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BOOK OF ABSTRACTS

SESSION I: FLAMES AND REACTION KINETICS

- FLAME STRUCTURE OF SUPERCRITICAL CH₄/O₂/CO₂ NON-PREMIXED
TURBULENT OXY-COMBUSTION BY MEANS OF 3D-DNS 11
D. Cecere, E. Giacomazzi, N.M. Arcidiacono, A. Di Nardo
- GENERALIZED ENTROPY PRODUCTION ALGORITHM FOR ON-THE-FLY
REDUCTION OF DETAILED MECHANISMS IN CFD CODES 12
L. Acampora, F.S. Marra
- LARGE EDDY SIMULATION OF A GASEOUS H₂ / LIQUID O₂ NON-
PREMIXED FLAME 13
E. Giacomazzi, D. Cecere, N.M. Arcidiacono
- LARGE EDDY SIMULATION OF MULTI-REGIME DARMSTADT
BURNER WITH FINITE RATE CHEMISTRY AND EDDY
DISSIPATION CONCEPT CLOSURE 14
L. Angelilli, P.P. Ciottoli, F.H. Perez, R.M. Galassi, M. Valorani, H.G. Im
- LES SIMULATION OF 100% H₂ COMBUSTION IN A SWIRLED
STABILIZED BURNER 15
T. Capurso, D. Laera, E. Riber, B. Cuenot
- CHARACTERIZATION OF THE EFFECTS OF A NEEDLE-RING
PLASMA ACTUATOR ON METHANE-AIR SWIRLED FLAME
STRUCTURE 16
S. Bonuso, G. Mehdi, M.G. De Giorgi
- EFFECT OF HYDROGEN ADDITION ON PREMIXED FLAMES
ISSUING FROM A MULTIHOLE BURNER IN DOMESTIC BOILERS 17
R. Lamioni, C. Bronzoni, M. Folli, L. Tognotti, C. Galletti
- ROLE OF INTRINSIC FLAME INSTABILITY IN TURBULENT
PREMIXED COMBUSTION MODELING 18
F. Creta, P.E. Lapenna
- CHAOTIC AND WAVELET DETECTION OF THERMOACOUSTIC
INSTABILITY 19
T. Pagliaroli, R. Hernandez, G. Troiani, E. Giacomazzi, R. Camussi

| | |
|--|-----|
| H ₂ EFFECTS ON AMMONIA OXIDATION AND DYNAMIC BEHAVIOR <i>M.V. Manna, P. Sabia, T. Viola, R. Ragucci, M. de Joannon</i> | I10 |
| RETARDANT EFFECT OF AMMONIA ON HYDROGEN REACTIVITY <i>M.V. Manna, R. Ragucci, M. de Joannon, P. Sabia</i> | I11 |
| AN EXPERIMENTAL, THEORETICAL AND KINETIC-MODELING STUDY OF H ₂ S OXIDATION IN IDEAL REACTORS <i>A. Stagni, L. Pratali Maffei, S. Arunthanayothin, O. Herbinet, F. Battin-Leclerc, T. Faravelli</i> | I12 |

| |
|---|
| SESSION II: ENGINES AND GAS TURBINES INCLUDING FIRE AND SAFETY |
|---|

| | |
|---|-----|
| COMBUSTION DEVELOPMENT ANALYSIS IN LEAN HEAVY-DUTY CNG ENGINES WITH ACTIVE PRE-CHAMBER <i>G. Onofrio, P. Napolitano, C. Guido, C. Beatrice</i> | I11 |
| FLAME PROPAGATION OF FLAMMABLE DUSTS: A MALLARD-LE CHATELIER INSPIRED MODEL <i>M. Portarapillo, G. Luciani, R. Sanchirico, A. Di Benedetto</i> | I12 |
| MULTI-PHYSICS MODELING OF LIQUID ROCKET ENGINE COMBUSTION CHAMBERS <i>A. Remiddi, G. Indelicato, P.E. Lapenna, F. Creta</i> | I13 |
| FROM TURBULENT COMBUSTION TO LIQUID ROCKET ENGINES: AN OVERVIEW OF APPLICATIONS <i>G. Indelicato, A. Remiddi, P. E. Lapenna, F. Creta</i> | I14 |
| CH ₄ CONVERSION AND NH ₃ FORMATION MODEL ASSESSMENT OVER A PD-RH THREE-WAY CATALYST FOR AUTOMOTIVE APPLICATION <i>D. Di Maio, C. Beatrice, C. Guido, V. Fraioli, P. Napolitano</i> | I15 |
| NUMERICAL MODELING OF CHEMICAL VAPOR INFILTRATION FOR PRODUCTION OF CARBON DISK BRAKES <i>A. Cuoci, A. Frassoldati, R. Passoni, M. Rosa</i> | I16 |
| AN UNCONVENTIONAL INTERNAL COMBUSTION ENGINE AS A RANGE EXTENDER FOR LOW CARBON MOBILITY <i>G. Vorraro, J. W.G. Turner</i> | I17 |
| COMBUSTION OF CRYOGENIC GASES <i>G. Pio, E. Salzano</i> | I18 |
| INVESTIGATION OF ULTRA-HIGH INJECTION PRESSURE ON A GDI SPRAY AT ENGINE-LIKE CONDITIONS <i>A. Montanaro, L. Allocca</i> | I19 |

SESSION III: SOLID FUEL COMBUSTION, PYROLYSIS AND GASIFICATION

| | |
|---|-------|
| CONTAMINATED BIOMASSES TO BIOFUEL <i>D. Amato, R. Ragucci, P. Giudicianni</i> | III1 |
| TOWARD A THOROUGH VALORIZATION OF HAZELNUT PRODUCTION RESIDUES: FOCUS ON FLUIDIZED BED TORREFACTION <i>M. Miccio, M. Fraganza, P. Brachi, M. Casa, G. Ferrari, P. Iuorio, M. Volpe</i> | III2 |
| HYDRODYNAMICS OF A COLD FLOW MODEL FLUIDIZED BED FOR FAST PYROLYSIS OF BIOMASS <i>S. Padula, M. Troiano, R. D'Onofrio, A. Cammarota, R. Solimene, P. Salatino</i> | III3 |
| EXPERIMENTAL AND THEORETICAL STUDY OF CELLULOSE PYROLYSIS <i>F. Serse, A. Locaspi, A. D. Ure, E. Krock, M. Pelucchi, S. Dooley, A. Cuoci, T. Faravelli, A. Frassoldati</i> | III4 |
| THERMAL DEGRADATION OF NYLON-6 AND REAL MIXTURES OF SOLID PLASTIC WASTE. AN EXPERIMENTAL AND KINETIC MODELLING STUDY <i>A. Locaspi, M. Pelucchi, R. Batista da Silva Junior, M. Mehl, A. Cuoci, A. Frassoldati, A. Beretta, L. Lietti, T. Faravelli</i> | III5 |
| GASIFICATION OF TANNERY SLUDGES IN FLUIDIZED BED: FATE OF Cr(III) <i>R. Migliaccio, M. Urciuolo, G. Ruoppolo, M. Balsamo, F. Di Lauro, F. Montagnaro, E. Imperiale, D. Caracciolo</i> | III6 |
| A STATISTICAL APPROACH FOR PYROLYSIS PROCESS DESCRIPTION AND OPTIMIZATION <i>D. Damiano, V. Del Duca, R. Chirone, A. Coppola, F. Scala, P. Salatino</i> | III7 |
| INVESTIGATE THE POTENTIAL SYNERGISTIC INTERACTIONS FOR CO-PYROLYSIS OF OLIVE STONE AND POLYOLEFINIC PLASTIC TO INCREASE THE QUALITY OF PYROLYSIS OILS <i>E.T. Ganda, R. Migliaccio, A. Coppola, G. Ruoppolo, M. Urciuolo, P. Brachi, F. Scala, P. Salatino</i> | III8 |
| SYNGAS FERMENTATION: ASSESSMENT OF KINETICS AND REACTOR SET-UP <i>F. Lanzillo, F. Raganati, M.E. Russo</i> | III9 |
| THE HEMICELLULOSE STRUCTURAL COMPLEXITY AND ITS ROLE IN PYROLYSIS PRODUCTS DISTRIBUTION AND SPECIATION <i>V. Gargiulo, A. I. Ferreira, P. Giudicianni, S. Tomaselli, R. Ragucci, M. Alfè</i> | III10 |
| BIOCHAR FROM LEAD CONTAMINATED BIOMASSES AS COKE | III11 |

SUBSTITUTE IN METALLURGY

C.M. Grottola, P. Giudicianni, N. Fiorentino, M. Fagnano, R. Ragucci

DECARBONISATION OF STEEL HEATING PROCESSES: MILD
COMBUSTION OF HYDROGEN/NATURAL GAS MIXTURES

III12

A. Della Rocca, D. Astesiano, E. Malfa

SESSION IV: FORMATION AND CONTROL OF POLLUTANTS

NO_x EMISSIONS AND COMBUSTION STABILITY OF AMMONIA/METHANE
MILD COMBUSTION

IV1

G.B. Ariemma, G. Sorrentino, R. Ragucci, M. de Joannon, P. Sabia

WET OXIDATIVE SCRUBBING (WOS) FOR FLUE-GAS CLEANING
ENHANCED BY OXIDATIVE MECHANISMS UNDER ACIDIC CONDITION

IV2

D. Flagiello, F. Di Natale, A. Erto, A. Lancia

BIOGAS UPGRADING BY ADSORPTION ONTO ACTIVATED CARBON AND
CARBON MOLECULAR SIEVES: EXPERIMENTAL AND MODELING
STUDY IN BINARY CO₂/CH₄ MIXTURE

IV3

F. Rainone, O. D'Agostino, A. Erto, M. Balsamo, A. Lancia

THERMOGRAVIMETRIC AND CHEMICO-PHYSICAL ANALYSES
OF SOOT OXIDATION

IV4

V. La Matta, B. Apicella, S. Cimino, F. Stanzione, A. Tregrossi, C. Russo

SOOT FORMATION IN OME_n DOPED PREMIXED FLAMES

IV5

F. Ferraro, R. Schmitz, C. Hasse, M. Sirignano

PRELIMINARY RESULTS ON THE EFFECT OF LASER HEATING
ON CARBON NANOPARTICLES SAMPLED FROM A PREMIXED
FLAME

IV6

*F. Migliorini, S. Belmuso, S. Bocchicchio, R. Dondè, M. Commodo, P.
Minutolo, A. D'Anna, S. De Iuliis*

THERMO-OPTICAL-TRANSMISSION OC/EC AND RAMAN
SPECTROSCOPY ANALYSES OF FLAME-GENERATED
CARBONACEOUS NANOPARTICLES

IV7

S. Bocchicchio, M. Commodo, A. D'Anna, P. Minutolo

3D PRINTED COMPOSITE ZEOLITE CATALYSTS FOR THE SCR OF
NO_x

IV8

E. M. Cepollaro, S. Cimino, L. Lisi, R. Botti, G. Franchin, P. Colombo

APPLICATION OF ATOMIC FORCE MICROSCOPY
NANOINDENTATION FOR THE MECHANICAL
CHARACTERIZATION OF SOOT NANOPARTICLES

IV9

G. De Falco, F. Carbone, M. Commodo, P. Minutolo, A. D'Anna

THE EFFECT OF KEROSENE ADDITION ON PARTICLE
FORMATION IN ETHYLENE PREMIXED FLAMES

IV10

G. De Falco, M. Sirignano, A. D'Anna

THE EFFECT OF POLLUTANTS ON WATER DROPLETS EVAPORATION IV11

F. Mattia, M. Commodo, A. D'Anna

PECULIARITIES OF PYROMETRY IN PARTICULATE-GENERATING FLAMES IV12

S. De Iuliis, R. Dondè, I. Altman

SESSION V: NOVEL CONCEPTS AND TECHNOLOGIES

OVERVIEW FOR RETROFITTING COAL POWER PLANTS BY IRON V1

P. Debiagi, R.C. da Rocha, C. Hasse

PERFORMANCE OF MODELING PARADIGMS FOR THE SIMULATION OF A CYCLONIC BURNER V2

G. Sorrentino, G.B. Ariemma, C. Genovese, L. Giuntini, C. Galletti, R. Ragucci

USING DATA SCIENCE FOR COMBUSTION PROCESSES MODELING, MONITORING AND CONTROL V3

T. Viola, P. Sabia, G. Sorrentino, M de Joannon, R. Ragucci

UNCERTAINTY QUANTIFICATION IN RANS OF LOX-CH₄ PINTLE INJECTOR V4

J. Liberatori, R. Malpica Galassi, D. Liuzzi, M. Valorani, P.P. Ciottoli

NUMERICAL MODEL OF THERMALLY-INDUCED SECONDARY ATOMIZATION V5

P. Guida, W.L. Roberts

CYCLIC CO₂ CAPTURE AND METHANATION OVER ALKALI PROMOTED RU CATALYSTS V6

S. Cimino, C. Allouis, L. Lisi

REACTIVE VOLUME OF FLUID MODEL FOR THE SIMULATION OF THE EVAPORATION AND COMBUSTION OF FPBO SURROGATE COMPONENTS V7

E. Cipriano, A. E. Saufi, A. Cuoci, A. Frassoldati, T. Faravelli, R. Calabria, P. Massoli

DEVELOPMENT OF A SMALL-SCALE BIOFUEL PROCESSOR: MODELLING OF AUTOHERMAL ETHANOL REFORMING V8

V. Troisi, A. Stagni, A. Frassoldati, G. Groppi, A. Beretta

PERFORMANCE OF DIFFERENT SORBENTS FOR CARBON CAPTURE AND THERMOCHEMICAL ENERGY STORAGE SYSTEMS V9

F. Di Lauro, C. Tregambi, F. Montagnaro, R. Chirone, R. Solimene, P. Salatino

SIMULATION OF FLUIDIZED BED SORPTION-ENHANCED V10

METHANATION

A. Coppola, G. Ferraro, F. Massa, F. Scala

ENHANCEMENT OF CARBON NANOPARTICLES FILMS FLAME
SYNTHESIS WITH ELECTRIC FIELD

V11

*A. Parisi, G. De Falco, D. Salvoni, M. Sirignano, C. Carotenuto, F. Di
Natale*

A SUSTAINABLE ROUTE FOR HYDROGEN PRODUCTION:
SOLAR-DRIVEN SYSTEM BASED ON A NANOCOMPOSITE
PHOTOCATALYST

V12

M. Muscetta, R. Andreozzi, R. Marotta, I. Di Somma

SESSION I

FLAMES AND REACTION KINETICS

Flame Structure of Supercritical CH₄/O₂/CO₂ non-Premixed Turbulent Oxy-Combustion by means of 3D-DNS

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Abstract

Turbulent non-premixed methane oxy-combustion in an atmosphere rich in CO₂ at supercritical conditions (300 bar) is investigated by means of 3D Direct Numerical Simulation. A simple shear-layer configuration typical of slot burners is considered: the fuel flows through the central slot, the oxidant O₂/CO₂ (90% O₂ by mass) mixture flows on both sides of the slot. Compressible N-S equations coupled to the Peng-Robinson cubic equation of state (PR-EoS) in its translated volume formulation (VTPR) are solved with a reduced 23-species kinetic scheme derived by ARAMCO 2.0 full mechanism. Diffusive mechanisms and transport properties are accurately modelled, including Soret effect, pressure gradient diffusion, Takahashi high-pressure correction for mass diffusivity. Fugacities are used instead of partial pressures for better accuracy in chemical-equilibrium calculation.

