44th Meeting of The Italian Section of The Combustion Institute

Combustion for Sustainability

Naples
June 5-8, 2022

Book of Abstract
edited by
Mario Commodo, Giancarlo Sorrentino, Gianluigi de Falco, Antonio Tregrossi, Heinz Pitsch
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Cover image courtesy of Michela Alfè

The foreground image is the statue of **Concordia Augusta**, exposed in the Atrium of the National Archaeological Museum of Naples (MANN) from the beginning of the Ukraine-Russia conflict as a sign of peace and stability.

The images in the circles refer to the meeting location (City of Naples and the Church and cloister of “Complesso SS. Marcellino e Festo”), to an ancient fountain in Naples located close to the conference site (Fountain of the Spinacorona, depiction of the siren Parthenope, icon of Naples) and to the main topics of the conference (energy transition and combustion sustainability).
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SESSION I

Novel concepts including multi-physics phenomena
Abstract

Lean and premixed combustion concepts are one of the most promising techniques for lowering combustion temperature and consequently NOx emissions. Reductions in fuel consumption and hazardous emissions are the main goals of aerospace engines since the major problems of aerospace combustors are LBO and ignition in high altitude conditions.

In this context, several passive control strategies have been used to investigate flame stabilization by permanently modifying the combustor geometry. However, plasma-assisted combustion (PAC) technology provides a promising method to actively control the flow characteristics and combustion dynamics of the combustor under real-time operating conditions [1, 2]. PAC improves flame stabilization, extends LBO limits and increases combustion efficiency. The effects of plasma on combustion are broadly classified into thermal, chemical, and aerodynamic effects. Currently, PAC researchers focus mainly on non-thermal plasma (NTP). PAC refers to the collision of high-energy electrons/ions with fuel molecules and breaks the long fuel chain into a large number of active particles.

This study investigates the characterization of attached and lifted flame behavior and blowout limits at different air preheating temperatures in plasma assisted lifted swirl methane/air stabilized combustor. The combustor was equipped with a needle-ring type plasma actuator driven by a 20 kHz sinusoidal generator directly coupled to the methane-air premixed flame close to the injector exit. The experimental tests were performed at different air preheating temperatures, air-fuel ratios (AFR) and plasma power. The application of plasma discharges to flame stabilization leads to plasma-attached flames or plasma-enhanced lifted flames, depending on the air and fuel flow rates.

The comparative analysis of electrical characterization and LBO limits at different preheating temperatures and plasma actuation conditions was performed.

In addition, near flame LBO is in the intermittent state, where usually partial or complete extinction, followed by re-ignition of the flame was noted. Therefore, optical diagnostic techniques and spectrometry analysis could help to understand the phenomena. The pressure oscillations of the combustion chamber, particularly near the LBO, were acquired by a calibrated microphone probe with a high sampling rate with or without plasma conditions. The acoustic signals were analyzed using wavelet decomposition techniques and the LBO limit was also performed. The Proper Orthogonal Decomposition of the flame images of broadband emission and chemiluminescence has allowed to detect the most relevant flame structures, in combination with the modal frequency spectra.

References


Experimental tests of a novel Directly Irradiated Fluidized Bed Autothermal Reactor (DIFBAR)

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³ Dipartimento di Ingegneria, Università degli Studi del Sannio, Benevento, Italy

Abstract
Thermochemical Energy Storage (TCES) is pointed out as a promising integration of Concentrating Solar Power plants [1]. Several gas-solid reactors have been proposed to this end [2]. A novel Directly Irradiated Fluidized Bed Autothermal Reactor (DIFBAR) has been recently conceptualized [3]. The key feature of the reactor is the autothermal operation: the sensible heat of the solid product is recovered to preheat the reactants. This is obtained by means of a solid-solid counterflow heat exchanger composed of two vertical coaxial tubes connected at the bottom of a conical receiver. The bed material is fed to the receiver through the inner tube (riser) by a fluidizing gas stream and exits through the outer tube (annulus) separating from the gas stream. By descending through the annulus, the particle bed transfers heat to the riser. A lab-scale stainless steel prototype was designed and built up, in which the material continuously circulates between the receiver and a reservoir. The system is tested with a high-flux solar simulator, made of a xenon arc lamp and an elliptic reflector. In this study first experimental results are presented. Figure 1 depicts the experimental apparatus.

Fig. 1. Experimental set-up.
A standpipe connects the bottom of the reservoir to the riser. A fluidizing stream (Q₁) is fed to the riser, through a nozzle. A secondary stream (Q₂) can be fed to the reservoir, through a sparger. Two auxiliary streams can be fed to the annulus (Q₃) and to the standpipe (Q₄). Q₃ also controls the solid discharge from the annulus into the reservoir. Two needle valves regulate the reservoir and receiver pressure. Cold flow tests were carried out with Geldart B quartz sand to investigate the hydrodynamic characteristics. Solid circulation rates were obtained by observing the particles flow through a Plexiglas copy of a segment of the annulus. Pressure profiles were recorded for different operating conditions. Gas tracing tests were conducted to understand internal gas paths.

Fig. 2. Solid circulation flowrate. Asterisk-labelled data (*) refer to an increased reservoir pressure.

The solid circulation flowrate (W) increases with the superficial velocity (u₁) of the riser feeding gas (Figure 2). A limiting value is reached when the reservoir is not aerated. By-passing streams normally flow from the receiver to the reservoir and can be reversed for some conditions. The results are coherent with the pressure profiles. Preliminary tests of heating of the reactor have been also carried out.

References
Advanced structured X-packing produced by 3D foam-printing for packed towers in FGD process intensification

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Abstract
In the last decade, 3D printing technology has largely spread in industrial applications to substitute conventional manufacturing processes and to allow faster, cheaper, and in-situ production of commercial products. Recently, 3D printing technique has also been successfully adopted in chemical engineering for process intensification to produce column internals and multi-phase contactors for Unit Operations and monoliths for catalytic reactors with very promising results [1–4].
Packed columns are largely adopted in chemical engineering processes for the synthesis and purification of compounds for petrochemical, food, chemical and pharmaceutical industries, and many others targeted applications, e.g. flue-gas cleaning from coal-fired power units and waste-to-energy plants.

In this work, we report the results of a first experimental study on design, manufacturing and characterization of an innovative tailor-made 3D foam-printed packing X-type in polylactic acid (PLA) having the advantages to be light, cost-effective, and easy-to-produce, used for process intensification of Flue-Gas Desulfurization (FGD) plants. The physical properties of the 3D foam-printed packing are characterized in terms of density, wettability, and surface roughness. Subsequently, the packing is tested in a pilot-scale FGD plant using air/water system to estimate the pressure drops in dry and wet-mode and the overall mass-transfer efficiency with typical absorption experiments using a simulated flue-gas with local tap water (western area of Naples).

The results show that the packing prototype has slightly higher mass-transfer efficiency and pressure drops than other similar commercial packing in the same ranking range of nominal surface area. A comparison with state-of-art Mellapak 250X in Hastelloy, tested in our previous FGD applications [5] with the same experimental set-up, shows that the improvement in mass-transfer rate overwhelms the increase in pressure drops and makes the prototype more convenient. The overall performances of both packings are determined by calculating a trade-off index ($\Psi_{index}$), which considers both the pressure drops and overall mass-transfer resistances (Figure 1). The experimental results are explained in terms of the superficial properties of the packing, in particular: both pressure drop and mass-transfer rate data can be correlated with the morphology of the packing surface roughness, in turn both deriving from the printing and the foaming processes, and also by new mechanical design of baffle rings, which probably reduce liquid-maldistribution between packing elements. Besides, the foam-printing material has higher sheet wettability than the Mellapak 250X in Hastelloy, thus improving the liquid-film dispersion on packing surface.

Fig. 1. Comparison of the overall performance of the prototype and benchmark for pilot FGD application by calculating the trade-off index, $\Psi_{index}$ (temperature $T=25°C$, gas flow rate $Q_{G}=32 m^{3}/h$, liquid flow rates $Q_{L}=40-130 L/h$ and $SO_{2(g)}$ concentration $C_{SO2(g)}=500-1000 ppm$).

In summary, the overall performance and the production process of 3D foam-printed packings can be a valuable option for the design of next generation of column internals for FGD process intensification, and the topic worth further efforts to better understand their large-scale industrial applicability and the physical phenomena behind which characterize their performances.

References
Advances in the optical diagnostics of nanosecond non-equilibrium discharge plasmas for CO₂ valorization and energy storage

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Abstract

Low-temperature plasmas are gaining increasing interest as a tool to initiate thermodynamically unfavorable chemical reactions. The successful and widespread use of gas discharge technologies relies on their being systems in highly non-equilibrium conditions, where the significant production of reactive species compared to gas heating can initiate non-thermal chemistry. Plasma-assisted combustion and ignition, pollutant remediation, activation of stable molecules (e.g., N₂, CO₂, CH₄ etc.), and solar fuel production are just some examples of the applications that have been developed so far. Among them, plasma-mediated conversion of CO₂ and CH₄ represents a valuable strategy to simultaneously convert two major greenhouse gases into value-added compounds and store renewable energy in solar fuels. In fact, plasma is a turn-key process that can flexibly follow the irregular and sometimes intermittent supply of renewable electricity. Atmospheric nanosecond repetitively pulsed (NRP) discharges show one of the highest efficiencies in converting CO₂ and CH₄ [1, 2, 3]. Atmospheric pressure plasmas are highly transient, non-homogeneous, highly affected by surface process, and influenced predominantly by collisions. Due to the harsh nature of plasma environments, the development of non-invasive, time-resolved optical diagnostics is of topical interest. It represents a step forward in understanding chemical processes and the non-equilibrium nature of plasma. This contribution will focus on the recent developments in optical diagnostic techniques, especially optical emission spectroscopy (OES) and laser-induced fluorescence (LIF) and their application to atmospheric pressure NRP discharges for CO₂ conversion. Time-resolved OES allows the study of transient conditions in the discharge and the identification of underlying mechanisms or reaction pathways for the emission. Physical parameters, such as electron temperature and density and gas (translational) temperature, can also be accessed [4]. The possibility of estimating the time dependence of the CO₂ dissociation (see Fig.1) by Collisional Energy Transfer LIF (CET-LIF) [5, 6] is presented. CET-LIF is a quantitative optical diagnostic method, applicable at high pressure, based on the detailed knowledge of molecular energy-transfer processes [7].

Fig. 1. CET-LIF measurement of the CO₂ conversion as a function of the time after one nanosecond pulse compared with the computational model of [8].

Acknowledgements

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References

SESSION II

Novel concepts including Power-to-X and CCUS
Sorption-Enhanced Reaction Concept Applied to CO₂-methanation in a Fluidized Bed Chemical Looping System

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Abstract

Synthetic methane (SNG) represents a fundamental energy carrier with a well-developed infrastructure and social acceptance, and can be produced using “renewable” hydrogen from water electrolysis and CO₂, thus combining a chemical storage of intermittent renewable energy with a Carbon-Capture and Utilization (CCU) technique. Sorption-enhanced methanation (SEM), the application of Le-Chatelier principle to shift the equilibrium towards products by means of in-situ water removal, has been proposed to overcome the thermodynamic limits of the reaction at low pressure and to decrease the energy for gas compression [1-3]. In this work, a novel configuration for the catalytic CO₂ SEM process was studied in a lab-scale dual interconnected fluidized bed system, achieving a chemical looping process where methanation and sorbent hydration occurred in one reactor, while sorbent regeneration took place in the other one. Calcium oxide from natural limestone, an abundant, unexpensive and eco-friendly material, was the selected sorbent. The experimental campaign investigated the sorption-enhanced effect at temperatures of 300°C and 350°C, and for two feed ratios (H₂/CO₂=4 and H₂/CO₂=3). During 5 SEM cycles, the amount of produced methane with respect to the H₂ fed was calculated and compared to traditional methanation. For both temperatures considered, the first SEM cycle was clearly affected by the undesired carbonation of the fresh CaO fed: a significant decrease in the methane productivity with respect to the conventional case occurred. When considering an over-stoichiometric feed in terms of CO₂ (H₂/CO₂=3), the CO₂ fed in excess seemed to partly counteract this negative effect. The CaO hydration led to the “enhanced-behaviour”, detectable from the second or subsequent SEM cycles, depending on the operating conditions considered. By way of example, Fig. 1 reports the methanation test results for a temperature of 300°C and a stoichiometric feed ratio (H₂/CO₂=4) as a function of time. During traditional methanation (black line) the ratio between the molar flow (mol/h) of the outlet CH₄ and that of H₂ fed shows an increasing trend, reaching a stable value after about 240 s. During the first SEM cycle (grey line) a distinct slowing down in reaching the asymptotic value with respect to conventional methanation was observed due to the above mentioned negative carbonation effect, which subtracts CO₂ reactant from the methanation reaction. Under the reported operating condition (300 °C and H₂/CO₂=4) the sorption-enhanced effect was already visible in the second SEM cycle, and even more evident in the subsequent three cycles.

References

Combined CO₂ capture and catalytic methanation over highly performing Li-Ru/Al₂O₃ dual function materials

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Abstract

Highly optimized Carbon Capture and Utilization (CCU) technologies are required to reach the ambitious goals of net-zero greenhouse gas emissions in the European Union by 2050. However, current multistage CCU technologies using renewable electricity to yield fuels suffer from low energy efficiency and require large capital expenditures. An innovative solution is represented by the Combined Capture and hydrogenation of CO₂ to Methane (CCCM). This is a catalyst-assisted chemical looping process wherein CO₂ from a point-source (e.g. combustion flue gases, anaerobic digestion, or even air) is captured using a Dual Function Material (DFM) composed of a supported adsorbent which also includes a catalytically active phase to produce CH₄ upon reaction with H₂ from renewable sources, by this way completing its regeneration. The two process steps (CO₂ adsorption and methanation) require a temporal or a spatial separation and are mediated by the solid DFM, which is a CO₂-carrier and a methanation catalyst [1-2]. As for all emerging chemical looping processes, the key to success is the DFM mediator that needs to fulfil a number of stringent characteristics, including high catalytic activity and selectivity at low temperature, high mechanical stability and long durability under cyclic operation, easy reducibility, large and selective CO₂ adsorption capability and easy regeneration [1].

In this work, we prepared a set of novel DFMs with low (ca. 1% wt.) Ru loading at fixed dispersion and variable Li contents (up to 5% wt.) dispersed on γ-Al₂O₃ spheres. DFMs were characterized by BET, PSD, XRD, H₂ chemisorption, CO₂-TPD, TG-MS, H₂-TPSRx, in-situ DRIFT and CO₂ catalytic methanation under continuous flow. Transient CO₂ storage/methanation cycles were studied in a fixed bed reactor operated with alternate feed conditions. Fig. 1 shows results obtained at 263 and 293°C: after the CO₂ capture step on the DFM, CH₄ production occurred quickly as soon as H₂ was admitted to the reactor and it was highly repeatable during following cycles whereas the formation of CO was negligible. The CO₂ conversion during the hydrogenation phases was as high as 98% at 263°C and ca 97% at 293 °C.

Eventually, a parametric study demonstrated that CH₄ productivity as high as 0.5 mmol/g can be achieved with the Li-Ru/A catalysts that are optimally operated at milder temperatures (around 280 °C) than the previous state of the art DFMs [1-2], and guarantee a very high methane selectivity and an outstanding methane turn-over (5.7 molCH₄/molRu) due to their limited Ru content.

It was also shown that by splitting the Sabatier reaction into two half phases mediated by the solid DFM, the heat release during the methanation step can be reduced by ca. 50%, thus substantially simplifying the thermal management of the methanator reactor.

References

Carbon Capture and Power-to-gas: a dynamic analysis of the use of hydrogen in a cogeneration plant


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Abstract
The current climatic situation requires the implementation of important changes already in the short term: the capture of carbon dioxide and the use of hydrogen are considered among the main solutions.
Hydrogen, thanks to the possibility of storing energy, especially from renewable sources, is the basis of the main national and international development plans, while Carbon Capture and Utilization approaches are increasingly at the center of research to optimize the already numerous solutions available and to limit the damage of this pollutant to the environment.
The present work, therefore, after an analysis of the current technological solutions for CO$_2$ capture, has focused on the analysis of a cogeneration plant fed by methane in dynamic regime, foreseeing the capture of carbon dioxide from the engine exhaust gases in order to be able to use it later in one of the Power-to-gas solutions: the methanation process with green hydrogen produced through electrolysis and electricity obtained from a photovoltaic field.
Using the TRNSYS software, the main components of the system were modeled (e.g. cogenerator, photovoltaic system, electrolyser) thus allowing an hourly analysis of the hypothesized configuration to be carried out; in particular, for a 20 kW$_e$ cogenerator at the service of a small company, the capture of different percentages of CO$_2$ from the exhaust gases and the subsequent reuse in a methanation process with green hydrogen produced by the excess electricity of the photovoltaic field was simulated.
The simulations carried out have shown the significant advantage in terms of both CO$_2$ emissions avoided and economic benefits obtained by exploiting the potential of all the cogeneration plant components, while a blind adoption of carbon capture and methanation is difficult to implement due to the too large amount of green solar energy required.
This case study shows the need to optimize some of the components needs (e.g. the electricity requests for the electrolysis process) by identifying alternative solutions, such as the use of hydromethane, to cope with the pollution problem.
Simulation of Sorption-Enhanced Methanation in a Chemical Looping System using CaO as Sorbent

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Abstract

Catalytic methanation for synthetic renewable methane production is gaining interest in the framework of bio-energy technologies development since methane benefits from an extensive infrastructure and social acceptance. Biomass gasification to syngas as feedstock for bio-methane represents a possible path among the different choices. The sorption enhanced methanation (SEM) concept has been recently proposed, based on in-situ water removal to shift the equilibrium towards a higher CH₄ conversion [1-4]. Such concept would overcome thermodynamic limits and allow to carry out the process at lower pressures with a subsequent energy duty decrease.

