the direct formation pathways of C70 and other tubular molecules like larger fullerenes and multi-walled nanotubes, whose presence has been detected by Merchan-Merchan et al. [8], would probably decrease the C70 concentration to more realistic values. Fullerenes formation can be considered as branching from soot/flat PAH weight growth sequence at the point where the internal 5-rings introduce significant curvature [5]. In contrast to soot, fullerenes have specific well-defined molecular structures, so the number of precursors is considerably small, compared with the number of other PAH species contributing to the soot formation.

CONCLUSIONS

The presence of fullerene material in atmospheric pressure opposed flow oxy-flames has been confirmed by HPLC and TEM analysis. Experimental results show that C60/C70 ratio is nearly constant along the flame axis and the highest fullerene concentration is just above the oxidation zone.

According to numerical simulations, the fullerenes formation has a low sensitivity to the O₂ content in the oxidizer. Conversely, an increase of acetylene content in the fuel and a lowering of strain rate positively affects the production of fullerenes. Future experiments will be needed to validate these numerical predictions. The numerical predictions of C60 concentration ($\sim 3 \mu\text{g/L}$) agree well with the experimental data, allowing for the uncertainty associated with possible disturbance of the flame by the sampling probe. At the same time some important pathways are to be added to kinetic model to account for significant discrepancies for predicted C70 concentrations and C60/C70 ratios.

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High-Rate Growth of Vertically Aligned Carbon Nanotubes (VACNT's) and Carbon Nanofibers in Opposed Flow Oxy-Flame of Methane

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ABSTRACT

Carbon nanotubes and carbon nanofibers are synthesized by the application of a Ni-based catalyst and a counter-flow diffusion flame. Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) are applied to study the morphology of the formed nanostructures. Observed nanoforms include multiwalled carbon nanotubes (MWNTs), MWNT bundles, helical coiled tubular nanofibers, and ribbon like coiled nanofibers with rectangular cross-section. The electric field is applied to control structure and purity of formed carbon nanomaterial. A coating layer of nanotubes possessing a thickness of 35 to 40 microns and a high degree of alignment was formed along the surface of the catalytic probe with variation of probe potential. The application of electric field shows a great promise in controlling the structure and synthesis rate of flame generated carbon nanostructures.

INTRODUCTION

The application of flames as a relatively inexpensive, robust, pyrolysing carbon source for growing tubular nanomaterials was recently studied in a number of publications. Synthesis methods with introduction of catalyst as a particle in the gas phase and in the form of solid support are implemented using mainly co-flow diffusion flame configurations [1-5]. The formation of filamentous carbon on a wire probe [1] or metal screen [2] inserted in the fuel side of the diffusion flames were reported in very early flame studies. The formed filaments were hollow with metal granules at the tips. The reported deposit structures closely resembled structures of carbon filaments formed by CO and CH₄ decomposition over metal catalysts [6]. Recently, Yuan et al. [3,4] studied flame-based growth of nanotubes on a Ni/Cr support in laminar co-flow methane-air diffusion flame. Formation of entangled MWNTs with a diameter range of 20 to 60 nm was reported. The metal catalyst dispersed on TiO₂ substrate was used by Vander Wal [5] to generate MWNTs in ethylene/air and acetylene/air diffusion co-flow flames. The importance of the catalytic substrate positioning in flame is emphasized by the co-flow studies. However, the influence of this factor has not been adequately studied due to the small flame volumes and strong flame-probe interactions. Use of counter-flow flame configuration can provide better sampling possibilities and improve interpretation of results. Additionally, it was shown recently [7], that a counter-flow oxy-flames have a strong potential for nanotube growth producing high temperatures and high radical concentrations. Requirements for high purity carbon nanofibers with controllable structure and properties call for development of novel growth control methods. In this paper the electric control method is implemented by variation of the probe potential relatively to the potential of the grounded burner nozzles.

EXPERIMENTAL

Opposed flow oxy-flame (Fig. 1) is formed by an oxy-fuel counter-flow burner forming two opposite streams of gases. The fuel (methane seeded with 4% of acetylene) is supplied from the top nozzle and the oxidizer (50% O₂+50%N₂) is introduced from the bottom nozzle. A detailed description of the burner is provided by Beltrame et al. [8]. A 40-mm long catalytic probe is introduced through the flame-protecting shield to the yellow soot-containing region of the flame. The central part of the probe (~25mm) was used to study the structure of deposit materials. Experiments were performed with grounded probe and probe at floating potential. The respective modes of operation are referred in the text as a grounded probe mode (GPM) and a floating probe mode (FPM). Transmission and scanning electron microscopy was used to study the morphology of the grown nanostructures.

RESULTS AND DISCUSSION

A variety of carbon nanostructures are observed with variation of catalyst position in flame in GPM sampling. In GPM, observed carbon structure include: MWNTs and MWNT bundles, nanofibers with varying degree of crystallinity, helical regularly coiled tubular carbon nanofibers, ribbon-like coiled nanofibers with rectangular cross section, and finally extremely long nanofibers with lengths approaching ~200 microns with diameters from 50 to 200 nm were also observed. Characteristic structures grown in the opposed flow flame are shown in Figs. 1(a-c). The diversity of formed nanomaterials is attributed to the strong variation of flame properties along the flame axis including temperature, hydrocarbon and radical pool. SEM images collected on a catalytic probe inserted at 9.5 mm from the edge of the fuel nozzle reveals a high concentration of helically coiled carbon nanofibers. Fig. 1(c) shows a typical regularly coiled carbon nanofiber surrounded by the specimens of the similar structure. The observed diameters of coiled fibers varied from 20 to 100 nm; length exceeded several microns. High-resolution TEM imaging performed on these structures revealed the presence of ordered carbon layers. Carbon micro-coils obtained by chemical vapor deposition, e.g. by catalyzed pyrolysis of acetylene, were studied by several researches [9,10]. This unique morphology structures are expected to have numerous applications including microsensors, nanomechanical devices and advanced composite materials.

Bundles of irregular carbon nanotubes are synthesized in the flame region close to $Z = 8.5$ mm (Fig. 1b). The nanotube bundles possess a length of only few microns and are grown in a disordered manner. The tube diameters typically vary from 10 to 45 nm. Another distinctive coiled carbon structure revealed by SEM analysis is shown in (Fig. 1a). These structures are found to be present in the low temperature zone. The nanofiber has a distinctive ribbon-like appearance. It was reported previously [11], that growth of this rarely observed ribbon-like filaments could be catalyzed by small iron-containing particles in CO containing atmosphere. Even though all current experiments were conducted with fixed flame parameters and single catalyst material, the synthesized forms of carbon nanomaterials change dramatically. It is observed that change of flame position induces variation in macro-morphology and in the microstructure of the carbon nanomaterials formed. The modification of growth conditions is directly related to variation of the flame environment pertinent to the specific flame location. Temperature, radical and hydrocarbon concentrations are strong functions of axial position in the flame. Availability of specific hydrocarbons at given temperature conditions alters the growth mechanism leading to the selective production of various nanoforms.

An effective control method is to be applied to stabilize growth of carbon nanomaterials with specified structure and morphology. The electric field control was implemented in this study by electrically isolating the probe from the grounded support and operating it at floating potential. Recently, the application of electric fields in plasma and in CVD has been reported

by several authors, e.g., Avigal et al. [12] grew short aligned nanotubes by positively biasing the substrate during the nanotube formation in CVD. The application of electric field to control growth of carbon nanostructures in flames has not been reported previously.

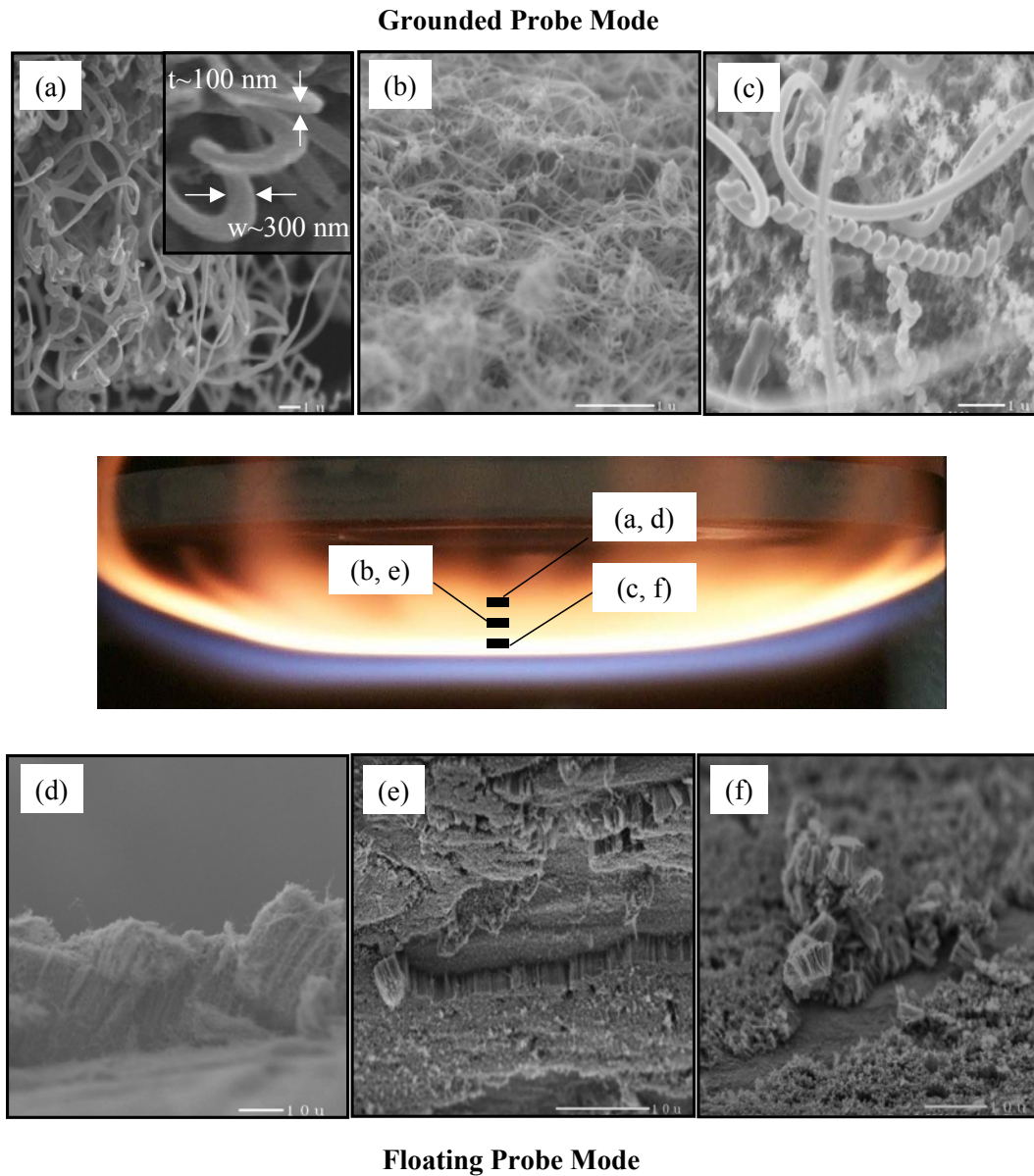


Fig. 1. Carbon nanostructures formed in various locations of opposed flow oxy-flame. The catalytic probes of similar compositions are used in GPM (a-c) and in FPM (d-f). Strong influence of probe position in flame on structure and morphology of grown nanostructures is observed in GPM. In the presence of an electric field (FPM) the growth of vertically aligned carbon nanotubes is stabilized at all tested positions.

Figs. 1(d-f) represent structures grown on the similar catalytic probe in FPM. Three similar catalytic probes were inserted in FPM at positions of 7.5, 8.5, and 9.5mm from the edge of the fuel side nozzle. At 7.5 mm formation of VACNTs layer averaging 40 microns is

observed (Fig. 1d). It was found that the thickness of the VACNT layer decreases with the distance from the fuel nozzle. Figs. 2(e-f) represent arrays of nanotubes formed at 8.5 and 9.5 mm from the edge of the fuel nozzle; an average layer thickness of 10 and 3 microns are measured for these positions. One of the interesting aspects depicted in Figs. 2(d-f) is a high-purity and well-ordered formation of nanotubes. The samples in both types of experiments were never exposed to any kind of chemical and/or physical cleaning. High resolution TEM and SEM imaging on VACNTs shows only small variation of nanotube diameter over average value of 35nm.

CONCLUSIONS

Carbon nanomaterials formed on the Ni-based catalytic probe positioned on the fuel side of opposed flow oxy-flame are studied experimentally. Transmission and scanning electron microscopy imaging was used to study the morphology of the grown nanostructures. These include MWNTs and MWNT bundles, nanofibers with varying degree of crystallinity, helical regularly coiled tubular carbon nanofibers, ribbon-like coiled nanofibers with rectangular cross section, and, finally, long (~0.2 mm) uniform-diameter (~100 nm) tubular nanofibers with regular internal structure of carbon layers

Application of electric field as a method to control structure, properties and purity of produced nanomaterials is evaluated experimentally. Particularly, the strong influence of the probe potential on flame-based nanomaterial synthesis is observed in experiments with grounded probe and probe at floated potential. The floating potential method shows great enhancement of production rate and quality of grown nanomaterials.

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Experimental Investigations of High Pressure Catalytic Combustion of Methane

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INTRODUCTION

Natural gas, with its main constituent methane, has become an abundant fuel supply for stationary gas turbines in energy generation field. Natural gas is generally considered as a clean fuel. However, the formation of the oxides of nitrogen, NO_x, at the high temperature zones created in the conventional gas turbine combustors are of a great environmental concern. It is a well-observed fact that the modern combustion techniques developed for limiting NO_x emissions in the gas turbine combustors in some way influence negatively on the emissions of carbon monoxide (CO) and unburned hydrocarbon (UHC) [1].

Catalytic combustion is an environmentally driven combustion technology for achieving ultra-low emissions from gas turbines [2]. Catalysts could stabilise the combustion well below the typical lean flammability level of the fuel, resulting reduced adiabatic temperature. The reduced temperature eliminates the thermal NO_x formation and the combustion stability over the catalyst ensures the complete oxidation of the fuel. The catalytic combustion technology has been going through development stages since last couple of decades and its capability of achieving ultra low emission levels has been demonstrated [3]. The technology has made it to the gas turbine market recently. A small-scale gas turbine (1.5 MW), running on natural gas and equipped with a catalytic combustor was introduced in 2002. The manufacturers of the system guarantee emission performances of NO_x, less than 3 and the CO and UHC, less than 5 ppm respectively [4].

COMBUSTION CATALYSTS

Suitable candidates for the gas turbine applications must cope up certain set of requirements. Catalysts should be able to ignite air fuel mixture at compressor delivery temperature such as 200°C to 400°C and it should withstand at combustor exit temperatures as much as 1400°C. Since there is no single catalyst available today to fulfil both end requirements, it is a common approach to comprise catalytic combustor design with several number of catalyst elements which has different characteristics. Catalysts segments placed at the entry of the combustor have to be precious metal catalysts, since they have to be very active for igniting fuel at lower temperature. Catalysts occupy at the middle and the latter part of the combustor should be stand at high temperature environment with out decaying their properties. Hexaaluminate catalysts are found to be suitable for a range of applications limiting catalyst temperature for about 1200°C. There are no promising catalytic materials available for the high end of the range.

It should be noted that the natural gas or methane is considered to be one of the most difficult fuels to ignite catalytically. Noble metal catalysts, mainly palladium or Palladium/Platinum combined catalysts are used for the applications with natural gas. Ignition temperature reported for atmospheric combustion tests are as high as 450°C – 500°C [5].

EXPERIMENTAL SETUP

The high pressure test facility consists of a high pressure air compressor (40 bar, 100g/s air delivery), pressure vessel containing catalytic combustor, electrical pre heaters for combustion air and pressure reduction system. Figure 1 illustrates the design of the test facility. The fuel capacity of the test facility is 100 kW. Combustion can be performed at any pressure level up to 35 bar. Air pre-heating system is capable of rising air temperature to the maximum of 600°C. The sizes of the catalysts tested are in 35 mm diameter and 20 mm length.

Air flow and fuel flow rates are controlled by mass flow controllers. Data obtain from the tests are temperature, flow rates, pressure and emission levels. A computer controlled data acquisition and control system has been established. Compressed air, fuel and water (in the case of humidification cycle) flows are accurately controlled and measured. Several number of N type thermocouples are placed inside the combustor to trace all important temperature variations from inlet to the outlet. Pressure in side the combustor is monitored. Online gas analysers take emission information. All the data collecting instruments communicate to the data acquisition program at the frequency of 1Hz and the data are stored in the computer at same speed.

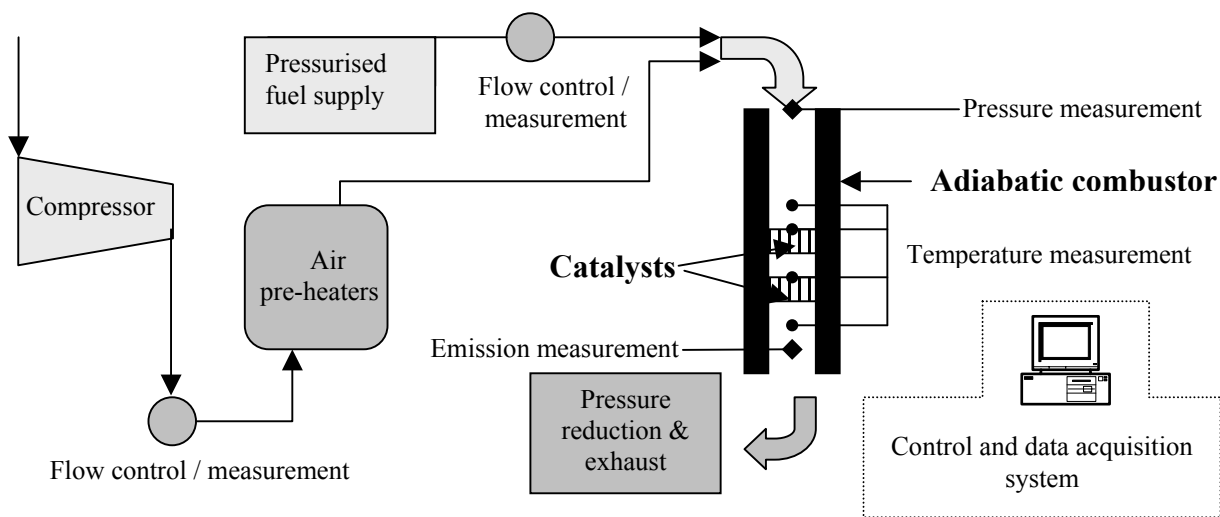


Fig. 1 Design of the high pressure catalytic combustion test facility

RESULTS

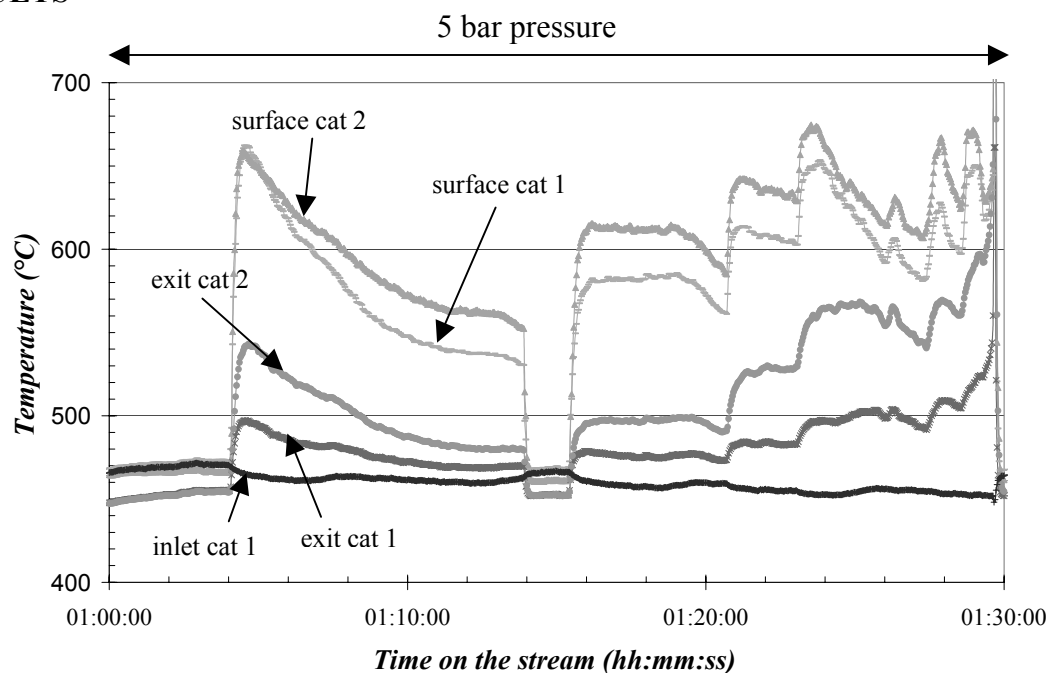


Fig. 2 Inlet, exit and surface temperatures of two catalytic test configuration at 5 bar pressure test

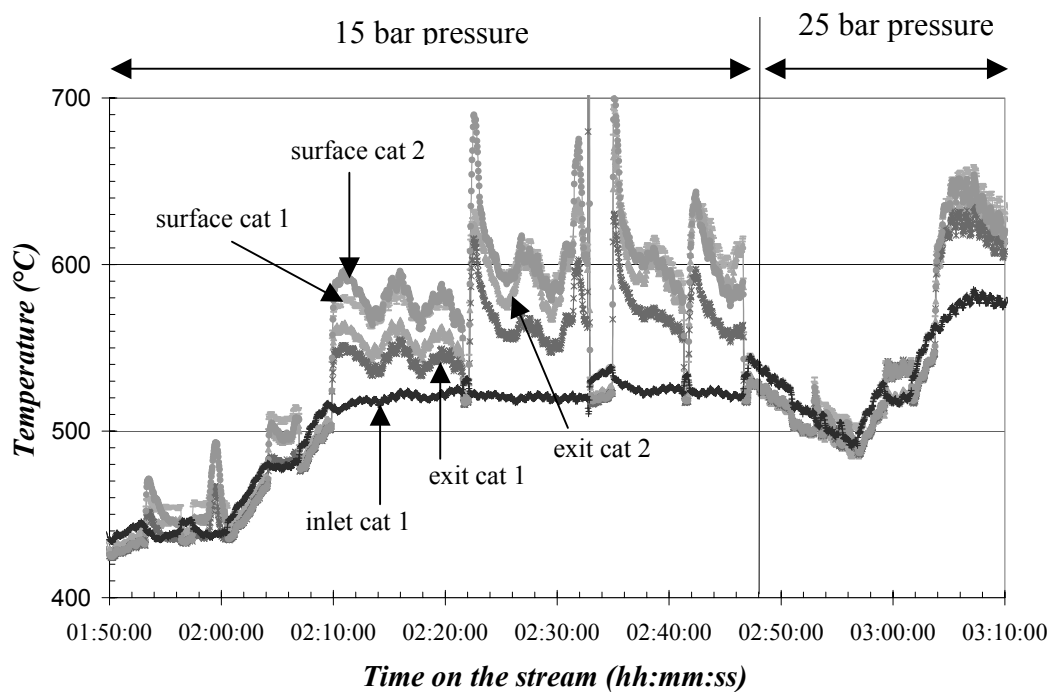


Fig. 3 Inlet, exit and surface temperatures of two catalytic test configuration at 15 bar and 25 bar pressure tests

The results present in the paper are the ignition test results of CH₄/air mixture at different pressure levels. The catalytic configuration considered here consists of two catalytic segments. Each segment is 35 mm in diameter and 20 mm in length. Both are Pd based catalysts, placed sequentially as Pd on Al₂O₃ and Pd on LaAl₁₁O₁₉. The palladium loading on the catalysts is 5% by weight, reference to the washcoat. The air is preheated electrically and the inlet temperature to the catalyst section controlled. In this tests inlet air temperature was kept between 450°C and 550°C as required for the ignition. In the case of catalytic combustion the quality of the mixing between fuel and air is utmost importance. The fuel is injected into the pre-heated air stream upstream of the catalysts allowing 150 mm mixing length in the 35 mm diameter reactor tube. The fuel injection head is placed at the centre of the reactor tube injects fuel into the air stream. At the point of fuel injection, reactor tube takes a shape of contracting its cross section for increased air velocity and enhanced the mixing. The well-mixed pre-heated air fuel mixture then passing through the catalysts for the oxidation reactions. Several numbers of thermocouples placed on the gas stream across the catalysts and the catalysts surfaces monitor the temperature changes and acquired by the computer based data acquisition system. The temperature variations along the catalytic configuration are shown in figure 2, 5 bar, and figure 3, 15 bar and 25 bar. The traces are air inlet, exit and surface temperatures of the catalysts against the time of the flow stream. In the tests the lambda values (air fuel ratio to stoichiometric air fuel ratio) were maintained between 2 and 4. The results clearly show the difficulties in maintaining a stable conversion over the catalysts. The ignition temperature of the catalysts also seems to be affected negatively by pressure. However, the negative effect may also be due to catalyst deactivation.

CONCLUSIONS

Catalytic combustion of methane over the precious metal catalysts (2 segments in the configuration) Palladium on alumina and palladium lanthanum hexaaluminate was experimentally investigated at different pressure levels. Results show that the ignition the fuel mixture below 450°C is a difficult task with the considered catalysts. At high pressures ignition seems to be further difficult and conversion rates of fuel across the catalysts has also reduced.

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Improved-performance premixed metallic burners with perovskite catalysts

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GENERAL ASPECTS

In accordance to the modern climate policy (e.g. Kyoto Protocol), the increasing use of natural gas in all the applications where a source of thermal energy is requested has promoted strong efforts for developing new highly efficient and clean combustion appliances. In light of the numerous stringent European regulations being proposed or adopted for NO_x and CO emissions from domestic appliances, a greater penetration of low-NO_x burners into the overall boiler market is expected (Fig. 1). One can figure out that such a strong production growth will be potentially accompanied by an increase in the low NO_x burner business from 23.3 million EURO obtained in 2000 to 29.9 million EURO estimated for 2005.

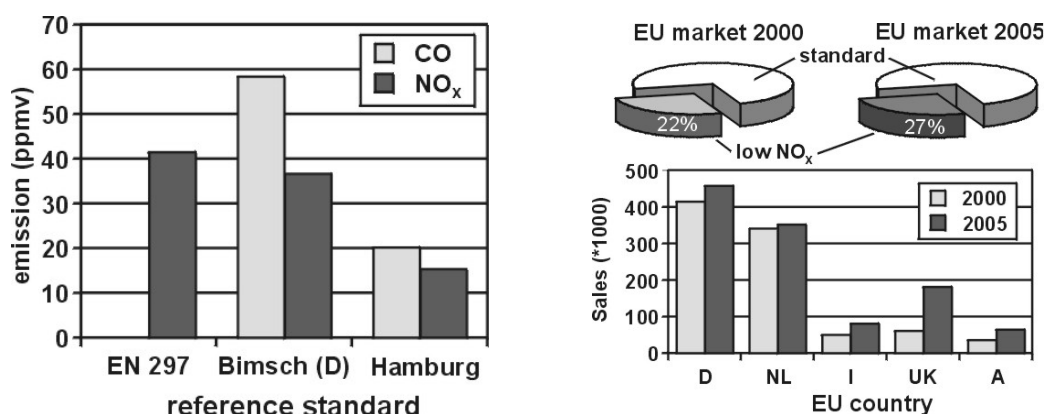


Fig. 1 EU reference standard for CO and NO_x emissions from domestic appliances (left side) and EU low-NO_x burners market for domestic appliances (right side)

In such a context, the generally recognized technical solutions being pursued to improve the efficiency and the environmental impact of domestic boilers (30-35 kW), besides the problems of noise and costs, can be the water cooled burners, the wing flame burners and the premixed (catalytic or non-catalytic) burners. In the present contribution, attention is focused on the premixed burner technology and particularly on the activation of FeCrAl alloy metal fibre panels with a suitable perovskite-based catalyst [1].

In the catalytic or non catalytic surface-flame burners, the combustion process can stabilize at the burner surface or just over it, where the laminar flame speed and the unburnt gas speed find a balance [2]. The aim of the present study is the development of a catalytic burner to be adopted in a low-emission domestic boiler, enabling a large power modulation (turndown ratio 10÷1) in order to contemporary satisfy heating (2-3 kW) and hot water production needs (25 kW), without any water storage, expensive in energetic or equipment terms.

The developed catalyst should be capable of promoting complete methane oxidation even under those critical conditions (specific power density <400 kW/m²) that would lead to unacceptably high concentrations of CO and HC with non-catalytic panels. Moreover, the presence of a catalyst should guarantee an as wide modulation range as the one

above mentioned (10÷1 turndown ratio). The catalytic activation of the burner through deposition of a suitable perovskite-based (ZrO_2 -promoted LaMnO_3) catalyst was considered and a test campaign on a boiler test rig has been carried out so as to prove the achievement of the above claimed advantages.

EXPERIMENTAL

Virgin burners and related pre-treatments

The metal burner employed in the present study is the commercial knitted fibre mat NIT 200/S made of FeCrAl alloy (Cr: 15%; Al: 5 wt%; Fe: balance) by ACOTECH (Zwevegem, Belgium). The FeCrAl alloy has an outstanding resistance to high temperature oxidation because of the formation of an $\alpha\text{-Al}_2\text{O}_3$ protecting layer that, in this case, offers a useful basement also for the anchoring of the catalyst phase. For non-catalytic burners this $\alpha\text{-Al}_2\text{O}_3$ layer is formed during operation, whereas for catalytic ones it must be promoted, prior to catalyst deposition, by means of an *ad hoc* developed high-temperature treatment under oxidising conditions. For this purpose, all panels were kept at 1200°C for 10 minutes in flow of oxygen (0.5% in N_2). Under these conditions, the aluminium present within the alloy migrates towards the fibre surface and forms a uniform coating of acicular $\alpha\text{-Al}_2\text{O}_3$, suitable for catalyst dispersion and anchoring purposes; the temperature, duration of the treatment and mildly oxidising atmosphere were chosen as optimal parameters in order to favour the regular growth of the alumina grains into a uniform layer [3]. Such pre-treated panel was then submitted to catalyst deposition.

Catalyst deposition over the pre-treated support

In view of the interesting results obtained when synthesising perovskite-based catalyst powders via a *combustion synthesis* route [4], a new deposition technique was developed. The attention was focused on perovskite $\text{LaMnO}_3 \cdot 2\text{ZrO}_2$, a catalyst which was previously characterised and tested with promising results. Combustion synthesis operating conditions - i.e. temperature, nature of the organic fuel employed, fuel-to-oxidiser ratio in the starting mixture - have been adjusted and tailored for such application in order to find the best compromise between the adhesion and the specific surface area of the deposited catalyst layer. As for the fuel, urea and glycine were considered: both play a double role within the starting mixture. Not only do they react with the precursors (metal nitrates) but also, by forming complexes with metal cations in aqueous solution, they guarantee a good homogeneity of the solution and are supposed to avoid preferential precipitation of one of the ionic species. Starting from a solution containing $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2$, $\text{ZrO}(\text{NO}_3)_2$ and urea or glycine, two deposition routes were then considered and investigated on small samples of NIT 200/S fibre mat:

- *Combustion synthesis combined with spray pyrolysis*: the solution was sprayed over the downstream surface of the small panels, just taken out of an electric oven where pre-heating at 600°C had been carried out. Due to the *in situ* pyrolysis occurring on the hot panel surface, catalyst formation was obtained. The panel samples were then placed back into the hot oven to stabilise the coating. The spray deposition cycle was repeated on a number of small panels to achieve different catalyst loads. For a further stabilisation and complete crystallisation of the catalytic phase, burners were finally calcined at 900°C for two hours in calm air.
- *Combustion synthesis on panels previously immersed in the precursors solution*: small panels were directly immersed into the precursors solution and left there for a few minutes at room temperature. They were subsequently placed into an electric oven set at

600°C. The reaction took place in the oven only, as opposed to the spray pyrolysis technique. After the deposition, the panels were once again kept at 900°C in calm air for 2 hours.

Scanning Electron Microscope (SEM) analyses were carried out on all samples to verify the effectiveness of the combustion-synthesis-based deposition techniques. Attention was paid to the coating uniformity and thickness and the presence of the desired perovskite/zirconia phase was verified via EDS. From this preliminary study, it was evident that an optimum solution has to be sought, aiming at the best uniformity of the coating coupled with a load of catalyst sufficient to promote the complete oxidation of methane: when employing urea, the better results came with samples deposited via spray-pyrolysis, in fact a rather uniform coating was obtained with a load of about 2% w/w ; on the contrary, when glycine was used, combustion synthesis on panels immersed in the precursors solution apparently behaved better with a load of about 1.5% w/w (Fig. 2).

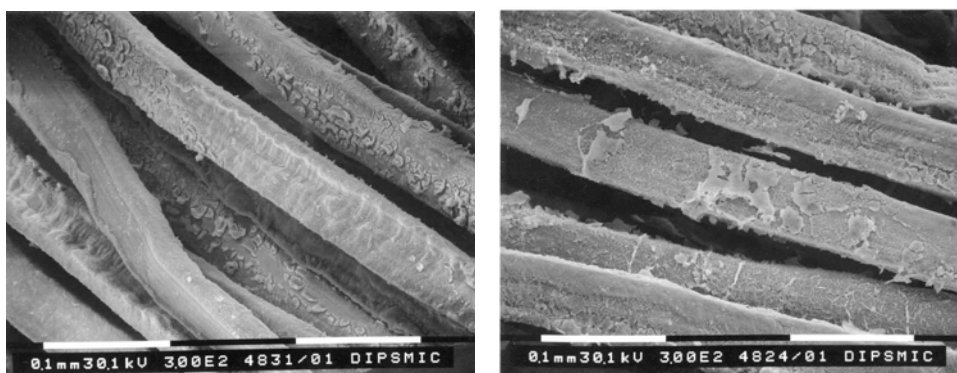


Fig. 2 Catalysed metal fibre mats; left side: sample prepared via urea/spray-pyrolysis (load ~2% w/w); right side: sample prepared via glycine/immersion (load ~1.5% w/w)

Burner testing

Two full size (210x280 mm²) catalytic burners were thus developed according to the two optimised routes just mentioned and tested together in a boiler test rig (maximum nominal power: 30 kW) together with a reference non-catalytic counter part. By varying the input power (200-800 kW/m²) and the excess air (2-70%) the pollutants emissions in the flue gases were monitored by means of a multiple gas analyser (Hartmann&Braun), meanwhile measuring the panel temperature with a K-type thermocouple and observing the flame pattern (radiant, transition, blue flame [1]) through a peep hole.

RESULTS AND DISCUSSION

The main results related to the performance of the catalysed burners compared to the non-catalysed counterpart are shown in Figure 3. As a general issue, it has to be underlined that by increasing the E_a values, the average NO and CO levels decrease. As for CO emissions, as expected, the catalyst was found to reduce the CO emissions with respect to the non-catalysed burner, especially when the excess of air is low ($E_a=4\%$); with reference to the two different ways of preparation of the catalysed metal fibre burners, there is no significant difference between the burners obtained by the urea/spray-pyrolysis or glycine/immersion methods: the CO emission curves are practically coincident. As for NO emissions, things are less promising and easy to understand: the NO emissions of the catalytic burners are lower than those of the non-catalytic burner when operating at low specific power densities ($Q_s < \sim 450-500$ kW/m²), whereas an opposite behaviour is observed at high Q_s values. The

presence of the catalyst help maximising methane conversion within the burners when operating in the radiant regime (low Q_s), which turns into higher heat transfer towards the radiating solid fibres and to lower combustion temperatures. This occurrence also maximises the heat transfer efficiency of the burner. However, when the premixed feed gas flow rate increases (higher and higher Q_s values) the presence of the catalyst becomes detrimental as it reduces the burner porosity and facilitates formation of high- NO_x generating blue flames. Also in this latter case there is no significant difference between the two methods of catalyst preparation. Anyway, the NO levels are quite low.

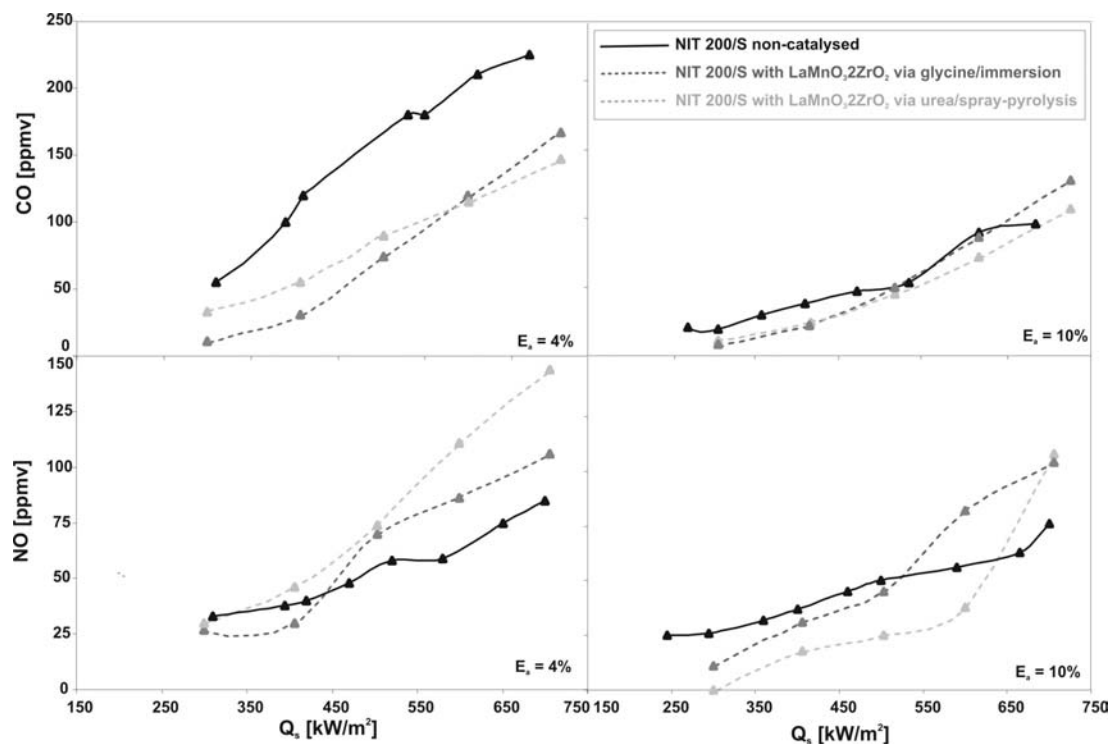


Fig. 3 Experimental CO and NO emission levels (dry gases) at different E_a values for the tested catalytic and non-catalytic burners

CONCLUSIONS

The primary goal of the present contribution was the development of a catalytic pre-mixed fibre burner for household applications, characterised by a markedly lower environmental impact in terms of NO_x and CO, compared to the non catalytic counterpart. The deposition of the perovskite-based catalyst over the metallic mat was found to stabilise the combustion process especially in the radiant regime ($Q_s < 450 \text{ kW/m}^2$), thereby maximising the heat transfer efficiency and improving the combustion completeness (reduced CO emissions). Further investigations related to the behaviour of the metal fibre mats after ageing conditions under high temperature and SO_2 rich environment (SO_2 is originated by the combustion of odorants) are in progress.

