# Book of abstracts

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# Hydrogen combustion

# Designing Combustion Systems for the Use of Hydrogen in Domestic Fires

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Decarbonising the provision of heat in domestic properties is one of the biggest challenges posed by the need to transition to net zero CO2. Currently within the UK, most properties are heated by natural gas (NG) through a combination of central heating boilers and domestic gas fires that provide secondary heat in main living spaces. The fires provide a focal point to a room through the use of a living flame concept, and hence are designed to mimic coal or wood fires with radiating flames giving a colourful visual effect. The replacement of NG with 100 % hydrogen within the gas network is currently under discussion, and this poses many challenges for domestic appliances such as boilers, fires and cookers. When operating on hydrogen, the appliances must pass safety tests, must provide a visible and attractive flame where necessary (e.g. for fires and hobs) and they must at least match the emissions levels for NOx met by the current NG versions. Since hydrogen has a higher flame speed and flame temperature than NG and is of lower visibility, the current designs for appliances cannot be used with hydrogen. New design principles need to be developed that i) avoid the possibility of flame flash back, ii) lower flame temperatures in order to meet NOx emission requirements iii) provide sufficient flame visibility to make the fire as attractive as the NG equivalent appliance, iv) provide adequate shutdown and explosion venting procedures for the use of hydrogen given its flammability limits. A key question is also whether new designs could be developed that allow the use of either NG or hydrogen within the same design (a dual fuel design). Should this be possible, such appliances could be brought to market very quickly, thus easing the transition to hydrogen when the gas network becomes ready. This however poses additional challenges since the same strategies used for reducing NOx, may lead to CO quenching when using NG. The presentation will use a case study based on domestic gas fires to show how such a dual fuel design can be met using non-premixed burners for both fuels. The design must consider important properties such as quench distance, flame temperature and heat transfer mechanisms, NOx and CO emissions, flame visibility and appearance, ignition and shut-down procedures. The project is an excellent example of using combustion theory and design in meeting the societal challenge of transitioning to low carbon fuels. It is funded through the BEIS Hy4Heat programme that is currently exploring the feasibility of transitioning the domestic gas network to hydrogen. The presentation will cover general design principles for prototype fire designs and will discuss how these affect operational, flame visibility and emissions properties for each fuel.

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[*] Speaker

# Numerical study of a confined hydrogen-enriched premixed methane/air swirling flame using detailed chemistry

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The growing interest in hydrogen as a fuel for energy production and transportation demands specific scientific investigations. Hydrogen combustion is well known as the simplest possible fuel in terms of chemical kinetics and it has been used for decades by the space industry to fuel rocket engines. It is however much complex in terms of transport and mixing properties, and its very light weight raises issues for storage. Recently, interest has grown around the idea of adding hydrogen to hydrocarbons that are more commonly used in industry, with two objectives: 1) lower the carbon content of the exhaust gases and 2) sustain stable combustion in lean conditions. In ground-based gas turbines for example, hydrogen may be added to natural gas. The properties of this dual fuel then need to be studied.

In this work a confined turbulent Methane/Hydrogen/Air swirling premixed flame stabilized over a bluff-body [1] is studied with numerical simulation. Two levels of enrichment are considered: 1) 90% of hydrogen in mole (very high level) and 2) 60% of hydrogen in mole (high level). For both levels, Large Eddy Simulations (LES) are performed with either adiabatic or non-adiabatic boundary conditions to assess the impact of heat losses on the flame structure. The DTFLES approach is used for turbulent combustion modelling. Chemical kinetics are described with Analytically Reduced Chemistry (ARC) enabling an accurate insight on the chemical phenomena. It allows in particular to capture and explain the transition from V to M shape when increasing the hydrogen proportion. The specific species and reactions that are sensitive to the thermal boundary condition can also be identified with ARC. The simulation results are compared with measurements and with a previous numerical investigation using tabulated chemistry (F-TACLES) [1] that was deemed to not well predict the combined effect of local strain rate and heat losses. Direct comparison with experiment is also done using detailed OH* chemistry, calculated with two strategies: either OH* is calculated as a transported species, or it is calculated in a post-processing step from the other computed species. Finally, the prediction of NOx and its sensitivity to the various above-mentioned conditions is presented.

R. Mercier et al., " Experimental and Numerical Investigation of the Influence of Thermal Boundary Conditions on Premixed Swirling Flame Stabilization ", *Combustion and Flame* 171 (september 2016): 42-58, https://doi.org/10.1016/j.combustflame.2016.05.006.

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# On the dynamics of H2 – CH4 turbulent flames in bluff body burner

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The reduction of CO2 and NOx becomes an ever-increasing trend across the globe. The addition of hydrogen (H2) proves to be a favorable candidate in reducing such emissions. However, insights pertaining to the effect of H2 addition over the local interaction dynamics in the turbulent flames are limited. Hence, this study aims at investigating the effect of H2 addition in lab-scale bluff-body burner using time-resolved optical diagnostic tools. We have employed, PIV and chemiluminescence imaging (OH*)/ PLIF (OH) in simultaneous fashion to delineate the flame – flow interaction dynamics across various concentration levels of hydrogen in a CH4-H2 fuel mixture. The operating modes such as constant thermal power and momentum flux ratios are considered. Across the two modes, experiments are carried out with the different H2 volumetric concentration levels viz. 20 %, 50%, 80%, and 100 %.

In a global sense, reduction in flame length and increased levels of OH concentration are observed for the hydrogenated flames. Furthermore, a localized extinction event namely *hole* formation causes the intermittent ejection of flame pockets in the pure methane flame. However, the same phenomenon is ceased with H2 addition. This reveals hydrogenated flames exhibit higher strain resistance than methane flame. Finally, proper orthogonal decomposition (POD) is implemented over the instantaneous flow/scalar fields to capture the dominant flow structures associated with various operating modes.

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# Overview and recent progress in hydrogen fire and explosions at Warwick FIRE

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This presentation will provide an overview of the modelling approaches and recent progress for hydrogen fire and explosions at Warwick FIRE, a multidisciplinary research laboratory for both fundamental and applied research into fire and explosion hazards as well as accidental release of hazardous materials. It will start with a brief introduction to the potential hazards related to hydrogen. This will be followed by a description of our approaches to model spontaneous ignition in pressurised hydrogen release, jet fires, hydrogen deflagration, deflagration to detonation transition (DDT) and detonation. The materials from this presentation are mostly be drawn from published papers from Warwick FIRE but will also include some unpublished latest results about the ignition and combustion of cryogenic hydrogen jets.

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# Experimental investigation of conventional domestic burners fueled with increasing hydrogen content up to pure hydrogen operation

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The necessity to reduce the carbon footprint of energy production has sprung the development of renewable electricity production via windmills and photovoltaic panels. Because these sources are intermittent, long-term storage in the form of hydrogen via the electrolysis of water is seen as a promising technology.
The objective of this work is to use 'green H2' for heat production in domestic heaters. Because of the peculiar properties of hydrogen, its combustion characteristics are quite different from other fuels, e.g. flame speed, flammability limits, ignition energy, etc. It is therefore investigated how two existing burners, developed for pure methane combustion, can safely burn a mixture with increasing hydrogen content.

The burners, presented as B1 and B2 in Fig. 1, are characterized by different porosity, hole pattern and internal structure, providing versatility of results which are not restricted to unique and specific configuration. Since two fuels are simultaneously used, two parameters are needed to univocally defined the mixture: global equivalence ratio (Fg) and hydrogen power percentage (PH2), which fix the relative amount of hydrogen and methane in fuel. A methodical approach is used to generate constant power maps in which both burners are tested from pure methane to pure hydrogen combustion, following step of 10% in PH2. For each fuel blend a well-defined range of Fg is investigated.
Results exhibit the following trends: the increase of PH2 shifts blow-off towards leaner mixtures, while it simultaneously reduces the upper equivalent ratio achievable due to limit wall temperature or flashback occurrence. It is worth mentioning that both burners can be run with pure hydrogen, achieving flame stabilization at equivalence ratio well below 0.5. The burnt gas temperature is therefore quite low, which is notably favorable to limit NOx emissions.

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*Speaker

# $CO_2$ CAPTURE AND UTILIZATION

# RCM studies on CO2 utilization by dry reforming

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The conversion of carbon dioxide (CO2) and methane (CH4) to syngas under internal combustion engine (ICE) conditions is studied in a Rapid Compression Machine (RCM). The conversion (dry reforming) according to the overall reaction
CO2 + CH4 $\leftrightarrow$2 CO + 2 H2

has to overcome large activation energies, since CO2 and CH4 are quite stable species at ambient conditions. We present a methodology that allows reaching high temperatures in an ICE environment, and thus, to overcome the activation energy. A key factor is the selection of a suitable initial mixture composition, which can be determined by an optimization procedure, involving numerical simulations. Experimental studies in an RCM show CO2 conversion levels of up to 50 %. Thermodynamic analysis shows that this operation, besides converting CO2 and producing syngas, can also deliver a net output of mechanical work.