A robust numerical scheme (AUSM⁺-up coupled with a second-order accurate interpolation with a TVD, linear preserving limiter for non-uniform grids) is adopted for the convective terms to reduce spurious oscillations.

Local dilution due to the sCO₂ coflow seems to decrease the local CO production; the very high pressure results in turbulent scales smaller than at lower pressure with an inner cut-off larger than the Kolmogorov scale, likely related to the Prandtl number larger than one; the flow exhibits uphill (counter-gradient) diffusion, with the main contribution due to the Hirshfelder and Curtiss' mass flux. Flame index distributions reveal a nonnegligible amount of premixed combustion regions, their contribution is negligible in terms of heat release. Furthermore, temperature iso-surfaces fractal dimension is calculated.

Generalized Entropy Production Algorithm for on-the-fly reduction of detailed mechanisms in CFD codes

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Abstract

To widen the adoption of renewable fuels, new combustor designs, often working in new combustion regimes, are required. The Computational Fluid Dynamics (CFD) approach is a well-established methodology to help in the design of combustion systems, but to deal with the detailed mechanisms required for accurate predictions of the new fuels is very challenging, because of the huge computational effort required. Current CFD codes adopt several algorithms to reduce significantly this effort. The chain of steps adopted in the reactingFoam application distributed with the open-source code OpenFOAM is an excellent example [1]: first, the ISAT method is applied to avoid re-computation of the kinetic evolution starting from states of the reactive mixture close to already computed states. To further reduce the required effort, without losing the generality of a detailed mechanism, an on-the-fly reduction of the kinetic mechanism is performed when a new starting state is detected that cannot be evolved from previous states. The advantage expected is that, having the new reduced mechanism be valid only for a single state, it can be much smaller than an a-priori reduced mechanism to be applied for every state, with computational benefits also on the stiffness of the resulting ODE to solve.

The authors proposed a new algorithm for the full automatic generation of reduced chemical mechanisms [2]. It showed the advantages of an efficient detection of the main reactions, leading to small skeletal mechanisms and without any need of knowledge of the starting species. Therefore, this algorithm appears a good candidate for an on-the-fly reduction procedure in a CFD code. The results of such an implementation in the OpenFOAM code, alongside the discussion of the performance obtained in comparison with the methods already available in the public distribution of the code, will be the object of the presentation.

- [1] Li, Z., M. T. Lewandowski, F. Contino, A. Parente. 2018. *Energy & Fuels* 32 (10): 10121–31.
- [2] Acampora, L., M. Kooshkbaghi, C. E. Frouzakis, F. S. Marra. 2019. *Combustion Theory and Modelling* 23 (2): 197–209.

Large Eddy Simulation of a Gaseous H₂/Liquid O₂ Non-Premixed Flame

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Abstract

Aerospace applications, and in particular liquid oxygen rocket engines and cooling systems, largely promoted research on real gas flows. In the last decade, high-pressure combustion of reactants exhibiting real gas behaviour has been focusing more attention not only for the renewed interest in space exploration, but also for its application in electric power generation, as in advanced supercritical CO₂ gas turbine cycles, organic Rankine cycles, and diesel engines.

This work is devoted to the analysis of the flame anchoring mechanism in the test case MASCOTTE C-60 on supercritical hydrogen/oxygen combustion at 60 bar, with transcritical (liquid) injection of oxygen. The divergent tapered injector is included in the simulation to investigate its effects.

The simulation is performed by means of the in-house parallel code HeaRT in the three-dimensional LES framework. The cubic Peng-Robinson equation of state in its improved translated volume formulation is assumed. Diffusive mechanisms and transport properties are accurately modelled, including Soret effect, pressure gradient diffusion, Takahashi high-pressure correction for mass diffusivity. A finite-rate detailed scheme involving the main radicals, already validated for high-pressure H₂/O₂ combustion, is adopted. Vreman's subgrid scale model and the Localised Turbulent Scale Model (LTSM) are used as turbulence and turbulent combustion closures. A robust numerical scheme (AUSM⁺-up coupled with a second-order accurate interpolation with a TVD, linear preserving limiter for non-uniform grids) is adopted for the convective terms to reduce spurious oscillations; numerical dissipation is locally increased (by forcing such a limiter to be first-order accurate when the compressibility factor is less than 0.8) in most of the liquid jet to avoid large spurious pressure oscillations due to the compressible solver.

Continuous ignition is provided by a stable hot spot at the tip of the O₂ injector. Since at supercritical conditions no atomization occurs, the flame evolves in a very thin mixing layer (with small shed eddies) between the gaseous hydrogen and liquid oxygen jets. Although the high turbulence level, the flame thickness remains limited and the flame front confined close to the LO₂ jet. At the present grid resolution, the O₂ jet does not exhibit any ligaments (shown in non-reacting conditions) but only some small wrinkles, sometimes tending to isolated ligament structures. At the external boundary of the faster H₂ jet, another shear-layer evolves, characterized by larger shed structures.

Large eddy simulation of multi-regime Darmstadt burner with finite rate chemistry and eddy dissipation concept closure

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Abstract

Although combustion processes are mainly classified as premixed and non-premixed in terms of mixing, in a number of practical configurations both regimes are present and coexist, leading to partially premixed and multi-regime combustion modes.

Recently, a novel multi-regime burner (MRB) was developed by Butz [1] which is composed of a cone jet and two different pilots. Differently from the previous burners, the temperature of the wall between the two pilots is kept constant to avoid re-condensation close to the nozzle exits. This allows the in-homogenous conditions to develop because of enhanced turbulence generated by mixing layer interaction outside of the pilots. This configuration is suitable not only for the experimental investigation of multi-regime combustion under well controlled conditions, but also for the validation of combustion models. In a first attempt to model a multi-regime flame of the MRB configuration, the Darmstadt group employed the artificial thickened flame (ATF) to close the chemical source term, obtaining an overall satisfactory agreement with the experimental results.

The aim of this work is to present the numerical results obtained by means of the application of the operator splitting to solve the chemistry with the finite rate model. This approach is particularly suitable to preserve a certain degree of accuracy when the transition from non-premixed to premixed flame occurs. However, due to high dimensionality of the chemical kinetics mechanics for methane, the reduction of the traditional GRI-3.0 is performed with an algorithm based on the CSP-TSR analysis. The numerical results are compared to experimental one in terms of the averages and fluctuations and conditional averages respect to mixture fraction to highlight the capabilities of the eddy dissipation concept combustion closure of catching the experimental features.

[1] Butz, D., Hartl, S., Popp, S., Walther, S., Barlow, R. S., Hasse, C., Dreizler, A., and Geyer, D., “Local flame structure analysis in turbulent CH₄/air flames with multi-regime characteristics, “Combustion and Flame”, Vol. 210, 2019, pp. 426

LES SIMULATION OF 100% H₂ COMBUSTION IN A SWIRLED STABILIZED BURNER

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Abstract

The effects of climate change are leading to further restrictions applied by the government to contrast the excessive greenhouse gas production. Simultaneously, the persistent installation of renewable energy source plants, is demanding more efficient and reliable ways to store the excess energy.

Hydrogen has been pointed out as the main player for the energy transition towards zero emissions. Indeed, hydrogen can be used as chemical storage through electrolysis. This can be either used in fuel cells or directly burnt, e.g., in gas turbines to produce electricity. Even if the combustion of hydrogen does not produce CO₂, thus reducing positively the greenhouse gas production, it is responsible of large NO_x emissions.

Hence, in order to fill the gap in simulating H₂ flames with an accurate estimation of NO_x production, herein a 100% H₂ technically premixed burner designed by the TUBerlin has been numerically investigated with a new chemical mechanism. The swirled stabilized burner has been designed with peculiar features to efficiently burn hydrogen with the aim to contrast flashback phenomena.

To perform effective LES simulations with the high fidelity AVBP solver, an analytical reduced kinetic mechanism for H₂-air combustion with NO_x has been proposed. This has been assessed on a wide range of temperature and pressure and then validated through experimental data.

Firstly, LES simulations of the cold case have been run to perform a grid sensitivity analysis. Then, one stable flame operating point with global equivalence ratio equal to 0.6 has been investigated and the results compared with experimental PIV and OH* data. Furthermore, a deep analysis of the mixing process has pointed out that compressible effects need to be considered to capture the right flow dynamics for both the air and hydrogen injection.

Finally, an evaluation of the hot spots responsible of the NO_x production close to the combustion chamber entrance and a global evaluation of the NO_x downstream of the combustion chamber has been carried out numerically.

Characterization of the effects of a needle-ring plasma actuator on methane-air swirled flame structure

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Abstract

Non-Thermal Plasma (NTP) is considered as a most prominent technique to improve the ignition and combustion by shortening the ignition delay timings, increasing lean flame stabilization, improving engine performance, extending lean blowout limits and reducing emissions. The first part of the work consists of experimental and numerical characterization of flow dynamics and combustion characteristics in presence of a ring plasma actuator driven by a high-voltage nanosecond pulse generator under atmospheric conditions in a quiescent environment. Smoke flow visualizations, Digital Particle Image Velocimetry and Proper Orthogonal Decomposition (POD) were performed to identify relevant flow structures. Numerical modelling of plasma ignition, validated with experimental studies, was performed by coupling ZDPlasKin with CHEMKIN. Plasma discharges on the methane/air mixture produced radicals that played a key role in enhancing the combustion process. The second part of study investigated the effects of continuous volumetric discharge of sinusoidal plasma actuator (needle electrode connected with high-voltage and the nozzle acted as a grounded electrode) at 20 kHz coupled directly on methane-air premixed flame in the near field of the injector exit. The ionic wind induced by the electrical body force given by the flow ionization leads to velocity disturbance and subsequently affects the flame. Flow quiescent visualizations showed that by increasing the electrical power used for the actuation a recirculation zone is formed in the non-reacting flow field. The study found that despite the low energy consumption in terms of electrical power, the plasma is effective in controlling flow and combustion. Comparative experiments between conventional and plasma assisted combustion were carried out to analyze the combustion enhancement in terms of lean blowout performance. It was found that a relevant extension of LBO limit was observed in presence of plasma discharges. At the highest air flow rate equal to 14.6 kg/hr, the LBO fuel flow rate was extended by 51.85% with an electrical power $P = 40.5$ W. Lowering the air flow rate the effect of the plasma actuation was more relevant and the LBO limits were significantly extended with a maximum reduction of the LBO fuel flow rate equal to 53% with $P=30.7$ W.

EFFECT OF HYDROGEN ADDITION ON PREMIXED FLAMES ISSUING FROM A MULTI-HOLE BURNER IN DOMESTIC BOILERS

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Abstract

Hydrogen can play a major role in the transition towards a decarbonized energy system. Indeed, green hydrogen can be produced through electrolysis from excess wind or solar energy and, then, can be injected into the existing natural gas grid, thus making use of the large available infrastructure for storage and transportation. Such integration between power-to-gas and the gas grid can thus face the challenges posed by the variability and intermittency of renewables. Soon the European natural gas network could undergo significant variations in the gas composition, as it has been estimated that 25 TWh of H₂ will be injected by 2030. The projections state that hydrogen could fulfill about 18% of the energy required for domestic heating in the EU by 2050. However, even though maximum hydrogen fractions up to 20% are foreseen, there is little proof of the adequate performance of end-user appliances. Hydrogen is much different than natural gas, exhibiting higher adiabatic flame temperature and much higher flame speed; this may lead to significant challenges for the safe and efficient operation of domestic burners and boilers.

Modern domestic condensing boilers are equipped with perforated burners which inject a premixed fuel-air mixture and ensure short-length flames. So far, the burner design has mainly relied on the manufacturers' experience; however, the upcoming variations in the gas composition, along with the more severe environmental regulations, will certainly ask for a better knowledge of the combustion process.

To this purpose, we carry out numerical simulations based on Computational Fluid Dynamics with detailed kinetics of premixed flames issuing from a multi-hole geometry emulating a portion of a typical burner installed in a condensing boiler. Different H₂ contents in the fuel mixture will be considered and compared to the natural gas case. The operating condition of the boiler, i.e. air excess, is preliminarily identified through a preliminary analysis based on the Wobbe index. The reaction zone anticipates with increasing H₂, however the downstream temperature decreases because the boiler naturally works in leaner conditions

Role of intrinsic flame instability in turbulent premixed combustion modeling

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Abstract

The planar configuration in premixed flames is almost invariably unstable. Two distinct intrinsic instability mechanisms exist, the Darrieus-Landau (or hydrodynamic) instability, caused by the thermal expansion across the flame, and the thermodiffusive instability, generated by unbalanced heat and mass fluxes in the reaction region. While the former is ubiquitous and always destabilizing, the latter can be either stabilizing or destabilizing depending on the effective Lewis number of the controlling reactant. The ensuing cellular morphology of premixed flames can be rather complex, even in the complete absence of an incident turbulent field.

