

XXXVIII

Meeting of the Italian Section of the Combustion Institute



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PROCEEDINGS

edited by

A. D'Anna, A. Ciajolo, M. Commodo, M. G. De Giorgi, Ö. L. Gülder, A. Tregrossi



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Meeting of the Italian Section of the Combustion Institute



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Ömer L. Gülder, Antonio Tregrossi

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1 Istituto di Ricerche sulla Combustione - C.N.R., Napoli - Italy

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* Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università degli Studi di Napoli Federico II, Napoli, Italy

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*DICMAPI-Università degli studi di Napoli Federico II, Naples, Italy
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* Istituto di Ricerche sulla Combustione - CNR – Napoli, Italy
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* Istituto di Ricerche sulla Combustione – CNR, Naples, Italy
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* Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale,
Università degli Studi di Napoli Federico II, Napoli (Italy)

** Istituto di Ricerche sulla Combustione, Consiglio Nazionale delle Ricerche, Napoli (Italy)

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* Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale,
Università degli Studi di Napoli Federico II, Napoli (Italy)

** Istituto di Ricerche sulla Combustione, Consiglio Nazionale delle Ricerche, Napoli (Italy)

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*Istituto di Ricerche sulla Combustione - Consiglio Nazionale delle Ricerche, Napoli, Italy

** Enel Ingegneria e Ricerca S.p.A, Pisa, Italy

*** Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale - Università
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*Istituto di Ricerche sulla Combustione - CNR – Naples, Italy

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*Universidad Nacional de Colombia, Departamento de Química, Bogotá (Colombia)

**Università degli Studi di Napoli Federico II, Dipartimento di Ingegneria Chimica dei Materiali e
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*Istituto di Ricerche sulla Combustione, CNR, Napoli, Italy

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*Politecnico di Milano, Dip. di Chimica, Materiali e Ingegneria Chimica "G. Natta", Milano, Italy

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*Istituto di Ricerche sulla Combustione, CNR, Napoli, Italy

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*Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale – DICMAPI, Università degli Studi di Napoli Federico II, Napoli, Italy

**Department of Experimental Medicine-Occupational Medicine, Hygiene and Industrial Toxicology Section, Naples, Italy.

***Istituto di Ricerche sulla Combustione, CNR, 80125 Napoli, Italy.....

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* Università del Salento, Department of Engineering for Innovation, Lecce, Italy.....

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*Istituto di Ricerche sulla Combustione – CNR, Napoli - Italy

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* University of Salento - Dept. of Innovation Engineering, Lecce, Italy.....

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*Department of Mechanics Mathematics and Management, Politecnico di Bari, Bari, Italy

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* Sotacarbo S.p.A., c/o Grande Miniera di Serbariu, Carbonia, Italy.....

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*ENEA - Italian Agency for New Technologies, Energy and Sustainable Economic Development, Rome, ITALY

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* University of Salento - Dept. of Innovation Engineering, Lecce, Italy

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* Istituto di Ricerche sulla Combustione - C.N.R., Napoli - Italy

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*Istituto Motori - CNR Naples, Italy

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* Dipartimento di Ingegneria - Università degli Studi del Sannio, Benevento, Italy

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*Dipartimento di Scienze e Tecnologie Biologiche e Ambientali, Università del Salento, Lecce, Italy

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CNISM-BRIT China-Italy Joint Research Center for Laser Remote Sensing

1CNR-SPIN, Napoli, Italy

2 Dipartimento di Fisica, Università degli Studi di Napoli "Federico II", Napoli, Italy

3CNR-IMAA, Potenza, Italy

4 CETEMPS, Dipartimento di Scienze Fisiche e Chimiche, Università degli Studi dell'Aquila,

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* Istituto di Scienze dell'Atmosfera e del Clima, ISAC-CNR, 73100, Lecce, Italy

** Istituto per la Dinamica dei Processi Ambientali, IDPA-CNR, 2137, Venezia,

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*ISAC-CNR via Gobetti 101, Bologna, Italy

**IENI-CNR, via Cozzi 53, Milano, Italy

*** Finnish Meteorological Institute, Helsinki, Finland **XI.5**

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M. Commodo*, L.A. Sgro*, M. Chiari**, G. De Falco***, A. D'Anna***, P. Minutolo*

*Istituto di Ricerche sulla Combustione, Napoli – Italy

**I.N.F.N. - Sezione di Firenze - Sesto Fiorentino (Firenze) - ITALY

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Magliulo***, P. Toscano****, A. Zaldei****

*Università di Napoli "Parthenope", Napoli, Italy

** Istituto Motori (IM-CNR), Napoli, Italy

*** Istituto per i Sistemi Agricoli e Forestali del Mediterraneo (ISAFoM-CNR), Ercolano, Italy

**** Istituto di Biometeorologia (IBIMET-CNR), Firenze, Italy **XI.7**

PLENARY LECTURES

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SOOT AEROSOL FORMATION AT HIGH PRESSURES IN LAMINAR DIFFUSION FLAMES

Ömer L. Gülder

ogulder@utias.utoronto.ca

University of Toronto Institute for Aerospace Studies
4925 Dufferin Street, Toronto ON M3H 5T6 Canada

Abstract

The formation of soot is an artifact of the non-premixed (diffusion) combustion and the pressure has a significant degree of influence on soot processes. In gas turbines for aircraft propulsion and in diesel engines, where the mode of operation is for the most part is non-premixed and partially-premixed combustion, a reliable and consistent combustion process is possible with overall equivalence ratios much lower than the lean flammability limits. In addition, these engines operate at pressures exceeding 40 atm in gas turbines and 100 atm in diesel engines for thermal efficiency and compactness concerns. However, tractable soot related measurements at elevated pressures are extremely limited and most of the information available is at atmospheric pressure. Since the chemical reactions governing the various flame processes are intrinsically nonlinear, the responses of combustion events to pressure changes are not usually monotonic. Therefore, it is extremely difficult to scale measurements at atmospheric flames to high-pressure combustion.

In this presentation, the experimental methodology of the high-pressure laminar diffusion flame experiments and the description of the UTIAS high-pressure soot rig will be summarized emphasising the challenges and pitfalls involved. Then, soot measurements at elevated pressures at UTIAS in laminar diffusion flames of various gaseous and liquid fuels will be presented and the relevance of the results to practical combustion systems will be discussed. Results will include comparisons of sooting sensitivities of various gaseous and liquid fuels to pressure. Also, recent results from thermophoretic sampling and TEM imaging of soot particles from diffusion flames at elevated pressures will be presented and the influence of pressure on primary soot particle size in laminar diffusion flames will be discussed.

Atmospheric Aerosols: from Physico-Chemical Properties to Sources

R. Vecchi*

roberta.vecchi@unimi.it

*Dipartimento di Fisica, Università degli Studi di Milano & sezione INFN-Milano
Via Celoria 16, 20133 Milano

Abstract

Aerosols play a key role in the atmosphere; they act as clouds condensation nuclei, are responsible for visibility reduction, contribute to global change and carry on a number of toxic components and heavy metals inducing adverse health effects.

The effects of aerosols strongly depend on their size and on their chemical composition in relation to size-classes: both parameters show a significant spatial and temporal variability, which makes the nature of the particles very complex.

On a global scale, the atmospheric particles influence directly the radiative properties of the atmosphere scattering and absorbing solar radiation and indirectly acting as condensation nuclei and influencing the albedo, the type and residence time of clouds and rainfall.

As far as air pollution is concerned, the detailed knowledge of physico-chemical properties of atmospheric aerosols is mandatory for the identification of emission sources, the application of models that quantify the contribution from different sources and the evaluation of the environmental impact of particulate matter.

The talk will focus on the linkage between the most relevant aerosol properties and the aerosol emission sources.

DUAL FUEL COMBUSTION IN ICE: A PERFECT COCKTAIL FOR FUTURE HAPPY HOURS

S.Di Iorio, E. Mancaruso, P.Sementa, B.M.Vaglieco

b.m.vaglieco@im.cnr.it

Istituto Motori- CNR Naples, Italy

Abstract

Dual fuel configurations can be considered one of the promising solution to fulfill the strict regulations on pollutants emissions both spark ignition and compression ignition engines. The talk is specifically focused on use of these innovative strategies on future light duty engines, since the dual fuel concept application already implemented in heavy duty engines. The use of optical and CFD diagnostics is reported in order to understand the chemical and physical phenomena involved in the cylinder engine to further implement this combustion mode and create an adaptive future model based.

Advanced Biofuels for road and aviation: processes and industrial initiatives

David Chiaramonti

david.chiaramonti@unifi.it

RE-CORD and CREAR

Department of Industrial Engineering, University of Florence

Viale Morgagni 40, 50134 Florence ITALY

Abstract

Process and technologies for Advanced Biofuels steadily developed during the recent years. Even if – from the market point of view - today conventional biodiesel and bioethanol still dominate the EU scenario (with a total biofuel production of approximately 12 MTOE in 2013) and the International scene, a significant number of industrial demo and pre-commercial plant came into operation during the last five years.

This article addresses the main routes towards advanced biofuels, and discuss what technically can be considered an advanced biofuel and a drop-in biofuel, and the current status of industrial development of the different possible types of biofuels, placing this in the framework of the overall trend of major fossil transport fuels.

Biofuel technologies status is here distinguished among Basic R&D, Demonstration, Early-Commercial and Commercial, and the major investment needs and constraints to introduce these new systems are discussed, together with the reduction cost opportunity. In this context, bioethanol from sugar cane in Brasil is examined as the major successful example of this development pathway.

The most relevant industrial plants in the EU, US and Brasil are listed, and some reference source of data given. As regards solid biomass and the gasoline-like chain, lignocellulosic ethanol is dominating the scene worldwide, while in the diesel-like pathway advanced diesel from crude tall oil is so far the main option that achieved industrial scale. Nevertheless, the largest share of new biofuel is largely dominated from hydrotreated vegetable oil and lipids.

In this respect, the issue of the definition of “advanced” versus “conventional”, a significant issue in the regulation of the biofuel sector, is analysed, focusing on the EU situation.

Finally, process routes and ongoing EU projects on aviation biofuels are reported: lignin and algae are discussed in this context.

SESSION I

Turbulent Combustion

Towards an Unsteady/Flamelet Progress Variable method for non-premixed turbulent combustion at supercritical pressures

P. E. Lapenna*, F. Creta*

pasquale.lapenna@uniroma1.it

francesco.creta@uniroma1.it

*Dept. of Mechanical and Aerospace Engineering University of Rome "La Sapienza"

Abstract

Combustion devices operating at elevated pressures, such as liquid rocket engines (LRE), are usually characterized by supercritical thermodynamic conditions. Propellants injected into the combustion chamber experience real fluid effects on both their mixing and combustion. Transition through super-criticality implies abrupt variations in thermochemical properties which, together with chemical reactions and high turbulent levels introduce spatial and temporal scales that make these processes impractical to be simulated directly. Reynolds-Averaged Navier-Stokes (RANS) and Large Eddies Simulation (LES) equipped with suitable turbulent combustion modeling are therefore mandatory to attempt numerical simulation on realistic length scales. In the present work, the building blocks for extending the unsteady/flamelet progress variable approach for turbulent combustion modeling to supercritical non-premixed turbulent flames are presented. Such approach requires a large number of unsteady supercritical laminar flamelet solutions at supercritical pressures, usually referred as flame structures, to be preliminarily established by solving the flamelet equations with suitable real fluid thermodynamics. Given such unsteady flame structures, flamelet libraries can then be generated for all thermochemical quantities. The explicit dependence on flamelet time is usually eliminated using mixture fraction, reaction progress parameter, and maximum scalar dissipation rate as independent flamelet parameters. Real fluid thermodynamics used for such unsteady supercritical laminar flamelet solutions, is taken into account by means of a computationally efficient cubic equation of state. In order to have a better handling of real gas mixtures, the real gas equation of state is written in a comprehensive three-parameter fashion. A priori analysis at supercritical pressures of transient flame structures is performed in order to study how solutions populate the flamelet state space which is usually characterized by the S-shape diagram representing a collection of steady solutions. High-pressure conditions ranging from 60 to 300 bar are chosen as representative of a methane/liquid-oxygen rocket engine operating conditions.

AN EXPERIMENTAL INVESTIGATION ON ISOTHERMAL FREE SWIRLING JET

F. Cozzi*, R. Sharma*, A. Coghe*, F. Arzuffi*

rohit.sharma@polimi.it

*Department of Energy, Politecnico di Milano, via Lambruschini 4, 20156, Milano, Italy

Abstract

This paper reports an experimental investigation on the dynamics of turbulent unconfined swirling flows. Isothermal free swirling jets with five different swirl numbers (S) and fixed Reynolds number ($Re = 21800$) are investigated to analyze the effect of swirl intensity on the recirculation, vortex breakdown and the occurrence of the precession vortex core (PVC) by means of 3C-2D Stereoscopic Particle image velocimetry (PIV). The contours and radial profiles of mean axial velocity confirmed the central recirculation zone (CRZ) for high swirl number. The importance of central recirculation zone is to ensure a good mixing of air/ fuel and combustion products and to generate a low velocity region for flame stabilization. Results shows that swirl intensity increases the backflow rate in the recirculation zone and jet spreads almost linearly with much higher spread rate as compared to non swirling flow. The frequency characteristics have been measured with a capacitive microphone. The frequency spectrum indicates the presence of oscillation and the existence of a central jet precession as observed in experiments. The Strouhal number varies almost linearly with swirl intensity.

Hydrogen enrichment effects in premixed Methane/Air flames

D. Cecere, E. Giacomazzi, F.R. Picchia, N.M. Arcidiacono

donato.cecere@enea.it

*Process and Enrgy Systems Engineering Laboratory, Rome, Italy.