Experiments with CO2/CH4 mixtures are conducted in an RCM, which is a piston-cylinder device that rapidly compresses a gas mixture in a near adiabatic fashion. At top dead center, the piston is stopped, granting isochoric conditions for the cylinder load. The operation is therefore similar to that of a piston engine; however, the RCM offers better defined initial conditions with respect to temperature, mixture composition and flow field.

To initiate reaction among the quite unreactive species CO2 and CH4, several measures are taken, including dilution by Argon to increase the heat capacity ratio of the mixture, and adding small amounts of DME as a reaction enhancer and oxygen to allowing exothermal reactions to run in parallel to the CO2 dry reforming process.

The achievable conversion depends on the initial conditions, and in particular, on the initial composition. Without addition of oxidizer, the temperature levels remain too low for significant conversion. Too much oxidizer, while providing sufficiently high temperatures for reaction, will cause some of the formed CO and H2 to be oxidized to CO2 and water (H2O), thus diminishing conversion.

In previous work [1] we show an optimization of this conversion processes with the aim to maximize the CO2 conversion $C$, defined as

$C = 1 - n1/n0 = 1 - m1/m0.$

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Here, $n$ denotes the amount of substance and $m$ the mass in the system for the species CO2. Indices 0 and 1 refer to the state before and after reaction, respectively.

In an attempt to maximize the conversion, an optimization procedure was applied which involves joint experiment and numerical simulations. The optimization treated the initial mixture composition as an independent variable, and the conversion $C$ (for given compression ratio and initial temperature and pressure) was the objective function. CO2 mole fractions in the initial mixture were varied between 10 mol-% to 50 mol-% in the total mixture, which included also CH4, Ar, O2, and DME. We found conversions up to $C$= 51% with an initial CO2 mole fraction $X$CO2,0 $\approx$ 20 mol–% and an overall initial fuel-air equivalence ratio (including CH4, DME and O2) of  = 2.8. Both, the initial CO2 mole fractions and the conversions of CO2 $C$ of the optimized mixtures, agreed well in the simulation and in experiment.

Analysis of the process shows that the initiation of the reaction is kinetically controlled. For high temperatures (exceeding about 1500 K), activation energies can be overcome, and the system approaches chemical equilibrium within the time scales of an ICE compression cycle (some milliseconds). At the compressed state with high temperatures, the equilibrium composition is shifted towards syngas production and thus, CO2 will be converted. At expanded conditions (low pressure, low temperature), equilibrium composition is on the side of CO2 and CH4, and therefore unfavorable. If the gas is allowed to attain equilibrium states at any time, any cooling of the reacted mixture would then lead to a back-formation to CO2 and CH4. However, the system can be hindered forming again CO2 and CH4 from syngas by reaching the low-temperature equilibrium states by cooling down quicker than CO2 will be formed. This can be achieved by heat losses and/or volume expansion. This essentially exploits that also the backwards reactions are subject to strongly temperature dependent reaction speeds, and cannot proceed at low temperatures.

Since the amount of CO2 decreases from the initial state to the state after reaction/combustion, this process essentially converts CO2, and could be used in CO2 removal and negative emission technologies

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# A combined modeling and experimental study on low- and high-temperature oxidation chemistry of OME3 as novel fuel additive

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The present research focuses on combined modeling and experimental work on the combustion of oxymethylene ethers (OMEs). OMEs are promising synthetic fuels which can be produced in a carbon-neutral manner starting from captured CO2 and renewable energy. Moreover, blending them with conventional diesel reduces soot emissions because of the absence of carbon-carbon bonds. This results in less harmful emissions and contributes to a more sustainable transport sector as aimed by the Paris climate agreement objectives. To promote the use of these kind of molecules as fuel additive, it is important to understand their low- and high-temperature combustion kinetics. The development of detailed microkinetic models provides this fundamental insight and enables predictive simulations for combustion applications.
During the last decade, great progress has been made in the construction of reliable kinetic models for numerous technologically important radical chemistry processes. The resulting models typically contain hundreds of species, and several thousands of associated reactions. The manual generation of microkinetic models would be a tedious, error prone and often incomplete process. To prevent this, automatic kinetic model generation routines have been developed to systematically develop models, such as Genesys at the Laboratory for Chemical Technology (Ghent University) [1]. A kinetic model for both oxidation and pyrolysis has been developed for OME3 based on first principles using Genesys.

A prerequisite for the generation of detailed kinetic models is the availability of accurate thermodynamic and kinetic data for species and reactions respectively. Ideally, these parameters are available from experiments or high-level quantum chemical calculations. Since these methods are expensive and time-consuming, Genesys instead often relies on approximation methods such as group additivity and rate rules. In this work, thermodynamic and kinetic parameters are obtained from quantum chemical calculations at the CBS-QB3 level of theory for important reaction pathways for both low- and high- temperature oxidation of OME3. The results of these calculations are extrapolated to be valid for long-chain OMEs by regression of new group additive values and rate rules.

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Within Genesys, the possible reactions are generally defined in terms of reaction families, e.g. hydrogen abstraction by molecular oxygen from a secondary carbon atom. Reaction families from earlier studies on smaller oxymethylene ethers such as dimethoxy methane [2] are taken over and applied for the OME3 model. The outcome is a model containing the chemistry for OME3. To include the chemistry of smaller (oxygenated) hydrocarbons in the final model, the Genesys model is merged with the AramcoMech 1.3 base model [3].

Both flat flame burner and rapid compression machine experiments have been performed with OME3 for validation of the combustion model. The flame experiments are performed at 0.053 bara and with a fuel composition of 20 mol% OME3 and 80 mol% CH4. Some measured concentration profiles in function of the height above burner (HAB) of small species (i.e. OME3, CH2O, CH3OH, H2, CO2 and CO) are shown in Figure 1. Other important species which are observed include ethane, ethylene, dimethyl ether, methyl formate, dimethoxy methane and methoxymethyl formate.

Ignition delay times have been measured via rapid compression at 5 bara for and to additionally validate the low-temperature section of the model. Samples were taken to identify the reactants and products, including OME3, methyl formate, methoxymethyl formate and methoxymethoxymethyl formate. Similarly, pyrolysis experiments are performed for OME3 in a bench-scale steam cracker setup over a broad range of temperatures (723 K – 1073 K) to validate both the primary and secondary chemistry of the pyrolysis model.

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# Membrane-based technologies for CO2 capture and mineralization from energy-intensive industries

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Mitigation of the adverse effects of climate change requires a transition to a CO2 economy with recycling of CO2 to (carbon-neutral) fuels and (carbon-negative) chemicals and minerals using renewable sources. Mineralization (Carbonation) technology is based on reacting carbon dioxide with calcium (Ca) or magnesium (Mg) oxides or silicates to form a solid carbonate mineral structure. These materials can be found either in natural form or in waste streams. The mineralization of CO2 is an alternative to conventional geological storage and results in permanent storage as a solid, with no need for long term monitoring. The carbonation reaction can be accelerated by using high CO2 concentrations and optimized reaction conditions. The reaction is exothermic (releases energy as heat) and does not require any significant input of renewable energy. CO2 mineralization is an attractive option for the cement industry, one of the most energy- and carbon-intensive manufacturing processes where CO2 releases are inherent in their fundamental chemistry.

Novel technologies for CO2 capture and mineralization involve the use of gas-liquid membrane contactors for post-combustion capture. Hollow fiber membrane contactors are well established in the field of gas separation/bubbling/extraction applications since very high and well defined surface areas can be obtained in hyper compact membrane modules. The membrane contactor process has several advantages compared to conventional bubbling columns since the gas-liquid interface lies at the pores edge with no dispersion of the gaseous phase into the liquid solvent. Membrane contactors can be used for direct CO2 capture from the flue gases and simultaneous conversion to useful chemical compounds, depending on the appropriate solvent selection.

In this study the process of simultaneous CO2 capture from flue gases and direct mineralization to nano-CaCO3 is evaluated. A CO2/N2 (19/81% v/v) binary gas mixture was fed in the lumen side of the membrane module (1x5.5 Liqui-Cel™ MiniModule), while a CaCl2/NH3 aqueous solution was used as liquid feed (shell side). Gas and liquid streams were co-currently fed to the membrane module in a once-through contactor mode. The Ca2+ concentration, gas (Qg) and liquid (Ql) flowrates, as well as the Qg/Ql ratio were identified as the main process parameters affecting the performance of the process (mass transfer coefficient, CO2 removal efficiency), as well as the morphological properties of CaCO3 particles produced. Benchmark tests were also performed with a 100% CO2 stream with continuous recirculation of the CaCl2/NH3 aqueous phase, both in contactor and bubbling mode.