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Nanostructured Pd perovskite catalysts for Natural Gas Combustion in CNG engines exhaust gases

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Catalytic combustion of methane with air was studied on $\gamma\text{Al}_2\text{O}_3$ -supported LaMnO_3 and palladium catalysts deposited on cordierite monoliths. The catalytic combustion of methane (4 vol%) was investigated in a lab-scale test rig in the temperature range 400-900°C and at a GHSV of 10,000 h^{-1} under realistic conditions. The combination of Pd and perovskite catalysts enables complete methane conversion with half the amount of noble metal used in conventional Pd- $\gamma\text{Al}_2\text{O}_3$ catalysts.

INTRODUCTION

Advanced natural gas engines guarantee considerable advantages over conventional gasoline and diesel engines. Since compressed-natural-gas (CNG) is widely recognized as the cleanest hydrocarbon fuel, CNG engines could lead to very low pollutant emissions. However, unburned methane is much harder to oxidise than gasoline-derived unconverted HCs. The strong greenhouse potential of methane (more than an order of magnitude higher than that of CO_2) forces to abate methane emissions from natural gas engines [1]. Catalytic combustion of methane on honeycomb converters similar to those used for the treatment of gasoline engine exhausts is the way to go.

Particular demands are imposed on the catalysts for methane combustion. They must resist thermal and mechanical shocks and exhibit high activity, which is not trivial owing to the high stability of CH_4 molecule and the low temperature of the exhausts of CNG vehicles (seldom exceeding 500°C). Commercial catalysts are mostly based on $\gamma\text{-Al}_2\text{O}_3$ -supported Pd catalysts [2,3], having a three times higher noble metal loading compared to conventional three-way catalysts. A research line of ours, funded by the European Community (Growth Project CAT-NAT), is aimed at developing nanostructured Pd-perovskite catalysts with lower Pd content than conventional ones. In the present contribution such catalysts are deposited by “*in situ* combustion synthesis” over ceramic honeycombs to produce reliable catalytic converters, tested on a specific test rig and compared to conventional converters.

EXPERIMENTAL SECTION

Catalyst preparation

A layer of γ -alumina - thermally stabilised with 10%^{w/w} La_2O_3 - was deposited on cordierite ($2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$) monoliths (Corning honeycombs with a cell density of about 600 cps; length: 40 mm; diameter: 20 mm) via a *combustion-synthesis* technique. The monoliths were repeatedly dipped in an aqueous solution containing the suitable amount of precursors ($\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$, from Aldrich and $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, from Alfa) and urea (from Alfa). The optimum urea amount was found to be 40% of the theoretical amount dictated by propellants chemistry (e.g. ratio between ammoniacal hydrogen and nitric oxygen equal to 2).

Subsequently, the monoliths were placed into an electric oven set at 500°C, where the synthesis reaction took place completely within a few minutes. Several deposition cycles were repeated until a load of 25% w/w with respect to the original weight of the monolith (about 12 g) was achieved. Calcination for two hours in calm air at 700°C was then performed to stabilize the obtained coating.

The LaMnO_3 active phase was added by combustion synthesis as well, by dipping again the alumina/lantana-deposited monolith in a solution containing $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2$ and urea. As suggested by previous studies [4], a 150% excess of urea was used in this case, with a view to promoting the one-step formation of the perovskite phase. After impregnation with the perovskite precursors solution, the monolith was placed again into the oven set at 500°C and subsequently calcinated at 700°C for 2 hours in calm air in order to improve the crystallisation of the LaMnO_3 phase. The cycle was repeated until a loading of 15% w/w with respect to the $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$ layer was attained.

On some monoliths, palladium was deposited on a monolith by dipping it into an aqueous solution of $\text{Pd}(\text{NO}_3)_2$ (8.5% w/w , from Aldrich) which was further diluted so as to eventually have a 1 or a 2% w/w final Pd load with respect to the alumina/lantana layer. The monolith was then kept at 500°C in order to promote the stabilisation of palladium and the formation of finely dispersed Pd clusters. Calcination at 700°C for 2h was repeated at the end of the Pd-deposition step.

Characterisation

The adhesion properties between the catalyst and ceramic surface was checked by means of ultrasonic bath test: a piece of the catalytic monolith was weighted before and after the ultrasonic treatment to quantify the catalyst loss.

Physicochemical characterization was performed on sections of the catalytic monolith; in particular, scanning electron microscopy (SEM) analyses were performed using a Philips 515 SEM apparatus equipped with an energy-dispersive spectrometer (EDAX 9900 EDS), in order to investigate the morphology and composition of the deposited catalytic layer.

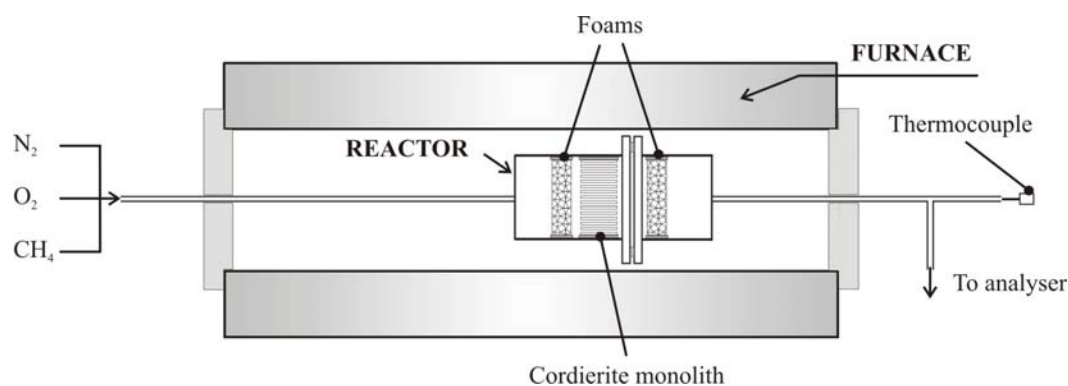


Fig. 1 Scheme of experimental set-up.

Isothermal Catalytic Activity Measurements

Catalytic combustion experiments were carried out in a steel reactor (Fig. 1) heated in a Carbolite horizontal split tube furnace with a heated length of 60 cm. The catalytic monolith was sandwiched between two mullite ceramic foams. A thermocouple, inserted along one of the central channel, was used to control the temperature within the monolith. The gaseous flow rates were regulated by Brooks 5850 mass flow controllers. Lean inlet conditions were fixed (0.4% CH_4 , 10% O_2 , N_2 balance). The temperature gradient produced in the axial

direction was not significant. The GHSV space velocity was set to $10,000 \text{ h}^{-1}$. The composition of the product stream was monitored by continuous analysers (Hartmann & Braun URAS 14 for CH_4 , CO_2 and CO concentrations, and MAGNOS 106 for O_2).

RESULTS AND DISCUSSION

After a large screening of methane-combustion perovskite catalysts obtained by combustion synthesis [4], in line with the literature [5], the best catalyst was found to be LaMnO_3 . Figure 2a shows SEM pictures of the LaMnO_3 perovskite catalyst produced via combustion synthesis. Its microstructure is foamy. During combustion synthesis, the decomposition-combustion of reacting precursors generates a large amount of gaseous products in a very short period of time, which leads to a spongy catalyst morphology. This feature represents a great advantage, as it favours the formation of rough interfaces for the catalyst clusters agglomerates, which in turn increase the specific surface area. Obviously this effect is further maximised by the presence of the $\gamma\text{-Al}_2\text{O}_3$ washcoat obtained in advance by analogous means. Shifting to the issues related to catalyst deposition, it has to be stated that the adhesion between the deposited catalyst and the channel walls of the traps was excellent, as the loss of catalyst by ultrasonic treatment was lower than 1%. To these merits, Fig. 1b shows SEM pictures of catalyst lined via *in situ* deposition on the channel-walls cordierite monolith which are evenly covered by the catalyst layer.

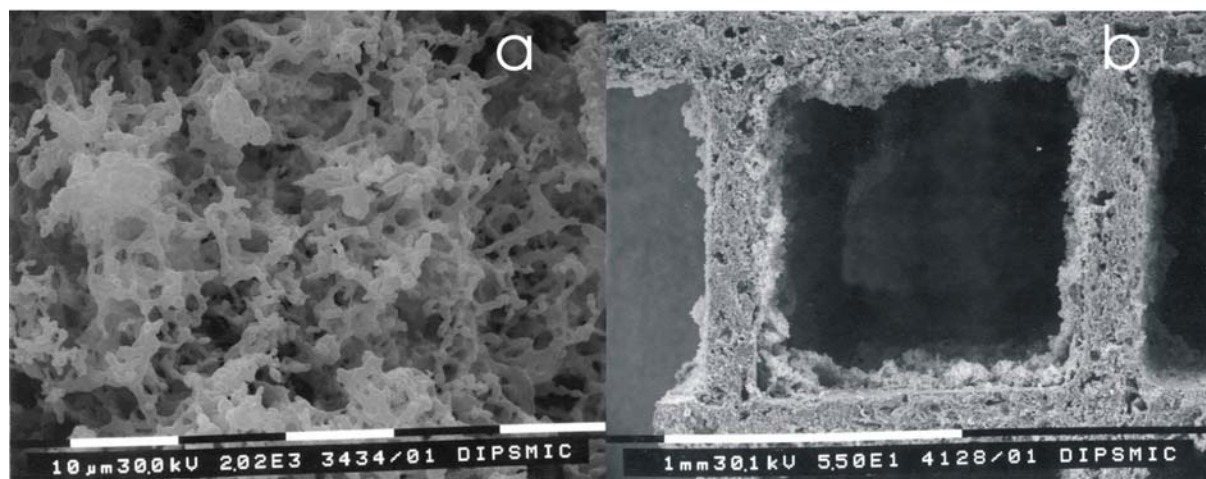


Fig. 2 SEM images LaMnO_3 : a) fresh catalyst; b) front view of a channel monolith.

As far as the comparative analysis of the activity of the catalysts towards methane combustion is concerned, specific experiments were carried out either with pure LaMnO_3 or on with supported catalysts (i.e. either LaMnO_3 or Pd-LaMnO_3 or only Pd on $\gamma\text{-Al}_2\text{O}_3$). Homogeneous reaction tests have also been carried out with the reactor equipped with uncatalysed monolith in order to evaluate the onset temperature of gas phase reactions. The isothermal catalytic curves plotted in Fig. 3 show that all $\gamma\text{-Al}_2\text{O}_3$ -supported catalysts, significantly shift the combustion temperature range towards temperature values more than 350°C lower than those typical of non-catalytic combustion. Starting from the pure LaMnO_3 catalysed monolith, the shape of this curve is quite similar to the plot obtained for the blank monolith; only a slight improvement of the activity at low temperature is noticeable: obviously this unsatisfactory behaviour is due to the rather low specific surface area of the

unsupported perovskite. Undoubtedly, it appears that the dispersion of active perovskite phase (LaMnO_3) on alumina is successful to enhance the activity in methane oxidation. The half-conversion temperature is reached at 450°C , compared with 750°C achieved for the monolith catalysed with only pure LaMnO_3 and/or by the uncatalysed converter.

It is interesting to note how the addition of 2wt% Pd to $\gamma\text{-Al}_2\text{O}_3$ shifts the results back to 350°C . Several studies are available in literature which deals with mechanistic details on the superior activity of Pd catalyst [3, 6, 7]. It is even more interesting to show that the combination of half-the-above amount of Pd with LaMnO_3 produces an equivalent performance, which helps reducing the catalyst costs.

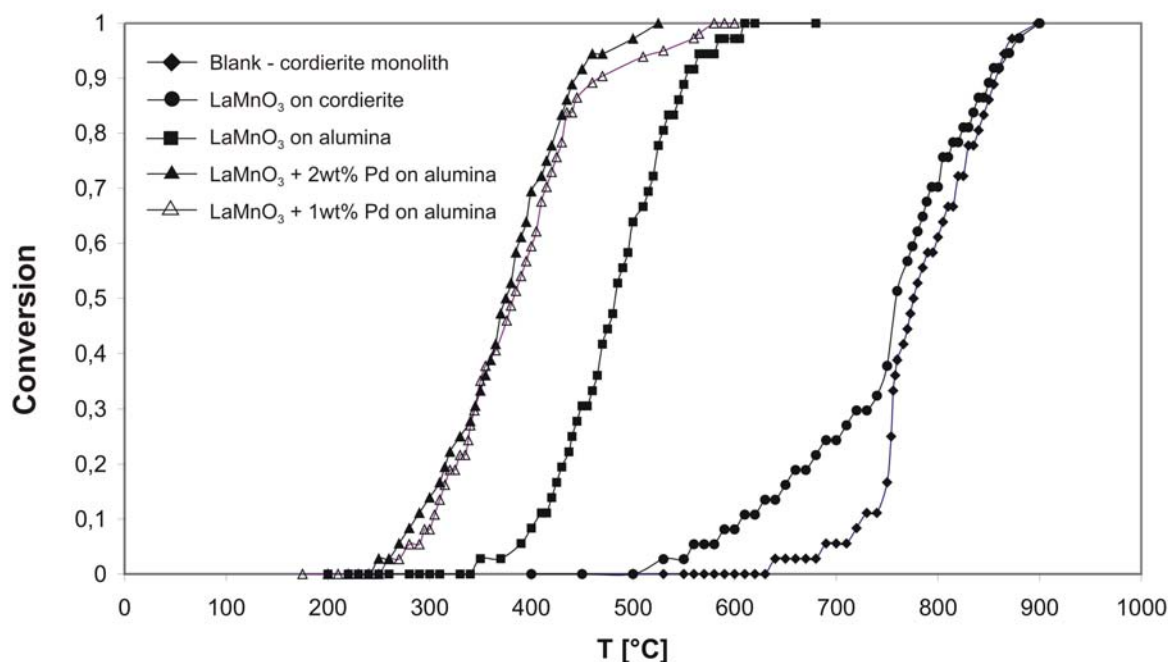


Fig. 3 Methane conversion as function of temperature over different catalysts deposited on cordierite monolith. ($10,000 \text{ h}^{-1}$ GHSV ; 0.4% CH_4 , 10% O_2 , N_2 balance)

CONCLUSION

Experimental tests on a series of *ad-hoc* prepared CNG exhaust gas aftertreatment converters have demonstrated a superior activity towards methane conversion by coupling the effects of lanthanum manganate and Pd active species. This should entail a reduction of the overall catalyst costs compared to conventional Pd-only catalysts currently employed. Specific activities are currently in progress to optimize the deposition of Pd in order to gain a further reduction of this costly noble metal in the catalyst formulation.

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Comparison Among Different Catalysts for Methane Combustion Under Very Lean Conditions

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INTRODUCTION

Catalytic combustion can be regarded as an intrinsically clean and safe technology which allows a primary air pollution control, since energy is produced with high efficiency burning fuel/air mixtures also outside the flammability limits, at operating temperatures far lower than those of flame combustion and without the instability problems and pollutants (CO, NO_x, soot and unburned hydrocarbons) typical of the traditional processes [1-3].

Typically, catalyst compositions for such process have included precious metals (and/or rare earths) since Pt and Pd are commonly recognised among the most effective active components; nevertheless, their application in high temperature applications is strongly limited by problems of stability (PdO) and volatility (Pt) [3-5].

In recent years, a lot of research effort has been devoted to the study of alternative active phases such as perovskite-type oxides with general formula $A_{1-x}A'_xB_{1-y}B'_yO_{3\pm\delta}$ [6]. Indeed, such materials offer potential better features in terms of elevated chemical and thermal stability (up to 1100°C) and lower cost. The well known drawback related to their low porosity and strong tendency to sinter [6-7] has been faced by dispersing perovskites onto high surface area refractory oxides (La/γ-Al₂O₃, MgO, ZrO₂) and coating suitable substrates (ceramic and metal honeycombs/foams) to obtain structured catalytic reactors [8-12].

In this work, the catalytic properties of PdO and LaMnO₃ active phases dispersed on La/γ-Al₂O₃ coated honeycombs have been compared in autothermal combustion tests with lean CH₄/O₂/N₂ mixtures (methane concentration ranging from 3 to 5 % vol.) carried out under operating conditions of interest for premixed fully catalytic radiant burners for industrial or domestic applications.

EXPERIMENTAL

Commercial cordierite honeycombs (400 cpsi) were first washcoated with a La₂O₃ stabilised γ-Al₂O₃ via a modified dip-coating procedure [8]. PdO (1.5% w./w.) was dispersed by repeated impregnation of washcoated monoliths in diluted Pd(NO₃)₂ aqueous solution, while LaMnO₃ perovskite (30% w./w.) was deposited using in situ Deposition-Precipitation (DP) method [8], or co-impregnation. After each deposition cycle the monoliths were calcined at 800°C in air for 3 hours.

Catalytic combustion experiments were carried out in a quartz down flow reactor electrically heated using monolith reactors with 25 channels on the cross section and various lengths. The gaseous flow rates were regulated by Brooks 5850 mass flow controllers and pre-mixed at atmospheric pressure to obtain a feed containing 3-5% vol. CH₄, in air or 10%vol. O₂. Total flow rate was varied in the range 16-72 Nl/h (GHSV = 2.2-13.2·10⁴ h⁻¹). The feed and product streams were continuously analysed using independent ND-IR detectors for CH₄, CO₂, CO and NO. Catalyst wall temperatures were measured with K-type thermocouples (d=0.5mm) placed at different axial positions in the central channel of the monolith [9-11].

RESULTS

Intrinsic CH₄ oxidation activity

Preliminary catalytic activity measurements for the different systems were carried out directly on monolith catalysts to take advantage of their favourable heat and mass transfer properties in order to obtain pseudo-isothermal conditions. As expected, catalytic monoliths based on PdO as active phase showed the best performances in the total oxidation of methane at low temperature: the specific activity on a mass basis of total active washcoat layer was 1-2 order magnitude higher than that of the perovskite based catalysts. In fact it must be noted that the noble metal based monoliths exhibited a large variability of activity depending on the pretreatment conditions and the thermal history experienced by the catalysts. Indeed, initial activation upon exposure to reaction conditions has been often reported and related to transformation of initially amorphous PdO state to a crystalline state and /or interaction with the support [4,5]. Moreover, the catalyst undergoes spontaneous reduction which when heated at temperatures above 700°C also in oxidising atmospheres, and is usually reoxidised only at lower temperatures giving rise to a characteristic hysteresis red-ox loop whose width is largely function of the oxygen partial pressure and the nature of the support and dopants [4,5]. Such feature was recognised as the main cause for apparent negative activation energy during methane combustion at temperatures above the PdO decomposition threshold [4,5].

Even if less active than the precious metal based system, the perovskite based catalysts displayed total selectivity to CO₂, a constant apparent activation energy of ~20 Kcal/mol, and an overall activity enhancement by a factor 6 with respect to the bulk LaMnO₃ obtained through the dispersion of the active phase on the high surface area alumina support [8,9].

Autothermal combustion

Fresh PdO based monoliths are able to ignite a mixture of 3% CH₄ 10% O₂ already at preheating temperatures between 350-375°C, slightly variable depending on the thermal history of the catalyst. The typical conversion plot for the operating condition examined is characterised by a sharp increase in conversion in correspondence of the light-off temperature, but in fact methane is not converted completely. As shown in Fig. 1 at fixed preheating of 375°C CH₄ conversion is about 85% and the catalyst displays an almost flat temperature profile with a maximum not exceeding 720°C.

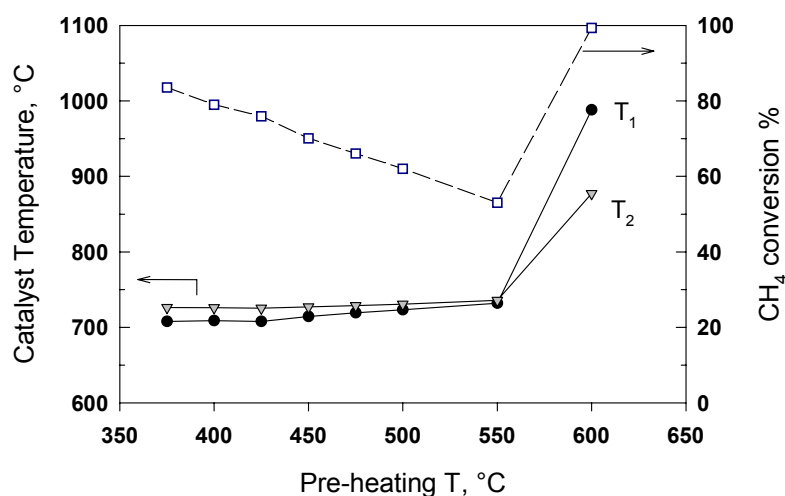


Fig. 1 Steady state CH₄ conversion and catalyst temperatures ($T_1=5$, $T_2=15$ mm from inlet, $L=22$ mm) over a PdO/La- γ -Al₂O₃ monolith as a function of preheating temperature. Feed: CH₄=3%, O₂=10%, GHSV=1·10⁵ h⁻¹

The unusual feature of PdO active catalyst clearly emerges by increasing the preheating level from 375°C to 550°C (Fig.1): while the catalyst temperature stays almost unchanged, the CH₄ linearly decreases down to 55%. The maximum temperature appear to be fixed to that of the decomposition from PdO to metallic Pd, which is reported as being far less active than the corresponding oxide [4,5]. Therefore the systems is able to convert only the amount of methane necessary to raise the temperature up to the level where a kind of dynamic equilibrium between the active and inactive forms of palladium is established and the two forms coexist. At still higher preheating levels (600°C) it became possible to ignite the large remaining fraction of methane also on the less active Pd species, giving complete conversion and with catalyst temperature raised up to maximum values of about 1000°C held at the entrance of the reactor.

The reversible transformation between PdO and Pd species on the surface of the catalyst can induce strong oscillating phenomena [5]. For example Fig.2 shows that as a response to a step change in methane concentration from 4% to 3% at fixed preheating temperature, large oscillations appeared in both CH₄ conversion and catalyst temperatures, centred around 730°C, with an amplitude of ~65°C, a characteristic time of 1h and a complex spatio-temporal pattern along the whole reactor. It appears that safe and convenient operation of such a catalytic burner would be a very hard task due to the intrinsic instability of the active phase and its inability to assure full conversion in a large window of operating conditions.

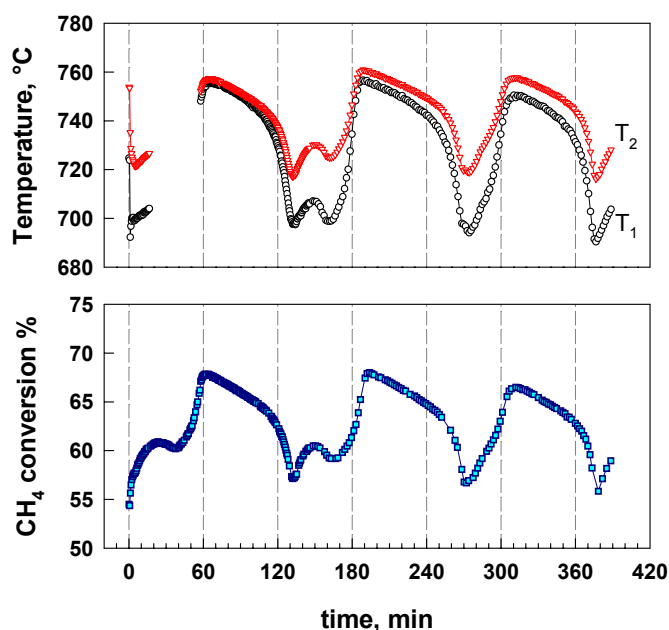


Fig. 2 Typical oscillatory behaviour of the PdO/La- γ -Al₂O₃ monolith induced by a step change in CH₄ concentration from 4% to 3% in air at time 0. Preheating $T=425^{\circ}\text{C}$, $GHSV=1\cdot 10^5\text{ h}^{-1}$

On the other hand the fresh monolithic catalyst with LaMnO₃ active phase is able to ignite a the same lean mixture (CH₄ 3% O₂ 10%), at minimum inlet gas temperature of about 485°C (Fig. 3A), giving stable temperature profiles and almost complete methane conversion associated to negligible CO and NO_x emissions [9]. Methane is consumed basically through heterogeneous reactions, since gas temperature in the first part of the reactor was still too low for significant homogeneous contributions [11]. Moreover, in contrast to Pd based system, temperatures on the LaMnO₃ catalyst monotonically increased with increasing preheating levels [9].

Transient ignition behaviour over perovskite based monolithic reactors was characterised and catalyst long term durability tested up to 120h under reaction conditions of interest for radiant burners (Fig. 3 A). After about 60 hours working time, minimum ignition temperature levelled off to a constant value, which is still 370°C lower than that required on a nude cordierite monolith, keeping complete selectivity to CO₂ [11]. As shown in Figure 3 B, an aged catalyst (after about 40 h in ignited conditions) ensured stable and almost complete conversion of methane during 9 h of continuous operation: in this case temperatures as high as 1000°C were constantly held at the reactor inlet (T₁), indicating no appreciable deactivation of our LaMnO₃-based monolith.

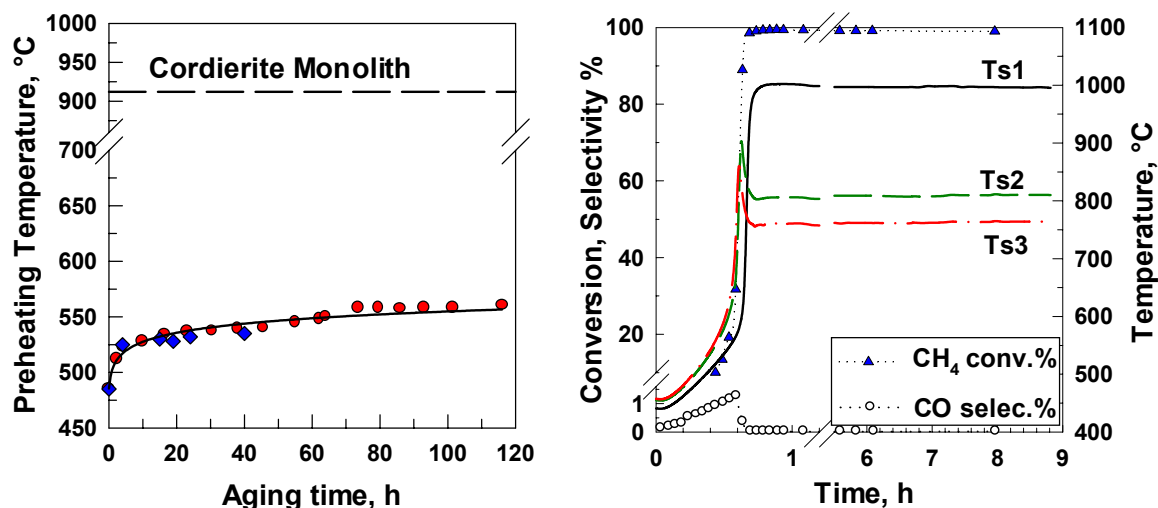


Fig. 3 A) Minimum ignition temperature measured over LaMnO₃/La- γ Al₂O₃ monolithic catalysts of different length: ($\diamond$) 46 mm, ($\bullet$) 23 mm.; Feed: CH₄ 3%, O₂ 10%; GHSV=4.4 or 8.8 10⁴ h⁻¹. B) Typical catalyst axial temperature profile (T₁=5, T₂=25, T₃=34, L=46mm), CH₄ conversion ($\blacktriangle$) and CO selectivity ($\circ$) vs. time on stream. Preheating T=580°C; GHSV=7.2 10⁴ h⁻¹.

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Effects of a Fast Exothermic Wall Reaction on Heat and Mass Fluxes in the Entrance Length of a Monolith

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ABSTRACT

A two-dimensional mathematical model of the catalytic propane combustion in a monolith reactor was a means to investigate the effect of superficial reaction and its coupling with the fluid flow on mass and energy fluxes between bulk gas and catalytic surface. Simulations, performed at different values of the Re number, showed that at the light-off location a spike appears in Nu (Sh) number due to the development of new temperature, concentration and velocity profiles.

INTRODUCTION

The wide range of application of monolithic reactors in the field of oxidation of hydrocarbons [1-3] calls for reliable mathematical models, capable of correctly predicting the behavior of the system, yet not excessively computationally expensive. Three- and two-dimensional models, even under simplifying assumptions, such as the boundary-layer approximation [4, 5] take hours to be solved for presently available computer power [6], and are not suitable for real time simulations or kinetic parameters estimation. More desirable in terms of computation time (of the order of seconds) are one-dimensional models, even though their accuracy, for applications of catalytic combustion, lays in the correct evaluation of the mass and thermal fluxes between bulk gas phase and surface [7].

As regards external heat and mass transfer, among the correlations proposed for their prediction, the most widely used is the one proposed by Hawthorn [8], based on the solution of the Graetz problem for constant wall temperature (Nu_T) and constant wall heat flux (Nu_H). However, in the presence of a fast exothermic reaction at the surface, such as in the case of catalytic combustion or partial oxidation, Nu and Sh numbers may be severely affected. Groppi et al. [9] proposed an interpolation of Nu_T and Nu_H via the Damkohler number (Da). Nevertheless, Hayes & Kolaczowski [7] claimed that Nu numbers depend not only on reaction parameters (Da) but also on gas inlet temperature and composition.

Recently, Di Benedetto, Marra & Russo [10] varying fuel mass fraction and inlet temperature, found a strong correlation between the perturbation generated by the light-off of the reaction on the mass and heat fluxes with the adiabatic temperature of the reacting mixture.

In this work we investigate the effect of the surface reaction on mass and heat fluxes to the wall, evaluating with a two-dimensional model Nu and Sh numbers at different Re numbers coupled with the entrance effects.

REACTOR MODEL

We developed a two-dimensional dynamic model to simulate the behavior of an adiabatic monolithic reactor in the shape of a circular channel of radius $R=0.00045$ m, in which a superficial reaction occurs. Internal mass transfer, wall heat conduction and homogeneous reactions have all been neglected to focus on the mere effect of the superficial reaction on heat and mass fluxes. The model superficial reaction is the catalytic combustion of propane, assumed as a one-step irreversible reaction, zeroth order with respect to oxygen and first order

with respect to propane mass fraction:

$$\omega_{y,C_3H_8} = 10^6 \exp\left(-\frac{10900}{T}\right) y_{C_3H_8} \left[\frac{\text{mol}}{\text{m}^2\text{s}}\right] \quad (1)$$

Mass and energy balances are coupled to the full Navier-Stokes equations and have been discretised by adopting the control volume approach: the entire domain has been divided into 19200 elementary cells according to a non-uniform structured mesh, with a finer discretisation where sharp gradients are expected. Numerical solution has been performed by means of the commercial software package CFD-ACE+ [11].

The propane-air mixture was considered at an inlet temperature of 600K and propane mass fraction of 0.015. The inlet gas velocity was varied from 1 to 36 m/s, corresponding to a Re number at inlet conditions ranging from 18 to about 640.

Nu numbers (and Sh analogously) have been calculated at bulk conditions as follows:

$$\text{Nu} = \frac{2R}{T_w - T_b} \frac{\partial T}{\partial r} \bigg|_{r=R} \frac{k_w}{k_b} \quad (2)$$

where R is the channel radius, and k thermal conductivity, and pedexes b and w indicate wall and bulk conditions respectively. Details of the model are reported elsewhere [10].

RESULTS AND DISCUSSION

Figure 1 shows the computed Nu for different Re numbers (Fig. 1a), the wall temperature (Fig. 1b), which identifies the location of the light-off, and the radial velocity profiles at $r=0.0004$ m (Fig. 1c) as function of the dimensionless coordinate x^* ($x^* = x/2r \text{ Pe}$). In Fig. 1a the constant wall heat flux (Nu_H) and wall temperature (Nu_T) obtained in absence of superficial reaction in a developing flow [12] are also plotted as a function of x^* . When plotted vs. x^* , Nu_H and Nu_T overlap for all Re numbers, provided that $\text{Pe} > 50$, and they take into account the entrance effect on temperature, concentration and velocity profiles. Conversely, it is possible to note that in the presence of a fast superficial reaction, Nu numbers are no longer correlated by x^* (Fig. 1a) also at $\text{Pe} > 50$, and Nu_H and Nu_T reported in Shah and London [12] can satisfactorily predict the calculated Nu numbers only far from the ignition point. It is worth saying that the calculated Sh numbers are equal to Nu numbers.

Once reaction has taken place, wall temperature can be considered quite safely constant (Fig. 1b), and the heat exchange problem may be assimilated to a Graetz problem for constant wall temperature ($T = T_{\text{adiab}}$, $\text{Nu} = \text{Nu}_T$). The asymptotic value of all the calculated curves is always in agreement with the theoretical asymptotic value ($\text{Nu}_{T\infty}$), confirming the accuracy of our simulations.

At the inlet, before ignition occurs, heat exchange in the reactor may be assimilated to a Graetz problem with constant wall heat flux (Nu_H) depending on the relative position of light-off and entrance effect. At high Re numbers ($\text{Re} > 160$) ignition does not occur at the inlet, but it is moved at x^* in the range $2 \div 3 \cdot 10^4$, while at low Re numbers ($\text{Re} < 320$) ignition is located close to the entrance (Fig. 1b). Consequently, at $\text{Re} < 320$ when light-off position overlaps to the entrance length, calculated Nu significantly differ from Nu_H at the inlet, and only for $\text{Re} = 320$ and 640, at which light-off is shifted, Nu is reasonably approximated by Nu_H .

A significant displacement of the calculated Nu with respect to the Nu_T and Nu_H curves can be observed in correspondence of the light-off, with the appearance of a spike, also reproduced in the past by the simulations of Groppi et al. [9], due to the exothermic nature of the surface reaction that takes place on the reactor walls.

The spike has a physical meaning: at light-off the fast exothermic reaction generates strong temperature and concentration gradients, which leads to a mixing in the bulk of the gas, with the formation, similarly to what occurs due to entrance effects, of brand new thermal and

concentration boundary layers. Moreover, the heat produced by reaction, generates local gas expansion thus perturbing fluiddynamic boundary layers, as shown by the radial velocity profiles reported in Fig. 1c. The negative value of the radial velocity suggests that a net convective flux from the wall towards the gas bulk arises.

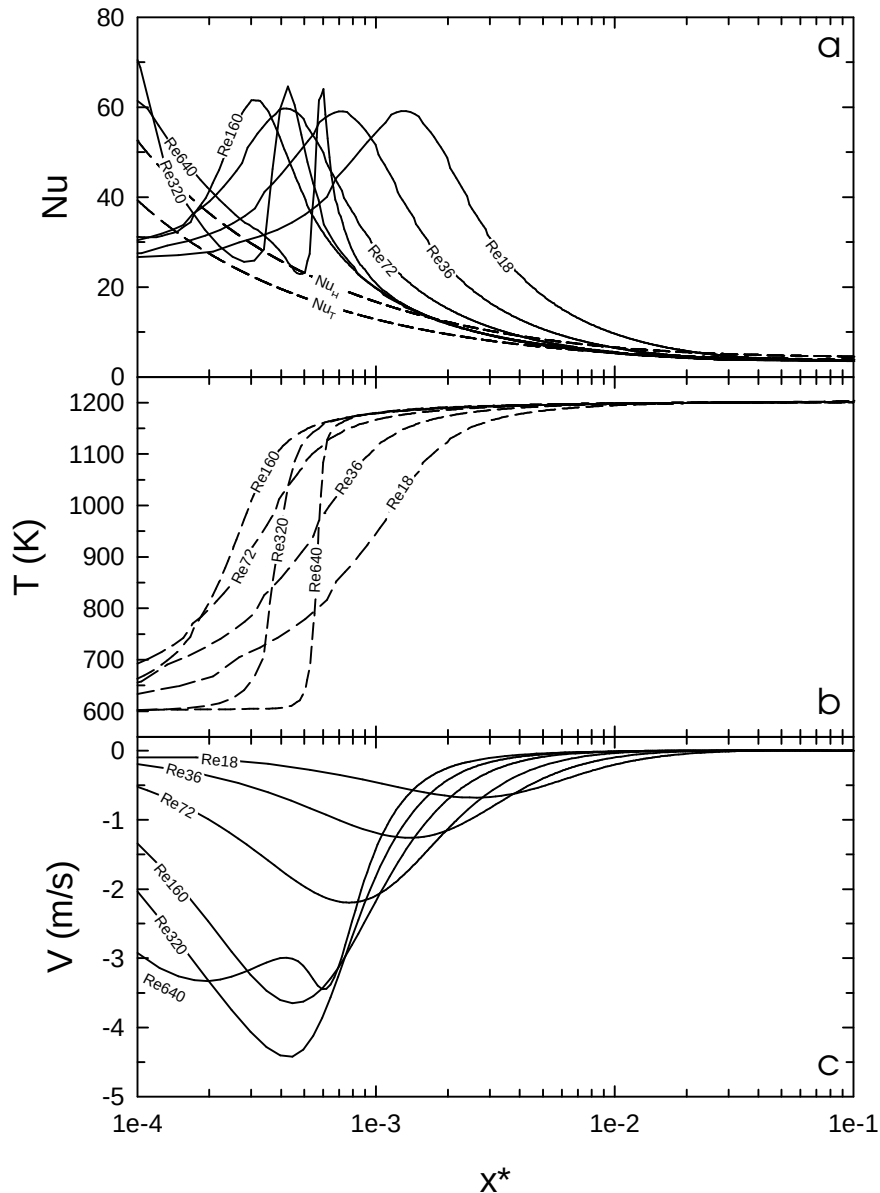


Fig. 1. Calculated (solid lines) and theoretical Nu (dashed lines) [12] (a), wall temperature (b) and radial velocity at $r=0.0004$ m (c) along the dimensionless coordinate x^* .

At low Re numbers ($Re < 320$) ignition is located close to the entrance of the channel and then entrance and reaction effects are close to each other and mostly overlap. The radial velocity exhibits a single peak, witnessing the concurrence and superimposition of the perturbations, even though such peak is always located in correspondence of the light-off. In the case of $Re = 320$ and 640 , surface reaction starts downstream of the main entrance effects. Entrance effects, always located at the same position, are separated from reaction effects, and for $Re = 640$ they are so markedly separated that it is possible to distinguish two peaks of the radial velocity, the first one due to entrance effects and the second to the reaction.

At varying Re number, the spikes differ in position and width, but not in intensity. The spike position depends on the relative position of light-off and entrance effect. At increasing Re from 18 to 640, the spike position (and then the light-off position) exhibits a non-monotonic trend, decreasing from Re = 18 to 160 and increasing from Re = 160 to 640.

Light-off position decreases on Re in the hypothesis of independent transfer coefficients [13], as the residence time is decreased and the Pe number is increased at increasing Re. Hence, light-off position should be constant or shifted at lower values of x^* the lower Re, when plotted versus x^* . Nevertheless, at low Re, when Pe is low, entrance effects are less pronounced but spread on a longer x^* [12]. Consequently, when Re is increased from 18 to 160, entrance effects become more pronounced and heat and mass transfer more efficient: the spike moves upstream along x^* . Conversely, when Re increases above 160, the superficial reaction is far less affected by the entrance effects, as entrance effects are less spread, and light-off position moves downstream. The intensity of the entrance effect at varying Re can be quantified by looking at the radial velocity profiles (fig.1c) at $x^* < 2e^{-4}$.

The width of the peaks instead constantly decreases from Re = 18 where it is the widest, to 640. This fact reflects both the width of light-off and the overlapping of entrance and light-off. In addition, also the flow conditions of the channel affect the width of the peak.

All these results point out that in the presence of a superficial reaction Nu (Sh) are not correlated with a fixed coordinate (x^*) as in the Greatz problem but a more realistic coordinate has to be identified.

CONCLUSION

The present investigation showed that when a fast exothermic superficial reaction ignites in the entrance length of a monolith, heat (mass) fluxes are affected in a not predictable way with the available correlations, due to the superimposition of entrance and reaction effects. In particular a spike in Nu (Sh) appears in correspondence of light-off, which depends on flow conditions and reaction rate.