Abstract

Nowadays, in the context of CO₂ reduction and gas turbine fuel flexibility, the interest in acquiring know-how on lean Hydrogen Enriched Natural Gas (HENG) is growing. This article provides a detailed analysis of a turbulent ($Re_{jet}=2476$, $Re_t=236$) lean ($\Phi=0.7$) CH₄/H₂-air premixed slot flames (unconfined and at atmospheric pressure) highlighting the effects of two different hydrogen contents in the inlet mixture (20% and 50% by volume). The data were generated and collected setting up a three-dimensional numerical experiment performed through the Direct Numerical Simulation (DNS) approach and using high-performance computing. Finite difference schemes were adopted to solve the compressible Navier-Stokes equations in space (compact sixth-order in staggered formulation) and time (third-order Runge-Kutta). Accurate molecular transport properties and the Soret effect were also taken into account. A detailed skeletal chemical mechanism for methane-air combustion, consisting of 17 transported species and 73 elementary reactions, was used. The analysis reports average and rms fluctuation of velocity components, temperature and main chemical species mass fractions. New scientific insight is delivered by analysing the probability density functions of several quantities: curvature, shape factor, alignment between vorticity vector and flame surface normal, displacement speed and its components. Correlations between the flame thickness and the progress variable and curvature are also investigated, as well as correlation between strain rates and curvature, and equivalence ratio and curvature. An expression of displacement speed, with diffusion terms taking into account differential diffusion of progress variable species components is derived. The effect of thermal diffusion is also considered. The effects of differential diffusion of several species on the local equivalence ratio are quantified: the maximum variation from the nominal inlet value is $\pm 9\%$ and it is due to H₂ and O₂.

The addition of Hydrogen reduces the displacement speed at negative curvatures in a range that depends on the local progress variable value, with a maximum variation of -33% between the two flames. The database will also be helpful to validate subgrid models for Large Eddy Simulation.

Reaction-Diffusion Equation and G-Equation Approaches Reconciled in Turbulent Premixed Combustion Modelling

G. PAGNINI*, R.A.D. AKKERMANS, N. BUCHMANN**,
A. MENTRELLI*****

gpagnini@bcamath.org

*BCAM – Basque Center for Applied Mathematics Ikerbasque – Basque Foundation for Sciences Alameda Mazarredo 14, 48009 Bilbao, Basque Country - Spain

**Technical University of Braunschweig and BCAM Hermann-Blenk-Str. 37, 38108 Braunschweig, Germany

***University of Bologna and (AM)² and BCAM via Saragozza 8, 40123 Bologna, Italy

Abstract

Stochastic fluctuations described by an adequate probability density function are imposed to the average flame position in order to give a proper formulation of the flame surface propagation in turbulent premixed combustion. An evolution equation of reaction-diffusion type is derived for an observable that can be understood as the effective burned fraction. When stochastic fluctuations are removed, the G-equation along the motion of the mean flame position is recovered suggesting that approaches based on reaction-diffusion equations and G-equation are indeed complementary and they can be reconciled. Moreover, when a plane front is assumed, the Zimont & Lipatnikov model is recovered. This last result suggests that the proposed equation can be considered as the natural extension of the Zimont & Lipatnikov model to the case with non null mean curvature.

EFFECT OF ACTUATION PARAMETERS ON STABILIZATION OF METHANE DIFFUSIVE FLAMES USING PLASMA ACTUATORS

M.G. De Giorgi*, A. Ficarella*, A. Sciolti*, S. Campilongo*, E. Pescini*, G. di Lecce**

mariagrazia.degiorgi@unisalento.it

*University of Salento, Dipartimento di Ingegneria dell'Innovazione, Lecce, Italy

**NANOTEC, Istituto di Nanotecnologie (CNR) - UOS Bari - Italy

Abstract

The reduction of nitric oxides (NO_x) in aircraft engines, gas turbines, or internal combustion engines is a main issue in the design of novel combustion systems. The reduction of the NO_x emissions might be reached by lean combustion. However, the major issue is the stabilization of the flame under lean conditions.

In this context, the present work investigates the possibility of increasing the combustion efficiency of a lean flame through the employment of a plasma actuator, operated by both nanosecond repetitively pulsed high voltage (NRPP) and sinusoidal DBD high voltage (HV). Different actuation conditions have been tested to stabilize and improve the efficiency of a lean non premixed methane/air flame in a Bunsen-type coaxial burner with central fuel jet. An image processing approach was used to characterize the flame behavior near blowout conditions.

LIBS and Chemiluminescence Measurements for Fuel/Oxidizer Mixing Monitoring

L. Merotto*, R. Dondè*, F. Migliorini*, and S. De Iuliis*

merotto.laura@gmail.com

*IENI-CNR Milano, via Cozzi 53, Milano, Italy

Abstract

Real-time monitoring of local equivalence ratio is of primary importance for chemical combustion efficiency improvement. In this context chemiluminescence and LIBS measurements have been presented and performed in premixed and diffusion flames. The ratio of radicals chemiluminescence emission is proved to be related to equivalence ratio in premixed flames. H/O LIBS measurements giving the ratio of two characteristic spectral lines of fuel and oxidizer is also related to the equivalence ratio. In this work, the calibration curves of radicals chemiluminescence as well as LIBS measurements versus equivalence ratio have been derived for premixed flames. Moreover, the application to diffusion flames is here considered and for both sets of measurements the calibration curves derived from premixed measurements have been applied. Results concerning the equivalence ratio evaluation in the diffusion flame by using LIBS measurements have been compared with those obtained from chemiluminescence at the external cone. These results are discussed in the text.

STRUCTURES FLAME DETECTION BY USING ADVANCED IMAGING TECHNIQUES

C. Allouis*, A. Amoresano, G. Langella**, V. Niola**, A. Quaremba**.**
amedeo.amoresano@unina.it

* Istituto di Ricerche sulla Combustione, Consiglio Nazionale delle Ricerche - CNR,
Piazzale V. Tecchio 80, 80125 , Napoli, Italy

**Università di Napoli "Federico II", Dipartimento di Ingegneria Industriale, Via Claudio
21- 80125 Napoli, Italy

Abstract

Numerous experimental studies and numerical models have been developed to understand the behavior of burners in gas turbines. In particular, there are current researches aimed to understanding fuel/air interaction in the premixing duct or region, upstream of the combustion chamber. Unstable combustion refers to self-sustained combustion oscillations at or near the acoustic frequency of the combustion chamber, which are the result of the closed-loop coupling between unsteady heat release and pressure fluctuations. However, the mechanisms whereby pressure fluctuations result in a heat release fluctuations are not well known.

Electrophoretic aerosol focusing for soot particle analysis

G. Trunfio*, G. De Falco*, M. Commодо, P. Minutolo**, A. D'Anna***
gianluigi.defalco@unina.it

* Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale -
Università degli Studi di Napoli Federico II, P.le Tecchio 80, 80125, Napoli, Italy

** Istituto di Ricerche sulla Combustione, CNR, P.le Tecchio 80, 80125, Napoli, Italy

Abstract

In this work, a focused deposition technique was developed and applied to soot particles produced in a laminar premixed flame of ethylene and air. Particles were collected by means of an Electrostatic Precipitator (ESP), coupled with a Corona charger device used for unipolar charging of particles. Charged aerosol particles were electrostatically focused on a mica muscovite disks positioned on the ESP electrode by an electrically grounded metal mesh. Particle dimensions were measured by means of a Scanning Mobility Particle Sizer system, constituted by a nano-Differential Mobility Analyzer (DMA) and an Ultrafine Condensation Particle Counter (CPC). The collection efficiency of the system constituted by the corona charger and the ESP was calculated to be 99%, by measuring particle concentration exiting the ESP when the voltage is applied, and comparing it to particle concentration exiting the ESP when no voltage is applied.

The focusing method was tested with an optical microscope observing focused carbonaceous nanoparticles in spots of tens of microns in dimension. This method can be used as an effective sampling procedure for *ex-situ* analysis of carbonaceous nanoparticles, since it allows obtaining reduced sampling times and enhanced analysis resolutions.

MASS SPECTROMETRIC TOOLS FOR STRUCTURE ELUCIDATION OF CARBONACEOUS MATERIALS

M. Passaro^{1,2}, B. Apicella¹, A. Carpentieri³, A.D'Anna², A.Ciajolo¹, A. Tregrossi¹

mariadellarcopassaro@gmail.com

¹ Istituto di Ricerche sulla Combustione - C.N.R., Napoli - Italy

² Chemical Engineering, Materials and Industrial Production Department, University of Naples "Federico II", P.le Tecchio 80, 80125 Napoli, Italy

³ Chemical Sciences Department, University of Naples "Federico II", Via Cintia, 80126 Napoli, Italy

Abstract

Mass spectrometry has currently achieved a mass resolution capable of discerning chemical composition and structure in complex mixtures. However, whatever is the mass spectrometric system used, complex mixtures produce spectra with a huge number of peaks which generally make difficult the data analysis.

In the present work, a method involving Fast Fourier Transform (FFT) analysis and a home-made software was applied for interpreting the mass spectra of complex PAH-laden samples derived from combustion systems and from heavy fossil fuels, thereby giving information on their composition.

Large polycyclic aromatic hydrocarbons (LPAHs) were found to be the major components in the complex mixtures. Iso-abundance plots were introduced to sort and visualize the molecular constituents into different types based on the carbon and double bond equivalence (DBE) numbers. The differences between the different carbonaceous materials could be easily observed by comparing their iso-abundance plots.

NANO-TiO₂ COATINGS OF ALUMINUM SURFACES PRODUCED BY AEROSOL FLAME SYNTHESIS

G. De Falco*, M. Liberini*, F. Scherillo*, A. Astarita*, M. Commodo, P. Minutolo**, A. Squillace*, A. D'Anna***

gianluigi.defalco@unina.it

* Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale,
Università degli Studi di Napoli Federico II, Napoli, 80125, Italy

** Istituto di Ricerche sulla Combustione, CNR, Napoli, 80125, Italy

Abstract

This work reports the development of a one-step method for the coating of aluminum surfaces with titania nanoparticles. Narrowly sized, ultra-fine TiO₂ nanoparticles were synthesized by Flame Aerosol Synthesis and directly deposited by thermophoresis onto cylindrical samples of aluminum alloy AA2024. Submicron coatings of different thickness and porosity were produced by varying the total time of deposition. Two flame synthesis conditions were investigated in order to study the effect of titania particle dimension and phase composition on the characteristics of coatings. Pure anatase nanoparticles of 3.5 nm diameter were produced in fuel-lean synthesis condition, while fuel-rich non-sooting condition was used to synthesize a mixture of rutile and anatase nanoparticle of 22 nm in diameter, rutile being the predominant phase. Confocal Microscopy measurements allowed to calculate coatings thickness. The electrochemical behavior of the coatings was characterized by means of Electrochemical Impedance Spectroscopy by analyzing the impedance phase angle and modulus, which is an index of the capability of the coating to protect the aluminum substrate. The results obtained show an improvement of the electrochemical behavior of the AA2024 substrate when TiO₂ nanoparticles are deposited. Specifically, processed samples have a capacitive behavior with a higher impedance modulus in a larger range of frequencies. Substrates processed with rutile phase nanoparticles of 3.5 nm in diameter and with a lower exposition time showed better results with respect to all the other operating parameters.

ADVANCED MATERIALS FORM CARBON BLACK MODIFICATION: A FOREVER YOUNG NANOMATERIAL

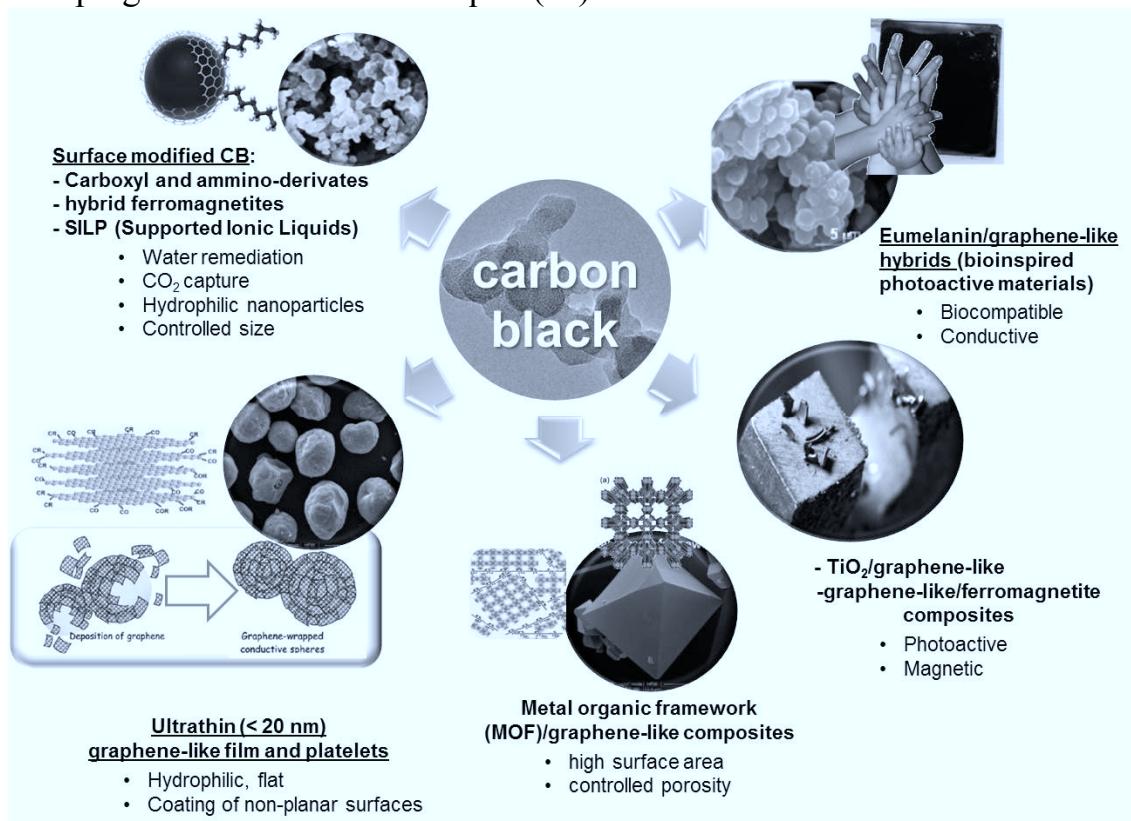
M. Alfe', V. Gargiulo

alfe@irc.cnr.it

* Istituto di Ricerche sulla Combustione - C.N.R., Napoli - Italy

Carbon black (CB) is a versatile carbonaceous material prone to be structurally and chemically modified in quite mild wet conditions. Recently, in our group, the potentiality of CB has been exploited producing a highly varied array of advanced materials for innovative applications in energetics. Among them:

- Graphene-like (GL) layers and ultrathin (GL) films;
- TiO₂/GL nanoparticles;
- Eumelanin/GL bioinspired conductive composites;
- Metal-Organic Framework (MOF)/GL conductive composites;
- Magnetite/GL composites;
- Tailored materials by CB surface modifications: i) oxidation and functionalization with amino-groups; ii) coating with iron oxides; iii) impregnation with an ionic liquid (IL).