The typical small-scale, thermodiffusive cells generally interact with large-scale hydrodynamic structures, giving rise to intricate, intrinsic wrinkling patterns. This is especially true for hydrogen and hydrogen-enriched flames in applications and devices dedicated to greenhouse gas mitigation. The understanding of such phenomena is therefore crucial in LES and RANS numerical simulations of such configurations as such wrinkling occurs at a sub-grid level and ad-hoc modeling is therefore required.

This study focuses on two possible strategies, amenable to LES and RANS implementation, providing sub-grid models for the unresolved wrinkling due to intrinsic instabilities. The first approach provides a wrinkling factor model, representing the amount of sub-grid flame area, to be used in the context of flame surface density (FSD) approaches. The second strategy represents a data-driven, filtered-tabulated approach based on a preliminary, minimal, two-dimensional direct numerical simulation (DNS) of an unstable flame. Both approaches are tested in an a-priori fashion and their accuracy and peculiar features assessed.

Chaotic and wavelet detection of thermoacoustic instability

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Abstract

Lean premixed (LPM) combustion is the state-of-the-art technology in stationary gas turbines for highly efficient low NO_x emission. However, especially when operated close to the lean blowout limit, flames tend to experience large amplitude pressure oscillations due to the coupling between heat-release fluctuations and some acoustic resonant modes of the combustion chamber. These phenomena are commonly known as thermoacoustic instability. They may have detrimental impact on reliability and availability of machines. Hence, the need for further knowledge of the mechanism of transition from stable to unstable behavior, which eventual early warning detection techniques should be based on.

To this purpose, recurrences in the reconstructed pseudo-phase space typical of chaotic analysis as well as bi-variate and mono-variate continuous wavelet transform of pressure and chemiluminescent radiative emission are analyzed. The two signals are recorded in a liquid rapid premixed oil swirled burner, as a test case that well represents a transition from stable combustion to thermoacoustic instability.

The main goal of the present analysis is the early detection of the combustion instabilities which translates into the prompt detection of transient states between stable and unstable regimes.

A comparison between indices obtained by chaotic and wavelet analysis highlights the same three stages appearing in the combustor behavior: a low amplitude Combustion Noise regime with some over-shoots caused by intermittent bursts of higher amplitude, transiting to a central part of thermoacoustic instability regime and then a return to a stable combustion. By contrast wavelet analysis of pressure and radiant energy appears to give further information about the energy transfer from low to high frequencies during the stable/unstable transition process.

This characteristic lies mainly in the locality of the wavelet transform and the different resolution achievable at different scales. In particular wavelet cross-spectrum modulus and its phase well evidence the coupling between pressure and radiant energy during the transition process and along the whole persistence of thermoacoustic instability.

spacing as uniform as possible.

H₂ Effects on Ammonia Oxidation and Dynamic Behavior

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Abstract

In a recent publication authors demonstrated the oxidation of ammonia under MILD condition comes through three different oxidation regimes, namely low, intermediate and high temperature ones. The shift from the low-intermediate to the high temperature regime can come through instabilities, with a strong dependence on the mixture stoichiometry. H₂ is conventionally used as a fuel “enhancer” of ammonia chemistry, as it improves the oxidation features of ammonia.

Based on these considerations, the goal of the present work is to study the hydrogen-ammonia combustion under low-intermediate temperature conditions, focusing on the effect of hydrogen on the thermokinetic instabilities.

To this aim, several experimental tests were performed in a Jet Stirred Flow Reactor, by parametrically varying the external system parameters (pre-heating temperature T_{in} , equivalence ratio ϕ , dilution level) and the hydrogen content in the H₂-NH₃/O₂/N₂ mixtures. The oxidation chemistry was characterized in terms of temperature profiles and stable species profiles. In addition, maps of combustion behavior in the T_{in} - ϕ plane were delineated as a function of the H₂ concentration.

Damped and periodic temperature oscillations were identified for all the mixtures. The overall effect of H₂ on the ammonia oxidation chemistry is to enhance the NH₃ reactivity. In particular H₂ shifts towards lower T_{in} the onset of instabilities, reducing the extension of the dynamic region with respect to both T_{in} and ϕ within the T_{in} - ϕ plane.

Following, numerical simulations were realized with different detailed kinetic schemes available in the scientific literature. Models were able to predict the H₂ effects on the ammonia oxidation chemistry. Kinetic analyses were performed in order to explain the interaction between H₂ and NH₃ oxidation pathways. Analyses highlighted a mutual inhibiting effect of H₂ and NH₃ oxidation chemistry.

Retardant Effect of Ammonia on Hydrogen Reactivity

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Abstract

Ammonia has been extensively studied as a hydrogen-vector and an energy carrier in combustion systems. The interest in the ammonia oxidation chemistry has boosted the development of detailed kinetic mechanisms, validated under several operative conditions. Although their recent improvements, several aspects have to be still considered.

Ammonia is a polar molecules, thus it is plausible to have a strong collisional efficiency in third-molecular reactions, likewise H₂O. To address this issue, experimental tests were realized in a Jet Stirred Flow Reactor considering its effects on the simplest oxidation system, namely H₂-O₂. The hydrogen oxidation chemistry is governed by third-body reactions, relevant also for conventional and unconventional fuels, within the concept of a hierarchical structure of detailed kinetic schemes.

Experimental tests were run for different H₂-O₂ mixtures in several bath gases (Ar, N₂, H₂O, NH₃) as a function of mixture inlet temperature. The experimental results show that NH₃, as well as H₂O, inhibits H₂ conversion, since the onset of reactivity shifts at higher temperatures as the NH₃ or H₂O concentration in the mixture increases. It has to be highlighted that NH₃ conversion can be considered as negligible under the explored operative conditions.

Following, numerical analyses were run using several kinetic mechanisms. They suggested a mutual inhibition effect of hydrogen and ammonia, along with the importance of ammonia as a third body species in third-body reactions. The mechanisms are very sensitive to the declaration of a third-body collisional efficiency for NH₃ in the reaction $H+O_2+M=HO_2+M$.

An experimental, theoretical and kinetic-modeling study of H₂S oxidation in ideal reactors

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Abstract

Bio-gas and bio-oil have been recently considered as an alternative to fossil fuels: due to their natural origin, they contain a number of contaminants, several of which harmful for the human health. Among them, H₂S is present in trace amounts, but still constitutes an issue because even tens or hundreds of ppm can quickly bring to permanent damage, and ultimately death. Several treatment options are available, including direct combustion and oxy-combustion. As a result, a wide-range understanding of H₂S combustion kinetics is of the utmost importance to get predictability on the related pollutant emissions.

In this work, pyrolysis and oxidation mechanisms of H₂S were investigated through a multifaceted approach: an experimental campaign covering different compositions, temperatures and residence times was carried out in a Jet Stirred Reactor and two Flow Reactors. All the three reactors had to undergo a proper coating procedure via boric acid, in order to limit wall effects in the presence of oxygen. At the same time, the key reaction steps at the lowest temperatures were re-evaluated by using *ab initio* tools. They were included in a detailed kinetic model, which was then leveraged to interpret the experimental data, thus identifying the governing pathways.

The results showed the substantial capability of the kinetic model in predicting H₂S pyrolysis and oxidation throughout the whole operating range. Specifically, it was found out that the thermal decomposition (H₂S + M = H₂ + S + M) reaction becomes critical at the lowest temperatures in pyrolysis conditions, where literature data are particularly scarce, and the proposed reaction rates differ by orders of magnitude. Still at the lowest temperatures, the biggest challenge is represented by an accurate prediction of the amount of HO₂ formed. This becomes particularly important in very lean conditions, where HO₂ is mainly formed by H-abstraction by O₂ on H₂S (H₂S + O₂ = SH + HO₂), then further enhances reactivity by performing again H-abstraction on H₂S (H₂S + HO₂ = SH + H₂O₂), thus creating the necessary SH radical pool to trigger the reactivity onset.

Acknowledgements

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SESSION II

ENGINES AND GAS TURBINES INCLUDING FIRE AND SAFETY

COMBUSTION DEVELOPMENT ANALYSIS IN LEAN HEAVY-DUTY CNG ENGINES WITH ACTIVE PRE-CHAMBER

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Abstract

Lean and ultra-lean CNG engines require innovative strategies to allow stable combustion while maintaining performance standards and emission reduction. One of these strategies is the employment of active pre-chamber configurations which represent a viable solution for Heavy-Duty engines, with their larger cylinders and space availability compared to smaller engines. Active pre-chambers are auxiliary combustion chambers that can initiate the stable combustion of lean mixtures (with air-to-fuel ratios, λ greater than 1.5) without compromising efficiency and stability requirements. In this work three pre-chamber nozzles differing for the orifice diameter were tested in a stationary heavy-duty 6-cylinder engine (originally a compression ignition engine) converted to work with a single cylinder and spark ignition operated. An extensive test matrix was carried out to perform spark timing, global lambda and load target sweeps in order to assess the behaviour of the three nozzles with respect to the changing operating conditions. Analysis of in-cylinder pressure traces and heat release rate allowed to unveil the characteristics of the combustion phasing starting from the pre-chamber to the development in the main chamber, relating these to the performance of the engine in terms of emissions, efficiency and stability. The key role of pre-chamber combustion development on the overall in-cylinder combustion phenomena was assessed, determining the more effective values of the varied parameters in terms of efficient operation and emissions.

FLAME PROPAGATION OF FLAMMABLE DUSTS: A MALLARD-LE CHATELIER INSPIRED MODEL

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Abstract

Many combustible dusts, if dispersed as a cloud in air and ignited, will allow a flame to propagate in a manner similar to the propagation of flames in premixed fuel–oxidant gases. Such dusts include common food-stuffs, synthetic materials, chemicals and pharmaceuticals, metals, traditional and unconventional dusts such as biomass. Once ignited, most of these dusts are characterized by a flame propagation in the homogeneous phase: the dust-air mixture is pre-heated up to the volatile point (*VP*), at which the devolatilization (pyrolysis, melting/boiling, sublimation) occurs, thanks to a thermal loop from the flame to the colder zones. The produced gases are heated up to the ignition temperature. Consequently, the flame burning velocity is the results of the coupling between heating rate, pyrolysis and/or evaporation/sublimation rate and volatiles combustion rate [1]. In this work, we formulated a three-layers Mallard-Le Chatelier inspired theoretical model to fully characterise the steps occurring during the flame propagation of dusts/air. To this end, we measured the devolatilization rate by means of the simultaneous thermogravimetric and differential scanning calorimetry (TG/DSC). To determine the composition of produced gases, literature data or FTIR analysis were used.

The laminar burning velocity of gases was computed by simulating the gas flame propagation in a tube starting from the measured gas compositions by means of the CHEMKIN code. The dust burning velocity, as well as the explosibility parameters, is strongly dependent on the turbulence level, on the equipment geometry and on the experimental conditions. As a consequence, the theoretical dust flame propagation model here developed is a quite important support for the experimental evaluations and/or to make preliminary considerations.

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MULTI-PHYSICS MODELING OF LIQUID ROCKET ENGINE COMBUSTION CHAMBERS

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Abstract

A thorough understanding of the multi-physics phenomena occurring inside a combustion chamber and its injection system is an imperative aspect of the characterization and design of an optimized propulsion system, particularly when dealing with challenging operating conditions as for Liquid Rocket Engines (LREs). Computational Fluid Dynamics (CFD) and numerical simulations are in this context valuable tools to replace experimental investigation and actively support the design process. Among the many, two aspects are inquired in this work: the geometrical layout effect over injector elements belonging to the same firing plate and the interaction between the hot gas mixture and the surrounding walls. More specifically, the former aspect is investigated in terms of injectors mutual distance and distance from the combustion chamber wall, through the collection of two-dimensional databases with the parametric variation of the confinement length, i.e. the transverse dimension available to the recirculation development. It is found that larger confinements cause wider recirculation regions both for near-wall and internal injectors, resulting in increasing thermal loads [1,2]. The interaction between neighboring continua is investigated by means of a recently developed multi-region solver for Conjugate Heat Transfer (CHT) in the context of LRE [3]. The solver tackles the concurrent solution of fluid and solid domains, coupling them at the interface through a boundary condition that guarantees heat flux and temperature continuity. The aforementioned results have been obtained with a flamelet-based approach accounting for non-adiabatic effects, coupled with an unsteady-RANS fluid-dynamic solver [4]. Also, the employment of thermal wall functions bridging the near-wall field with the fully turbulent flow allows the computational cost reduction, avoiding the solution of the boundary layers [5]. The numerical frameworks are developed in the context of OpenFOAM open-source platform [6].

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From turbulent combustion to liquid rocket engines: an overview of applications.

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Abstract

With the recent increase of High Performance Computing (HPC) resources, an higher demand of Computational Fluid Dynamic (CFD) investigations have been observed in the context of Liquid Rocket Engines (LRE) combustion chamber simulations. Associated to this technological advancement, the minimum standards of numerical analysis have raised a bar, in terms of reliability, robustness and performance. As an example, Large Eddy Simulation (LES) is nowadays considered the reference numerical framework for unsteady turbulent problems (such as those involved in the turbulent combustion process of a LRE) in place of Reynolds Averaged Navier Stokes (RANS) analysis, being Direct Numerical Simulations (DNS) still prohibitive for industrial and large scale applications. In particular, the widespread diffusion of wall-modeled LES (WMLES) simulations is nowadays largely discussed [1], given the computational bottleneck associated to the simulation of wall-bounded flows. However, the intrinsic complexity and interdisciplinary nature of LRE combustion chamber problems, still require proper modeling solutions in order to, on one hand, separately describe the main physical phenomena involved (heat exchange towards the chamber walls, expansion in the nozzle, flame-flame and flame-wall interactions) and, on the other, let all these models harmonically and consistently play to achieve the final aim: the simulation of the entire injection-mixing and combustion problem in LRE. To this end, this work aims at addressing the main physical aspects beneath LRE combustion chambers, with associated challenges in their numerical simulation. Concurrently, it presents some of the authors' solutions. Particular emphasis is given to the propellants injection problem and to non-adiabatic phenomena at the chamber walls. Regarding the former, the effects of heat exchange phenomena inside the propellants inlet ducts is discussed [2] and some modeling strategies and solutions are proposed. Concerning the latter, the effect of large stratifications in the near wall region, as for instance those induced by the combustion process, is discussed and some recent advancements with respect to the state of art in the context of wall models are presented.