In this work, a SEM process using biomass-derived syngas in a dual interconnected fluidized bed system was simulated in ASPENplus using CaO as the sorbent for steam capture. The SEM section was modelled as a chemical looping system operated at nearly atmospheric pressure: in one reactor methanation and hydration occur while the spent sorbent is continuously sent to the other fluidized bed for regeneration. The flowsheet of the process is shown in Fig. 1. Different operating conditions, in terms of syngas composition and recirculation of CaO between the reactors were investigated, with the aim of achieving methane streams suitable for injection into the natural gas grid. The effect of the methanation temperature in the range 250-350°C was also investigated. Three dimensionless parameters were introduced to characterize the SEM performance, two of them representing the syngas composition: \( \alpha = \frac{(\text{H}_2\text{-CO}_2)}{(\text{CO}+\text{CO}_2)} \), \( \phi = \frac{\text{CO}_2}{(\text{CO}+\text{CO}_2)} \), and a third one: \( \theta = \frac{\text{CaO}}{\text{CaO}_{st}} \). This last parameter is the ratio between the CaO fed to the methanator with respect to that necessary for the capture of the total steam theoretically produced by complete methanation.

Under a stoichiometric gas feeding (\( \alpha = 3 \)), the results showed that the undesired CaO carbonation reaction had a negative impact with a significant increase of H₂ concentration in the product gas.

This effect increases with the CO₂ content in the feeding gas, since a higher CO₂ concentration implies faster carbonation, subtracting both CaO for the SEM, and CO₂ reactant for the methanation reaction, and leading to a lower conversion of H₂. Under stoichiometric gas feed ratio, no conditions are appropriate for the direct injection in the gas grid, with the only exception at 250°C, \( \phi = 0 \) and \( \theta = 0.5 \). However, with hydrogen-lean syngas suitable streams for the injection could be obtained. Under these conditions the surplus in carbonaceous compounds in the feeding gas tends to be compensated by the CaO carbonation. At 300°C for \( \alpha = 2 \) and \( \theta = 2 \) the produced gas composition is suitable for the gas grid independently by the relative content of CO and CO₂ in the feeding gas. Similar results were obtained at 250°C for specific values of \( \phi \) (0.75 and 1). At 350°C only values of \( \theta > 2 \) ensure a suitable gas composition.

Fig.1 Aspen flowsheet of the SEM process

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References

SESSION III

Energy carriers: utilization, storage and safety
Abstract
The combustion of ammonia has received a lot of attention over the last few years due to challenges associated with its burning speed and the emission of nitric oxides [1]. One way to improve the reactivity of NH3 is to pre-crack the fuel into mixtures containing NH3/H2 before introducing it into energy systems. Previous studies have shown that pre-cracking ammonia produces hydrogen which promotes its combustion behavior and reduce NO and unburnt NH3 emission [2,3]. Verkamp et al. [4] showed that mixtures of partially cracked NH3 (28% vol.), reproduces the minimum dissociation energy, and quenching distance of CH4 flames. Hussain et al. and Pacheco et al. [5-7] in their various studies demonstrated that NH3/H2 flames could be stabilized by combining swirling and a bluff-body burner with staged fuel injection. They also showed that NOx can be reduced by initially operating fuel rich mixtures to reduce amount of NO formed, then followed by a lean injection to oxidize the remaining products. It is quite established from above literatures that ammonia dissociation produces H2 which increase the reactivity of ammonia fuel as it burns further. However, what is not clear is what percentage cracking produces mixtures capable of mimicking the basic combustion properties of hydrocarbon fuels. Previous studies have shown that ammonia dissociates into mixtures containing hydrogen and nitrogen in a 3:1 ratio. This study seeks to understand the turbulent flame structure of NH3 stabilized in a non-premixed bluff-body burner. Combustion in many industrial systems occurs in non-premixed turbulent modes with complex recirculating flows. Bluff-Body burners have recirculating zones (RZ) which are found in practical combustors. The RZ is essential for the flame's stabilization as it carries hot recirculated products to the bluff-body surface and serves as a re-ignition source for incoming fuel jet [8]. Therefore, the aim of this study is to see if the recirculation zone on a bluff-body would act as a cracking region for ammonia flames and as a means to reduce the need for ‘pre-cracking’ of the fuel. To do this, an attempt is first made to see if an NH3/air flame will be stabilized in a bluff-body burner, and then to study the turbulent flame properties of various mixtures of NH3/H2/N2 flames.

References
Explosion Behavior of Ethanol-Ethyl Acetate in Air

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Abstract

Alcohol-ester mixtures and, specifically, ethanol-ethyl acetate mixtures are widely used as solvents in the packaging industry. Such mixtures are flammable and, thus, in order to design adequate prevention and mitigation measures for the industries where they are stored, handled and used, reliable safety data are required.

According to the National Fire Protection Association, the key parameter for classifying flammable liquids is the flash point [1]. However, although liquid fuels are not explosive by themselves, explosive conditions may arise at temperatures higher than the flash point: fuel evaporation and subsequent mixing with air may result in the formation of a flammable cloud, the accidental ignition of which may lead to explosion [2]. Hence, in some conditions, explosion parameters – maximum pressure and the maximum rate of pressure rise (i.e., the deflagration index) – for flammable liquids in their vapor state are also needed. The flash point is 12.8°C for ethanol and -4.4°C for ethyl acetate [3]. This means that both ethanol and ethyl acetate are prone to generate explosive conditions at ambient temperature or higher.

Recent research efforts have been focused on predicting the flash point for ethanol, ethyl acetate, and their mixtures [4]. For ethanol-ethyl acetate, it has been found that, over a rather wide range of mixture compositions, synergistic effects arise resulting in the so-called “minimum flash point behavior”: the flash point of the mixture is below the flash points of the individual components [4]. This behavior increases the explosion risk for ethanol-ethyl acetate mixtures compared to ethanol and ethyl acetate.

Explosion data for ethanol and, above all, for ethyl acetate are rather scarce (see, e.g., Refs. [5-7]), whereas there is a complete lack of data for ethanol-ethyl acetate mixtures. Non-linear effects could affect the explosion behavior of such mixtures. Thus, in principle, this behavior cannot be extrapolated from the individual components, but it requires a dedicated investigation.

The present work fits in this context focusing on the explosion behavior of ethanol-ethyl acetate in air. Closed-vessel explosion tests were carried out for an ethanol-ethyl acetate composition of interest to the packaging industry, varying the fuel/air equivalence ratio. Tests were also extended to ethanol/air and ethyl acetate/air to quantify the effects of the possible interaction between the two fuels in the mixture. All tests started from 25°C and 1 bar.

Experimental results show that, as the fuel equivalence ratio is increased, a transition occurs from a regime in which synergistic effects arise making the explosion behavior of ethanol-ethyl acetate more severe (i.e., making the rate of explosion pressure rise of ethanol-ethyl acetate higher) than both ethanol and ethyl acetate, to a regime in which, as a result of a completely different interaction between ethanol and ethyl acetate, the explosion behavior of their mixture is less severe than both the individual components. The maximum rate of pressure rise falls within an intermediate regime in which non-linear interaction effects substantially disappear and, thus, the value of deflagration index for the mixture can be obtained by averaging the values of the two fuels according to their molar proportions.

References

Influence of NH\textsubscript{3} on CH\textsubscript{4} oxidation regimes


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Abstract
The use of pure NH\textsubscript{3} as alternative no-carbon fuel for conventional combustion systems is nowadays a challenging topic, due to ammonia poor oxidation properties. Blending ammonia with fossil fuels represents a feasible solution to improve process stability, exploiting the higher reactivity of such “fuel-enhancer”, while reducing at the same time the CO\textsubscript{2} emissions.

In this context, the present work aims at exploring CH\textsubscript{4}-NH\textsubscript{3} interaction, with particular focus on the effect of NH\textsubscript{3} on CH\textsubscript{4} oscillation regimes [1].

Experimental tests were carried out in Jet Stirred Flow Reactor, changing the system operating parameters. Fuel-lean CH\textsubscript{4}-NH\textsubscript{3}/O\textsubscript{2}/N\textsubscript{2} mixtures were considered, at fixed equivalence ratio ($\phi=0.8$), dilution level (d=90%) and residence time ($\tau=0.4$s), changing the inlet temperature within the range $T_{in}=800-1300$K and the fuel-mixture composition. In particular, the NH\textsubscript{3} content was increased from 0 up to 100%, with an increment of 10%. The experimental tests were carried out at nearly atmospheric pressure ($p=1.1$ atm).

Simulations and kinetic analyses were performed with different detailed kinetic mechanisms, modelling the system as non-adiabatic with a global heat transfer coefficient equal to 1.6-$10^{-3}$ cal/(cm\textsuperscript{2} s K).

Experimental results revealed a different influence of NH\textsubscript{3} on CH\textsubscript{4} oxidation depending on the NH\textsubscript{3} concentration. In particular, mixture reactivity is slightly enhanced when NH\textsubscript{3} is increased from 0 up to 30%, while CH\textsubscript{4} conversion is shifted to higher $T_{in}$ for NH\textsubscript{3}$>40\%$.

NO emissions are boosted for the CH\textsubscript{4}-NH\textsubscript{3} blends in comparison with the oxidation of both pure CH\textsubscript{4} and NH\textsubscript{3}. Indeed, while for the combustion of pure CH\textsubscript{4} the NO formation is negligible under the explored conditions, increasing NH\textsubscript{3} content from 0 up to 10%, NO emissions drastically increase up to a maximum of 180ppm. The highest NO concentrations were detected for NH\textsubscript{3} content from 20 to 40%, reaching 300ppm of NO for $T_{in}=>1150$K.

A further increment of NH\textsubscript{3} concentration results in a reduction of NO emissions.

Maps of instabilities were outlined for CH\textsubscript{4}-NH\textsubscript{3} blends ranging from pure methane to pure ammonia, following the evolution of the reactor temperature ($T_{r}$) in time at different $T_{in}$ and fixed equivalence ratio ($\phi=0.8$). Results are reported in Fig. 1.

Both periodic (dark grey area) and damped (light grey area) oscillations were detected, with different shapes, amplitudes and frequencies depending on $T_{in}$ and NH\textsubscript{3} concentration. Examples of both the dynamic phenomena are reported in the insets of Fig.1.

Low concentrations of NH\textsubscript{3} (10-30%) promote the onset of periodic oscillations, as they occur at lower $T_{in}$ compared to pure CH\textsubscript{4}. Increasing the NH\textsubscript{3} content in the fuel blend, the window of periodic oscillations is shifted to higher $T_{in}$ and confined in a narrower $T_{in}$ range. For NH\textsubscript{3}$>70\%$ only damped oscillations were found.

Fig. 1. Maps of dynamic behaviors as a function of NH\textsubscript{3} concentration and inlet temperature.

Numerical results show that the selected kinetic schemes well reproduce the experimental data for pure CH\textsubscript{4}, while discrepancies between models predictions and experiments get worse for NH\textsubscript{3} containing mixtures. Despite such inconsistencies, models reproduce the overall effect of NH\textsubscript{3} on mixture reactivity and pollutant emissions.

Kinetic analyses revealed a strong interaction between CH\textsubscript{4} kinetic paths and NO-NO\textsubscript{2} loop from NH\textsubscript{3} oxidation.

References
Risk Assessment of the Large-Scale Hydrogen Storage in Salt Caverns

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Abstract

The use of hydrogen-based technologies requires infrastructure for small, medium, and large-scale production, transportation, storage, and distribution. Now, the focus is on the optimization of technological performance. However, hydrogen infrastructures must be developed above all in compliance with safety principles. The development of safety indications and procedures is mandatory to guide the development of H\textsubscript{2} storage technologies, transport systems and infrastructures. In this context, salt caverns are accepted as a technological solution for large-scale high-pressure hydrogen storages.

Underground hydrogen storages (UHS) pose severe safety issues due to high energy densities, low leakage rates and big storage volumes. As a consequence, risk analysis of UHS is a required step for assessing the suitability of this technology.

Up to date, quantitative risk assessment of underground hydrocarbon storage has been widely performed [1], [2] while no previous work has been published on the risk analysis of salt caverns used for hydrogen storage. Generally, hydrogen has low ignition temperature and wide flammability range, making leaks a significant hazard for fire and explosion, especially in confined spaces.

Moreover, in the case of UHS in salt caverns, due to the phenomena of hydrogen contamination by bacterial metabolism, the hazards associated with the presence of methane and hydrogen sulfide must also be considered.

In a recent paper we performed the risk analysis of hydrogen storage in salt caverns by considering the release of H\textsubscript{2}, CH\textsubscript{4} and H\textsubscript{2}S. The frequencies used in the calculations were obtained from historical data of CO\textsubscript{2} storage [3].

In this work, we extended the calculations of the risk of UHS to evaluate the sensitivity of the results to the frequency of the initiating event which is assumed as the rupture at the ground of the riser pipe from the salt cavern to the ground. Empirical models were used for the consequence analysis coupled with the event and fault tree analysis for the evaluation of the effect zones.

First, the bow-tie analysis (Figure 1) was used to highlight all the possible causes (basic events), as well as the outcomes (jet fire, UVCE, toxic release), and then the consequence and risk analyses were performed.

![Bow-tie diagram](image)

**Fig. 1.** Bow-tie diagram with “Rupture of vertical riser pipe at the ground” as initiating event/top event.

Calculated results showed the peculiar safety issues related to this storage system.

In particular, the UVCE turns out to be the most frequent outcome, but its effect zone decreases with time due to the hydrogen contamination and the higher contents of methane and hydrogen sulfide. Consequently, for long times, in addition to the contamination and safety problems linked to hydrogen alone, the effects related to the toxicity of H\textsubscript{2}S, produced by anaerobic bacteria, and of SO\textsubscript{2}, main product of the combustion of H\textsubscript{2}S, become more crucial.

References


MILD Combustion features of NH3/Alcohols blends

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Abstract
High hydrogen-density and well-established production processes [1] makes NH3 a valuable energy vector in the context of the energy shift toward Renewable Energy Sources integration. Despite that, high fuel NOx emissions, low flammability and difficult reactor design compromise the NH3 wide utilization. In this context, MILD Combustion [2] is becoming a first choice technology to oxidize ammonia, both for its inherent reaction stability, remarkable fuel flexibility and very low NOx emissions [3]. Another relevant aspect that is gaining relevance, in the framework of the general effort to increase e-fuels usage and reduce the dependence on specific fuels availability, is the set-up of thermal conversion technologies capable of oxidizing blends of e/fuels and traditional fossil fuels. For instance, e-fuels/fossil fuels blends may help achieving greater stability and conversion degree [4], entailing only marginal modifications to the burner design. Moreover, the blend of a potentially interesting e-fuel like ammonia and bio-derived fuels, like low molecular weight alcohols, may have beneficial effects similar to those due to fossil fuels addition. These blends may indeed better sustain the global energy transition by further reducing the overall carbon dioxide emission.

In this framework, the present work presents experimental results and discusses these results, with the support of numerical chemical kinetics and fluid-dynamical simulations. Combustion performance, overall stability and pollutants emission (in particular nitrogen oxides) of NH3/alkohols blends are studied in a cyclonic burner. In this reactor MILD Combustion is attained by means of a strong internal recirculation induced by two inlet streams from the opposite corners of a nearly prismatic chamber.

In the reported cases the oxidant was standard air at ambient temperature. All the tests here reported are relative to a 7 kW power load. Main results were also compared with those obtained with NH3/CH4 blends to better clarify the role of the blend composition. Experiments confirmed that alcohols widen the region where stable ammonia combustion is achieved, in terms of both operational temperature and mixture compositions.

In lean conditions (at $\phi=0.7$) NOx emissions suddenly increase at increasing NH3 content in the fuel mixture, being higher than the pure NH3 case for a wide range of blending ratios, both with alcohols and CH4. In particular, a non-monotonic trend is detected for NOx profiles as a function of NH3 content. As matter of facts, when NH3 is added to pure CH4, NOx emissions increase up to about 1200 ppm when NH3 percentage is 50%, and then decrease for higher % of NH3 [3].

On the other hand, the NH3 addition to pure alcohols more gradually increases NOx emissions, with a maximum emission when the ammonia is 90% of the blend. On the other hand, comparable NOx levels are detected for pure NH3 and NH3/alkohols blends at with a 25% of ammonia.

By comparing the relative behaviour of investigated alcohols, slightly higher NOx are detected for ethanol blends with respect to methanol and 1-butanol. Remarkably, the blends of ammonia with these two latter alcohols show very similar NOx emission levels up to a NH3 content of 50%.

At corresponding NH3 percentage in the blend, NH3/alkohols blends show lower NOx levels than NH3/CH4 mixtures for ammonia content up to about 75%. At higher NH3 percentages the situation is reverted and higher NOx emissions are observed for NH3/alkohols mixtures.

Chemical kinetics analysis highlights that CO and NH3 species differently compete for OH radical consumption when alcohols or methane are blended with NH3. This behaviour affects the NOx distribution, shifting their peak toward higher %NH3 for NH3/alkohols blends.

References
Numerical simulations of ammonia/methane and ammonia/methanol blends in a lab-scale cyclonic burner

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Abstract
In the context of the energy transition and the need for alternative fuels utilization, NH3 appears to be one of the most suitable because of its high hydrogen density and ease of production [1]. Despite that, high fuel NOx emissions, low flammability and difficult reactor design compromise the NH3 wide utilization. In this context, MILD Combustion is becoming a first choice technology to oxidize ammonia, both for its inherent reaction stability, remarkable fuel flexibility and very low NOx emissions. This peculiar combustion mode requires the development of new modelling paradigms for the prediction of both reactor behaviour and thermo-chemical state.

The presented activity was purely simulative and was performed on an anti-symmetrical feed cyclonic burner (LUCY) [2], developed at STEMS-CNR. In particular, the focus was on the use of innovative methods for the tabulation of detailed chemical kinetics in turbulent reactive flows for strongly internally diluted systems with recirculating burned gases.

The objective of this work has concerned the analysis and modelling of the cyclonic flow burner emulating MILD combustion conditions and operating with both conventional and alternative energy carriers and blends of them. In particular, the advancement proposed by this work concern the characterization of the interaction between turbulence field and chemical kinetics using detailed kinetics for innovative fuels. To obtain such results, reactive fluid dynamic analyses were performed using the Ansys Fluent software. In particular, an optimized mesh has been built in order to catch in a proper way the peculiar flow-field and large velocity gradients inside the burner, then several steady-state simulations with a RANS approach were performed with different turbulence models, in order to find the best one for the investigated case, considered through a tabulated chemistry method for the application of detailed chemistry.