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Kinetic Modeling of the Influence of Fuel Composition on Ignition and Combustion Rate in HCCI combustion

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INTRODUCTION

The homogeneous charge compression ignition (HCCI) engine has the potential to meet the increasingly stringent emission regulations. The concept is quite old [1, 2], but the challenge is to develop practical HCCI 4-stroke engines that are able to exploit the advantages of HCCI over the whole operating range. The main problems are that at low loads it is difficult to ensure that auto-ignition always occurs, and at high loads the combustion can be noisy and pressure rise rate unacceptably high because of high heat release rates. The critical problems are therefore the control of ignition timing and combustion rate. As HCCI combustion is controlled by chemical kinetics, kinetic modeling may be a valuable complement to experiments in order to gain increased understanding of the fuel chemistry. A challenge is that realistic fuels in addition to paraffins contain for example aromatics, olefins and alcohols, for which the kinetics has to be modeled correctly. In this study we have by kinetic modeling with complex chemistry modeled HCCI combustion of fuel mixtures containing primary reference fuels and toluene. The purpose is to see how the ignition and combustion rate depends on the fuel type. Comparisons with experiments are made and the limitations of the model are discussed.

MODEL

A single-zone modeling approach is used, where we employ the AURORA software, which is part of the CHEMKIN package [3]. To model the variation of the volume in combustion cylinder in an internal combustion engine, AURORA use the equations provided by Heywood [4] ($V(t) \cdot \rho$ is constant). The computational domain was from -180 crank angles ATDC to 25.2 crank angles ATDC. The CPU time varied between 30 and 40 min (DASPK time step $2.5 \cdot 10^{-6}$ s) on a Dell Precision Workstation (Pentium II) with 1 GB of RAM.

Chemical Kinetic Models

To describe the combustion chemistry of primary reference fuel mixtures, a mechanism from the literature could be retrieved [5]. It consists of 2386 reaction steps among 645 species. The reaction mechanism for toluene combustion was taken from [6]. It consists of 921 reaction steps among 120 species. However, combustion mechanisms for mixtures including primary reference fuels and toluene have not yet been well established. A first approximation, used here, is to superimpose the individual mechanisms from [5] and [6] and to remove duplicate reactions. This approach should be seen as a first step in developing a chemical kinetic model for mixtures of a paraffinic and an aromatic fuel. The compiled mechanism consisted of 2964 reaction steps among 719 species.

Initial conditions

Four different fuel mixtures were investigated: iso-octane 94 mole % and n-heptane 6 mole %

(denoted fuel A), iso-octane 84%-n-heptane 16% (fuel B), n-heptane 25%-toluene 75% (fuel C) and n-heptane 35%-toluene 65% (fuel D). The total number of moles (1 mol fuel+4.762 mol air) in the mixture was the same in all calculations. The operating conditions for the engine were as follows: $\lambda=3.5$, compression ratio 17, revolutions per minute 900, intake pressure 1 bar, and total volume 2112 cm³ (bore 127 mm, stroke 154 mm, and clearance volume 124.4 cm³). The problem set-up is influenced by a recent experimental study on HCCI combustion [7].

RESULTS AND DISCUSSION

Effect of fuel type on burn-rate

Fig. 1 explains the definitions used to calculate the burn-rate for fuel A-D where dP is defined as the difference in pressure between a reacting mixture and a mixture where the chemistry is turned off. As the chemical kinetic mechanisms are not optimized, the initial temperature of the unburned fuel-air mixture was chosen as the parameter to adjust the time of combustion.

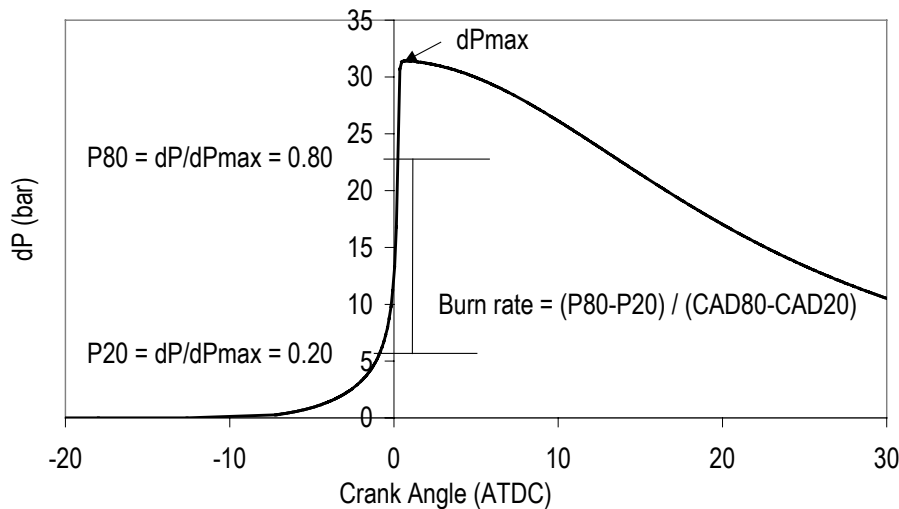


Fig. 1 Definitions used to calculate the burn-rate for fuel A-D.

Fig. 2 shows the burn-rate as a function of inlet temperature for fuel A-D. The burn-rate increases more rapidly as the inlet temperature is changed for fuel A and C compared to fuel B and D, indicating a larger sensitivity for these fuels. This would be as expected, as fuel C and D has a lower Motor Octane Number (MON) than the corresponding primary reference fuel. However, fuel A and B has a higher burning rate for the same initial temperature. The higher burning-rates for fuel A and B can be explained by their shorter ignition delay times (see Fig. 3) predicted by the primary-reference-fuel mechanism used [5], which lead to an earlier combustion time for the same initial temperature.

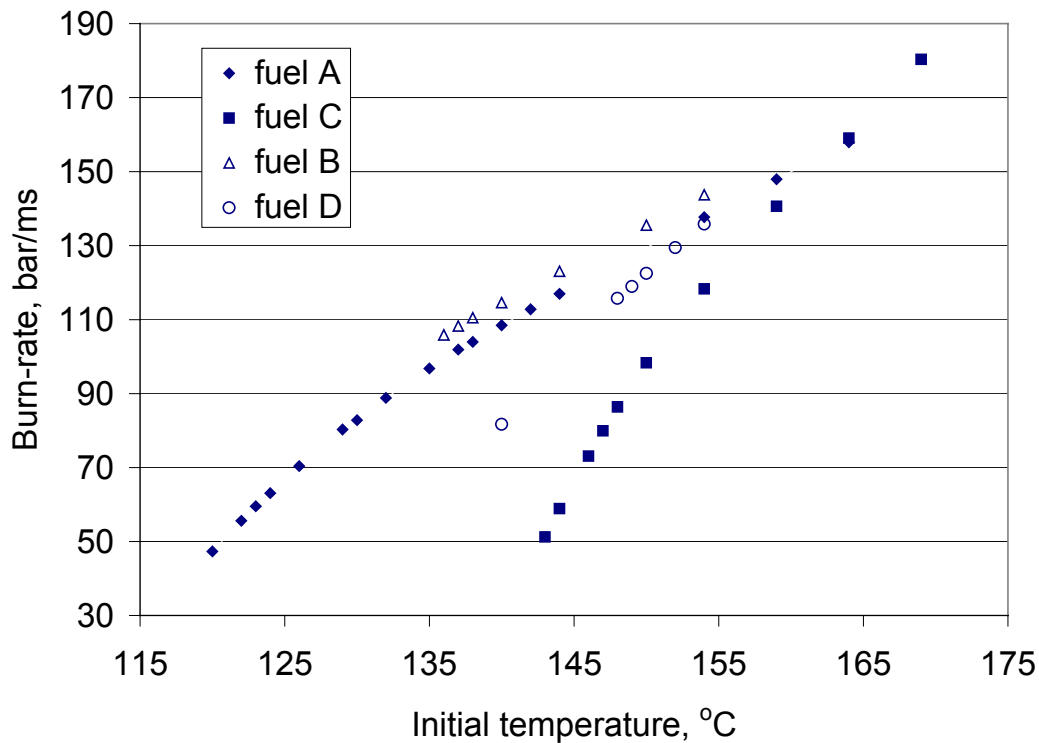


Fig. 2 Burn-rate as a function of initial temperature for fuel A-D. $\lambda=3.5$, $p_{in}=1$ bar, compression ratio=17, rpm=900.

Comparison with experiments

Fuel A and C has similar Research Octane Number (94) but different Motor Octane Number (i.e. fuel C with its aromatic content is more sensitive than fuel A). This is also true when fuel B (RON 84) is compared with fuel D. Fuel A and C are less prone to auto-ignite than fuel B and D. Accordingly, the experimental data in [7] revealed that for the same inlet temperature (120°C) fuel A and C auto-ignited at a crank angle of 5 to 7 degrees after top dead center compared to fuel B and D that auto-ignited at top dead center. The experiments in [7] also revealed that the heat-release rates were significantly larger for fuel B and D compared to fuel A and C. Our calculated burn-rates for fuel B and D at top dead center are ~ 90% higher compared with the calculated burn-rates for fuel A and C at ~ 6 crank angle degrees after top dead center. The results are in reasonable agreement with the experimental study [7] considering the approximations in the model, e.g. a single-zone model for the cylinder and uncertainties in the chemical kinetics. Anyway, as shown in Fig. 3, the current kinetic mechanisms are not able to predict the expected ignition delay times for fuel A-D. Fuel B and D with RON 84 should have similar and shorter ignition delay times compared to fuel A and C with RON 94.

Work in progress

To be able to predict the ignition delay times correctly, a sensitivity analysis is under way in order to modify the chemical kinetic models. Furthermore, a much more comprehensive modeling study will be done where relevant engine parameters are varied.

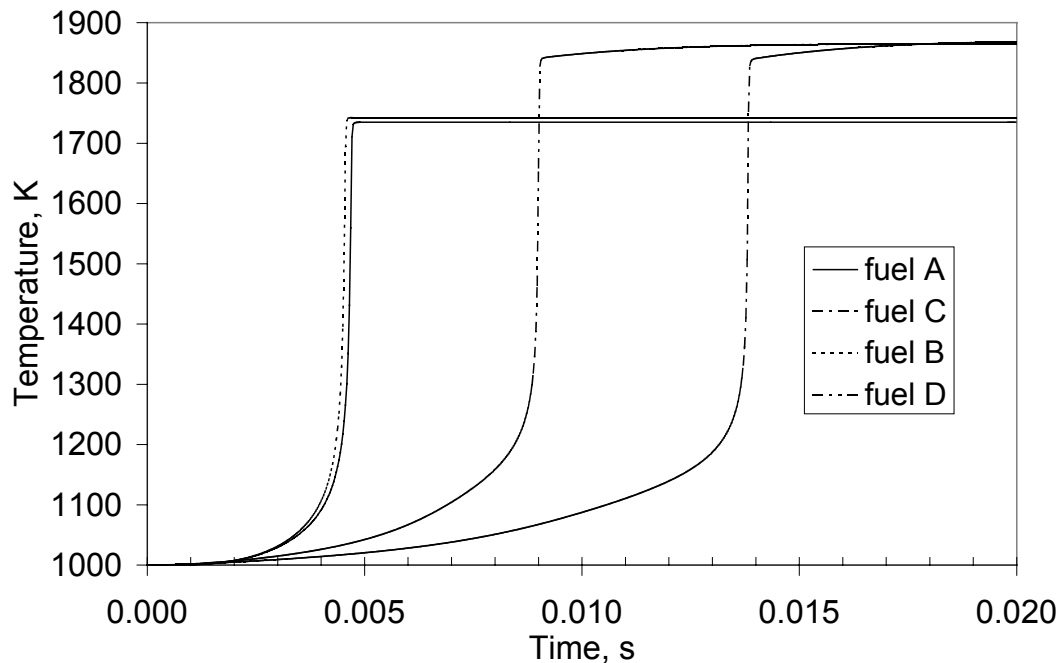


Fig. 3 Ignition delay times from a constant volume calculation for fuel A-D. The initial state is temperature 1000 K, pressure 45.6 bar (volume 124.4 cm³) and $\lambda=3.5$.

ACKNOWLEDGMENT

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Knock Modeling: an Integrated Tool for Detailed Chemistry and Engine Cycle Simulation

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KEYWORDS: engine knock, detailed kinetics, SI engine simulation

INTRODUCTION

For the analysis of a wide range of engine issues, inclusively the engine knock, in nowadays engine development full cycle engine simulation tools (EST) are in use [1]. Meanwhile, in the engine research with relevance to knock the kinetic processes that lead to the autoignition of the end gas are often analyzed by the help of simple zone models. Though these models neglect the influence of turbulence on the autoignition process, they are still very useful in the analysis of the chemical processes that lead to autoignition. The recent engine research brought forward in a number of publications that the autoignition in the end gas of the engine is influenced by the composition of the rest gas, or – if exhaust gas recirculation (EGR) is applied – by the composition of the EGR. Particularly the amount of NO that was formed during one cycle is found to influence the occurrence of autoignition during the next cycle.

Today neither the tools for engine development, nor the tools for engine research are able to fully take such effects into account. This motivates the combination of an EST with a zonal model that is able to predict the composition of the burned gases and the autoignition chemistry, including complicated chemical processes such as the two stage autoignition and the influence of NO on the autoignition.

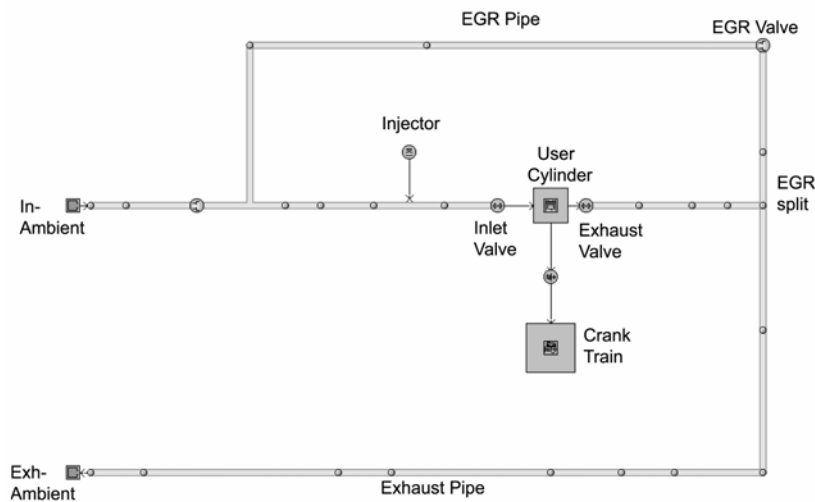
In this paper we combine the commercial EST (GT-Power) with our in-house code (Ignition) that employs a two-zone model [2]. The developed tool allows engine researchers to take at the same time into account the overall engine and powertrain behavior and the complex chemical processes during the combustion. The current paper is a further development of the homogeneous charge combustion ignition (HCCI) model connected to the EST [3] and the two-zone model as it was developed in [2]. The results obtained by means of the coupled simulations are compared to the experimental data. Finally, the capabilities of the new interface are demonstrated by addressing an issue known to have a strong influence on engine knock occurrence - the nitric oxide content in the cylinder gas charge.

NUMERICAL MODEL

Engine data and model

The engine used for the analysis is a single cylinder Ricardo Hydra with a Volvo B230 cylinder head, modified to have a horseshoe shaped combustion chamber for enabling temperature laser measurements. The engine parameters are given in the Appendix. The engine numerical model has been devised using the engine simulation software GT-Power. The fluid dynamic and thermodynamic equations resulting from the engine model are formulated in the form of time dependent finite differences. The layout of the EST model created for the engine studied in this paper is presented in Fig.1. Standard pipe, connection

and cylinder objects constitute the model. Basically we make use of two models for the in-cylinder processes. The model in our in house Ignition code is explained in detail in [2]. The model applies the Wiebe function to account for the propagation of the flame front. Further



heat release from the autoignition process in the end gas is calculated by means of a detailed kinetic mechanism. From this calculation Ignition provides an overall reaction progress variable (based on the generated heat) that is used by the in-cylinder model of the EST. The approach did not demand any changes of the EST.

Fig.1 General layout of the test engine modeled with the EST

The detailed reaction mechanism is also used to calculate the chemical processes in the burned gas zone, in particular the formation of NO. In-cylinder processes are described by conservation equations for mass and energy. The mass equation accounts for the changes of the in-cylinder mass due to flow through valves. Also, the standard EST combustion model based on a prescribed burn rate profile (provided by Ignition) is applied by the 1-D code.

Chemical kinetic mechanism

The present chemical kinetic mechanism [4] was compiled from different sources. Some refinements of the mechanisms were necessary. The whole mechanism includes 141 species and 1401 chemical reactions. Emphasis during mechanism development was put on the parts important for the autoignition timing ignition onset: the reactions and on the transition from low-temperature to high-temperature chemistry.

1-D Model and kinetic code interface

As a basis for the realization of the interface, a preliminary created interface for the HCCI combined simulation was used [3]. The connection between the two numerical tools is achieved through the mentioned user combustion model. The original interface was built flexible enough to enable studies for all the engine types, without limitations concerning the type of injection, the fuel mixture or the exhaust gas recirculation (EGR). In order to save computational time, Ignition Code is called only during the closed valves interval. Also, in order to limit the cycles with the detailed kinetic calculation, the flow inside the engine is firstly initialized by means of a user-provided number of cycles, in which only the 1-D model is used.

RESULTS AND DISCUSSION

A comparison with experimental measurements for the knocking cases was carried out in order to test the integrated simulation tool. For the reference case, a stoichiometric composition of the mixture was chosen. Four other lambda cases and one EGR case extend

the investigation.

Fig.2 present numerical against measured in-cylinder pressure traces. Concerning the combustion period, the autoignition crank angle is accurately evaluated by the numerical code. The slightly higher Ignition-calculated pressure after autoignition can be explained by the only two-zone approach of the kinetic code. This ignores the near wall low temperature, which determines a slightly more reactive system. This drawback is however negligible given the achieved general aim of this paper: to investigate global operation coupled with detailed chemistry, an aim that required a relatively simple model. The heat release curve plotted in Fig.2 clearly indicates the two stages of autoignition. As known in the literature the chemistry related to the first stage of autoignition is involved to a large extent in the knocking phenomenon. Further more, the nitrogen oxides can influence a lot the cool flames chemistry, especially the NO, which -as we will confirm later in this work- plays an essential role in autoignition occurrence.

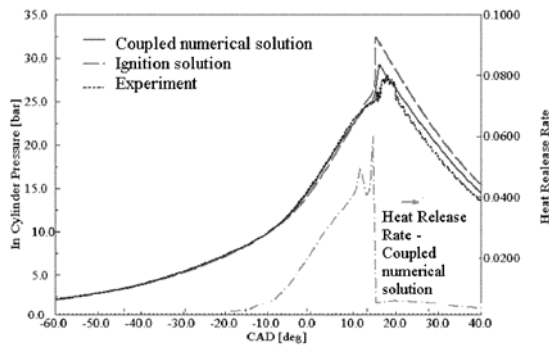


Fig.2: Comparison between experimental [5] and calculated pressure values near firing top dead center (TDC) and calculated rate of heat release ($\lambda=1$).

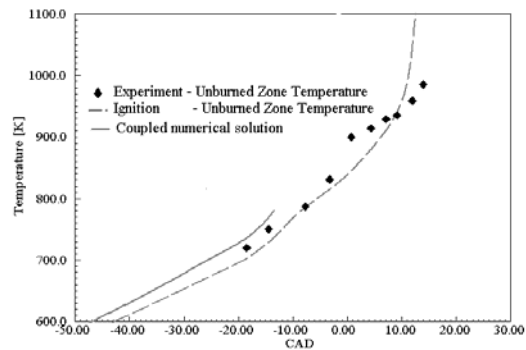


Fig.3: Comparison between the experimental [5] (diamonds) and calculated temperature for the unburnt zone (kinetic code - dashed line). Solid line represents the EST results assumes only one zone ($\lambda=1$).

Figure 3 displays the calculated temperature (dashed line – Ignition, solid line – EST) against the measured one in the near wall unburned region. The kinetic code gives a good estimation of the temperature for the unburnt zone. The EST evaluation on the other hand is also fairly good, considering its only 1-zone assumption that makes sense for comparison only up to little after the spark timing (19 CAD before the firing TDC).

For the consideration of mixture stoichiometry, the air to fuel equivalence ratio (λ) was varied ($\lambda = 1.3, 1.16, 0.83, 0.78$) in order to address its influence on the engine performance and combustion behavior. Good pressure fittings were obtained by running with the coupled code for all 4 non-stoichiometric mixtures as well as for the one EGR case. The autoignition onset was predicted with accuracy of 1 CAD for all these cases. Also the indicated mean effective pressure was predicted with 3.4% precision in all investigated cases..

As found in earlier work [2] the nitric oxide is a species holding a main responsibility regarding autoignition occurrence. Therefore we applied the newly created tool in order to obtain confirmation on previous finding. Figures 4 and 5 show the pressure calculated with the combined tool for low, respectively high NO amounts, for the $\lambda=1.0$ reference case. The results obtained with different NO amounts from the rest gas within the initial cylinder charge confirmed the trends found in [2]. Low NO content has -up to a certain level- a promoting

effect on autoignition (Fig.4), while increased NO amounts above this critical value inhibit the phenomenon (Fig.5).

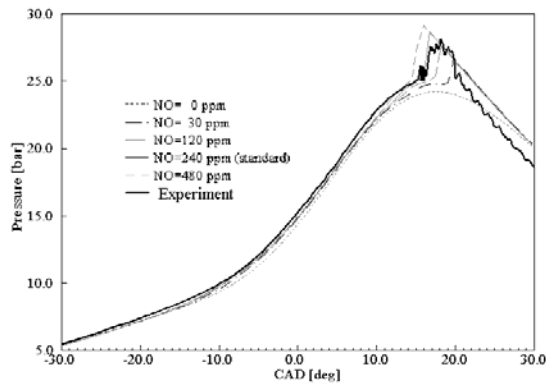


Fig.4: Parameter study of the influence of low NO amount on autoignition. By decreasing the NO concentration in the initial charge, autoignition is moved later and later.

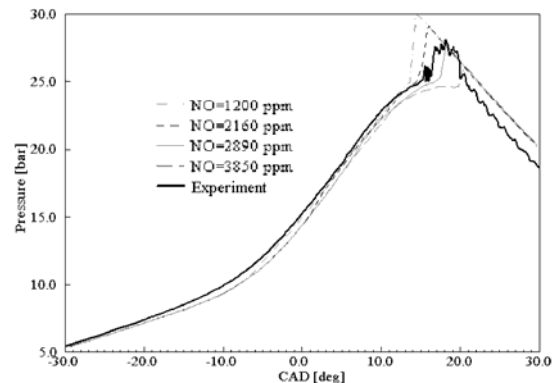


Fig.5: Parameter study of the influence of high NO amount on autoignition. By increasing the NO level in the initial charge above 1200 ppm the autoignition onset is delayed.

CONCLUSION

This work presents a new SI engine simulation tool, built by coupling the commercial one-dimensional fluid-dynamic GT-Power code and our in-house detailed chemical kinetic code. The new interface was validated by comparing the numerical results to the experimental values obtained with a single cylinder test-engine. The simulation results obtained with the coupled tool predicted the autoignition onset and the pressure fairly well for mixtures with different stoichiometry and with or without exhaust gas recirculation. Concerning the Indicated Mean Effective Pressure, the numerical results matched the experimental values quite accurately. Therefore it can be concluded that the combined code proves to be a useful and powerful tool in both global and sensitive SI engine analysis.

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APPENDIX:

Engine parameters for the reference case

Bore/ Stroke/ Rod	96/ 103/ 158 mm
Compression Ratio	7.7
Crankshaft rotational speed	1200 rev/min
Fuel /RON	n-Heptane – Isooctane / 75

Laser diagnostic applied to Homogeneous Charge Compression Ignition (HCCI) engines.

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ABSTRACT

The major advantages with Homogeneous Charge Compression Ignition, HCCI, compared to the diesel engine are low NO_x emissions and less problem with soot formation. The benefit with HCCI compared to the Spark Ignition (SI) engine is a much higher part load efficiency. Several optical measurement techniques have been applied in order to investigate the HCCI-combustion process. This paper will briefly show some of the generated results.

The absorption of light propagating through the combustion chamber has been spectrally resolved for different fuels. Complementary information was obtained by time resolved chemiluminescence, captured during combustion. The homogeneity of the fuel charge was monitored by the use of two-dimensional tracer LIF.

The distribution of OH-radicals and formaldehyde was monitored simultaneously by PLIF imaging. In addition, the HCCI combustion progress was studied by means of high-speed fuel tracer PLIF imaging using a high-speed laser and detector system that can acquire a sequence of eight images within less than one crank angle.

INTRODUCTION

As the name applies, in a Homogeneous Charge Compression Ignition (HCCI) engine, the fuel and air are most often premixed to create a homogeneous charge. During the compression stroke, the charge is heated to achieve auto-ignition. Preferably this occurs close to Top Dead Center (TDC). These two traits carry similarities to the conventional spark ignited engine and the direct injected diesel engine. Due to this, the HCCI engine has been described as a hybrid between an SI and a diesel engine. However, the operating characteristics of an HCCI engine differ significantly from both SI- and diesel engines.

The major advantages with HCCI compared to the diesel concept are low NO_x emissions in combination with significantly less soot formation. In diesel engines, a reduction of NO_x emissions often results in an increase of soot volume fraction and vice versa. Furthermore, the cycle-to-cycle variations of the HCCI combustion process are generally very small compared to those in an SI engine [1]. This is related to the fact that HCCI-combustion has no normal flame front propagation. Instead, initiation occurs in many places simultaneously and the whole mixture burns rather heterogeneously. As the whole bulk burns almost simultaneously, the overall combustion rate is very high. As a consequence, highly diluted mixtures have to be used in order to limit the rate of heat release. With HCCI, there are no direct means to control the start of combustion as the ignition process relies on spontaneous auto-ignition. By adjusting the remote operating parameters, i.e. fuel properties, inlet air temperature or exhaust gas recirculation (EGR) rate, ignition timing can be controlled.

OPTICAL ENGINES

The presented investigations have been performed in two truck-sized heavy-duty engines (a Scania D12 and a Volvo TD-100) and in one passenger car sized diesel engine (Volvo D5). The Scania D12 single cylinder engine and the Volvo D5 were equipped with a Bowditch-type optical access to enable imaging of most of the combustion chamber. In Fig. 1, the optical engines are shown. The fuel (iso-octane, ethanol, methanol or a mixture of iso-octane/n-heptane) was fed to the engine using a port fuel injection system. For the fuel visualization, acetone was mixed into the base fuel to act as a fuel tracer. The fuel was injected either in the intake port or 1.5 m upstream of the inlet, promoting good mixing and the forming of a homogenous charge. In some cases ethanol was used as fuel instead of iso-octane, since problems with laser light absorption are then less significant. It is well known that pure iso-octane does not show any absorption at typical UV laser wavelengths such as 248 and 266 nm. The mentioned absorption is introduced by intermediate species created during the latter part of the compression stroke and in the early phase of combustion [2]. The inlet air was preheated with an electrical heater to initiate HCCI combustion, with proper timing, for the selected compression ratios and fuel types. For the Volvo TD-100, a spacer with four quartz windows between the engine block and the cylinder head was used to provide optical access.

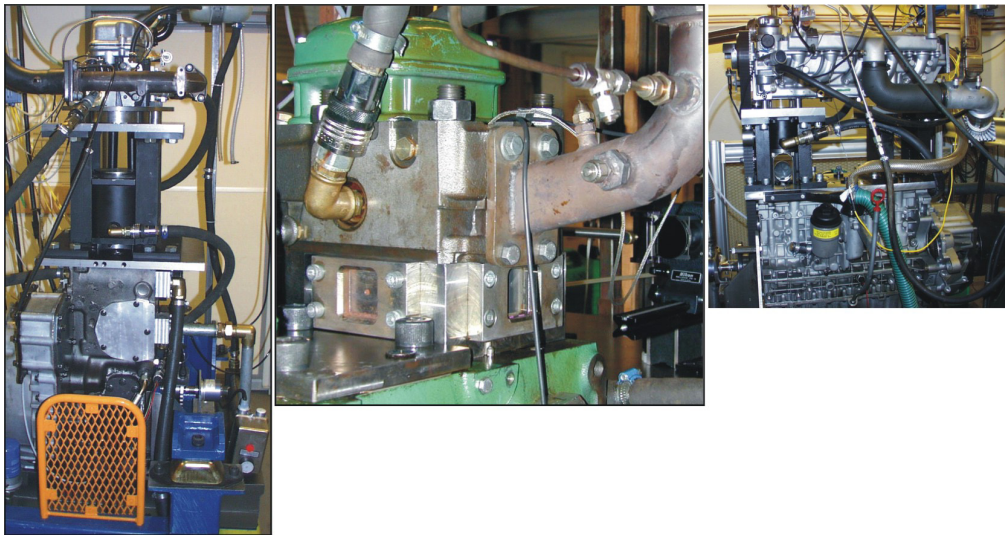


Fig. 1 To the left; Scania D12 with Bowditch-type piston extension. Middle; Volvo TD100 with optical spacer. To the right; Volvo D5 passenger car diesel engine, also with Bowditch-type piston extension.

EXPERIMENTAL SETUP

Since the presented work covers experiments performed in different engines and since several measurement techniques have been applied to each engine, it is not possible to provide a detailed description of each setup. In general, a setup similar to the one shown in Fig. 2 has been used for the visualization experiments. The laser beam is formed to a horizontal sheet and then guided through the quartz cylinder liner. The resulting fluorescence signal is collected through the piston, via a mirror in the piston extension, and detected with an image intensified CCD camera. For the spectrally resolved measurements, the signals were collected through a spectrometer.

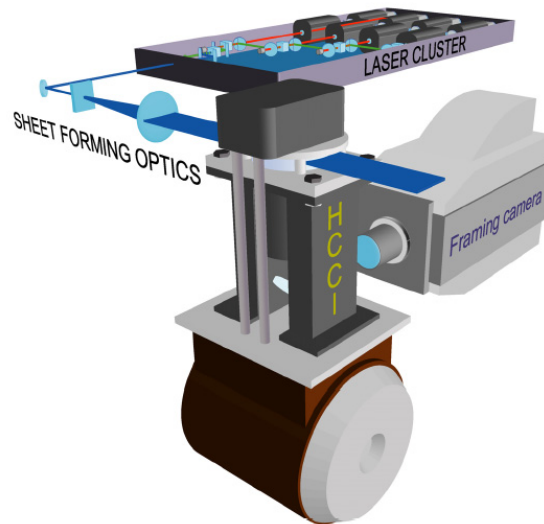


Fig. 2 Typical experimental setup for visualization through the Bowditch-type piston extension.

EXAMPLES OF RESULTS

Fig. 3 shows spectrally- and crank- angle resolved absorption data for an HCCI engine running on an n-heptane/iso-octane fuel mixture. It is clear that the spectral transmission through the combustion chamber varies significantly during the combustion process. The strong absorption that starts at about 20 CAD BTDC is related to the occurrence of cool-flame reactions.

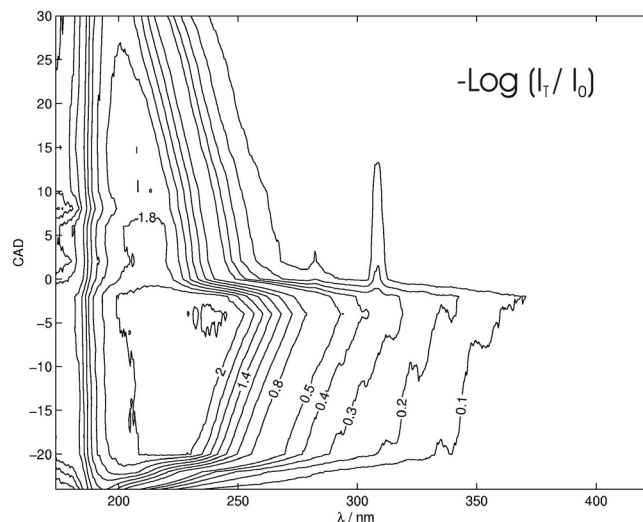


Fig. 3 Spectrally resolved absorption through the combustion chamber of a HCCI engine running on a mixture of n-heptane/iso-octane.

By using two laser systems and two ICCD cameras, it was possible to simultaneously perform two-dimensional imaging of formaldehyde and OH-radicals. A typical example can be seen in Fig. 4. When studying sequences covering the entire cycle, it can be seen that the formaldehyde is formed at an early stage of auto ignition. Later, the formaldehyde is consumed and OH is formed in the corresponding regions.

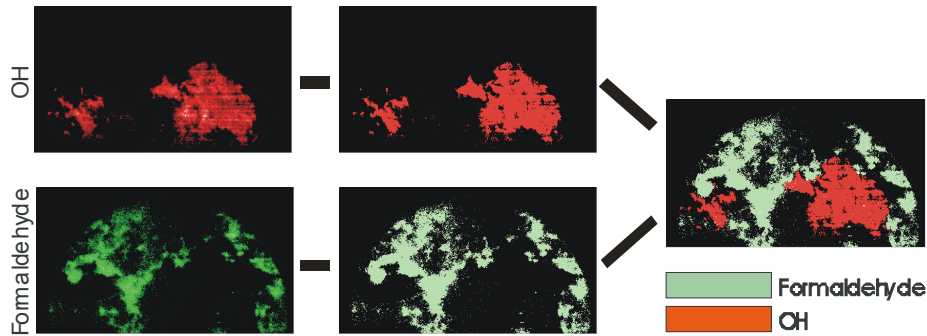


Fig. 4 Example of simultaneous detection of formaldehyde and OH. After the background has been removed, the images are flattened to enhance areas with the probed molecule, thereafter the image pairs are combined into one image.

An example of high-speed fuel tracer LIF is presented in Fig. 5. Note that there is no conventional flame propagation in HCCI combustion. Instead the oxidation occurs gradually through distributed reactions.

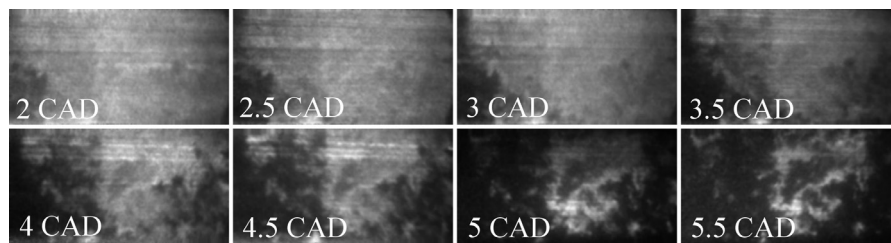


Fig. 5 High-speed fuel visualization in an HCCI engine. The eight images above are recorded within a single cycle by use of a unique high repetition rate laser/camera system. Bright areas correspond to unburned fuel and dark areas represent burnt regions.

For more details regarding diagnostics in HCCI engine please refer to [3-7].

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Simulation of a Two-Stroke Free Piston Energy Converter

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ABSTRACT

In a free piston engine, the piston motion is not prescribed by a crank mechanism, but is the result of the equilibrium of forces acting on the piston. The linear motion of the pistons is directly converted to electricity in an alternator and a compact energy converter is the result. The lack of a crank mechanism gives means to easily vary the compression ratio, and it is possible to run the engine on a multitude of fuels in HCCI combustion mode.

In this paper, the effect of different fuels on the performance of the free piston engine has been studied. It is shown that both efficiency and power increase, but not dramatically, with higher octane rating.

INTRODUCTION

Increasingly stringent legislations on emissions have raised interest for new advanced automotive prime movers. A great deal of research has been aimed at hybrid vehicles [1, 2], where an internal combustion engine (ICE) is combined with an electrical motor (EM) batteries. The idea is to have the ICE running at its most efficient operating points over a wide load and speed range in order to lower emissions and fuel consumption. Although promising, this concept has some downsides. The incorporation of both an ICE and an EM gives not just an efficient power source, but also a heavy and bulky one. The high weight parasites on the vehicles total efficiency, since it takes more energy to propel a heavier vehicle. Furthermore, the higher number of components in such an engine will increase costs and make it less competitive [3].

The free piston engine offers a more integrated design, leading to a more compact and less expensive engine. There are many types of free piston engines [4], but the one under consideration in this study is of the dual piston type with a linear alternator integrated in between the two cylinders. With the use of HCCI (Homogeneous Charge Compression Ignition) combustion, high efficiencies and low emissions are the expected results. Combustion at alternating cylinder ends drives permanent magnets fixed on the connecting rod back and forth through the coils of the alternator. The alternator is primarily used to generate electricity, but also to control the piston motion by varying the electric load.

DYNAMIC MODEL

Piston motion is governed by the equilibrium of forces acting on the pistons and is described by Newton's second law:

$$m \frac{d^2x}{dt^2} = A_p (P_{c,2} - P_{c,1}) - F_{el} - F_f$$

$$\begin{aligned} \frac{d^2x}{dt^2} &: \text{acceleration} \\ m &: \text{moving mass (translator)} \\ A_p &: \text{piston area} \\ P_c &: \text{cylinder pressure} \\ F_{el} &: \text{electric force} \\ F_f &: \text{friction force} \end{aligned}$$

The electric force is a constant value applied for 90% of the stroke, but not at the turning points when piston speed is low. An estimation of the friction force can be deduced from the friction mean effective pressure, f_{mep} . For engines with rolling element bearings, the following formulas can be used [7, 9]:

$$f_{mep} = 6300 L_{st} f \quad (2)$$

$$F_f = \frac{V_d}{2L_{st}} f_{mep} \quad (3)$$

$$\begin{aligned} L_{st} &: \text{stroke} \\ f &: \text{frequency} \\ V_d &: \text{displaced volume} \end{aligned}$$

Cylinder pressure and temperature is obtained by applying the first law of thermodynamics in conjunction with the ideal gas relation:

$$\delta Q = dU + dW \quad (4)$$

$$PV = mRT \quad (5)$$

Substitution of variables and some mathematical treatment result in:

$$\frac{dp}{dt} = \frac{dQ}{dt} \frac{p}{mc_v T} - \frac{\gamma p}{V} \frac{dV}{dt} \quad (6)$$

$$\frac{dT}{dt} = \frac{1}{mc_v} \frac{dQ}{dt} + \frac{T(1-\gamma)}{V} \frac{dV}{dt} \quad (7)$$

The results (piston motion, frequency and compression ratio) from the dynamic model are used as input in SENKIN and BOOST.

RESULTS AND DISCUSSION

As seen in Fig. 1, the maximum temperatures for all three fuels are low enough to achieve very low levels of NO_x . The rate of formation of NO_x shows a rapid increase above

temperatures of about 1800 K, and only the natural gas case exceeds this value, but only slightly with its maximum value of 1834 K. Furthermore, the free piston engine spends less time in the high temperature region, since its velocity around the turning points is much higher than for conventional engines, which further reduces the emissions of NO_x .

In Tab. 1, some of the main results of the simulations are presented. The less prone a fuel is to ignite (higher octane rating), the higher the compression ratio must be. The “worst” case is natural gas, with a compression ratio of almost 56. This is also reflected in the high pressures for the natural gas case. As the compression ratio increases, so does power, frequency and efficiency as well. It can also be seen that the benefits of increasing the compression ratio decreases with higher compression ratio. The compression ratio increases from 35.16 to 55.72 when using natural gas instead of gasoline, but the benefits in increased power and efficiency are modest. It is questionable if it is wise to use extremely high compression ratios, as the mechanical stresses due to high accelerations and high pressures increase, as well as higher levels of combustion noise. The best compromise would be using gasoline as fuel. It combines high efficiency and power, with tolerable values of accelerations and pressures. Furthermore, gasoline is much better suited for HCCI combustion than diesel, as it evaporates easier to form a premixed air/fuel mixture.