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CH₄ conversion and NH₃ formation Model Assessment over a Pd-Rh Three-Way Catalyst for automotive application

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Abstract

The growing diffusion of Heavy-Duty engines powered by Natural Gas (NG) has made it necessary to investigate specific Three-Way Catalysts (TWC), with the consequent development of reliable numerical models.

This reactor allows a high conversion efficiency exclusively in a limited range of Air-to-Fuel Ratio (AFR) around the stoichiometric. In highly dynamic conditions, its behavior can differ from Steady-State ones due to numerous phenomena of Oxygen Storage and oxide formation on palladium surface, not fully detected from Engine Test Bench (ETB) data.

Goal of the present research activity was to develop a 1D chemical reaction model of a Pd/Rh TWC for NG application with the use of a Synthetic Gas Bench (SGB) through an extensive and innovative experimental characterization.

Specific Steady-State experiments have shown a dynamics in the methane conversion, not only to λ variation but also at fixed λ and temperature conditions, linked to the reversible Pd \rightleftharpoons PdO transformation.

Through dedicated temperature-programmed oxidation and reduction (TPO / TPR) tests, hysteresis phenomena in the methane oxidation rate were highlighted. Furthermore, with fast Rich-Lean λ transitions tests, it has been also demonstrated that the presence of NO reduces the methane oxidation reaction rate.

A dedicated experimental protocol has shown the high impact of Steam Reforming reaction on methane conversion, partly responsible of a particular decrease in CO conversion efficiency at high temperatures in rich and stoichiometric conditions.

In addition, given the high reliability of the experimental data and the possibility of managing the chemical composition of the gas entering the catalyst, important aspects related to the NH₃ formation and decomposition were analyzed.

The proposed reactions kinetic scheme describes in an acceptable way the behavior of a TWC for NG application

NUMERICAL MODELING OF CHEMICAL VAPOR INFILTRATION FOR PRODUCTION OF CARBON DISK BRAKES

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Abstract

Chemical Vapor Infiltration (CVI) is the one of the leading techniques for the production of carbon disk brakes for aircrafts or high-performance vehicles. In CVI, porous preforms are placed in a reactor heated up to temperatures of the order of ~1100 °C. A gaseous stream (mainly composed of light paraffins) flows around the preforms and pyrolyzes. The decomposition products infiltrate the porous preforms, where heterogeneous reactions take place in the pores of the solid substrate, leading to the deposition of graphitic carbon.

CVI is a complex process, in which multi-physical and multi-chemical phenomena occur at the same time: homogeneous gas phase reactions, heterogeneous surface-deposition reactions, molecular diffusion, mixed convection gas flow, radiative heat transfer, etc. The numerical modelling of CVI reactors is significantly complicated by the wide range of temporal scales of these phenomena, from fractions of ms (associated with pyrolytic reactions) to days (which is the typical time to complete the densification), preventing the possibility to adopt a fully-coupled approach. Alternative numerical techniques have to be implemented.

In this work we present and apply a modelling strategy based on the partial decoupling between the evolution of pyrolysis in CVI reactors and the densification process occurring over the porous substrates. More specifically, a recursive 2-step procedure is proposed: 1) a steady-state CFD simulation of the whole reactor is performed, in which only the gaseous phase is modelled (no heterogeneous reactions are accounted for and no equations are solved inside the porous preforms); 2) the CFD solution (Step 1) is used to provide the proper boundary conditions for modelling the densification process in each porous preform for a duration of several hours. Then, the procedure is repeated by providing the CFD simulation (Step 1) with mass fluxes released and consumed by the preforms inside the reactor. This strategy assumes that, being the gaseous reactions much faster than densification (usually limited by porous diffusion), they can be considered as *quasi-steady* with respect to the densification.

The proposed algorithm was initially validated on experimental data available in the literature. Then, it was applied for the modelling of CVI reactors currently adopted by Brembo S.p.A. for industrial production.

AN UNCONVENTIONAL INTERNAL COMBUSTION ENGINE AS A RANGE EXTENDER FOR LOW CARBON MOBILITY

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Abstract

The automotive sector is facing an extraordinary time as a consequence of several announcements by different countries on the future ban of the internal combustion engine vehicles (ICEVs) in favour of the battery electric vehicles (BEVs). Although the BEVs, with their zero tailpipe emissions, represent a valid solution in countries producing electricity from renewable sources, a series-hybrid powertrain layout for range-extended electric vehicles (REEVs), based on a small internal combustion engine used as a range extender and an electric motor for the vehicle traction, is representative of an optimal solution where charging infrastructures are not fully developed yet or the production of electricity is still based on coal.

In that respect, an interesting engine architecture is represented by the rotary Wankel engine. With its extraordinarily favourable power-to-weight ratio and high power density in addition to a compact design with low vibrations, the rotary engine has the potentiality as the ideal range extender, especially when fuelled with alternative fuels as the Hydrogen.

This work will present the experimental activities on the 225CS rotary Wankel engine (225cm³) produced by Advanced Innovative Engineering UK (AIE UK). Specifically, it will illustrate the particular combustion analyser developed to collect the indicated pressure cycles together with the other experimental results regarding the performance and the emissions of the engine fuelled with conventional fuel. Relying on those data, further considerations will be made on the development of a dedicated injection system in order to run the engine on Hydrogen fuel, while performance predictions using the alternative fuel will be made by modelling activities. Finally, the numerical results will represent the base for a future development strategy able to reduce the carbon footprint of the rotary engine as applied on range-extended electric vehicles.

Combustion of cryogenic gases

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Abstract

The innovation in several industrial sectors, including power generation, has been recently characterized by the need for reducing the operative temperature either for economic or environmental related aspects. For the same reasons, the use of light or carbon-neutral fuels is largely desirable. In this framework, direct combustion of cryogenic fuels such as liquefied natural gas (LNG) and liquid hydrogen (LH₂) represent promising alternatives. However, innovative solutions require the acquisition of fundamental-based knowledge to produce safe and robust systems. Since reactive systems are often the bottleneck, this work is focused on the integration of chemical (i.e., detailed kinetic mechanism) and physical (i.e., computational fluid dynamics, CFD) models. A theoretical-based kinetic mechanism mimicking the behaviour of light fuels and their intermediates under oxidative conditions in a wide range of temperature and pressure was reduced and tested against experimental data. More specifically, the most influential species and reactions were identified and included in a reduced detailed kinetic mechanism via a combined analysis including flux diagram determination and sensitivity analyses. The range of temperature was selected to be representative for the ultra-low, low, intermediate, and high temperatures. The resulting mechanism was implemented in an open-source computational fluid dynamics model to characterize pool fires caused by the accidental release of cryogenic fuels. In this case, a cylindrical pool was considered as already formed after an accidental release on the ground. The evaporation rate model developed by Conrado and Vesovic [1] was imposed. The obtained heat fluxes were compared with the traditional approach commonly adopted for the evaluation of the chemistry of the pool fire in CFD, i.e., the single step reaction, showing fair agreement especially on mid- and far-field distances. However, the implementation of a reduced mechanism has allowed for the characterization of the composition and dispersion of combustion products, unfeasible for the traditional approach since the need for empirical values of the yields of partially oxidized byproducts at the investigated conditions.

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Investigation of Ultra-High Injection Pressure on a GDI Spray at Engine-like Conditions

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Abstract

In GDI injection systems, a challenge remains the improvement of the spray parameters in terms of atomization, smaller droplets and their spread in the combustion chamber in order to enhance the combustion efficiency. A recognized general trend is the increase of the injection pressure to improve the fuel atomization degree and contribute to a fast evaporation, and consequently a better mixture formation. In this framework, very high pressures for injecting gasoline in internal combustion (i.c.) engines are recently explored for improving the air/fuel mixing process in order to control unburned hydrocarbons (UBHC) and particulate matter emissions such as for investigating new combustion concepts. This paper aims improving the knowledge of the spray behaviour for gasoline at high pressures useful to understand and enhance the benefits on combustion systems.

The tests were performed by a multi-hole GDI injector in a constant volume vessel filled with gas (N_2) at diverse pressures and temperatures. The effects of very-high injection pressure on gasoline spray development will be discussed for a wide range of ambient conditions, including sub-atmospheric ones. A complete set of operative conditions was explored ranging the injection pressure (p_{inj}) between 40 and 100 MPa, ambient temperature (T_{amb}) between room and 200°C and the ambient density (ρ_g) from 0.2 up to 11.5 kg/m³. Spray development was observed by a combined optical technique: high-speed Mie scattering imaging was utilized to visualize the liquid phase while shadowgraph one for determining the global structure, including liquid and vapor, by using the light beam passing the sampling volume and hitting the camera. The results, including spray morphology, penetration, cone angle, and area for both liquid and vapor phase under different engine-like conditions, will be discussed in detail. They could give a contribute towards a comprehensive database to develop CFD numerical models as well as to explore advanced combustion strategies.

SESSION III

SOLID FUEL COMBUSTION, PYROLYSIS AND GASIFICATION

CONTAMINATED BIOMASSES TO BIOFUEL

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Abstract

Worldwide, there is a general increase in the demand for renewable energy sources, which is often encouraged by legislative actions. One of the main sectors affected by this trend is transportation: according to the revised Renewable Energy Directive 2018/2001/EU, a minimum of 14% of fuel for transport purposes must be biofuel produced from renewable sources by 2030.

The use of biomasses for energy purposes is often criticised because of the combination of soil shortage and increasing world population: the cultivation of specific energy crops could subtract high-quality agricultural land to food crops. A possible solution could be to use contaminated land areas to grow energy crops; moreover, choosing the appropriate crops, there could be partial remediation of these contaminated lands through phytoremediation, leading to a win-win situation. While in principle contaminated biomass from crops grown on contaminated lands can be used to produce biofuels, the presence of potentially toxic compounds (such as heavy metals) poses some technical difficulties in biofuel production, especially for fermentation. A reliable technique for the treatment of contaminated biomasses is pyrolysis, a thermochemical process that, given appropriate operative conditions, can concentrate and stabilize heavy metals in the solid product (char) while obtaining a combustible liquid phase (bio-oil) free from contaminants.

Framed into CERESiS European project, a fast pyrolysis plant has been developed and designed aiming to produce bio-oil from heavy metals contaminated biomasses. The plant is based on an auger reactor and includes a complex condensation section that can achieve a fractional condensation of bio-oil.

The fast pyrolysis plant will be involved in future researches to investigate the speciation of heavy metals and their distribution in the pyrolysis products under different operative conditions, other than heavy metals effect on pyrolysis products properties. The final aim is to define the best operational parameters needed for the production of a clean, good-quality bio-oil.

TOWARD A THOROUGH VALORIZATION OF HAZELNUT PRODUCTION RESIDUES: FOCUS ON FLUIDIZED BED TORREFACTION

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Topical Area

Biofuels, Biochemicals and Biorefinery

Abstract

The cooperative R&D Project "Pastificio Lucio Garofalo toward the 2030 Agenda: commercializing products of the Italian gastronomic tradition, upgrading agri-food by-products and implementing new solutions for environmental sustainability - PASTA FOR FUN" is presently ongoing within the EU-Italy National Operating Program (PON) "Businesses and Competitiveness 2014–2020, Axis I, Action 1.1.3" issued by the Ministry of the Economic Development. The University of Salerno through its Department of Industrial Engineering is the Academic partner to Pastificio Lucio Garofalo.

In the action plan of the "PASTA FOR FUN", the Workpackage 9 is dedicated to a new hazelnut "pesto" formulation and characterization on selected raw materials, and the Workpackage 14 is devoted to the valorization of hazelnut wastes.

The present work is within the framework of the above Workpackage 14.

The following residues as non-edible parts originated by the traditional field collection and industrial processing of hazelnut (*Corylus avellana*) have been here taken into consideration: i. leafy husk (*brattee fiorali*), ii. dry shell (*pericarpo*) and toasted cuticle (*perisperma*).

Presently, leafy husk is an unused residue as it is partly left on the tree or, more abundantly, resting on the cultivation soil; shell fragments are generated as an industrial residue after breaking and separation of the kernel (*achenio*); toasted pellicles represent another kind of residue whenever the kernel is toasted for further processing in food and pastry-making.

Campania has been the leader region in the field production of hazelnut in 2020, with an amount of about 480000 q and less than half in the province of Avellino.

Samples of leafy husk had been collected fresh directly from the trees in a small harvesting field in Pizzolano (SA). Samples of dry shell and toasted pellicles have

been provided by Prodal.

All of the above mentioned non-edible parts are actually a source of bioactive compounds like polyphenols (e.g., p-cumaric acid) and tannins. This feature makes them candidate to valorization processes for obtainment of the bioactive compounds through steps of extraction and separation. In turn, this makes the spent post-extraction residues available for thermochemical valorization processes, *in primis* torrefaction.

Preliminary, the present paper briefly discusses the lab-scale activity based on adoption of water rather than organic solvents for extraction of bioactive compounds.

Then, the paper presents as work in progress the investigation on torrefaction of hazelnut residues before- and post-extraction by means of bench-scale fluidization. The fluidized bed torrefaction of such highly fragile matters is feasible and works smoothly in the temperature range 200-300 °C. Samples are to be reduced from their original un-processable size and put in a biomass-to-inert ratio of about 1% wt. The mass yield by torrefaction turns out in the range 50-75% (ar).