Rapid pH reduction was found in both modes of operation (once-through, recirculation), and the CO2 recovery was monitored at 50-90%, in the whole Qg/Ql ratio, examined. CaCO3 particles were precipitated in any mode of operation. In bubbling mode, CaCO3 demonstrated all its crystalline structures, while in the contactor mode only calcite was detected. Average particle

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size was estimated to approximately 1$\mu$m, while nanoparticle aggregates were also observed. The average size of CaCO3 particles was slightly smaller in the case of bubbling mode operation compared to those from the contactor mode. Membrane precipitator operated in the bubbling mode had higher productivity than in the contactor mode.

The experimental results revealed that membrane-based precipitation of carbonates offers an ideal route for mineralization with controllable morphological and structural properties of the precipitated particles. A very promising potential application could be calcium carbonate nanoparticles production for partially substituting cement in high-performance concrete.

# Modelling the performance of a syngas fuelled engine: Effect of excess air and CO2 as combustion diluents

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Bio-syngas, derived from the pyrolysis and gasification of a biomass feedstock, can be used as an alternative fuel in reciprocating engines. This mixture of CO, H2, CH4, and CO2 is less calorific than traditional fuels and has different in-cylinder combustion properties, ultimately resulting in a power derating for syngas engines when compared to traditional engines of a similar size. Nevertheless, syngas remains an attractive renewable, low-carbon fuel suitable for use in spark-ignited (SI) internal combustion engines. The current study investigates syngas engine performance across varying air/fuel ratios and the effect of substituting CO2 for excess air.
In the present work, a representative time-dependent, thermodynamic model of a four-stroke internal combustion engine is derived (eqs. 1 – 3). Fuel combustion is sub-modelled using a Weibe function tuned specifically for the combustion characteristics of syngas mixtures of predominantly H2, CO, and CO2 in air (eq. 4). Instantaneous heat lost to the cylinder wall is calculated using a convective heat transfer model with the heat transfer coefficient determined using a Nusslet-Reynolds correlation (eq. 5).

dP/d
*theta*=(γ-1)/V·(ΔH_c·(dX¬_b)/d
*theta*-(dQ¬_L)/d
*theta*)-(γ·P)/V·dV/d
*theta*+(γ-1)/V ((γ_0 T_0 R)/(γ_0-1))·dm/d
*theta* (1)
V(
*theta*)=V_c+(V_c (r_c-1))/2 (1-cos(
*theta*)+·sin^2(
*theta*)/2) (2)
dV/d
*theta*=(V_c (r_c-1))/2 sin(
*theta*)·(1+ cos(
*theta*) ) (3)
X¬_b (
*theta*)=1-exp^(-2.23((
*theta*-
*theta*_s)/

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*theta*_d )ˆ1.71 ) (4)
h_c=a Bˆ(b-1)/k ((ρ U _p )/μ)ˆb (5)

When validated against experimental data (Shivapuji & Dasappa, 2013), this model can predict brake power output and in cylinder pressure profiles, as highlighted in Table 1. Additionally, the model predicts the overall energy distribution between the brake power, friction losses, jacket cooling load, and exhaust sensible heat as shown in Table 2 (Shivapuji, 2015).

Table 1: Experimental and modelled values for brake power output at different engine loads (Shivapuji & Dasappa, 2013)
Measured brake power (experiment) 27.32 kW 16.41 kW 5.23 kW
Calculated brake power (simulation) 27.25 kW 16.83 kW 5.30 kW
Relative error 0.26% 2.56% 1.34%

Table 2: Experimental and modelled energy distribution for an engine with 123.5 kW input energy rate (Shivapuji, 2015)
Brake power Cooling load Exhaust sensible heat Friction losses
Measured output (experiment) 22.1% 31.9% 26.2% 14.8%
Calculated output (simulation) 20.0% 32.5% 30.8% 15.6%

Engine simulation was set up by maintaining a constant mass flow of the syngas mixture while varying the mass flow of air from sub-stoichiometric conditions to an excess air-fuel ratio of $\lambda$=2.15, representing the lean limit for syngas combustion (Dasappa, Sridhar & Paul, 2011). Intake conditions were set to constant temperature and pressure conditions of 298 K and 100 kPa, respectively.

To simulate the effect of using CO2 as a substitute diluent instead of excess air, a mass flow stream of CO2 was introduced into the intake mixture while a stoichiometric airflow was maintained. The mass flow rate of CO2 was increased for successive iterations of the model. For comparison to excess air cases, an equivalent $\lambda$ parameter is calculated for the CO2 cases such that the mass flow of air remains at the stoichiometric flow rate while the CO2 mass flow substitutes the equivalent mass flow of excess air. Equation (6) illustrates the calculation.

λ_eq=(1+m _(CO_2 )/m _(air,st) ) (6)

Under stoichiometric combustion conditions, the peak cylinder temperature is calculated to be 1941.4 K. For engine operation at excess air of $\lambda$=2.0, peak temperature is limited to 1519.1 K. This falls to a peak temperature of 1470.3 K for an equivalent CO2 dilution of $\lambda$eq=2.0.

By substituting CO2 for excess air as the engine diluent gas, the indicated mean effective pressure at high $\lambda$ ratios remains slightly higher, indicating more available work per engine cycle. For $\lambda$(eq)=1.50, this translates to a 1% increase in IMEP with a trend that rises to 2% for $\lambda$(eq)=2.15.

Additionally, lower cylinder cooling loads are required and exhaust gas temperatures remain higher under the CO2 diluent regime. For example, at $\lambda$(eq)=2.0 the cooling load reduces from 37.48 kW in excess air to 36.56 kW in CO2 while exhaust temperatures are 629.7 K and 688.2 K, respectively. This is attributable to the increased heat capacity of the exhaust gases since they have a higher CO2:N2 ratio. Such an effect is beneficial for potential down stream processes like removal of pollutants or CHP applications.

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# Ammonia combustion

# Low NOx combustor development for NH3 applications

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Renewably generated NH3 offers a form of carbon-free chemical energy storage to meet the differences between uncertain renewable supply and fluctuating demand, and has the potential to support future energy requirements as a power-to-X concept. Consequently, there is increasing research interest in developing combustor designs and fuelling concepts that reduce harmful emissions production. Through the introduction of fuel staging, pathways have been identified that limit NOx production from fuel-bound nitrogen, whilst improving combustor efficiency and reducing unburned H2 and NH3. However, the efficacy of secondary air staging is sensitive to the primary flame behaviour, and whilst low NOx emissions can be achieved at rich conditions, high unburned NH3 results in greater global NOx concentrations from downstream production. Presented work summarises the development and optimisation of a fuel-flexible burner, enabling partial and full premixing, together with operation of a swirl-stabilised non-premixed flame. NH3/air and NH3/H2/air mixtures have been employed for a range of increasing inlet conditions of temperature and pressure. Parametric experiments have been performed to characterise individual influences, with inlet conditions also proportionally scaled to maintain residence time in the combustor. Time-resolved OH*, NH2* and NH* chemiluminescence data have been captured alongside the measurement of product NO and NO2 concentrations, with optical trends complementing changes in sampled exhaust emissions. Contrasting trends were identified as functions of fuel composition, delivery mechanism and equivalence ratio, with a comprehensive database of optical and analytical results generated. Changes in secondary air loading and reactant humidification were also explored as pathways to NOx reduction with each fuel blend and flame configuration, and captured trends summarised. Chemical kinetic simulations were performed with reactor network modelling facilitating a comparison between numerical and experimental data. The sensitivity of NOx emissions to inlet condition, fuel-air equivalence ratio, and humidification was captured by the models, allowing the detailed breakdown of intermediate reaction chemistry.