SESSION IV

Kinetic of Combustion

CHEMISTRY OF SMART ENERGY CARRIERS AND TECHNOLOGIES: A EUROPEAN COST NETWORK

M. de Joannon*, G. Skevis**

dejoannon@irc.cnr.it

* Istituto di Ricerche sulla Combustione-CNR, Naples, Italy

** Aerosol & Particle Technology Laboratory CPERI-CERTH – Thessaloniki, Greece

Abstract

The Cooperation in Science and Technology (COST) is a European framework that enables breakthrough scientific developments leading to new concepts and products for Europe's innovation. The aim of a COST Action is to make the people collaborate on common topics, already founded by national and international research programs, and share competences and results in synergistic way, providing support for networking activities. In March 2015 the four year SMARTCATs COST Action (CM1404, www.smartcats.eu), focused on Chemistry of Smart Energy Carriers and Technologies started, so far bringing together 23 European and cooperating countries and led by the Istituto di Ricerche sulla Combustione-CNR. The primary aim of this COST Action is to create a Europe-wide network of world leading academic and research institutions and key industries to promote the use of Smart Energy Carriers, SECs (fossil, unconventional and renewable) on a large scale in order to increase fuel flexibility and carbon efficiency of energy production and to support distributed energy generation strategies.

Oxidation of C₃ and *n*-C₄ aldehydes at low temperatures

M. Pelucchi*, A. Frassoldati*, E. Ranzi*, T. Faravelli*
matteo.pelucchi@polimi.it

* CRECK-Department of Chemistry, Materials and Chemical Engineering “G. Natta”,
Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

Abstract

Due to the increasing interest in the use of biofuels such as alcohols mainly in blend with fossil fuels, it is of great importance to assess the combustion characteristics of intermediate species such as aldehydes, both in the high and in the low temperature combustion regime. Starting from the high temperature mechanism for *n*-C₃-C₅ aldehydes recently developed at Politecnico di Milano (*Combust. Flame* 2015, 162 (2), 265-286), and from the low temperature kinetics of acetaldehyde, a detailed kinetic mechanism has been developed to describe the low temperature oxidation of propanal and *n*-butanal. The validation has been carried out by comparison with recently published species measurements in isothermal Jet Stirred Reactors by Veloo et al. (*Proc. Combust. Inst.* 2013, 34 (1), 599-606; *Combust. Flame* 2013, 160 (9), 1609-1626) at T=500-1100 K, p=10 atm and $\phi=0.3, 0.5, 1.0$ and 2.0 . Aldehydes reactivity is largely dominated by H-abstraction from the carbonyl site (α) leading to the formation of R_n•C=O radical, which rapidly decomposes to form CO and the corresponding •R_n alkyl radical. Therefore, the low temperature oxidation of R_nCHO aldehydes is strictly related to the low temperature oxidation of the corresponding R_nH alkane. According to both the experimental measurements and model predictions the low temperature reactivity increases as *n*-butanal>propanal. This is due to the fact that *n*-propyl radical has more pronounced low temperature reactivity than ethyl radical. The scarcity of experimental measurements at engine relevant conditions in other facilities (shock tubes, rapid compression machines) preclude any wide range validations of the present model. Reduction of the number of species in the aldehydes sub-mechanism through lumping will follow in a future study.

Kinetic modeling of the low temperature cool flames of acetaldehyde in a well stirred reactor

M. Pelucchi*, A. El Ziani*, M. Mensi*,
E. Ranzi*, A. Frassoldati*, T. Faravelli*
matteo.pelucchi@polimi.it

* CRECK-Department of Chemistry, Materials and Chemical Engineering “G. Natta”,
Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

Abstract

Due to the increasing interest in the use of biofuels such as alcohols in blend with fossil fuels, it is of great importance to better understand the combustion characteristics of species such as aldehydes, both in the high and in the low temperature regime. Starting from the high temperature mechanism for C₃-C₅ aldehydes recently developed at Politecnico di Milano (*Combust. Flame* 2015, 162 (2), 265-286), its extension to the low temperature conditions firstly requires to assess acetaldehyde and acetyl radical (CH₃•C=O) reactivity at low temperatures. Acetaldehyde low temperature mechanism is used in this paper to reproduce different oscillatory ignition regimes such as cool flames, experimentally observed in well stirred reactors by Gray et al. (*Proc. Roy. Soc. London, Ser. A*, 1981, 374, 313-339). The periodicity of cool flames depends on the self-quenching kinetics. In fact, the competition between the endothermic acetyl radical decomposition (CH₃•CO+M=•CH₃+CO+M) and the addition to oxygen to form acetyl-peroxide (CH₃•CO+O₂=CH₃•CO₃) explains the observed phenomena.

Considering the dominant abstraction channel leading to the formation of carbonyl radicals in C₂-C₄ aldehydes oxidation [1] and its subsequent fast decomposition to CO and alkyl radical, it is reasonable to assume that the low temperature oxidation of heavier aldehydes (R_nCHO) is mainly related to the low temperature branching path of the R_{n-1} alkyl radicals.

KINETIC MODELING STUDY OF H₂S PYROLYSIS

A. Bassani*, C. Frau, M. Fontana*, E. Maggio**, E. Ranzi*, A.
Pettinau**, F. Manenti***

flavio.manenti@polimi.it

*Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica “Giulio Natta”, Centre for Sustainable Process Engineering Research (SuPER), Piazza Leonardo da Vinci 32, 20133 Milano, Italy

** Sotacarbo S.p.A., c/o Grande Miniera di Serbariu, 09013 Carbonia, Italy

Abstract

This article proposes a detailed kinetic scheme for the pyrolysis of H₂S. The H₂S pyrolysis is involved in different processes such as, for instance, Claus process, coal gasification and hydro-desulfurisation. Moreover, the H₂S pyrolysis is an important key-step for a new and promising route to reduce CO₂ by means the oxidation-reduction reaction between H₂S and CO₂. For these reasons, there is the interest in a better understanding of the reactions involved in H₂S pyrolysis. The kinetic scheme, used in this work, differs from the literature ones since it involves the presence of light and heavy hydrocarbons, ammonia, and other species usually present in H₂S containing feedstocks. Aiming at a hierarchical validation of the mechanism, different experimental conditions of H₂S pyrolysis are analyzed. In particular, the scheme is in comparison with experimental data of pure pyrolysis, of pyrolysis with S₂ addition, and the effect of H₂S on the pyrolysis hydrocarbons is also investigated.

EXPERIMENTAL STUDY OF THE EFFECT OF CO₂ ON PROPANE OXIDATION IN A JET STIRRED FLOW REACTOR

M. Lubrano Lavadera*, P. Sabia, G. Sorrentino*, R. Ragucci**, M.
de Joannon****

marco.lubranolavadera@unina.it

*DICMAPI-Università degli studi di Napoli Federico II, Naples 80125, Italy

**Istituto di Ricerche sulla Combustione-CNR, Naples 80125, Italy

Abstract

The influence of CO₂ on the combustion chemistry of hydrocarbons is important in several advanced technologies (MILD combustion, oxy-fuel combustion, combustion with exhaust gas recirculation in diesel). It has been assessed that the presence of diluents, required for temperature control and pollutant mitigation, leads to failure of the consolidated kinetic models in predicting the fundamental combustion features. In order to better understand and characterize the effect of CO₂ on the oxidation kinetics of simple hydrocarbons, experimental tests were carried out on propane oxidation in presence of variable amounts of CO₂ in a quartz jet stirred flow reactor (JSFR) at atmospheric pressure, over the temperature range 720-1080 K and at a residence time of 0.5 s. Three equivalence ratios (0.5, 1, 1.5) and three CO₂ dilution (90% N₂, 45% CO₂-45% N₂, 90% CO₂) were considered. Sampling and GC-TCD/FID analyses of exhaust gases allowed the measurement of the concentration of the stable species. Temperature and concentration measurement results obtained varying the inlet CO₂ concentration suggests that the oxidation of propane is significantly altered by CO₂ depending on temperature and equivalence ratio.

Comparison between experimental and numerical results pointed out that the adaptation of detailed kinetic mechanisms when CO₂ dilutes reactant mixtures is mandatory.

SESSION V

Catalytic Combustion

Soot Combustion over Ceria-Praseodymia Nanocatalysts

T. Andana, M. Piumetti, S. Bensaid, D. Fino, R. Pirone, N. Russo

Department of Applied Science and Technology, Institute of Chemical Engineering,
Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129, Turin, Italy

e-mail of principal author: samir.bensaid@polito.it

Abstract

Ceria-based catalysts are among the most active systems for soot oxidation either under O_2 or in a NO_x/O_2 atmosphere. Indeed, ceria alone or in combination with other oxides is effective towards the soot combustion. Among the various properties of ceria that could affect the surface reactivity, the redox capacity and the availability of surface oxygen species are likely the most important. Moreover, the number of soot-catalyst contact points may influence the activity of ceria for soot oxidation and hence it is necessary to maximize the interactions between the soot particles and the catalyst.

The present work investigates the catalytic activity of a set of nanostructured ceria-praseodymia with various molar compositions, as well as their morphologies, in soot combustion. Tailoring the morphology of nanoscale ceria confers interesting surface reactivity properties, thus leading to promising oxidation activities.

Therefore, a set of ceria-praseodymia catalysts with different Pr loadings (namely 10%, 25%, and 50%-mol, denoted further as Ce100, Ce90Pr10, Ce75Pr25, and Ce50Pr50, respectively) was synthesized through hydrothermal process using nitrate metal salt precursors and concentrated sodium hydroxide. For comparison purposes, another set of ceria-praseodymia and a pure CeO_2 catalyst were also synthesized through solution combustion synthesis (SCS). Then, all prepared ceria-praseodymia have been characterized by means of complementary techniques.

Catalytic activity tests in a fixed bed micro-reactor were firstly performed to gain initial insights into the effect of praseodymium doping and morphology on soot combustion activity. A typical “tight contact” condition between soot and catalyst in the reactor bed was preferred since it allows better discrimination of the activity of each catalyst. As a result, the Ce50Pr50 catalyst (where 50 indicates the atomic percentage of cerium as well as of praseodymium) with well-defined nanostructures (nanorods and nanocubes) has attained the best performances in terms of soot combustion, thanks to its high lattice oxygen mobility and its high reducibility.

Catalytic oxidation of volatile organic compounds over cerium-copper oxide catalysts

M. Piumetti, S. Bensaid, N. Russo, D. Fino

Department of Applied Science and Technology, Institute of Chemical Engineering, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129, Turin, Italy

e-mail of principal author: marco.piumetti@polito.it

Abstract

In this work, several Ce-Cu mixed oxide catalysts with different Cu/Ce contents (denoted hereafter as $\text{Cu}_x\text{Ce}_{1-x}$ where x indicates the Cu/Cu+Ce atomic ratio) have been synthesized by the solution combustion synthesis (SCS) method. Their catalytic activity has been examined in the total oxidation of ethylene, as probe molecule for VOC abatement. All the prepared catalysts have been characterized by complementary techniques, including powder XRD, FE-SEM, N_2 physisorption at -196°C , H_2 -TPR and XPS analysis.

It is generally accepted that the catalytic oxidation of VOCs over transition metal oxides, such as Cu-Ce mixed oxides, occurs according to a redox mechanism and proceeds through lattice oxygens (nucleophilic attack) of the metal oxide catalysts. Thus, the redox activity of CuO-CeO_2 catalysts is created by the ability to reduce and re-oxidize both CuO and CeO_2 , which is enhanced by a strong interaction between these phases. As a whole, $\text{Cu}_x\text{Ce}_{1-x}$ catalysts have revealed better activities compared to pure CuO and CeO_2 , likely due to their easier reducibility and redox properties, as confirmed by H_2 -TPR and XPS analysis. The most active catalyst has been the $\text{Cu}_{0.6}\text{Ce}_{0.4}$ and complete oxidation of ethylene to CO_2 occurred at ca. 450°C . On the other hand, further increase of Cu-content has diminished the catalytic activity. The lowest ethylene conversion has been reached for pure CeO_2 . These findings means that beneficial synergistic effects between CuO and CeO_2 can be observed during the catalytic oxidation of VOC, which are kinetically described by Mars-van Krevelen-like mechanisms. Finally, the most active powder catalyst was then deposited on a cordierite-type monolith through a direct synthesis and tested for the total oxidation of the VOCs. The $\text{Cu}_{0.6}\text{Ce}_{0.4}$ -based monolith exhibited high activity towards the total oxidation of VOCs, which is comparable to that obtained with powdered $\text{Cu}_{0.6}\text{Ce}_{0.4}$.

ON THE PARTIAL CATALYST-COATING OF MONOLITHS FOR HIGH PRESSURE METHANE COMBUSTION: AN EXPERIMENTAL AND MODELING APPROACH

P.S. Barbato*, G. Landi*, V. Di Sarli*, A. Di Benedetto**

barbato@irc.cnr.it

* Istituto di Ricerche sulla Combustione - CNR – P.le Tecchio 80 – Napoli

** Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università degli Studi di Napoli Federico II – P.le Tecchio 80 - Napoli

Abstract

Catalytic combustion is a valuable route to generate power with near-zero emissions and through an inherently safe operation. However, a commercial breakthrough has never been attained mainly for cost and durability limitations of catalytic materials. The occurrence of combustion at the catalytic surface poses serious thermal management issues associated with the generation of hot spots and consequent catalyst aging and/or deactivation, eventually affecting the lifetime of the catalyst itself.