HYDRODYNAMICS OF A COLD FLOW MODEL FLUIDIZED BED FOR FAST PYROLYSIS OF BIOMASS

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Abstract

The production of biofuels is one of the most promising routes to satisfy the increasing global transportation demand and to reduce greenhouse gas emissions in the transport sector. Biofuels can be obtained from biomass via thermochemical/biochemical processes. Biomass sources are well distributed all over countries and are very heterogenous. These two features together with a small storage density make large scale processing operations very difficult from a logistic point of view. For this reason, a two-level biofuels production chain can be taken into consideration. It involves a first conversion of biomass to an intermediate carrier at a local, decentralized level, then the transport of this biofeedstock to large centralized production sites, for up-grading and refinery operations.

The present work deals with the development of an internally circulating fluidized bed reactor for the production of bio-oil (biofeedstock) by fast pyrolysis of biomass in the frame of the project “Biofeedstock”. In this reactor hot inert sand particles are continuously circulated between a fluidized and a moving bed, separated by a vertical baffle and interconnected by an opening at the bottom. In the fluidized bed particles are transported upwards over the baffle and then settle in the other region. There, they flow down by gravity as a moving bed and return in the fluidized bed across the opening. Biomass can be continuously fed at the top of the moving bed and dragged down by sand particles toward the fluidized bed, where the pyrolysis reactions take place. The present work is about hydrodynamic study conducted in a cold flow model. As fast pyrolysis is a non-equilibrium process, residence times have to be carefully limited below 1s, in order to avoid secondary pyrolysis reactions, and hydrodynamic control is essential for a successful operation. For this reason, the experiments aimed at investigating the driving force and the mechanism of particle circulation in the system. Experimental tests allowed the measurement of the circulation rate of sand and the assessment of particle residence time distributions (RTD) under different operating conditions and for different values of the clearance ratio between the fluidized bed and the moving bed sections.

EXPERIMENTAL AND THEORETICAL STUDY OF CELLULOSE PYROLYSIS

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Abstract

A combined experimental and theoretical approach is applied for the study of liquid phase pyrolysis of cellulose and Fast pyrolysis of Bio-Oils. Due to the complexity of the reaction environment, pure levoglucosan (LVG) has been selected as model system. Levoglucosan is in fact the major intermediate in cellulose pyrolysis and a key-component of the sugar fraction of the Fast Pyrolysis Bio-Oils. The high boiling temperature of this compound (above 380 °C) causes a competition between evaporation and liquid phase chemical reactions. The former phenomenon leads to the gas phase decomposition into lighter compounds whose mechanism has been extensively studied [1], whereas the latter leads to polymerization into oligo and polysaccharides [2]. Still to this day, little is known about the liquid phase reactivity of pure levoglucosan, however newly developed computational tools such as enhanced free energy sampling methods [3] and QM/MM calculations can be exploited to get insights into the liquid mechanism. In this work, the capabilities of these methods are explored in order to evaluate kinetic and thermodynamic parameters which can be incorporated into a Thermogravimetric analysis model. The scope of the theoretical investigation is to provide a fundamental background and possibly to extend a newly developed mechanism of LVG liquid pyrolysis. The results of the simulations are then compared with ad hoc fabricated experimental data in terms of concentration profiles.

References

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THERMAL DEGRADATION OF NYLON-6 AND REAL MIXTURES OF SOLID PLASTIC WASTE. AN EXPERIMENTAL AND KINETIC MODELLING STUDY

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Abstract

The current challenges related to plastic waste disposal motivates the renewed interest in understanding the chemical and physical phenomena involved in the thermal treatments of plastic polymers (i.e., pyrolysis and gasification) [1], embracing the current trends and incentives towards the implementation of circular economy strategies for chemical recycling of solid plastic wastes (SPW). In general, SPW is a complex mixture involving different polyolefins (PE, PP, PS), heteropolymers (PVC, PET, PA) and numerous additives [2]. This work addresses nylon-6 (PA) pyrolysis presenting new thermogravimetric analyses (TGA) together with a preliminary semi-detailed kinetic model, extending the plastic degradation models developed at Politecnico di Milano for vinyl polymers [3]. The semi-detailed kinetic model, whose parameters were estimated according to the approach developed for the other polymers, is validated with additional literature TGA and GC-MS data. The resulting pyrolysis models were also assessed with a real SPW mixture under the completely segregated mixture (CSM) assumption. Further developments of the kinetic model will be performed through detailed information of intermediates from speciation measurements performed at POLIMI. Such information will allow to carefully expand the description of PA thermal degradation including also radical pathways. Further work will also address describing interactions between the different polymers.

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GASIFICATION OF TANNERY SLUDGES IN FLUIDIZED BED: FATE OF Cr(III)

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Abstract

Italy is the main supplier of leather in Europe, contributing 65% to European production of bovine leather and 15% to the world production. The tanning industry produces wastewater rich in pollutants, especially Cr, which is the chemical species with the strongest environmental impact. The purification process of this wastewater, produces a tanning sludge (TS) with high concentration of Cr(III), generally stored in authorized landfills with high costs. Due the high production of TS, it is necessary to implement sustainable management strategies that aim both to reduce the volume of TS to be disposed of and to produce energy vectors. Therefore, Sludge-to-energy ("StE") technologies are adopted. However, due to the high content of Cr(III) in TS, special attention must be paid to limit/avoid the oxidation of Cr(III) to Cr(VI), extremely harmful. In this context, gasification is particularly suitable for the treatment of TS because, operating in oxygen-deficient conditions, it reduces the risk of oxidation of Cr. In this work, were carried out gasification tests, in a fluidized bed reactor (ID=0.041m and H=1m), of a dried Italian TS, supplied by SSIP. Tests were conducted at 850°C, at a velocity of 0.3 m/s. The volumetric flow rate of fed gas was 350 NL/h, consisting of 85.7% N₂ (300 NL/h) and 14.3% air (50 NL/h). The TS (ID<1mm) was sent to the reactor with mass flow rates of 99g/h and 63g/h to obtain two different air/fuel equivalence ratio (ER) values of 0.15 and 0.24, respectively, in order to observe its effects on hexavalent Cr formation. In the test with ER=0.15 (less oxidative conditions) 22% more syngas was produced (CO+H₂=77.07%), compared to that with ER=0.24 (CO+H₂=59.74%). Consequently, HHV in the test with ER=0.15 (12.0 MJ/Nm³) is greater than that obtained with ER=0.24 (11.6 MJ/Nm³), while the CO₂ content is lower (16.16% for ER=0.15 vs 30.10% for ER=0.24). The concentration of Cr(VI) (absent in the raw TS) determined in bottom-ash, fly-ash and tar is always four orders of magnitude lower than the concentration of Cr(III) in the raw TS (25.38 g/kg), demonstrating the correct choice of gasification operating conditions, aimed at limiting oxidation to Cr(VI).

A statistical approach for pyrolysis process description and optimization

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Abstract

According to RED II targets by 2030 the renewable energy consumption must be raised up to 32%, particularly 14% of the energy supplied for road and rail transport must be renewable. As part of renewable energy sources, residual biomass plays a significant role, because of its availability and the possibility of obtaining advanced biofuels and biochemical through several thermochemical and biochemical processes, such as pyrolysis, gasification and aerobic digestion. The main challenge of using residual biomass is its properties variability (e.g., O/C ratio, ashes content, extractives, cellulose, hemicellulose, lignin and so on) according to type, geographic localization and seasonality. For this reason, properties and yields of the products are highly variable. Furthermore, the complexity of the processes involved in biomass valorization often makes the classical chemical-physical modelling approach very challenging. In this framework, the research community as well as the industrial sector are focusing their attention on the adoption of new provisional tools, based on advanced statistical methods, machine learning techniques and operative research techniques for decision-making support, in order to improve the sustainability utilization of the biomass resources.

In particular, this work represents the first attempt to this new modelling approach, focusing its attention on the thermochemical valorization of residual biomass. The principal components analysis (PCA), which projects the original data in principal component (PC) space for assessing which input parameters have the highest score on the PC reducing the input data dimension, without losing valuable information, is used for the fast pyrolysis process. A broad database with about 450 observations is developed collecting data from scientific literature. The database includes both qualitative and quantitative information regarding main biomass characteristics (e.g., type, proximate and ultimate analysis), operative parameters (e.g., temperature, pressure, type of reactor) pyrolysis products and byproducts (e.g., yields, quality). PCA is applied to a subset of the original data considering only fast pyrolysis process, non-catalytic, in a fluidized-bed reactor with a temperature range of 450-550°C.

Investigate the potential synergistic interactions for co-pyrolysis of olive stone and polyolefinic plastic to increase the quality of pyrolysis oils

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Abstract

The development of sustainable, clean modern energy carriers has swept across the energy sector in line with the goals of moving towards low carbon economies. This has resulted in the increased utilisation of previously neglected solid organic waste resources as alternative carbon feedstocks for fuels and petrochemicals, as evidenced by more research towards valorisation of lignocellulosic and plastic waste resources. Co-pyrolysis has been identified as a potential pathway to benefit from this readily available stream of residual carbon providing a platform to produce valuable products that may fit into the different energy vector streams. Despite a lot of work being done at microscale pyrolysis to determine the synergistical potential of co-feeding, less work has been done on large scale reactors with potential for commercialisation on the impact of co-pyrolysis to improve the quality of pyrolysis oils. In this study, our focus is identifying potential synergy between devolatilization and condensation products that may occur in the presence of an inert and catalytic bed under bench scale fluidised bed conditions.

The product distribution from non-catalytic pyrolysis of olive stone and polyethylene was comprised of derivatives indicative of a combination of the individual pyrolysis products i.e., oxygenated biomass derivatives plus olefinic monomers plastic derivatives. This could suggest that condensation synergy as suggested by Gunasee, et al. [1] may be the dominant process, requiring changes in operating procedure to allow for secondary reactions. For the catalytic experiments, the product distribution was shifted due to secondary reactions, however there was no conclusive information to distinguish the type of synergy that may have occurred, i.e., devolatilization/condensation synergy. There is still ongoing work on this project to try to optimise the process parameters towards increasing the interactive devolatilization synergy towards improving the quality of pyrolysis oils.

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SYNGAS FERMENTATION: ASSESSMENT OF KINETICS AND REACTOR SET-UP

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Abstract

Fermentation of H₂/CO/CO₂ mixtures to fuels has been recently developed as an effective gas-to liquid biocatalytic process that enables the valorization of syngas and other carbonaceous waste gas streams (e.g. steel mill off gas). The use of syngas from both biomass and non-biogenic residues (e.g. plastic waste) allows the potential exploitation of the full carbon content of the feedstock as an alternative to the sugar-based biorefinery [1].

Current technologies for C1 gas fermentation have been developed up to demonstration scale [1] for the production of ethanol as fuel compound and as building block for polymer synthesis. Open issues related to the scientific research are: i) selection of optimal syngas compositions and effect of polluting species (e.g. NH₃, HCN, H₂S) on bacteria growth; ii) optimization of cell and products yields, iii) maximization of gas-liquid mass transfer rate in the bioreactor [2].

Concerning the first issue, CO consumption, as main carbon source is characterized by substrate inhibition kinetics in most of the microbial species. This contribution reports results from batch fermentation tests of *Clostridium carboxidivorans* aimed at the assessment of the effect of CO partial pressure (0.5-2.5 atm) and liquid-to-gas volume ratio (0.28-0.92) on cells growth rate and butanol-ethanol yields. Results provided growth rate as a function of CO concentration, the data were fairly fitted by a substrate inhibition model (maximum rate at CO=25 mg/L). In addition, growth rate resulted affected by liquid-to-gas volume ratio with a maximum rate ranging between 0.22 and 0.18 h⁻¹.

The kinetic model has been used to design and set-up stirred bioreactors (0.25 L) for syngas fermentation tests with continuous gas (99.97% CO at ~0.6 L/h) and liquid feeding.

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THE HEMICELLULOSE STRUCTURAL COMPLEXITY AND ITS ROLE IN PYROLYSIS PRODUCTS DISTRIBUTION AND SPECIATION

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Abstract

Pyrolysis has gaining increasing relevance as a feasible thermochemical route for converting biomass into value-added products. To date, many aspects of the mechanisms leading to the conversion of a lignocellulosic biomass into liquid, gaseous and solid products deserve dedicated studies to optimize the overall process in terms of desired product yields. In this framework, a detailed investigation on the slow pyrolysis of xylose-based materials was conducted since many years in our group to shed light on the pyrolytic behavior of hemicellulose (that is the most tricking sugar-based biomass component) and identify and circumscribe the role of alkali and alkaline earth metals.

Xylose-based feedstocks, mimetic of real hemicellulose types, have been used in the present work to investigate the relationship between the pyrolysis products yields and distribution and the hemicellulose structural characteristics. Three xylose-based hemicelluloses differing in composition, molecular weight (MW), chain branching, monomers composition and origin were selected: a commercial glucuronoxylan (beechwood xylan), a commercial mixture of low MW xylo-oligosaccharides with a low acetylation degree (corn cob xylan) and an arabinoglucuronoxylan extracted from grape pruning. These materials were structurally characterized and used as feedstock for slow pyrolysis tests up to 700°C. We observe that the production of char and gas species is promoted by higher MW, branching and composition with the ashes playing a prominent role. As concerns the speciation of compounds in pyrolysis liquids, we found that the production of anhydrosugars, furfural, formic acid and acetic acid is suppressed by the presence of ashes, while the chain branching seems to favor the production of linear ketones and to inhibit the production of cyclic and hydroxylated ketones. The production of water seems to be favored by the increase of MW and branching and suppressed by the presence of ashes. These results are intended to drive an increase in the knowledge on the main structural features affecting the hemicellulose decomposition mechanisms.