All the simulated test-cases refer to 7 kW of power load, while standard air (300K) was used as oxidizer. Main results obtained for pure NH3 were compared with those obtained with NH3/CH4 and NH3/CH3OH blends, to better clarify the role of the blend composition on system reactivity, stability, temperature profiles and emissions (Fig. 1). Numerical results were compared with experimental data, in order to overlay the local temperature profiles and chemical species monitored inside and at the exit of the burner, respectively, in order to verify and validate the numerical model.

Fig 1. Temperature contours and streamlines for LUCY burner.

The CFD model here obtained showed quite good agreement with the experimental data with respect to the measured temperature, for all the different investigated NH3 blends. However, the model was less accurate in predicting the chemical species at the reactor outlet, showing very good agreement only for mixtures with a low ammonia content, but losing its effectiveness as the percentage of NH3 in the fuel mixture increases.

References
SESSION IV

Biomass and waste thermochemical processing
Effect of pyrolysis atmosphere on PETs behavior during contaminated biomass pyrolysis

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Abstract
Hyperaccumulators plant conversion into biofuels or value-added products via pyrolysis processes is considered as a prospective approach owing to its safe solution for potentially toxic elements (PTEs) contaminated biomasses disposal. The feasibility of phytoremediation coupled with pyrolysis can be accomplished via the targeted production and utilization of by-products such as gaseous volatile fraction and biochar. Nevertheless, the fate and transformation of PTEs during the thermal treatment is fundamental considering the volatility difference of PTEs and their distribution in pyrolysis products. Previous study revealed that in presence of Cd it is necessary to operate at low-temperature (lower than 430 °C) to obtain a heavy metals free vapor phase fuel [1]. In case of one or more metals among Pb, Cu, and Zn, it is possible to pyrolyze at higher temperatures retaining PTEs in the biochar, characterized by lower metals mobility. The safe application of the contaminated biochar in different fields (fertilizer, activated carbons precursor, filler in wood and polymer composites, contaminants adsorbent in wastewater and soil, catalyst or adsorbent in gas cleaning [2]) is a key factor for the feasibility of the entire process. In contrast, the pyrolysis gaseous products, that contain a large percentage of CO₂, is particularly suitable for feeding MILD combustion burners. In these peculiar combustion condition fuel is, indeed, fed under high dilution (fuel concentration outside the flammability limits) and preheating (higher temperature than self-ignition one) conditions [3].
The purpose of this study is to compare the effects of the carrier gas on both PTEs fate during pyrolysis and on biochar and pyrolysis gas properties at different operating conditions. Carrier gas composition was be varied using N₂, CO₂ and mixture of them. Slow pyrolysis experiments of contaminated Populus nigra (Pb= 21.65 mg kg⁻¹) from phytoremediation were studied, and products yield and gas composition were measured. Biochar chemical and physical characterization as well as the analysis of potential environmental risks (BCR extractions) related to the use of biochars derived from contaminated Populus nigra were conducted. The preliminary results show that the nature of the carrier influence pyrolysis process at higher temperature, products yield and PTEs recovery in the biochar. Moreover, temperature strongly influence the physico-chemical characteristics of biochar, as expected.

References
Hydrochar and postprocessing water as potential energy sources from the hydrothermal co-carbonization of waste

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Abstract

According to Eurostat Statistic 225 million tonnes of municipal waste (MW) were generated in the EU in 2020 of which 23% was landfilled. In the case of sewage sludge (SS), there was c.a. 8.7 million tonnes of dry sludge and 6%, respectively. Both materials have the same properties: high moisture and organic contents [1,2]. In the EU, undersieved fractions (USF) from the mechanical-biological treatment (MBT) of MW undergoes an aerobic biological stabilization before being landfilled. Sewage sludge, in many cases, meets the same fate. Therefore, the main aim of this work was to study hydrothermal carbonization and co-carbonization of both materials dedicated to feedstock with a high moisture content and the potential energy application of its products.

The USF of mixed MW was collected from an MBT plant from Florence. Although 75% of the USF was unrecognizable, the remaining percentage included paper, plastics, glass, wood, textiles, food waste, coffee pods, inert materials, and metals. Digested sewage sludge was collected from the wastewater treatment plant in Żory, Poland. USF, SS, and a mixture of SS with 20% of USF were hydrothermally pretreated under the same conditions: 200 °C, and 2 h, and 150 rpm in a Zipperclave® Stirred Reactor (Parker Autoclave Engineers, USA). The combustion process was performed by thermal analysis with a Netzsch STA 449 F3 Jupiter in an air atmosphere (40 mL min⁻¹), at a heating rate of 10K min⁻¹ up to 700 °C and depicted in the form of TG and DTG curves. The postprocessing water (PW) from every test and reference sample (inoculum) was evaluated for biomethane potential within 500 ml reactors in Bioprocess Control’s AMPTS II for at least 20 days.

The results are summarized in Fig. 1 and Fig. 2. In brief, the combustion of hydrochars took place at higher temperatures and finished earlier than in the case of the feedstocks. Hydrothermal co-carbonization decreased the time of combustion, which occurred at higher temperatures in more stabilized way.

Fig. 1. TGA analysis

Fig. 2. Biochemical Methane Potential results.

PW SS was the most effective in methane production, whereas the USF addition slightly decreased its potential.

Concluding, hydrothermal carbonization proved to be an appropriate treatment of these wet waste under investigation with the potential for energy recovery.

Acknowledgements

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References

Abstract

In a circular economy perspective, solid plastic wastes (SPW) are a valuable source of chemicals, energy vectors and fuels, providing more efficient and environmentally sound options compared to landfill disposal [1]. Product distribution optimization, experiment, reactor, and process design as well as pollutant formation control can largely benefit from fluid dynamics and chemical kinetic modelling tools [2]. This work proposes a semi-detailed kinetic model for polyethylene (PE), polypropylene (PP), and polystyrene (PS) pyrolysis that, upon further model reduction, is directly applicable to CFD simulations. Based on the functional group approach implemented for polyvinylchloride (PVC) [3] and biomass pyrolysis [4], the kinetic model proposed adopts a simplified description of high molecular weight species (HMW) while preserving a detailed description of low molecular weight species (LMW). The same approach is extended to other polymers offering a powerful tool for the investigation of fundamental aspects in chemical recycling processes for SPW and biomass/SPW mixtures.

The present kinetic model (in CHEMKIN format) classifies polymeric liquid-phase chains in LMW and HMW according to the chain carbon-number. LMW species can evaporate forming stable gas-phase products, while HMW chains are described by a few chain functional-groups representative of mid-chain (MC) and end-chain (EC) moieties. Chains with different carbon-number are simply characterized by different amounts of the same functional groups, therefore the HMW chain-distribution is described through MC and EC pseudo-species only. Direct information on the chain distribution is lost, but the average molecular weight is inferred from the MC to EC groups ratio. The resulting models involve 75 liquid-phase species for PE, 120 for PP, and 42 for PS. The main computational cost of the present model stems from product distribution description as the reactivity HMW distribution is described with less than 15 species.

Model performances have been assessed by comparison with experimental data and detailed models from the literature [e.g., TGA]. Figure 1 shows model predictions for the different polymers at heating rate 5 °C/min. The model agrees with experimental data with an error <10°C in terms of temperature, well within experimental uncertainty. The present model has also been assessed by comparison with more computationally expensive models from the literature [5], [6], although not reported herein, resulting in similar predictions both in terms of mass profiles and product distribution.

Fig. 2. Comparison of model predictions (solid line) with experimental data (symbols) on liquid mass loss at 5 °C/min for PS, isotactic PP, and high-density PE.

Acknowledgements

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References

Modeling fast pyrolysis of biomass in fluidized bed reactors: the role of heterogeneous secondary reactions and char loading

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Abstract

Biomass is one of the most promising renewable sources for the substitution of fossil feedstocks in several industrial applications. Biomass fast pyrolysis favours the formation of bio-oil, which offers significant advantages in storage and transport. A scenario based on a decentralized production of biooil as an intermediate biofeedstock for the final upgrade in a biorefinery was proposed.

The present study is focused on fluidized bed fast pyrolysis, selected due to its several advantages. However, particle heating, gas and solid phases residence time and contacting, need to be carefully controlled to drive conversion along the prescribed chemical pathway. Primary biomass decomposition reactions and secondary homogeneous reactions of vapours have been largely investigated through kinetic mechanisms and kinetics of variable degree of complexity. Instead, heterogeneous secondary reactions between volatile products of biomass decomposition and biomass char were often overlooked in modeling biomass fast pyrolysis, as well as in the process and reactor design guidelines.

The relevance of heterogeneous vapor-char interaction to bio-oil production emphasizes the role of char loading establishing at steady state during operation. Char hold-up is regulated by the balance that occurs as fresh biomass is continuously fed while some of the char is subject to entrainment and elutriation, possibly enhanced by attrition. For this reason, bed drain and ex-situ regeneration are typically accomplished to control biomass and char inventories. A model-based assessment of the relevance of heterogeneous secondary reactions between pyrolysis vapors and biomass char is undertaken. A 1-D distributed parameters model based on a simplified representation of the fluidized bed pyrolytic converter has been developed based on a shallow bubbling fluidized bed with overbed feeding of the biomass particles. The reactor operates under steady-state conditions at atmospheric pressure. Solids are considered well stirred while the gas flow pattern is modelled according to the axial dispersion model with variable mixture density and velocity. A semi-lumped reaction scheme, similar to that suggested by Shafizadeh and Chin [1], has been assumed, while the kinetics of the heterogenous secondary reaction has been modelled using an expression proposed for tar decomposition over char [2]. Material balances on the species and constitutive equations describing elutriation, entrainment, attrition and drainage are solved. In Fig.1 the effect of reactor temperature on gas and oil yields is shown while varying the drainage space-time. Results highlight the optimal range of the drainage time and temperature to maximize oil yield, considered the combined effects of kinetics and char loading.

**Fig. 1. Oil and gas yields as a function of drainage space-time for different values of temperature.**

Acknowledgements

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References

The integration of pyrolysis and pavement production processes: toward a more sustainable waste management


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Abstract
This work proposes the use of residues (bio-oil and char) obtained from the pyrolysis of Refuse Derived Fuels (RDF) as additives for producing improved asphalts and for recycling aged asphalts to regenerate new ones. The ambitious double goal of this approach is i) the reduction of the consumption of resources for the production of new road pavements and ii) the landfill wastes reduction. The optimization of the processes for the production and the use of pyrolysis by-products is expected to fully integrate the urban waste and asphalt cycles, as shown in Fig. 1.

Fig.1: Integration of pyrolysis and road pavement production processes.

The use of pyrolysis products for asphalt preparation is an emerging research topic [1] and opens to an alternative use of pyrolysis products (liquids and solids) outside of fuel and chemicals industries and to the replacement of petroleum-derived products (e.g. crude oil) with products deriving from waste thermoconversion.

A RDF provided by Calabra Maceri e Servizi s.p.a. (Rende, CS) was used as feedstock for the production of bio-oil and char samples. Preliminary pyrolysis tests in a tubular quartz micro-reactor were performed and a full characterization of all the pyrolysis product was carried out to identify the more suited pyrolysis conditions for RDF transformation (550°C, 30°C/min). The pyrolysis residues were used as bitumen additives (char and bio-oil) and as aged asphalt rejuvenator (bio-oil). Mechanical properties of the bitumen samples enriched by char or bio-oil were evaluated by rheological characterization [2]. Possible anti-aging effects exerted by char or bio-oil addition have been also evaluated by applying ad-hoc bitumen aging protocols [3]. The ability of bio-oil to exert regenerative properties on aged asphalt, through the its maltenic fraction restoring, was also tested by analyzing the rheological properties of aged asphalts treated with growing amounts of pyrolysis liquid. Interestingly enough, this study has also confirmed that bio-oil has all the suitable characteristics to be used as bitumen additive both as fluxing agent and (in the better cases) as asphalt rejuvenator. This work confirms the feasibility of the use of char as bitumen additive thanks to its highly compatibility with bitumens (given their organic nature) with the goal to reinforce the overall bitumen structure increasing its mechanical properties and slowing down the molecular kinetics of its aging process. This circumstance is particularly advantageous since carbon-based nanoparticles purposively used (among them, fullerenes, nanotubes and graphenes) are available at higher costs [3].

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References
SESSION V

Engines & Propulsion
Insights on strategies for particle emissions control in HD SI Natural Gas engines in view of EURO VII limits

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Abstract
Engines fed by gaseous fuels, such as Natural Gas (NG), are proving to be an alternative to the traditional gasoline and Diesel engines. Considering the more and more restrictive regulations on pollutant emissions and the global direction towards decarbonization, Natural Gas could represent a mid-term alternative solution. Methane is the primary component of NG and it has the highest H/C ratio among the hydrocarbons, providing lower carbon based emissions. In Heavy Duty sector, historically represented by Diesel vehicles, NG engines show comparable performance and benefits in terms of emissions [1]. The upcoming EURO VII regulation for gas engines is pointing the attention to the sub-23 nm solid Particle Number (PN) emissions which can represent a critical aspect, even for this kind of engine [2].

The authors evaluated the potentialities offered by three different strategies in the abatement of PN emissions, mainly focusing on sub-23 nm particles control. An extensive experimental campaign has been carried out on a test bench Euro VI NG HD Spark Ignition engine. It is recognized that the main source of PN emissions from gaseous fuels engine is linked to the lube oil consumption [3] and its introduction into the combustion chamber. In this sense, the effect of improved rings pack design was studied, comparing two configurations of the same engine characterized by different oil rings pack. The upgrading of the rings pack reduces the oil deposits in the crevices and in the ring seats thus lowering the oil access to the combustion chamber. The results demonstrate a significant abatement (95%) of engine out PN emissions with the new designed rings pack.

Since oil consumption is also influenced by the oil quality [4], the impact of specific lubricant properties has been studied. Typical automotive lubricants consist of base oil (roughly 75-90% by mass) and an additive package; the ash content is the incombustible component of the oil. The effects of different base oils and ash contents on PN emissions have been evaluated. The experimental tests have been performed on the engine with upgraded rings pack. The results show that the improvement of oil quality determines a further PN reduction up to 70%.

Differently from the previous described approaches, the last strategy is not headed to the control of particle formation processes, but towards the abatement of PN at the exhaust through the addition of a CNG Particulate Filter (CPF) coupled with a Three Way Catalyst (TWC). Such technology is derived from the well consolidated DPF for Diesel engines. The potentiality of the filter has been studied when applied to a NG engine, characterized by different working conditions and significative low level of emitted particle. The study also provides insights future optimization of the system. The CPF has been tested on the engine with improved rings pack. The abatement efficiency has been calculated through a comparison of the PN emitted with and without the CPF. Although the CPF technology is still under development and optimization, the results are very encouraging and show its high potential to achieve an important PN decrease from a NG engine of roughly 85%

A recap of the strategies tested and the achieved results is presented in Figure 1.

Fig. 1. Technologies and abatement efficiencies on particle emissions

The analyzed methods can lead to a proper sub-23 particles control toward the future regulation limits.

References
Role of lubricant oil on particle emissions from a PFI/DI SI engines powered with gaseous fuels

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Abstract
The objective of reducing the pollutant emissions and in particular those of particles has motivated researchers to explore alternative fuels to replace the conventional fossil ones. It is well known from literature the contribution of spark ignition (SI) engines to the emission of particles too [1].

Among the liquid biofuels for SI engines, pure and blended alcohols are recommended due to their low sooting tendency as well pointed out by study involving optical diagnostics of combustion process [2].

Gaseous fuels, as compressed natural gas (CNG), have the advantage over liquid fuels of reducing particle emissions thanks to their lower carbon content. In this case, particle formation depends on the gas components concentration which can vary with geographical source, time of year, and treatments applied [3]. Although the strong reduction of particles when gaseous fuels are used, their concentration at exhaust still cannot be considered negligible. Their presence can be attributed to the lubricant oil that participates to the combustion. Hydrogen fuel could have great potentiality to diminish the particle emissions due to the absence of carbon atoms in its molecule. Nevertheless, lubricant oil can play an important role on particle emissions.

This study aims to provide a better insight on the effect of oil on the particle emissions at exhaust of small displacement SI engines equipped with direct (DI) and port fuel injection (PFI) systems fueled with commercial gasoline (G) and gaseous fuels, both CNG and hydrogen. A methodology able to evaluate the oil contribution was developed considering several percentage of oil to simulate in the medium and late time oil effect [4].

Fig. 1 shows the percentage of particles emitted from CNG, GPFI and GDI at different oil content. The particle emissions are classified in particles smaller than 23 nm which will be likely subject to the next emission regulation and those larger than 23 nm actually regulated. Oil addition produces a significant increase of particle emissions whatever the fuel and the engine configuration. The different proportion between the two range classes of the particles depends on the role played by the nucleation and agglomeration processes. Generally, the higher volatility species of the oil tend to nucleate contributing to the formation of sub-23 nm particles. On the other hand, the heavier organic components are more prone to condense on existing particles resulting in more pronounced accumulation mode. The effect of oil is also evident for H₂ fueled engine as reported in Fig 2. A large number of sub-23 nm particles was measured at the engine conditions characterized by a more oil consumption as high engine speed and low load.

These results highlighted the significant role played by the lube oil on particles emitted from gaseous fueled engines, and the necessity to improve its quality to reduce their impact on the atmosphere and then improve the urban air quality.

Fig. 1. Particle number percentage at different oil content for the CNG, GPFI and GDI configuration.

Fig. 2. Particle size distribution for H₂ fueling

References
Chemical characterization of the condensed exhaust from a DI SI hydrogen-powered engine

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Abstract

Lower ignition energy (0.02 mJ), wider inflammability range (0.21<Φ<7.34), higher calorific value (141.9 MJ/Kg) and higher flame propagation speed, compared to gasoline, make hydrogen an interesting and suitable substitute for application in spark ignition (SI) engines [1]. As a gaseous fuel, hydrogen, once introduced into the intake manifold and well mixed with air, improves combustion efficiency compared to a liquid fuel and results in a reduction of exhaust emissions [2]. In the present work, we studied the emissions of a hydrogen-fueled SI engine for investigating if it can be considered totally "green".