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# Large-eddy simulations of ammonia spray combustion under direct injection engine-like conditions using a hybrid Stochastic Fields/Flamelet Progress Varible methods

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This paper, for the first time, investigates ammonia spray combustion in combustion engine-like conditions using Large-eddy simulations (LES) approach based on a hybrid Stochastic Fields (SF)/Flamelet Progress Variable (FPV) method. In the recent International Energy Association report, ammonia has been identified as "the low hanging fruit" for carbon-free hydrogen alternative energy carriers for the following reasons: (1) Compared to hydrogen, ammonia storage is easily achievable. It is liquefied at room temperature at 9.90 atm (similar to propane, a fuel with widespread domestic applications), whereas hydrogen storage essentially requires very low temperature (below -239.95 C) or very high pressure (e.g., 700 atm in fuel cell vehicles). (2) Liquid ammonia has a very high hydrogen density (kg H 2 per litter of liquid ammonia), even higher than liquid hydrogen. (3) Mass production and shipping technologies of ammonia have been long established due to its applications in the fertilizer industry. Despite great economic and technological advantages, ammonia cannot be directly used in conventional-based Internal Combustion Engines (ICEs). The main problem is that these engines have been traditionally designed to operate with highly reactive fossil-based fuels which are not compatible with the fundamental combustion characteristics of ammonia. Nonetheless, a very long ignition delay time (IDT) of ammonia/air mixture compared to most hydrocarbon-based fuel counterparties makes is an ideal fuel for future engines that are operating with advanced modes of combustions, namely, the Homogeneous Charge Compression Ignition (HCCI) engines and its derivates. To date, there is very little known about the structure of ammonia spray combustion under practical ICEs conditions. For example, it is not very clear how IDT of ammonia can affect the structure of ammonia spray when it is injected into an engine-like environment. Whether the mixture reaches to a homogeneously mixed condition, as it is intended in an HCCI engine, or it involves some levels of stratification in mixture' temperature or composition, is predominately affects the combustion progress and its efficiency. In this paper, first, we formulate a new spray combustion modeling approach based on our previous work in which a hybrid (ES/FPV) was developed and used for modeling non-premixed jet flames. The method is then used to simulate the so-called Sandia' Spray A - a benchmark for diesel srpay combustion in modern engine-like conditions. This follows by modeling ammonia spray in an advanced DI-engine like conditions. The results will be analyzed and the dominate combustion modes in each case are identified. We shall discuss the combustion performance of each case in terms of heat release modulations, combustion efficiency, and NOx emissions.

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# Probing Nitrogen Chemistry: a Theoretical Study for Important Reactions of NxHy, HCN and HNCO Oxidation

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Ammonia ($NH_3$) is a carbon free energy carrier with relatively high energy density, but its combustion produces nitrogen oxides ($NO_x$) and other harmful pollutants. Therefore, understanding its oxidation chemistry is necessary to develop industrial combustion applications. Diazene ($N_2H_2$), diazenyl radical (NNH), amidogen radical ($NH_2$), hydrogen cyanide (HCN) and isocyanic acid (HNCO) are important intermediates in the $NH_3$ combustion, and HCN and HNCO are highly toxic compounds [1]. However, there are very few experimental and modeling work of HCN [2] and HNCO [3] oxidation in literature, and limited fundamental studies were found regarding the rate coefficients determination of the key reactions for the two compounds' oxidation. Therefore, this study aims to systematically perform high level quantum chemical calculations for the rate constants of important reactions of $N_2H_2$ ($N_2H_2$, NNH and $NH_2$), HCN and HNCO oxidation, as well as the thermochemistry of species involved.

NxHy System:

- $NNH + M \leftrightarrow N_2 + H + M$
- $N_2H_2 + H \leftrightarrow NNH + H_2$
- $N_2H_2 + O \leftrightarrow NNH + OH$
- $NH_2 + H \leftrightarrow NH + H_2$
- $NH_2 + OH \leftrightarrow NH + H_2O$

HCN System:

- $HCN + M \leftrightarrow HNC + M$
- $HCN + H \leftrightarrow NC + H_2$
- $HCN + O \leftrightarrow NC + OH$
- $HCN + OH \leftrightarrow NC + H_2O$
- $HCN + HO_2 \leftrightarrow NC + H_2O_2$

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- HCN + O2 ↔ NC + HO2

HNCO System:

- HNCO + H ↔ NCO + H2
- HNCO + O ↔ NCO + OH
- HNCO + OH ↔ NCO + H2O

Regarding the calculation method, the M06-2X [4] method with the 6-311++G(d,p) [5, 6] basis set was used for the geometry optimizations, vibrational frequency calculations and also the hindered rotation treatments for lower frequency modes. All vibrational frequencies and zero point vibrational energies (ZPVEs) were scaled by 0.983 and 0.9698 respectively, which was recommended for the M06-2X functional by Zhao and Truhlar [4] The electronic single point energies (SPEs) were calculated at the CCSD(T)/cc-pVXZ level of theory (where X = T and Q) [7, 8], and the resulting SPEs were extrapolated to the complete basis set (CBS) limit using the following formula: [9, 10]

ECBS = ECCSD(T)/cc-pVQZ + (ECCSD(T)/cc-pVQZ - ECCSD(T)/cc-pVTZ) * 44 / (54 – 44)

The internal rotations that correspond to low frequency torsional modes were scanned in 10 degree increments as a function of dihedral angle using the M06-2X/6-311++G(d,p) method. This method was also used to perform intrinsic reaction coordinate (IRC) calculations [11] on each transition state (TS) to ensure it was connected to the desired reactants and products. The quantum mechanical tunneling was taken into account for an unsymmetrical Eckart barrier model [12].

For the MultiWell [13] program suite calculation, the Lamm module was used to calculate both external rotational constants and reduced moment of inertia for the hindered internal rotations. The calculated results were then fitted to truncated Fourier series, which were further used as 1-D hindered internal rotation input in the Thermo module. The high-pressure limit (HPL) rate coefficients were finally calculated by the Thermo module as a function of temperature (298.15 – 2000 K) based on canonical transition state theory (TST) [14]. The calculated rate coefficients were fitted to a modified Arrhenius expression as a function of temperature:

*k = A (T/Tref)n exp(-E/RT)*

Where A is the A-factor, *T* is the temperature in units of Kelvin, *Tref* = 1 K, *n* is the temperature exponent at 1 K, and *E* is related to the activation energy (by *Ea = E + nRT*).

As to the quantum chemical methods for the thermodynamic properties calculation, the average atomization formation enthalpies for all of the nitrogen containing species were carried out using a combined compound method CBS-APNO/G3/G4 [15-17], which was found to yield results approaching "chemical accuracy" (arbitrarily, ≈ 4 kJ mol–1 or 1 kcal mol–1) when benchmarked against enthalpy of formation values in the Active Thermochemical Tables (ATcT).[18-20] The thermochemical values of interest (enthalpy of formation, entropy and heat capacity) were calculated as a function of temperature (298.15–3000 K), and these resulting values were fitted to NASA polynomials [21] using the Fitdat utility in ANSYS CHEMKIN-PRO [22].

Eventually, the rate constants of 14 reactions and thermodynamic properties of 9 species were systematically carried out. The rate coefficients have been comprehensively compared based on 1) different systems: N2H2 (N2H2, NNH and NH2), HCN and HNCO systems; 2) different reaction types: abstraction, decomposition and isomerization reactions. Both reaction rates and thermochemistry have been compared with the experimental and theoretical results in literature, and excellent agreement was obtained.

# Experimental and numerical validation of ammonia combustion in oxygen at high pressures and temperatures

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The combustion of fossil fuels produces large quantities of carbon dioxide which participates in the global warming. Due to alarming concerns, initiatives are taken to promote the use of 'zero-carbon fuel'. Ammonia stands as a potential fuel as it is carbon-free and relatively safe to store and transport. The well-known Haber-Bosch process is used for its production.
The use of ammonia as an alternative fuel in gas turbines and spark-ignition engines has already been tested. Ammonia flames are characterized by a low combustion intensity, low laminar burning velocities, and narrow flammability limits. The low speed leads to an early blow-off and a difficulty in ignition. Nevertheless, ammonia combustion has anti-knock characteristics because of its high-octane number which makes it favorable to use in the spark-ignition engine.

Studies on ammonia flame speeds for different equivalence ratios have been done for a narrow range of pressures and temperatures. The maximum flame speed data available in the literature is for a pressure and temperature of 5 bar and 473 K respectively. As high pressures and temperatures are encountered in spark-ignition engines and gas turbines, it is essential to obtain accurate flame speed data for these conditions. Moreover, the existing kinetic mechanisms for ammonia combustion have not been assessed for elevated conditions. It is important to identify the key reactions and to check if pressure dependency is accounted well at high pressures.

The present study affords new flame speed results at elevated temperatures and pressures conditions using the constant volume method. The tests were performed at an initial temperature of 300 K for 3 different equivalence ratios (0.8,1.1 and 1.3) and an initial pressure ranging from 1 to 4 bar which allows to obtain laminar flame speeds upto a pressure of 20 bar and temperature of 485 K.

At these conditions, hydrodynamic and thermo-diffusive instabilities are favored. In order to stabilize the flame, a mixture of argon and helium was used. The ratio of argon and helium was chosen based on the ability to easily ignite the mixture. Helium has a high thermal diffusivity. Therefore, larger quantities of helium were used only for the high-pressure conditions. A mixture containing a mole fraction of 30% of oxygen and 70% of diluents was used.