Biochar from Lead Contaminated Biomasses as Coke Substitute in Metallurgy

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Abstract

A partial replacement of the coke used in the blast furnaces with the solid product of biomass pyrolysis (biochar) would contribute to significantly reduce CO₂ emissions associated to the metallurgic industry. However, the introduction of biochar could affect the standard operation of the blast furnaces since its chemical and physical characteristics may differ significantly from those typical of coke fed to these types of furnaces (density, calorific value, ash content and composition, mechanical strength, etc.). The critical limit for coke replacement depends on the type of furnace as well as on the chemical and physical characteristics of biochar.

The idea underpinning the present work is to integrate pyrolysis for biochar production with contaminated sites restoration through biomass (phytoremediation), thus increasing the energetic and environmental sustainability of the whole production chain.

Biomasses from a Pb contaminated site were harvested, collected and characterized in terms of agronomic parameters. Then biochar samples were produced exploring different pyrolysis operating conditions. A rich set of classical and advanced analytical techniques supported the whole activity in order to obtain detailed information on the physical and chemical properties of produced biochar in dependence on production methodologies. A particular care was given to identify the best procedure capable of sequestering Pb in the biochar, thus reducing its leakage caused by the devolatilization during the pyrolytic treatment.

DECARBONISATION OF STEEL HEATING PROCESSES: MILD COMBUSTION OF HYDROGEN/NATURAL GAS MIXTURES

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Abstract

The Paris Cop21 agreement, the European Green Deal and the EU roadmap for a competitive low-carbon economy in 2050 set several targets of greenhouse gas emissions for many industries. In this contest, hydrogen will cover the roles of feedstock, fuel and energy storage mean.

Today, the use of hydrogen in the steel industry is limited to annealing processes. A complete transformation of the steelmaking production route from liquid steel production to rolling and finishing processes requires development and validation of specific combustion technologies. A massive use of hydrogen in steel industry is envisioned in many proposed scenarios and creates substantial challenges in terms of NO_x emissions, product surface quality and plant safety.

This work summarizes the current efforts of Tenova with the SmartBurner platform: recuperative and self-recuperative flameless burners that are able to use hydrogen/natural gas mixtures while controlling NO_x emissions below the next envisioned limits even in high temperature processes, i.e., above 1000°C. A massive use of embedded sensors allows continuous monitoring of the combustion process performance, as well as of the integrity of key burner components.

SESSION IV

FORMATION AND CONTROL OF POLLUTANTS

NO_x Emissions and Combustion Stability of Ammonia/Methane MILD Combustion

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Abstract

Ammonia is broadly considered as a valuable energy vector in the framework of the energy shift toward Renewable Energy Sources, due to its very high hydrogen-density and well-established production processes. Despite its many potential advantages, several drawbacks, characterising the ammonia oxidation process (high fuel NO_x emissions, low flammability, high auto-ignition temperature and difficult reactor design), compromise its wide utilisation. An intermediate and bridge solution to overcome these issues may be the use of “fuel enhancers”. In this respect, blends of ammonia and fossil fuels, entailing only marginal modifications to the burner design, have been proposed as effective strategy.

In this framework, the present study deals with the ammonia/methane combustion characteristics under MILD combustion conditions. Gaseous pollutant emissions (NO_x, NH₃, H₂, CO) and process stability limits were identified in a cyclonic burner as a function of the equivalence ratio and NH₃/CH₄ fuel composition.

Results highlight the beneficial effect of using NH₃/CH₄ fuel blends to extend the stable operational window of the system, with respect to the pure NH₃, in terms of both working temperatures and equivalence ratio. Nevertheless, fuel blends produce higher NO_x emissions than both the pure NH₃ and CH₄ cases.

In particular, the oxidation chemistry of the two fuel components can be assumed decoupled. On the contrary, NO_x emission levels depend on the NH₃/CH₄ ratio in a non-linear and, nevertheless, relevant way.

Chemical kinetics analysis highlighted that, as a result of its faster oxidation chemistry, methane boosts the production of OH radicals, thus sustaining the ammonia oxidation. At the same time, even at low ammonia percentages, OH produced along the CH₄ oxidation pathway, consumes NH₂ radicals, thus limiting the concentration of the DeNO_x agent and leading to higher NO_x emissions.

Wet Oxidative Scrubbing (WOS) for flue-gas cleaning enhanced by oxidative mechanisms under acidic condition

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Sustainable Technologies for Pollution Control (STPC-Lab)

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Abstract

For several applications, after-treatment processes are the only available options to comply with the recent regulations for SO_x and NO_x emission in land-based installations. These technologies commonly include dry-scrubber or wet-scrubber units for SO_x capture, and Selective Catalytic Reduction (SCR) or thermal Selective Non Catalytic Reduction (SNCR) units for NO_x control. Despite the efforts to improve these technologies and their mutual integration, the combined use of these units still requires high Capex and O&M costs, also having a large footprint for the plant installation.

In this work, we propose a promising technology for the simultaneous SO₂ and NO_x emission control as an alternative to traditional after-treatment systems. The process consists in a wet scrubbing by an aqueous solution doped with sodium chlorite (NaClO₂), which allows to simultaneously reduce SO₂ and NO_x emissions. The experiments were performed in a fully instrumented pilot-scale scrubber, having a DN 100, equipped with Mellapak 250.X structured packing with height of 892 mm. A simulated flue-gas stream with a constant gas flow rate of 32 m³/h (1.15 m/s) containing 500 ppm_v of SO₂ and 1030 ppm_v of NO_x at a temperature of 60 °C was used as a reference case. The scrubbing solution consisted of an aqueous solution containing NaClO₂ with a concentration ranging from 0 to 1% w/w, fed with a liquid-to-gas ratio between 1.25 - 4.06 L/m³ at 25 °C. Further experiments were carried out with 1% w/w NaClO₂ scrubbing solution with addition of HCl up to pH values of 6 and 3.

The experimental results showed that the scrubber is able to completely remove the SO₂ and to reduce NO_x emissions up to 65%. We found that SO₂ plays a synergistic role in the simultaneous absorption, improving the de-NO_x efficiency by about two times compared to the results achieved in our previous work. Although an excess of NaClO₂ was necessary to achieve higher removals for NO_x, we also found that a joint effect due to the acidification of the scrubbing solution at pH < 6 and the presence of SO₂ in the flue-gas allows activating faster reaction mechanisms by achieving a further improvement in the de-NO_x efficiency up to the complete removal. Finally, the experiments allowed determining the main oxidation pathway, while the acidic conditions significantly increased the oxidation rates of NO_x.

BIOGAS UPGRADING BY ADSORPTION ONTO ACTIVATED CARBON AND CARBON MOLECULAR SIEVES: EXPERIMENTAL AND MODELING STUDY IN BINARY CO₂/CH₄ MIXTURE

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Abstract

Biomethane (BM), a renewable form of natural gas, can be produced by biogas upgrading and its utilization is promoted to mitigate CO₂ emissions. In Italy, the production of BM with purity levels suitable to the input in national gas lines has been recently supported by an incentivization program, which allows achieving significant economic benefits for those companies that started or converted to this activity their core business. In this work, biogas upgrading via adsorption on commercial carbonaceous adsorbents, an activated carbon (AC) provided by Desotec and two carbon molecular sieves (CMSs) produced by Carbotech and Xintao, is experimentally investigated in a fixed-bed column, testing CO₂/CH₄ mixtures at different concentrations as feed gas.

The experimental campaign highlights that AC has a higher adsorption capacity for both CO₂ and CH₄, as well as better kinetic performances (i.e. higher bed usage efficiency and lower desorption times), than CMSs. On the other hand, the CMSs show a much lower CH₄ adsorption capacity than the AC due to their combined thermodynamic/kinetic sieving properties, which emerge from dynamic breakthrough curves and equilibrium adsorption data alike. Therefore, the CMSs show a much higher selectivity for the separation of the CO₂/CH₄ mixture, and Xintao sample shows a better overall performance thanks to its faster kinetics; moreover, experimental cyclic adsorption/desorption runs on Xintao confirmed its complete regenerability.

Breakthrough curves modelling, performed in MATLAB environment and aimed at evaluating the CO₂ mass transfer coefficients, points out that intraparticle diffusion is the rate-limiting step for CO₂ adsorption process. It can be concluded that CMSs show better performances for biogas upgrading due to their high selectivity and despite their lower CO₂ adsorption capacity, which cannot be taken as the main controlling parameter in the adsorbent selection devoted to this specific application.

THERMOGRAVIMETRIC AND CHEMICO- PHYSICAL ANALYSES OF SOOT OXIDATION

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Abstract

Carbon particles are widely distributed in the atmospheric aerosol as they mainly originate from a large variety of combustion sources emitting from micrometer sized soot aggregates down to ultrafine nanosized particles. Carbon particulate affects Earth's energy balance by scattering and absorbing radiation and by modifying the amount and properties of clouds, consequently causing climate changes. Moreover, nanometric particles have harmful impact on human health, thus the control of their emission is fundamental to limit their detrimental effects.

Internal combustion engines are a significant emission source of carbon particles, especially as regards road vehicles for which particle filters are required to meet the limit of number and mass particles established by environmental regulations. Soot oxidation is the process at the basis of the regeneration of the particulate filters. This work aims at getting insights into the structural evolution of soot during its oxidation through an experimental study combining thermal analysis and chemico-physical characterization. Soot was collected from a laminar premixed flame and subjected to thermogravimetric analysis to extract its kinetic parameters. The activation energy of soot sample was found to be within the range of values typically found for carbon black and soot. A programmed thermogravimetric analysis was performed and stopped at different values of mass loss in order to obtain samples, which are representative of different advancements of soot oxidation, starting from the raw unoxidized soot: at the beginning (M70, 70% mass remaining after oxidation), in the middle (M50, 50% mass remaining) and almost at the end of soot oxidation (M20, 20% mass remaining). Raman spectroscopy allowed studying the nanostructure of partially oxidized soot samples. The Raman analysis showed that the more amorphous soot fraction burns first, thereafter soot does not undergo any significant change in the aromatic layers composing its turbostratic structure. The specific surface area was evaluated through the Brunauer–Emmett–Teller (BET) method for raw soot and partially oxidized soot (M70) showing a remarkable increase of the surface area after the oxidation process. This indicates that oxidation, after having preferentially removed the organic part, behaves in a non-preferential way towards the soot particle, suggesting the occurrence of internal burning of the particles.

Soot formation in OMEn doped premixed flames

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Abstract

Reducing and controlling particulate matter is still a main issue despite the growing share of electrified and hybrid vehicles for transportation. In fact, for the large production of energy and for hard-to-decarbonize sectors, the presence of traditional and innovative fuels is far to be excluded. For its potential use of chemical storage for hydrogen oxymethylene ethers (OMEs) represent a foreseeable option for the forthcoming future. However, to satisfy the present and the future regulation in terms of pollutant emissions and their impact on human health, systematic studies on OME combustion behavior are mandatory.

To analyze particle formation, OMEs were burned in premixed flames as dopant up to 20% in terms of total carbon fed to the flame. The reference fuel used was ethylene, which well represents the paraffinic fuel behavior. An array of in situ and ex situ techniques have been adopted, including Particle size distribution (PSD) and Laser-Induced Fluorescence (LIF) and Incandescence (LII) along with numerical (Conditional Quadrature Method of Moments – CQMOM, based on D'Anna physico-chemical soot model) investigations.

The experimental technique suggested that OME has a significant impact in reducing large soot aggregate formation, not so much for particles with sizes smaller than 7 nm. The numerical analysis, in agreement with experimental data, evidences an important role of OME in more complete oxidation pathways that subtract carbon from the soot precursor formation pathways. However, large soot aggregate formation is mainly affected by the reduced formation pathways due to the general reduced formation and growth processes. The small particles are still formed and since they are not able to fast move to larger aggregates are present in a significant amount at the flame exhaust. This behavior has been found for all the OME investigated and can be assimilated to other oxygenated fuels.

PRELIMINARY RESULTS ON THE EFFECT OF LASER HEATING ON CARBON NANOPARTICLES SAMPLED FROM A PREMIXED FLAME

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Abstract

Carbon nanoparticles produced as by-product of combustion processes are actually considered an interesting resource to be employed in different applications, spanning from gas sensing to electronics. This interest is due to the peculiar properties of the nanoparticles sampled from flames at first stages of their formation. By changing the experimental conditions of the flame or simply the sampling height of the particles from flame, it is possible to tailor nanoparticles with specific property. In this context, following our previous studies on the effect of laser irradiation on carbon nanoparticles, laser heating of nanoparticles is suggested as an interesting tool to change and control their optical properties.

In this work we investigate the effect of laser heating on carbon nanoparticles produced in a premixed flame. Particles are sampled from flame and irradiated on-line by using the fundamental beam of a pulsed Nd:YAG laser. On-line wavelength-resolved extinction measurements are carried out in the visible range on pristine and laser heated nanoparticles. To this purpose a laser heating unit is employed consisting in a tube where the nanoparticles are sent in line with the extinction measuring section. The aerosol sampling flow rate and laser frequency are adjusted in order to heat the particles by a single shot. Particles are then collected on filters for Raman spectroscopy. By coupling our results information on optical properties, and in particular optical band gap, and particle nanostructures are obtained and discussed.

The authors would like to acknowledge the financial support from the PRIN project 2017PJ5XXX: "Modeling and Analysis of carbon nanoparticles for innovative applications Generated directly and Collected During combustion (MAGIC DUST)".

THERMO-OPTICAL-TRANSMISSION OC/EC AND RAMAN SPECTROSCOPY ANALYSES OF FLAME-GENERATED CARBONACEOUS NANOPARTICLES

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Abstract

Soot nanoparticles produced under different operating conditions have been analysed using two different techniques, one to determine the different contributions of total carbon, i.e. thermo-optical-transmission analysis and another to characterize the particle carbon structure, i.e., Raman spectroscopy analysis. Particularly the first analysis allowed dividing the total carbon into three different fractions: organic, pyrolytic and elemental carbon.

Once the amounts of organic carbon and elemental carbon were calculated it was also possible to evaluate the mass absorption coefficient, in fact, various studies have shown a correlation with OC/EC fraction.