The experiment was performed on a small displacement direct injection SI engine upstream of the Three-way catalyst (TWC) [3]. By using a condensation sampling line connected to the tailpipe, the condensed exhaust was collected and extracted by an organic solvent (dichloromethane, DCM), in order to separate the organic fraction present in the water. The sampling was carried out at different engine operating conditions chosen as representative of the typical urban driving conditions. Whatever the operating conditions, the results evidenced the presence of similar species, but with different concentrations. In particular, the untreated water, before the extraction treatment, presented an intense fluorescence emission, in a wavelength range typical of aromatic species [4, 5]. Similar fluorescence was measured also on DCM extract of the samples. It was hypothesized that some of the lubricating oil, used for avoiding wear between parts in relative movement of engines, passed into the combustion chamber. DCM extract of the samples were analysed by Gas Chromatography - Mass Spectrometry (GC-MS) analysis and compared with the lubricating oil mass spectrum (Figure 1). The spectra presented the following features, typical of a mineral oil:

- they have the same unresolved curve
- in both cases a sequence of alkanes was detected by ion extraction.

Moreover, in the DCM extract samples the presence of certain PAH (Polycyclic Aromatic Hydrocarbons) and oxygenated PAHs such as Fluorenone, Phenalenone and Anthracenedione were also detected. These results highlighted the presence of organic compounds at engine exhaust even when a carbon neutral fuel is used. Therefore, it was confirmed a leakage of the mineral oil in the combustion chamber, which in part has undergone a combustion or a thermal degradation in oxidizing environment, showing the typical products (PAHs and oxygenated PAHs) and in part, instead, reached the exhaust, unburned. Finally, the extent of the contamination due to the lube oil depends on the operating condition.

![Mass spectra of mineral oil and DCM extract](image)

Fig. 1 Mass spectra of mineral oil and DCM extract from condensed exhaust obtained through GC-MS analyses at 3000 rpm and λ=1.67.

References

Abstract
The use of gaseous fuels has been considered as a valid solution for reducing the dependence from oil as well as a way for decreasing the environmental impact of energy conversion systems. In fact, gaseous fuels have a low carbon content, which means low CO$_2$ emissions, and the good mixing with air allows emissions lower than conventional fuels. Unfortunately, recent geopolitical events demonstrated that also the price of natural gas can suffer big fluctuations, limiting the advantages coming from the use of such alternative fuels. For this reason, developing technologies to produce gaseous fuels of non-fossil origin, as well as innovative combustion systems for their efficient use are of seminal importance nowadays.

Biogas is produced from the anaerobic digestion of organic materials, with a composition dependent on the feedstock and on the production processes [1–4]. Though the use of biogas in internal combustion engines (ICE) is very attractive, the presence of CO$_2$ has adverse effects on combustion, reducing combustion speed, narrowing flammability limits, and deteriorating combustion stability. A possible way to improve the combustion performances of biogas is to have hydrogen among the constituents. Innovative anaerobic digestion processes, which maximize the H$_2$ yield, can end up with biogases made of CH$_4$, CO$_2$ and H$_2$. The biogas, generally adopted as fuel in positive ignition ICEs, is also suitable for Controlled Auto Ignition (CAI) engines. Recently, it was shown that the use of innovative biogases made of CH$_4$, CO$_2$ and H$_2$ in CAI helps reducing the NOx emissions with respect to conventional biogases without H$_2$. This was demonstrated numerically with a single zone cylinder model and with a simplified reaction mechanism, the GRIMech 3.0 [5]. The auto-ignition was controlled by varying the EGR rate, the intake charge boost pressure and temperature. The intake charge temperature dependence on the amount of hot recirculated exhaust gas was considered, due to its impact on the combustion process. Authors investigated the effect of these engine control parameters on the emission formations.

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References
Physical and chemical characterization of particles emitted during passive regeneration of medium-duty diesel engine

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Abstract
Passive regeneration is an approach used to oxidise particulate matter (PM) in the diesel particulate filter (DPF) [1]. It uses normal exhaust temperatures and nitrogen dioxide (NO₂) as the catalyst to oxidize PM in the DPF. PM was collected from a medium duty diesel engine running at 3500rpm and full load operation. At this steady state condition, the exhaust temperature was higher than 500°C. For the physical and chemical characterization of the particles, PM was sampled at engine out (B-DPF), after the DPF (A-DPF) and after the selective catalytic reactor (A-SCR).

Improved information about the chemical and physical composition of PM could be essential to understand the contribution of each component, to model PM oxidation through exhaust aftertreatment system, to implement more efficient abatement systems and to assess health protection programs.

The organic fraction extracted by PM with dichloromethane was analyzed by fluorescence spectroscopy (Fig. 1 top) and the spectra were deconvoluted in three main contributions, corresponding to species whose emission is peaked in the UV region (<400nm) and in the visible, at 430 and 500nm. It can be observed that passing through the aftertreatment systems, a change of the species distribution occurs. In particular, a decrease of light species can be noticed, together with an increase of heavier species (fluorescing in the visible range of wavelengths).

The application of transmission electron microscopy (TEM) and high resolution TEM (HRTEM) to PM provided statistically significant measurements of the primary particles dimensions and nanostructure parameters (fringe length, tortuosity and separation), respectively. It was found an increase of primary particles diameter, passing through the aftertreatment systems, but no significant change in the nanostructure parameters (Fig.1, bottom).

It can be concluded that the effect of aftertreatment systems is not only the PM reduction in terms of mass and numbers at the exhaust and the change in PAH composition already demonstrated [2], but also a chemical transformation of the fraction not identified by GC-MS along with morphological change of PM. In particular, the size of the primary particles increases without significantly changing their nanostructure. This behavior suggests a decrease in their reactivity when emitted, with a minor adverse effect on human health. However, emission standards will also need to take into account the presence of volatile particles [3].

Fig. 1. Fluorescence deconvolution at 350nm of emission wavelength (top) and HRTEM (bottom) of samples collected at 3500rpm B-DPF (left) A-DPF(center) and A-SCR (right).

References
Abstract
In the last years, small scale satellites (e.g., Cubesats) represent one of the main attractions from the space market point of view. Thus, research is moving towards proper propulsion systems for attitude, trajectory, and orbit control. Chemical engines are preferred to electric ones when the low thrust capability of electric propulsion systems is not compatible with maneuver requirements, such as impulsive boost. Since the employment of solid, liquid bi-propellants or hybrid thrusters have several drawbacks and design issues [1], monopropellant thrusters are considered a good solution given their structural simplicity coupled with re-ignition and throttling capability. In this context, the interest in the study, development and testing of both monopropellants and hybrids for nanosatellites is growing more and more. Consequently, thruster breadboards are ground-tested, based on the catalytic decomposition of hydrogen peroxide, that finds its application as monopropellant or oxidizer, in the case of hybrid system, in combination with polymeric fuel grains.

In the present work, a particular attention has been dedicated to the decomposition efficiency and catalytic bed responsiveness for applications involving HTP (High-Test Peroxide) monopropellant thrusters, whose ignition performance directly affects the time needed to reach the nominal values of chamber pressure and thrust, therefore influencing propellant consumption and system performance. For this kind of applications, the widely used propellant is hydrazine, able to give good performance in terms of efficiency and durability [2], but its high level of toxicity [3] and relatively high freezing point can cause some problems during space mission [4]. So, the interest has shifted to storable, easy handling and green propellants, such as hydrogen peroxide, despite it presents a theoretical specific impulse that is the 69% of that one obtainable with hydrazine [5]. 87.5 wt% HTP was employed, and several tests were performed for varying catalytic pellets characteristics. The performance of commercially available Pd-loaded alumina ceramic pellets was compared to that of some laboratory metal-free formulations of in-house manufactured ceramic pellets of similar shape but of radically different active species. The main parameters were measured during operation and the propulsive performance were estimated. Figure 1 shows, as an example, the transient temperature increase due to catalytic decomposition with three different catalytic bed made of commercial pellets (Comm.), and the two in-house developed formulations labeled “P1” and “P2”. The formulation “P2” nicely matches the responsiveness of the commercial pellets and also gives good performance in terms of steady-state decomposition temperature.

![Fig. 1. Measured HTP Decomposition Temperature versus time for different kind of Pellets.](image)

References
SESSION VI

Stationary and solid fuel combustion systems
Fluidized bed reactor modelling using multiphase reactor networks

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Abstract
Biomass is expected to be a key resource for fulfilling clean energy demands in the near future. Using detailed kinetic mechanisms with computational fluid dynamic (CFD) simulations for predicting pollutant emissions can easily become unfeasible in terms of required computation power. For this purpose, reactor network (RN) modelling can be a viable alternative with significantly less computational power requirements.

In RN modelling, depending on mixing behavior, the real system is represented by a combination of ideal reactors: Perfectly Stirred Reactor (PSR) and Plug Flow Reactor (PFR). However, the standard ideal reactors are only capable of solving gas-phase reactions. When applied on solid fuels, the gas and solid-phase reactions are usually decoupled. First, the solid pyrolysis is calculated and second, gas-phase pyrolysis products are used in RN modelling.

In this study, a novel solid-gas Perfectly Stirred Reactor (sPSR) was developed which calculates both phases in a fully coupled manner. The simultaneous solution of two phases also allows including the surface reactions in a volumetric basis, which are usually neglected in previous studies. The steady-state equations for respectively gas and solid species are given in Eq. (1) and (2):

\[
\frac{m_{\text{in,gas}} \cdot \omega_{\text{in,gas}} - m_{\text{out,gas}} \cdot \omega_{\text{out,gas}}}{V_{\text{solid}}} + MW_{\text{i}} = (R_{\text{in,gas}} + \frac{R_{\text{gas,from solid}}}{P_{\text{gas}}}) \cdot \frac{m_{\text{gas}}}{m_{\text{solid}}} \cdot \omega_{\text{solid}} + MW_{\text{i}} \cdot \frac{R_{\text{solid}}}{P_{\text{solid}}} = 0
\]

Eq. (1)

where \( m_{\text{in,gas}} \) and \( m_{\text{out,gas}} \) are the mass flow rates of gas entering and leaving the reactor, \( \omega_{\text{in,gas}} \) and \( \omega_{\text{out,gas}} \) are the gas compositions, \( V_{\text{solid}} \) is the volume of solid phase, \( MW_{\text{i}} \) is the molecular weight of the i-th component, \( R_{\text{in,gas}} \) and \( R_{\text{gas,from solid}} \) are the reaction rates of gas phase and gasification reactions, \( P_{\text{gas}} \) is the pressure of gas phase, \( m_{\text{gas}} \) and \( m_{\text{solid}} \) are the mass of gas and solid phase, and \( \omega_{\text{solid}} \) is the mass fraction of solid phase.

The sPSR is implemented in the previously introduced reactor network solver NetSMOKE [1]. The approach is applied on biomass gasification in a bubbling fluidized bed reactor.

The representation of the bubbling fluidized bed reactor, shown in Fig. 1, and estimation of the residence times of each reactor in the figure are done similarly to the work from Stark et al. [2] and Bates et al. [3]. The main novelty of this work is using the sPSR in the network instead of gas-phase PSR. In Fig. 1, emulsion phase, which includes solids, is shown with brown color and is represented by the novel sPSR (R1). Bubbles (shown in white) and freeboard (shown in pink) are represented by gas phase PFRs, R3 and R2 respectively.

Fig. 1. A bubbling fluidized bed and its RN representation, including the novel sPSR.

Fig. 2 reports the dry \( \text{N}_2 \)-free gas concentrations from RN models with and without the sPSR, compared with the experiments from Pecate et al. [4], using \( \text{N}_2 \) as the fluidizing gas. Adding the new sPSR resulted in significantly better predictions. With sPSR, self-gasification is also calculated which has an effect on water-gas shift equilibrium due to steam consumption.

Fig. 2. Comparison of experimental data with RNs predictions with and without using sPSR.

Acknowledgments
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References
Multi pattern cylindrical perforated burner: numerical simulations of interacting flames

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Abstract

Hydrogen may help the transition to a decarbonized energy scenario as it can be produced from excess wind and solar power and then injected into the existing natural gas grid. In this manner, the available infrastructure is exploited for the storage and distribution of renewable energy sources, thus mitigating challenges due to intermittent and variable nature. However, hydrogen exhibits very different properties from those of natural gas. This behavior requires a better understanding of the effect of adding H2 on consumer appliances such as domestic burners and boilers, as well as on industrial systems. Among these, domestic condensing boilers are equipped with perforated burners that generate multiple laminar premixed flames. This contribution analyzes the possible onset of intrinsic instabilities, which are well known to influence the behavior of pre-mixed flames of pure hydrogen or methane [1, 2, 3] for different mixtures of H2. In these works, the hydrodynamic and heat diffused instabilities on methane/propane premixed air and hydrogen flames have been analyzed, however, no information is available for fuel mixtures, and in particular for those enriched with H2. The literature still lacks a fundamental analysis of these phenomena given the use of these mixtures in industrial and domestic applications. The present work aims to shed light on the occurrence of the aforementioned instabilities with mixtures enriched with H2 and to derive usage maps in relevant conditions for end-user equipment based on premixed laminar flames. Representative direct numerical simulations (DNS) of practical flames will be performed by emulating portions of real burners. To do this, a strategy is suggested to reduce the DNS computation effort. For this purpose, the critical wavelength that triggers flame instabilities for different H2 contents is determined, at equivalence ratios typical of the aforementioned user systems. It has been found that the critical wavelength decreases strongly by adding hydrogen; for example, with 80% H2, it is about a quarter of the value with pure methane. Direct numerical simulations of practical flames are then carried out which emulate portions of real burners to evaluate the occurrence of the aforementioned instabilities (Fig. 1). Operatively, the massively parallel spectral element code nek5000 is employed using a one-step deficient reactant approach capable of faithfully reproducing the instability length-scales at play for each mixture using a in-house developed conversion toolbox for the non-dimensional parameters. In particular, to have a correct estimate of the flame-wall interaction, a conjugate heat transfer approach between flame and burner was applied.

Fig 1. Temperature distribution for different time steps for 80% of H2.

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References

Hydrodynamic investigation of hot dense fluidized beds for thermochemical conversion of solid fuels


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Abstract

Thermochemical conversion of solid fuels (e.g., combustion, gasification, pyrolysis) efficiently occurs in properly designed and operated fluidized bed reactors. In this regard, solid mixing of both inert bed and fuel particles is an essential condition to be optimized as it strongly affects process performance and emission levels. Solids mixing requirements depend on the thermochemical process under investigation. For example, conventional combustion of solid fuels relies on relatively intense solids mixing to ensure complete burn out of fuel and to minimize the number of feeding ports. In allothermal gasifiers, characterized by two interconnected beds, the aim is to control the fuel mixing to give the fuel sufficient residence time within the gasifier. Too high lateral mixing results in a loss of char from the gasifier to the connected combustor. Also, in CLC fuel reactors, in contrast to direct combustion, moderate levels of lateral mixing increase the fuel residence time, thereby minimizing losses of unconverted char to the secondary reactor. Moreover, the variability in physical properties of different solid fuels, especially for biomass, is another aspect, which directly influences the mixing behavior.

Despite previous studies on solids mixing in gas-solid dense fluidized beds, few works address units operated at typical industrial conditions. Therefore, proper characterization of mixing/segregation phenomena within the inert bed and among dissimilar solids, in hot large-scale units operated at relevant superficial gas velocities requires further research studies.

The major challenge of such studies is to find the suited diagnostic technique to trace the patterns of a fuel-like solid once it is injected in the inert fluidized medium. In this regard, in the present study home-made uncooled capacitance probes are tested in a bubbling-regime laboratory scale unit operated at high temperature.

To reliably interpret the capacitive signal of the dense phase in mixing tests, a perfect knowledge of the single-solid bed material behavior at fixed superficial gas velocity is required. As a result, the probability distribution function (PDF) of bed voidage is computed, providing significant information about bubbles and emulsion phase. One of the main outcomes is that the dense phase voidage can hardly be modeled with the two-phase theory, according to which all the excess gas respect to minimum fluidization joins the bubble phase (Figure 1). This result, registered as early as room temperature, is of significant importance, not only to correctly measure solid tracer concentration in the dense phase of the bubbling bed, but also because the dynamic gas–solid distribution in the fluidized bed can have a considerable effect on the apparent reaction and heat and mass transfer rates of a generic thermochemical process. The traditional two-phase theory is incapable of predicting these rates properly.

![Fig. 1. Emulsion voidage mode at 3 different radial positions in the bed column (r/R=0: circles; r/R=1/2: squares; r/R=7/9: diamonds) VS excess gas velocity U-Umf. Fluidized bed of grey quartz sand (dp=358μm, ρf=2650kg/m³) at 600°C. Capacitance probe sensing volume placed at h/H=0.7; fluidized bed aspect ratio is about 1.78.](image-url)

Thus, the present study deals in detail with the issue of gas-solid distribution in the dense fluidized bed and shows results on first experiences about tracking tests on binary systems of solids.
Soot effect on heat transfer in large furnaces: CFD modelling and validation by field test data

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Abstract

Energy transition represents a challenge for the energy market, involving mainly scientists, engineers and designers to properly produce and efficiently use bio-fuels, waste-fuels as well as new energy vectors, like hydrogen and ammonia, which are likely to replace gradually the fossil fuels.

Steam generation remains essential for industrial activities and power generation and represents a highly energy demanding activity. Moreover, the increasing stringent regulations on pollution constitute an additional element pushing toward innovation. Specifically in the boilers context, optimizing energy conversion is essential, ensuring high thermal efficiency along with lower emissions regardless of the fuel employed, even for extremely different liquid and gaseous fuels with completely variable characteristics, ranging from bio-oils to low calorific value waste gases.