These experiments were conducted in the OPTIPRIME facility of ICARE, CNRS. This experimental device is a perfectly spherical chamber with full optical access and allows the simul-

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taneous recording of pressure and flame radius inside the chamber during the combustion process.

A literature survey was conducted to choose and evaluate the most recent kinetic mechanisms in ammonia combustion. It was seen that most of the chosen mechanisms could reproduce the experimental flame speed trend for any given test condition: flame speeds increase with the pressure and its corresponding isentropic temperature. Sensitivity analyses for a set of mechanisms were performed to further understand the working of these mechanisms.

From the sensitivity analyses, it was seen that the driving reaction of all the mechanisms is the well-known reaction. It is the most dominant reaction and its rate constant is pressure independent. It was observed that the recombination reaction of ammonia flames showed very low pressure dependency unlike the methane flames' reaction , which is highly pressure dependent playing a major role at high pressures. The absence of this sensitive recombination reaction and the domination of the $OH$ reaction could explain why most of the mechanisms can predict a consistent trend for elevated conditions. However, only a few mechanisms can predict the flame speed values that lie within the experimental range.

It is interesting to note that for the mechanisms of Nakamura [1] and Stagni [2], the flame speeds for all conditions are quite close to each other and within the experimental range even if the sensitivity tests result in two different sets of the top 10 reactions with only 3 reactions in common for all the given initial conditions. It was seen that the reactions are dependent on the equivalence ratio rather than the initial pressure.

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# Interaction of NH3 on the H2 oxidation chemistry

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The transition of the energy scenario towards no-carbon economy is becoming mandatory within 2050, because of fossil fuels depletion and CO2 strict emissions regulations, while worldwide energy demand is increasing [1-2]. Within this panorama, the role of green and blue hydrogen (from renewable sources) as energy carrier for stationary and transport applications is recognized as the main leading challenge [3]. Hydrogen is considered to be the ideal fuel because of its high heat value (on mass basis), the absence of CO2 emissions and limited NOx emissions, when burned in the appropriate conditions.
Nonetheless, the attempt to reach an energy system based on the hydrogen economy is a long-term project, since issues related to NOx emissions and to hydrogen storage/delivery and safety. The H2 conversion to other energy vectors more easily transportable and with high-energy density represents a relatively cheap alternative capable of guaranteeing energy supply within the constraints of the energy trilemma [4].

Within the palette of new fuels [5, 6], ammonia has received a lot of attention because of its high hydrogen density and heating value, the absence of CO2 emissions with already available storage and delivery infrastructures, as well as some well-established production technologies and plants. Nonetheless, its physical/chemical properties represent an hindrance to its practical use both in stationary and transportation systems [7, 8].

MILD Combustion has been proven to allow the use of pure ammonia. The role of third-molecular reactions is emphasized, in virtue of relatively low working temperatures and the massive presence of "strong" colliders (H2O and CO2) [9]. Many authors have attributed the high collisional efficiency of water high to a very strong polar-polar interaction between HO2 radicals and H2O [10]. In this respect, it has to be also accounted for that ammonia is a four-atom molecule with a relatively high polarity, and a dipole moment comparable to water. Its third body effect cannot be ruled out "a priori" in chemical kinetics modeling of ammonia combustion, but it has to be addressed through experimental evidences.

Therefore, experimental tests were realized for H2/O2/Ar mixtures as reference cases in a Jet Stirred Flow Reactor (JSFR) [11], in presence of H2O and NH3, for a fuel-lean H2/O2 mixture diluted in Ar at d=94% as a function of mixture inlet temperature (Tin), at a fixed residence time (t=0.5 s) under atmospheric pressure (p=1.2 atm).

The experimental tests suggest that ammonia strongly interacts with the H2 oxidation chemistry

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within the considered operative conditions, with an overall delaying effect on H2 characteristic chemical times. As a direct evidence, the onset of the system reactivity is shifted towards higher inlet temperatures as the ammonia concentration increases. In addition, hydrogen instabilities, identified for the mixtures H2/O2/Ar, disappear as soon as ammonia is added to reactants. This effect is even more evident with respect to the delaying effect of ”water” on hydrogen oxidation. All these considerations contribute to conceive a plausible role of ammonia as a ”strong” collider in ter-molecular reactions.

All these considerations may have a strong impact on the development of detailed kinetic schemes for ammonia oxidation under low-intermediate temperatures.

In addition, several practical issues towards the development of a H2 economy system can be deduced, overcoming problems related to an hydrogen safely delivery/storage systems while reducing ammonia production cost through Haber-Bosh processes.

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# CFD modelling of an ammonia cracker for the on-board generation of NH3/H2 mixture as a COx-free fuel

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The climate change caused by global warming has become the main crisis for human race in the last century, and the major player is carbon dioxide having a large portion of greenhouse gas emissions. The CO2 emissions caused by human activities mostly come from electricity, transportation, industry, residential and agriculture. Among these sections, transportation has a noticeable portion of CO2 emission as well as NOx, and unburnt hydrocarbons. Using electric vehicles and fuel cell technology are two well-known solutions. Both of these technologies are comparably immature and expensive with considerable limitations.

In search of zero-carbon fuels, apart from nuclear energy, hydrogen has been attracted much attention in the last few decades. Hydrogen can be used either in internal combustion engines or in fuel cells, and in both cases the exhaust product is water. However, hydrogen technology has not been successful in the industry mainly due to the limitations on fuel storage and transportation. Alternative solutions to H2 delivery and storage obstacles are using chemical or thermal processing of hydrogen carriers for on-demand generation of hydrogen. Ammonia (NH3) has been repeatedly reported in the literature as a potential H2 carrier for the on-site production of hydrogen. Ammonia has superior H2 content (17.8 wt%) and energy density compared to alternative carriers with well-established production and transportation infrastructures.

It is worth noting that H2 can be produced directly from NH3 by cracking with the aid of a heterogeneous catalyst. Hence, in case of transportation applications hydrogen could be generated on-site and directly injected into the internal combustion engine together with ammonia. Therefore, expensive and large consuming H2 tanks are not required, and this makes the on-board NH3 cracking feasible for vehicular applications. Ammonia decomposition is an endothermic reaction that yields high conversions at high temperature and low-pressure conditions in the presence of heterogeneous catalysts. Ru-based catalyst series were reported as the most active for the ammonia cracking reaction; however, numerous studies have focused on enhancing the reaction conversions at low temperature using novel catalysts. Hence, the overall operation efficiency can be improved by decreasing the reaction temperature, and the process costs can be reduced using abundant, inexpensive catalysts.

While the main investigation area is related to the application of ammonia as a COx-free hydrogen carrier, it can also be used as an alternative fuel for combustion systems, e.g., internal combustion engines (ICE). Nevertheless, in conventional ICEs, NH3 should be co-fed together with a combustion promoter. Due to the low laminar burning velocity, high ignition energy and narrow flammability limits of pure NH3, it is feasible to use ammonia as a primary fuel together with other fuels used as combustion promoters such as H2 for combustion. Hydrogen, on the other hand, is characterised by low ignition energy and wide flammability range, and the

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complementary properties of NH3/H2 mixture could be operated in combustion engines. Some studies proposed H2 as a potential promoter, reporting that a small ratio of H2 in ammonia/air mixture ($>$ 1 wt%) could speed up the combustion significantly and allow satisfactory engine running. The required H2 ratio can be directly generated from ammonia through decomposition reaction at the upstream of the engine system. For example, 14% conversion of NH3 is sufficient to produce approximately 2.5 wt% hydrogen mixture.

This work presents a numerical methodology to model a macro-scale heater-reactor system for hydrogen generation from the ammonia decomposition reaction. A kinetic rate expression was developed and for the reaction and implemented in the CFD model based on the experimental data obtained. The kinetic model parameters for the macro-scale cracker were calculated and used based on a commercial catalyst. A CFD solver was used to solve the governing equations, and measuring the reacting flow properties from temperature, velocity and density distributions to the species mole fraction profile and outlet NH3 conversions. The CFD models were solved at various reaction temperatures and NH3 flow rates and compared with the empirical data obtained from the literature. The solved CFD model showed good accuracy with respect to the experimental data in the model. Therefore, the developed rate expression could effectively predict the experimental kinetic conversions along the ammonia decomposition reactors. Furthermore, a heat transfer analysis was performed on the heater-reactor model to assess the temperature gradients all over the heater section and the reactor part and to optimise the internal heating system. The heat transfer analysis for the macro-scale heater-reactor showed that increasing the heater lengths increases the surface contact and reduces the overall heat flux in the heater and reactor parts leading to lower temperature gradients. Therefore, there is less possibility of hot spots inside the system, and the overall process efficiency could be enhanced. Finally, a scale-up calculation was conducted to analyse the feasibility of the NH3/H2 mixture generation process in larger scales for internal combustion engines.