Computational Fluid Dynamics (CFD) has demonstrated itself to be a powerful tool to simulate the occurrence of temperature excursions over the catalyst as a result of complex interplay among fluid flow, chemical reaction and heat exchange. Hence, through the use of CFD models, it is possible to gain more information about the phenomena that take place in catalytic combustors and also to develop novel reactor configurations.

By developing a two-dimensional CFD model, we successfully simulated both steady and unsteady behavior of a 20 wt. % $\text{LaMnO}_3/\text{La-}\gamma\text{-Al}_2\text{O}_3$ catalytic monolith fueled with methane and operated at high pressure. In particular, simulation results have demonstrated the strongly synergistic coupling established between gas-phase and catalytic reactions. Starting from these results, we have showed that complete fuel conversion can be obtained in novel partially catalyst-coated honeycomb reactors. In particular, in the “core-shell” reactor configuration we proposed, the catalyst is deposited only over the external channels, thus allowing for cost saving. Catalytic reactions are responsible for activation of homogeneous reactions, and fuel ignition first takes place in the coated channels and then in the un-coated ones (thanks to radial heat transfer). We experimentally prepared these novel catalytic monoliths and successfully tested them for high-pressure methane combustion. This work reviews the most relevant results of the modeling/experimental activity we carried out, highlighting the importance of CFD when coupled with appropriate experimental campaign.

Technical and Economic Analysis of the Combustion of Mixed Poultry Litter/ Olive Pomace Pellets for Energy Recovery

C. Allouis*, S. Cimino*, M. Gallo**, R. Nigro**

rnigro@unina.it

* Istituto di Ricerche sulla Combustione – CNR, Naples, Italy

** Dipartimento di Ingegneria Chimica dei Materiali e della Produzione Industriale
– University of Naples “Federico II”, Naples, Italy

Abstract

Currently, due to the stringent and explicit European environmental legislation about land spreading of nitrates, the direct land application of the poultry litter (PL) is not anymore the most appropriate disposal technique [European law 1991/676/CEE]. According to the recent European guide lines concerning the smart grids, the generation of electricity and heat from poultry derived wastes based on high-temperature thermal destruction techniques, i.e. combustion, could be a promising local waste management solution.

In this work we set out to investigate the technical and the economic feasibility of the combustion of poultry litter blended with olive pomace in a domestic burner (35 kW) initially designed for wood pellets. Flue gas and solid by-products during combustion tests were characterized at varying poultry litter content in the pellets. Compared to the combustion of wood pellets, CO and particulate emissions increased with PL content, whose inorganic fraction was mainly concentrated in the ashes. Under optimized conditions, the burner could be satisfactorily fuelled with pellets containing up to 50% PL by weight.

Moreover, the economic analysis further confirmed that a concentration of poultry litter around 50% represents a good compromise between its technical feasibility as an alternative fuel and the total costs for heating energy production.

PARTICLE-WALL INTERACTIONS IN ENTRAINED-FLOW SLAGGING GASIFIERS

M. Troiano*, R. Solimene, F. Montagnaro***, P. Salatino***

maurizio.troiano@unina.it

* Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale,
Università degli Studi di Napoli Federico II, P.le V. Tecchio 80, 80125 Napoli (Italy)

** Istituto di Ricerche sulla Combustione, Consiglio Nazionale delle Ricerche,
Piazzale Vincenzo Tecchio 80, 80125 Napoli (Italy)

*** Dipartimento di Scienze Chimiche, Università degli Studi di Napoli Federico II,
Complesso Universitario di Monte Sant'Angelo, 80126 Napoli (Italy)

Abstract

The slagging conditions occurring during combustion/gasification of solid fuels play a key role in the design of modern entrained-flow reactors. In these systems, solid particles migrate toward the reactor walls, due to swirled/tangential flow and to turbophoresis, generating a slag layer that flows along the reactor internal walls and is drained to the bottom of the reactor. The recent literature on entrained-flow gasification has addressed the fate of char particles as they impinge on the wall slag layer. Different micromechanical char–slag interaction patterns may establish, depending on the stickiness of the wall layer and of the impinging char particle.

This study aims to contribute to the development of a phenomenological model of the fate of coal/ash particles which considers the establishment of particle segregated phases in the near-wall region of the gasifier. Near-wall phenomena were investigated and mechanistic understanding of particle–wall interaction patterns in entrained-flow gasifiers was pursued using the tool of physical modeling. Montan wax was used to mimic, at atmospheric conditions, particle-wall interactions relevant in entrained-flow gasifiers. As a matter of fact, this wax had rheological/mechanical properties resembling under molten state, those of a typical coal slag and, under solid state, those of char particles. Experiments have been carried out in a lab-scale cold entrained-flow reactor, equipped with a nozzle whence molten wax atomized into a mainstream of air to simulate the near-wall fate of char/ash particles in a real hot environment. The partitioning of the wax droplets/particles into the different phases was characterized by their selective collection at the reactor exhaust. Results showed that the particle–wall interaction mechanisms and segregation patterns are affected by the stickiness of both the wall layer and the impinging particle and by local hydrodynamic conditions. In particular, the micromechanical interaction of a particle with a sticky wall enhances particle transport to the wall and the tendency to reach a segregation–coverage regime with the formation of a dense-dispersed phase in the near-wall region of the reactor.

THERMAL BEHAVIOUR OF FLUIDIZED BEDS DIRECTLY IRRADIATED BY A CONCENTRATED SOLAR RADIATION

Claudio Tregambi*, Riccardo Chirone, Fabio Montagnaro***, Piero Salatino*, Roberto Solimene****

claudio.tregambi@unina.it

*Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università degli Studi di Napoli Federico II, Piazzale Vincenzo Tecchio 80, 80125 Napoli (Italy).

**Istituto di Ricerche sulla Combustione, Consiglio Nazionale delle Ricerche, Piazzale Vincenzo Tecchio 80, 80125 Napoli (Italy).

***Dipartimento di Scienze Chimiche, Università degli Studi di Napoli Federico II, Complesso Universitario di Monte Sant'Angelo, 80126 Napoli (Italy).

Abstract

Directly-irradiated fluidized bed reactors are very promising in the context of solar chemistry and concentrated solar power applications as they can be operated at process temperatures high enough to perform thermochemical storage with high energy density (e.g. solar fuels production). Bed surface overheating is a critical issue because it determines the efficiency of fluidized beds as thermal receivers and possible sintering and/or degradation of the fluidized particles, hence the reduction of the efficiency of thermochemical cycles. Conditioning the hydrodynamics of the bed close to the surface may disclose effective measures to improve the interaction between the impinging radiative flux and the bed, and mitigate bed surface overheating. The present study aims at experimentally investigating the direct interaction between a concentrated simulated solar radiation and a fluidized bed by measuring the time-resolved bed surface temperature by an infrared camera. A 0.78×0.78 m fluidized bed filled by silicon carbide particles (0.127 mm) was directly irradiated by a highly concentrated solar radiation, simulated by a 4 kW_{el} short-arc Xe lamp coupled with an elliptical reflector. The interaction between the fluidized particles moving under the action of bubble bursting and the concentrated solar radiation was analysed by the time-resolved bed surface temperature varying the fluidization gas velocity. The effect of a localized generation of bubbles was also investigated injecting a chain of bubbles through a nozzle located just at the centre of the concentrated solar beam. The obtained results encourage the localized generation of bubbles, just at the larger value of the impinging radiative heat flux, as a strategy to reduce the overheating of the bed surface and, as consequence, the energy losses related to fluidizing gas and to radiative re-emission. This strategy can be also applied to preserve the chemico-physical properties of reactive materials involved in high-temperature thermochemical cycles.

COMBUSTION OF SOLID LIGNIN-RICH RESIDUES FROM BIOETHANOL PRODUCTION IN FLUIDIZED BED REACTORS

R. Solimene*, A. Cammarota*, R. Chirone*, P. Leoni, N. Rossi**, P. Salatino*****

solimene@irc.cnr.it

*Istituto di Ricerche sulla Combustione - Consiglio Nazionale delle Ricerche, Piazzale V. Tecchio 80, 80125 Napoli, Italy

** Enel Ingegneria e Ricerca S.p.A, Via Andrea Pisano 120, 56122 Pisa, Italy

*** Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale - Università degli Studi di Napoli Federico II, Piazzale V. Tecchio 80, 80125 Napoli, Italy

Abstract

The deployment and the exploitation of alternative automotive fuels, e.g. ethanol produced from lignocellulosic biomass and scraps of agricultural crops, became more and more relevant to reduce the emissions of greenhouse gases. The composition of lignocellulosic biomass is typically: cellulose (35-45%), hemicellulose (25-30%) and lignin (25-30%). The cellulose and hemicellulose are made of fermentable sugars, while the lignin is a polymer consisting of several units of not fermentable phenylpropane. The residues of bioethanol production characterized by high lignin content can be used only in part to energetically support the process of bioethanol production (about 40%). The aim of this work was to study the co-combustion of high lignin content residues coming from a second-generation bioethanol production plant, with coal in fluidized beds with the aid of different experimental apparatus, at lab and pilot-scale, and of different diagnostic and experimental protocols. The lab-scale experimental investigation showed that: 1) comparing devolatilization times with transversal mixing time of typical industrial-scale fluidized bed combustors, wet fuel larger than 10mm can be fed mixed with coal directly in the combustor chamber, whereas dry fuel was extremely reactive and once fed to the fluidized bed it can generate localized emissions of heat and micro- and macro-pollutants; 2) the particles do not undergo primary fragmentation; 3) secondary or percolative fragmentation is active in late stage of char burn-out; 4) fines are mainly produced by fragmentation during char burn-out rather than generated by surface abrasion. The pilot-scale experimental investigation showed that: 1) the gaseous emissions do not significantly change at least until a percentage of 30%w of residues is considered; 2) the particulate emissions increase with the percentage of residues content, but, at the same, the carbon content is significantly reduced; 3) agglomerates of bed particles are not observed; 4) long and high-temperature operation can cause a significant enrichment of metals coming from residues ash.

CFD model for pyrolysis of thick biomass particle

G. Gentile, A. Cuoci, A. Frassoldati, T. Faravelli, E. Ranzi

giancarlo.gentile@polimi.it

Politecnico di Milano, dip. CMIC, p.zza Leonardo da Vinci 32, 20133 Milano, Italy

Abstract

The present work addresses the study of the pyrolysis of biomass particles, with the aim to improve the comprehensive mathematical model of the thermochemical processes involving solids decomposition.

The motivation of the work resides in the fact that biomass materials represent an area of growing interest and development in the current energy scenario. In this context it is important to spend more modeling efforts in the direction of a deeper understanding of the chemical and physical processes controlling the pyrolysis and gasification of biomasses. The final goal of the activity is to develop numerical tools able to support the technological implementation of new processes for the effective exploitation of biomass potential.

A comprehensive CFD model for the biomass pyrolysis was developed at the particle scale in order to describe the simultaneous effect of reaction kinetics and transport phenomena. This tool allows to solve the Navier-Stokes equations for both the solid porous media and the gas contained within its pores. The code employs the open-source OpenFOAM[®] framework to effectively manage the computational grids and the discretization of governing equations.

The model is able to properly describe the shrinking of the biomass particle due to the decomposition of the porous media through the introduction of moving unstructured meshes.

In order to validate the reliability of the model, the results of the CFD simulations were compared to the corresponding results obtained using a 1D algorithm independently implemented. The latter solves mass and energy balance equations for gas and solid species employing a finite volume method (FVM) discretization of 1D isotropic spherical domain.

In this work, pyrolysis of centimeter-scale of wood particles was been studied under “thermally thick” conditions. It represents an ideal benchmark for the new tool because heat transfer and chemical kinetics exhibit comparable timescales.

INTERACTIONS BETWEEN BIOMASS COMPONENTS IN BIOMASS PYROLYSIS: A CASE STUDY ON POPULUS NIGRA

P. Giudicianni*, C.M. Grottola, R. Ragucci*, M. Alfè*, V. Gargiulo*,
M. Rabacal***, A. I. Marquez Ferreiro***, M. Costa*****

giudicianni@irc.cnr.it

*Istituto di Ricerche sulla Combustione - CNR - Naples

**DICMaPi - University Federico II – Naples

***IDMEC – Instituto Superior Tecnico – Lisbon

Abstract

Pyrolysis of biomass represents an interesting thermochemical process given its excellent flexibility with respect to the desired products yields and characteristics. Slow steam pyrolysis is proposed as possible process for the recovery of biochar with characteristics that make it suitable for agronomic applications. In view of the evaluation of the feasibility of such a process, products yields, composition and energetic content of gaseous products needed to assist energetically the process are relevant data to be evaluated. Biomass main components (hemicellulose, cellulose and lignin) contribute to a different extent to the determination of products yield and characteristics both for their own intrinsic chemical nature and for the onset of possible interactions due to their simultaneous presence in a real biomass. In the present paper the influence of possible interactions between biomass main components on pyrolysis of *Populus nigra* has been studied. To this aim TG analysis have been performed on *Populus nigra* and on a model mixture of xylan, cellulose and lignin resembling its composition. The weight loss curves have been compared with two non interacting cases: the experimental one obtained superimposing the TG curves of xylan, cellulose and lignin and the numerical one obtained adopting the Bio-PoliMi kinetic model. Then, steam assisted pyrolysis tests have been carried out and products yields, gas releasing rate as function of temperature and gas composition obtained processing the real biomass and the model mixture in both the interacting and not interacting case have been compared. The results show that a detailed description of pyrolysis behavior of *Populus* should take into account mainly the interactions between biomass components even though a rough prediction of the product yields can be made on the basis of knowledge of biomass biochemical composition.

Validation of the twoPhaseEulerFoam solver for jet inlet fluidized beds

G. Tretola, F.S. Marra,

marra@irc.cnr.it

Istituto di Ricerche sulla Combustione - CNR, via Diocleziano 328 - Napoli, ITALY

Abstract

Gas–solid fluidized beds operating in the bubbling regime have been widely used in various fields of chemical engineering and of the power industry due to the highest contact efficiency between the phases, which leads to a higher conversion, and to a better heat distribution these systems can grant for their nature.