In this framework, advanced design tools are strategical to meet market needs: in particular, for boiler design, CFD is an extremely useful tool for both the analysis and development of single equipment – e.g. the burners, over-fire-air ports etc. – and for optimization of the full system. On the other hand, simulation software have grown more and more complex, requiring highly experienced users to give back affordable quantitative results, and remains the need of reliable parameters and models reproducing correctly the physics of the problem, both ingredient requiring validation.

For the specific application of CFD to furnaces of large boilers, it is essential using accurate heat exchange parameters, mainly the emissivity of membrane walls and a fouling coefficient, as well as employing physically consistent modelling of injection by the steam-assisted atomizers, including the soot production, since it affects gas absorption such having significant effect on heat transfer.

Taking advantage of AC Boilers activity on boilers – starting from design and up to on-site testing and operation – affordable plant data are available even for quite different boilers, such providing ideal basis for CFD analysis validation.

In particular, gas and oil testing on a 6-burner refinery boiler allowed the tuning of heat exchange parameters and the development of a simple and effective modelling procedure for liquid fuel injection and soot production. The optimal value found for wall emissivity is 0.6, along with usual values for fouling thermal resistance. The approach proposed for soot is based on the use of a simple 1-step Kahn and Greeves model, just with tuning of the soot-formation-constant, to be varied in order to get suitable mean (2-3%) and peak values (<5%) of soot mass fraction in flames.

The study ends with, a validation of the overall CFD set-up, obtained comparing simulations and test data on a 32-burner super-critical boiler, fed with heavy fuel oil: keeping unchanged heat exchange parameters and soot modelling, an excellent matching is obtained on a completely different test case.

Fig. 1. Flame shapes and temperatures in a refinery boiler by post processing of CFD simulation: gas (left) and heavy-fuel-oil (right) combustion.

Acknowledgements

The present paper summarizes the results obtained in a study – carried out within the “BE4GreenS” R&D project supported by Regione Puglia through FESR funding by European Union.
Assessment of the possibility of using ammonia-based nano-additives for lean combustion

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Abstract

To reduce emissions and improve the combustion performance of lean fuels, considerable research progress has been made [1]. Reducing total nitrogen oxide (NO\textsubscript{x}) emissions can be achieved in several ways, as by lowering the flame temperature with the use of fuels emulsified with water. A novel approach is evaluated in the present work, by using fuel emulsified with ammonia-based nano-additives, such as urea.

The use of water as part of the hydrocarbon fuel represents one of the prospective directions in the development of new type of fuel systems. For fuel preparation, on the other hand, it is desirable to achieve greater stability of the emulsified fuel with minimal chemical expenditure, so that the emulsified fuel can be used for a longer period. The stability of an emulsion is influenced by water-fuel ratio and the amount of surfactant. We investigated the influence of nano-dispersed urea particles, glycerol, and surfactants (SPAN 80 and TWIN 80) on the combustion performance and emission characteristics of aviation fuel.

The experimental campaign was conducted in a swirl combustor; the test rig (300kW liquid swirl combustor, Fig. 1) consists of a cylindrical combustion chamber with four optical windows and equipped with pressure sensors, thermocouples, and an exhaust gas analyzer for emission recording.

Fig. 1. Section of the swirl combustor.

The experimental campaign was conducted with different fuel/air ratios (Φ). The focus is on the stability of the emulsion and surfactants and glycerol were therefore used. To characterize the effects of the additive on flame emissions, chemiluminescence flame images were acquired. A statistical and spectral analysis was then performed using the pressure sensor for instability analysis. A nine-component wavelet analysis of the frequency signal was performed, each of which has a particular frequency content; in this way, it was possible to identify the signal from very lower to very high frequencies. For each decomposed signal component, the root mean square (RMS) value was determined: an increase in the RMS value towards the leaner conditions was noted. The second spectral moment was also calculated to be used as an indicator of combustion stability. Exhaust gas analysis was performed both with the Jet-A1 additive described above and without additive for the different Φ and it was carried out for nitrogen oxides (NO\textsubscript{x}), carbon monoxide (CO) and carbon dioxide (CO\textsubscript{2}) emissions.

References

Numerical simulations of interacting flames in perforated burners of domestic condensing boilers

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Abstract
The injection of hydrogen, produced by water electrolysis from excess wind and solar power, into the natural gas network could help the decarbonization of domestic heating; indeed, forecasts state that hydrogen could provide about 18% of the energy demand in the EU by 2050. Modern condensing boilers are equipped with perforated burners injecting a premixed mixture into the combustion chamber. So far, the burner design comes from the manufacturers’ experience [3]; however, the upcoming changes in gas composition, with the introduction of fuels with reactivity and power density differing significantly from those of natural gas, ask for a better understanding of the combustion process.

In this context, the application of mathematical models based on computational fluid dynamics (CFD) is partially hampered by the complexity of premixed flames, as well as by the computational cost required to describe transport, reaction, and heat exchange in complex domains. Only a few numerical simulations of burners in domestic boilers can be found, and most of them are limited to the mixing problem (e.g., [2]) or to simplified computational domains (i.e. just single or group of holes [4]).

The present work aims to improve the comprehension of the structure of the laminar premixed flames in real domestic condensing boilers with the ultimate purpose to provide a tool to optimize the burner design, especially in the perspective of addressing gas variations, e.g. H2-admixtures. More specifically, we carry out three-dimensional numerical simulations of the whole combustion chamber with detailed kinetic mechanisms, i.e. KEE-58 [1] oxidation scheme with 17 chemical species and 58 reversible reactions. The burner is cylindrical with a pattern of over 2000 slits and holes and is equipped with an upstream cylindrical distributor, which affects the velocity of each hole and slit. Hence, to better represent the real combustion process, the numerical model encompasses also the distributor section. The flow is laminar with typical Reynolds numbers $Re < 50$, as the holes and slits are very small. The pressure-based solver available in ANSYS Fluent is used for numerical simulations, with second-order discretization and a coupled pressure-velocity algorithm.

A significant interaction between neighbor flames occurs as shown in Fig. 1 for 0%, i.e. natural gas, and 50% of H2 content in the fuel mixture. Numerical predictions are compared with experimental data on pollutant emissions available for different H2 contents.

![Temperature field on a plane passing through a row of slits for 0% (a) and 50% (b) of H2 content in the fuel mixture.](image)

Fig. 1

Acknowledgements
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References
Abstract
Carbon nanotubes (CNTs) are a family of hollow cylindrical carbon-based structures whose walls consist of one graphitic sheet (SWCNT), two (DWCNT) or more (MWCNT) rolled up to form long carbon tubes. Due to their outstanding physicochemical properties (e.g., high thermal and electrical conductivity and excellent mechanical properties), they can have many potential applications. For these reasons, since their discovery in 1991 by Iijima et al. [1], many efforts have been made by researcher and industrial companies in developing CNT synthesis methods with industrial applicability.

Among the most used methods to produce these materials, the floating catalyst chemical vapour deposition (FCCVD) is one of the most promising for large-scale CNT production. FCCVD are heated cylindrical reactors in which a hydrocarbon feedstock (e.g., methane/natural gas) is introduced along with a carrier gas (usually Ar and H₂) and either a catalytic precursor (typically ferrocene) or a metal aerosol. The formed CNTs, which grow while crossing the reactor chamber, are collected at the outlet by spinning methods. This process potentially enables the continuous production of high-value carbon nanomaterials and “turquoise” hydrogen.

On the laboratory scale, FCCVD has been successfully employed for the synthesis SWCNTs. However, despite the high potential of FCCVD, its industrial implementation is still a challenge due to low production, process performance variability and uncertainties and operational difficulties arising from competing amorphous carbon formation. A well-directed CNT kinetic model can be game-changing in driving process optimization needed to accelerate scale-up efforts.

In this view, this work proposes a CNT model for describing the chemical steps involved in FCCVD processes. This semi-detailed chemical kinetic framework, hierarchical and modular in nature, is able to qualitatively and quantitatively describe the relationships between catalyst, reaction conditions and CNT yields in the thermo-catalytic pyrolysis of methane. The chemical pathways in the model were developed based on experimental evidence to account for the main reactive steps involved in CNT production. The early catalytic reactions between the hydrocarbon and the free catalysts and those involved both in the nanotube cap nucleation and in the subsequent growth of the nanotube walls were carefully implemented in the model.

Fig. 1. Graphic representation of the main step involved SWCNTs evolution

The extreme complexity related to the different chemical routes to carbon formation and aggregation and its evolution from the gas-phase chemistry is decoded by applying a discrete sectional model approach on the analogy with the soot particle growth-model [2]. The surface kinetic model is coupled with an already widely validated gas-phase pyrolysis mechanism to account for both carbon nanotube and soot formation. Finally, the developed kinetic framework has been tested by adopting a FCCVD numerical model implemented in the OpenSmoke++ suite [3] allowing to describe the interactions between the phenomena at the microscale with the fluid dynamics description of the system at the macroscale.

The paucity of quantitative kinetically controlled data on these processes, especially in terms of methane conversion and nanotube yield, limits in-depth validation of the model. However, the analysis of the dynamics of gas-phase products distribution, surface species, and CNT growth as a function of reactor operating conditions (temperature, feedstock composition, catalyst size) shows agreement with the main experimental trends already driving lab-scale experimental design and paving the way for further analysis of the chemical physics aspects of this process.

References
Electrophoretically-driven in-flame deposition of Carbon Nanoparticle films


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Abstract

Gas-fuel combustion in premixed flames is emerging as a viable method for the synthesis of Carbon nanoparticles (CNPs) films with fascinating properties, which turn them into potential candidates for many industrial applications [1].

In fact, a fuel-rich flame provides the chemical reactive environment capable of generating CNPs in a fast and tunable way by varying the combustion parameters. CNP films can be produced by harvesting particles from a specific flame position. One of the most common methods consists of the rapid insertion of a cold collector into the flame. In this case, particles deposition is driven by thermophoretic forces. Chemical and physical film properties can be fine-tuned controlling the flame parameters, and the insertion conditions (the insertion time, the cooling time and the height above the burner at each the collector is inserted) [2].

This work provides novel experimental results on the use of electric fields to improve the harvesting process and modify the properties of the CNP films without changing the operating flame conditions. To this aim, a novel collector device has been designed. The collector includes a metallic holder which is kept at a desired DC potential, a controlled pneumatic actuator and a vertical micrometric slide which allowed operations at given insertion time, cooling time and flame positioning. The holder hosts a thin circular substrate (which acquires the same potential of the holder) where CNPs deposit.

In these experiments, a flat laminar premixed ethylene-air flame with carbon-to-oxygen ratio equal to 0.67 stabilized on an electrically-grounder McKenna burner has been tested. The cold electrified CNP collector has been operated to have up to 400 insertions at insertion time of 100 ms, cooling time of 1 s, height above the burner of 15 mm, and applied potential from 0 to -3 kV.

CNPs deposited on substrates have been analyzed by atomic force microscopy (AFM), UV-visible light absorption and Raman spectroscopy. AFM images acquired over freshly cleaved mica substrates with a single insertion in flame reveal that deposited CNPs increase linearly as the absolute value of the electric voltage increases. In particular, the estimated degree of coverage increases by six times, from 5% at 0kV to 30% at -3kV. Interestingly, these experimental results are consistent with the predictions of a recently developed CNPs deposition model [3].

CNP films have been also deposited on glass substrates. Light absorption analysis of CNP films reveals that the presence of an electric field increases the growth rate of the film thickness by a factor of 6, passing from 0 to -3kV. Moreover, the analysis of the spectra in terms of Tauc’s plot shows that the energy band-gap decreases as the electric voltage increases. This effect is confirmed by a reduction in the ratio between the slope of the linear photoluminescence background, $m$, and the intensity, $I(G)$, obtained from the Raman spectra.

At date, the mechanisms governing film formation and morphology in the electrophoretically driven process are still unclear. Nevertheless the deposition model and the Raman spectra suggest possible effects deriving from the presence of a larger fraction of coarser particles, bearing higher charge levels, in the CNP films.

Acknowledgment

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References

In-situ Laser Diagnostics to Monitor the Flame-Assisted Synthesis of Pt Nanoparticles in the Reactive Spray Deposition Technology (RSDT)


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Abstract
The Reactive Spray Deposition Technology (RSDT) is a flame-based process that combines the synthesis of nanoparticles and their deposition on the substrate of choice in one step. This unique technology allows us to manufacture performant and durable Membrane Electrode Assemblies (MEAs) to be used in the next generation Proton Exchange Membrane Fuel Cells (PEMFCs) and Water Electrolyzers (PEMWEs). The optimization of the RSDT process involves ex-situ analysis of the products at the end of the deposition. Laser diagnostics can expedite the RSDT process parameters optimization by characterizing the synthesized nanoparticles in-situ and in real-time.
RSDT relies on a horizontal turbulent diffusion flame fueled by a fuel solution containing a metal precursor component. The fuel solution is atomized by a heated nozzles nozzle so that the metal undergoes decomposition/oxidation, nucleation, and growth, as it is transported across the flame [1]. This work characterizes the nanoparticles synthesized in two flames (Pt-Type1 and Pt-Type2) fueled by different flowrates of a mixture of xylene, acetone, propane, and 10mM platinum acetylacetonate (Pt-AcAc). To this end, measurements are performed also in the correspondent metal-free flames (Blank 1 and Blank 2) fueled by a solution deprived of Pt-AcAc to remove the contribution of the carbonaceous flame products from the measured signals.
Laser-Induced Incandescence (LII) measures a signal proportional to the volume fraction ($f_{v,p}$) of the nanoparticles [2]. The proportionality constant is determined at the edge of the luminous zone of the flame from the value of $f_{v,p}$ that can be inferred from the mass balance of Pt under the two extreme assumptions of the nanoparticles being composed of either pure Pt or PtO. Static Laser Light Scattering (LLS) measures the fraction of light being diffused that, in the spherical shape approximation, is proportional to the nanoparticle $f_{v,p}$ and the average sixth power of their diameter ($d^6$) and inversely proportional to the average third power of their diameter $d^3$ [3]. The combination of LII and LLS measurements enables the measurement of an average diameter of the synthesized Pt nanoparticle, $d_{av}= (d^6/d^3)^{1/3}$, whose profile as a function of the distance from the fuel nozzle, $L$, is shown in Fig.1. The figure includes the $d_{av}$ of nanoparticles sampled via thermophoresis from the flame and imaged with High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy (HAADF-STEM) to validate the in-situ results.
Results indicate that the coagulation efficiency of the synthesized nanoparticles is very low since they grow at a rate that is orders of magnitude slower than the collision rate of non-interacting Brownian nanoparticles predicted by the gas kinetic theory.

Acknowledgments
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References
Cu- and Mg- activated carbon honeycombs monoliths for H₂S removal from biogas at low temperature

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Abstract
Hydrogen sulfide is one of the main impurities present in reformate, natural gas and raw biogas. The purification of these gas streams is a mandatory step before their use in downstream processes as H₂S is toxic, corrosive for engines and fuel processing devices and poisonous to catalysts even in small concentrations. One of the most effective techniques for H₂S removal is the adsorption due to its easy management, high efficiency and low cost. The surface chemistry, the high internal surface area and porosity are the main features that make Activated Carbons (AC) good H₂S sorbents. Application of ACs, generally produced as powders, is limited when high pressures are required. Therefore, the use of ACs in structured form is preferred but this generally requires the use of binders that while they improve the mechanical properties of sorbents they reduce the adsorption capacity due to the partial blockage of porosity. Otherwise, the introduction of suitable metals can lead to the improvement of original ACs properties [1, 2].
In this work, copper and magnesium oxides were dispersed both separately and mixed on commercial honeycomb ACs to improve the H₂S capture capacity. Dynamic catalytic tests (100ppmv H₂S) have been carried out at room temperature in the co-presence of humidity and O₂ to evaluate the sulfur capture capacity and to investigate the oxidation reactions involved by varying the composition of the two metals. The adsorption performance and the activated mechanism were significantly different depending on the nature of the metal. The basic MgO active sites promote the formation of elemental sulfur through a path faster than the deeper oxidation mechanism promoted by CuO, resulting in the formation of sulfates/sulfuric acid along with elemental sulfur. The easy dissociation of H₂S into HS⁻ and H⁺, occurring for Mg-modified sorbents, is the reason for the higher capture capacity of these materials in the presence of wet streams compared to Cu-modified ACs for the same load level. Nevertheless, the Cu-Mg catalytic sorbents coupled the fast kinetic features of MgO, promoted by the presence of water vapor, to the deeper oxidation activity of CuO, exerted also under dry conditions, thus representing materials with tunable properties.
Both fresh and spent honeycomb sorbents were characterized by N₂-adsorption at -196°C, PSD, XPS, TG-MS in order to investigate the specific nature of S-species formed during the catalytic adsorption.
A thermal treatment up to 620°C under inert gas flow of the bimetallic spent sorbents restores the original porous structure of the modified AC monoliths due to the decomposition of sulfate species at lower temperature and the evaporation of elemental sulfur at higher temperature. The honeycomb monoliths can operate several capture cycles without detectable loss of capture capacity releasing only SO₂ and S by the thermal regeneration. This makes these structured metal-modified ACs very good candidates for H₂S capture process at room temperature for natural and raw biogas purification.

References
SESSION VIII

Numerical combustion - part 1
Self-updating Digital Twin of a semi-industrial furnace via data assimilation approach

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Abstract

Data assimilation (DA) is a set of mathematical techniques in which observation data and a numerical model are used synergically to generate predictions that are more accurate than the ones obtained using the data or the model independently. More specifically, data assimilation includes a wide spectrum of tools which aim to the estimation of an optimal state of a given system integrating a model and observations, both affected by uncertainties [1]. Considering its successful application in weather forecasting [4], DA can enable significant advancements also in the combustion field.

In the present work, we propose a methodological DA approach, which efficiently integrates experimental data in a numerical model for a specific combustion system. In particular, we will apply a DA methodology to a semi-industrial furnace (Fig.1), where a great number of experimental and numerical data is available [3]. For the latter, a Digital Twin (DT) has been developed [2] in order to predict the entire state of the chamber, in particular the spatial fields of temperature and the main chemical species. The DT is derived from 2D numerical simulations with Computational Fluid Dynamics (CFD) techniques solving the Reynolds-averaged Navier-Stokes (RANS) equations. These simulations are analysed using a dimensionality reduction method, i.e. Proper Orthogonal Decomposition (POD), and an interpolation method, i.e. Kriging, used to find a response surface for the unexplored operating condition.