# Ammonia-methane interaction in Jet-Stirred and Flow reactor: an experimental and kinetic modeling study

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The influence of the addition of ammonia on the oxidation of methane was investigated both experimentally and numerically. Experiments were carried out at atmospheric pressure, using a fused silica jet-stirred reactor, and a recrystallized alumina tubular reactor designed on purpose to reach temperatures as high as _˜2000 K. A temperature range of 600-1200 K was investigated in the jet-stirred reactor at a residence time of 1.5 s, while experiments in the flow reactor were carried out between 1200 and 2000 K, for a fixed residence time of about 25 ms in the reactive zone. A methane/ammonia mixture, diluted in helium, was used in both reactors with equivalence ratios varied between 0.5 and 2 in the first reactor, while stoichiometric conditions were investigated in the second one. The measurement indicates that CH4 reactivity was promoted by NH3 addition below 1200 K, but not so much influence above. These results were interpreted and explained using a comprehensive kinetic model, previously validated in a wider range of operating conditions. The mechanism allowed to shed light on the underlying causes of the anticipated methane reactivity at low temperature, and of the major role played by NOx in it. This effect was shown to become less significant at higher temperatures, where the reactivity is mainly governed by H-abstractions on

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both fuels.

# Biomass combustion

# Parametric study of Syngas laminar flame speed for varying compositions

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The present work introduces new laminar flame speed experimental resultsfor three compositions of Syngas with varying initial pressure, initial temperature and equivalence ratios. Syngas compositions consist of five gases (H2, CO,N2, CO2, CH4) as mentioned Bridgwater (1995), with volume fractions relatedto different gasification techniques. Moreover, as a wide range of H2/CO ratios can be obtained, most of the studies on the combustion of Syngas considered mainly binary mixtures of H2 and CO. The objective of this study is to evaluate the effect of the other components on the laminar flame speed, one fundamental combustion parameter. For that, experimental measurements were realized by means of an optically accessible spherical vessel coupled with the high speed Schlieren technique to obtain images of the outwardly propagating spherical flame. The initial pressures and temperatures tested are ranged from 1 to 5 bar and 298 to 423 K with equivalence ratios ranging from rich mixtures to rich ones. The results obtained allow the determination of the parameters of the correlation proposed by Metgalchi and Keck (1982) for each Syngas composition. The accuracy of the correlation is also improved by comparing the laminarflame speed data obtained by kinetics simulation from Ansys CHEMKIN with different kinetics mechanisms available (San Diego Mechanism, Polimi Mechanism).

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# A two-dimensional pyrolysis model for thermally thick particles

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A fundamental understanding of the chemical and physical characteristics of particles is essential for accurate bed modelling in large-scale furnaces for waste and biomass combustion. In recent years, the pyrolysis of biomass particles has been studied extensively, mostly by means of one-dimensional models. Even though these models have been successful in describing the main chemical and physical phenomena, they have also addressed the need for developing a multi-dimensional single particle model that can account for the anisotropy of the solid fuel and for the gas phase movement in the interior and exterior of the particle.
This paper presents a fully transient two-dimensional CFD (computational fluid dynamics) model for simulating the pyrolysis of thermally thick particles. The solid conversion process is programmed via a C++ routine and embedded into the CFD code, allowing the gas flow field and the solid conversion process to be resolved simultaneously. The complete model was validated with experimental data from the literature, and a good agreement has been obtained.

The established model was used to study the anisotropy of woody particles (near-spherical and cylindrical particles, diameters from 9.5 to 40 mm) and the dynamics of particle conversion at different pyrolysis temperatures (600K-1300K). The anisotropy of thermal conductivity was investigated for radial and longitudinal samples, which have grain direction coinciding with the particle radial and axial direction, respectively. It was found that the radial sample is converted faster than the corresponding longitudinal sample, which is explained by the effect of anisotropic thermal conductivity on the heating profile and product yields. The permeability, even though it has little impact on the overall conversion process, can determine where and when overpressure occurs. As the permeability is anisotropic, the pressure peaks are observed at the outer layer of the particle during the initial heating and when reaction rates are maximum. The pyrolysis temperature can be used to primarily assess the interaction between the heat transfer and the conversion process of thermally thick particles. At pyrolysis temperatures below about 650K, the conversion time is much longer than the heating time, the thermal degradation process is purely kinetically controlled. At a temperature of 700-800K, not only the internal heat transfer and the conversion process are important, but also the convective external heat transfer should be taken into account. At higher temperatures (800-1300K), the coupling between heat transfer and thermal conversion is prominent as the conversion time and the heating time are in the same range.
The simulation results demonstrate that the developed two-dimensional model is capable of capturing the internal and external flow field and of including the anisotropy of the solid fuels. The model and its results will be of interest for future research into the combustion of biomass/waste

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for packed and fluidized-bed applications.

# Experimental Study of the Pulverized Biomass Flames in a pilot-scale reactor using OH* Chemiluminescence Imaging and In-flame Probe Measurements

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Experimental Study of the Pulverized Biomass Flames in a pilot-scale reactor using OH* Chemiluminescence Imaging and In-flame Probe Measurements

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The world efforts to reduce the dangerous levels of pollution present biomass as an attractive fuel for the industrial power plants. In many ways, biomass is regarded as an economical solution of energy production and waste management. Its abundance and sustainability and its resemblance to coal, makes it a potential candidate of incorporating it with coal in the existing infrastructure.

An experimental study is performed on a pilot-scale combustion facility to evaluate the structure and characteristics of pulverized biomass flames. The design of the 20kW bluff-body burner and the 4m-length vertical combustion chamber is made in a way to allow analyzing the different involved phenomena using chemiluminescence and in-flame probe measurements of temperature and gas concentrations (O2, CO, CO2, NO). Pine (82% volatiles) was grinded ($< 500$ $\mu$m) and thermally treated into two degrees to produce a moderately torrefied pine (72% volatiles) and a pyrolyzed one (44% volatiles). The chemiluminescence signal of OH* excited radicals marks

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the zone of the volatiles reactions. The intensity of the signal is strongly dependent on the fuel volatile content. However, the position and structure of the reaction zone is rather affected by the particle size distribution in the first order than by the biomass thermal treatment. Despite having low volatile content, pyrolyzed pine flames show earlier OH* chemiluminescence radiation than pine flames thanks to the finer granulometry. The wide granulometry of pine produces a first close-to-burner reaction zone, which is penetrated by the large particles that devolatilize further in the reactor forming a second reaction zone. This decreases the reaction zone intensity near the burner and explains why the finer moderately torrefied pine has a more intense reaction closer to the burner despite lower volatile content and less devolatilisation reactivity observed at particle level. The probing results validate these conclusions where the two-stage devolatilisation of pine has the advantage of reducing the NOx fraction in the second devolatilisation region. Moreover, higher and earlier devolatilisation, oxygen consumption and temperature rise are detected on the jet axis for the treated pine compared to their raw counterpart. The confined jet aerodynamics creates in the combustion chamber a large recirculation zone around the main central jet where hot combustion products are entrained upstream. The earlier release of volatiles reduces the particle density and prepares them to follow the air streams to undergo their char conversion in this outer recirculation zone.

# Particle, CO and NOX emissions during the combustion of wood pellets as a function of the feeding mode and air staging.

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The results that will be presented concern the combustion of wood pellets in a domestic boiler. The objective of this study is to analyse the influence of the feeding mode and air staging on the quality of emissions. Different feeding methods are considered (pulsed and continuous feeding) in a pellet boiler (20 kW) with a drop feed. Gaseous and particulate emissions were sampled in the vicinity of the smoke exhaust and close to the boiler. The particle mass concentration is measured with a PPS and the particle size for submicronic particles with a mobility diameter analyzer (SMPS). Finally, a gas analyzer (CO-NOx) is used. The results show an increase in emissions between 400 and 800 ppm carbon monoxide with the pulsed feed mode. Whereas the values observed for continuous feed were 100 to 200 ppm. The typical particle size is between 50 and 60 nm. The air staging was done close to the granule bed at about 2 cm from its surface and we could observe significant variations in NOx and CO emissions depending on this air staging. This point will be analysed and discussed

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# Conception and elaboration of a prototype of pellet domestic stove and combustion tests with DIN+ pellets

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The present study deals with the possibility to use waste from Cameroonian forest- and agro-industries as combustible for energy production in a circular economy. Such waste may first be assembled in pellets for easier transportation from the production zone to the final destination and for preparation of a combustible with higher energy density. Selected Cameroonian and more generally sub-Saharan waste (palm nut shells, palm nut fibers and coffee husks) and the associated pellets were characterized,and their thermodynamic profile was determined through pyrolysis and combustion processes performed in a thermobalance. These materials were proved to be appropriate candidates for combustible, [1].