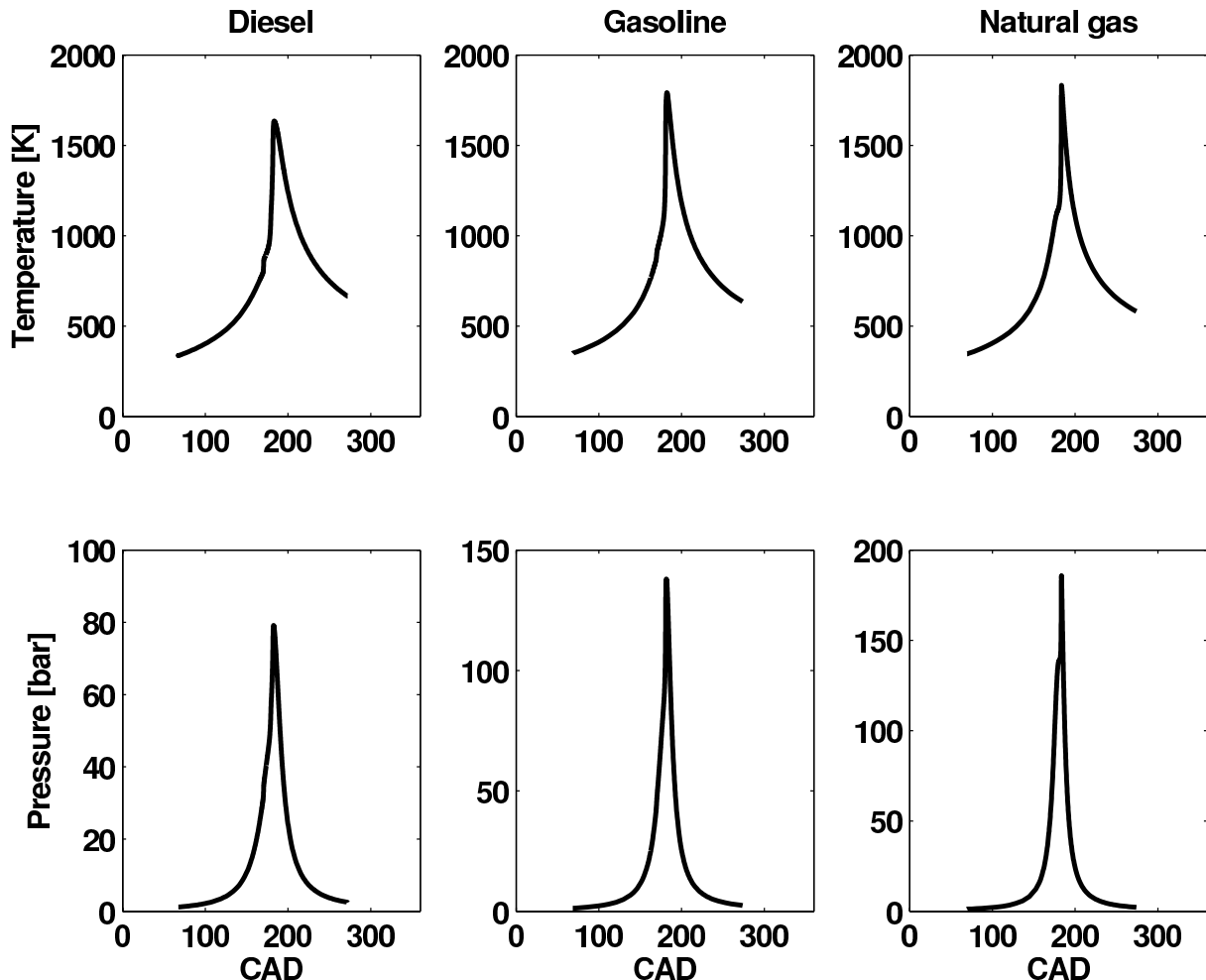


Fig. 1 Temperatures and pressures for the three different fuels. Note the different scales of the pressure plots.

Fuel	Diesel	Gasoline	Natural gas
Frequency [Hz]	27.01	30.84	34.40
Compression ratio	22.66	35.16	55.72
Indicated efficiency [%]	50.75	51.77	53.39
Effective efficiency [%]	42.71	44.29	45.38
Effective power/cylinder [kW]	5.58	7.05	7.37

Tab. 1. Main results of the simulations

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Future trends in fuel design for compression ignition engines

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INTRODUCTION

This paper reports some results on the performance of an advanced CR DI diesel engine burning twelve model diesel fuels. The experiments are part of the co-operative European research program “NeDeNeF” (New Diesel Engines and New Diesel Fuels). Within this program, the Diesel Engines and Fuels Department of Istituto Motori dedicated to assess the effect of fuel quality on exhaust emission, identifying the fuel parameters that are most relevant. In fact, even if engine emission performances are strictly dependent on the characteristics of the combustion system and the setting of injection parameters [1, 2], new fuel specifications planned for 2005 [3] lead the research to deepen on the correlation between fuel quality and new CR engine technologies. The results showed a quite insensitivity of the advanced common rail engines to the quality of conventional fuels while interesting emission performance were observed with oxygenated non conventional fuels.

EXPERIMENTAL EQUIPMENT

The engine employed in the tests was a Fiat four-cylinder CR diesel engine -EURO3 version- of 1910 cc of displacement, installed on Alfa Romeo 156. At the engine exhaust, smoke was measured by an high-resolution (0.01 Bosch number) smoke meter (AVL 472), while gaseous emissions were measured upstream and downstream the catalyst by an analyzer test bench (AVL-CEB-2). Particulate measurements were performed by a dilution mini-tunnel (AVL SmartSampler PC). The test points chosen were 1500 rpm at 5 bar of B.M.E.P. and 2500 rpm at 8 bar of B.M.E.P., as ones of the main representative points of the emission test cycle ECE 15+EUDC. Engine emissions measured in these two conditions are in the top side of the emission equivalent schedule, therefore the improvement on emissions achievable in these points is more significant than in others. However, for conciseness, in the following only the results obtained at 1500 rpm and 5 bar of B.M.E.P. will be described.

FUELS

The fuel matrix, prepared by Fortum Oil and Gas Company, consists of twelve fuels. All fuels have low sulphur content (< 20 ppm), a narrow end of distillation and a narrow density range. Also the cetane numbers were kept in a narrow range, with cetane number always higher than 50. The fuel matrix is divided into two batches. Batch 1, made by normal refinery components, has been designed to investigate the influence of different values of surface tension, viscosity, density and compressibility on fuel performance. Table 1 reports the relative characteristics of fuels of batch 1. On the other hand, batch 2 was designed to investigate on the role of the total oxygen content and includes three oxygenated blends (Oxy1, Oxy2, and Oxy3) prepared adding to the base fuel some bio-derived or synthetic compounds. In particular Oxy1 was prepared with RME, while diglyme and butyl-diglyme

were adopted for blends Oxy2 and Oxy3. The first two oxygenated fuels have the same mass percentage of oxygen equal to 3%, while Oxy3 has the highest oxygen content equal to 9% in mass.

SURFACE TENSION: Base>Surface tension2>Surface tension3
DENSITY: Density1<Base<Density2
VISCOSITY: Viscosity1<Base<Viscosity2
COMPRESSIBILITY: Base<Compressibility2<Compressibility1

Table 1. Fuels characteristics.

RESULTS AND DISCUSSION

All fuels of the matrix were tested in the chosen engine test point showing a very similar behaviour among the fuels in terms of indicated data: cylinder pressure, energizing current (E.C.) and rate of heat release (R.O.H.R). The most significant differences among all fuels of the matrix with respect to the base fuel were found testing the three oxy fuels and they are reported in Figure 1.

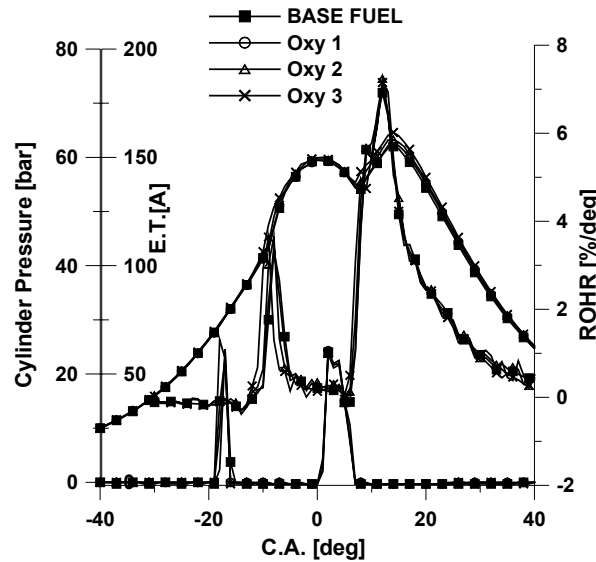


Fig. 1 Cylinder pressure, heat release rate and energizing current for base and oxygenated fuels at 1500 rpm @ 5 bar of B.M.E.P..

Only in the case of Oxy3 fuel, characterised by the highest cetane number, a small reduction of the pilot ignition delay time can be observed. Looking at the combustion of the main injection, no significant ignition delay variations were observed increasing the fuel cetane number (from 53,3 of the base fuel to 54,6; 60,1; 72,9 of Oxy1 Oxy2 and Oxy3 respectively). However, the pilot injection activation reduces drastically the ignition delay time, hiding the cetane number influence. Concerning again Oxy3 fuel, due to the little increase of the rail pressure dependent on the higher injected fuel mass (derived in turn from its lower heat of combustion), the combustion pressure slightly increases as well.

From figure 2 to 4 results obtained in terms of pollutant emissions are plotted as emission indices percentage variation with respect to the base fuel. Figure 2 shows HC and CO emissions upstream catalyst. As well known, unburned emissions derived from a pilot+main injection strategy should be mainly due to the fuel injected during the pilot injection in which case some fuel may ends up to the combustion chamber walls or into the squish volume.

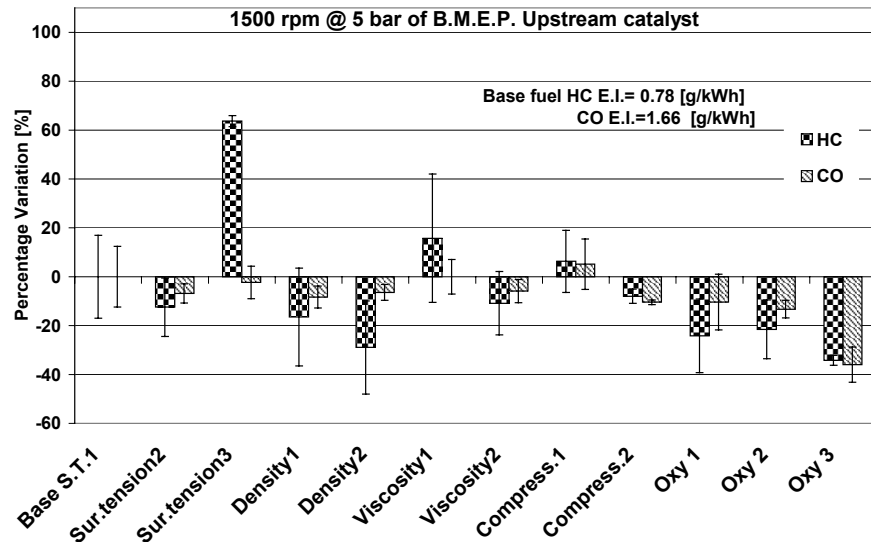


Fig. 2 Unburned gaseous emission indices percentage variation for all tested fuels.

Looking at the surface tension fuels behaviour, it can be noticed a foreseeable effect of increasing HC with a decrease of surface tension. As regard to the effect of fuel density on HC and CO emissions, Density1 presents about the same emissions of base fuel, while Density2 shows a reduction and this is in agreement with other trends reported in literature. Taking into account the relation among fuels, the results confirm that a reduction of viscosity tends to increase the in-cylinder air-fuel mixing and so to decrease unburned emissions. Compressibility shows no significant influence on HC, while fuel oxygenation is effective on HC and CO reduction, especially burning Oxy3, that also has the highest cetane number. In figure 3 results in terms of particulate emissions are reported together with the correspondent soluble and dry fractions.

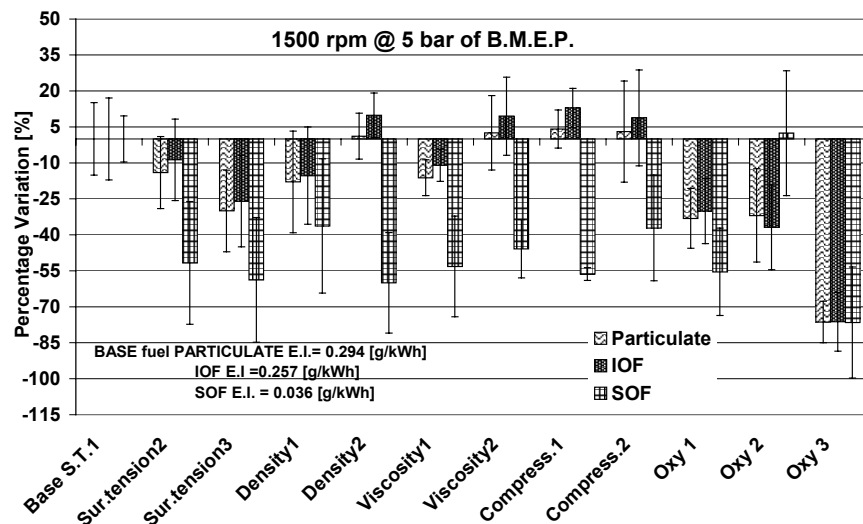


Fig. 3 Particulate, IOF and SOF Emissions for all tested fuels.

The measurements outline that only fuel oxygenation gives a marked improvement on particulate reduction, while among all the other fuels there are no significant differences. One of the most evident conclusion is that the SOF emission index is very low for all the fuels and is below the base fuel. This is a well-known characteristic of the modern DI diesel engine, but it's also due to the presence of the oxy-catalyst.

To put in evidence the improvement achievable with fuel reformulation on both, NO_x and particulate emissions, in figure 4 there is NO_x-particulate trade-off for the twelve fuels. Results confirm that fuel oxygenation is still a good way to obtain remarkable effects on smoke reduction. The emissions are quite scaled with the oxygen content, so, increasing the percentage of oxygen, smoke emissions decrease and of course, NO_x emissions increase. It's evident that Oxy3 has the most interesting behaviour. In particular the soot reduction gain with this fuel could be partially used to lower NO_x emissions, optimising engine parameters such as EGR rate, injections parameters and so on.

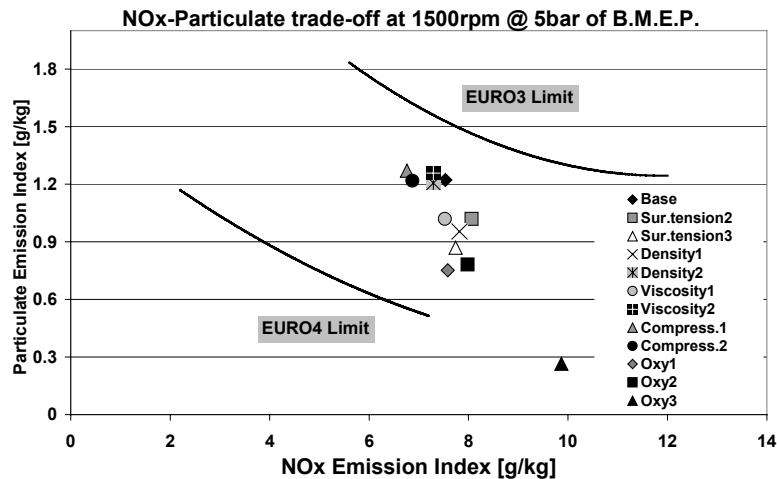


Fig. 4 NO_x-Particulate trade-off for all tested fuels.

CONCLUSIONS

Modern CR engines employing pilot+main injection strategy, confirm their little sensitivity in terms of combustion evolution to fuel quality variation, except when oxygenated fuels are blended with fossil fuels. As regard to exhaust emissions, the reduction of fuel surface tension, increasing the air-fuel mixing, evidenced a good influence on smoke emissions, but NO_x, HC and CO tend to increase. On the contrary, fuel density variation showed no so significant effects on all emissions, while viscosity and compressibility have a quite moderate effect.

Fuel oxygenation confirms its marked influence on pollutant emissions reduction, especially on smoke, while tends to increase NO_x. In particular in the case of low oxygenation level, no differences were found varying the kind of oxygenated compound (bio-derived or synthetic). In the case of high oxygenation level, in spite of the high NO_x emissions, a great potentiality of the fuel-engine interaction to meet EURO4 limits was outlined. To this reason it will be interesting to evaluate, in the future, the effect of interaction between reformulated oxy-fuels and advanced engine technology strategies (multiple injection, high cooled EGR and so on).

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The effect of Oxygenated Fuels on in-cylinder Soot Evolution via Two-colour pirometry technique

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INTRODUCTION

Aim of this work is the characterization of the development of combustion in a modern DI common rail diesel engine, fed by oxygenated fuels, via two-colour pirometry technique.

The engine adopted is an optical research single cylinder DI diesel engine with 500 cm³ of displacement [1], which reproduces the main characteristics of the production engine FIAT 1.9 JTD-F3, 4 cylinders and two valve for cylinder. The research engine is equipped with a modern second generation common rail injection system and with a VCO 6 holes double guide injector.

The optical access to the combustion chamber is achieved by a cylindrical disk of quartz that constitutes the bottom of bowl. Its upper part is characterized by re-entrant lips, which is able to reproduce quite the same fluidynamic characteristics of the combustion chamber of the real reference engine.

Two flame images at two different wavelengths were processed in order to evaluate instantaneous and local values of flame temperature (T) and soot volumetric fraction (fV).

Engine conditions at 1500 rpm and 22mm³/stroke of injected fuel were chosen for tests on the transparent engine, correspondent to the 1500 rpm and 5 bar of B.M.E.P. on the reference diesel engine.

Tests have shown the effect of oxygen concentration on local soot concentration and global in-cylinder soot loading.

THE EXPERIMENTAL SYSTEM

Flame images were acquired by a couple of high-speed CCD. Frame rate was fixed to 4000 frame/s as the best compromise between spatial (100x98 pixels) resolution and temporal resolution. The electronic shutter was fixed to an exposure time of 100μs.

Images of combustion were reflected by an elliptical mirror and collected on a beam-splitter that divided the light emitted from incandescent soot particles into two equal parts. The two beams, emerging from the beam-splitter, were filtered by two 20nm bandpass filters, centred on 750nm and 900nm [2]. A tungsten lamp was used for the calibration. This arrangement have been considered as the best between the influence of wavelength values on the measurement uncertainty and the overall efficiency of the optical system.

To calculate flame temperature, the raw data of flame light have been corrected in order to consider the effect of window fouling.

Five fuels of different blends were tested in the optical engine and their characteristics are reported in Table 1 [2]. Because the aim of the work was to assess the potential of blending fossil fuels with oxygenated compounds on in-cylinder soot loading, the base fuel used for tests was the Finnish Summer Grade diesel fuel (FSG named as D1 in the table) that is an high quality fuel. Different blends with different oxygen content and different type of oxygenated compound (bio-derived or synthetic) were tested (named as DO1 to DO4).

FUEL SPECIFICATIONS	D1	DO1	DO2	DO3	DO4
Composition [% in volume]	100%	70% D1 30% RME	90,7% D1 5,0% Diglyme 4,3%B-Diglyme	71,4% D1 15% Diglyme 13,6%B-Diglyme	60% D1 40% Diglyme
Density @ 15° [g/liter]	833,7	848,2	840,5	854,9	880,2
Cetane number	53,3	54,6	60,1	72,9	85÷90*
LHV (MJ/kg)	43,2	43,1	41,5	38,7	35
Oxygen (% wt)	-	3	3	9	15

Table 1. Specifications of tested fuels (* estimated).

RESULTS AND DISCUSSION

As mentioned above all fuels were tested in the engine conditions of 1500rpm and about 22mm³ injected fuel/stroke correspondent to one of the main test points for engine emission optimization. The setting of injection parameters in this test point is reported in [2]. Because of the different heat content of tested fuels, the injected fuel quantity was adjusted in order to achieve, for each test, the same PMI value.

The analysis of the combustion evolution was performed for the reference fuel D1 in appendix 1 in terms of radiance at 750nm, flame temperature and soot volume fraction (fV) versus crank angle for one engine cycle.

No luminous spots derived from pilot combustion are visible because they were under the luminosity threshold of the measurement system. As confirmed by past studies first flame spots are located in the middle part of the spray path downstream of swirl direction. Then the flame develops in an annulus between the combustion chamber centre and its walls and moves toward the centre of the combustion chamber, because of the re-entrant shape of the bowl. A large portion of the flame pattern is calculable via the two-colour method and then a good characterization of fuels in terms of soot loading and flame temperature can be drawn. Results shows that the temporal and spatial matching of both images of calculated flame temperature and fV shows an acceptable agreement with images of luminosity.

The maximum local values of flames temperature and fV, measured during the engine cycle, are about 2400K and 4.0E-5 [a.u] with the maximum temperature zones quite overlapped to the maximum fV ones.

For an appropriate and critical analysis of results obtained from two-colour pirometry technique, some parameters indicating the local ($fV_{averaged}$) and global (fV_{global}) fuel sooting tendency were defined. In this way the comparison between fuels was possible in terms of average flame temperature, $fV_{averaged}$ (medium local fV value) and fV_{global} (medium fV value in the measurement volume).

Figure 1 shows the flame temperature values as calculated by the two-colour method for each fuel. Each curve has been averaged on five non-consecutive cycles. Only DO4 presents higher flame temperature in agreement with its higher oxygen content, while no significant differences are appreciable for the other fuels.

$FV_{averaged}$ curves reported in figure 2 assess the importance of a high percent of oxygen on soot loading. In agreement with higher flame temperature, local fV values exhibited by DO4 are lower with respect to other fuels. On the contrary figure 3 shows that DO4 is marked by fV_{global} peak values similar to D1 fuel. This is easily explainable considering that, even if DO4 presents lowest local soot concentration, the sooting zones are more extended so giving higher value of fV_{global} . This higher soot formation rate is probably due to the higher combustion rate of synthetic oxy-fuels. In spite of this, DO4 exhibits fV_{global} values that decrease rapidly during the expansion stroke, due to both the presence of low local fV values and high oxygen content so improving the oxidation rate. The different soot distribution and evolution between

the base fuel D1 and the DO4 are confirmed in appendix 2, while the integral values of fV_{global} versus crank angle are reported, for all tested fuels, in figure 4.

Results obtained from the two-colour method outlined that this technique shows appreciable differences among fuels only for remarkable oxygen content in the fuel (>15%). No important differences were evidenced by maintaining the same fuel oxygen content while varying the quality of the oxygenated compound, so results obtained for the bio-derived oxy fuel (DO2) and the synthetic one (DO3) are very similar.

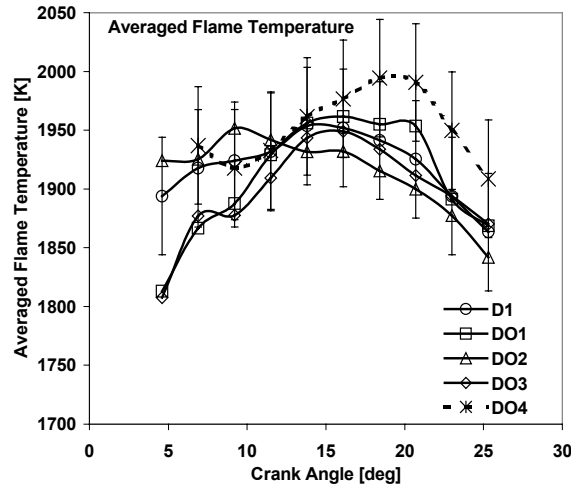


Fig. 1: Average flame T for all tested fuels

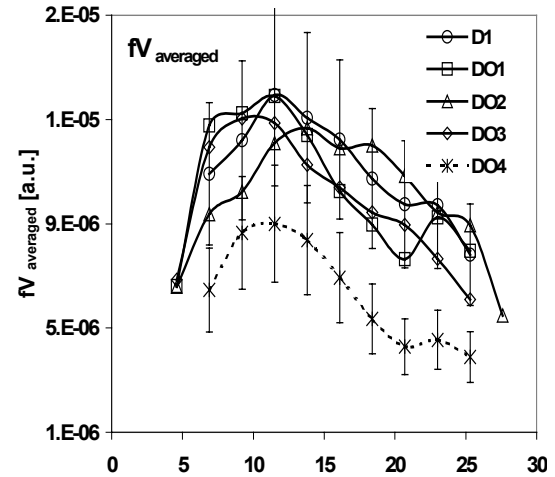


Fig. 2: $fV_{average}$ for all tested fuels

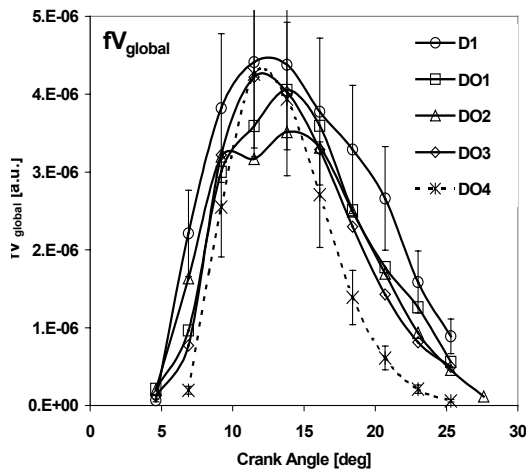


Fig. 3: fV_{global} for all tested fuels

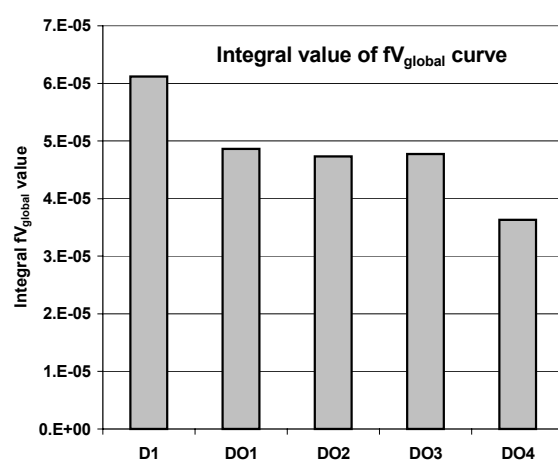


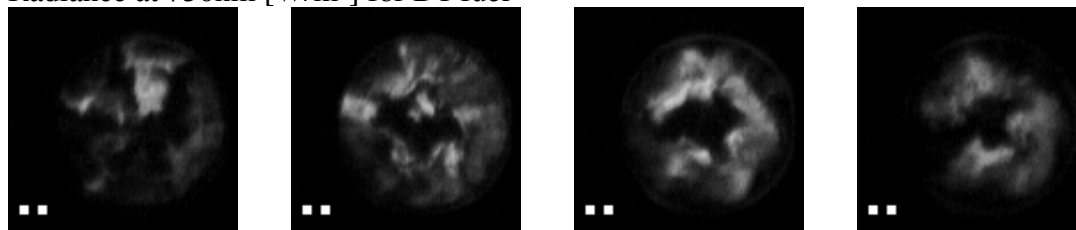
Fig. 4: Integral value of fV_{global} for all tested fuels

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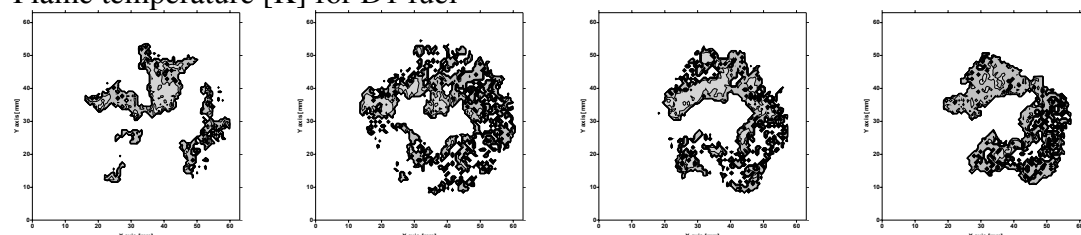
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APPENDIX 1

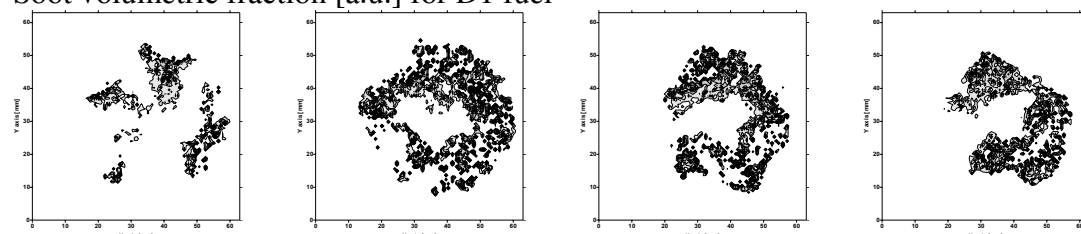
Radiance at 750nm [W/m³] for D1 fuel



Flame temperature [K] for D1 fuel



Soot volumetric fraction [a.u.] for D1 fuel



6.9 c.a. ATDC

11.5 c.a. ATDC

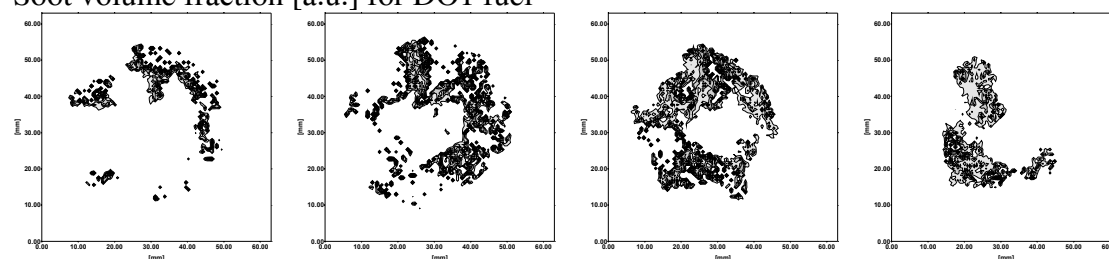
16.1 c.a. ATDC

20.7 c.a. ATDC

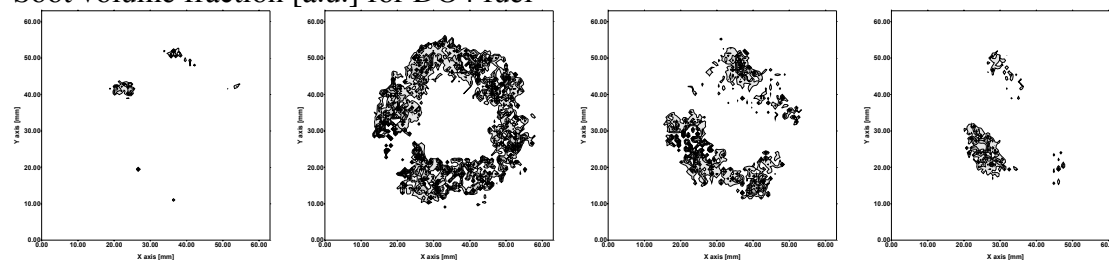


APPENDIX 2

Soot volume fraction [a.u.] for DO1 fuel



Soot volume fraction [a.u.] for DO4 fuel



The evolution of fuel injection equipment for very small displacement diesel engine

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INTRODUCTION

In the last years a great attention is dedicated to engine downsizing as the more interesting solution to win the challenge of a 3-liter car. In this field, due to the combustion characteristics and the recent progress, especially in the injection technology, it is possible indicating the diesel engines as the most promising to equip small passenger cars [1].

The fuel mixture preparation process is one of the aspects that must be deepened to achieve the objective of reducing raw emissions of a small size engine, while maintaining advantages in terms of fuel economy. Once optimised the swirl level, the improvement of spatial fuel distribution can be achieved via a suitable design of the injector nozzle as well as through multiple closely injections.

In this paper the importance of an appropriate combustion system design is outlined in a small size (0.3L) CR diesel engine equipped with a last generation CR system that permits the use of multiple sequential injections. Spray visualizations are performed in an optical research engine varying the injection strategy and the injector design. Experiments are focused on the study of spray/wall interaction in a reduced bowl volume demonstrating that the problem of the spray impact can be easily exceeded coupling new CR injection systems with appropriate injector nozzle designs.

RESULTS AND DISCUSSION

Experiments were performed on a four cylinder turbocharged engine equipped with a second generation Common Rail system and with a total displacement of 1.25L. The engine characteristics are reported in [2]. The visualization of spray evolution was realized in a single-cylinder optically accessible prototype engine with the same main characteristics of the real engine (inlet and exhaust valves, cam profile, etc.) [3]. The engine has a classical elongated piston and the optical arrangement is described in [4].

The engine design allows the use of different optical diagnostics: in these tests a high-speed CCD camera, with a maximum resolution of 480x420 pixels and maximum speed of 8000f/s, and a copper vapour laser for spray illumination were used. The optical engine has a modular structure in order to reproduce different engines characteristics. In particular this structure permits to vary the combustion chamber geometry and as a consequence the compression ratio.

The 1.25L engine was settled at 1500 rpm, 5 bar of B.M.E.P., corresponding to 14.5 mm³/stroke of injected fuel mass. Tests were performed with rail pressure equal to 600 bar and without EGR. The injector used was a Microsac, 6 holes, $\phi=0.125$ mm. The same setting was used for the four cylinder engine as well as for the transparent engine.

Experimental activity [2] on the real engine has outlined that, in the class of small engines and with the new generation of Common Rail systems, with respect to more complex injection strategies (multiple injections like the pre-main-after injections) a simpler one (one injection before the main one) may be sufficient to obtain good results both in terms of fuel economy

and emissions levels. Therefore the attention was focused on using a pre injection very close to the main one that is more convenient in terms of fuel economy with respect to using the standard pilot-main strategy. On the contrary some problems deriving from the fuel wall interaction must be considered adopting the pre injection strategy due to the injection timing very close to the TDC. To this reason the present study is limited to analysing both experimentally and numerically the pilot-main and the pre-main injection test cases as reported in Table 1.

As evidenced from Figure 1 numerical results obtained from KIVA3V simulations [4] in a previous paper showed that, in this kind of engine, the pre-main injection strategy is convenient with respect to the pilot-main one in terms of soot and NOx emissions. The analysis of fuel spray and air/fuel mixture obtained from computations outlined that the pre injection is characterized by lower penetration and higher vaporization with respect to the pilot injection, due to the different in-bowl pressure and temperature conditions at the moment of their injection timing. In the pre injection test case no wall impingement is evidenced and a better fuel vapor distribution in the whole chamber bowl is obtained.

In order to understand these results relative to the real engine, a deepen analysis of the fuel spray behavior in the pre-main injection test case is necessary and can be accomplished on the optical engine. Therefore the transparent engine was used to analyze the cold phase and the interaction of the liquid fuel jets with the combustion chamber walls, that is the main topic to investigate in the class of small size engines [5].

Test cases	Start First E.C. [c.a.]	First injected mass	Start Main E.C. [c.a.]	Main injected mass	First-Main Dwell Time [μ s]
Pilot-Main Injection	18 BTDC	10%	5 BTDC	90%	1150
Pre-Main Injection	9 BTDC	10%	5 BTDC	90%	150

Table 1: Selected injection strategies (E.C. = Energizing Current of the Electro-injector)

In Figure 2 visualizations of the whole chamber of a Pre-Main injection sequence are displayed: pictures have been taken at 8000 frames/s with a temporal resolution of 1.125 crank angle. The nozzle injector of new technology (hole diameter and hole type) is very suitable for small displacement engines, producing a good atomisation level and high jet momentum near the nozzle exit also at a moderate rail pressure. It can be noted that, as regard to the pre injection, there is a full evaporation of liquid jets and no kind of wall impingement.

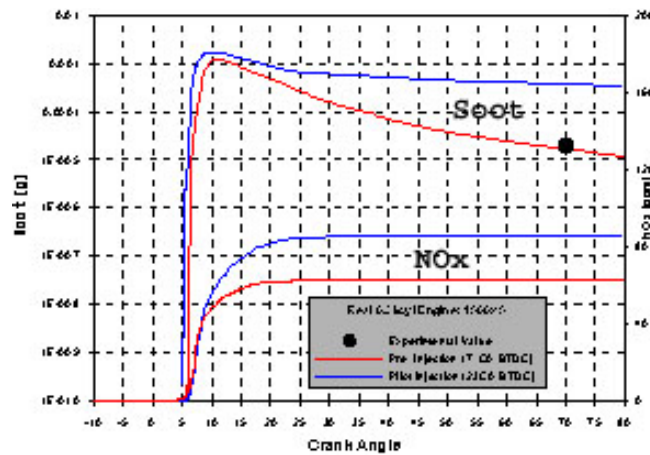


Fig. 1: Comparison between Pilot-Main and Pre-Main Numerical Combustion Patterns for the real 1.25L Engine.

Also concerning the main fuel jets, the liquid fuel doesn't splash on the wall before the start of combustion. Different repetitions of the same test case confirmed this behaviour. Figure 3 shows the same evolution for the pilot-main strategy, confirming also in this case the numerical results. In fact, the penetration of pilot injection is quite higher with respect to the pre injection test. This could probably lead to the impact of some fuel droplets on the chamber wall as carried out from computations. Unfortunately the adopted optical technique doesn't permit to investigate on this aspect. Taking always in mind that the temporal uncertainty is of 1.125 c.a., until 2.25 c.a. BTDC the main injection presents almost the same evolution.