The goal is to determine if and how combined TOT and optical/spectroscopic measurements allow monitoring nanoparticles formed under "clean-like" combustion conditions and differentiate them from those produced in sooting flames with the perspective to improve the carbon balance in the atmosphere and to consolidate source apportionment.

The study has included an analysis of four samples: two samples of young and mature particles belong to the nucleation particles, namely particles with a size of the order of 2-4 nm and other two soot samples, belong to the category of the so-called primary or grown soot particles.

The results show that the amount of EC is higher for mature than young soot while the amount of OC has an opposite behaviour indicating a similar trend in the graphitization order of the different soot particles. This observation was also confirmed by the Raman spectroscopy analysis.

3D PRINTED COMPOSITE ZEOLITE CATALYSTS FOR THE SCR OF NO_x

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Abstract

NO_x removal from emission of diesel engines by Selective Catalytic Reduction (SCR) requires catalysts which, in addition to high catalytic performances, must have good thermal and mechanical properties. They should operate in a wide temperature window, to cope with cold start phases as well as high temperature regeneration treatments for the upstream particulate filters. Zeolites, such as ZSM-5, are very active in a wide temperature range when exchanged with copper or iron. Unfortunately, ZSM-5 cannot be produced in bulky structured monolith reactor because of their scarce adhesion properties; therefore, they are typically applied at limited loadings as a washcoat on preformed (inert) honeycomb monoliths.

In this work, a ZSM-5 (up to 60% by weight) was incorporated in a geopolymer matrix and directly formed as a structured monolith by an additive manufacturing method (Direct Ink Writing).

The monoliths were suitably pre-treated to remove alkaline residues and subsequently ion-exchanged with a copper solution. The geopolymer, an amorphous low cost analogue of zeolite, provided a good mechanical resistance and a hierarchical porous structure (from macro to micropores) which enhanced the intrinsic catalytic activity of the Cu-ZSM-5 phase. On the other hand, the geopolymer matrix did not affect the crystalline and porous structure of the zeolite as well as the intrinsic catalytic behavior of the copper sites in the zeolite.

A deep characterization (XRD, SEM, BET and pore size distribution, compressive strength, ICP-MS, H₂-TPR and NH₃-TPD and NH₃-SCR testing) was carried out in order to investigate the improved catalytic performance with respect to a pure Cu-ZSM-5 monolith previously developed.

APPLICATION OF ATOMIC FORCE MICROSCOPY NANOINDENTATION FOR THE MECHANICAL CHARACTERIZATION OF SOOT NANOPARTICLES

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Abstract

In this work, we report an experimental characterization of the nanomechanical properties of flame-formed carbon nanoparticles performed for the first time using the atomic force microscopy (AFM) nanoindentation technique. Layers of soot particles with different size and nanostructure were produced in atmospheric laminar flames of ethylene and air and collected by thermophoresis on mica substrates. Atomic force microscopy was used to image the topology of the samples in semicontact mode. Then, force-distance curves were acquired by measuring the tip-sample interaction forces in contact spectroscopy mode. The instrument was operated so that the tip of the AFM probe acted as a nanoindenter and the maximum applied force was derived from the force curves. The hardness of the sample was determined from the maximum applied force in combination with semicontact atomic force microscopy images of the indents performed on the sample surface. Also, the Young's modulus of the sample was measured by fitting the linear part of the retraction force curves. AFM nanoindentation showed the potential to furnish information on the layer properties, as well as on the nanostructure and composition of particles composing the layers when in combination with a numerical simulation analysis.

THE EFFECT OF KEROSENE ADDITION ON PARTICLE FORMATION IN ETHYLENE PREMIXED FLAMES

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Abstract

This work reports a characterization of lab-scale laminar flames of kerosene and ethylene in terms of carbon nanoparticle emissions. To this aim, particle size distribution functions (PSDs) were measured in atmospheric pressure, laminar premixed ethylene/air flames at different equivalence ratios, from the onset of soot particles formation up to heavily sooting conditions. The flames so produced constituted the reference cases for studying the effect of kerosene on carbon particulate matter formation. In order to have a direct comparison with PSDs measured in pure ethylene flame, kerosene/ethylene mixture containing 20% of total carbon fed as kerosene were burned keeping constant the equivalence ratio, the cold gas velocity and the total carbon flow rate fed to the premixed burner with respect to ethylene pure flames. The temperature profiles of pure ethylene and kerosene/ethylene flames are quite similar and thus the difference found in particle formation can be attributed mostly to the fuel formulation.

The results showed that the number of particles with size greater than 10 nm, which are responsible of the total volume of particles emitted, is similar for ethylene and kerosene/ethylene flames in the same conditions. On the other hand, the addition of kerosene resulted in a reduction of the number of particles produced with diameter lower than 10 nm. This can be likely attributed to the presence of a small, but not negligible, percentage of aromatic compounds in the kerosene composition.

The present study was conducted as a part of the Horizon 2020/Clean Sky JU project "LEAFINNOX", whose aim is the development of a novel low-NO_x and low-emission "Lean Azimuthal Flame (LEAF)" combustor burning aviation kerosene. The experimental results herein obtained represent a useful database for the development and validation of new kinetic schemes for kerosene combustion in the LEAF combustor.

THE EFFECT OF POLLUTANTS ON WATER DROPLETS EVAPORATION

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Abstract

In front of the recent sanitary emergency, due to the Covid-19 pandemic, great emphasis has been placed on the determination of a possible correlation between air pollution and respiratory viral infections. During respiratory events, a bioaerosol of droplets, made mostly by water, is produced; these droplets can interact with air pollutants, enhancing their lifetime and hindering their natural evaporation process. In this study, the evaporation rate of water droplets has been evaluated in terms of particle size distribution at different residence times. Exhausts emitted by internal combustion engines were bubbled in demineralized water; the resulting solutions, after an absorption spectra analysis, were aerosolized and sent to a specially designed flow reactor to estimate droplets evaporation rates in polluted environments. Subsequently, diluted exhausts from selected vehicles were sent directly to the reactor along with an aerosol of demineralized water droplets. Using demineralized water solution as reference, the first results showed in both cases an important delay in the evaporation process after 4 seconds; the strongest effect was detected when the emissions directly invested the water droplets. According to the experimental results, average evaporation rate constants were evaluated following the classical d^2 law and corrective factors were estimated to apply the law in the case of a polluted environment. The study indicated that in the presence of combustion related products an increase of water droplets lifetime can be observed; in particular, for the system of diesel engine emissions and water droplets the effect of the presence of pollutants can be detected after 1 second and a global delay of 2 seconds in the evaporative process is observed compared to the reference.

Peculiarities of Pyrometry in Particulate-Generating Flames

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Abstract

The pyrometry technique is a powerful diagnostic tool widely used in combustion to retrieve information on concentration and temperature of emitting particles. Thanks to the use of minimal optical access, fast and cheap qualitative and quantitative measurements can be carried out with high temporal and spatial resolution. It is widely applied to characterize carbon particles produced in hydrocarbon flames as well as nanoxide in synthesis flame.

The technique is essentially based on the detection of light emission from particles in flame, assumed to be in equilibrium with the gas and at a uniform temperature in the probe volume.

In this work, a synthesis flame is considered and the evidence of non-isothermality is proved, that means the coexistence of hot and cold particles in the probe volume. This coexistence strongly affects pyrometry measurements, both in terms of the effective temperature of the system under analysis and in terms of the concentration of the emitting particles.

The non-isothermality is evidenced by comparing light emission from titania nanoparticles produced in a flame spray with that obtained irradiating the flame with a pulsed laser. In order to interpret the experimental results, a thought experiment is performed to model the possible occurrence in the probe volume of different percentages of particles with varying temperature. The results here presented are also discussed considering the implications of the pyrometry measurements to measure carbon particles in hydrocarbon flames.

SESSION V

NOVEL CONCEPTS AND TECHNOLOGIES

OVERVIEW FOR RETROFITTING COAL POWER PLANTS BY IRON

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Abstract

Metals are being investigated as alternative energy carriers for green energy production. Some of them are combustible, generating thermal energy when oxidised, similarly to traditional solid fuels. Due to their high energy density, stability and abundance, they present optimal capabilities to transport and store energy generated from renewable sources. Among them, iron is being considered an ideal solution, due to its abundance, low toxicity, low price and existing production infrastructure and transport network. Electricity from solar, wind or other sources can be used in green reduction processes, generating particles that can be burned in retrofitted coal power plants, making use of existing infrastructure and rapidly substituting the fossil fuel. Oxides formed in the process can then be recycled, in what can be called "clean circles". The present work evaluates the feasibility of this solution, giving an overview of the technological, logistic and economic challenges, the resources and possibilities in light of the different scenarios in terms of climate change and advancements in green iron and energy production, focusing on the present and future scenarios for Germany, Europe and the World. The data employed for this investigation was obtained from reliable and updated sources, including the International Energy Agency (IEA), the British Petrol energy outlook, global energy monitor, the European hydrogen roadmap, the intergovernmental panel on climate change, among others. The assumptions, estimations and projections were done using a combination of the quantitative data for demands and production of raw materials and products, and technical information on the properties of both coal and iron as fuels. The required efforts to develop and operate this retrofitting are aligned with the current European plans for a rapid energy matrix transition, including the role of H₂ as an intermediate carrier in this process, and offers a solution that takes advantage of existing infrastructure. The obtained projections reveal a challenging but feasible alternative, which would support the transition to a sustainable economy, also establishing valuable and durable assets that increase energy security.

Performance of Modeling Paradigms for the Simulation of a Cyclonic Burner

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Abstract

The design and development of MILD Combustion systems in different fields and applications is hampered by a lack of knowledge of such oxidation mode; therefore new tools are required when compared to conventional combustion systems. In fact, when MILD combustion is used, reactants are diluted with large amounts of burnt products prior ignition, enabling therefore the stabilization of autoignition kernels under peculiar conditions, thereby avoiding high-temperature regions that promote pollutants formation. On the basis of this scenario, computational fluid dynamics (CFD) for the design, prediction and optimization of the burner and combustion chamber behavior, is a key step for the beneficial introduction of these novel concepts in the energy conversion field. More specifically, there is a pronounced sensitivity to the reaction chemistry in the modeling of diluted reactive structure and thus detailed chemical kinetics are needed.

In order to include detailed chemistry in fluid-dynamics simulations, two different combustion paradigms are used, namely the Eddy Dissipation Concept (EDC) and the Flamelet Generated Manifold (FGM). In particular, the present study investigates the combustion characteristics of MILD Combustion in a cyclonic lab-scale burner, mimicking locally diluted and preheated conditions of the reactants. The numerical computations are performed incorporating turbulent combustion models in RANS simulations to determine the effect of several parameters on models performance.

An assessment of models is carried out on the basis of an experimental/numerical comparison by evaluating several variables of interest such as temperature, major species composition and pollutants. Results suggest that both the paradigms represent promising tools for modeling the complex flame structures of the cyclonic MILD burner, although in several conditions they exhibits some aspects that need to be further investigated.

Using Data science for Combustion Processes Modeling, Monitoring and Control

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Abstract

Continuous developments in information and communications technology (ICT) have enabled the transition from an industrial society to an information society. The widespread diffusion of Big Data is increasing in many fields of science and technology, where data are generated, stored, and still grow in the cyber space.

In the combustion process domain, the variety of fuels and the associated measurable quantities can be considered typical sources of Big Data, due to the huge amount and large heterogeneity of data generated over time. In relation to this last, it is quite possible to imagine the basis of the existence of big data on combustion based on the experimental data and reaction models, which are traditionally available through books, published papers and online databases.

The aim of this work is to define a valid and general adaptation of the Big Data philosophy to the Combustion domain trying to outline criteria to identify, collect, organize, evaluate, manage Big Data of Combustion Processes (henceforth referred to as BDCPs). The expectation is the possibility to create an appropriate methodology for modeling large volumes of complex and varied real-time and non-real-time combustion data. Moreover, looking far into the future, this approach could allow the implementation of effective monitoring and control strategies aimed at improving the overall efficiency and sustainability of any experimental process projected to be sustainable in industrial applications.

Finally, with this in mind, the modeling of BDCPs presented is also intended to propose in its statement a simple, unabbreviated, no-nonsense nomenclature that is practical and effective.

In this sense, the conceptualization and schematization of BDCPs realized in this work wants to be the concretization of a guideline for constitution of a robust and effective model for Big Data on combustion in their generality and vastness.

Uncertainty quantification in RANS of LOX-CH₄ pintle injector

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**AVIO SpA

Abstract

This work presents the numerical characterization under uncertainty of a pintle-injector liquid rocket engine thrust chamber, fueled with LOX-CH₄, and operated at subcritical pressure. Being the design optimization the ultimate goal of this effort, the numerical characterization is carried out employing a Eulerian-Lagrangian Reynolds-averaged Navier Stokes equations approach within the OpenFOAM CFD toolbox. The numerical model of choice, as well as the rich variety of physical phenomena taking place in such a device, require the knowledge of a large number of model parameters, many of which are challenging to be calibrated under the severe thermophysical conditions of interest. A possible way to overcome this lack of knowledge is to resort to the Uncertainty Quantification (UQ) framework to estimate the effects of model and parameter uncertainties on the solution accuracy. In particular, this research aims at propagating the uncertainty associated with the most probable diameter d_0 which characterizes the injection Rosin-Rammler distribution for the liquid droplets, employing a Polynomial Chaos Expansion (PCE) representation of the uncertainty. The pintle configuration consists of a horizontal gaseous methane inflow and a vertical LOX spray injection. A set of RANS are conducted to generate the PCEs surrogate model for the estimation of the probability distribution of the quantities of interest, as well as the visualization of their credibility intervals. Lastly, to assess whether the uncertainty on d_0 can overshadow the sensitivity to the pintle design, the same study is performed for two geometries, which differ in the so-called skip length, i.e., the distance between the annulus final section and the fuel-oxidizer impingement location. The results provided by the UQ analysis show how the temperature axial distribution in proximity of the pintle head and the extension of the core recirculation region, although affected by input parametric uncertainty, remain distinct for the two configurations. On the other hand, the confidence intervals associated with the radial temperature distribution in correspondence of the chamber region mainly occupied by evaporated LOX almost overlap. Provided these considerations, the present work still has to be intended as a preliminary feasibility study which paves the way for further investigations, aimed at including parametric uncertainty deriving from different models.