The numerical modelling of bubbling fluidized beds presents particular difficulties due to the high number of particles involved in the system, which makes the adoption of Lagrangian models impossible for the simulation of devices of practical interest due to their high computational cost. As a consequence, the Eulerian–Eulerian two-phase approach is the choice to simulate these systems. where the normal stresses of the particulate phase are modelled with the kinetic theory of the granular flow, or with some rheological model to calculate the normal stresses of the particulate phase, in order to avoid an unphysical increase in its phase fraction .

The aim of the work is to perform the validation of the solver twoPhaseEulerFoam, presents in OpenFOAM ver. 2.3.x, for the numerical simulation of a fluidized bed with an inlet jet. The experimental set-up proposed in Kuipers et al. [1] is used to compare numerical simulation with experimental results.

With a proper choice of the available models and correlations whose effect will be illustrated, it is confirmed the ability of the solver at reproducing the transient phenomenon. Nevertheless, several numerical caveats emerged, making the selection of numerical parameters crucial for a successful integration.

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METAL RECOVERY FROM SEWAGE SLUDGE ASH FOR CLC OXYGEN CARRIERS PRODUCTION

A. Coppola*, R. Chirone*, G. Ruoppolo*, R. Solimene*, M. Urciuolo*

ruoppolo@irc.cnr.it

*Istituto di Ricerche sulla Combustione, CNR, P.le Tecchio 80 – 80125 Napoli

Abstract

Chemical looping combustion (CLC) is a promising strategy to produce energy from fossil fuel coupling the CO₂ sequestration. The CLC process is typically realized adopting two interconnected fluidized beds with a solid, the oxygen carrier, circulating between them. The solid, i.e. the oxygen carriers (OC), promotes fuel oxidation without direct contact with atmospheric oxygen. Typical OCs consist of an active phase, which could be a suitable metal oxide, supported on an inert material for ensuring chemical, thermal and mechanical stability. The process involves two cyclic reactions which take place alternately in the Fuel Reactor (reaction 1) and in the Air Reactor (reaction 2):

1. $C_nH_{2m} + (n+\frac{1}{2}m)Me_xO_y = nCO_2 + mH_2O + (n+\frac{1}{2}m)Me_xO_{y-2}$
2. $Me_xO_{y-2} + O_2 = Me_xO_y$

where C_nH_{2m} is a generic fuel, while Me_xO_y and Me_xO_{y-2} are the metal oxide in the oxidized and reduced form, respectively.

The oxygen carriers should have high reactivity with gaseous fuels and oxygen and oxygen transport capacity, low fragmentation, attrition and agglomeration tendency and high stability to a large number of redox cycles. However, the choice of the proper oxygen carrier is still open and it deserves further investigations. Usually the oxygen carrier is made of a metal oxide. Among transition metals, Fe-based oxygen carriers are considered an attractive option for the chemical looping combustion owing to their low cost, abundance and environmental compatibility. The aim of this work is the production of low-cost CLC oxygen carriers by sewage sludge fluidized bed combustion. In particular, the metals (Fe, Ca, Mn) present in sewage sludge ash have been deposited during sewage sludge fluidized bed combustion on high-surface γ -alumina which is characterized by high mechanical resistance and it was used as bed material. The produced oxygen carrier has been characterized using ICP-MS, X-ray diffraction (XRD), Scanning Electron Microscopy (SEM-EDX) and surface area (BET) analysis. The redox behaviour of the oxygen carrier has been investigated using H₂ reduction experiment. Reduction/oxidation cycles have been performed to assess the stability of the systems. The reactivity of the carriers and their oxygen transport capacity have been also evaluated under repeated cycles of methane combustion/air regeneration carried out in a fluidized bed reactor.

PRE-TREATMENT OF THE ORGANIC FRACTION OF THE MUNICIPAL SOLID WASTE AT DOMESTIC SCALE

P. Bozza*, P. Giudicianni, A. Cavaliere*, R. Ragucci****

pio.bozza@unina.it

* DIC-MAPI - Università degli Studi di Napoli Federico II– ITALY

** Istituto di Ricerche sulla Combustione- C.N.R. Napoli – ITALY

Abstract

In the present study a thermo-mechanical treatment for the disposal of the Organic Fraction of Municipal Solid Waste (OFMSW) at apartment or condominium scale is proposed. The process presents several advantages allowing to perform a significant volume and moisture reduction of the produced waste at domestic scale thus producing a material with an increased storability and improved characteristics (e.g. calorific value) that make it available for further alternative uses. The assessment of the applicability of the proposed waste pretreatment in a new scheme of waste management system requires several research steps involving different competences and application scales.

In this context, a preliminary study is needed targeting to the evaluation and minimization of the energy consumption associated to the process. To this aim, in the present paper, two configurations of a domestic appliance prototype have been presented. The performances of the prototype have been tested on three model mixtures representing a possible daily domestic waste and compared with an existing commercially available appliance.

The results obtained show that a daily application of the process is feasible given the short treatment time required and the energy consumption comparable to the one of the common domestic appliances. The evaluation of the energy recovered in the final product per unit weight of raw material shows that in most cases it is comparable to the energy required from the treatment.

CO₂ ADSORPTION FROM SIMULATED FLUE-GAS ON ACTIVATED CARBON MONOLITHS

D. P. Vargas*, M. Balsamo, L. Giraldo*, A. Erto**, A. Lancia**, J.C. Moreno-Piraján*****
aleserto@unina.it

*Universidad Nacional de Colombia, Departamento de Química, Bogotá (Colombia)

**Università degli Studi di Napoli Federico II, Dipartimento di Ingegneria Chimica dei Materiali e della Produzione Industriale, Napoli (Italy)

***Universidad de los Andes, Departamento de Química, Bogotá (Colombia)

Abstract

In this work, CO₂ adsorption tests are carried out in a lab-scale fixed-bed reactor from simulated flue-gas, at different temperatures (303 and 353 K) and CO₂ concentrations (3-25%), in order to investigate both the kinetic and thermodynamic aspects. To this purpose, two different activated carbon monoliths were synthesized starting from an African palm stone (*Elaeis guineensis*), activated with H₃PO₄ (48% w/v) or with a combination of H₃PO₄ (32% w/v) + CaCl₂ (2% w/v), respectively. In order to increase the affinity toward CO₂, the monolith samples were subjected to a same surface modification post-process, conducted with a 30 % w/w ammonium hydroxide aqueous solution.

The textural characterization of the monolith samples was carried out by N₂ and pure CO₂ adsorption at 77 K and 273 K, respectively, allowing the determination of micro- and mesopore volumes as well as pore size distributions.

The adsorption tests shows a maximum CO₂ adsorption capacity for the sample with the greatest ultramicropore volume, while the adsorption rate increases in presence of mesopores and for higher temperature. Moreover, dedicated regeneration studies demonstrate that both the monoliths samples can be fully regenerated at each investigated adsorption temperature and their CO₂ adsorption capacity keeps almost constant in five consecutive cycles of adsorption-desorption. It can be concluded that activated carbon monoliths can be a good alternative to granular or powdered sorbents for CO₂ capture in fixed-bed plants.

SUSTAINABLE ENERGY ACTION PLAN FOR REDUCTION OF THE EMISSION OF GREENHOUSE GASES IN VALLE CAUDINA AREA

R. Chirone*, R. Formato, L. Lisi*, G. Ruoppolo*, M. Urciuolo***

g.ruoppolo@irc.cnr.it

*Istituto di Ricerche sulla Combustione, CNR, P.le Tecchio 80 – 80125 Napoli

** Responsabile progetto Joint Paes “La Valle Caudina...VIVE

Abstract

The climate changes related to CO₂ emission from combustion of fossil fuels increased more and more in the last 50 years. According to Protocol of Doha, extending the Protocol of Kyoto, the European Union decided 20% (or even more) reduction of CO₂ emission levels of 1990 by 2020.

The Covenant of Mayors is a European movement where local/regional authorities, voluntarily commit to increasing energy efficiency and use of renewable energy. This paper describes and analyzes the overall scenario of greenhouse gases emissions from urban, industrial and agricultural activities in the reference year 2011 of a covenant of 13 small towns located in Valle Caudina (about 50.000 citizens) area and proposes, on the base of the emissions inventory data, strategies to reduces emissions by 20-30%. The work was carried out in the context of *Piani di Azione per l'Energia Sostenibile (PAES)*.

The inventory of 2011 baseline emissions was done both by a top-down and bottom-up approach and the estimation in the reference year of total CO₂ emission was 257.762 ton/year taking into account also other greenhouse gases as methane, nitrogen oxides etc. which were calculated as CO₂ equivalent.

Transportation represents the main source of CO₂ emission followed by electrical and thermal consumptions and, to a lesser extent, by livestock. This is related to lack of public transports connecting the small towns which involves an overuse of cars. Excluding transports, the energetic consumption are mostly related to domestic/residential sector, Valle Caudina being a poorly industrialized area.

Strategies to reduce greenhouse gases emissions were based on improving energy efficiency of public and private buildings through thermal insulation, promotion of car sharing and substitution of old and polluting cars, promotion of use of bikes, public education campaign etc. Nevertheless, here we limit the discussion to proposals basically aimed at substituting fossil for renewable fuels thus enhancing local production of energy from biomass in order to exploit agricultural and wooded waste which represent a large heritage of the valley. Among projects proposed one involves the chipping of wooded waste and their use as fuel for heating of school buildings. Others involve collection and use of floricultural waste or animal livestock manure for anaerobic digestion to produce biogas to be transformed into thermal and/or electrical energy.

SESSION VIII

Fire & Safety

EXPLOSION PARAMETERS OF AMMONIA/ETHANOL-AIR MIXTURES

Francesco Cammarota^{*}, Almerinda Di Benedetto^{}, Valeria Di Sarli^{*},
Ernesto Salzano^{*}**

f.cammarota@irc.cnr.it

^{*}Istituto di Ricerche sulla Combustione, CNR, Piazzale Tecchio 80, 80125, Napoli, Italy

^{**}Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale,
Università degli Studi di Napoli Federico II, Piazzale Tecchio 80, 80125, Napoli, Italy

Abstract

Over the last few decades, growing environmental concerns over the depletion of fossil fuels and gradual increase in energy demand have stimulated interest in alternative fuels such as biofuels. Bioethanol is mainly of interest as a petrol additive or substitute, because ethanol-blended fuels undergo cleaner and more complete combustion, thus reducing greenhouse gas and toxic emissions [1]. Bioethanol can be produced from agricultural feed-stocks, forestry wood wastes and agricultural residues [2]. One of the examples for bioethanol production is rice straw, which is the most abundant lingo-cellulosic biomass worldwide [3]. The feedstock is typically pretreated by using ammonia fiber expansion (AFEX) and enzymatically hydrolyzed [4]. Safe industrial use of this fuel needs explosion data as maximum pressure, maximum rate of pressure rise and burning velocity, which are the most important parameters for the safe design of process equipment.

In this work, the explosion parameters of $\text{NH}_3/\text{C}_2\text{H}_5\text{OH}$ -air mixtures have been measured. Experimental tests were carried out in a 5 dm³ closed cylindrical vessel. Results allow quantifying the combined effects of initial temperature and equivalence ratio on maximum pressure, maximum rate of pressure rise and burning velocity.

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Keywords: Ammonia, Ethanol, Combustion, Explosion parameters, Burning velocity

CFD ANALYSIS OF SPRINKLER EFFECTS ON ENCLOSED FIRES

S. Favrin*, A. Parente, M. Derudi***

simone.favrin@polimi.it

*Politecnico di Milano, Dip. di Chimica, Materiali e Ingegneria Chimica “G. Natta”,
Milano, Italy

**Université Libre de Bruxelles, Service d'Aéro-Thermo-Mécanique, Bruxelles, Belgium

Abstract

Fire dynamics and smoke dispersion inside buildings are complex phenomena involving many variables; some of these are related to firefighting systems behavior and their effects. CFD simulations involving water based firefighting systems require a high level of knowledge about main characteristics of the model. An effects-based analysis over some input parameters of sprinkler systems has been conducted.

The software chosen is NIST Fire Dynamics Simulator, an open source LES solver widely used in fire engineering.

An initial stage of validation and calibration of the model has been done in order to guarantee an acceptable confidence level about the results of the analysis. This first part focused on reproducing a known experimental layout, which consists in a wide room with a single opening and a gas burner located in a corner of the enclosure. A series of tests has been performed with the sprinkler system activated and compared with another series without the sprinkler system activation. CFD results showed a good level of agreement with literature experimental data.

Main characteristics of the sprinkler model investigated are flow rate, particle diameter, initial velocity, and spray angle.

Results are quantified respectively to fire characteristic variables, such as temperature and smoke layer height, instead of water distribution on the floor as commonly done.

Conclusion highlights the relevance of water flow rate and particle diameter over the others in fire controlling themes; loss of visibility inside the enclosure has been reported due to altered smoke layer stratification during the sprinkler activation.

SESSION IX

Pollutant Formation and Control

SOOT FORMATION PROPERTIES IN A PREMIXED TOLUENE-DOPED METHANE FLAME

C. Russo*, L. Giarracca, F. Stanzione*, A. Tregrossi*, A. Ciajolo***

carmela.russo@irc.cnr.it

*Istituto di Ricerche sulla Combustione, CNR, Piazzale Tecchio, 80, 80125 Napoli, Italy

**Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale,
Università degli Studi di Napoli Federico II, P.le Tecchio 80, 80125 Napoli, Italy

Abstract

The sooting structures of premixed methane and toluene-doped (0.8 vol.%) methane flames were analyzed by sampling and analysis of gaseous and condensed phases. It was shown that the addition of very small amounts of toluene drastically changed sooting yield and the properties of soot formed as inferred by detailed chemical and spectroscopic analysis.