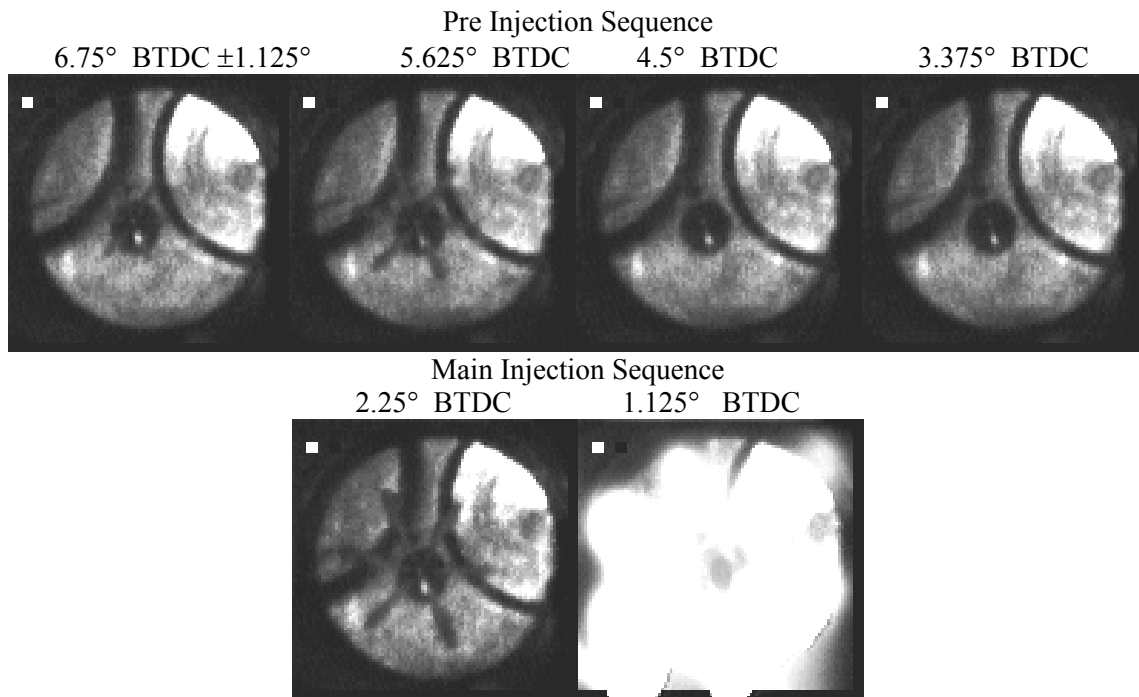


Fig. 2: Pre-main injection test case at 8000f/s visualizations

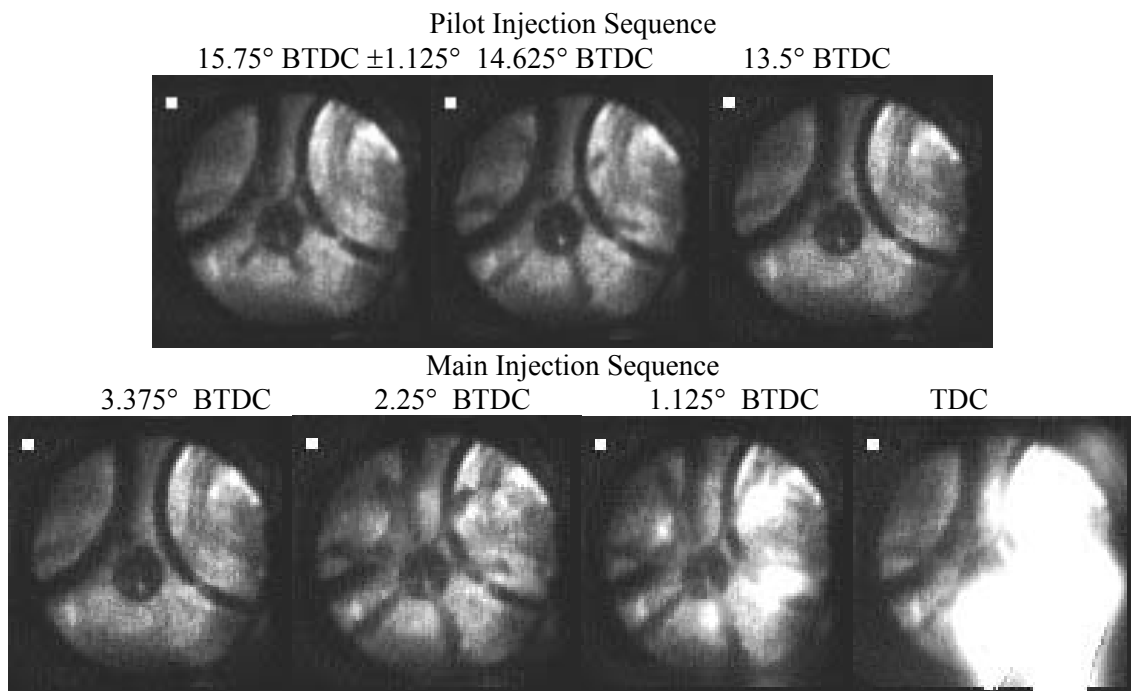


Fig. 3: Pilot-main injection test case at 8000f/s visualizations

Subsequently, the main injection penetrates more before the start of combustion that is not so rapid than in the previous case and some initial spots of combustion are evident at the fuel jets tip downstream the swirl direction. This different evolution of the ignition process can be justified by the more favourable fuel vaporization and the better fuel vapour distribution of the pre-main test case with respect to the pilot-main one. Due to high temporal resolution of previous visualizations and because of the fouling window phenomena during combustion the spatial resolution and image quality are limited for a detailed analysis of the fuel spray impact. In fact, in the pilot-main test, even if no macroscopic impact of the main injection is evident, it could be interesting increasing the spatial image resolution for a detailed analysis at the spray tip. Therefore some visualizations were performed at the same CCD speed but zooming the image on a single jet of the main injection. Figure 4 evidences a very poor liquid contact on the bottom part of the bowl lips at 2.25 c.a. BTDC with the jet tip shape weakly deflected by the swirl.

Concluding in the class of small size engines a simpler strategy with the injected fuel mass splitted over only two close-coupled injections, that is a pre-main strategy, produces good results in terms of emissions. Using small combustion chambers a proper nozzle design assures good levels of mixing also at moderate rail pressure, and fuel jets have a good level of atomization without any fuel wall interaction.

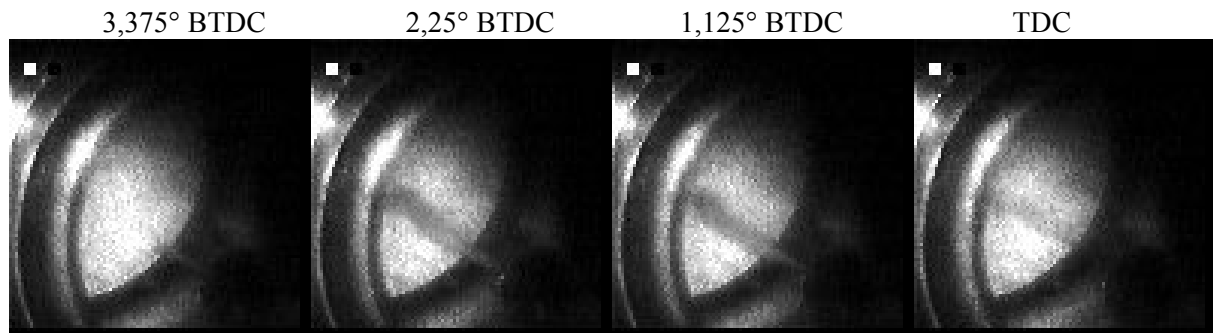


Fig. 4: Visualization of the main injection in the Pilot-Main Test Case at 8000f/s.

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Use of alternative fuels in heavy duty engines

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BACKGROUND

Emission standards as proposed in Europe and the United States for diesel engines will require a NO_x and particulate emission reduction by more than 90 % relatively the already very stringent requirements of today in the next 6 years. To comply with the proposed limits heavy cooled exhaust gas re-circulation (20 % at full load up to 50 % at low load) plus particulate traps and DENOX by SCR are proposed. The systems not only impose a fuel economy penalty but are very costly, unreliable and not fully developed yet. In addition their combination, as required, does not seem to be feasible. Heavy, cooled exhaust gas re-circulation not only requires a doubling of the current cooling systems but also strongly reduces the exhaust temperatures and thus makes continuous trap regeneration and operation of SCR and other catalytic systems impossible. Thus, without a technological breakthrough achievement, the required drastic emission reduction is questionable, which jeopardizes the very existence of diesel engine industries in the future.

The expected shortage of fossil fuels as well as the demand for reduction of CO₂ emissions from fossil fuels is another threat to the diesel engine industries. Synthetic bio-based fuels as well as alcohol fuels will therefore be more and more important as alternative fuels and need to be matched both to the engines and to the after-treatment system.

Optimisation of heavy-duty diesel engines for different alternative fuels will be reported, including ethanol and methanol with different ignition improver systems and synthetic Fischer-Tropsch fuels. Based on these findings as well as literature reviews a forecast of future alternative fuel usage will be given.

ALCOHOL FUEL

Alcohol fuels, ethanol or methanol, have low cetane number, 9 respectively 3, and are therefore not possible to use in diesel engines without engine modifications. Normal practice is to add an ignition improver to the alcohol fuel. Ignition improvers available on the market are rather expensive and are normally mixed directly into the alcohol fuel. An early concept was to inject a small amount of diesel fuel into the cylinders before injecting the alcohol. This gives satisfactory operation but requires two fuel injection systems which increases cost and maintenance.

Dissolved ignition improvers of type polyethylene glycol (PEG) are used in Scania and Volvo engines with good success but alternative additives are of interest to investigate. A promising solution is to use an on-board reactor to generate ethers from the alcohol fuel. From ethanol (EtOH), diethyl ether (DEE) may be dehydrated and from methanol (MeOH), dimethyl ether (DME) may be dehydrated. Both these ethers have high cetane numbers, 90 respectively 60, and may be used as ignition improvers.

Alcohols, as non-soot fuels, do not provide the starting materials, necessary for the formation of aromatic rings, upon which the soot formation is initiated, nor the acetylenic species, which contribute to its growth. It is this characteristic, which makes alcohol an attractive candidate

for use in diesel engines. Furthermore, lower NO_x levels are already reported in different papers, but the effect of alcohol fuels on exhaust emissions, particularly those which are currently unregulated, is uncertain and under discussion.

Two Volvo diesel engines have been developed to run on alcohol fuel, TD73 used in heavy-duty trucks and AH10A245 used in buses. The modifications for using alcohol are mainly increased compression ratio and larger fuel pump and fuel nozzles. Both engines were developed to run on ethanol with 7% PEG as ignition promoter and the bus engine was later also developed to use ether. Those tests have not included on-board manufactured ethers at the present stage, instead purchased ether has been premixed with alcohol in the initial tests and injected into the engine air inlet during the fumigation tests.

When using the premixing of EtOH and DEE it has proven to be necessary to mix in 60% DEE in order to run the engine over the whole range of operation. This agrees well with experience from other researchers when running on MeOH with mixed in DME. Performance as well as emissions are comparable with those obtained when running the engine on EtOH with PEG as ignition improver. All tests have been done according to the ECE R49 13 mode test and evaluation procedure. Comparing 7% PEG with 60% DEE shows the following emissions for the bus engine:

Fuel	EtOH + 7% PEG	EtOH +60% DEE	EtOH +fum. DEE	MeOH +fum. DME	
NO _x	4.96	5.01	3.58	3.48	g/kWh
HC	0.23	0.27	1.27	0.80	g/kWh
CO	7.89	7.98	5.91	5.48	g/kWh

When using the fumigation technique, i.e. injecting a mixture of ether, alcohol and water into the air inlet of the engine in order to simulate the output from a dehydration reactor, testing has been completed using ethanol as well as methanol as the main fuel and the resulting emissions are shown above. When using an oxidizing catalyst both CO and HC will easily be reduced to levels of 0.1-0.2 g/kWh.

The amount of DME used in the tests was similar to the amount of DEE used i.e. 2-15% of the fuel flow, the higher values corresponding to low loads. These amounts of ether is easily produced on board the vehicle in a dehydration reactor of size similar to an oxidizing catalyst.

In addition to the regulated emissions reported above also the following unregulated emissions were measured. Formaldehyde (0.01 g/kWh), Acetaldehyde (0.02 g/kWh), Methanol (0.12 g/kWh), Ethanol (0.18 g/kWh), Acetic acid (0.16 g/kWh). All values are evaluated according the ECE R49 13 mode test cycle.

Further information on the tests may be found in references [1-3]. As a conclusion of using alcohol in diesel engines, NO_x will remain as a problem as it only may be reduced by a factor of 2-3 compared with conventional diesel fuels. Soot is no problem and HC and CO may be reduced using an oxidizing catalyst. The combination of alcohol and ether may, however, pave the road for new combustion concepts.

GAS TO LIQUID FUEL

GTL fuels can be processed by the Fischer Tropsch (FT) process, which gives a diesel fuel of high quality. Having low aromatic compounds, high cetane rating and almost zero sulphur content, the FT diesel fuel shows advantages over conventional diesel fuel. This fuel has been investigated to reveal and analyse its effect on a research diesel engine performance. Since the engine performance is closely related to in-cylinder processes, a detailed thermodynamic analysis is revealing the real thermo-chemistry history.

The test engine consists of the basic AVL Type 501 cylinder block and Volvo – 2 l cylinder head equipped with C-3 Lucas unit injector. Turbocharger performance of a six cylinder production engine was simulated by the AVL 5153 supercharging group according to discrete parameters red from Volvo test.

Experimental investigation has shown that FT fuels have a significant impact not only on the emissions levels, but also on other energetic parameters of the engine such as ignition delay, cylinder peak pressure, heat release gradient, indicated efficiency, fuel consumption etc.

The regulated emission, emitted by the diesel engine when it runs on FT fuels, are lower than those of MK1. The ECE R49 13 mode evaluation of specific weighted values have shown a general NO_x reduction by 6%, HC reduction by 17%, CO reduction by 10%, and Soot reduction by 19%. A small reduction by 1% in BSFC was observed as well. At some loads (from light load 10% to medium load 50%) the emission reductions were higher. Hence, reduction of NO_x reached 25%, HC 50% and CO 30%. Generally speaking, FT fuels are shown to be effective over the operating range of the engine, and particularly at high load and rated speed. These tests are reported in reference [4] and another test with the same engine but comparing regular diesel fuel and a FT fuel did give similar results, reference [5].

Detailed measurements of organic compounds in the exhaust showed that none of the FT-fuels produced any significant amounts of dangerous higher organic compounds for example PAH. The emissions were dominated completely by fuel components. There are only paraffins in the fuels, and there are basically only paraffins in the exhaust.

As a conclusion of the experimental investigation on single cylinder research engine it may be stated that FT fuels can be used in unmodified compression ignition engines with significant reduction of regulated emission and smoother thermodynamic performance. FT-fuels can also be produced from biomaterial, thus no CO₂ penalty, and the exhaust gases are much less toxic than from diesel fuels. NO_x will remain as a problem and a new combustion concept is required.

FUTURE USE OF ALTERNATIVE FUELS

From the testing reported above it is quit clear that future emission requirements will not be possible to archive without a new combustion concept.

The Homogeneous Charge Compression Ignition, HCCI, concept is a hybrid of the Spark Injection, SI, and Compression Ignition, CI, engine concepts. As in a diesel engine, the fuel is exposed to a sufficiently high temperature for auto-ignition to occur, but in HCCI, a homogeneous fuel/air mixture is used. The homogeneous mixture is created in the intake system, as in a SI engine, using a low-pressure injection system or a carburetor. No ignition system is necessary. To limit the rate of combustion very diluted mixtures must be used. This high dilution can be achieved by high air/fuel ratio and/or with Exhaust Gas Recycling, EGR. If the mixture is too rich, the rate of combustion becomes too rapid and will generate knock-related problems. A too lean mixture will lead to incomplete combustion or misfire.

With HCCI, cycle-to-cycle variations of combustion are very small, since combustion initiation takes place at many points at the same time. The whole mixture burns almost homogeneously. In this way, unstable flame propagation is avoided. One of the most appealing

attributes of HCCI is the homogeneous combustion. This means that the temperature should be the same in the entire combustion chamber. This, in combination with the ultra lean mixtures required to control the combustion rate, gives a very low maximum temperature during the cycle. The NO_x emission levels reported from tests at LTH in Lund [6] are very low, less than 0.02 g/kWh, indicating that the maximum temperature during the cycle is approaching the limit of thermal NO_x production.

An alternative road to achieve HCCI, called Heat-Re-circulating Combustion, HRC [7], is used in industrial furnaces. In heat-recirculating combustion, the reactants are preheated prior to combustion by recycled exhaust gases. This has proven to be an effective method for energy savings and reduction of NO_x emissions. In this technology, for example, the only diluted air can be preheated to high temperatures, while rich fuel/air mixtures can be injected into preheated air to realize diffusion or partially premixed combustion.

In order to provide fundamental understanding of the physical and chemical processes that occur during combustion in high temperature air or exhaust gases with a low content of oxygen a study using a detailed chemistry approach has been performed at Chalmers [8]. The numerical solution methodology employed in the modelling uses a coupling of a generalized partially stirred reactor, PaSR, model with a high efficient numerics. The results clearly illustrate that the flame structure is significantly affected by oxygen concentration. Contrary to the hot air case, which shows a normal flame development, the case of the oxygen-depleted mixture shows a barely distinguishable flame front: the combustion zone is distributed over the chamber volume and the maximum temperature is only 150 K higher than the surrounding temperature. The predicted NO_x concentration was found negligible.

These concepts are still requiring much more research efforts and will be developed for conventional as well as alternative fuels. The alternatives might, however, due to their larger flexibilities in composition have a better chance of success.

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Progress Variables for Homogeneous Charge Compression Ignition (HCCI) Engine Combustion

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INTRODUCTION

Combustion progress variables are parameters, giving a measure of how far a combustion process has proceeded. Frequently they are used for connecting fluid dynamics calculations with kinetic calculations, for example through flamelet libraries¹.

A progress variable is a property of the combustion system, and the change in this property, weighted to range from 0 to 1, will define the progress of the combustion. Possible properties are the consumption of the reactants², the fuel components or the oxidiser³, the formation of an end product such as CO₂ or H₂O⁴, or the energy in the system, through temperature, internal energy or sensible enthalpy^{5,6}.

The vast amount of different definitions of progress variables reflects the different needs for different problem formulations. To give a simple example, different engine types have different modes of combustion. In a CI engine, the combustion occurs through diffusion flames, in an SI engine through a premixed flame, and in an HCCI engine the combustion occurs through chemical oxidation.

Especially the latter puts special demands on the progress variable as a fraction of the fuel is partially consumed through low-temperature oxidation and ensuing reactions, giving rise to a small but from a phenomenological viewpoint important heat release. The end products CO and CO₂ are not formed at the low-temperature regime, meaning that a CO or CO₂ based progress variable will not detect these important pre-reactions. On the other hand, the CO and CO₂ forming reactions account for a large portion of the heat release in the engine, meaning that a progress variable studying one of the reactants in the system will instead give an over-weight to the first, early heat release. Further, the chemical oxidation is considered a slow process, meaning that the main heat release will most likely be too early predicted.

In this paper we perform a full cycle engine simulation using the engine simulation tool (EST) *GT-Power* by Gamma Technologies Inc., to model the intake and exhaust flows, all aggregates connected to the engine and a simple combustion model based on a progress variable. We couple the EST to our in-house-code *Ignition* that calculates the HCCI engine auto-ignition process using a detailed kinetic model. *Ignition* calculates the progress variable and transfers it to the EST at each time-step. If the reaction progress variable is accurate, we achieve a tool that performs full cycle simulations with detailed chemistry.

NUMERICAL INVESTIGATIONS

Six different progress variables were compared through numerical investigations. The temperature trace calculated through *Ignition* was compared to its subsequent temperature trace as described by the progress variable in the EST.

Numerical model

The numerical model used in this work consists of the kinetic code *Ignition* coupled by a user-interface to the EST *GT-Power*. A semi-detailed kinetic model consisting of 157 species and

1552 reactions is used. The engine simulation tool is set to give a full description of a laboratory setup of a 6-cylinder 12-liter Scania DSC12 truck engine converted to HCCI operation. The turbocharger, inlet heater and exhaust system differ from the normal CI operation layout. The kinetic calculations are only performed for one of the cylinders; the remaining 5 are slave cylinders.

Investigated progress variables

Six different progress variables (pv.) were studied. One of them is based on reactant consumption. (b =burned, u =unburned):

$$C = \frac{Y_{O_2}^u - Y_{O_2}^b}{Y_{O_2}^u - Y_{O_2}^b} \quad (\text{pv. } O_2)$$

Four are based on the relative mass fractions of common end-products:

$$C = 1 - \frac{Y_{H_2O}^b - Y_{H_2O}^u}{Y_{H_2O}^b - Y_{H_2O}^u} \quad (\text{pv. } H_2O)$$

$$C = 1 - \frac{Y_{CO_2}^b - Y_{CO_2}^u}{Y_{CO_2}^b - Y_{CO_2}^u} \quad (\text{pv. } CO_2)$$

$$C = 1 - \frac{Y_{H_2O+CO_2}^b - Y_{H_2O+CO_2}^u}{Y_{H_2O+CO_2}^b - Y_{H_2O+CO_2}^u} \quad (\text{pv. } 2\text{prod})$$

$$C = 1 - \frac{Y_{H_2+H_2O+CO+CO_2}^b - Y_{H_2+H_2O+CO+CO_2}^u}{Y_{H_2+H_2O+CO+CO_2}^b - Y_{H_2+H_2O+CO+CO_2}^u} \quad (\text{pv. } 4\text{prod})$$

Finally a progress variable based on the reaction enthalpy is investigated

$$C = \frac{H_{298}^o - H_{u,298}^o}{H_{b,298}^o - H_{u,298}^o} \quad (\text{pv. entalp})$$

Calculation cases

In all calculations, the engine speed was 1500 rpm, compression ratio 17:1.

- case 1.* 100% iso-octane, strong pre-heating. Ignition occurs close to top-dead center (TDC) with the first signs of heat release occurring at 5-7 crank angle degrees (CAD) before TDC at roughly 1020-1030 K. Pre-reactions are difficult to detect in the temperature trace, as is shown in Fig. 1.
- case 2.* 60% iso-octane, 40% n-heptane, moderate pre-heating. Pre-reactions are starting 21 CAD before TDC at 760 K, the majority of the n-heptane is consumed at 5 CAD before TDC while the rest of the heat release occur slightly after TDC. The results are shown in Fig. 2.
- case 3.* 40% iso-octane, 60% n-heptane, no pre-heating. The ignition is here phased slightly later than in the previous case, giving pre-reactions at 17 CAD before TDC at 790 K, the majority of the n-heptane is consumed at TDC while the rest of the heat release occur slightly about 5 CAD after TDC.

Two cycles with the kinetics code replaced by a Wiebe function are run before the kinetic calculations in order to stabilize the in-cylinder physical parameters. In case 2, two subsequent kinetic calculations are performed in order to let an adaptive algorithm adjust the borders for where heat release is detected and thereby allow for as good prediction of the total heat release as possible. In cases 1 and 3 this is not ensured, meaning that the temperature increase from chemical reaction may cease to continue before all chemical heat is released.

RESULTS

The results are shown as temperature profiles in Fig. 1 and 2.

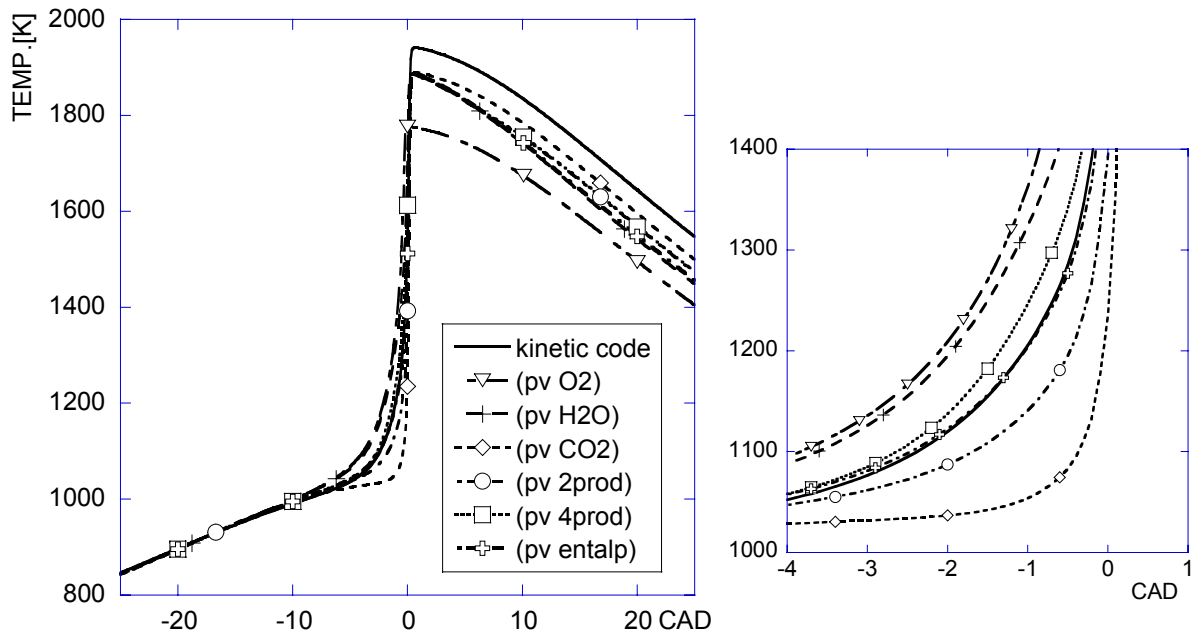


Fig. 1 100% iso-octane. Note that the lower total heat release and end-temperature for the progress variable based on O_2 consumption (pv O_2) originate from a calculation error.

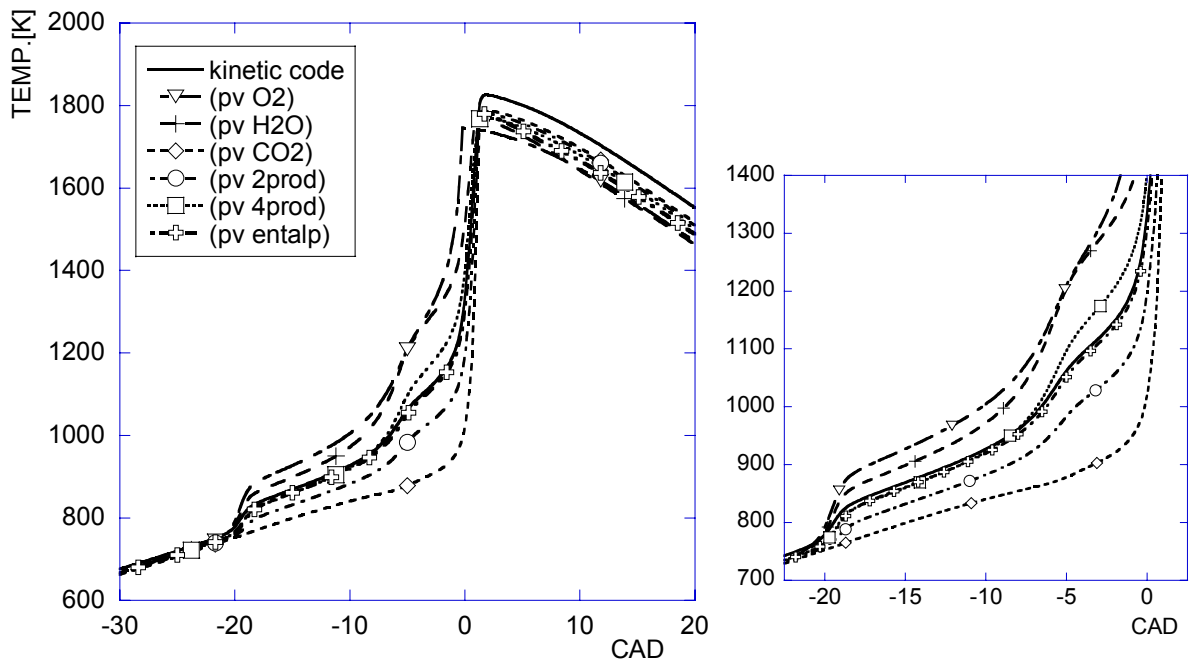


Fig. 2 60% iso-octane, 40% n-heptane. It is here very visible that (pv. O_2) and (pv. H_2O) overpredicts the importance of the early reaction, whereas (pv. CO_2) does not detect the low-temperature reactions at all.

CONCLUSION

The tested progress variables are ranked in order of increasing truthfulness, and the following judgments may be given on them:

- (pv. O₂) predicts a too early timing of the ignition and puts too much emphasis on the pre-reactions
- (pv. CO₂) does not identify any influence whatsoever from the pre-reactions since they do not produce any CO₂. The prediction of the main heat release is slightly delayed
- (pv. H₂O) exaggerates the importance of the early stages of ignition, and gives a slightly too early ignition
- (pv. 2 prod) is better than any of the previous three, and gives a good prediction of the main heat release but tend to underestimate the importance of the pre-reactions
- (pv. 4 prod) gives a good prediction of the ignition timing as well as the weighting between low- and high-temperature reactions
- (pv. entalp) is the best of the tested progress variables and follows the temperature trace excellently.

We choose to compare the progress variables to the temperature trace, since both the low-temperature oxidation and the high temperature reactions needed to be accounted for. Evidently the progress variable based on sensible enthalpy gives the best correlation to the temperature trace. The progress variable based on the accumulated formation of {H₂+H₂O+CO+CO₂} offers an interesting alternative, whereas the superposition of H₂O and CO₂ is maybe acceptable but far less accurate.

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Prediction Tool for the Ion Current with Reference to SI Combustion

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INTRODUCTION

The ionization sensor is an electrical probe for combustion diagnostics. Its signal contains information on both the early phase of the combustion process due to chemical ionization in the flame front and the main combustion due to ionization equilibrium in the post-flame gases. All factors influencing the ion-current in spark ignited combustion are not fully understood. The sensor signal consists of two major parts, a first peak and a second one. The first peak occurs when the flame is in contact with the spark plug electrodes. It is caused by the chemical ionization in the flame, and its magnitude is related to the local equivalence ratio close to the electrode gap. The second peak is located close to the position of the pressure peak. A theory presented by S. Yoshima et al. [1] also explained the second peak as flame front ionization. A bomb experiment showed that the second peak appeared when the flame front was in contact with the combustion chamber wall. Another proposed model for the second ion-current peak was presented by Saitzkoff et al. [2]. In this model the main factor influencing the second ion-current peak was thermal ionization of NO. Franke et al. [3] presented a theory based on thermal ionization of alkali metals (potassium) where it was stated that thermal ionization of NO is a major factor at high temperatures. At low temperatures, where not enough NO is formed, the alkali metals play an important role for the occurrence of the second peak. The combustion model used in the present work is a zero-dimensional zonal model. The gas in the combustion chamber is divided into two different zones, burned and unburned gases, separated by the flame front. Due to the zero-dimensionality, the flame front is assumed thin, i.e. the flame stretch and curvature are neglected [7]. The assumption of zero-dimensionality is valid for the whole model. Detailed chemical kinetic mechanisms are implemented for both the unburned and burned zones. The walls of the combustion chamber can be either kept at a constant temperature T_w or a wall heat flux $\dot{Q}_w$ can be specified. An external cooling system of the walls may also be considered. However, for such approach the convective heat transfer coefficient and the temperature in the cooling system must be known. The adiabatic temperature of the flame front is calculated by minimizing Gibb's free energy and using the unburned gas temperature and pressure. The flame front propagation is modeled using Wiebe function with adjustable parameters [4].

MATHEMATICAL MODEL

It is assumed that the gas in each zone has a homogeneous structure and uniform properties. Consequently each zone is assumed to be a control volume. The unburned zone was treated as a plug flow reactor and the burned one as a well stirred reactor the following equation have been solved [4].

- Conservation of mass

$$\sum \dot{m}_i - \sum \dot{m}_e = \frac{dm_{cv}}{dt} \quad (1)$$

- Conservation of energy

$$\dot{Q}_{total} - \dot{W} = -\sum \dot{m}_i h_i + \sum \dot{m}_e h_e + \frac{dE_{cv}}{dt} \quad (3)$$

The conservation of species is written for the unburned and burned zones in equation (4) and (5) respectively:

$$\frac{\partial y_{j,u}}{\partial t} = \frac{M_{j,u}}{\rho_u} \sum_{k=1}^{Nr} \nu_{j,k} \omega_k \quad (4)$$

And

$$\frac{\partial y_{j,b}}{\partial t} = \frac{M_{j,b}}{\rho_b} \sum_{k=1}^{Nr} \nu_{j,k} \omega_k + \frac{\dot{m}_b}{m_b} (y_{j,b} - y_{j,b}) \quad (5)$$

IONIZATION EQUILIBRIUM

The ionization equilibrium is representing the thermal ionization of both Nitric Oxide (NO) and Potassium (K) can be written as



The balance between generation and regeneration of ions caused by thermal excitation forms the basis for the ionization. The ionization process is assumed to be fast compared to the combustion process and specifically the combustion temperature development. Therefore the electrons and ions are in thermodynamic equilibrium and the balance can be described below by the Saha's equation:

$$\frac{n_{A^+} n_e}{n_A} = \frac{Z_e Z_{A^+}}{Z_A} \exp\left(-\frac{E_i}{k_B T}\right) \quad (6)$$

The ionization equilibrium above (R1) is controlled by the non-linear equation system calculated according to [3]:

$$\frac{n_{A^+} n_e}{n_A} = K_e \quad (7)$$

$$n_A + n_{A^+} = n_{A,T} \quad (8)$$

$$n_{A^+} = n_e \quad (9)$$

where the Z_i are the molecular partition functions of species (j), which contain translational, electron, rotational and vibrational contributions. The exponential dependency on the ratio between the ionization energy E_i and the temperature dominates the behavior of the equilibrium constant. The solution of the system (6-9) yields the electron density n_e . Free electrons contribute most to the current in the heated gas because of their very high mobility. Ions become important when their concentration exceeds the electrons concentration by about two orders of magnitude and this can happen in the presence of electronegative species combined with low temperature [3]. Thus the current density depends on the electron density as

$$j = n_e e X \mu_e \quad (10)$$

where X is the electric field, μ_e the electron mobility, e the charge of the electron, n_e the electron density [9].

RESULTS

Existing models for the ionization current assume nitric oxide as the main electron donor in the post-flame gases [2, 3, 5, and 10]. This is reasonable as long as NO is the combustion product with the lowest ionization energy. This hypothesis will be tested in the following section compared to other species which can be a strong candidate as main electron donors. First let's start by comparing the

results from the simulation to those measured in the cell experiment. The pressure cycle calculated from the model is compared to the experimental result and they are both presented in figure 1 and a good agreement between the two results is noticed. As stated before, the scope of this paper is to study the contribution of two different species in the process of thermal ionization namely nitric oxide and potassium. This process is known to be strongly dependent on temperature; the model used is supposed to give more accuracy in the estimation of the burned gas temperature than the one-zone model. In a recent study, Andersson [10] found that a one-zone model underestimates the burned gas temperature by about 16% compared to the two zone model. This agrees with the figures previously presented by Heywood [7]. Figure 2 shows the calculated current from the ionization of NO compared to the experimental measurement. The calculated current peak is about 8% lower than the measured one, and this is probably due to the simplified geometry chosen for the two electrodes in the simulation model, where the geometry of the electrodes in the experimental set up was quite complex. The nitric oxide ionization is strongly dependent on temperature as shows in figure 3. Both profiles reach the maximum at the same time. The potassium ionization is found to be strongly dependent on temperature, and this can be seen below in figure 4, where the maximum electron mole fraction, produced from the thermal ionization of potassium is reached slightly before the maximum temperature.

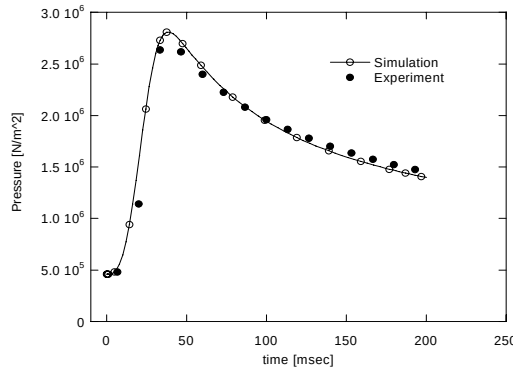


Fig. 1. Calculated and measured pressure cycle.

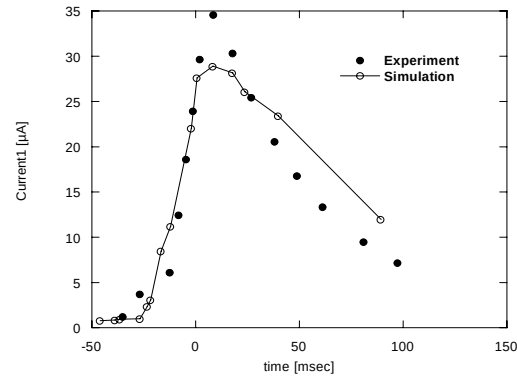


Fig. 2. Calculated current vs. a measured one

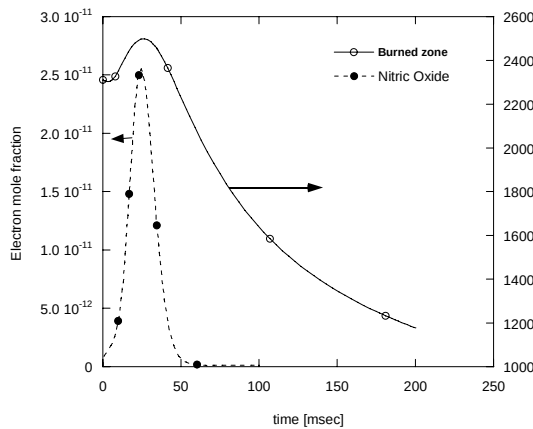


Fig. 3. Burned gas temperature and electron mole fraction produced from the ionization of NO both vs. time.

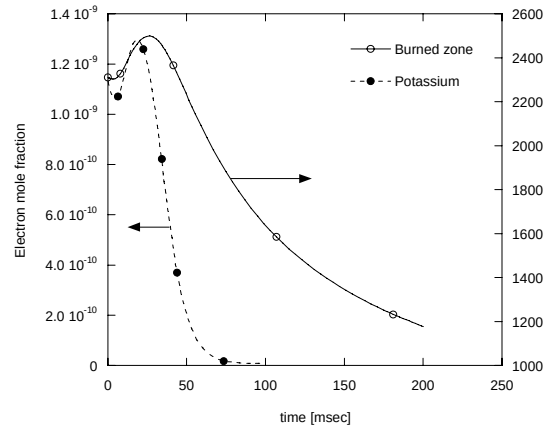


Fig. 4. Burned gas temperature and electron mole fraction produced from the ionization of Potassium both vs. time.

CONCLUSION

A simplified zero-dimensional, two-zone model has been developed by applying principles from classical thermo-dynamics. The combustion chamber has been divided into two zones, burned and unburned gases, separated by an assumed thin flame front. The detailed chemical mechanisms are included in both zones. The effects of compression by the flame front propagation are included in the model. A simple chemical equilibrium is used for the calculation of the thermal ionization of NO and K. The numerical code, used for the calculations, is found to be an efficient tool. Despite the detailed chemical analysis, the calculations could be performed within a minute on a regular personal computer. Nitric oxide has always been known as the main electron donor in the compressed hot post-flame gases, and thus considered to be the most important species for the ionization sensor current during main combustion. A theoretical effort has been made to verify the assumptions above, and to identify the most important contributors to equilibrium ionization in the hot compressed post-flame gas. The investigation above indicated that species with much lower ionization energy than the one for NO make a significant contribution to the conductivity of the gas in the post-flame zone. Among the species with lower ionization energy than the one for NO, alkali metals and specifically the thermal ionization of potassium and its contribution to the sensor current was studied within this model. It has been observed that the presences of species with lower ionization energy e.g. alkali metals (K, Na), might have significant contribution to ionization, the contribution level of nitric oxide ionization in the sensor current is still not very clear, here the sensor signal and NO concentration relationship is mainly due to the dependence of both variables on temperature, which affects in the same time NO formation and the ionization process. Potassium not only seems to be the main electron donor but it also affects the NO/NO⁺ equilibrium indirectly. Since high electron concentration is produced due to the early ionization of potassium, the NO/NO⁺ equilibrium is forced towards NO (electron attachment). Future work will consider more complex ionization equilibrium to study the real effect of each species, where electronegative species will be included.

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Diesel Fuel Surrogate Oxidation Mechanism with Application to Spray Combustion Modelling

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ABSTRACT

A numerical study has been carried out on the application of a detailed chemistry mechanism for diesel fuel surrogate to spray combustion modelling. The fuel surrogate vapour is represented by a mixture of 70 % n-heptane and 30 % toluene and is modelled on the basis of detailed mechanisms for n-heptane and toluene, individually developed. The mechanism is validated using shock-tube auto-ignition data and reduced using sensitivity analysis. The diesel surrogate mechanism developed consists of 68 species and 280 reactions. The mechanism is implemented into the KIVA-3V [1] code for spray combustion modelling in a constant-volume vessel.

Using the diesel surrogate model, the essential features of fuel auto-ignition at engine relevant conditions are reasonably well reproduced. The aliphatic fuel component controls spray auto-ignition, while the aromatic one significantly contributes to soot formation. The effect of toluene on auto-ignition is predicted as moderate, since its ignition is promoted by a radical pool formed by easily oxidised n-heptane.