More specificaly, the present study focuses on the elaboration of a low-cost domestic stove which could use such pellets for example for cooking purpose at a domestic scale. The combustion zone of the pellet stove consists of a cone placed in a cylinder to concentrate the hot gases in the upper part of the stove. A pan filled in with 5 liters of water was placed on the thick (6 mm) plate or circular crown posed on the upper part of the stove. Normalized DIN+ pellets were used during the combustion tests in this stove. The temperatures were measured during the combustion test through thermocouples type K placed at different zones of the stove. The thermal efficiency of the stove was determined first determining the HHV of the DIN+ pellets and observing the time necessary to bring the water to ebullition with a pellet flux of 900 g/h. The thermal efficiency was measured at low levels in the case of the thick plate and slightly higher in the case of the thick circular crown. The thermal behavior of the stove was simulated writing balances in the complete system and assuming simplifying hypotheses, among which a uniform temperature of the thick plate. The model predicts a faster increase of the temperature of the water in the pan than observed during the experiment.

The exhaust gases (especially CO, as NOx emissions are very low in biomass combustion) were measured at around 50 cm above the stove with a TESTO 350-XL analyzer, to determine the exposition levels of a person during the stove activity. The CO emissions were measured below 5 ppm. For comparison, OMS suggests a maximal level of 9 ppm CO emissions at human height close to a stove during 8 h without health risks.

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The next stages of the study will consist to improve the combustion process in an improved domestic stove and to test the combustion of pellets built with Cameroonian waste in this domestic stove.

. T. Vitoussia, A. Brillard, D. Kehrli, A. Kemajou, E. Njeugna, J. Brilhac, Thermogravimetric analyses and kinetic modeling of pellets built with three Cameroonian biomass. Biomass Conversion and Biorefinery (2020), 10.1007/s13399-019-00558-3

# The Combustion of Biomass Char in a Fluidised Bed: The Influence of CLOU Particles on the Rate of Combustion

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This research concerns the combustion of biomass char in a fluidised bed using Chemical Looping Combustion with Oxygen Uncoupling (CLOU). Here, gaseous oxygen for reaction comes from a solid oxide, called an oxygen carrier. To evaluate the influence of the CLOU material on the rate of combustion, experiments were performed in a fluidised bed (i.d. 30 mm) using either an active oxygen carrier (CuO supported on mayenite) or inert SiO2 sand, as the bed material. To avoid other mass transfer effects in the fluidised bed, a small mass of birch wood char ($\leq$ 0.1 g) was combusted in the bed, with a partial pressure of oxygen, $p$O2, close to the equilibrium pressure of O2 of the Cu-based oxygen carrier. Despite the same $p$O2 for both experiments, the presence of the oxygen carrier resulted in a significant increase in the combustion rate of char. As a result, at 1173 K, the burn-out time of 0.1 g of char particles in the CLOU setup was around five times faster than in the inert bed of SiO2. To investigate the origin of this apparent enhancement of rate of combustion of the birch char in CLOU, an analytical model has been developed based on a simplified scenario, *i.e.* gaseous mass transfer external to the fuel particle was taken as a stagnant system, ignoring advective flow. The model accounted for: (1) the combustion of char with oxygen to CO and CO2, (2) the homogeneous reaction of CO with oxygen, and (3) gaseous oxygen release from the oxygen carrier. The combustion of a char particle was modelled as a shrinking particle. Results from the analytical model of CLOU agreed with the experimental observations despite the simplified assumption of a stagnant system, *viz.* a system in which the mass transfer boundary layer, is infinite. This agreement results from a creation of an effective boundary thickness, rather than a conventional boundary thickness for the system, . Moreover, in CLOU, is independent of , provided . Finally, the modelling work evidences that the rate of combustion in CLOU was enhanced due to the improved mass transfer of O2 from the bulk phase to the surface of the char particle, *i.e.* the interphase mass transfer.

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# Influence of air flow and radiative heating on oxidation of wood char at atmospheric pressure

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INFLUENCE OF AIR FLOW AND RADIATIVE HEATING ON OXIDATION OF WOOD CHAR AT ATMOSPHERIC PRESSURE

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ABSTRACT

A series of experiments and analysis were carried out to comprehend the influence of air flow and external radiative heat flux on oxidation of wood char by using the Cone Calorimeter Test apparatus and a fan to generate the air flow. Two types of char specimens are compared, namely char produced from un-charred specimen following flaming or char produced from pre-charred specimen, in the experiment to grasp the influence of initial condition of specimen on char oxidation. Un-charred specimens were air-dried at atmospheric temperature whereas pre-charred specimens were charred in electric furnace with inner temperature500 oC before experiments. The main parameters were external heat flux and air flow velocity including cases without air flow. From the results we found that the weight of specimens after flame went out were about 20 % to 30% of the initial mass of wood. The heat of combustion (HC) during char oxidation is in the range of 25 to 35 kJ/g. The Heat Release Rate (HRR ranges from 20 to 45 kW/m2) and Mass Loss Rate (MLR ranges from 0.5 to 1.5 g/s.m2) of un-charred wood after flame went out and of pre-charred wood are approximately the same at the same external heat flux. The time to char oxidation of pre-charred wood is approximately inversely proportional to the square of external heat flux at values over 5 kW/m2 whereas pre-charred specimens at 5 kW/m2 external heat flux did not glow. The HRR and MLR increased with increasing air flow velocity. Pre-exponential factor $A$ and activation energy $E$ for the chemical reaction rate of char oxidation were calculated by using a model based on the balance of diffusion of oxygen in air and reactivity of char. The overall objective is to investigate how environmental conditions and the created process affect char reactivity, porosity and mode of oxidation (Regime III to Regime II).

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## SUMMARY OF RESULTS

The points of a special mention from results of the present research are the following:

- Mass of un-charred specimen at flame going out ranges from about 20 % to 30% of initial mass. Time to flame going out decreases with increasing external heat flux and is similar to the time at second peak of heat release rate (HRR).

- From the experiment using pre-charred specimen without air flow, time to char oxidation tends to be inversely proportional to square of external heat flux except at 5 kW/m2 of external heat flux where pre-charred specimen at 5 kW/m2 did not glow.

- From the results in the presence of air flow, higher velocity of air flow causes higher intensity of luminous of glowing. Note that a major part of ash layer covering on char surface was blown away over 1.6 m/s of air flow. In addition, the Mass Loss Rate (MLR) and surface temperature greatly increases with increasing air flow velocity.

- The Heat of Combustion (HC) of un-charred specimen remains at a constant level after ignition (about 12kJ/g) and shifts to another level (from 25 to 35 kJ/g) after flames went out. It is thought that the former one is caused by combustion of pyrolysis gases, while the latter one by char oxidation. On the other hand, the HC of pre-charred specimen kept approximately a constant level as high as the one of un-charred wood after flame went out.

- The ratios $Xco/Xco2$ in exhausted smoke of the present experiment ranging from 0.05 to 0.2 are approximately the same as the calculated values by using experimental empirical equations proposed in the literature. Furthermore, Heat of combustion (HC) calculated as heat release rate measured by oxygen consumption method divided by mass loss rate is approximately the same as the estimations based on thermo-chemical equation.

- The Pre-exponential factor $A$ and activation energy $E$ for calculating the chemical reaction constant of oxidation of wood char plate were estimated corresponding to reaction order $n$ by using the model based on the balance of diffusion of oxidizer (e.g. oxygen in air) and reactivity of char (Regime III). From the results, estimated values of $E$ and $A$ are 47.7 kJ/mol, 7.68 m3/s.m2 , respectively at $n$=1.0. Calculated HRR using the estimated $A$ and $E$reproduce within 12.7 % of average relative error. In addition, the temperature of char surface in steady state is well estimated by the consideration of heat balance on char surface including the reaction rate relation obtained in this work. Note that modeling of ash influence on char oxidation is future work because knowledge and data regarding diffusivity of oxygen in ash and combustion catalysis of ash is necessary.