Combustion-generated Particles Nucleation: Molecular Dynamics Approach

L. Pascazio, M. Sirignano, A. D'Anna

laura.pascazio@unina.it

Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale -
DICMaPI, Università degli Studi di Napoli Federico II, Napoli, Italy

Abstract

Nucleation of combustion-generated particles remains the less understood process in particle formation in combustion and it is a challenge for both experimental and modelling sides. Despite of the efforts spent on the topic, a conclusive description of the process is not reached yet, particularly the formation of the first molecular clusters and their morphology.

Molecular dynamic (MD) approach allows to describe punctually the evolution of the particles and of their principal constituent, i.e., the polycyclic aromatic hydrocarbons (PAHs). In this paper, a study of the evolution of PAHs and their possibility to form cluster has been performed by using a commercial MD code (GROMACS v4.6). By molecular dynamics it is possible to get a detailed description of molecule evolution, monitoring the internal coordinate over the time. Knowing the location of all atoms in space, it is possible to identify the formed clusters and to study their time evolution and their internal structure.

Simulations of homomolecular systems have been performed at a temperature of 500 K using the velocity Verlet algorithm coupled with a Nosè-Hoover thermostat. Two representative PAH molecules, pyrene ($C_{16}H_{10}$) and coronene ($C_{24}H_{12}$), have been selected as starting molecules in order to study the influence of the different extension of the aromatic island on particle inception, size and morphology.

In the investigated conditions, pyrene shows a small amount of formed clusters whereas coronene form large number of clusters with different sizes. Looking at the evolution of the cluster size distribution, it is evident in the coronene simulation the formation of clusters of size up to 50 molecules, although a large part of the cluster are mainly constituted by 2-4 molecules. Molecular dynamic approach also allowed to analyze the morphological arrangement of the coronene clusters, showing a peculiar pile-structure for clusters constituted by less than 10 molecules.

THERMAL TREATMENT OF CARBON-BASED MATERIALS RELEVANT IN THE COMBUSTION FIELD

C. Russo, B. Apicella, F. Stanzione, A. Tregrossi, A. Ciajolo

carmela.russo@irc.cnr.it

Istituto di Ricerche sulla Combustione, CNR, Piazzale Tecchio, 80, 80125 Napoli, Italy

Abstract

In the context of searching for alternative sources of carbon materials this work concerns the study of the structure of carbon materials obtained by carbonization at low temperatures ($<700\text{ }^{\circ}\text{C}$) of soot and tar-like material sampled in fuel-rich premixed flames. The structural evolution of flame-formed tar under thermal treatment was investigated by spectroscopic tools and compared to that of naphthalene pitch, a commercial analogue catalytically-produced from organic precursors.

Thermocouple particle densitometry for quantification and characterization of combustion-formed particulate matter

G. De Falco*, G. Trunfio*, M. Commodo, P. Minutolo**, A. D'Anna***
commodo@irc.cnr.it

* Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale -
Università degli Studi di Napoli Federico II, P.le Tecchio 80, 80125, Napoli, Italy

** Istituto di Ricerche sulla Combustione, CNR, P.le Tecchio 80, 80125, Napoli, Italy

Abstract

In this work, thermocouple particle densitometry (TPD) has been demonstrated to be a valid tool for the analysis of combustion-formed carbon nanoparticles. The TPD methods has been successfully used to describe both particle volume fraction and the chemical evolution of carbonaceous nanoparticle in an ethylene/air premixed flame. Scanning mobility particle sizer (SMPS) and Raman spectroscopy have been used in comparison with the TPD analysis and to corroborate the TPD results. As a result, TPD has shown excellent agreement to the SMPS particle volume fraction measurements along the entire flame, starting from the very low values at the inception region. Furthermore, TPD has shown a clear evidence that the two classes of carbon nanoparticles, i.e. the two modes of the particle size distribution, strongly differentiate in terms of their graphitization degree based on the different values of emissivity of the material deposited on the thermocouple. While primary soot particle, i.e. those with diameter 10-20 nm, present emissivity of approximatively 1, thus acting as a black body, nucleated nanoparticles present emissivity values of about 0.5-0.6 indicating that they have a lower graphitization degree, i.e. higher content of organic carbon as compared the grown ones. Finally, Raman scattering, measured directly on the thermocouple previously coved by carbon nanoparticle, supported the TPD analysis. The possible use of TPD as valid, reliable and cost-effective combustion aerosol sensor in hot gas-stream is discussed.

EFFECT OF 2,5-DIMETHYLFURAN ON PARTICLES FORMATION IN PREMIXED FLAMES: AN EXPERIMENTAL STUDY

M. Conturso*, M. Sirignano, A. D' Anna

marielena.conturso@unina.it

Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale -
DICMAPI
Università degli Studi di Napoli Federico II
Italia

Abstract

Particulate matter pollution is one of the most common problems of the big town and industrial areas. Epidemiological studies carried out in last years have demonstrated a correlation between particulate presence in atmosphere and an increased mortality rate. To cope with this problem, research efforts address the pollution reduction and the search of alternative sources of the transportation fuels like biodiesel, methanol, bioethanol, butanol, dimethylether. Furanic biofuels have been investigated in last months because considered possible fossil fuel substitutes thanks to their high energy density close to gasoline one, the renewable source from they come and low green-house gas emissions. Not a rich literature is present about the behaviour of these compounds in laboratory flame reactor, thus after their study in counter-flow diffusion flames, we have expanded the knowledge about their particulate formation propensity during the combustion employing them in premixed atmospheric flames of ethylene at four different equivalence ratios: 2.01, 2.16, 2.31 and 2.46. Liquid 2,5-dimethylfuran has been added at the inlet stream as 10% and 20% of total carbon fed. In-situ spectroscopy, namely laser UV-induced emission, has been used as diagnostic tool to detect different types of nanoparticles by changing the detection wavelength from the UV to the visible. Laser induced incandescence has instead been used to detect soot particles. Results show that 2,5-dimethylfuran addition in high percentage causes a reduction of particulate formation: the highest reduction is for the incandescence emission at high equivalence ratio.

The Effect of Support on Mercury Capture Performance of MnO_x Regenerable Sorbents

S. Cimino*, F. Scala**

stefano.cimino@cnr.it

* Istituto di Ricerche sulla Combustione – CNR, Piazzale Tecchio 80, 80125 Napoli, Italy

** Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale,
Università degli Studi di Napoli Federico II, Piazzale Tecchio 80, 80125 Napoli, Italy

Abstract

Mercury is well known to cause adverse effects in human body and animals. Coal combustion on its own contributes to 30% of the global anthropogenic Hg emissions. Elemental mercury (Hg^0) is the most difficult species to remove with conventional air pollution control devices due to its high volatility and insolubility in water. Oxides of transition metals (in particular Mn) have been recently indicated as possible alternatives to activated carbon as regenerable sorbents for Hg removal from combustion flue gas. Moreover MnO_x based catalysts are widely studied for their high activity and selectivity for NO_x reduction in flue gases via the low temperature ($<200\text{ }^\circ\text{C}$) NH_3 -SCR reaction, which is a typical redox process. This observation opens the possibility of simultaneous SCR and mercury capture in a single process unit in tail-end configuration. Following previous studies in this work we set out to investigate the effect of the type of support (TiO_2 vs. Al_2O_3) on the Hg^0 removal performance of MnO_x -based adsorbents under oxidizing conditions. The adsorbents were fully characterized by means of ICP-MS, XRD, BET, H_2 -TPR, NH_3 -TPD, and Hg-TPD. Moreover, the effect of the simultaneous presence of other species in the flue gas such as NO and NH_3 was also studied in view of the possible development of a single-step process integrating low temperature SCR and mercury capture.

PRELIMINARY STUDY ON MILD COMBUSTION CHARACTERISTICS OF ALCOHOL FUEL BLENDS

M. Derudi, R. Rota

marco.derudi@polimi.it

Politecnico di Milano, Dip. di Chimica, Materiali e Ingegneria Chimica “G. Natta”, Milano

Abstract

This preliminary study has been focused on the investigation of the sustainability of mild combustion for liquid hydrocarbons and alcohol fuel blends using a dual-nozzle laboratory-scale burner; the proposed experimental setup allows sustaining mild combustion conditions by directly injecting different liquid hydrocarbons in a mild combustion environment previously obtained using a gaseous fuel. A liquid kerosene fuel, with its well-known properties has been used as a reference fuel; the kerosene fuel performances in terms of NO_x and CO emissions, temperature profiles and mild combustion stability have been compared to those of different alcohol fuel blends, mainly constituted by butanol-kerosene mixtures. The investigated fuels evidenced mainly a similar behavior, low temperature gradients within the combustion chamber and very low NO_x emissions.

Concerning the use of liquid fuel blends, the mild combustion region in the usual T vs K_v diagram slightly enlarges towards higher average furnace temperatures when using an alcohol fuel blend with respect to the kerosene. In this region very low amounts of NO_x and CO are produced for the fuels investigated, thus supporting the idea that a mild combustion furnace can create a suitable environment also for PAH and soot depression, allowing the use of a wide range of liquid hydrocarbons and blends.

CHARACTERIZATION AND INFLAMMATORY POTENTIAL OF SUB-10NM PARTICLES GENERATED FROM GAS COOKING APPLIANCES

M. Conturso*, P. Pedata, S. Scantone*, M. Sirignano*, F.
Stanzione**, A. Ciajolo***, A. D' Anna***

marielena.conturso@unina.it

*Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale –
DICMAPI, Università degli Studi di Napoli Federico II, Piazzale V. Tecchio 80, 80125
Napoli, Italy.

**Department of Experimental Medicine-Occupational Medicine, Hygiene and Industrial
Toxicology Section, Second University of Naples, Via L. De Crecchio 7, 80138 Naples,
Italy.

***Istituto di Ricerche sulla Combustione, CNR, Piazzale V. Tecchio 80, 80125 Napoli,
Italy.

Abstract

Combustion generated ultrafine particles are believed to have an effect on human health. Their presence in the atmosphere is mainly attributed to outdoor sources, but they may also form indoor. Gas cooking is commonly considered very clean, and particle free. However, even bluish flames of natural gas may produce a considerable number of sub-10nm particles if operating conditions deviate from stoichiometry and mixing at atomic level. These particles negligibly account for particulate mass but, due to their very low sizes, they can deposit far inside the airways and potentially reach target organs being dangerous although present in low mass concentration. The objective of this study is to characterize the exhausts of a domestic cooktop burner measuring stable compounds, gas-phase aromatic compounds and particulate matter and to collect nanoparticles for in vitro toxicological studies and to analyse their possible inflammatory effects. Combustion exhausts, including polycyclic aromatic hydrocarbons (PAH) and nanoparticles, have been sampled at 60cm above a mid-range cooktop burner fed with network natural gas. Tests have been performed in a free flame and by putting a pot on the burner in order to simulate operating conditions closer to the usual ones. Speciation of PAHs and the distribution of the particles generated during combustion has been measured. Measurements show that the flames produce and emit PAHs and particles in the size range 2.5-20nm in huge number concentration. Tests of cell viability when exposed to nanoparticles have been performed. Preliminary results of crystal violet assay have shown that reduction in cell viability is not observed with nanoparticles collected in a free flame whereas a small effect is observed by putting a pot on the burner.

SESSION X

Stationary and Engine Combustion

PERFORMANCE OF A CYCLONIC BURNER FOR TECHNOLOGIES WITH HIGH LEVEL OF DILUTION AND INTERNAL RECIRCULATION

G. Sorrentino*, P. Bozza*, P. Sabia, M. de Joannon**, A. Cavaliere*, R. Ragucci****

pio.bozza@unina.it

* DICMAPI - Università Federico II, Naples, Italy

** Istituto di Ricerche sulla Combustione - C.N.R., Naples, Italy

Abstract

The present study describes the performance and stability characteristics of lab-scale burner with high level of dilution and strong internal gas recirculation.

A cyclonic flow is realized inside the combustor and it could represent a very effective system in realizing mixing processes in very short time and small size while allowing for a reasonable long residence time for the development of combustion reactions.

The stabilization process of MILD combustion for propane/oxygen/nitrogen mixtures was studied varying the system external parameters, namely inlet temperature (T_{in}), equivalence ratio Φ (lean to rich mixtures) and inlet oxygen percentages X_{O_2} (from 8% to 18%). The process features were characterized by means of temperature measurements inside the chamber, a quartz window and gas sampling analysis at the stack of the burner.

Different combustion regimes were achieved and characterized: low reactivity, dynamic regimes and MILD Combustion. The last regime showed a uniform temperature distribution within the chamber with a stable volumetric combustion characteristics and very low pollutant emissions in the exhaust gases. MILD regimes were established for inlet preheating temperature higher than about 900 K for each mixture composition. The main contributing factor for combustion stability was found to be pronounced internal recirculation.

Moreover, once achieved MILD operating condition, it was possible to maintain this regime by decreasing the preheating temperature of the reactants, thus identifying a hysteresis behavior. As matter of fact, for the stoichiometric condition the present burner configuration proved to operate without the need for external preheating, and achieved a high degree of temperature uniformity with low emissions. Such results suggest that the advantages of MILD can be partly achieved without the preheating of combustion air and with moderate flue gas recirculation. This enables a simplified and more economical construction, applicable for instance in small-scale boilers and CHP systems.

FLAME INSTABILITY IN A LIQUID FUEL BURNER: COMPARISONS BETWEEN SINGLE AND MULTIPOINT INJECTIONS

M.G. De Giorgi*, A. Sciolti*, Stefano Campilongo*, Antonio Ficarella*
mariagrazia.degiorgi@unisalento.it

* Università del Salento, Department of Engineering for Innovation, Via Monteroni, 73100,
Lecce, Italy

Abstract

With the aim to characterize the flame behavior when ultra-lean combustion conditions are reached, an experimental investigation was performed on a liquid-fuel gas turbine derived burner, at different fuel/air ratios and comparing different fuel injection modes. Ultra lean conditions have a negative impact on combustion efficiency for the instabilities insurgence. High speed acquisitions by a CCD camera were performed to investigate the behavior of the spray and the flame close to lean blowout. Statistical and spectral analyses were also applied to the flame acquisitions to extract suitable parameters for blowout recognition.