INTRODUCTION

Diesel oil is characterized by an enormous variation of its chemical makeup. In order to model combustion processes within a realistic computational time, a simplified model of the diesel fuel is needed. The ignition behaviour, combustion process development and emission formation, especially soot, depend on the fuel properties to a significant degree. Therefore it is important to have a realistic diesel fuel surrogate model. Diesel fuel surrogate models consisting of single component aliphatic hydrocarbons, such as n-heptane or n-dodecane, have been used in the Computational Fluid Dynamic (CFD) modelling of diesel spray combustion. However, since real diesel oil is a mixture of different hydrocarbons, both aliphatic and aromatic, modelling of diesel fuel as a single component, pure aliphatic substance is unlikely to reproduce accurately all of its properties.

This motivates the development of a diesel fuel surrogate model consisting of both aliphatic and aromatic components. In this model, the fuel vapour is represented by a mixture of 70 % n-heptane and 30 % toluene and the chemical mechanism integrates the kinetics of fuel component combustion with kinetics of Polycyclic Aromatic Hydrocarbon (PAH) formation as soot precursors.

The mechanism developed has been implemented into the KIVA-3V combustion code and numerical solutions have been used to evaluate auto-ignition of real diesel oil in a constant-volume vessel.

DIESEL FUEL SURROGATE MODEL

Currently, only single component fuels are implemented in the KIVA-3V library. The thermodynamic properties of diesel fuels in the liquid phase are represented by those of real

diesel oil, i.e. the enthalpy-temperature curve is similar to n-dodecane with enthalpy of formation of -9.8 kcal/mole.

Since diesel surrogate vapour is represented by a mixture of n-heptane and toluene, it is assumed that the combination of their respective properties will give a good approximation of real diesel oil properties. The choice of n-heptane is motivated by its cetane number around 56, which is similar to the cetane number of real diesel oil. This promotes correct auto-ignition behaviour. In order to get a more accurate prediction of soot formation, the aromatic hydrocarbon is also included in the model. Toluene, which is a product of benzene alkylation, has been selected as the aromatic component in the diesel fuel surrogate makeup. The presence of toluene does not affect significantly ignition delay time because its oxidation is promoted by high radical concentrations, produced when n-heptane oxidation proceeds.

The main reaction pathways for n-heptane combustion are well established [2] and in addition to its reduced mechanism, the simplified reaction scheme of toluene oxidation [3] is included into the diesel surrogate model. The toluene oxidation promotes direct formation of acenaphthylene, A2R5, which is a gaseous precursor of soot. Soot formation is modelled as a finite-rate transition of A2R5 to graphite. The complete mechanism, in which the dominant reaction rate coefficients are tuned on a basis of a sensitivity analysis [4], consists of 68 species and 280 reactions and has been validated using auto-ignition shock tube experimental data.

RESULTS AND DISCUSSION

Shock tube auto-ignition calculations

The suggested reaction mechanism is evaluated by comparing predicted ignition delay times with shock tube experiments for n-heptane [5] and toluene [6], respectively.

Comparisons of calculated and experimental ignition delay times for different temperatures and n-heptane/air compositions are shown in Fig. 1. The predictions are in reasonable agreement with the experimental data

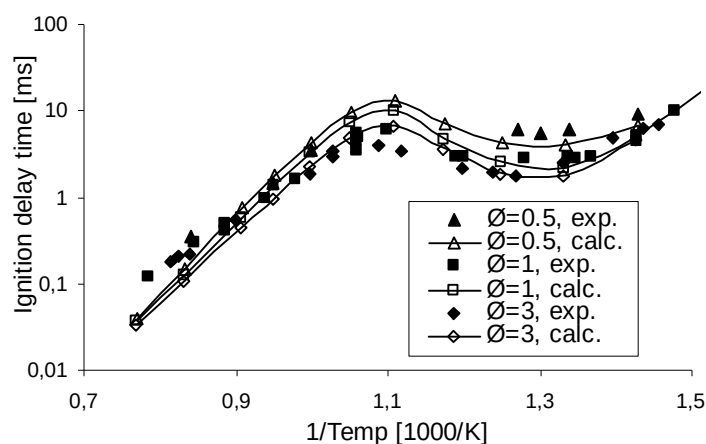


Fig. 1 Ignition delay times for n-heptane in shock tube experiments. $p_0=13.5$ atm.

Experimental and calculated data for toluene ignition delay times for different pressures and compositions, summarized in Table 1, are compared in Fig. 2. The calculated values agree well with the experimental data.

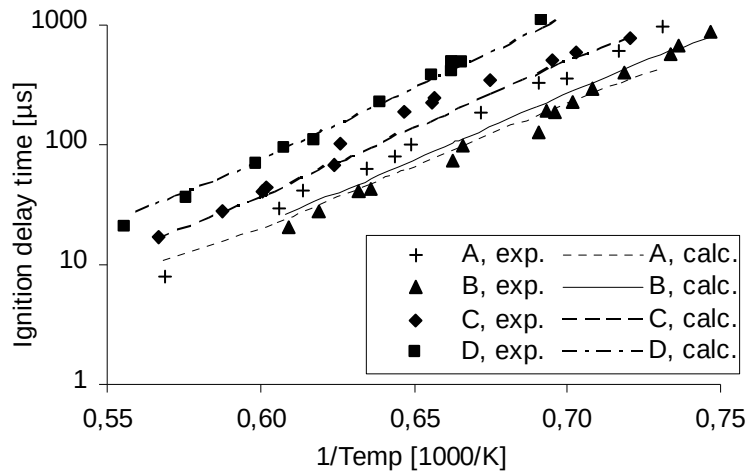


Fig. 2 Ignition delay times for toluene in shock tube experiments. The experimental conditions are summarized in Table 1.

Table 1. Mixture compositions and initial pressures for shock tube experiments.

Case	p (atm)	Ø	C ₆ H ₅ CH ₃ (%)	O ₂ (%)	Ar (%)
A	2.8	1	1.495	13.45	85.055
B	2.3	0.33	0.497	13.51	85.993
C	6.8	1	0.497	4.48	95.023
D	2.3	1	0.497	4.48	95.023

Fig. 3 presents calculated ignition delay times for stoichiometric mixtures of n-heptane, toluene and the diesel fuel surrogate. This illustrates that the auto-ignition behaviour of the fuel surrogate model is mainly characterised by the properties of n-heptane.

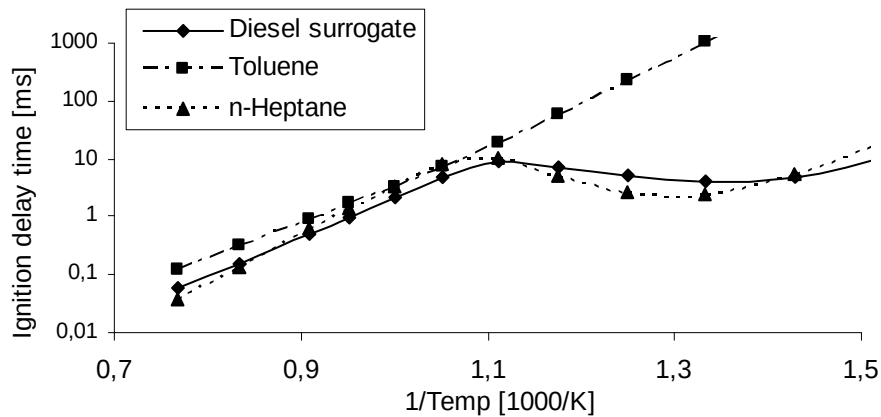


Fig. 3 Calculated ignition delay times for n-heptane, toluene and diesel surrogate combustion in air. $p_0=13.5$ atm. Equivalence ratio, $\phi=1$.

Constant volume spray combustion

The model predicts accurately shock-tube n-heptane and toluene auto-ignition, but the important question is whether the fuel surrogate model can reproduce the ignition properties of real diesel oil at engine relevant conditions. This is evaluated by simulation of constant-

volume spray auto-ignition experiments. Calculations of ignition delay times in a constant volume vessel were carried out using the KIVA-3V code.

Constant volume experimental data are available in [7], where ignition delay times were measured for different initial temperatures for both turbulent and non-turbulent cases. In the experiments, diesel fuel (6 mg) has been injected with the injection duration 1.27 ms. To simulate different levels of turbulence, different initial values of turbulent kinetic energies are used in the calculations, while the initial turbulent length scale is kept constant. The ignition delay time was defined as the time for the average temperature to increase by 1% of its initial level. The results are presented in Fig. 4 and the predictions show reasonable agreement with the experimental data.

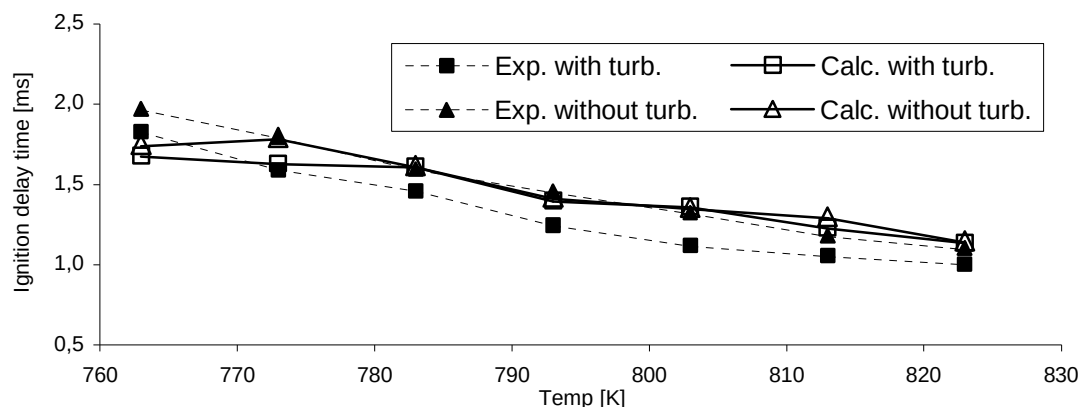


Fig. 4 Ignition delay times for constant volume ($p_0=50$ atm.) combustion; comparisons between experimental data and simulations.

CONCLUSIONS

A diesel fuel surrogate model has been developed, consisting of 68 species and 280 reactions representing the oxidation kinetics of a mixture of 70 % n-heptane and 30 % toluene. The model has been validated by comparison of simulated ignition delay times for the fuel components with shock tube experimental data.

The validated model has been integrated into the KIVA-3V code to simulate diesel spray combustion in a constant-volume vessel. Comparisons with spray auto-ignition experimental data show that the model reproduces reasonably well the diesel spray auto-ignition process.

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Validation of a Flux Method for Radiative Heat Transfer in Plug Flow Reactors

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INTRODUCTION

Flux methods are *conceptually approximate* methods for the calculation of the rate of radiative heat transfer with remarkable computational advantages with respect to *conceptually exact* methods like Hottel's zone method and the MonteCarlo method. The attention has been focused here on the *quantitative aspects* of the flux method approximation in order to distinguish cases where Roesler's one-dimensional flux method can be applied safely from those where caution is required.

ANALYSIS

The steady state temperature profile of a medium along a PFR is governed by the energy balance:

$$\frac{d}{dx} [\rho u (c_p T + Y_f HV) - k_{\text{eff}} \frac{dT}{dx} + q_R] = 0 \quad (1)$$

where the contributions of sensible and chemical enthalpy, effective diffusion and radiation appear in this order, to be solved together with the auxiliary equations for the mass velocity $\rho u = \rho u(x)$, the equivalent unburned fuel mass fraction $Y_f = Y_f(x)$, the effective thermal conductivity k_{eff} , and the absorption coefficient of the reacting medium k_a . The temperature profile of the bounding walls where the heat flux is assigned, and the heat flux profile where the temperature is specified are then also determined.

With reference to the elementary volume located by point P along the duct of fig. 1, where a beam of incident radiation of intensity $I^i(P, \underline{\Omega})$ is visualized together with the relevant elementary solid angle $d\Omega$, the radiative contribution to the energy balance eq. (1) is

$$dq_R / dx = k_a [4\sigma T^4(x) - \int_{4\pi} I^i(x, \underline{\Omega}) d\Omega] \quad (2)$$

The intensity of the incident radiation $I^i(x, \underline{\Omega})$ being governed by the radiative transport equation, the radiative contribution confers non-linear integro-differential form to the energy balance eq. (1). In the zone method approach [1] the volume and the bounding walls are subdivided in N_v and N_s zones, and the integral contribution of absorption in eq. (2) is obtained by the sum of the contributions of each zone, so that with reference to the volume zone V_n

$$\int_{4\pi} I^i(x, \underline{\Omega}) d\Omega = [\sum_{j=1}^{N_s} \overline{S_j G_n} \sigma T_j^4 + \sum_{p=1}^{N_v} \overline{G_p G_n} \sigma T_p^4] / k_a V_n \quad (3)$$

where the blackbody emissive power of each zone is weighted by the relevant total exchange area [1]. The radiative contribution expressed by eq. (3) is *conceptually exact*. However, this is a form that adds a considerable computational burden to the solution of the set of algebraic equations generated

by the discretization of eq. (1), because all elements of the matrix of the coefficients, which is tridiagonal in a non-radiating medium, become non-zero if the medium absorbs/emits thermal radiation. The radiative contribution can, however, be brought to yield a tridiagonal set of algebraic equations by discretization if expressed by the flux method approach. The *flux method approximation* consists in the assumption of the angular distribution of incident intensity $I^i(x, \underline{\Omega})$. The discrete ordinate one-dimensional flux method originated by Roesler [2] is characterized by a constant intensity profile within each 2π solid angle centred about the positive and negative direction of the axis, as shown in fig. 2.

A function $G(x)$ such that

$$G(x) = \frac{1}{4} \int_{4\pi} I^i(x, \underline{\Omega}) d\Omega$$

can then be introduced, whereby the radiative contribution to the energy balance eq. (1) takes the form

$$dq_R / dx = 4k_a[\sigma T^4(x) - G(x)]$$

$G(x)$ is governed by the ordinary differential equation

$$d^2G / dx^2 = c_3(c_1G + c_2) \quad (4)$$

so that the matrix of the coefficients of the set of algebraic equations generated by the discretization of eq. (1) is now tridiagonal for radiating as well as for non-radiating media.

The heat fluxes absorbed at the side and end walls $q_{sw}(x)$ and $q_{ew,i}$ are related to $G(x)$ by the relationships:

$$q_{sw}(x) = \varepsilon_{sw}[G(x) - \sigma T_{sw}^4] \quad , \quad q_{ew,i} = c_{ew,i}[G_{ew,i} - \sigma T_{ew,i}^4] \quad i = 1, 2$$

The explicit dependence of the coefficients $c_1, c_2, c_3, c_{ew,i}$ on the absorption thickness of the medium and on the nature, temperature and emissivity of the side and end walls, as well as the boundary conditions of eq. (4), can be found in Ref. 2.

VALIDATION

PROCEDURE - The accuracy of the flux method above has been determined by comparison of the heat flux profile at the absorbing walls of a cylindrical PFR combustor obtained for assigned temperature profile of the medium with the corresponding exact profile. The differences between approximate and exact heat fluxes are functions of the emissivity of the absorbing walls ($\varepsilon_{sw}, \varepsilon_{ew,i}$), absorption thickness of the medium ($k_a D$), and aspect ratio of the chamber (L/D), namely:

$$\Delta q_i(x) = f(x, \varepsilon_{sw}, \varepsilon_{ew,i}, k_a D, L/D)$$

For any given pair of values of $k_a D$ and of L/D the discrepancy $\Delta q_{i,max}$ is a maximum when the walls are black. The Δ_i 's reported in figs. 3 and 4 in function of the absorption thickness of the medium for selected values of the aspect ratio are these maximum relative differences.

In the case of isothermal medium the PFR combustor is also a CSTR, a well known case for which the flux absorbed by the bounding walls is given by Hottel [1] in the form

$$q_s = \bar{F}_{sG}(\sigma T_G^4 - \sigma T_s^4)$$

which is exact as long as the total exchange factor $\bar{F}_{sG}$ is determined using the exact emissivity of the medium, i.e. that determined by the definition

$$\epsilon_G = \bar{g}_s / A_s \quad (5)$$

where $\bar{g}_s$ is the gas-surface direct exchange area of the enclosure [1].

The validity of the results obtained being independent of the shape of the temperature profile, as shown in Ref. 3, this elementary case is as good as any other for the purpose of validation of the flux method in object.

RESULTS – The percentage differences between the rates of heat transfer to the walls obtained by the flux method and those obtained by Hottel's method for black wall cylindrical chambers of aspect ratio $L/D = 1$ and $L/D = 10$ confining an isothermal medium of absorption thickness $k_a D$ are shown in fig. 3. The flux method underpredicts the rate of heat transfer with a maximum difference in correspondence of absorption thicknesses of the order of unity, and tends to become exact in both the transparent and thick medium limits. A more complex behaviour becomes apparent as the difference of the rates of heat transfer to the side wall are considered separately from those to the end walls, indicating that the result above is due to a compensation between an underestimation of the former and an overestimation of the latter. Moreover, the approximation of the heat flux to the side wall increases with increasing aspect ratio, i.e. as the weight of the rate of heat transfer to the end walls decreases.

A very significant measure of the magnitude of the discrepancies introduced by the flux method approximation is now obtained by the comparison with that introduced in the exact zone method by the widespread practical approximation by which the emissivity of a grey medium is calculated using the estimate of the mean beam length $L_e = 3.5V/A$ in the relationship:

$$\epsilon_G = 1 - \exp(-k_a L_e)$$

as an alternative to the exact but laborious determination by eq. (5).

The discrepancies in the heat flux profiles at the side wall of a cylindrical chamber with radiatively adiabatic end walls are shown in fig. 4 for the two values of the aspect ratio $L/D = 1$ and $L/D = 10$. The rate of heat transfer is underestimated by both approximations with a maximum of about the same magnitude in correspondence of $k_a D \approx 1$. The two differences differ by amounts of the order of 1% in media of increasing absorption thickness ($k_a D > 1$), whereas in more transparent media ($k_a D < 1$) the flux method tends to become exact, while the underestimation of the rate of heat transfer due to the $L_e = 3.5V/A$ approximation on ϵ_G reaches the order of 10%.

CONCLUSIONS

The rate of heat transfer to the end walls of a one-dimensional chamber is overestimated by Roesler's flux method, and that to the side walls is underestimated.

The approximation to the exact rate of heat transfer to the side walls can be even better than that of the zone method when the $L_e = 3.5V/A$ approximation of the mean beam length is used for the determination of the gas emissivity, e.g. as the rate of heat transfer to the end walls tends to become negligible and/or the aspect ratio of the chamber exceeds the order of unity.

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FIGURES

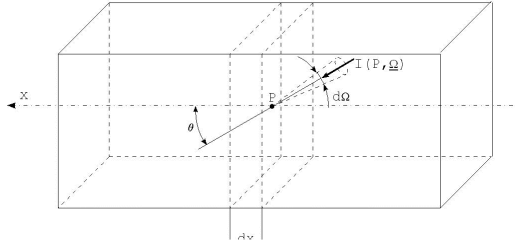


Fig. 1 – The intensity of incident radiation $I^i(P, \underline{\Omega})$ on the elementary volume along a 1-D duct is a function of the point $P(x)$ and of the direction of the impinging beam $\underline{\Omega}$.

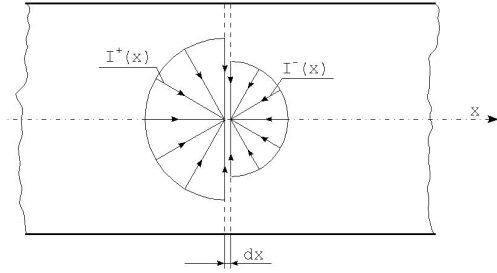


Fig. 2 – The incident intensity profile on the elementary volume in the discrete ordinate 1-D flux method approximation.

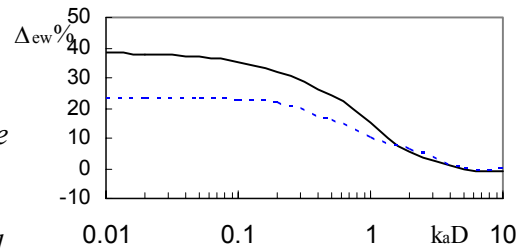
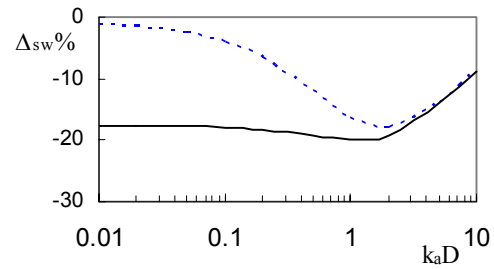
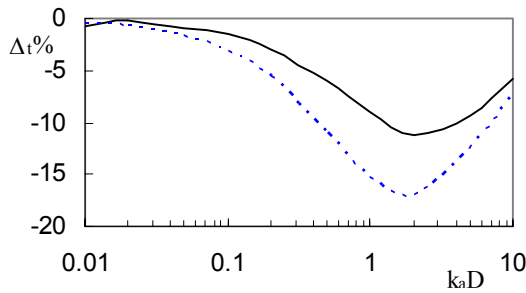


Fig. 3 – Percentage differences between the flux method and the exact rates of heat transfer to the total ($\Delta_t\%$), side wall ($\Delta_{sw}\%$) and end walls ($\Delta_{ew}\%$) of a black cylindrical enclosure of aspect ratio $L/D=1$ (full line) and $L/D=10$ (dotted line).

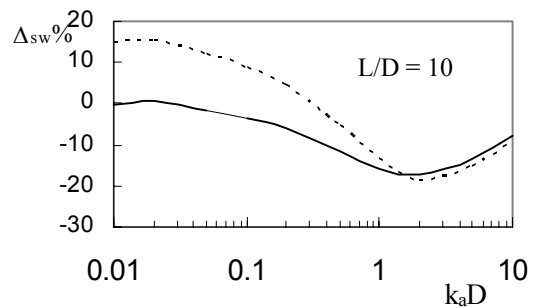
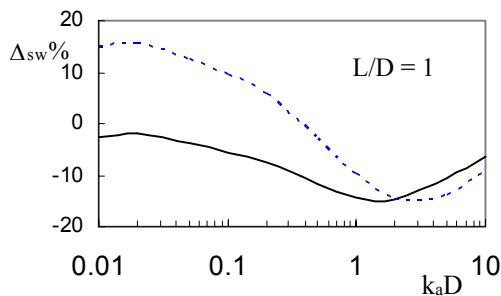


Fig. 4 - Percentage differences with respect to the exact rates of heat transfer to the side wall ($\Delta_{sw}\%$) of a black cylindrical enclosure due to the flux method approximation (full line) and to the $L_e=3.5V/A$ approximation on the emissivity ε_G in the zone method (dotted line) for the two key values of the aspect ratio.

NO Emission Formation in a Full-scale Power Plant Co-Firing Biomass Gas and Pulverized Coal: a CFD-modeling Study

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INTRODUCTION

The combustion in the 350 MW_{in} boiler at the Kymijärvi power plant in the city of Lahti, Finland, was studied. The boiler is fired with pulverized coal (300 MW_{in}) and gasification gas from a separate biomass/waste fluidized bed gasifier unit (50 MW_{in}). Taking into consideration the local supply of suitable biomass/waste the gasification gas is estimated to potentially replace up to 30 % of the coal burned annually in the boiler. The aim in this work was 1) to study the combustion process under various operational conditions in order to gain a better understanding of how, where, and why nitric oxide (NO) is formed in the boiler. An objective was also 2) to come up with recommendations on how to further reduce the NO_x emissions from the boiler, and 3) to illustrate the factors that affect the oxidation of fuel-N (NH₃) in the gasification gas to NO_x. The method used was computational fluid dynamics (CFD). The commercial CFD-program Fluent (versions 5 and 6.0) was used for the simulations with the state-of-the-art submodels for turbulence, radiation, and turbulence-chemistry interaction. Concerning submodels on chemistry certain own improvements were introduced.

BOILER GEOMETRY AND COMPUTATIONAL GRID

The boiler is 50m high and has a base of 10m x 7m. The coal is fired in twelve burners on three levels on two opposing walls. The eight burners on the two lower levels (1 and 2) are low-NO_x burners, and the four on the third level are conventional burners. On the front wall, below the bottom level of coal burners, there are two burners for the gasification gas with a capacity of 25 MW_{in} each. Over-fire air is fed from eight ports on the sidewalls 1.8m above the third level coal burners. The boiler is symmetrical with respect to a vertical plane stretching between the burner pairs from the front to the back wall. The computational domain covers half of the boiler: an unstructured grid was used (Fig. 1), and is made up of 166 000 tetrahedral cells.

MODELING APPROACH AND BOUNDARY CONDITIONS

In the simulations, most of the models used are standard models included in Fluent. Turbulence was modeled with the standard k-epsilon model, and radiative heat transfer with the discrete ordinates method. The coal/char particle tracking was done with the Lagrangian combusting particle model. The gas phase hydrocarbon combustion was modeled with a six-reaction chemical scheme. The scheme is a slightly modified combination of Fluent's scheme for oxidation of coal volatiles to CO and H₂, and the mechanism for hydrocarbon combustion presented by Jones and Lindstedt (1988). Coal volatiles are represented by the macromolecule CH_{3.086}O_{0.131}. The gasification gas was described as a mixture of CO₂, H₂O, CO, CH₄, H₂, NH₃, and N₂.

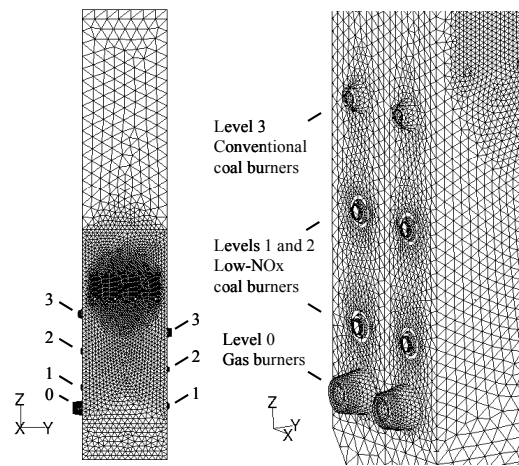


Fig. 1. The computational grid seen from the right boiler wall (left) and a close-up (including the grid and its mirror image over the vertical symmetry plane) of the lower part of the front and right walls (right).

For NO formation, three principal paths were included in the estimates: thermal NO, prompt NO, and fuel NO (coal NO, gas NO). For fuel NO formation the performance of three different mechanisms were compared: two variations of the De Soete mechanism in Fluent (HCN and NH_3 intermediate), and also an alternative, two-step mechanism by Brink and Kilpinen (2000). This last one has especially been developed to describe ammonia oxidation at biomass combustion conditions, and was here used to describe the NH_3 oxidation of the gasification gas. The nitrogen in the char was assumed to be released as NO during the char combustion (Lockwood et al., 1992). The heterogeneous NO reduction on the char surface was treated with the model by Levy et al. (1981). Turbulent mixing typically has a strong influence on the predicted gas combustion rates and on the formation and destruction rates of NO. For the hydrocarbon chemistry and for the Brink&Kilpinen reaction scheme, the turbulent mixing was described with the Eddy dissipation combustion model (EDCM) as implemented in Fluent. For the rest of the NO_x models a PDF-approach was used. A more detailed description of the modeling approach is given in Jungar (2001) and in Boström et al. (2003).

SIMULATED CASES

Five operational cases (I–V) with different combinations of load on the gas and coal burners were simulated (Table 1). Three more cases were simulated where the coal and gas load was as in Case I. In two of them (VI–VII), alternative assumptions were made regarding the amount and form of reactive nitrogen in the gasification gas, and in the third one (VIII), the gas was assumed to contain 50 % more water vapor. A total of 32 NO_x predictions were performed in a post-processing step after the main combustion simulations (Table 2). Predictions were made for one, two, or all the three principal NO formation paths (thermal, prompt and fuel). Fuel NO from the coal was predicted with Fluent's model (De Soete) either assuming the nitrogen intermediate species to be NH_3 (Estimates 2b, 3a, 3b) or HCN (2a, 2c). Fuel NO from the gasification gas was predicted either with the same model as for coal NO (2a, 2b, 2c), or with the Brink&Kilpinen model (3a, 3b).

Table 1. Basic features of the simulated cases.

Case	Operational condition	Other
I (base case)	Full coal and gas load	
II	Load on level 1 coal burners decreased to 60%	
III	Gas load decreased to 50%	
IV	No gas. Full coal load.	
V	No gas. Coal load increased to 133%	
VI	As Case I	Double NH ₃ in gasification gas
VII	As Case I	Half NH ₃ in gas replaced with NO
VIII	As Case I	50 % more H ₂ O in gas

The influence of the coal nitrogen content on the predicted NO_x formation was tested by reducing the nitrogen content from 1wt- % to 0.5wt-% (2c). Also, the influence on the ammonia oxidation by disabling the option of mixing limited reactions was tested (3b).

Table 2. The NO_x estimation methods used in the predictions.

Estimate	Paths considered	Fuel NO model	Intermed. N species	Other
0	Thermal	-	-	
1	Thermal, prompt	-	-	
2a	Thermal, prompt, fuel	De Soete	HCN	
2b			NH ₃	
2c			HCN	50 % N in coal
3a		Coal: De Soete Gas: Brink & Kilpinen	NH ₃	
3b				Reactions kinetically limited

RESULTS

Flow field and main combustion. The simulation results predicted very reasonable flow, temperature, and concentration fields in the furnace as compared to available measurements. Areas of high oxygen content existed close to the burner air inlets and at the over-fire air ports. In the middle of the boiler, a low-oxygen area stretched all the way up to the boiler exit. The temperature field showed high-temperature areas especially near the conventional coal burners, and in comparison, much lower temperatures close to the low- NO_x burners and the gas burners. At the conventional coal burners, no re-circulation zone was created as was the case at the low NO_x burners.

NO formation in the boiler. Figure 2 shows net NO formation rate calculated for the five operational conditions with the different model assumptions. (The codes 0, 1, 2a, 2b and 3a for the predictions are explained in Table 2.) The simulations clearly show that both thermal NO and fuel NO from coal are significant. Prompt NO and fuel NO from the gasification gas are of minor importance. The formation rate of thermal, prompt, and fuel NO combined was 100–150 gNO/s (2a, 2b, 3a). The predicted NO_x emission per unit fuel input ranged at Case I from 270 mgNO₂/MJ (0.5wt-% N in coal) to 470 mgNO₂/MJ (1wt-% N in coal). Compared to the typical measured emission 200-240 mgNO₂/MJ, the predicted absolute NO amounts were, thus, somewhat too high.

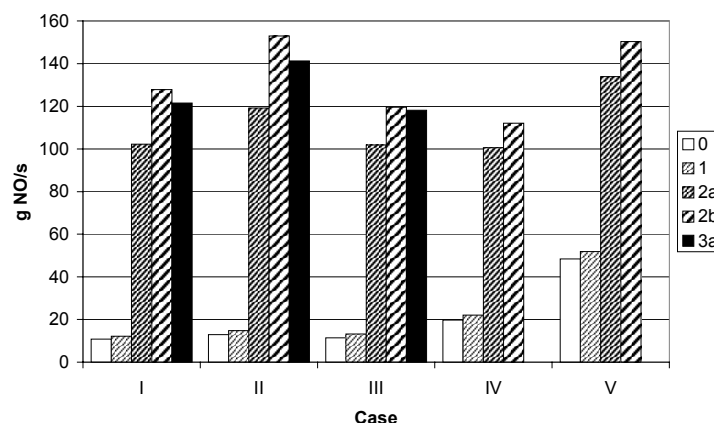


Fig. 2. Net NO formation rate (g NO/s) under the various operational conditions.

CONCLUSIONS

It can be concluded from the simulations that the conventional coal burners (level 3) dominate the NO formation in the boiler. Replacing them with low-NO_x burners, e.g., of the type used on levels 1 and 2, would obviously lower the NO_x emission from the boiler. The cooling effect of the wet, low-calorific gasification gas does have a significant effect on reducing the formation of thermal NO from the coal burners. According to the simulations, all ammonia in the gasification gas is consumed in or very close to the gas burners, and does not reduce any NO formed at the coal burners. In order to do this, the burners should be located closer to the coal burners. Typically about 60% of the ammonia in the gasification gas reacted with O₂ to NO, and 40% was reduced with NO to N₂. The predicted fate of gasification gas ammonia was not sensitive to whether the reaction rates were limited by turbulence or chemical kinetics. De Soete's model predicted higher NO formation when the intermediate species was assumed to be NH₃ (2b) than when it was HCN (2a). Also the Brink&Kilpinen model (3) clearly predicted lower NO formation than the De Soete model (2b).

ACKNOWLEDGEMENT

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Experiments in the New High-Pressure Combustor Rig at Lund

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INTRODUCTION

At the Lund Institute of Technology (LTH), a new facility to perform combustion tests at high-pressure has been built and is currently undergoing shakedown tests. The main parameters for this new test rig are: up to 1.3 kg/s air flow rate at an inlet temperature of up to 1000 K and inlet pressure up to 16 bar. The high-pressure test rig is designed for investigation of combustion phenomena, to provide data for validation of combustion models, and for development of new diagnostic methods. The scale of the facility ensures that experimental studies can be performed up to industrially relevant size and conditions.



Figure 1. Photograph of house for the new high pressure facility at LTH.

FACILITY

Figure 2 contains a schematic of the equipment associated with the rig. Air for the facility is compressed up to 16 bar by a large Roots blower located on the lower floor, while natural gas is compressed in a neighboring room (both are depicted on the first floor in Figure 2). The facility also has pumps for liquid fuels including kerosene, diesel fuel, and volatile liquids such as naphtha. A gas cylinder facility can be used to supply hydrogen or other bottled gases.

The compressed air flows up to the next floor where it is introduced into the burner housing (see Figure 3), which is located in the center of the flow system. This housing, which was designed and proven at Volvo Aero, is square in cross section with windows on all sides. There is actually an inner wall and an outer wall, and both sets are fitted with windows. The outer set contains the system pressure while the inner set isolates the high combustion temperatures.

The compressed air flows from the center towards the right in Figure 2, between these two walls, cooling the inner window

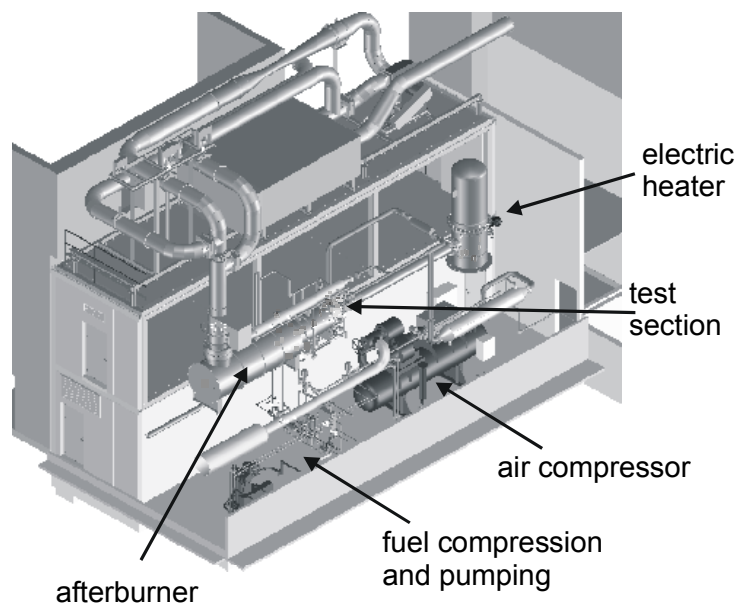


Figure 2. Schematic of the new high-pressure facility at LTH.

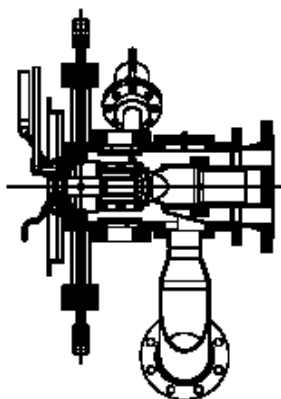


Figure 3. Test section in rig. Air enters from the bottom, flows right to cool the inner chamber, is heated and returns inside

set. In fact, a small amount of inlet air is allowed to flow along the boundary layer of the inner duct, to cool the insides of the inner windows. Most of the air, however, flows towards the right in Figure 2 (inside the annulus of the long horizontal cylinder) until it reaches the electric preheater (the vertical structure on the second floor), which heats the air up to a maximum of 1000 K. Electric preheating provides excellent control over the inlet temperature. The air then flows inside the inner cylinder back to the left, towards the combustor. Combustion can occur within various ducts that are mounted inside the optically accessible, 10 cm x 10 cm housing. Combustion products then pass through an adjustable orifice, which controls the pressure drop down to ~1 bar downstream (a system also designed and proven at Volvo Aero). Water jets cool the combustion products and they flow out the exhaust system mounted on the roof.

As an alternative, jet mixing can be studied without combustion. The resulting mixture of fuel and air is then burned in the natural gas-fired afterburner (the thick horizontal housing to the left on the second floor).

In addition to these facilities, the rig has fully automated control and safety systems. A water-cooled probe extracts gas samples through a modified scuba regulator for on-demand sample extraction. The sample then flows through a heated line to a standard gas analysis (O_2 , HC, CO, CO_2 , NO) rack. Measurement of pressure fluctuations via piezoelectric transducers is also provided.

The rig is purposely attached to the Enoch Thulin laboratory in order to place it in proximity to the numerous laser diagnostics systems available at LTH. These systems include standard diagnostics, truly unique diagnostics, and new techniques under development. Standard techniques available for use in the facility include: 1) Temperature at single point via CARS, 2) Minor gas-phase species via absorption (line of sight), LIF (single point), PLIF (imaging), 3) Major gas-phase species via Raman scattering (single point or line image), 4) Fuel imaging via Mie scattering, Rayleigh scattering and PLIF, 5) Soot via LII (single-point or images), and 6) Velocity via LDA (single point) or 3-D PIV (images).

LTH has several genuinely unique diagnostics capabilities. A fast framing camera and tunable laser system provides LIF imaging in a sequence of up to 8 images with repetition rates ranging from 100 Hz up to 100 MHz. This system can also rather easily be used for 3D visualization. A high power, narrow band alexandrite laser provides access to species with unusual spectral features. It can also be used in a filtered Rayleigh scattering experiment to acquire temperature images of a flowfield. Ultrafast laser systems (fs pulsewidths) allow detection of rapid transients and imaging through highly scattering media such as liquid fuel sprays. Polarization spectroscopy provides a spatially resolved measurement of trace species that do not fluoresce.

In recognition of the unique character of the rig, it is one of the main facilities included in a European Union Large Scale Facility for combustion that is based in Lund. Under this designation, researchers from other EU member nations can visit Lund for an extended period of time, and the interaction is fully funded by the EU.

COMMISSIONING

In the last year, the rig has been tested and modified. The compressor has been operated over the range of mass flow rates and pressures of interest, and the sensors and controllers have all been tested and trimmed. The mass flow meters have been calibrated and the igniter has been redesigned for more reliable operation. The electric heater has failed several times, been repaired and retested but it remains the weak link in the system.

Early experiments were conducted for an EU project entitled FLAMESEEK. Here, a small non-premixed flame stabilized on a backward facing disk (see Figure 5) was operated at up to 5 bar. Images were acquired using a fast-framing planar laser induced fluorescence (PLIF) imaging system (see Figure 6). These results were used to evaluate an emission-based sensor.



Figure 5. FLAMESEEK flame stabilizer; flow is left to right.