The dataset selected to train the Digital Twin takes into account different operating conditions in terms of fuel composition (methane-hydrogen mixtures from pure methane to pure hydrogen), considering an air injector diameter of 16 mm to adjust the air jet entrainment, and an equivalence ratio of $\phi = 0.8$.

The goal of this work is to develop an adjusted DT model through one of the many DA methods, the Kalman filter, as it allows robust predictions by reducing the model and experimental data uncertainties. In this way, the level of confidence of the whole system will be high.

The state of the system we wish to optimize regards the temperature profile, sampled at different axial and radial locations inside the chamber, and the NO emissions measured in the exhaust gases.

The obtained results will show how the assimilation of the available data provides a substantial improvement, thus highlight the effectiveness and robustness of the DA framework paving the way to its application within the development of combustion systems.

References

A data driven Filtered Wrinkled Flamelet model for premixed hydrogen-air flames

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Abstract
In the next decades, hydrogen is expected to be used as a zero-carbon fuel for a plethora of applications ranging from heat generation, transportation and energy distribution. However, the development of hydrogen-based combustion devices is often hindered by the lack of reliable predictive numerical simulations tools. A peculiar and key aspect of hydrogen-based flames is the intrinsic thermal-diffusive (TD) instability of the flame front which is promoted by the elevated mobility of the hydrogen molecule. This happens especially for lean hydrogen-air mixtures when the fuel Lewis number $Le$ decreases below a critical, sub-unity, Lewis number $Le_0$ [1]. The onset of TD instability locally modulates the flame speed along the front, amplifying small perturbations leading to self-wrinkled, unsteady cellular flames [3]. Such effects are also amplified by the thermal expansion and the ensuing, ubiquitous Darrieus-Landau (DL) instability mechanism as shown in Fig.1.

The impact of intrinsic instability, both TD and DL, is currently overlooked by state-of-art models used in LES simulations of turbulent premixed flames therefore motivating this contribution. A first step toward their inclusion, has been done in a recent work [5] where a data-driven, laminar, wrinkling factor model has been proposed. In the present contribution, we follow a different strategy [4] which takes advantage of the filtered tabulated chemistry approach and the FTACLES formalism [2]. The present data driven Filtered Wrinkled Flamelet model, is based on the data driven generation of tables for each unclosed term. The data are collected from a filtered, fully resolved 2D simulation of a self-wrinking intrinsically-unstable flame, using a filter $\Delta_{filt}$ and tabulated as conditional averages with respect to two filtered progress variables, $\phi(C_1,C_2;\Delta_{filt})$, being $\phi$ a generic unclosed term.

The effectiveness of the model is measured a-posteriori in terms of the capabilities of filtered simulations (see Fig.2) to reproduce the flame area and the consumption speed of a large-scale flame with $L=400\ell_D$, being $L$ the hydrodynamic lengthscale and $\ell_D$ the flame thickness. The main advantage of this approach is that the tables can be generated using data from a significantly smaller $L\sim100\ell_D$, and therefore computationally cheaper, simulation compared to the target large-scale flame.

Acknowledgements
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References

Fig. 1. Experiments and simulations of intrinsically unstable, self-wrinkling flames.

Fig. 2. Filtered simulations of a large scale self-wrinkling flame using different filter sizes.
On the dynamic determination of the micro-mixing constant in Transported joint-composition PDF models

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Abstract

Developing more efficient, clean and fuel-flexible combustion technologies is crucial to prompt the energy transition, especially in those industries with high operating temperatures that cannot be achieved by electrification. In this context, Moderate or Intense Low-oxygen Dilution (MILD) combustion has gained increasing attention as it can fulfil all the aforementioned features. MILD combustion is achieved by diluting the reaction region through recirculation of hot flue gases; in such regime, enhanced mixing and lower reaction rates induce strong turbulence-chemistry interactions, leading to Damköhler numbers approaching unity (Da≈1). Despite its advantages, MILD combustion presents many challenges. Besides, the lack of validated numerical models, which have been developed for conventional combustion systems where Da >> 1, partially hampers its application.

For this reason, in the last few years several modifications of the available combustion models have been proposed for MILD combustion in the Reynolds-Averaged Navier-Stokes (RANS) framework, showing improved numerical predictions. However, dealing with the highly non-linear average reactive source term is still an open research issue. In this regard, Transported joint-composition Probability Density Function (TPDF) methods represent a promising solution as the highly non-linear reactive source term is in a closed and exact form. On the other hand, it is necessary to close the molecular mixing term by employing a micro-mixing model. In particular, all of these models depend on a mixing constant, $C_\phi$, which is typically set to the fixed value of 2. However, $C_\phi$ is not constant at all and can vary widely depending on the case study investigated, hence needing costly trial-and-error tuning procedures to find its optimal value.

In this work, a novel methodology for the dynamic estimation of $C_\phi$, based on the transport of a passive scalar, is presented. RANS joint-composition TPDF simulations are performed on two MILD-related test cases: the Adelaide Jet-in-Hot-Coflow (AJHC) [3] emulating MILD combustion through a vitiated coflow, and a semi-industrial furnace (temperature in-flame profiles are shown in Fig.1) equipped with a MILD-capable burner, both fed with methan-hydrogen mixtures. The dynamic approach developed in this work permits generalizing the applicability of TPDF methods for cases where the combustion regime is not known a-priori, and hence it allows avoiding the time-consuming trial-and-error tuning procedure of $C_\phi$, achieving, with a single simulation, a satisfactory agreement with the experimental data.

Fig. 1. Radial profile of temperature for the MILD combustion furnace feeding 50% H2.

References

Abstract

In the context of the ecological transition asked by the EU Green Deal, hydrogen (H\textsubscript{2}) is playing a central role as a possible candidate to replace fossil fuels for providing heat and power. Hydrogen can be produced by electrolysis from renewable resources, injected into the existing natural gas network and directly burnt in domestic and industrial systems. Moreover, the EU is promoting the development of "hydrogen valleys", i.e., regional ecosystems exploiting the local availability of renewable energies to favor the decarbonization of domestic heating and local industries using hydrogen as an energy vector. On the other hand, the physical and chemical properties of hydrogen are significantly different from those of natural gas (NG), resulting in a lack of validated schemes for hydrogen and H\textsubscript{2}-enriched mixtures combustion under the typical conditions of existing end-user systems usually fed with natural gas, such as domestic condensing boilers. In particular, due to higher reactivity and power density, hydrogen shows a larger adiabatic flame temperature and an extreme difference in the flame propagation, with a laminar flame speed of 2.5 m/s, which is nearly ten times that of natural gas (0.3 m/s).

Under these conditions, flashback phenomena can severely compromise the safety and the performance of the burners, with the flame returning back towards the injection and heating the burner plate to undesirable operating temperatures. In this context, a better comprehension of the flashback phenomenon and the conditions under which it can occur is of fundamental importance to guarantee the safety and efficiency of the burners. Even if some experimental data concerning the characteristic speeds of H\textsubscript{2}-enriched mixtures already exist, no validated schemes and reliable numerical models have been proposed to predict the minimum velocity required to avoid flashback in perforated cylindrical burners when feeding them with NG/H\textsubscript{2} admixtures.

The present work proposes a numerical model which aims to evaluate the conditions leading to flashback in multi-hole burners, typically encountered in condensing boilers, in terms of operating parameters, such as the fuel velocity and the distance between burner holes. To this purpose, we perform 2D axisymmetric transient simulations with Computational Fluid Dynamics techniques with detailed kinetics, i.e., with the KEE58-Mech [1], having 17 species and 58 reactions to characterize a premixed hydrogen-natural gas flame out of a circular hole emulating a real cylindrical burner in a condensing boiler. Since the typical dimension of the hole is very small, the flow is completely laminar and no turbulence model is needed. Importantly, we model the conjugate heat transfer between the flame and the burner, including the radiation effects, to take account of the flame-wall interaction, which plays a crucial role in the flashback phenomenon. We investigate the flashback limits, in terms of velocity, for various H\textsubscript{2} contents.

We believe the present approach may also be useful to investigate how the burner design, as for instance dimension and hole-to-hole distance, may be improved to prevent flashback phenomena.

Figure 1: Temperature field in flashback conditions.

References

A Family of Skeletal Mechanisms for Methane Oxidation at High Pressure


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Abstract

The use of methane as a fuel in a wide range of rocket engine applications represents one promising route due to its benefits at a system level. Although several detailed kinetic mechanisms for methane oxidation exist, only a small subset proved to adequately reproduce the fundamental reaction pathways that appear under oxygen-fuel conditions and high-pressure levels, typical of liquid rocket engines’ thrust chambers.

Nonetheless, the search for computationally cheap schemes, eventually specialized for specific applications, represents an unavoidable theme in the space propulsion field. This is accompanied by the need for simplified mechanisms that may deal with off-stoichiometric mixtures, that deserve special attention in closed-cycle, staged combustion, liquid-fueled rocket engines.

In this work, the generation of a set of skeletal mechanisms for methane oxidation at high pressures is carried out starting from the C1 – C4 version of the detailed kinetic mechanism by Zhukov [1].

The mechanism reduction process is accomplished via an improved algorithm proposed by Malpica Galassi et al. [2], that builds on the computational singular perturbation (CSP) framework by introducing an additional layer of automation based on the tangential stretching rate (TSR) and the species’ participation index to TSR [3]. Based on this, the intrinsic target species set is dynamic and automatically identified through the process, leading the algorithm to include a minimal number of species/reactions that ensure global observables replication without any a-priori knowledge of the chemical pathways.

Various reduction strategies are carried out, targeting different applications and operating conditions of interest in space propulsion, as reported in Fig. 1. The objective is to provide a set of compact mechanisms that may cover a wide range of O/F ratios and chemically reacting flow conditions that characterize aerospace applications.

In this regard, the entire set of CSP-based skeletal mechanisms is tested against the corresponding validation targets, including ignition delay time, laminar flame speed, counterflow diffusion flame extinction, and perfectly stirred reactor (PSR) calculations showing appreciable predictive accuracy compared with the detailed parent kinetic scheme.

Fig. 1. Kinetic mechanism simplification strategies.

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References

Kinetic Evaluation of Hydrogen Supersonic Combustion and Chemical Emissions of Airbreathing Ramjet Vehicles

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Abstract

The MDO and Regulations for Low-boom and Environmentally Sustainable Supersonic aviation (MORE and LESS) is a research project pursued by a consortium of European government and academic institutions, including the Italian Aerospace Research Centre (CIRA) and coordinated by Politecnico di Torino under the EC Horizon 2020 financial support.

MORE and LESS aims to address the challenges regarding the environmental impact of the supersonic, air-breathing aviation implementing a holistic approach based on a synergic coupling between low and high-fidelity modelling of several processes e.g., aerodynamics, jet-noise, sonic-boom, propulsion, and above all pollutant and climate-changing chemical emissions.

Hydrogen is a promising candidate as fuel for supersonic, air-breathing, trans-atmospheric, long-term passenger transportation aircraft, because it can be burned in an efficient and reliable manner in supersonic combustion engines. Furthermore, H₂ is esteemed as a clean fuel with lower greenhouse gas emissions compared to hydrocarbons, since the overall product of its complete oxy-combustion is only water, even if, when reacts with air, it produces also NOₓ, due to the very elevated flame temperatures reached during combustion.

Since experimental investigations is often unfeasible due to several difficulties in measuring multispecies, reacting, high-speed, unsteady flow fields, the most convenient way to design and develop ramjet vehicles relies on CFD modelling and simulations, not only for an accurate description of the ignition and combustion behavior, but also for the pollutant i.e., NOₓ and the climate-changing i.e., water vapor chemical emissions evaluation.

In the work here proposed, the ignition characteristics of several H₂/O₂ detailed and skeletal combustion mechanisms i.e., Kéromnes, CREEK, Z22 [1], Aramco–II and GRI – Mech 3.0 were investigated through 0D calculations of the induction delay times by means of Cantera/Python simulations of homogeneous, adiabatic, isochoric, batch reactors.

Then, the computational predictions were compared against the experimental, high-pressure measurements of Hu et al. [2] carried out in shock tubes at inlet conditions i.e., pressures up to 10 atm, intermediate temperatures between 1030 and 1170 K and a fuel lean composition representative of the typical airbreathing, stratospheric, supersonic ramjet operations (see Fig. 1).

Secondly, the main H/O/N reaction paths followed by the chemical species in supersonic air-breathing combustion were theoretically analyzed.

Finally, a thermodynamic and kinetic 0D methodology, conceived to be applicable even in aeronautical conceptual design stage, was formulated to simulate also the electric spark ignition of the vehicle’s Air Turbo Rocket (ATR) engines. In this way, the pollutant and greenhouse gases emissions released by the ATR engines of a particular ramjet configuration, indicated as STRATOFLY MR5 and preliminary investigated by The von Karman Institute for Fluid Dynamics, were evaluated.

References


SESSION IX

Numerical combustion - part 2
Large Eddy Simulations of mean pressure and H\textsubscript{2} addition effects on the stabilization and dynamics of a partially-premixed swirled-stabilized methane flame


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Abstract

This work reports a numerical analysis on the pressure and hydrogen enrichment effects on the stabilization and combustion dynamics of a partially-premixed swirled-stabilized methane flame operated at 1, 3 and 5 bar, with H\textsubscript{2} admixture up to 40% by volume [1]. Large Eddy Simulations (LES) performed with the compressible parallel code AVBP (www.cerfacs.fr/avbp7x/) are performed to analyze flame stabilization and dynamics for all cases. When pressure is increased, both turbulence and chemical time scales are reduced leading to smaller turbulence scales and thinner flames which increases LES modelling challenging. To ensure that all flames are resolved similarly in the tested pressure range, the thickened flame (TFLES) model is used here with a Static Mesh Refinement (SMR) strategy. This necessitates a significant increase in the required mesh size. An Analytically Reduced Chemistry (ARC) scheme is employed to describe CH\textsubscript{4}-H\textsubscript{2}/Air chemistry. LES is validated against experimental multi-kHz repetition-rate OH* chemiluminescence, OH Planar Laser Induced Fluorescence (PLIF), stereoscopic Particle Image Velocimetry (sPIV) and pressure recordings. The dynamics of the different flames are then addressed. First, the impact of hydrogen at atmospheric pressure is investigated. While the reference natural gas flame (1 bar, 0% H\textsubscript{2}) presents a lifted M-shape, a strong Precessing Vortex Core (PVC), 40% H\textsubscript{2}-enrichment modifies the flame which becomes an attached V-shape, with a weakened PVC and the triggering of a thermoacoustic oscillation at the first system acoustic mode. Second, the impact of mean pressure is analyzed by fixing the H\textsubscript{2}-enrichment while increasing the mean pressure to 3 and then 5 bar. As the pressure increases, the flame assumes a more compact M-shape. It is proven that the interaction with turbulence smallest scales is not affected by pressure: Karlovitz number is constant. On the contrary, flame response to large turbulent structures is modified: Damköhler number reduces when mean pressure increased. If strong flame/PVC interactions are observed at atmospheric pressure leading to flame tip and root roll-up and local quenching, a more coherent flame is observed when pressure is raised. Furthermore, for these points, the thermoacoustic oscillation at the first system acoustic mode rapidly disappears and stable conditions are recovered.

Fig 1. Iso-surfaces of $q' = 10\% q'_{max}$ colored by thickening field $F$ (on the left) and temperature field $T$ (on the right) for Cases (a) 1 bar - 0% H\textsubscript{2} (23M mesh), (b) 1 bar - 40% H\textsubscript{2} (23M), (c) 3 bar - 40% H\textsubscript{2} (65M) and (d) 5 bar - 40% H\textsubscript{2} (144M). A similar thickening field is achieved for all the flames thanks to SMR.

Acknowledgements

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References

The effect of hydrogen and exhaust gas recirculation on NO\textsubscript{x} formation in laminar and turbulent CH\textsubscript{4}/Air flames at 25 bar

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Abstract

Hydrogen enrichment is a promising concept for reducing fuel consumption and pollutant emissions. It has been shown that in diffusion flames hydrogen enrichment can improve flame stability and reduce CO\textsubscript{2} emissions, but it increases NO production [1]. The net effect of hydrogen enrichment on NO formation in a hydrocarbon diffusion flame depends on the relative variations of the thermal and prompt paths [1]. The Exhaust Gas Recirculation (EGR) technique is a valid methodology to mitigate NO\textsubscript{x} emissions [2].

In this work, the effect of EGR on NO\textsubscript{x} emissions in a CH\textsubscript{4}/H\textsubscript{2}/air combustion at 25 bar, with an Equivalence Ratio \(\phi = 0.7\), is analyzed in laminar and turbulent partially premixed flames. Numerical simulations of twenty partially premixed counterflow flames with H\textsubscript{2} percentages ranging from 0% to 100%, with and without EGR, were carried out by mean of OpenSmoke++ code [3]. A sensitivity analysis showed that the thermal path is the main responsible for the NO\textsubscript{x} production in each flame, with a contribution of 80%. In laminar flames an increase of H\textsubscript{2} led to an increase in emissions of NO\textsubscript{x}. However, the addition of the exhaust gas decreases the flame temperature and therefore it decreases NO\textsubscript{x}. All laminar flames showed a NO\textsubscript{x} reduction of about 60% with the presence of exhaust gas.

Four turbulent slot jet flames with a premixed central core and air-exhaust as coflow were studied using Large Eddy Simulations (LES) through the ENEA's HeaRT code [4]. Accurate molecular transport properties is considered and, a reduced chemical mechanism for methane/hydrogen-air combustion, consisting of 48 transported species and 465 elementary reactions is adopted.

The four turbulent flames were simulated in a 2D domain with 0% and 50% hydrogen concentration, with and without EGR. The presence of hydrogen reduces CO\textsubscript{2} emissions, decreases the NO\textsubscript{2} production, but at the same time increases the NO concentration. However, the introduction of exhaust gas in the coflow leads to a NO decrease, as shown in Fig. 1. In particular, the flame with EGR has nitrogen monoxide peaks lower than the flame without EGR, at two different flame heights z with the same residence time. At \(z = 0.06\) m, the NO peak decreases by 11%.