EFFECT ON CO₂ DILUTION ON RAPESEED OIL COMBUSTION IN A STATIONARY BURNER

C. Allouis*, F. Chiariello**

allouis@irc.cnr.it

*Istituto di Ricerche sulla Combustione – CNR, P.le V.teccio 80, 80125 Napoli - Italy

**Istituto Motori – CNR, 1 P. Barsanti E Matteucci, 80125 Napoli - Italy

Abstract

Application of CO₂ diluted combustion to existing fossil fuel/biofuel energy systems to facilitate CO₂ capture presents several challenges. This paper investigates the combustion characteristics of Rapeseed oil and its blends with Diesel oil in swirling spray flames. It focuses on the stability of flames, NO_x, CO and particle emissions. We observed that CO₂ dilution decreased the NO_x emission (up to 20 times) due to the lower furnace temperature at fixed oxygen concentration. Although the dilution of combustion does not produce significant effect on the shape of the size distribution functions, this modifies significantly the absolute concentrations of the emitted particles. Finally, the produced diluted flames were stable and more luminous than the air/fuel flames.

Ignition of a homogeneous gaseous air/methane mixture through a flash light

A.P. Carlucci*, A. Ficarella*, D. Laforgia*, L. Strafella*

paolo.carlucci@unisalento.it

* University of Salento - Dept. of Innovation Engineering
via per Monteroni - 73100 Lecce, Italy

Abstract

This paper proposes a new ignition system for air-methane mixtures, based on the exposition of Multi Wall Carbon NanoTubes (MWCNTs), containing 75% in weight of ferrocene, to a low-consumption flash camera. The experiments were performed in a constant-volume chamber filled with an air-methane mixture and its combustion was triggered by exposing the nanotubes to the flash of a camera. During the experimental activity, two types of tests have been carried out. The first, compares the results of the combustion process varying the amount of nanoparticles introduced into the combustion chamber at fixed air/methane ratio; the second compares the results of the combustion process varying the air/methane ratio at fixed amount of nanoparticles. Dynamic pressure measurements show that the photo-ignition phenomenon takes place when a minimum amount of nanoparticles, equal to 10 mg (for the first tests session) is provided, and when an air/methane ratio not exceeding 61.5, i.e. three times higher than the stoichiometric (for the second test session), is used.

These results are considered to be of great scientific importance, since the combustion process has been obtained igniting a mixture extremely lean: the use of mixtures of this type would allow to reduce pollutant emissions, such as NO_x and particulate.

Coupling a Helmholtz solver with a Distributed Flame Transfer Function (DFTF) to study combustion instability of a longitudinal combustor equipped with a full-scale burner

D. Laera*, S.M. Camporeale*

davide.laera@poliba.it

*Department of Mechanics Mathematics and Management, Politecnico di Bari,
Via Re David 200, 70125 Bari (Italy)

Abstract

Lean premixed combustion chambers used in modern gas turbines for power generation are often affected by thermo-acoustic combustion instabilities. Previous experiments as well as theoretical and numerical investigations indicate that the modes involved in this process may develop in the longitudinal direction and the azimuthal direction depending on the geometry of the combustor. The present article reports a numerical analysis of instability coupled by longitudinal modes. This corresponds to experiments carried out in the LRIA (Longitudinal Rig for Instability Analysis) test facility equipped with a single full-scale industrial burner for power generation. The dynamic response of the flame is described by means of a distributed n - $\tau(\mathbf{x})$ flame transfer function (FTF) model, where the space distribution of the time delays is derived directly from Reynold averaged Navier-Stokes (RANS) simulations. Coupling this model with an acoustic Helmholtz solver results in a linear stability problem from which frequency and growth rate (α) of the thermo-acoustic modes of the system are analyzed. The influence on the stability analysis of the length of the combustion chamber is investigated in a second step. The numerical results are compared with experiments showing a good correspondence in the stability ranges and wave shapes of the unstable modes.

Oxycombustion optimization: pilot plant for sulfuric acid production from offgas

C. Frau*, E. Loria*, F. Loria*, E. Maggio*

c.frau@sotacarbo.it

*** Sotacarbo S.p.A., c/o Grande Miniera di Serbaniu, 09013 Carbonia, Italy

Abstract

Growing concerns over greenhouse gas emissions have driven extensive research into new power generation cycles that enable carbon dioxide capture and sequestration. Among possible options to capture carbon dioxide, pressurised oxy-fuel combustion is a promising one. Accordingly, Sotacarbo teams with Itea and Enea to develop a pressurised oxy-combustion technology.

Currently, extensive tests have been carried out at 4 bar on a 5 MWt facility installed in Gioia del Colle (Southern Italy). Starting from the knowhow gained on that scale, Sotacarbo and ITEA planned to build an experimental 48 MWt demo-plant, based on the same pressurised combustion process introduced above. This will be the necessary intermediate step for the further scale-up towards a zero emission plant of industrial scale.

This paper reports the process design and mass balances on the pressurized coal combustor fed with Sulcis coal and focuses on technology issues related to the process integration and optimization, particularly the offgas line ensuring not only clean energy and “zero emission”, but also the recovery of an industrial product of wide consumption.

SOTACARBO EXPERIENCE ON GASIFICATION AND CO-GASIFICATION IN 5 MWth DEMONSTRATION PLANT

**Gabriele Calì², Paolo Deiana¹, Enrico Maggio², Claudia Bassano¹,
Simone Meloni²**
g.calì@sotacarbo.it

¹ENEA - Italian Agency for New Technologies, Energy and Sustainable Economic
Development

Via Anguillarese 301 - 00123 Rome, ITALY

²Sotacarbo S.p.A. - c/o Grande Miniera di Serbariu - 09013 Carbonia, ITALY

Abstract

In the field of coal and biomass gasification for distributed power generation, ENEA and Sotacarbo are developing several activities on demonstration plant scale in order to test gasification technologies for combined production of synthesis gas and electric power in medium and small-scale industrial plants. In particular, the plant platform includes a 5 MWth air blown fixed-bed up-draft gasifier equipped with a wet scrubber for syngas clean up. The co-gasification of local biomass and coal can reduce CO₂ emissions improving thermal efficiency of the process and simultaneously producing electricity in an economically and environmentally sustainable way, partly alleviating the energy dependence on foreign oil and gas sources.

This presentation reports some results of the experimental activities related to the start-up of coal and biomass gasification carried out on a demonstration plant at Sotacarbo Research Centre in the South-West of Sardinia (Italy). The aim is to assess the system behaviour and to evaluate the gasification performance. In particular, during the experimental tests different types of fuel has been tested: wood chips, Colombian coal, blends of Colombian coal and wood chips. The experimental activity was carried out in order to check the operability of all components and to improve the knowledge of gasifier operation in the different phase of start-up, run and shut down. A characterization of the process was performed and the modalities and key parameters to achieve standard operating conditions were identified. The ultimate aim is to provide useful data so as to improve the system efficiency and to make electricity generation suitable by an internal combustion engine fed by clean syngas.

BEHAVIOUR OF A COMPRESSION IGNITION ENGINE FED WITH BIODIESEL DERIVED FROM CYNARA CARDUNCULUS AND COFFEE GROUNDS

**A.P. Carlucci*, A. Ficarella*, L. Strafella*, A. Tricarico*,
S. De Domenico**, L. D'Amico**, A. Santino****

paolo.carlucci@unisalento.it

* University of Salento - Dept. of Innovation Engineering
via per Monteroni - 73100 Lecce, Italy

** Institute of Sciences of Food Production - C.N.R. Section of Lecce
via per Monteroni - 73100 Lecce, Italy

Abstract

Biodiesel is one of the most tested and efficient amongst alternative fuels on the market and a considerable number of scientific papers show that its performance is similar to that of petroleum diesel. Moreover, it can work with existing engines and injection systems with negligible impact on the operating performance.

Aim of this work is to assess the performance of biodiesel derived from *Cynara cardunculus* and coffee grounds as fuels, in blend with standard diesel fuel, for feeding a compression ignition engine. The combustion behavior and its effect on engine performance and exhaust emission levels have been quantified during an extensive experimental activity and compared with the results obtained feeding the engine with standard diesel fuel, alone or in blend with biodiesel derived from *Brassica carinata*. Results show that an overall conversion efficiency comparable or only slightly lower compared to that obtained with standard diesel fuel is observed using the biodiesel blends, mainly due to the lower heating value, lower for biodiesel than for standard diesel fuel. Moreover, total hydrocarbons (THC), carbon monoxide (CO) and particulate matter (PM) are all lowered with biodiesel, mainly due to the oxygen present in the biodiesel molecule. For the same reason, on the other hand, nitrogen oxides (NO_x) increase.

Thanks to these results, it can be concluded that biodiesels derived from *Cynara cardunculus* and coffee grounds are good candidates for feeding, alone or in blend with standard diesel fuel, compression ignition engines.

GASOLINE SPRAY CHARACTERIZATION AND DROPLETS-WALL INTERACTION AT DIFFERENT PISTON TEMPERATURES

F.Catapano*, G. Marseglia*, P. Sementa*, B.M. Vaglieco*

g.marseglia@im.cnr.it

*Istituto Motori CNR, Napoli Via Marconi 4-80125

Abstract

Spray/wall interaction has a significantly influence on the mixture formation process in gasoline direct injection (GDI) engines. Moreover, the fuel wall film and the resulting delayed evaporation of the liquid fuel are the main sources of soot formation in the internal combustion engines. In this paper, the spray evolution from a multi-hole GDI injector was investigated into an optical accessible vessel and environmental controlled through optical diagnostic developed under different injection strategies varying the duration and pressure of injection. In particular, a set of measurements were performed to characterize the spray evolution and the spray impact at different wall temperature. 2D high temporal and spatial resolution images of fuel spray were collected to obtain information about the penetration length, and wall impact hence about mixture formation process. Firstly, the spray evolution was analysed through the measurement of penetration length by visible high speed camera; secondly, the impact on the wall piston was analysed by means infrared thermography. The results obtained highlight the influence of injection pressures on the penetration length and the importance of piston temperature during the spray/wall impact.

THE DUAL-FUEL ETHANOL-DIESEL COMBUSTION: A STUDY ON SIZE, NUMBER, NANOSTRUCTURE AND CHEMICAL FEATURES OF THE EMITTED SOOT

V. Gargiulo*, M. Alfe'*, G. Di Blasio, C. Beatrice****

alfe@irc.cnr.it/gargiulo@irc.cnr.it

* Istituto di Ricerche sulla Combustione - C.N.R., Napoli - Italy

** Istituto Motori - C.N.R., Napoli - Italy

In the field of second generation biofuels, ethanol is receiving a growing attention as a valid alternative to conventional fuels in internal combustion engines thanks to its storage facility, availability and handling. The most common use of ethanol is for gasoline engine applications, but the interest in burning ethanol in diesel engine is increasing. Several methods and systems have been examined in order to evaluate the applicability of ethanol in compression ignition engines, including dual fuel (DF) injection. In DF configuration, the port fuel injection (fumigation) of ethanol is coupled with the direct injection of the conventional diesel fuel. Besides the well-known effects of DF ethanol-diesel system on regulated engine raw pollutant emissions (HCs, CO, NO_x and PM), ethanol fumigation is very effective also in the reduction of the number of the emitted particles.

This study aimed to characterize the impact of the dual-fuel ethanol-diesel combustion system on size, number, nanostructure, reactivity and chemical features of the emitted carbonaceous particles. The tests were conducted on a single cylinder research engine provided with a modern architecture and properly modified in a DF configuration. The selected test points, critical in terms of soot emissions, were performed using engine calibration parameters (injection, boost, swirl, etc.) and exhaust recirculation gases (EGR) values derived from the real Euro 5 compliant four-cylinder engine of equal unit displacement.

Overall, the chemico-physical characterization of soot particles clearly indicates that soot features, including the oxygen incorporation and morphology, slightly vary with the increasing amount of injected ethanol, even at high ethanol loading. The thermal stability of soot occurs in the range of 500-550 °C, as typically estimated for other diesel soot. UV-Visible investigation indicates that diesel soot appears as high-graphitized soot with a specific absorption (6-8 m²/g in the UV and 3-4 m²/g in the visible) comparable to those of furnace carbon black and soot from a benzene laminar flames.

EXPERIMENTAL ANALYSIS OF THE ETHANOL/GASOLINE BLENDS AND DUAL-FUEL PARTICULATE EMISSIONS IN A SMALL DISPLACEMENT SI ENGINE.

S. Di Iorio*, L. Luise*, P. Sementa*, B.M. Vaglieco***

s.diorio@im.cnr.it

*Istituto Motori- CNR Naples, Italy

**University of study of Naples Parthenope, Naples, Italy

Abstract

Over the recent years, great attention has been focused on ethanol as alternative fuel for both port fuel injection (PFI) and Direct Injection (DI) spark ignition (SI) engines. The higher octane number allows to operate with high compression ratio improving the engine efficiency, and the larger oxygen content contribute to reduce PM emissions. Ethanol can be both blended and dual fueled with gasoline. In this latter case, ethanol and gasoline are separately injected.

The aim of this study is to analyze the different methods of ethanol fueling in order to understand the configuration that better exploit the ethanol effect on the reduction of soot formation. To address this issue, the particle emissions from both the ethanol/gasoline blend, E30, and the ethanol/gasoline dual fuel, EDF, were evaluated. In this latter case, ethanol was direct injected and gasoline was injected in the intake duct. For both the operating configurations, the same percentage of ethanol was supplied: 30 %v/v ethanol.

The experimental activity was performed in a small displacement single cylinder engine and the tests were carried out at 3000, 4000 and 5000 rpm under full load condition. The particle emissions were measured downstream of a three way catalyst (TWC) by a smoke meter. Particle sizing and counting was performed in the size range from 5.6 nm to 560 nm by an Engine Exhaust Particle Sizer (EEPS). For E30 the particle emissions are larger than for EDF because of the different contribution of gasoline. In EDF the better evaporation and mixing of gasoline, typical of PFI configuration, coupled with the soot reduction tendency of ethanol lead to low particle emissions.