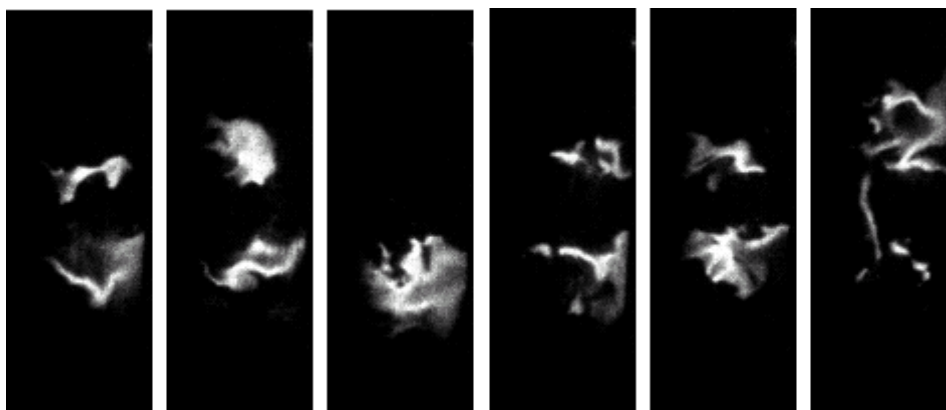


Figure 6. OH PLIF images of the flame produced by the stabilizer shown in Figure 5; flow is not right to left.

The test zone is currently fitted with a Rolls-Royce Deutschland (RRD) lean premixed prevaporized (LPP) combustor duct, which has been ignited several times (see Figure 7). We have not exceeded 5 bar absolute pressure because the current window set is not sized for higher pressures. New, higher-pressure windows will be mounted soon. After the new windows are installed we will operate the existing LPP duct up to the maximum design pressure. Following that, we will install and ignite a newer LPP duct as part of an EU FP5 program (LOPOCOTEP). This work will be followed by another FP5 program entitled AFTUR, and that will be followed by an FP6 program entitled INTELLECT.

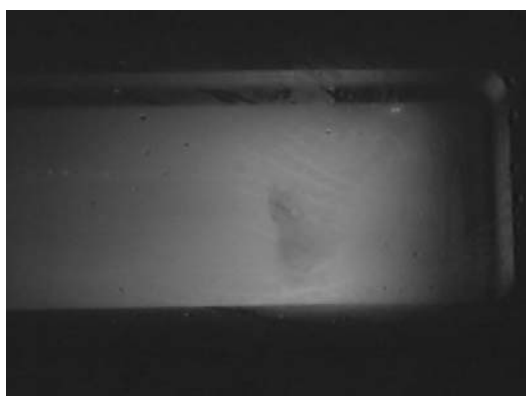


Figure 7. Photograph of LPP flame in the duct.

CONCLUSIONS

A new high-pressure combustion rig with optical access and laser diagnostics has been built at LTH. Interested researchers from the EU are invited to consider joint projects at LTH, funded by the Large Scale Facility.

UNCONVENTIONAL FUELS EXPERIMENTAL CAMPAIGNS IN ENEL SESTA FACILITY

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ABSTRACT

The paper describes the experimental campaign carried out in the ENEL Produzione Ricerca gas turbine experimental facility located in Sesta (Italy) on different industrial combustion system of the major gas turbine industrial group.

Those different projects had the scope to study and resolve different kinds of problems born during their gas turbine operation.

NOMENCLATURE

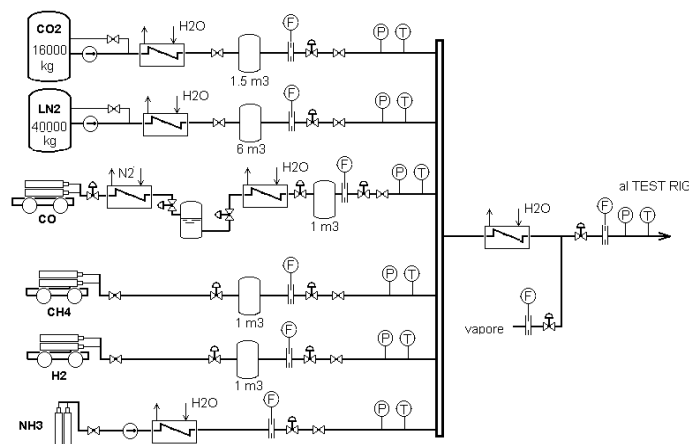
LHV	Lower Heating Value	NG	Natural Gas
DLN	Dry-Low-NO _x	LBO	Lean Blow Off
WI	Wobbe Index	HHC	Heavier Hydrocarbons
IGCC	Integrated Gasification Combined Cycle	ϕ	Equivalence Ratio
PFBC	Pressurized Fluidized Bed Combustion	LNG	Liquefied Natural Gas

1 INTRODUCTION

In the last decade, new electric power generation has been prevalently attained installing gas turbines in power plant, where NG was the primary fuel of choice. In a 10 – 15 years scenario the use of GT will keep its dominant position, but NG market could become saturated and combustion technology will be oriented towards to use of alternative fuels, such as syngas or industrial residual gases including hydrogen mixtures [1]. In the next future, the huge reserves of coal could be exploited by new coal based technologies like IGCC or PFBC and various alternative fuels could be considered as primary or back-up fuels especially in areas where gas and distillate oil are scarce.

2 UNCONVENTIONAL FUELS PLANT DESCRIPTION

Looking at this scenario, ENEL had started a program on GT problems from 1991, where an important activity was the realization of the ENEL Gas Turbine Test Facility located in Sesta (I). The first testing campaigns developed in Sesta were conducted with conventional fuels (NG and light-oil). In 1998,



ENEL decided to build a specific plant capable of unconventional fuels by mixing of different pure components.

The gases that can be added to the NG to simulate the syngas are: H₂, CO, CO₂, N₂, steam, and ammonia (NH₃) (Fig. 1). The designed syngas mass flow rate is 5 kg/s. The disposition of the different gases can be defined on the bases of each storage area, that are “Cryogenic gas”, “High pressure gas”, “Heaters gas mixture”. In the first area N₂ and CO₂ are stored in tanks in liquid phase.

Fig. 1. Schematic of the syngas plant

Each gas liquids pumped and vaporized with a steam heater to fill a buffer tank. The gases from these buffer tanks are fed into a manifold where the mixing occurs. The high-pressure gas storage area is

inside the restricted fuel area with 4 bunkers containing methane bottle trucks. When testing syngas, two methane bottle trucks will be replaced with the CO and H₂ bottle trucks. The CO is liquefied and stored in a tank to assure the daily quantities. The pressure of CO and H₂ is 200 bars and is regulated to the normal supply pressure (28 bars). Downstream of the syngas manifold, a heater placed near the test rig allows to increase the mixture temperature as required. A PLC system monitors and controls the pressure, temperature, and mass flow rate of each gas involved, and sets the alarms and trips. In order to simulate variations in natural gas composition, ENEL had installed a HHC plant (Fig. 2) capable of mixing heavier hydrocarbons into the methane. The ethane is mixed with NG in gaseous phase, and the liquid propane/butane is pressurized and injected into the hot methane/ethane mixture.

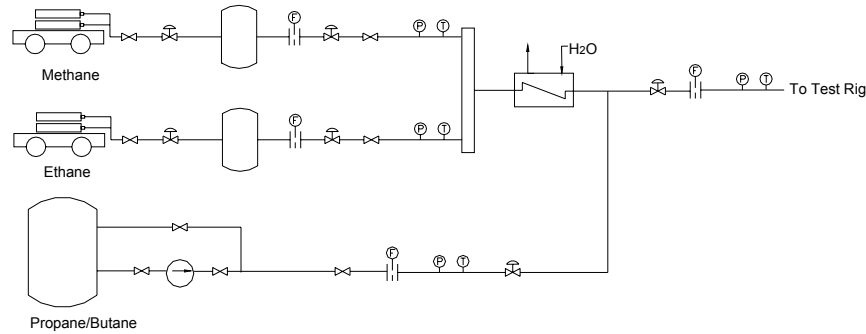


Fig. 2. Schematic of the HHC plant

3 ENEL INVESTIGATIONS ON GT COMBUSTOR FED BY H₂/CH₄ MIXTURES

3.1 Testing phase: scope and condition

The gas turbine combustor under investigation is a typical conventional reverse-flow can combustor at a pressure level of about 1 MPa [2]. Chemical reactions occur simultaneously with fuel injection and mixing, creating a diffusion flame combustion process. Tests were conducted using the syngas plant using pure NG, pure H₂ and the mixture with equal heat input from H₂ and NG. The test conditions simulated the same gas turbine working parameters: ignition and loading were conducted with only NG; at 40% of base load, H₂ was introduced in the fuel manifold to have the desired mixture.

3.2 Experimental results: Combustion noise

The combustor has shown wide ignition zone and also a good flame stability at each load, both using NG and H₂. The maximum pressure fluctuation was about 25 mbar (at 220 Hz) with NG. During fuel change over, no blow-off or flashback was encountered. With H₂ mixtures, pressure fluctuations were lower than using NG, due to the higher burning velocity that enhances flame stability.

3.3 Experimental results: Metal temperature distribution

Metal temperatures were measured on basket and transition piece. With different mixtures, from pure natural gas to pure H₂, temperature distributions were identical except for quite difference observed near the primary zone. LHV and burning velocity increased with higher H₂, moving the flame front to the flame holder, reducing the flame volume and increasing the maximum temperature level.

3.4 Experimental results: Pollutant emissions

Increasing of NO_x emission with the increasing of H₂ percentage in the fuel was encountered, up to 3.4 times greater than using NG. This was due to the higher flame temperature as well as the worse mixing quality. The overall ϕ_{pz} , fuel injection velocity, and flame temperature are listed in Table 1.

	ϕ_{pz}	T_{pz} [K]	$T_{\phi=1}$ [K]	Fuel Velocity [m/s]	Mach n°
Hydrogen	0,808	2354	2564	565	0,42
Natural gas	0,89	2308	2408	157	0,33

Table 1. Baseload fuel injection characteristics

With pure H₂, the fuel jet penetration was greater than NG, creating a very high fuel rich region with high production of thermal NO_x in the primary combustion zone. Using Lefebvre's empirical correlation for NO_x emissions with stoichiometric temperature values [3], the ratio between the NO_x emission from pure H₂ and from NG was about 3.8, fits well with the experimental data.

4 SIEMENS WESTINGHOUSE TESTS ON HEAVY HYDROCARBONS

4.1 Testing phase: scope and condition

High levels of HHC (ethane and heavier) have been observed in the power generation NG supply. The higher amount of HHC in the natural gas results in a higher WI. WI variation can cause bad fuel/air mixing profile in the lean premix burners. Furthermore, the lower autoignition temperatures of the HHC can lead to higher potential of flash back in DLN combustor [4]. Large amount of HHC in the NG supply could affect emission and cause combustion noise in DLN combustors.

Most LNG sources contain less than 12% ethane, less than 3.0% propane and less than 1.5% butane and heavier. However, few LNG sources contain higher propane and heavier (< 6% propane). In this testing, different fractions of heavier hydrocarbons were simulated.

The testing was conducted for the W501F DLN combustor using the HHC plant. The combustor was ignited with methane. Heavier hydrocarbons were introduced when the heaters were ready. The fuel compositions were monitored continuously with a gas chromatographer. When the gas compositions stabilized, steady state points were taken at different load levels.

4.2 Experimental results

In the tests, various parameters were monitored. The combustor behavior was as expected:

- No flashback was observed
- Significant increase of HHC in the fuel resulted in off-design fuel/air mixing profile, leading to higher combustion dynamics in intermediate frequencies and higher NO_x emission. However, the pressure fluctuation at low frequencies was quiet.
- With significant HHC in the fuel, the metal temperatures of the combustor basket increased. However, the changes were small and the metal temperatures were well below operational limit.
- With different fuel-staging schedule, the combustor was able to compensate for the high fuel Wobbe Index variation. And the combustor could maintain the performance both in emission and combustion dynamics for the reasonable level of the heavier hydrocarbons in fuel.

5 SIEMENS WESTINGHOUSE TESTS ON SYNGAS MIXTURES

5.1 Testing phase: scope and condition

Syngas is the LHV gas generated by gasifying solid or liquid fuels rich in carbon. Depending on the feed stock and gasification method, the heating value as well as the H₂/CO ratio varies. Typical oxygen blown syngas has a lower heating value between 11.2 and 13 MJ/Nm³. And the air blown syngas can have LHV as low as 1/3 of the oxygen blow syngas. The syngas compositions vary significantly depending on the gasification method, feed stock, and H₂ extraction. H₂ can vary from 10% to 60%, and the CO can vary from 20% to 60%. With the inerts in syngas (N₂ or steam), LHV is typically below 8 MJ/Nm³. Siemens has demonstrated the capability of GT design for IGCC application [5, 6]. This testing was to evaluate the extension of the W501D5 syngas modified conventional combustion system to the W501F operating conditions. A standard W501F conventional combustor basket was used. The burner design was similar to the syngas burner used in W501D5 [5] with syngas injectors enlarged to accommodate the larger fuel flows required for W501F conditions. The tested syngas consisted of CH₄, H₂, CO, and steam. It simulated typical oxygen blown syngas, with variation of H₂/CO ratio and steam dilution for NO_x control. The syngas mixture was heated to avoid condensation from the steam.

5.2 Experimental results

The testing started with NG to ensure stability at part and full loads; same conditions were tested on syngas while optimizing the steam content in the syngas for NO_x control. The tests demonstrated:

- Extremely stable flame during syngas operation over a wide range of loads and gas compositions.
- NO_x emission target at baseload can be achieved with steam as diluent; Near zero CO emission can be achieved except FSNL (Full Speed No Load).
- Reliable ignition and loading with NG; smooth transfer between NG and syngas operation.
- Higher combustor basket temperatures were observed. However, the temperature level was acceptable for safe operation.

6 ANSALDO ENERGIA TEST CAMPAING ON STILL MILL FUEL GASES

6.1 Testing phase: scope and condition

Following the increasing demand of burning alternative fuels other than the natural gas, Ansaldo Energia has been investigating the re-design of the original Siemens low BTU burner in order to meet

the new fuels requirements. Therefore a test campaign, following the design phase, has been arranged regarding to the following points:

- 1) Flame stability under all working conditions of the machine
- 2) NO_x emissions
- 3) Burner metal tip temperature

Combustion tests have been performed with the three still mill gases (Table 2). A pre-test campaign

ELETTRA A				
Species	mol. (%)	wt. (%)	Density (0° C, 1.013 bar)	1.167 kg/m ³
N ₂	45.90	49.53	Hu	7267.0 kJ/kg
H ₂ O	0.00	0.00	Mol mass	0.0261 kg/mol
CO ₂	13.63	22.99	Stoichiometric A/F ratio	2.28
H ₂	9.05	0.70	Laminar Flame velocity	0.40 m/s
CO	18.28	17.47	CO/H ₂	1.80 mol/mol
CH ₄	15.15	9.32		
ELETTRA B				
Species	mol. (%)	wt. (%)	Density (0° C, 1.013 bar)	0.977 kg/m ³
N ₂	23.58	31.31	Hu	10302.1 kJ/kg
H ₂ O	27.01	22.57	Mol mass	0.0216 kg/mol
CO ₂	8.11	16.56	Stoichiometric A/F ratio	3.36
H ₂	9.79	0.92	Laminar Flame velocity	0.36 m/s
CO	9.88	12.84	CO/H ₂	1.01 mol/mol
CH ₄	21.23	15.80		
ELETTRA C				
Species	mol. (%)	wt. (%)	Density (0° C, 1.013 bar)	1.241 kg/m ³
N ₂	48.29	48.98	Hu	7286.4 kJ/kg
H ₂ O	0.00	0.00	Mol mass	0.0278 kg/mol
CO ₂	14.50	22.99	Stoichiometric A/F ratio	2.334
H ₂	1.52	0.11	Laminar Flame velocity	0.32 m/s
CO	16.92	17.07	CO/H ₂	11.1 mol/mol
CH ₄	18.77	10.85		

has been performed at atmospheric conditions and a final verification test has been performed at actual machine pressure and temperature, where base load conditions were simulated by adjusting the combustion air velocity. In this case a flame flow field being independent from test pressure level and relevant to machine conditions is provided. During all test operation periods, the dried exhaust gas was online analysed for O₂ and CO₂ to have an independent control of the adjusted flow rates (air excess ratios). Only test periods for which the adjusted and measured air and fuel mass flows correlated correctly with the O₂ and CO₂ based calculated air excess ratios were used for evaluation.

Table 2: Still mill gases tested

The whole test campaign has been divided into two steps:

- a) atmospheric tests, performed at Ansaldo Caldaie test facility located at Gioia del Colle (Italy) whose main aim has been to get an overview of the burner performances of the different steel mill gas nozzle designs, especially in terms of flame stability and burner temperatures.
- b) pressurized tests, performed at ENEL facility in Sesta whose main aim has been to test the burner performance at actual pressure condition in order to verify the behaviour of the burner in a reasonable way at operating conditions of the machine.

6.2 Experimental results: Lean Stability Limits

Gas Turbine operation with still mill-NG mixture is foreseen in the load range between 60% and base load. To check for the burners' capability to burn the different fuels in stable way under all possible operating conditions, the weak extinction limit has been investigated; to cover the worst case condition, all LBO points were measured with the minimum machine air temperature of 280°C.

The results showed, in the variation range of the relative burner air velocity, the measured lean blow off curves were in general flat with a small increase of the blow off air ratios at reduced air velocity.

However, a different behaviour with respect to the pressure influence has been found out. The Fuel A and B looked not sensitive to the pressure whilst Fuel C (minor H₂ content) was showing decreasing stability when increasing pressure. Finally, the results showed wide stable flame region against flame extinction from 60% to base load thus confirming what expected.

6.3 Experimental results: NO_x emissions

Fuels	NO _x [mg/Nm ³]
A fuel	34
B fuel wet	24
C fuel	20
Natural gas wet	56

Table. 3. NO_x emission results

The emission measurements were tested at actual base load conditions not only for the three different fuels tested, but also for the natural gas mixed with steam. Furthermore with Fuel B and NG, a sensitivity analysis was performed on steam/fuel ratio in order to optimise the combined cycle efficiency to the emission level guaranteed. The results are shown in Table 3. No problems were found in complying the NO_x emissions guarantee for both ELETTRA fuels and the NG (70

mg/Nm³ @ 15% O₂ in the dry exhaust gas), which confirmed the very good behaviour of the new ANSALDO diffusion burner for typical low BTU fuels coming from gasification process.

6.4 Experimental results: Burner temperatures

Secure operation of a burner is only possible as long as the temperature limits of the burner materials are not exceeded. For this reason, the burner temperatures at the tip of the axial swirler and the diagonal swirler have been measured systematically at actual machine base load conditions.

The tests confirmed maximum metal temperatures for operation with A, B, and C fuels are far below the limit of the high quality material used (Hastelloy and Nimonic).

7 CONCLUSION

H₂ mixture were used by ENEL with quite good success on a conventional GT combustion system. Pressure fluctuations were under critical limits at each thermal load. Increasing the H₂ in the mixture, metal temperatures have shown negligible change, except in the primary zone region. NO_x emissions have shown an evident increase with H₂, confirming that having H₂ in the fuel the Zeldovich mechanism becomes the prevalent.

Tests were conducted with W501F DLN and conventional combustor running simulated LNG and syngas. Test results were reasonable and the combustor designs were proved to be able to burn the simulated LNG and syngas without sacrifice of combustor performance.

The performance of the ANSALDO V94.2K low BTU fuel burner, designed for operation with the steelworks gas – NG mixture, was systematically tested up to real machine conditions.

The weak extinction limit observed with increasing test pressure showed a constant flame stability limit for A, B fuel and regressive for fuel C. The present safety margins have been enlarged with the possibility to include the secondary air port option into the combustion. This gives a more stable operation with ELETTRA fuels for all lean machine conditions. NO_x emissions measured lay well below the guaranteed limit of 70 mg/Nm³ at full machine conditions, indicating the ideal combination of the simple diffusion mode combustion concept with LHV fuels. Burner metal temperatures at all pressure levels were below the critical limit for the material used at the most exposed parts.

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Influence of Air-Fuel Ratio and Air Temperature on Combustion Time of Air-Methane Mixtures in Stationary and Turbulent Condition

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INTRODUCTION

Within the sphere of combustion processes in the electric power production systems, the development of techniques and innovative procedures plays a major part in the design and the management of energetic systems oriented to the protection of environment.

The development of electric power production systems and CHP (combined heat & power) plants in the range of 5 up to hundreds of MW (electric) has been growing up basing on gas turbine technology, mostly burning methane. Particularly in gas turbine air-fuel global ratio is always in lean or very lean condition so the methodological approach to the analysis of combustion process is very complex also due to random parameters involved.

A critical role is played by turbulence: its influence as well as on transport phenomena, is directly connected to the reduction of airflow and on the improvement of fuel air mixing.

Chemical reactions and mixing are strongly influenced by turbulence intensity ([2]...[6]): that's why it's necessary to assign the right mixing condition for air fuel mixture in order to have a good combustion process.

Another critical role is played by residence time in combustion chamber which must be very small in order to minimize chamber dimension and very high to reduce pollutant formation; the lean condition combustion doesn't allow to have short residence times so the burning process has to be divided into a number of steps, starting from a richer pilot flame and going on with lean premixed ones.

OBJECTIVES OF THE WORK

The starting point of this work is the analysis of Dry Low NO_x combustion chambers of gas turbines for cogeneration plant in the range from 5 to 150 MW of electric output. In particular the attention was focused on the premixed air-methane stream and its interaction with the pilot flame. In fig. 1 a typical configuration of this type of combustion chamber is reported.

The lean premixed air-methane mixture, coming from premixers has to be heated from the pilot flame in order to reach the ignition condition and to burn completely and quickly during its passage through the chamber.

The main objective of the work has been the analysis of the correlation between the residence time and so the space needed from the lean mixture to burn completely and the heat needed to be achieved from the pilot flame in order to do it.

This is an useful information in design phase, in sizing the correct amount of heat to be delivered from the pilot flame to the lean mixture coming from premixers.

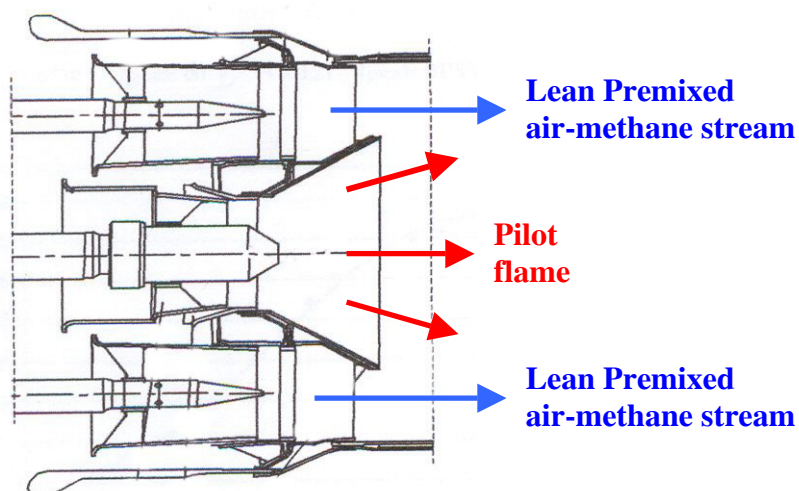


Fig.1: Scheme of the first section of a typical TG combustion chamber

NUMERICAL MODEL ADOPTED

The burning process of the lean premixed mixture has been simulated by a plug flow in a cylindrical duct. The heat transfer from the pilot flame has not been simulated but only taken into account by a temperature increase of the lean mixture before its passage in the combustion zone.



Fig.2 Mono-dimensional plug flow adopted for simulation

PLUG simulates the behavior of plug-flow chemical reactors. More specifically, the program is designed to model the non-dispersive, one-dimensional flow of a chemically reacting, ideal-gas mixture in a duct of essentially arbitrary geometry. The program makes use of the CHEMKIN and SURFACE CHEMKIN Utility packages to handle gas-phase and heterogeneous kinetics, as well as species thermodynamic properties.

PLUG solves the set of differential/algebraic equations describing the reactor using the implicit numerical software DASSL the set of differential/algebraic equations describing the reactor. These equations are briefly presented here, followed by the procedures for running PLUG.

The equations governing the behaviour of the plug flow reactor are simplified versions of the general relations for conservation of mass, energy, and momentum. They can be derived most easily by writing balances over a differential slice in the flow direction x , with the stipulations that (a) there are no variations in the transverse direction, and (b) axial diffusion of any quantity is negligible relative to the corresponding convective term. In this way the overall mass balance (continuity equation) for the gas is found to be:

$$\rho V \frac{dA}{dx} + \rho A \frac{dV}{dx} + VA \frac{d\rho}{dx} = a_i \sum_{gas}^{K_g} \dot{g}_k W_k \quad (1)$$

Here ρ is the (mass) density and V the axial velocity of the gas, which consists of K_g species; W_k is the molecular weight of species k , and $\dot{g}_k$ is the molar production rate of this species by all *surface* reactions. The quantities A and a_i are the cross-sectional (flow) area and the internal surface area per unit length, respectively, of the reactor; each can be a function of x . Equation (1) simply states that the mass flow rate of the gas can change as a result of generation or consumption by surface reactions. A similar equation can be written for each species individually:

$$\rho VA \frac{dY_k}{dx} + Y_k a_i \sum_{gas} \dot{g}_k W_k = W_k (\dot{g}_k a_i + \dot{\omega}_k A) \quad (2)$$

Here Y_k is the mass fraction of species k and $\dot{\omega}_k$ is its molar rate of production by homogeneous *gas* reactions. Such reactions cannot change the total mass of the gas, but they can alter its composition.

Turning now to the energy equation, one finds.

$$\rho VA \cdot \left(\sum_{gas} h_k \frac{dY_k}{dx} + \bar{C}_p \frac{dT}{dx} + V \frac{dV}{dx} \right) + \left(\sum_{gas} h_k Y_k + \frac{1}{2} \cdot V^2 \right) \cdot a_i \sum_{gas} \dot{g}_k W_k = a_e Q_e - a_i \sum_{bulk} \dot{b}_k W_k h_k \quad (3)$$

where h_k is the specific enthalpy of species k , $\bar{C}_p$ is the mean heat capacity per unit mass of the gas, T is the (absolute) gas temperature, and $\dot{b}_k$ is the molar production rate of bulk solid species k by surface reactions. The distinction between bulk and surface species is discussed somewhere else.

The momentum equation for the gas expresses the balance between pressure forces, inertia, viscous drag, and momentum added to the flow by surface reactions. Thus

$$A \frac{dP}{dx} + \rho VA \frac{dV}{dx} + \frac{dF}{dx} + V \cdot a_i \sum_{gas} \dot{g}_k W_k = 0 \quad (4)$$

where P is the absolute pressure and F is the drag force exerted on the gas by the tube wall, to be discussed below. The pressure is related to the density via the ideal-gas equation of state:

$$P \bar{W} = \rho RT \quad (5)$$

where R is the universal gas constant and $\bar{W}$ is the mean molecular weight.

Since the heterogeneous production rates will depend, in general, on the composition of the surface as well as that of the gas, equations determining the site fractions Z_k of the K_s surface species are now needed. Assuming that these species are immobile, the steady-state conservation equations are extremely simple:

$$\dot{s}_k = 0 \quad (6)$$

i.e., the net production rate of each surface species by heterogeneous reactions must be zero. the dependent variables ρ , u , T , P , ρ , Y_k and Z_k . The functions $\bar{W}$, h_k , $\bar{C}_p$, $\dot{\omega}_k$, $\dot{g}_k$, $\dot{s}_k$ and $\dot{b}_k$ can all be expressed in terms of these and are obtained from calls to CHEMKIN and SURFACE CHEMKIN subroutines.

NUMERICAL RESULTS

Numerical results are summarized in the diagram reported in fig. 3. Different duct lengths have been considered: for each of them the inlet temperature of the stream versus the

air/methane volumetric ratio is reported: that is the temperature needed from an assigned (air/fuel ratio) mixture to completely burn in the assigned duct length.

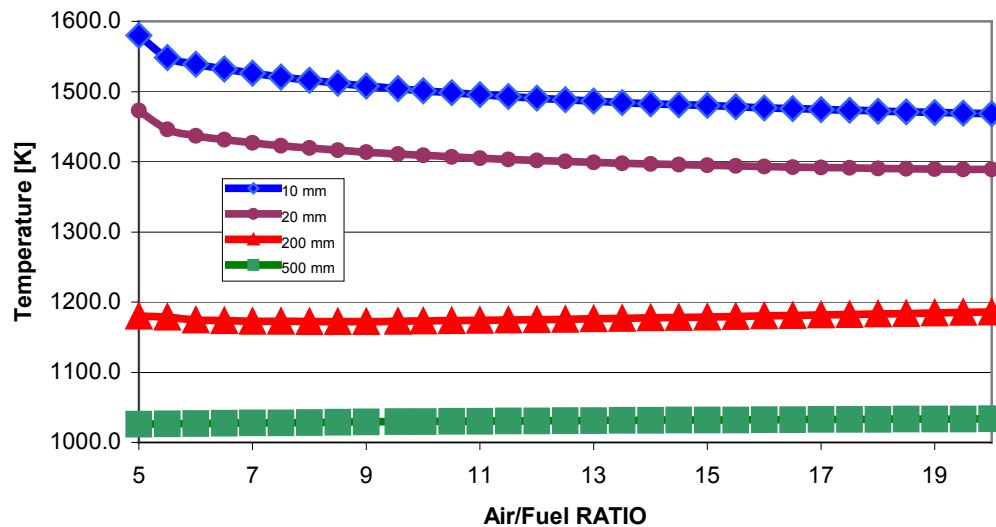


Fig. 3 Inlet mixture temperature vs air fuel ratio, for different geometrical configuration.

It can be noticed by this plot that the shorter is the duct length the higher is the influence of the air fuel ratio on combustion: that's for low air fuel ratio an higher inlet temperature is needed in order to burn completely along the duct length.

This diagram is an useful tool in combustion chamber design, because it allows to evaluate the heat amount needed by an air fuel mixture to burn in a given length, starting from a given inlet temperature and composition. Particularly it allows to size the pilot flame in order to give the right amount of heat to the lean premixed stream.

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Numerical Evaluation of Main Features of Chemical Models for Motor Fuel Surrogates.

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INTRODUCTION

To control Homogeneous Charge Compression Ignition (HCCI) engine operation, different means have been proposed such as variation of fuel injection timing (early injection of a portion of fuel), boost pressure, adjusting of trapped residual gas fraction, usage of ignition improvers, etc. Since chemical kinetics plays a larger role in HCCI engines than in other classes of IC engines, only the detailed chemistry modeling can provide the insight in the process development. However, because most practical hydrocarbon fuels are blends consisting of large amounts of aliphatic and aromatic components, satisfactory modeling of HCCI combustion would not be possible without development of simplified, but still comprehensive, models for motor fuel (diesel oil and gasoline) surrogates nevertheless representing the main features of auto-ignition and combustion of real fuels. In this paper, it is described how the gasoline surrogate model integrating the detailed oxidation kinetics of generic species such as iso-octane, n-heptane and toluene has been developed, validated and applied to the HCCI engine modeling. The chemical mechanism was constructed using the main steps outlined in Ogink and Golovitchev (2001) and then: 1) comparison of predicted ignition delays for the generic fuel components with the shock-tube experimental data, 2) investigation of mixture composition effects on auto-ignition of different blends representing gasoline fuel, and 3) investigation of natural combustion improvers (intermediate combustion products) effects on auto-ignition and combustion developments in the model HCCI engine described in Endo et al. (2001) have been carried out.

Since adjusting the retained residual gases in the HCCI engine cylinder (see Koopmans and Denbratt (2001)) is considered to be a strong candidate for controlling the ignition timing, the chemical effect of different species of the exhaust gas composition on ignition enhancement is analyzed.

CHEMICAL MODEL OF GASOLINE SURROGATE

Since the major reaction pathways in aliphatic hydrocarbon combustion are well established and since n-heptane and iso-octane are primary reference fuels, their detailed oxidation mechanisms were recently developed and available e.g. from Curran et al. (2002). Using sensitivity analysis, a remarkably reduced mechanism for reference fuels can be derived by neglecting unimportant side branches, see Golovitchev (2002). While significant advances have been made in the understanding of aliphatic hydrocarbon combustion kinetics, comparatively fewer progress has been achieved in the study of the aromatics kinetics. Although several kinetic models of benzene and toluene oxidation have been published and tested on the bases of individual experiments by Emdee et al. (1992), Howard (2001), the mechanisms were not included yet into the motor fuel compositions. The presence of toluene in the fuel surrogate model can be motivated by the fact that residual oil cracking produces alkanes and aromatic hydrocarbons with approximately the same number of carbon atoms. The mixture composition consisting of 55 % iso-octane, 35 % toluene and 10 % n-heptane is assumed to represent gasoline in the surrogate model under study.

Let us outline briefly the main steps of the toluene mechanism included into the gasoline surrogate model. The initiation step of toluene oxidation is assumed to be a benzylic hydrogen atom abstraction from the methyl side of the toluene molecule giving the benzyl radicals. These radicals are assumed to play a significant role: the radicals are very stable, but their recombination with HO_2 leading to the unstable benzylhydroperoxide species decomposing to benzylaldehyde is the key reaction at intermediate temperatures. The low temperature

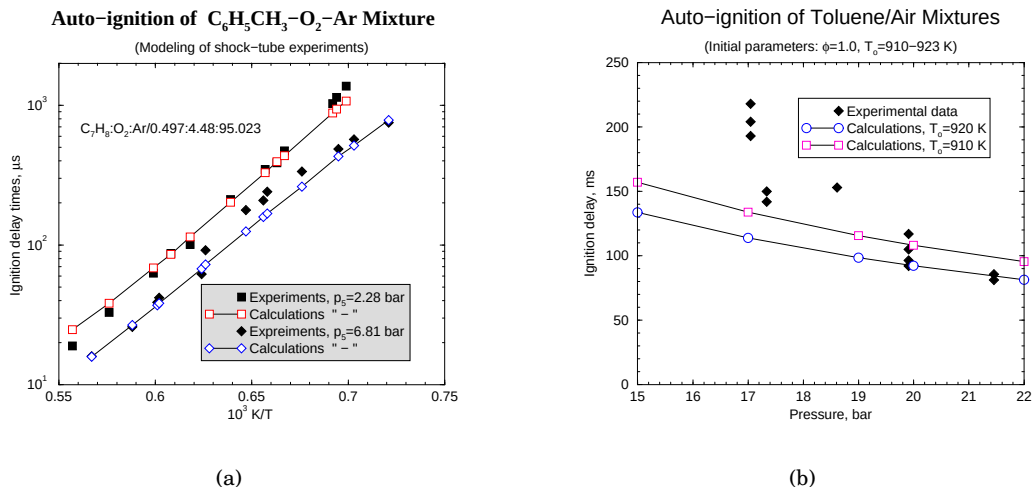


Figure 1: Experimental (filled symbols) and computed (lines) ignition delay times for a) toluene -oxygen -argon mixtures studied in shock tube experiments; b) toluene-air ($\phi=1.0$) mixture in RCM experiments.

mechanism involving benzylhydroperoxide as the intermediate adduct was highly simplified since the auto-ignition of toluene in the mixture with n-heptane and iso-octane will be mainly driven by the most reactive species. As far as soot formation was out of the scope of this work, the molecular mass growth reactions were not accounted for. The current model of the gasoline surrogate consists of 105 species participating in 537 reactions. Kinetic calculations were carried out using the Chemkin-2 code by Kee et al. (1992).

At first, the toluene mechanism has been validated against two sets of experimental data: 1) shock tube auto-ignition data presented in Burcat et al. (1986), and 2) rapid compression machine (RCM) auto-ignition experiments reported in Lemaire et al. (2001). From results presented in Fig. 1 a-b) it follows that the model

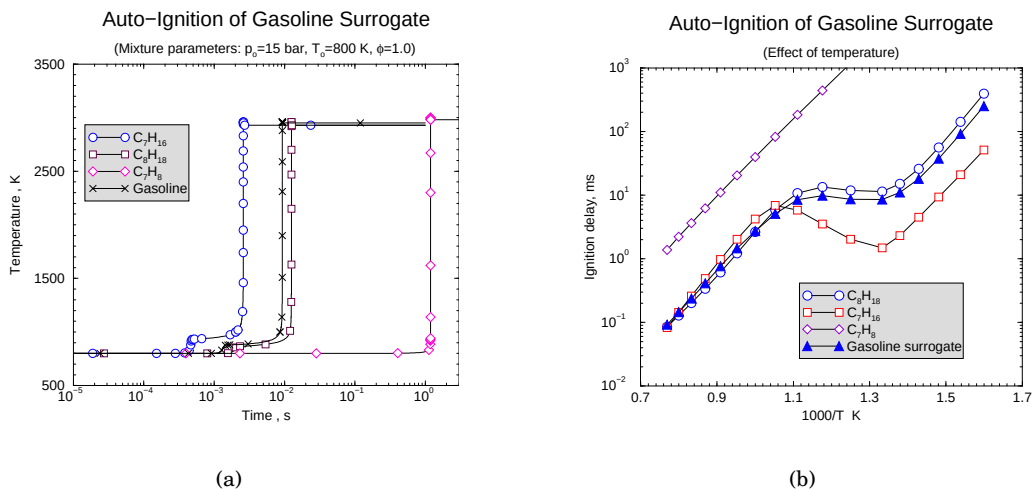


Figure 2: Calculated a) temperature vs time histories for gasoline surrogate (55 % iso-octane, 35 % toluene, and 10 % n-heptane) and its components, b) ignition delay times relevant to simulation of shock-tube ($v=\text{const}$) experiments. Initial mixture parameters: $p_0=15$ bar, equivalence ratio, $\phi=1.0$.

complies with Burcat et al. experimental data quite well for different pressures and toluene-oxygen-argon compositions. The discrepancy in the data involving high pressure RCM experiments could be the result of experimental inaccuracy because the measured values at lower pressures are scattered to such an extent which cannot be explained by the temperature variation at TDC of the rapid compression machine within the range 912-923 K specified in the experiments.

The predicted ignition delays simulating shock-tube experiments for gasoline surrogate and its components at the engine relevant conditions are presented in Fig. 2 a-b). From the predicted temperature vs time histories follow that the two-stage auto-ignition mechanism typical for n-heptane (most reactive component) and iso-octane is not revealed in the case of toluene. The auto-ignition properties of the gasoline surrogate are found close to those of iso-octane. The less reactive blend component (toluene) has a little impact on the gasoline surrogate auto-ignition due to the compensating effect of n-heptane.

FURTHER RESULTS AND DISCUSSION

The most important issue of the chemical model development was to simulate HCCI regimes in a combustion chamber of the test engine specified in Endo et al. (2001). The model engine geometry is characterized by following sizes: bore= 17.0 cm, stroke= 22.0 cm, squish=0.32 cm, $r_c=18$, etc. In this case, the initial value problem for the temperature, pressure, and composition of the mixture was solved with the help of the SENKIN code of the Chemkin-2 package specifying the engine volume change as a function of time. To simulate the piston reciprocating motion and the cylinder volume and surface changes, the model has been coupled with slider-crank and heat transfer models. The last one was formulated as a two-zone model with a given wall temperature and assuming an existence of a unique characteristic heat transfer time (equal to 4.4×10^{-5} s) chosen to be constant for all regimes studied. Auto-ignition of a homogeneous gasoline-air charge of different compositions has been investigated. The predictions corresponding to the intake (atdc=-180 deg) temperature 323 K, the intake pressure 2.182 bar, the engine speed 1200 rpm are presented in Fig. 3 a-b).