![Fig. 1. NO mass fraction trend along y at two different heights, z = 0.06 and 0.08 m.](image)

Hence, the results obtained in this work show that at high pressure, the enrichment of hydrogen in the EGR mode, leads to lower NO\textsubscript{x} as well as CO\textsubscript{2} emissions.

References

Performance assessment of numerical models for the simulation of a cyclonic burner fed with methane

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Abstract

Moderate or Intense Low-oxygen Dilution (MILD) [1] combustion is a promising technology within the energy transition scenario, as it is able to deal with complex and variable energy mix, by avoiding drastic changes in the operation of existing equipment. In such oxidation regime, reactants are diluted with large amounts of burnt products inducing distributed auto-ignition processes which suppress temperature peaks and so thermal NOx formation. However, to prompt the design and development of MILD combustion systems a deep understanding of such oxidation mode is required.

To this purpose, Computational Fluid Dynamics (CFD) represents a key tool despite the lack of reliable and truly validated models to describe the complex fluid-dynamical and chemical phenomena of MILD combustion. Based on this scenario, many MILD-related prototypes [2, 4, 3] have been developed in recent years to validate CFD simulations against experimental data.

In this work we present a performance analysis of three different combustion paradigms, namely the Flamelet Generated Manifold (FGM), the Eddy Dissipation Concept (EDC) and the Partially Stirred Reactor (PaSR) model, for the simulation of a cyclonic lab-scale burner [4], where pure methane is burnt in stoichiometric condition with air. This test case is particularly interesting as it achieves MILD combustion through a strong internal recirculation, hence mimicking industrial systems. As shown in Fig. 1, by exploiting the rotational periodicity of the burner geometry only a half of the domain is discretized, thus drastically reducing the computational efforts. An assessment of different turbulence models is also carried out in a Reynolds-averaged Navier-Stokes (RANS) framework incorporating a detailed chemistry. The comparison of numerical results with experimental profiles of temperature suggests that both the combustion paradigms and the turbulence models play a key role in the prediction of the complex flame structures inside the cyclonic burner. Despite the promising achievements, a further improvement of the numerical setup is needed to refine predictions.

Fig. 1. Computational grid.

References

Abstract
In the next decades, the continuous growth of the energy demand and the increasing share of renewable sources will challenge engineers to provide flexible, highly efficient solutions to supply energy. The storage of surplus energy and the use of alternative fuels as hydrogen are certainly two key technologies that will shape the future energy scenario. In this framework, gas turbines will continue play an important role thanks to their unique flexibility in load, size and fuels. In the past, a consistent effort was devoted to optimizing the gas turbine versatility and efficiency, approaching the limit of the thermodynamic cycle, except for the combustion process which always relied constant pressure combustion. Switching to other combustion modes which involve a pressure gain during the heat addition, such as detonations, could potentially provide a major increase of cycle efficiency, unlocking a new generation of gas turbines.

Among pressure gain devices, Rotating Detonation Combustors (RDC) are particularly promising for the adoption in gas turbines, as the high-frequency rotating detonation mitigates the turbine efficiency decrease due the flow unsteadiness. On the other hand, the complexity of these devices imposes the adoption of advanced analysis tools to overcome the inherent limitations of the experiments and allow for a detailed description of the physics behind the rotating detonation.

In the present work, the non-premixed rotating detonation combustor (RDC) installed at TU Berlin [1] is studied by solving the fully compressible, multispecies, reactive Navier-Stokes equations with the AVBP code [2]. The full hydrogen and air injection system is included in the numerical model to accurately describe both the reactants mixing and the resulting complex turbulent flow-field in the refill region. A global reaction mechanism is calibrated for the conditions of interest and adopted to describe the hydrogen detonation process in the combustor, without compromising the computational cost of the analysis. The numerical model is then applied to simulate a stoichiometric, single wave mode operating condition of the test rig, validating the results against the measurements of wave frequency and pressure gain.

After an overall description of the wave stabilization process and global parameters, the analysis of the results focuses on the characterization of key features of the RDC flow-field, such as the shocks structures, the spatial distribution and gas features in refill region. Then, the transient operation of the reactants injectors subject to the periodic blockage of the detonation is studied and discussed in relation to their geometric design. Finally, a time-resolved technique for tracking the three-dimensional evolution of the detonation front and evaluating its propagation speed is developed, obtaining a stochastic characterization of the local front speed, the fresh gas properties and their mutual correlation.

Acknowledgements
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References
NOx pathways in lean technically premixed swirling H2-air turbulent flame

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Abstract

Today’s climate and energy challenges are pushing the use of decarbonised and renewable alternative fuels in the field of power generation and transportation. Hydrogen as a fuel is a good candidate to meet these requirements since it offers no-carbon emissions and can play the role of energy vector to store energy in excess produced by renewable energy [1]. Nonetheless, NOx production needs to be assessed. This work deals with this problem by proposing high-fidelity LES simulations of NOx production of 100% technically premixed H2-air flame. This refers to experiments performed at the Berlin Institute of Technology rig [2]. With the purpose to properly solve the combustion process, the static mesh refinement (SMR) and the conjugate heat transfer (CHT) [3] techniques have been applied by showing their impact on the solution. To allow NOx prediction, a new reduced kinetic scheme for air-H2 combustion (15 species and 47 reactions) has been developed using Cerfacs in-house code ARCANE [4] on purpose taking into account the NOx pathways. The ARC chemistry is included in the compressible parallel code AVBP (www.cerfacs.fr/avbp7x/) in which turbulent combustion is handled by the dynamic formulation of the Thickened Flame LES combustion model (TFLES) [5]. While the application of the CHT does not change the global amount of NO emitted, it affects the amount of N2O obtained at the exit of the combustion chamber. Moreover, a detailed analysis of the NO formation is presented proving that the numerical model and the analytical chemical kinetic scheme are able to predict the NO dynamic formation accounting for the primary and secondary route: N2O and NNH (Fig. 1).

Acknowledgements

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References


Optimisation of a 2-step CH₄/air reaction mechanism to a CO₂ enriched environment for high fidelity combustion simulations

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Abstract

The unprecedented high levels of greenhouse gases in the atmosphere impose the adoption of concrete solutions for containing the pollutant emissions of the energy sector. Despite the increasing share of renewable sources, conventional systems based on fossil fuel combustion such as gas turbines still require new, clean technologies to mitigate the CO₂ emission.

A solution could be obtained by coupling gas turbines with Carbon Capture and Storage (CCS), however, high CO₂ concentrations at the exhaust are needed for an efficient capture.

The application of exhaust gas recirculation EGR in gas turbines allows the maximization of the CO₂ content in the exhaust plumes, significantly increasing the efficiency of CCS as well as reducing the size of the system and its investment cost. These aspects make the EGR an enabling technology for the convenient use of CCS systems in gas turbines. On the other hand, a high EGR level significantly alters the mixture composition, thus modifying the combustion properties and leading to a relevant decrease in the reactivity of the flame.

For investigating the effect of increasing CO₂ content in the reactants mixture, Cabot et al. [1] carried out an experimental campaign on a methane-air swirl stabilized flame, providing essential indications on the flame stability and extinction resistance in those conditions. Trying to numerically reproduce some of the experimental points investigated by Cabot et al. [1], in this work high-fidelity numerical simulations have been performed with the AVBP code and the Artificially Thickened Flame (ATF) model for describing the turbulent combustion. However, the simulations require, at the same time, a cost-efficient and accurate description of the fuel oxidation kinetics when the CO₂ content in the fresh air is increased, so a dedicated chemical scheme must be developed.

In this framework, this article is focused on the adaptation of the commonly used 2-step BFER mechanism [2] in a CO₂ enriched environment. As expected, the 2-step BFER mechanism has been found incapable to predict the consumption speed in laminar conditions with the increase of the CO₂ content. To overcome these limitations, starting from this mechanism, a novel 2-step mechanism has been developed with a multi-objective optimization process. The obtained scheme provides an accurate prediction of the laminar flame speed in a wide range of equivalence ratios (Figure 1) for a fixed CO₂ content in the oxidizer, thus enabling its application to technically premixed flames.

The results show that the trend in the decrease of the reactivity given by the CO₂ addition in the fresh gasses mixture is well captured, allowing an accurate reproduction of the flame characteristics in these conditions.

Fig. 1. Unstretched laminar flame speed predicted by different mechanisms at atmospheric pressure for different levels of temperature T₀=300, 450 and 600 K.

Acknowledgements

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References

SESSION X

Pollutants formation, monitoring and control
Abstract
Leachate is a liquid with high pollutants content resulting from the anaerobic transformation of organic substances present in waste inside landfills. The composition of the leachate is extremely variable both from landfill to landfill and within the landfill itself as both the concentration and the flow rate are closely linked to atmospheric precipitation. The quantity and quality of the leachate depend on many factors [1]; the most relevant are annual precipitation, surface runoff, infiltration into the landfill body, evapotranspiration, temperature, composition and density of the waste, initial moisture content of the waste and depth of the landfill. Leachate represents one of the most difficult sewages to purify. The difficulty is not only due to the extent of the polluting load, but also to the fact that this varies over time. Consequently, no conventional biological or chemical treatment is always able to achieve efficient levels of pollutant removal.

The choice and design of a leachate treatment plant is therefore not simple. The main aspects to be considered in the design are, first of all, the characteristics of the leachate, the different possibilities of discharging the purified water, the technologies available on the market and the construction and management costs of the plant.

Supercritical Water Oxidation (SCWO) is an innovative method of thermal destruction of organic waste which over the years has been tested on various types of special and hazardous waste, such as water polluted by pesticides, hospital waste, solid propellants, sewage sludge, welding oils and more [2]. In the SCWO, an oxidant (air or pure O₂) is added to the reaction medium in order to totally oxidize organic matter that is dissolved in water. Product gas is mainly composed of CO₂ and excess O₂. Thanks to the relatively low temperature of the process (T<700 °C), when compared to conventional combustion, NOx are not produced. Acid substances such as HCl, H₂SO₄ and H₃PO₄ remain dissolved in liquid water after the cooling of the reaction phase, and so do not pollute the effluent gas [3]. SCWO can convert organic matters with yields in the order of 99.9% in a short residence time. The reaction is exothermic, and a large part of the heat produced from the reaction can be recovered in properly designed energy recovery systems [4].

In this work, the SCWO of leachate was studied in a reactor operating in continuous mode with a volume of 200 mL, using compressed air as an oxidant. Residence time was changed in the range 1-5 min by varying the total flow rate that was fed to the reactor. Pressure and temperature were set at 24 MPa and 650 °C, respectively. The performance of the process was measured in terms of oxidation efficiency, defined as a percentage of COD knocked down. The effect of excess air, residence time and temperature were studied. EU Legislation regulates the discharge of industrial water on the abatement of COD, to determine whether to dispose of it directly in surface water (COD <160 mg/L) or in the sewer system (COD <500 mg/L). Starting from a leachate with COD = 13500 mg/L, we have experimentally verified that after treatment with SCWO it is possible to obtain an aqueous waste with COD value within the legal limits, with average abatement values higher than 99.0% (Fig. 1).

Fig. 1. Lecheate @ COD=13500 mg/L (left), water after SCWO @ COD=156 mg/L (right).

Acknowledgements
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References
Abstract
This work focuses on the spectroscopic analysis of carbonaceous particles produced in a fuel-rich ethylene flame. The cold gas velocity was set at 9.8 cm/s and carbon to oxygen atomic ratio was 0.67, equivalence ratio $\Phi = 2.03$. Soot particles were sampled using three different collection methods: sampling on a quartz filter, suspension in solution of dichloromethane and thermophoretic collection on a glass/quartz support.

In this work, a Uv-Vis/NIR spectrophotometer equipped with an integrating sphere, $\varnothing$ 60 mm, was used in addition to the classical double beam spectrophotometer. An integrating sphere is an optical component consisting of a hollow reflective spherical cavity that allows a uniform scattering or diffusing effect; indeed, light rays incident on any point on the inner surface and then they are distributed equally to all other points, by multiple scattering. The aim of this work is to understand the reliability and validity of the spectrophotometric measurements, thus also evaluating different sampling methods: the optical band gap is used as a comparison tool of methods.

From the transmittance and reflectance spectrophotometric measurements, the bandgap of soot particles, with different sizes in the range of 3 – 20 nm corresponding to inception and early grown particle, was derived by comparing Tauc's method [1] with Kubelka-Munk's method [2]. Specifically, absorbance measurements, evaluated from transmission data, ($A_{bs} = -\log_{10} T$) are analyzed in terms of the Tauc model, while diffuse reflectance measurements are elaborated with the Kubelka-Munk model.

The comparison between the two methods shows a slight difference in the obtained values, depending on the sampling methodologies.

Each of them has positive aspects, however, the diffuse reflectance measurement on quartz filter, introduced in this work, is very promising; the sampling procedure allows collecting enough material also in lightly sooting combustion conditions. The optical band gap evaluated from the diffuse reflectance data and the Kubelka-Munk model can thus be considered a valid procedure for soot samples. The results of this study, shown in Fig. 1, are in perfect agreement with the band gap obtained with complementary methods in literature and confirm the size dependent trend.

Fig. 1. Comparison between optical band gap value estimated in this work and data of literature [3].

References
Utilization of smart sensors for improving performance and reliability of combustion systems
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Abstract
Optimization of modern combustion systems in steel reheating furnaces requires additional levels of information from the installed equipment. The situation is even more complex in regenerative burners installations, where the combustion system behavior is highly dynamical due to the continuous alternation of the regeneration phase (when burners suck flue gases from the furnace in order to preheat solid bed of regenerators) and the firing phase (when cold air is provided to the regenerators to be preheated at very high temperatures). Keeping the combustion equipment always in the optimal design condition requires additional efforts from the furnace operation and maintenance teams. This issue can be overcome if one provides embedded sensors in each burner units with the aim to collect relevant physical quantities and to extract trends of key performance indicators (KPIs, representative of the combustion performance) and key health indicators (KHI, representative of the integrity of critical burner components).

In this work, we summarize the industrial experience obtained during six months long-term tests of an innovative burner concept (SmartBurner) applied to an existing regenerative combustion system of the rotary hearth furnace in Tenaris Dalmine. A couple of flameless regenerative burners with integrated sensors (Fig. 1) were tested against real furnace operation in order to better understand the real conditions of industrial burners in a highly dynamic furnace environment. After initial overheating problems due to the harsh industrial environment, the designs of the sensors and signal processing unit were reviewed. The architecture was integrated into the typical automation control system of industrial furnaces, in order to elaborate KPIs and KHI during the tests. In particular, the direct measurement of the oxygen level in regenerated flue gases allowed highlighting potential issues in terms of the air and waste gases cycling valves (Fig. 2). These findings potentially allow to directly take into account small mass flow imbalances into the control loop and explain why fine tuning of the air excess of regenerative combustion system is generally considered challenging after several years of operation.

Fig. 1. Tenova TRGX 16 SmartBurner prototype: (1)-(7) temperature sensors, (8)-(10) pressure sensors, (13)-(15) chemical species sensors, (16)(17) optical sensors, (18)-(20) mechanical sensors.

Additional results in terms of regenerator efficiency and potential issues in terms of clogging of the solid bed have also been investigated. Direct measurement of pressure drop and temperature gradient inside the solid bed provides useful data on which highly accurate dynamic models can be developed in order to further minimize specific fuel consumption. Continuous measurement of pressure drops in air and fuel circuit provided additional insight in order to optimize opening/closing delays of the cycling valves.

Fig. 2. Oxygen measurements in two locations evidences potential issue of the flue gas cycling valve.

Acknowledgements
This work is supported by the European Commission, Directorate for General Research and Innovation, under the RFCS project “BURNER 4.0” with Grant Agreement 847237.
Characterization of soot and NO\(_x\) emissions from an atmospheric LEAF combustor fuelled with Jet A-1 and H\(_2\)


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Abstract

The reduction of NO and soot emissions is a main driver in the design of novel combustors for aeroengine applications. In this framework, technologies burning in a clean and efficient way drop-in liquid fuels such as Jet A-1 or sustainable aviation fuels (SAF) with injection of a low amount of hydrogen are of particular interest. They combine the advantages of conventional liquid fuels (well-established infrastructure and aircraft design) and the ones coming from H\(_2\) combustion (reignition at high altitude and increase of the flammability limit towards leaner conditions [1]).

In the current work, we present a low-NO\(_x\), soot-free Lean Azimuthal Flame (LEAF) burner operated with Jet A-1 fuel and a small amount of hydrogen, building on the results obtained for gaseous fuels by El Helou et al [2] and kerosene by de Oliveira et. al. [3]. The concept is based on the opposite injection of swirled main air through top air orifices and fuel from the bottom by means of three air-blast atomizers. The combustion of each spray is mixed with the swirled air coming from the top, which provides the vitiated environment to the next one. The formation of the toroidal flow is linked to the atomizer air-to-liquid ratio (ALR), as this parameter affects both the Sauter Mean Diameter (SMD) and the jet-to-crossflow momentum ratio. Favourable conditions for the stabilization of the LEAF flame are achieved with fine atomization and good mixing. However, lower ALR conditions are more realistic for aeroengine applications due to the lower associated pressure drop. In order to extend the operation of the LEAF flame towards lower ALR conditions, a small quantity of hydrogen is injected tangentially from the bottom plate, in-between the three sprays.

The formation of soot in the combustor is reported by analysing the flow luminescence above 570 nm in the combustion chamber.

The reactive flow analysis is then related to the exhaust measurement in terms of soot and gaseous emissions. Measurements at the combustor exhaust show low amount of NO (20 ppm at 15% O\(_2\) dilution) at low ALR, which further reduce to single digit with increasing ALR. Also, the flue gases exhibit a 3-4 % vol. of O\(_2\) concentration, which means a negligible amount of unburnt fuel corresponding to full combustion.

Soot emissions are measured at the exhaust by means of a Scanning Mobility Particle Sizer (SMPS) at the exhaust. The measurements report absence of soot emissions and a low amount of nanoparticles, with a volume fraction of particles emitted at the burner exhaust in the range 0.03-0.06 ppb, even for the operating conditions exhibiting soot luminescence in the chamber.