Comparison of detailed reaction mechanisms for an alternative Jet Fuel surrogate by Parametric Continuation

L. Acampora*, F.S. Marra**

marra@irc.cnr.it

* Dipartimento di Ingegneria - Università degli Studi del Sannio, Benevento, Italy

** Istituto di Ricerche sulla Combustione - CNR, Napoli, Italy

Abstract

A comparison of selected detailed reaction mechanisms was performed in order to point out capabilities, limitations and mutual differences in modelling the combustion with air of an alternative Jet Fuel surrogate (Shell GTL) in a Perfectly Stirred Reactor.

Three different reaction mechanisms, having increasing number of species and reactions, have been adopted. Specifically, the mechanisms proposed by: the CRECK Group mechanism (Frassoldati et al. 2010, Ranzi et al. 2012); Naik et al. (2011); and by Malewicki et al. (2013).

The comparison was performed by studying the equilibrium curve. A specifically developed parametric continuation tool was used in order to manage the large chemical mechanisms adopted to model the surrogate combustion.

The results allow the identification of the differences among the three mechanisms. Generally, the proposed analysis approach can represent an useful tool for the study and validation of detailed reaction mechanisms.

SOURCES AND CHEMICAL COMPOSITION OF PM1 AND PM10 SAMPLES OVER SOUTH EASTERN ITALY

A. Genga*, M.R. Perrone**, Maria Siciliano*, Tiziana Siciliano***, Fabio
Paladini**, Pasquale Burlizzi**

alessandra.genga@unisalento.it

*Dipartimento di Scienze e Tecnologie Biologiche e Ambientali, Università del Salento,
Lecce, 73100, Italy

**Dipartimento di Matematica e Fisica, Università del Salento, Lecce, 73100, Italy

***Dipartimento di Beni Culturali, Università del Salento, Università del Salento, Lecce,
73100, Italy

Abstract

The aerosol size distributions and the contents of chemical species in the different size-ranges play an important role in determining visibility, air quality and human health effects. The aim of this work is to chemical characterize PM1 and PM10 samples and perform a Source Apportionment (SA) study to evaluate the source contributions to each fraction. Aerosol samples were collected in an urban background site (Lecce, SE of Italy), using a ($2.3 \text{ m}^3 \text{ h}^{-1}$) HYDRA-FAI dual Sampler to simultaneously collect 24-h PM10 and PM1 samples on 47-mm-diameter quartz fiber filters, pre-heated for 4 h at 700 °C. The monitoring campaign lasted from December 2011 to November 2012 and a total of 156 PM1 and PM10 samples, respectively were collected. Each analyzed filter was divided in 4 sections, which were used for the analysis of main ions, metals and organic and elemental carbon, respectively.

Saharan dust episodes have been identified and chemical characterized. Chemical composition of collected aerosol was used for source apportionment using EPA PMF5.0 software. Five sources have been individuated: marine, crustal, secondary inorganic aerosol, combustion and traffic emission.

Impact of agriculture biomass burning and preliminary results, on coastal site Lamezia Terme, integrating data of different instruments.

**T. Lo Feudo*, D. Gulli*, R. Calaudi*, E. Avolio*
M. De Pino* and C. R. Calidonna*.**

t.lofeudo@isac.cnr.it

*(ISAC)-CNR, UOS of Lamezia Terme, Italy

Abstract

In order to establish strategies for the influence of anthropic activities, continuously monitoring of particulate and greenhouse gases are required. Atmospheric aerosol particles together with greenhouse gases, according to the IPCC(2013), are playing a major role in climate change affecting the Earth's radiative balance: directly by absorbing and scattering of solar radiation and indirectly by supporting for cloud condensation. In the GAW Regional Coastal Observatory I-AMICA in Lamezia Terme (38.88 LAT 16.24 LON, 6m agl) in Calabrian Region, greenhouse gas and particulate are daily monitored in order to collect and investigate natural and anthropic sources affecting climate. The equipment allow us to detect local events of different nature that influence short lived gases and aerosol presence in our area. In particular here we present some evidence of forest fire smoke detection due to biomass burning caused from agriculture activities. Hourly and daily variation of several parameters are showed, correlation with local circulation is analysed. A further analysis on the correlations with back-trajectories technique based on Hysplit model outputs are also showed.

SYSTEM SIMULATION OF HIGH SPECTRAL RESOLUTION LIDAR FOR AEROSOL MONITORING

X. Wang¹, C. Song², A. Boselli³, M. Iarlori⁴, V. Rizi⁴, N. Spinelli²
changbo.song@unina.it

CNISM-BRIT China-Italy Joint Research Center for Laser Remote Sensing
and

1CNR-SPIN, Napoli, Italy

2 Dipartimento di Fisica, Università degli Studi di Napoli "Federico II", Napoli, Italy

3CNR-IMAA, Potenza, Italy

4 CETEMPS, Dipartimento di Scienze Fisiche e Chimiche, Università degli Studi dell'Aquila, L'Aquila, Italy

Abstract:

Atmospheric aerosols play very important roles in climate change and air particulate pollution. Due to their highly variable optical and physical properties as well as to short atmospheric lifetimes and large spatial and temporal gradients, the aerosol impact on climate models and air pollution is really a complex task. Lidars based on elastic scattering have been largely used to measure aerosol spatial distribution and to derive their properties, but elastic backscatter Lidar data require the assumption of the aerosol extinction-to-backscatter ratio to retrieve aerosol optical properties profiles. To overcome this disadvantage, two main methods, High Spectral Resolution Lidar (HSRL) and Raman lidar, can be used to measure aerosol optical properties without a-priori hypotheses. Compared to Raman lidar, HSRL has the advantage of day and night measurements and can be adapted to many kinds of carrying platforms.

HSRL can provide the vertical profile of aerosol extinction by separating the Mie signal by atmospheric aerosol and the Rayleigh signal by atmospheric molecules. Due to small spectral difference between Mie and Rayleigh signals, there are three difficulties: firstly, the laser source must have a narrow bandwidth, high energy and stable center wavelength; secondly, the receiver should have a very narrow spectral filter to separate aerosol scattering and molecular scattering; thirdly, the center wavelength of the receiver must be real-time locked to laser source.

In order to study the influence of system parameters and to optimize their values, a system simulation of high spectral resolution lidar for aerosol monitoring has been done and will be presented in this paper.

ATMOSPHERIC IMPACT OF SHIPS EMISSIONS IN TWO ADRIATIC HARBOURS: BRINDISI AND VENICE

A. Donateo*, E. Gregoris, E. Merico*, E. Barbaro**, A. Gambaro**,
D. Contini***

a.donateo@isac.cnr.it

* Istituto di Scienze dell'Atmosfera e del Clima, ISAC-CNR, 73100, Lecce, Italy

** Istituto per la Dinamica dei Processi Ambientali, IDPA-CNR, 2137, Venezia, Italy

Abstract

Emissions of atmospheric pollutants from shipping and harbour activities are a growing concern at International level and, specifically, in the Mediterranean area. The continuous increase of global trade and of harbour services made maritime transport a key contributor to atmospheric pollution. The objective of this work is to give a comparable assessment of the impact of ship traffic and harbour activities to atmospheric $PM_{2.5}$ and particle number concentrations (PNC) in two important port-cities of the Adriatic Sea: Venice and Brindisi. In Venice area, measurements were taken in 2007, 2009 and 2012 during summer, when the tourist ship traffic is at maximum. In Brindisi, measurements were performed in summer 2012 and in summer 2014. The two harbours have significant differences in the typology of ship traffic as well as in the volume of traffic and in the layout and logistic organization that could influence the impact of pollutant emissions on nearby urban areas. High temporal resolution measurements, both for particle number and mass concentrations, were used for identification of single ship plumes and for quantitative statistical evaluation of primary contribution of ship emissions to atmospheric aerosol concentrations. Results show that, in 2012, the contribution of ships emissions to $PM_{2.5}$ was 7.4 (± 0.5) for Brindisi harbour and 3.5 (± 1) for Venice harbour. The contribution to particle number concentration was 26 (± 1) and 6 (± 1), respectively, for Brindisi and Venice harbour. Results show that the ship traffic contribution increases when particle size decreases and it is significantly larger on particle number concentration with respect to $PM_{2.5}$. The inter-annual trends of the impact of shipping to atmospheric particles concentrations were investigated in the two areas showing a decrease in Venice correlated with the use of low-sulphur content fuel.

Characterization of ambient carbonaceous aerosol at high time resolution in the Po valley.

S. Gilardoni*, M. Paglione*, M. Rinaldi*, S. De Iuliis, F. Migliorini**, M. Aurela***, M.C. Facchini***

s.gilardoni@isac.cnr.it

*ISAC-CNR via Gobetti 101, Bologna, Italy

**IENI-CNR, via Cozzi 53, Milano, Italy

*** Finnish Meteorological Institute, Helsinki, Finland

Abstract

More than 20 million people living in the Po Valley are exposed to Particulate Matter (PM) levels well above the limits set by the World Health Organization and by the European Air Quality Directive, especially during the colder season. Carbonaceous aerosol (organic aerosol OA, and black carbon BC) accounts for the largest fraction of fine PM both at urban and rural locations. Effective policy measures aiming at reducing PM exposure require a better understanding OA and BC sources.

In the framework of the PoAir experiment, in February 2014, the chemical and microphysical properties of OA were characterized at minute-time resolution at four sites in the Po valley (Milano, Padova, Bologna, and San Pietro Capofiume), using aerosol mass spectrometric measurements. Organic aerosol sources were characterized by positive matrix factorization analysis of organic aerosol fragmentation spectra. We identified three primary OA sources, i.e. hydrocarbon like OA (10-20% of OA), biomass burning OA (14-36% of OA), cooking OA (5% of OA), and up to two different types of oxidized OA (OOA1 and OOA2), proxy of secondary/processed organics. OOA accounted for the largest fraction of OA (52-63%), highlighting the need to regulate OA precursors and to better understand OA atmospheric processing.

During the same experiment, we attempt to identify black carbon sources in Milano urban background area integrating OA source apportionment data with BC measurement by laser induced-incandescence (LII) technique.

CHARACTERIZATION OF FLAME-GENERATED CARBONACEOUS NANOPARTICLES BY OC/EC ANALYSIS, RAMAN AND UV-VIS SPECTROSCOPY

M. Commодо*, L.A. Sgro*, M. Chiari, G. De Falco***,
A. D'Anna***, P. Minutolo*
minutolo@irc.cnr.it**

*Istituto di Ricerche sulla Combustione, P.le V. Tecchio 80, 80125, Napoli – Italy

**I.N.F.N. - Sezione di Firenze - via Sansone 1, 50019 Sesto Fiorentino (Firenze) - ITALY

***DICMAPI - Università di Napoli Federico II, P.le Tecchio 80, 80125, Napoli, Italy

Abstract

Flames and combustion devices operated in rich hydrocarbon conditions produce a large variety of carbonaceous compounds from low and high molecular weight gas-phase polycyclic aromatic hydrocarbons (PAHs) to solid particles.

In addition to soot, which is often referred to as Black Carbon (BC) or Elemental Carbon (EC), recent works have demonstrated that nanoparticles with a more organic structure are formed in flames and combustion conditions near the onset of particle formation and are emitted into the atmosphere as primary emissions and are possible constituent of primary atmospheric organic carbon (OC). The mean size of these particles is about 2 nm, as was determined in previous works by in situ extinction and scattering measurements, on-line Differential Mobility Analysis measurements of the size distribution, and Atomic Force Microscopy (AFM) measurements on particles deposited on substrates.

In this work, we investigate carbon aerosols produced in various flame conditions, across the soot formation threshold, by thermo-optical- transmission (TOT), UV-vis and Raman spectroscopy in order to characterize their structural composition in correlation with their OC and EC content. The goal is to determine if and how combined TOT and optical/spectroscopic measurements allow distinguishing nanoparticles formed under “clean-like” combustion conditions from those produced in sooting flames with the perspective to improve and consolidate source apportionment.

The sample collected from the non-sooting flame is mostly OC with the lowest propensity to char during the heating procedure, transforming in pyrolytic carbon (PC), and contains a low percentage of EC.

Raman features are sensitive to the content of OC and PC in the particles as well as to the EC one.

Characterization of primary particulate vehicular emissions in an urban tunnel in Naples, Italy

A. Riccio*, E. Chianese*, D. Monaco*, M.V. Prati, M.A. Costagliola**, G. Perretta**, B. Gioli****, V. Magliulo***, P. Toscano****, A. Zaldei******

angelo.riccio@uniparthenope.it

*Università di Napoli "Parthenope", Centro Direzionale, Isola C4, Napoli

** Istituto Motori (IM-CNR) Via Marconi 4, Napoli

*** Istituto per i Sistemi Agricoli e Forestali del Mediterraneo (ISAFoM-CNR) Via Patacca 85, Ercolano (Napoli)

**** Istituto di Biometeorologia (IBIMET-CNR) Via Caproni 8, Firenze

Abstract

On-road particulate matter (PM) mass and size distribution were collected during a sampling campaign in March of 2015 in the '4 giornate' tunnel in Naples, Italy. This tunnel is part of the heavy-trafficked urban road network, connecting the city center to suburbs. Two sets of samples were collected at both sides of the tunnel, each set representing the daily cycle at a 1 hour time resolution. Distance-based – mass per kilometer – and fuel-based – mass per burned fuel – emission factors (EFs) were calculated using mass concentrations, traffic flow rates and wind speed as a function of fleet composition. Also, chemical analysis was performed for polycyclic aromatic hydrocarbons (PAHs), metals and trace elements.

Average particle mass concentrations in the tunnel atmosphere were more than 5 times higher than in the outside urban background air, revealing its origins almost exclusively from fresh vehicle emissions.

While EFs for most of gas species were within the range of expected values, the present study found much higher EFs for particulate matter and trace elements. This suggests that the sampling methods employed in this campaign are more efficient at capturing particles from sources such as resuspended road dust and wear from tires and brakes, which are usually not included in traditional sampling methodologies for assessing vehicular emissions (e.g. dynamometer studies).



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