In Fig. 3a), species of the mixture composition vs Ca histories are presented illustrating the HCCI process development. The ignition starts before TDC and is characterized by a rapid growth of intermediate and main product concentrations; among fuel components, at first n-heptane is consumed, then iso-octane and, finally, toluene. The mixture composition before and after TDC is characterized by high, nearly constant concentrations of such intermediates as formaldehyde and hydrogen peroxide. The effect of these species (which are stable and could be components of the exhaust gases retained in the combustion chamber) present in the initial mixture composition on the auto-ignition process has been studied, and the predictions are presented in

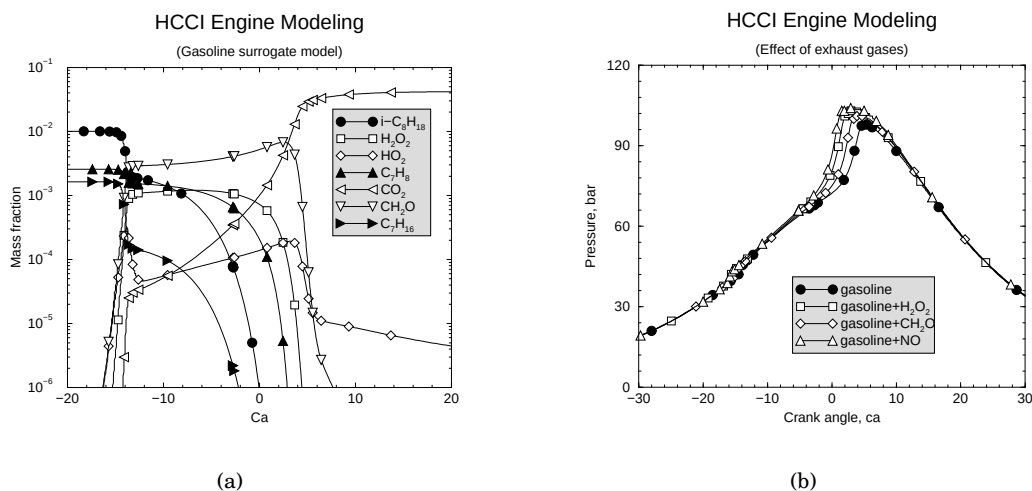


Figure 3: Calculated a) mixture composition vs Ca histories for gasoline surrogate (55 % iso-octane, 35 % toluene, and 10 % n-heptane), b) in-cylinder pressure vs Ca histories for different ignition improvers.

Fig. 3b). It can be seen that the presence of such species leads to acceleration of the auto-ignition process and the peak pressure rise at TDC. Hydrogen peroxide is a more efficient ignition improver than formaldehyde.

It was supposed (see Faravelli et al. (2003)) that at low temperature oxidation of hydrocarbons, nitrogen monoxide, NO, which is also the component of exhaust gases, can significantly enhance auto-ignition of the fuel charge in the engines. Under these conditions, the influence of NO on the oxidation process, as it discussed in Faravelli et al. (2003), is mainly to provide a more rapid build-up of the radical pool by activating peroxy radicals. The transformation of HO_2 to OH is responsible for ignition enhancement. Also NO can provide chain-carriers at low temperatures by interacting with methylperoxy, CH_3O_2 radicals. The reactions responsible for such a modification of the oxidation process were included in the mechanism developed.

The calculations (see Fig. 3 b) illustrate the mechanism capability to predict the promoting effect of NO (in a molar concentration twice less than the n-heptane content in the fuel composition) on the auto-ignition of gasoline surrogate. The NO ignition acceleration effect under the HCCI engine conditions is more significant than the effects of CH_2O and H_2O_2 .

CONCLUSIONS

The gasoline surrogate model represented as a mixture of iso-octane, toluene and n-heptane and consisting of 105 species participating in 537 reactions integrating kinetic mechanisms of the generic components has been developed and validated using the auto-ignition data for the generic species at different simulation conditions. The ignition properties of the gasoline surrogate were predicted close to those for iso-octane.

The mechanism has been applied to the analysis of the model HCCI engine; the promoting effects of different species which are component of the engine exhaust gases have been studied. The NO ignition acceleration effect at HCCI engine conditions was found to be more significant than the effects of hydrogen peroxide and formaldehyde.

ACKNOWLEDGMENTS

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Electrically Assisted Sprays for Combustion Purposes

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INTRODUCTION

Traditional atomizers operate on liquid breakup mechanisms by supplying energy, often using a subsidiary gas flow, or mechanic energy, by means of moving or vibrating devices. These systems allow to obtain fine and monodisperse sprays, but the atomization process is not very efficient, being a large part of the supplied energy retained by the drops as kinetic energy.

Higher efficiencies may be reached by EHD atomization. The first effect of charge injection is the jet striction, through a mechanism first modeled by Taylor [1]. This striction reduces the jet diameter so that the size of the droplets formed during the jet break-up is reduced accordingly. In addition, applied voltage induces an intensification of varicose instabilities and gives rise to kink instabilities that promote a better liquid disruption [2][3]. If the droplets are injected in a high temperature region the evaporation increases charge-to-mass ratio and, if the *Rayleigh limit* for the surface charge is reached, the droplet can undergo a secondary breakup producing an even finer spray. Moreover, because of electrostatic repulsion among charged drops, coalescence is reduced to a minimum and the spray angle is increased enhancing the dispersion of liquid in the gas phase.

In addition to the higher efficiency of the process, the use of electrosprays in combustion appears to be promising at least for two reasons: first of all, in theory it could be possible to keep suitably low the liquid velocity, making easier the stabilization of a flame; second, charge injection on liquid drops could allow for the realization of an active control on the atomization process and, hence, of the combustion process. This aim could be achieved with a modulation of some spray properties, such as drop size or spray angle, and applied voltage appears to be a flexible controlling parameter.

While electrosprays represent a commonly used tool for other technological applications, most of all electrospray ionization for mass spectrometry, few results have instead been achieved in the attempt to use EHD atomization in the spray combustion [4], essentially regarding some applications to special cases, for instance miniaturized combustors as components of energy conversion systems [5]. Nevertheless the physics governing the process of combustion of electrically charged fuels appears to be still out of our comprehension.

Previous studies on combustion of positively charged liquids have shown that the presence of flame significantly reduces the spray quality [6]. This fact could be due either to heat transfer phenomena and to the interaction between the electric charges on drops and the electric charges normally observed in flames. In particular it is possible to suppose that radical species, formed in the combustion process, induce a neutralization of drop charge. It is evident that the possibility to largely use charge injection for liquid fuel atomization passes through a better understanding of these complex mechanisms. In this context the motivation of the present study on the effects of polarity inversion on EHD atomization is to understand how the choice of the polarization of the liquid can affect the atomization, possibly obviating to charge neutralization, and then, acting on atomization, modify the combustion conditions.

The rich variety of regimes observed in EHD spraying suggested to study polarity inversion effects by comparing atomization conditions through stability maps obtained in either positive or negative polarization conditions, such as those presented by other authors [2][7-9].

Images collected by a digital camera, with a sufficient time resolution, can provide a first identification of the spraying modes. In this paper results obtained by means of direct spray visualization have been compared with quantitative information on droplet size and velocity,

measured by using a PDA system. The systematic comparison of the result of the two techniques allowed for an unambiguous identification of the atomization regimes and of their characteristic droplet size distributions. It is interesting to note that PDA systems have been largely used in the characterization of EHD sprays [10][11], but never for a systematic characterization of the regimes.

EXPERIMENTAL SETUP

The configuration adopted for the atomizer is the needle-to-plate scheme, showed in fig. 1a. An electric potential of up to 10 kilovolts is applied between the needle, used to supply the liquid, and a metallic plate placed 3 cm below the tip of the needle. The stainless steel needle inner diameter is 0.25 mm and the outer one is 0.4 mm. The capillary is shielded by an insulating cylinder and supported by a coaxial plexiglas prism, bound to a micrometric moving device. The metallic plate is placed in a basin for liquid recovering. The whole system has been insulated from external aerodynamic and electrostatic perturbations. To this purpose a cylindrical plexiglas shield and a coaxial iron mesh, kept floating, have been used.

Atomized liquid is n-heptane doped with 0.5% vol. of Stadis® 450 to enhance electric conductivity without significantly affecting other liquid properties. Electric conductivity of doped n-heptane is $6.76 \cdot 10^{-7} (\Omega\text{m})^{-1}$. A peristaltic pump provides for liquid feed. The flow rate operating range has been chosen between 10 and 55 cc/h. Polarity inversion is simply possible by exchanging terminals. It has been assumed, according to the generally accepted nomenclature, that when the positive potential was applied to the needle the condition was identified as “positive polarity” and when the positive potential was applied to the plate it was identified as “negative polarity”.

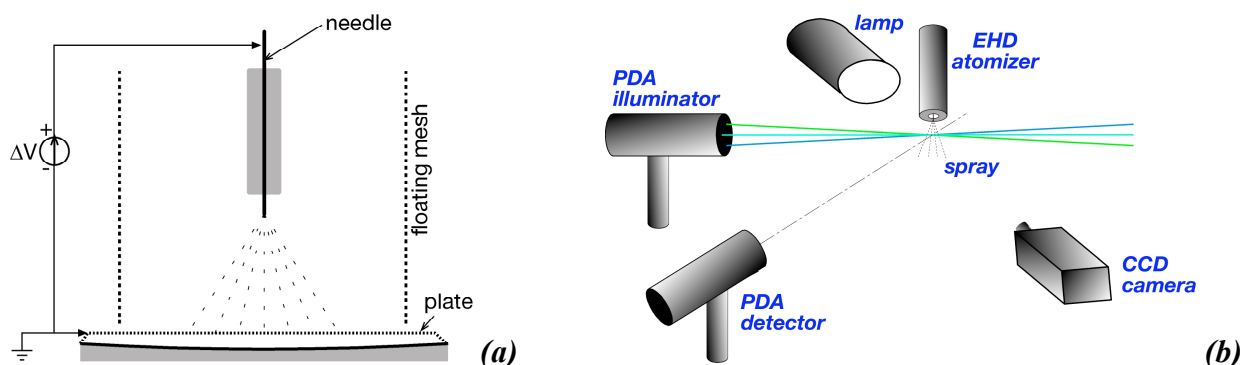


Fig. 1 Needle-to-plate configuration (a) and diagnostic setup (b)

All the experimental tests were conducted at atmospheric pressure and ambient temperature.

A schematic representation of the diagnostic setup is presented in fig. 1b. A visualization system was used for qualitative characterization of the atomization regimes. A Pulnix TM-6710 digital camera, with resolution equal to 640x480 pixels, and a halogenous lamp realized a configuration similar to a flash shadowgraph system. A National Instruments IMAQ PCI-1422 acquisition board installed on a PC collects images of the spray. The system was able to acquire images up to 240 Hz, shutter time being fixed to 1/32,000 s. A LabVIEW procedure was used to acquire and store the images for subsequent elaboration. In order to increase the readability of the images they were subtracted to a previously collected background image and then inverted.

A laser PDA system by Dantec was used for quantitative characterization of the spray. It indeed allowed to collect detailed single point measurements of the distributions of droplet size and of two components of their velocity. PDA measurements have been all collected at a distance of 6 mm from the tip of the capillary, on the needle axis every time it has been possible. For oscillating-jet mode and precession mode data have been acquired on both needle axis and spray boundary. A 100,000 droplets sampling and a limit acquisition time of 1000 s for each measurement have been fixed in order to obtain distribution histograms statistically representative of the spray.

RESULTS AND DISCUSSION

Each regime has been identified through spray images collected by the digital camera and quantitatively characterized by means of size and velocity data acquired by PDA system. Individuation of regime stability fields has made it possible to elaborate maps of occurrence, for both positive and negative polarities. Since the spraying regimes have been already largely described and classified [2][7-9], here just a brief summary of main features will be presented.

For every chosen flow rate, *dripping mode* is observed when no voltage or low voltage is applied. A voltage increase brings to the stabilization of *spindle mode*. In this conditions applied voltage is too low to establish a cone-jet, so that an emission of large drops alternating with thin jets, undergoing Rayleigh breakup in small droplets, is observed.

By increasing applied voltage, in the low flow rate field it is possible to observe the well-known *Taylor cone-jet mode*, firstly pulsed and then continuous when applied voltage is high enough to establish a steady jet. In both conditions data collected by PDA indicates that this spraying mode produces very small drops, down to $10\text{ }\mu\text{m}$, even if in the pulsed mode the size distribution appears to be less monodisperse. In the same voltage field, a flow rate increase gives rise and enhances kink instabilities that make no longer possible the stabilization of a cone-jet. For high liquid flow rate two spraying modes are observed: as voltage grows, first the *oscillating-jet mode*, characterized by strong oscillations in the plane containing the capillary axis, and then *precession mode*, differing from the previous one because jet rotates around the capillary axis, resembling a hollow cone spray. For each flow rate, above a certain value of the applied voltage, jet striction effects are so strong that a single jet cannot carry off the supplied amount of liquid. In this condition the jet divides in two or more streams and meniscus flattens. This condition is commonly named *multi-jet regime*. A comparison of spray images and PDA data indicates that each jet behaves like an insulated cone-jet. The experimental evidences have been summarized in two maps of occurrence of the atomizing regimes, one for each polarity, presented in fig. 2.

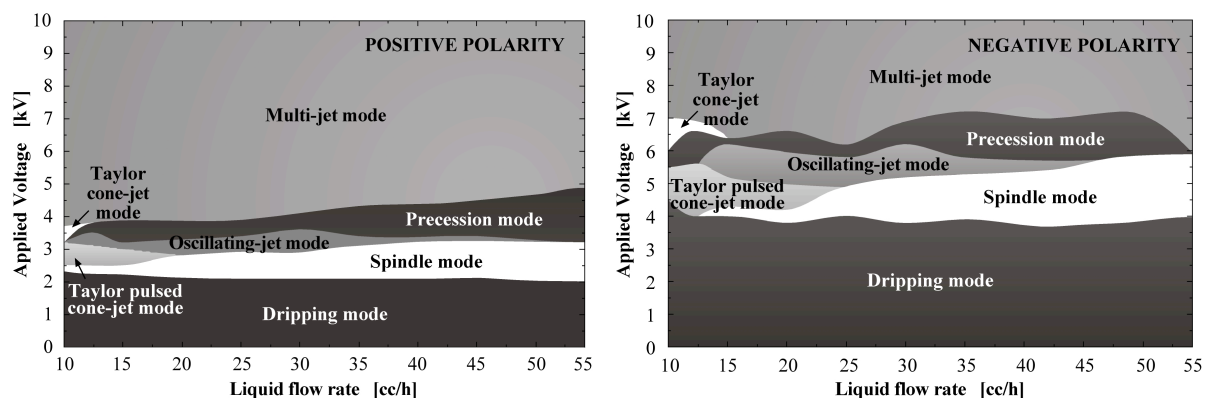


Fig. 2 Map of occurrence of stability regimes for positive and negative polarity.

The two maps do not differ much each other. It should, however, be noted that a significant difference exists between the two polarization cases in the voltage values where the different regimes could be observed. In essence the stability map in the negative polarity case appears both to be shifted toward the higher voltage values and the voltage intervals in which the regimes were observed are wider. The same shift can be clearly observed in fig. 3, presenting the behavior of the drop mean diameter against applied voltage and, parametrically, liquid flow rate. In general drop size grows with liquid flow rate and decreases with applied voltage. For higher flow rate a maximum appears in correspondence of the *oscillating-jet mode*. Actually, it must be underscored that in the *spindle mode* The PDA system can collect only data on aerosol droplets, since large drops are out of the chosen PDA setup: as a consequence, it should be expected that the effective mean diameter for this regime is much higher than the measured one.

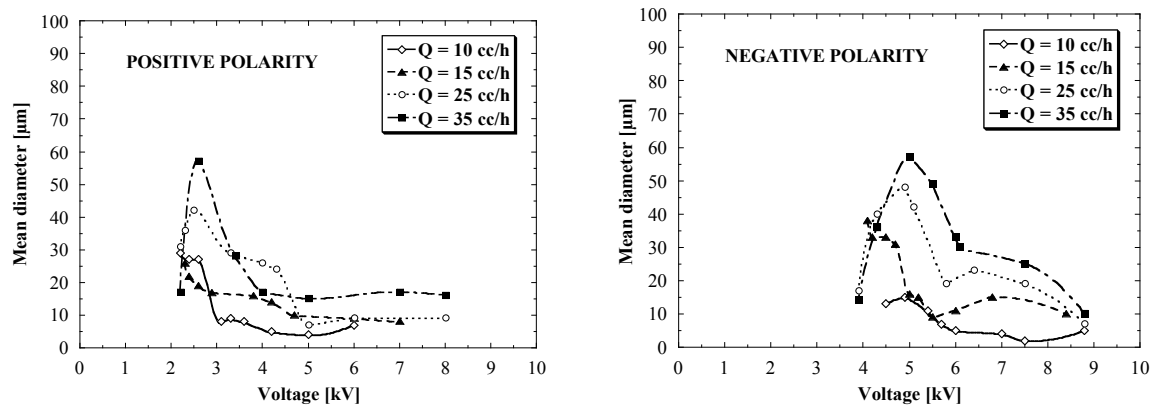


Fig. 3 Mean droplet diameters in positive and negative polarity as a function of applied voltage for different values of liquid flow rate.

Results indicate that the best spray quality is achieved by *cone-jet* and *multi-jet* modes, but aiming to apply the EHD atomization for combustion applications, cone-jet mode is no longer interesting because of the very low liquid flow rates this regime requires. Multi-jet mode can instead give a fine and extremely monodisperse spray also for high flow rates, most of all in negative polarity, as fig. 3 shows. Moreover, negative polarity, in the used experimental configuration, corresponds to wider stability regions for every spraying mode.

CONCLUSIONS

Negative polarity is more effective than positive in the atomization process. Unfortunately this better spraying quality does not seem to be able to produce a more stable flame.

The higher voltages required to achieve a satisfying atomization condition in negative polarity pose a problem in the practical application to combustion. As a consequence, the effect of the presence of the flame could, in this case, be even more effective than in the case of positive polarization, being the space charge due to the applied electric potential even larger.

The final result is an expected increased instability of the flame in consequence of the prevalence of pulsating regimes in the atomization process, instability which has been also observed in the first tests on the combustion of negatively charged sprays.

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Sequential Enlargement Combination of Separated Effect Contributions for the Analysis of Liquid Jet Atomization in Cross-flow Conditions

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1. INTRODUCTION

The study of the interaction between a liquid jet and a gas cross flow appears to be complex due to the simultaneous presence of a liquid column, subject to the stresses induced by the air cross flow, bended and deformed by drag forces, pressure drop between windward and leeward side, liquid fragments and drops stripped from jet surface. This reduces the coherent liquid jet's cross-section so the jet undergoes breakup and breakdown phenomena. The first one leads to the loss of jet continuity and to the formation of ligaments and droplets. The lack of coherence of the jet results in a substantial breakdown of the jet due to the fact that liquid particles, formed in the jet breakup, are easily dragged by the airflow surrounding the spray. In the literature two main atomization mechanisms [1,2] have been individuated in dependence of the value of the ratio of jet to airflow moments, expressed by means of the “ q ” parameter $\left[q = (\rho_L v_L^2) / (\rho_G v_G^2) \right]$. The first mechanism, characteristic of lower q values, is the column breakup; the jet appears to be already bended by the airflow before the occurrence of the breakup which is due to the onset and growth of waves on the windward side of the jet: a significant change in the jet trajectory could be observed in correspondence of the rupture point. At higher q values, the jet breakup occurs mainly through the surface breakup mechanism; liquid ligaments and droplets are detached from the jet surface due to the erosive action of the airflow: jet breakup can take place when the combined action of aerodynamic stresses and surface tension causes the rupture of the liquid column. The discriminating parameter in this case is the Weber gas number ($We_G = \rho_G v^2 D / \sigma$, where v is the relative velocity at the jet interface). At We_G values high enough the aerodynamic stresses become so strong to induce the stripping of liquid from the liquid column. At lower We_G values the only effect of airflow is the amplification of jet instabilities and a moderate bending of the jet. It is clear from these considerations the relevance of the jet size and of the surface tension of the liquid. Furthermore, the jet atomization due to the liquid velocity and to the ambience pressure (typical of high pressure jets injected in quiescent atmosphere) can play a relevant role in the phenomenology of jet breakup. In conclusion, inertia of the liquid jet, aerodynamic shear of the gas phase, surface tension and atomization are the main factors playing a rule in this process. Other effects that have to be taken in account are the viscosity, the convection inside liquid phase due to drag force and pressure drop, the energy transfer taking place at all turbulence scales and cavitation phenomena inside the nozzle.

A mathematical description of all the elementary sub-processes involved in the jet bending and atomization is far beyond the present capabilities of modeling. It comes, thus, helpful a multilevel approach to the study of the phenomenon that exploits a strategy based on the successive addition of physical effects and of the mutual interactions among them. This is a typical example of the Sequential Enlargement and Combination of Separated Effects

Contributions (2SEC) approach to the analysis of complex processes. It is not in the aim of this present paper an exhaustive discussion of the general aspects of 2SEC analysis strategy and it is in the intention of the authors only to show a possible application of such strategy in order to reduce the complexity of the problem by using different simplified models and analyzing their effectiveness in describing the experimental evidences. In the process the physical relevance of the different effects will be evidenced in terms of their influence on the models effectiveness.

2. MATERIALS AND METHODS

The approach followed is based on the elaboration of two numerical models of the jet and on the tight comparison of their results with the experimental results obtained by means of optical diagnostic of the jet behavior in a test device. Models outlines are presented in the following subsections along with the experimental facility main features.

2.1 Numerical modelling: model I

The first model, pertaining to the integral models class, used for the jet description resembles the approach largely followed in literature [1, 4] based on the numerical resolution of the momentum balance equations and the subsequent tuning of the model parameters by using experimental data available. In our case a momentum balance is written on a finite, thin slice of the liquid column delimited by two layers perpendicular to the initial velocity of the jet. A Cartesian system is chosen with the origin in the geometrical center of the nozzle outlet, under the hypothesis of two-dimensional problem and taking x and z axes respectively oriented along the gas flow and initial velocity of the jet. In this model the terms taken in account are only jet inertia and drag forces along x direction and z direction. For the evaluation of the drag coefficient in the x direction, the liquid jet is assimilated to an unlimited, unbending cylinder transversally invested by a gas flow. Under these hypotheses, even though Re varies significantly along the jet, due to the reduction of both relative velocity and jet diameter, nevertheless it remains in the range of high values, where C_{Dx} is practically constant with Re . Furthermore the cross section has to be referred to a cylindrical geometry. In order to take in account the lack of shape ideality, due to column deformation and surface roughness induced by the aerodynamical stripping of ligaments and drops, a correction factor Ψ is introduced. In the balance relative to z direction the surface exposed to the drag force is only the lateral area of the liquid element, cylindrically shaped in the ideal condition. Because of the stiffness of a theoretical evaluation of the drag coefficient in the z direction it appears to be useless the introduction of a correction factor in this equation too: ignorance, about shape and energy transfer effectiveness, is all put in the friction factor. To take in account the jet diameter reduction due to the atomization process, a linear reduction is utilized.

2.2 Numerical modelling: model II

In the second model proposed, that pertains to the numerical model class, the jet trajectory is determined by using a commercial fluid-dynamic problem solver (Fluent), retaining all the complexity of the airflow and of the jet air interactions, but schematizing the jet as a single nonspherical particle identified by a shape factor $\phi = s/S$ [5] where: s is the surface area of a sphere having the same volume of the particle and S is the actual surface area of the particle. The ϕ choice fixes, in conjunction with Reynolds number, the drag coefficient C_D that represents the model empirical input. This approach comes out from theoretical considerations [6] and experimental investigations [7,8] and concerns the deformation of the cross-section of a jet injected into a cross flow (from circular to 'kidney' shape) due to the

pressure gradients induced by the separation of the turbulent boundary layer. This strong distortion determines an increase of the drag coefficient with respect to its value in the solid cylinder hypothesis. The choice of the ϕ value (coupled with Reynolds number, value relative to the actual working conditions) give the opportunity of calibrate the C_D value with respect to the experimental data. The standard $\kappa - \varepsilon$ model have been used as turbulent model and the coupling between the phases and its impact on both the discrete phase trajectories and the continuous phase has been taken in account in the computation.

2.3 Experimentals

The experimental set-up is described in detail in reference [3] and consists of a fully optically accessible tunnel, with a square cross section of 25 X 25 mm, in which the jet is injected perpendicularly to the air cross flow. The air pressure and temperature were kept constant at 1.3 MPa and 300 K. The liquid used was distilled water and the nozzle diameter was 0.5 mm for all the reported conditions. The injecting system is a plane orifice one with a nozzle hole of 0.3 or 0.5 mm diameter. The optical set-up is a simple shadowgraphic scheme using a low-pressure xenon flash lamp as light source and a CCD digital camera. In each test condition forty 10 bits images (1024 different tonalities of grey) of the spray were collected. The analysis of the variations both in time and space of image boundaries obtained from averaged images were used to characterize the jet stability in statistical sense.

In order to clarify a possible correlation between jet stability and injection conditions a square average shifting indicator s has been introduced. A steepest increase of the s value in correspondence of a z coordinate value in dependence of the injection and airflow conditions was observed [4]. This increase could be tentatively attributed to the breakup of the liquid column. In this case the error increase can be explained by the different behavior of a cloud of droplets with respect to a liquid column. Although this is not a rigorous evaluation of the jet break-up position it appears to be at least a good first approximation estimation method of this position [4].

3. RESULTS AND DISCUSSION

The experimental trajectories have been compared, for different air and liquid injection velocities, with those obtained by using both the model I and the model II. Two typical results are reported in Fig. 1. For lower q values, the jet trajectory undergoes a strong bending and is characterized by an evident knee. The windward outline shows the rising of waves on jet surface, instabilities which initially promote the stripping of liquid ligaments, and then, for higher wave amplitude, take to the loss of column integrity, i.e. jet breakdown. Both models fit well the experimental points, even though they cannot depict the typical knee. When the conditions are favorable for the z_{jb} evaluations by the square average shifting indicator, the integral model works well, maybe because it reaches a good estimation of the jet diameter decrease. For higher q values, the trajectory simulated by the integral model is less bended than numerical model, which better fist the real jet behavior probably due to the more realistic simulation of a complex interaction between the liquid jet and the airflow. At q values above 100 the bending force induced by the aerodynamic action cannot prevent the jet impact on the opposed wall. In these conditions the kinetic energy of the jet is so strong, with respect to air, that liquid column moves straightaway towards wall with a less evident bending: both the models work reasonably well.

4. CONCLUSIONS

It has to be underlined the good description given by the proposed models of the jet trajectories. The integral model is very effective when the determination of the jet breakdown

allows for having a reliable estimation of the liquid column rupture; it gives reasonable good results also in other conditions for the assumption of a jet diameter consumption law. This confirms the general problem of integral models in requiring an experimental validation of controlling parameters to give realistic results. The second model, which is less dependent on the experimental determination of jet characteristics, is very effective in describing the jet trajectories, apart from some cases where the assumptions of the model are significantly different from the real processes. To this aim a more realistic determination of the drag coefficient (and as a consequence of the ϕ) could give better results. In this case too it appears important the assessment of a relationship between airflow and jet injection parameters and the drag coefficient, which does not only depend on the value of Reynolds number, but must also take in account the jet deformation and the occurrence of the aerodynamically induced atomization process. The relevance of the jet atomization by liquid stripping from jet surface (either as a direct consequence of stresses induced by the air cross flow or due to jet velocity induced atomization with a subsequent liquid drag acted by airflow) appears to be relevant for system operated at increasingly high pressures like gas turbines. To prevent the jet impact on the wall the onset of a surface breakup mechanism appears much more efficient than a column breakup one. It appears in this case that the parameters to be controlled are, apart from the q parameter, also the parameters governing the atomization process that are the Weber numbers relative to the gas flow and to the liquid jet. In these parameters are also taken in account the dimension of the jet and the surface tension of the liquid. This suggests that suitable choices of the nozzle size (i.e. of the jet initial diameter) and of the initial jet orientation can allow for the determination of the most efficient liquid dispersion in the duct.

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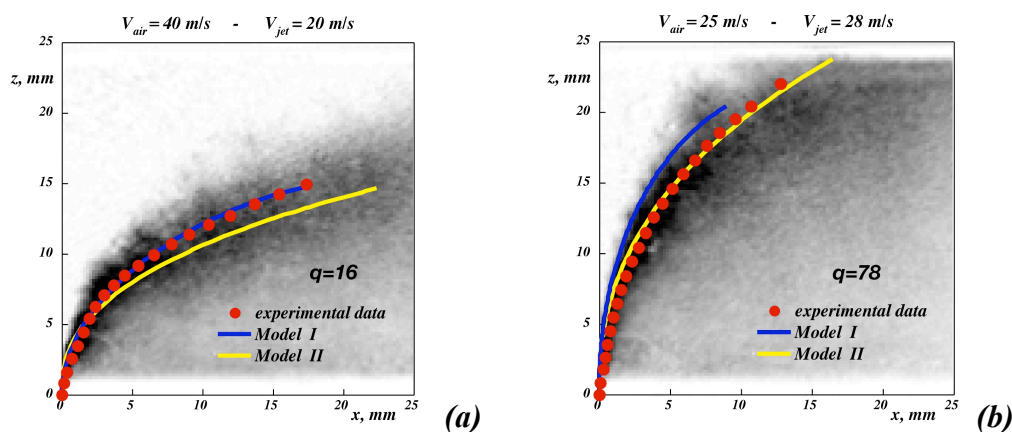


Fig. 1 Comparison of experimental determined trajectories and results of modelling.

Infrared analysis of the interaction between fuel jet and convective hot field in counter flow conditions

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ABSTRACT

The aim of this paper was to study the interaction between fuel droplets and a hot counter air flow. Infrared imaging was employed to better understand what were the mechanisms of heat and momentum transfer that govern the self-sustaining combustion. Working in counter flow and using an IR camera evaporation and mixing, phenomena are analysed . This preliminary work allowed to recover numeric, thermal field and dynamic field in counter flow injection condition.

INTRODUCTION

The exploitation of heavy fuel oils or other not precious liquid combustibles for heat generation through conventional combustion technologies is limited *de facto* by environmental policies, since they contain heavy hydrocarbons and undesired amounts of nitrogen and sulphur, which form NO_x and SO_x during standard combustion processes in an oxygen rich environment.

Nevertheless, they are economical alternatives for power generation due to their low cost, provided that they can be used in compliance with environment protection, heavy oils constitute a major energy source, which could be used for medium/large sized heat/power generation, providing an improved and full exploitation of natural resources.

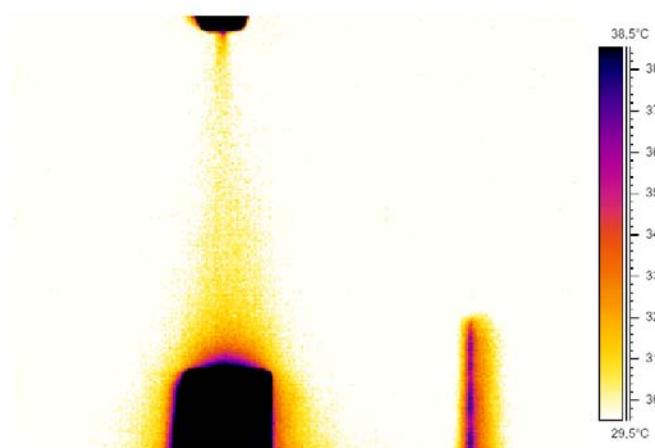


Fig.1

EXPERIMENTAL

In Fig 1 is showed the mouth of the electrical furnace generates hot air in free convection or in turbulent convection in a range of temperature until 1000. K

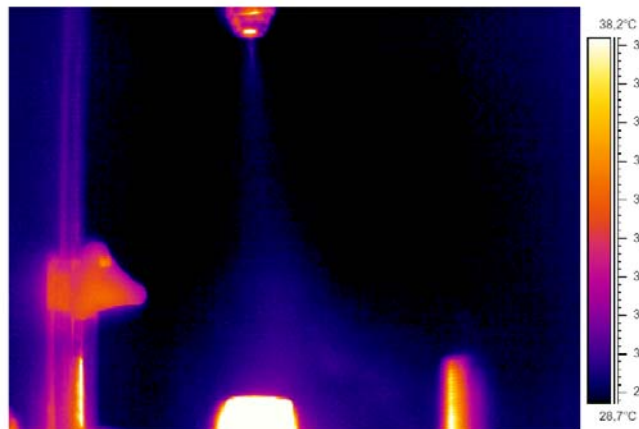


Fig.2

The fuel is injected in a convective thermal flow field generated by the furnace. The gas used in counter flow is nitrogen. This choice has been done to avoid that the thermal field was influenced by some burning phenomena, especially for high gas temperature.

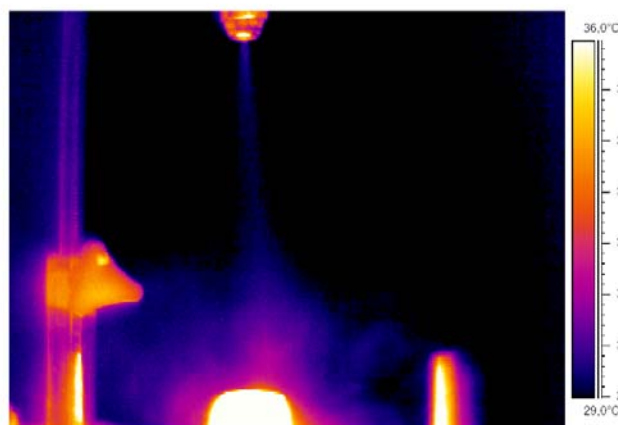


Fig.3

RESULTS

The tests are carried out working with the infrared camera. The range of diameters generated by this nozzle is [0.001/0.005 m]. The limit conditions of the first test are: fuel temperature $T_f = 293.23$ and the environment temperature $T_e = 373$ K. The pressure conditions of the air is fixed about 2 atm.

In this case the instability of the spray is due only to the stress between the droplets and the external air. The photo in fig 1 shows the behaviour of the spray in the conditions before indicated. It is possible to look the perfectly development of the entire cone spray. It is symmetrical and has an undistorted shape. The droplets arrive undisturbed until the mouth of the furnace. It is possible to notice the profile of the convective field near the mouth of the furnace. The entire jet doesn't fill the thermal convective field and the temperature is the environmental one. It is possible to note a little shadow near the mouth of the furnace. In real infrared camera colours it is visible clearly and it has a parabolic profile. The parabolic profile shows that the jet doesn't interact with the thermal field because of the very little difference of temperature between the gas and the liquid phase.

The second photo (Fig 2.) represents the spray visualization with the following limit conditions : $T_f = 293$ K, $T_{in} = 723.23$ K. The droplets spray now interact with the thermal convective field. The convective profile is still parabolic before of the spray impact. The

droplets spray fill the convective thermal field before than the previous case. The spray near the mouth of the furnace is less regular. The little droplets interacting with the thermal field and begin to evaporate influencing the superior share of the liquid jet. The jet opens quite symmetrically respect the vertical axis and follows the parabolic profile of the convective thermal field. Increasing the furnace temperature the interaction between jet and convective thermal field is more accentuated. The third photo fig 3 represents the behaviour of the spray when $T_f = 293^\circ\text{K}$, $T_{in} = 800^\circ\text{K}$. It is possible to notice that the colour of the cloud near the mouth of the furnace is darker than the first one. In infrared colours the cloud the colour is red. The droplets near the furnace evaporate and influence further the jet. In this case the mixing between the two phases is more evident. The jet begins to lose its symmetrical shape and the vapour phase became very important because influences substantially the behaviour of the spray. The velocity of the hot air due to the free convection flow field is now of 5 m/s. So the droplets are strongly applied by the counter air hot stream. The evaporation or stagnation region is 0.1 m far from the mouth of the furnace. The little droplets evaporate and begin very reactive.

Increasing the temperature of the furnace until 1000°K the presence of the convective flow field begins more important. In fig 5 the velocity of air vs. air temperature is reported

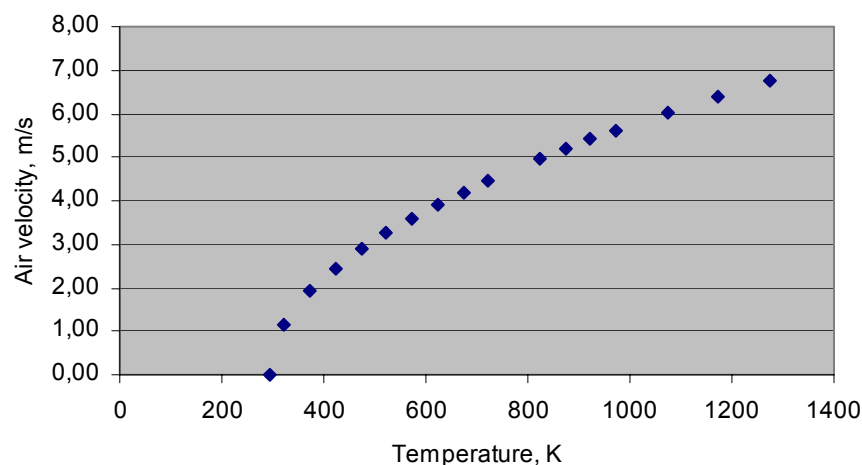


Fig.4

Near the 1000°K the air velocity is 5m/s approximately. The convective thermal field influences strongly the behaviour of the spray. Fig 5 put in evidence the new velocity profile of the thermal field. The spray fills the new conditions until the nozzle. The liquid jet increases completely its temperature. The little droplet evaporates quickly and also the big droplets begin to fill the thermal field.

REMARKS

The paper put in evidence the behaviour of the spray when injected in a free convective counter flow. Also if the application, especially in general industrial applications are few, has been considered that this analysis can be very explanatory to

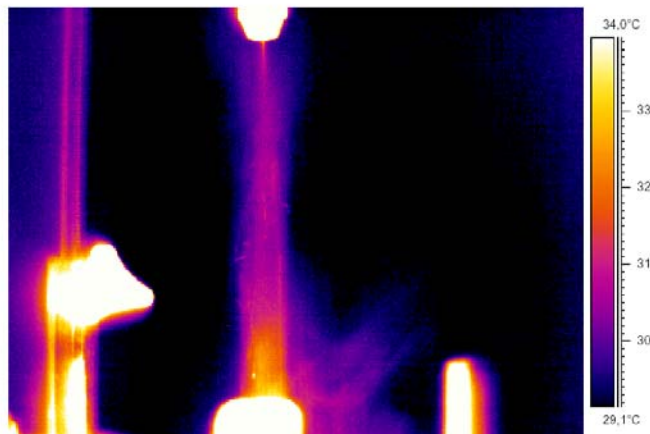


Fig.5

understand what are the mechanisms that govern the free combustion and the importance of the heat and mass fluxes inside these mechanisms. Working in counter flow conditions it is possible to reduce the area of the evaporation and burning phenomena and verify with fine precision the condition of ignition and burning phenomena. The extension of this initial work foresees to recover numeric information about size droplets, thermal field, and dynamic field, to support the choices especially in the applications for mild combustion with heavy fuel. Furthermore the infrared analysis put in evidence the interaction between the spray and the convective thermal field. In fig 4 is enhanced this behaviour. The spray is very sensitive to convective thermal field generated from the furnace and it is put in evidence because of the red color of the liquid injected.

This particular approach by means infrared camera is very interesting to visualize the mixing zone of spray. The infrared approach gives very important information about mixing phenomena but to follow the real development of the interaction between spray and gas it is important to follow the typical times of the phenomena. This is possible using the high frequency infrared camera. This kind of systems will visualize also locally the interaction in spray mixing with or without flame production.

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