The results in terms of pollutant emissions and flame stability make the Jet A-1-hydrogen LEAF burner an attractive clean technology for future aeroengines applications.

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References

Numerical modeling of soot formation and evolution in combustion of isolated, spherically-symmetric droplets

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Abstract
Spherically-symmetric, isolated droplets are ideal systems widely adopted to investigate the physics and the chemistry of combustion of liquid fuels. Despite of the simplicity of the system, most phenomena involved in spray combustion are still accounted for: evaporation- and diffusion-induced transport, complex liquid thermodynamics, radiation, aerosol chemistry.

In this work we analyzed the formation and evolution of soot nanoparticles from the combustion of hydrocarbon liquid fuels in isolated droplets. A detailed, heterogeneous kinetic mechanism, describing soot nanoparticles through a discrete sectional method was adopted. The resulting 1D model (already validated in previous works [1], [2]) accounts for (i) non-luminous and luminous radiative heat transfer, and (ii) incomplete thermal accommodation for the calculation of the thermophoretic flux of soot nanoparticles. The combustion of droplets of n-heptane, as the simplest representative species of real fuels, was investigated. More specifically, the temporal evolution of the system was analyzed through a comprehensive study, as a function of the droplet size.

Because of the competition between convective and thermophoretic velocities, soot nanoparticles accumulate in a thin region (soot shell) between the droplet surface and the flame front. Growth, coalescence, and aggregation are especially enhanced in that region, characterized by very high local residence times, with an evident modification of the particle size distribution if compared to what observed in conventional combustion conditions. Large droplets showed an increasing sensitivity to radiative heat transfer, with significant impact on the formation of soot, while scarcely affecting the location of the soot shell. Finally, the simulations confirmed the primary role played by thermophoresis on production and evolution of soot particles, as already found in literature through more simplified approaches.

References
WORK IN PROGRESS
POSTERS
Mixed-phase TiO$_2$ obtained through MOF mediated synthesis (MOFMS) for doubly-parametric O$_2$ optical sensor development

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Abstract
The detection of gaseous oxygen (O$_2$) in gas mixtures is relevant for air quality control, packaging, life sciences, automotive industry, and chemical industry. Starting from previous literature results on the ability of TiO$_2$ nanostructures to act as a photoluminescence-based probe of O$_2$, in this work we explored the possibility to produce a mesoporous mixed-phase TiO$_2$ by using a metal organic framework (MOF) as sacrificial template and to test it as dual-emitting O$_2$ optical probe. Mesoporous TiO$_2$ containing both anatase and rutile crystalline phases was produced starting from a 1,4-benzenedicarboxylate (BDC)-based MOF containing Ti as metallic center (MIL125-(Ti)). Two different calcination temperatures were explored with the aim of modulating the ratio between the two crystalline phases. The obtained samples were characterized by TGA, SEM, HRTEM, N$_2$ adsorption–desorption isotherms, XRD, FTIR, XPS and photoluminescence (PL) spectroscopies. Their capacity to act as doubly-parametric O$_2$ optical sensor was evaluated by measuring PL intensity changes during O$_2$ exposure (Fig.1). In particular, the time dynamics of the PL modulation for VIS-PL and NIR-PL emission bands were investigated by measuring PL spectra during exposure to flowing Air-N$_2$ mixtures at different relative concentrations. The results showed that the MOF-derived samples exhibited responses to air densities in the 2-20% range. Future work will be focused on the detection of lower concentrations of O$_2$ and to improve the responsivity of both NIR- and VIS-PL components also by metal doping.

Fig.1 Building mixed-phase TiO$_2$ by MOFMS for doubly-parametric O$_2$ optical sensors.
Abstract
The identification of suitable and sustainable energy carriers plays key roles in both supporting the energy shift toward Renewable Energy Sources integration and satisfying the energy demand. Moreover, the effective integration of such energy vectors needs the development of highly fuel flexible thermochemical conversion units, capable of operating with unconventional fuels ensuring high performances, process stabilization and low pollutants emission.
However, the fuel flexibility is not a simple task to pursue in a single combustion unit. In fact, traditional combustion systems, that rely on feedback flame stabilization mechanisms, have a rather narrow operational conditions useful range. This limitation is mainly connected to the need for realizing an optimal geometrical and fluid-dynamical condition to achieve performance and low environmental impact. This limit the capability of the systems to be easily adapted to satisfactorily working with a wide range of fuels. Innovative combustion modes, such as MILD combustion, may significantly enlarge the fuels palette allowing them to be efficiently used in a wide range of operative conditions.
With this background, in this paper the possibility to successfully burn a very wide palette of e-fuels in the same combustion unit, under MILD Combustion conditions, is demonstrated.
In particular, conventional hydrocarbons (CH$_4$-C$_3$H$_8$), low calorific fuel (Biogas), bio-derived alcohols (methanol, ethanol, 1-butanol), no-carbon fuels (NH$_3$, H$_2$) were used, both pure or blended, in order to characterize the oxidation process in terms of process stability, speciation and pollutant emissions. The influence of several operational parameters (equivalence ratio, thermal load, fuel blend composition) was investigated, in order to identify the optimal operational conditions.
In particular, slightly fuel-lean conditions were identified as the optimal ones to achieve NOx and CO emissions for hydrocarbon fuels, biogas and low molecular weight alcohols way below the normative limits. In the NH$_3$ case, NOx emissions lower than 100 ppm and sustainable NH$_3$ slip was attained at stoichiometric condition. On the other hand, blending NH$_3$ with more reactive fuels such as CH$_4$, H$_2$ or alcohols while extending the stable operational range of the system, require some cares to avoid a possible increase of NOx emissions due to the competing chemical routes of the mixture components.
Performance of an auger reactor for bio-oil production through fast pyrolysis of contaminated biomass

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Abstract
CERESiS (ContaminatEd land Remediation through Energy crops for Soil improvement to liquid biofuel Strategies) project, granted under EU Horizon2020 research and innovation programme, intends to promote land decontamination through phytoremediation by growing energy crops to produce clean biofuels. In this context, the project aims to demonstrate the potential of two thermochemical processes, i.e. Supercritical Water Gasification (SCWG) and Fast Pyrolysis (FP) for the production of key bio-fuel precursors suitable for further upgrading from contaminated biomass.

The aim of our research activity is to design a FP system which allows to obtain at the same time high yields and low levels of contaminants in the bio-oil.

The auger reactor configuration was chosen. The advantages of using an auger reactor are summarized as follows:
• Proven technology.
• Wide range of particle sizes that can be processed.
• Good control of residence time and temperature.
• Good mixing characteristics.

In contrast, the main disadvantage is the high cost of maintenance required, given the presence of moving parts and possible tar condensation on the shaft when an auger reactor heated only indirectly through the external wall is used. To deal with tar condensation problems the reactor is heated by three independent induction heaters that allow reaching high heating rates of the shaft with great efficiency. A two-stages fractionated condenser, a cyclone and an electrostatic precipitator are used to selectively capture solids and condensable products.

The auger reactor was designed to valorize contaminated biomass coming from phytoremediation adapting the plant and operational parameters to the presence of inorganic contaminants. Both pelletized and ground contaminated biomass can be used as feedstock for bio-oil production. Further investigations are needed to assess the possible effect of feedstock size on pyrolysis products yields and heavy metals speciation and distribution.
Abstract
Due to their eco-compatibility, low toxicity and chemical stability, Carbon Dots (CDs) are actually considered attractive candidates for applications in the fields of imaging, replacing organic dyes, electronics, as semiconductors, or sensors. This work has identified a fuel-rich premixed ethylene flame as a bottom-up system for generating blue, green, and yellow CDs. Particulate matter (PM) was sampled in an ethylene/oxygen (C/O=1) flame, through thermophoretic sampling, in the soot inception (6mm) and in the aged soot (14mm) region. In both cases, PM was separated in organic carbon (OC), soluble in dichloromethane, and refractory organic carbon (ROC), soluble in N-methyl pyrrolidinone. Chromatographic, mass spectrometric and spectroscopic analysis have been carried out to investigate the features of these pyrogenic products. It was found that OC, coming from PM sampled at both heights of the flame, presents the same fluorescence emission in the blue wavelength region (420-500nm). Therefore, the two samples were grouped under the name: blue CDs. Whereas ROC samples, derived from PM sampled at low and high heights, fluoresce in the green (500-550 nm) and yellow wavelength region (550- 600nm), respectively, and were named green CDs and yellow CDs. Insights on their structure and fluorescence mechanisms, which make them appealing for applications as CDs, have been reported.

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Direct numerical simulation of intrinsically unstable premixed ammonia flames

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Abstract
Carbon-free energy storage is a key enabler of renewable resources, given its role in overcoming the structural intermittency of such resources. Grid-scale storage can be flexibly provided by chemical energy via hydrogen or alternative carbon-neutral vectors, ammonia being a promising candidate. Ammonia possesses some crucial advantages over hydrogen, namely a lower cost per unit of stored energy, higher volumetric energy density, a widespread production and distribution capacity [1]. Ammonia can indeed be utilized via direct combustion in gas turbines and internal combustion engines although it poses challenges due to its low reactivity and high NOx emissions. This calls for an intense research effort in ammonia combustion both at experimental and numerical level. Computational fluid dynamics research on ammonia combustion is still in its infancy and new numerical tools are therefore needed. In this study we utilize an in-house, high order, low-Mach number reactive flow solver, especially suited for DNS, based on the massively parallel spectral element code nek5000. We utilize the CFD infrastructure on problems specifically targeting ammonia combustion. Given the high hydrogen content and the resulting low effective Lewis numbers of typical reactive ammonia mixtures, the focus is directed towards the analysis of thermodiffusively unstable ammonia flames, exhibiting a characteristic cellular conformation. Such flames are known to greatly affect the global consumption speed due to their wrinkling tendency which may also affect NOx emissions. Two-dimensional simulations are performed to analyse the main features of thermodiffusively unstable laminar ammonia flames. We also recently proposed novel data-driven models [2,3] for the sub-grid modeling of such intrinsic instabilities which can prove of great value in LES codes. In this context, we seek DNS datasets that are minimal in size and yet still fully representative of the morphological and propagative features of larger ammonia flames.

Ammonia to help decarbonization: validation of kinetic mechanisms.

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Abstract
A huge increase in the share of renewable energy sources is needed to meet the EU “Fit for 55” goals and diminish our dependence on fossil fuel suppliers. In this scenario, power-to-gas technologies are attractive as they can produce, from excess wind and solar power, fuels, like hydrogen, that can be directly burnt in existing furnaces. This may help the decarbonization of hard-to-abate industries, for which electrification cannot provide the required high process temperatures.

In this roadmap, an increasing interest is towards hydrogen carriers such as ammonia, because ammonia can be transported more easily than hydrogen. Indeed, NH₃ condenses at a significantly higher temperature than hydrogen (i.e., at -33°C while hydrogen at -252°C for atmospheric conditions), it has a higher volumetric energy density, and is less flammable, thus largely improving safety. Besides, its distribution infrastructure is already well developed, thanks to its extensive use in agriculture.

However, NH₃ is significantly different from traditional fuels such as methane and a better understanding of its combustion behaviour is required to design conversion systems. Here, the use of computational fluid dynamics is partially hindered by the lack of validated models, especially for oxidation kinetics.

The present work intends to carry out a comprehensive analysis of different mechanisms, characterised by a different number of chemical species and reactions, for predicting combustion parameters, such as the laminar flame speed (Sₐ) and temperature, for NH₃ oxidation. For this purpose, 1D simulations of NH₃- air premixed flames are performed for different equivalence ratios in the range φ= 0.8-1.5 using the Cantera code for kinetic analysis and implementing different chemical mechanisms. The results are validated against available experimental data[1] [2].

Morphology And Electronic Properties Of Incipient Soot By Scanning Tunneling Microscopy And Spectroscopy

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Abstract
Soot nucleation is one of the most complex and debated steps of the soot formation process in combustion. In this work, we used Scanning Tunneling Microscopy (STM) and Spectroscopy (STS) to probe morphological and electronic properties of incipient soot particles formed right behind the flame front of a lightly sooting laminar premixed flame of ethylene and air. Particles were thermophoretically sampled on an atomically flat gold film on a mica substrate. High-resolution STM images of incipient soot particles were obtained for the first time showing the morphology of sub-5 nm incipient soot particles. High-resolution single-particle spectroscopic properties were measured confirming the semiconductor behavior of incipient soot particles with an electronic band gap ranging from 1.5 to 2 eV, consistent with earlier optical and spectroscopic observations.
Abstract
Nowadays, the growing energy demand, together with the convenience in the implementation of a circular economy approach and the existing constraints due to environmental regulations have posed new challenges from both scientific and technological perspectives. In this sense, the development of appropriate processes for mass and heat recovery from municipal and industrial wastes represents an essential step toward sustainable solutions. Among them, the pyrolysis of biomass has been largely studied in a wide range of conditions because of the potential application of the resulting gaseous mixtures (producer gas) in turbines. Quite clearly, the composition of the producer gas is strongly affected by the operative conditions as well as by the compositions of the feeding stream. Hence, considering the nature of the raw material, large oscillations can be expected. Nonetheless, the combustion characteristics of these mixtures and the chemical interactions between their constituent species are still not fully understood. In this sense, a detailed kinetic mechanism suitable for the description of the behaviour of light species (i.e., lighter than C5) in oxidative conditions was developed to evaluate the overall reactivity in air.
Considering the investigated conditions, i.e., a temperature higher than 700 K, the ignition delay time was first selected as the standalone parameter for the evaluation of the chemical and thermal aspects. The model was validated against experimental data retrieved from the current literature, at first. Obtained results can be intended as a building block for the realization of a validated mechanism to be integrated with physical and fluid-dynamic models to control and design optimized systems for bio-syngas use and production.
Chestnut derived biochar for the adsorption of bioactive organic molecules

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Abstract
The chestnut peeling industrial process generates solid residues (inner and outer shells), which accounts for about 10–15% of the whole chestnut weight. In the present study an integration between a chemical and a thermochemical process is proposed as valorization route for the chestnut residues: the extraction of polyphenols, a class of strong natural antioxidants, and the slow pyrolysis for biochar production. The chestnut residues after the polyphenols extraction are used as pyrolysis feedstock, and the produced biochars are applied as adsorbing materials to simplify the recovery of the extracted polyphenols. The aim of this study is to evaluate how the physical and chemical characteristics of biochar from chestnut residues influence the adsorption of polyphenols. The biochar production was carried out in a slow pyrolysis reactor using two feedstocks (pre-extraction and post-extraction chestnut residues) and three pyrolysis temperatures (500 °C, 600 °C and 700 °C). Each biochar was used as adsorbent material for the polyphenols in the aqueous extracting solution obtained from chestnut residues. Adsorption tests were carried out at room temperature, with fixed biochar percentage (5% w/v) and contact time (1 hour). Specific classes of polyphenols were considered, such as non-tannin polyphenols, hydrolysable tannins and condensed tannins. The adsorption efficiency of biochar increases in the char produced at 700 °C for both the considered feedstocks. The analysis of the specific polyphenols groups shows that, despite having an overall adsorption capacity much lower than activated carbon, biochars have a great selectivity for the adsorption of non-tannin polyphenols. The correlation between the chemical and physical properties of the biochars with the polyphenols adsorption efficiencies allow to postulate that the main feature involved in the adsorption of polyphenols is the mesoporous surface of biochar; however, the surface chemistry of the biochars, especially the acidic functionalities, could also be involved in the adsorption mechanism.
Electrical Properties of Flame-Formed Carbon Nanoparticles for Electronics and Sensors Applications


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Abstract

Carbon nanoparticles generation in the combustion has been long investigated being a critical issue for the environment and human health. However, due to their unique optical and electrical properties, these nanoparticles can be implemented in a wide range of industrial applications such as sensors, diodes, and transistors, to mention few. Particularly considering the use of such carbon nanoparticles in optoelectronic devices and to get the real benefits of nanocarbon-based devices, we investigate the electrical properties of flame-made layers.

The synthesis of carbon nanomaterial devices (thin film) includes deposition of a proper amount of material (to obtain desired thickness) of flame-formed carbon nanoparticles on a substrate. Later, we perform electrical, optical and structural characterization, the latter by Raman spectroscopy to understand the properties and applications of the produced thin film. We present the results by changing the amount and tuning the properties of deposited material. Hence, they can be applied in various technologies.

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Development of an UV-absorption based smart sensor for the detection of nitrate and nitrite concentration in wastewater

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Abstract
Nitrates (NO$_3^-$) and nitrites (NO$_2^-$) are present in environmental, food, industrial and physiological systems. Sources of NO$_3^-$ in the environment can be natural. However, anthropogenic activities such as fossil fuel emissions and their influence on the biogeochemical cycle of nitrogen or as mining industries contribute most of the nitrates and nitrites that accumulate in different localized water bodies, resulting in devastating environmental and health impacts. Our need and desire to monitor these ions are unquestionable, yet their ubiquity can pose a significant challenge to the analytical community. Spectroscopic methods are most widely used for nitrates and nitrites determination due to correlation of absorbance and concentration commonly expressed by the Beer-Lambert law. However, these methods generally depend on the reaction between the monitoring solution and specific reagents, thus not allowing a continuous control.

The aim of this work is the development of a smart sensor probe for the simultaneous and continuous determination of nitrate and nitrite concentration in wastewater, based on a reagent-free, direct ultraviolet spectroscopic method. The continuous control of the species can be done by inserting the sensor probe in a cell, inside which the wastewater is conveyed, connected to a system of nitrate and nitrite abatement.

The spectra of nitrate and nitrite show an absorption peak respectively at 301 nm and 354 nm. A calibration curve for the single species can be easily obtained through the value of the absorption peaks obtained at different concentrations. On the other hand, if both species are present in the sample at the same time, the spectrum of nitrites can strongly affect the spectrum of nitrates. The model herein presented takes into account for the influence of nitrites, allowing a correct determination of both ions’ concentration in solution. This model can be considered as the basis for the development of the smart sensor for wastewater monitoring.

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