Numerical Model of Thermally-Induced Secondary Atomization

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Abstract

This study presents computational simulations of multi-component and multiphase flows to reproduce the physical phenomena in the secondary atomization of a droplet induced by a hot temperature environment. The computational fluid dynamics (CFD) model is based on the geometric volume-of-fluid (VOF) method, with piecewise linear interface calculation (PLIC) reconstruction for accurate determination of the curvature and phase-change fluxes at the interface. The purpose of the model was to faithfully reproduce complex physical processes, such as internal gas cavity formation, liquid-vapor interface instability, cavity collapse and liquid jet ejection, and the pinch-off of a secondary droplet, leading to the micro-explosion phenomenon that greatly enhances the evaporation rate of non-volatile liquid droplets. The solver was validated against the analytical solution in benchmark cases, and experimental data with bi-component droplets reported in the literature. The model was used to predict the atomization of vegetable oil and jet A-1 blends exposed to high temperatures under microgravity conditions. The choice was dictated by the availability of experimental observations on such blends. Different atomization regimes were identified, depending on the initial size of the internal bubbles. While small bubbles led to simple gas ejections, cavity collapse caused the larger bubbles to produce a jet formation. When the ratio between the bubble and droplet volumes was bigger than 0.35, micro-explosions occurred. The results were found to be consistent with cases of bubble burst on flat surfaces, showing a strong dependence on the Ohnesorge number (Oh). Key observable quantities, particularly jet velocity and bubble cap drainage velocity, were found to agree with correlations reported in studies. The similarities were also supported by studies extending over a wide range of simulations (4000 cases) at different Oh . An inversion in the dependence of the jet velocity on Oh (above a critical value Oh_c) was observed.

Cyclic CO₂ capture and methanation over alkali promoted Ru catalysts

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Abstract

Conversion of CO₂ captured from point emission sources (or air) into added-value chemicals and fuels can represent a smart solution for decreasing CO₂ emissions. One of these processes is based on the reaction of CO₂ with hydrogen from renewable sources to produce methane that can be used as synthetic substitute of natural gas (SNG). Recent studies have investigated the development of dual functional materials (DFM) containing both a sorbent and a catalytic active component that can capture CO₂ from a flue gas until saturation and subsequently convert it at the same temperature using H₂ from renewable sources to produce SNG while regenerating for the next cycle.

In this work we set out to investigate the effect of three different alkali metals (Li, Na and K) added by impregnation to a 1% Ru/Al₂O₃ methanation catalyst to develop a CO₂ storage capacity. A commercial γ -alumina shaped in the form of spheres (diameter 1mm) with high mechanical and abrasion resistance was employed as a support: this makes the dual functional catalysts potentially suitable for operation in a chemical looping process for CO₂ capture and utilization (CCU) utilizing either fixed or fluidized bed reactors.

Notably, stable and repeatable cyclic CO₂ capture and hydrogenation to pure methane were achieved operating a highly active Li-Ru/Al system at as low as 230 °C, that is 70-90 °C below the optimal temperature level previously reported for cyclic operation of similar Dual Functional Materials with much higher (5% wt.) Ru metal loadings.

Reactive Volume of Fluid Model for the Simulation of the Evaporation and Combustion of FPBO surrogate components

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Abstract

Fast Pyrolysis bio-oils are black-brownish liquids obtained by the condensation of vapors during the fast pyrolysis of wood and other vegetable biomasses [1]. FPBO are complex mixtures of hundreds of components that can be described by surrogate models. Like other liquid fuels, bio-oils are introduced into the combustor as sprays of droplets, whose behavior determines the combustor performances. Detailed CFD simulations of isolated droplets are a valuable tool which, by neglecting the interactions between droplets (breakup, coalescence, and fragmentation), allow to focus on the processes of vaporization, ignition, and combustion. Furthermore, they are useful to obtain sub-grid models that can be used for the multiscale simulations of sprays. However, detailed CFD simulations of droplet combustion are hindered by several numerical challenges, such as the chemical complexity and the calculation of the vaporization rate and the thermodynamic equilibrium at the interface. These issues were partially addressed in DropletSMOKE++ [2], a gas-liquid multiphase solver developed at Politecnico di Milano and based on the volume of fluid (VOF) methodology. In the present work, DropletSMOKE++ was extended by including gas-phase reactions and a novel model to characterize the interface phase change condition. The resulting model was used to simulate the vaporization, auto-ignition, and combustion of FPBO surrogate components. Simulations were performed with single and bicomponent isolated droplets suspended on a fiber in normal gravity conditions. The results were compared with experimental data, obtaining good agreement in terms of vaporization rate and ignition time. These encouraging results pave the way for the application of this model to the analysis of more complex liquid fuels like real bio-oils.

[1] Calabria, R., et al. "Combustion fundamentals of pyrolysis oil based fuels." *Experimental Thermal and Fluid Science* 31.5 (2007): 413-420.

[2] Saufi A.E., et al. "DropletSMOKE++: A comprehensive multiphase CFD framework for the evaporation of multidimensional fuel droplets", *International Journal of Heat and Mass Transfer* 131 (2019): 836-853.

DEVELOPMENT OF A SMALL-SCALE BIOFUEL PROCESSOR: MODELLING OF AUTOHERMAL ETHANOL REFORMING

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Abstract

On-board production of H₂ from liquid fuels represents a valuable solution to enhance the vehicle energy efficiency and solves the several issues (safety, energy density) related to hydrogen storage. In view of zero-emission strategies, bio-ethanol represents a promising model fuel as its combustion does not increase the net amount of greenhouse gas emissions. Catalytic partial Oxidation (CPO) on Rh-catalysts is an attractive technology for the on-board H₂ production. Because of the high exothermicity of the process, the reaction can be conveniently carried out in adiabatic reactors of compact size and fast response to variable loads.

In this work, a preexisting reactor model [1] was extended to describe ethanol/O₂ reacting system and validated by the simulation of experimental steady-state data of ethanol CPO in a lab-scale autothermal reformer.

Ethanol CPO tests were accomplished at atmospheric pressure and high flow rate by applying spatially resolved sampling technique to acquire temperature and concentration profiles along the axis of the reactor. To simulate the reactor behaviour, both heterogeneous and homogeneous chemistry were introduced in the 1D, dynamic, single channel, adiabatic model.

A heterogeneous scheme including total oxidation, oxidative decomposition and steam reforming of ethanol was derived from experimental data collected in an *ad hoc* annular reactor in LCCP group laboratories. In order to limit high computational costs related to large number of species and reactions, a detailed homogeneous mechanism was reduced with tools developed by CRECK Modeling group by coupling Directed Relation Graph with Error Propagation (DRGEP) to sensitivity Analysis on species. Ideal-reactor simulations of a set of experimental data validated the reduced scheme obtained in this way.

The modelling results revealed the important role of gas-solid mass transfer limitations which govern the rate of O₂ consumption and the growth of a hot-spot at the reactor entrance. Here, gas-phase reactions also contribute to ethanol conversion with the formation of C₂ species, such as acetaldehyde and ethylene, which are undesired coke precursors.

[1] M. Maestri et al., "Comparison among structured and packed-bed reactors for the catalytic partial oxidation of CH₄ at short contact times," *Catal. Today*, vol. 105, no. 3-4, pp. 709-717, 2005

PERFORMANCE OF DIFFERENT SORBENTS FOR CARBON CAPTURE AND THERMOCHEMICAL ENERGY STORAGE SYSTEMS

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Abstract

In the recent decades, the integration of a Calcium Looping (CaL) cycle with a Concentrated Solar Power (CSP) system has emerged as a means of reducing the high amount of CO₂ from fossil fuels and as a technology that allows to use a renewable source for energy production. The aim of this study is to investigate the performance of two different sorbents for Carbon Capture and Storage (CCS) applications or for ThermoChemical Energy Storage (TCES) purposes. Calcination/carbonation cycles were performed in a Fluidized Bed (FB) reactor directly irradiated by a simulator of concentrated solar radiation. Results indicate that dolomite, vs. limestone, is the sorbent with the highest CO₂ capture and energy storage values. On the other hand, dolomite is more friable and leads to production of elutriates during the process.

SIMULATION OF FLUIDIZED BED SORPTION- ENHANCED METHANATION

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Abstract

Methane is a crucial energy carrier with a massive use in all sectors and a well-developed distribution and storage infrastructure. In the framework of the efforts made to address the energy transition, it is of great interest the replacement of fossil methane by its synthetic alternative, the Substitute Natural Gas, coming from renewable sources. The reactants (CO/CO₂ and H₂) for catalytic methanation can be obtained from different pathways involving renewable sources: they could derive, for example, from biomass-produced syngas or from generated H₂, exploiting the surplus of renewable electricity to perform water electrolysis, and CO₂, which can be a pure captured stream, thus giving a Carbon Capture and Utilization solution. The studies on catalytic methanation have recently been developed with the concept of sorption-enhanced reaction, using a proper sorbent material to adsorb the water produced by the reactions, in order to enhance the equilibrium conditions even at low pressures.

The aim of this work was to analyze the Sorption Enhanced Methanation (SEM) in a Dual Fluidized Bed system at 300°C and 1 atm, by selecting CaO as water sorbent and using as simulator Aspen Plus®V10 software. The process was mainly analyzed under stoichiometric conditions, introducing dimensionless parameters to consider different relative quantities of CO and CO₂ fed, and different amounts of CaO compared to the stoichiometric one to capture all the generated H₂O. The purity of the methane is a sensitive aspect to assess, given the restrictions for injection in the grid, in particular with regard to the percentage of admissible H₂. SEM results on the outlet composition showed that H₂ on dry basis was never low enough to be fed directly into the grid. The undesired carbonation of CaO was found to be the main reason for this behavior. This secondary reaction seems to be able, by absorbing CO₂, to shift the equilibrium of important involved reactions towards the consumption of the methane itself, and the production of H₂. To fulfill the limits for injection, another kind of sorbent, not subject to carbonation and already being studied, may be selected, e.g. a zeolite, acting as molecular sieve and giving water selective adsorption. Another interesting condition to be verified may be to evaluate non-stoichiometric conditions, and in particular when H₂ is the limiting reactant.

ENHANCEMENT OF CARBON NANOPARTICLES FILMS FLAME SYNTHESIS WITH ELECTRIC FIELD

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Abstract

Carbon nanoparticles (CNPs) are receiving the attention of both academic and industrial worlds due to their properties, thanks to which CNPs can be applied in the fields of bioimaging, nanomedicine, electrocatalysis, energy storage and chemical sensing. Typically, CNPs collection during flame synthesis is mostly based on thermophoretic deposition: films of CNPs are deposited on the cold collector immersed in a controlled flame under a specific set of conditions. The film properties change by controlling flame conditions and deposition parameters. A portion of the CNPs moving along the flame carries electric charges so that the application of an electric potential to the collector could enhance the CNPs capture process and modify film properties by a combination of thermophoresis and electrophoresis.

This work, as part of the PRIN 2017 project "MAGIC DUST", presents preliminary findings on the application of electric fields to the flame synthesis of CNPs films. Experiments have been performed with a CNPs deposition system consisting of an ethylene/air premixed laminar flame with C/O ratio equal to 0.67 stabilized on a McKenna burner and equipped with an upgraded collector kept at fixed electric potential, spanned from -3 to +3kV, to activate the electrophoretic deposition. The cold collector consists in a circular mica substrate inserted in flame with a residence time of 100 ms one time at a height over the burner of 12 mm. Particle deposition on the mica collector has been analysed by Atomic Force Microscopy. To predict deposition efficiencies as a function of size and charge of the particles and the applied voltage, a dedicated particle deposition model has been developed and numerical simulations have been carried out. Both experiments and model results show that the electric field enhances the deposition process (up to five times) leading also to a change in the morphology of the CNPs deposits. By adding the electric field the deposits passed from compact to petal-like fractal islands.

A SUSTAINABLE ROUTE FOR HYDROGEN PRODUCTION: SOLAR – DRIVEN SYSTEM BASED ON A NANOCOMPOSITE PHOTOCATALYST

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Abstract

Global warming, greenhouse effect and acid rains are only some examples of the environmental problems related to the use of the fossil fuels, which nowadays represent the traditional, non-renewable, and exhaustive energy sources. Hydrogen, as stable and clean alternative energy carrier, has aroused great interest in the recent years: hydrogen powered internal combustion engines could promote infrastructure for fuel cell cars, and automakers such as Ford, Toyota or BMW have been planning to introduce hydrogen ICE cars to obtain very low emissions of air pollutants. However, the high costs of the production methods and the problems related to H₂ storage limited this technology. As concerns hydrogen production processes, photoreforming of organics, photoelectrolysis and photocatalytic water splitting by using solar radiation have been widely studied and are considered some of the best technologies for a sustainable H₂ production. Despite TiO₂ still represents the most used photocatalyst due to its positive characteristics, the poor absorption in the visible light range makes necessary the association of the material with other semiconductors, such as Cu₂O, largely studied due to its narrow bandgap (about 2.1 eV). As a p-type semiconductor, and when combined with an n-type semiconductor, Cu₂O can form a heterojunction photocatalyst, extending the light absorption in the visible range and reducing of electron-hole recombination rate.

In the present work, the photocatalytic hydrogen production in presence of a Cu₂O – TiO₂ composite material prepared through mechanical mixing is evaluated. The photocatalytic experiments are carried out in an annular glass batch reactor, in which selected amounts of the composite material are suspended in a doubly distilled aqueous solution, containing a fixed concentration of methanol or glycerol as sacrificial species. The activity of the photocatalyst under solar radiation is evaluated, noticing a great influence of the temperature of the system, as well as of the radiation intensity, on the photocatalytic activity.