# Experimental study of the influence of secondary air on the formation of pollutants and soot from wood pellets combustion

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Experimental measurements in a small-scale boiler have been performed to investigate the influence of secondary air supply on the formation of pollutants and soot during the combustion of wood pellets. The boiler used is a domestic automatic wood pellet boiler with a nominal power of 10 kW. It has coupled primary and secondary air injections in its factory configuration and the secondary air supply can be completely cut off by a plug. Gas analyzers are instrumented to measure the combustion gases which trapped separately from the chimney and the combustion chamber. A laser diagnostic bench is instrumented to acquire the signals from laser-induced incandescence (LII), including a YAG laser for soot excitation, a photomultiplier system for collecting the LII signals from the chimney, and an ICCD camera for collecting the LII images from the combustion chamber. The concentrations of CO2, CO and total hydrocarbons (THC) in the flame and in the chimney have been measured separately in the conditions with or without secondary air supply. With the presence of secondary air, the concentrations of THC, CO and CO2 in the flame increase strongly. In the chimney, a decrease of the concentration of CO2, a slight decrease of the concentration of CO and an increase in the concentration of THC are observed. The evolution of the average values of the LII peaks as a function of the primary airflow in the chimney has been investigated. There is a clear reduction of the LII peaks in the absence of secondary air and the temporal evolution of LII peaks without secondary air shows greater stability.

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# BIOFUELS COMBUSTION

# Combustion kinetics of C3-C5 ketones

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Most of the energy consumed in the world is produced by the combustion of fossil fuels. The combustion of these fossil fuels releases massive amounts of CO2, which was captured by forests and buried millions of years ago. The extraction and combustion of fossil fuels since the 1850s such as coal, oil and natural gas have led to a rapid increase in the concentration of greenhouse gases in the atmosphere with CO2 as the main contributor, threatening the humanity as global warming changes the climate. However, the population and the standard of living are increasing rapidly and the demand for energy is constantly increasing. In the field of transport fuel, solutions exist to reduce CO2 emissions. Biomass grows by capturing CO2 thanks to the photosynthesis process, harvested, transformed by catalytic process into biofuel to be finally used as fuel. This short cycle stabilizes the period during which CO2 remains in the atmosphere. A second solution is to reduce the fuel consumption of the engines by increasing the efficiency. In the case of spark-ignition engines, the quality of gasoline is the key to efficiency. Gasoline must be knock resistant, allowing higher operating pressure, leading to superior engine efficiency. Usually, knock resistance is estimated via the research octane number (RON).
Ketones meet both of these requirements. Ketones can be produced from biomass, as shown for butanone. In addition, the RONs measured for acetone (RON=110) and butanone (RON=117) are high compared to conventional gasoline (RON = 95) and can lead to an improved knocking behavior during engine operation. However, to ensure use of this family of compounds, their combustion behavior must be studied. In the literature, numerous studies are found on the kinetics of the oxidation of acetone or 2-butanone. The literature on longer carbon chain ketones is sparse. However, the length of the carbon chain influences the heating value of a fuel. The longer the chain, the higher the energy delivered by volume. However, increasing the length of the carbon chain is known to increase the knocking propensity of the fuel through the low temperature chemistry reaction pathway.

To investigate the reactivity of acetone, butanone, 2-pentanone, 3-pentanone and 3-methyl-2-butanone under engine-relevant conditions, experiments where conducted in a rapid compression machine and a shock tube. In this regard ignition delay time (IDT) measurements of ketone/air mixtures for pressures between 20 and 40 bar have been performed. The ignition delay time is a good indicator of knock propensity of a fuel and serves as validation target for kinetic models. Furthermore, the stable intermediates during the oxidation of butanone, 2- and 3-pentanone have been measured in laminar flow reactors in previous studies. These experimental data were used in this study to validate a detailed kinetic model for acetone, butanone, 2-pentanone, 3-pentanone and 3-methyl-2-butanone. The important aspect of this detailed kinetic model is the systematic use of consistant reaction rates constants, allowing the establishment of rate rules for kinetic modeling of longer carbon chain ketones. In addition, the thermochemical data for the fuels, their primary radicals and associated peroxyalkyl radicals were calculated (G4 compound method), and are sensitive on the IDTs in the low temperature range.
The predictive ability of the model is very good for the ignition delay time the mole fractions

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of the intermediates of oxidation. Thanks to this well validated kinetic model, the influence of carbonyl on the combustion behavior of ketones is examined and reveals the kinetics behind the octane booster propensity of ketones. For temperatures higher than 850 K, ketones are consumed by H-atom abstraction reactions followed by beta-scission reactions, with the exception of acetone which rapidly undergoes unimolecular reactions. At temperatures below 850 K, the low-temperature chemistry pathway is sensitive on the IDTs. However, the reactivity reduction of ketones compared to alkanes is explained by an equilibrium shifted to the reactants for the ketonyl stabilized by resonance addition to O2. Moreover, the carbonyl group in ketones prohibits the H-atom migration reactions peroxyalkyl radical = hydroperoxyalkyl radical. These two classes of reaction are kinetically limiting steps in the low temperature chain branching sequence.

# The Influence of iso-Butanol Blending on Spark-Ignition Engine Performance

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Bio-alcohols and other bio-derived fuels are attractive alternative fuel options for spark-ignition (SI) engines, as a means to achieve the required carbon emissions reductions from transport. Particularly for bio-alcohols, this is partly due to their similar physical and thermodynamic properties when compared with fossil fuels, as well as their viability in modern SI engine technologies and fuel distribution infrastructure, with little to no modification [1,2]. One such bio-alcohol (and the focus of this study) is iso-butanol. As SI engine technologies tend towards turbo-charged, downsized engines, the blending of bio-alcohols and gasoline may produce a further advantage over standard gasoline fuels by increasing knock resistance. This would allow engines to be operated at higher compression ratios without risking typical knock damage. However, there is also the potential to reduce the knock resistance of the fuel, which may lead to catastrophic engine damage. Therefore, it is necessary to characterise the fuels ignition behaviour over the entire range of possible fuel blends, for both engine performance and safety reasons.

This study investigates the impact of iso-butanol blending on the ignition behaviour of a reference gasoline ('PR5801' – RON 95.4, MON 86.6). To achieve this, the study applies both fundamental ignition and full-scale research engine studies, utilising the University of Leeds Rapid Compression Machine (RCM) and Leeds University Ported Optical-access Engine (LUPOE) respectively. This equipment is described fully in previous literature [3][4]. Blending ratios of 5-70% by volume iso-butanol are investigated, as are the individual components (gasoline and iso-butanol). A 5-component surrogate is also developed to match the properties of the reference gasoline, and the ability of this surrogate to mimic the ignition behaviour of gasoline and blends with iso-butanol is investigated.

From RCM experiments, the study shows that the addition of iso-butanol to gasoline does not produce a simple increase in knock resistance across all blends. At low volume percentages of iso-butanol, ignition delay times (and therefore knock resistance) are lower than those of the standard gasoline, indicating a higher reactivity. This is particularly true in the negative temperature coefficient (NTC) region. However, as iso-butanol volume percent increases beyond 10%, this behaviour changes and increasing the amount of iso-butanol in the blend increases ignition delay times, particularly at low temperatures ($< 800$ K). Similar behaviour has been observed at the University of Leeds RCM facility, during investigations of n-butanol blending [3, 5], where suppression of the NTC region by n-butanol can be observed at blends of 20% by volume n-butanol. The 5-component surrogate provided a good representation of the reference gasoline's ignition behaviour in the RCM in general. However, under a high degree of iso-butanol blending the surrogate produced significantly longer ignition delay times than the same conditions for the reference gasoline, particularly at low temperatures. Also, kinetic simulations of ignition delay time failed to represent the intensity of the NTC behaviour of the 5-component surrogate.

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The fundamental study results are consistent with the findings of LUPOE experiments. The 5-component surrogate continues to give a good representation of gasoline and the same knock resistance influence is seen in blends with iso-butanol, with blends below 10% iso-butanol producing an earlier knock onset at crank-angle spark advance timings of $> 10\circ$. Blends with more than 10% iso-butanol by volume again showed a continuous improvement in knock resistance. A drastic decrease is also observed in knock intensities for blends with greater than 10% iso-butanol. These results indicate that the supplementing of gasoline with $> 10\%$ iso-butanol by volume produces a significant knock resistance improvement and may allow for the safe increase of SI engine operating conditions, improving efficiency and performance.

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# A Study of the Physical Properties of Cellulose Derived Biofuel Components and Diesel Blends

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The decarbonisation of transport using alternative low carbon fuels, such as biofuels, will be a key component in achieving the reduction of greenhouse gas emissions required for Europe to become net zero in terms of CO2 emissions by 2050. Most biofuels currently used are first generation, however, the revised Renewable Energy Directive (RED) limits these to a maximum of 7% of the final energy consumption for any Member State of the European Union. Production of second generation biofuels from cellulose is an increasingly active area, with a range of conversion methods being developed, including the alcoholysis of cellulose to produce the corresponding levulinate ester and dialkyl ether from the dehydration of the alcohol. Biofuels based on mixtures of the alcohol, alkyl levulinate, and dialkyl ether have the potential to be a tailorable biofuel component mixture depending upon the final application. These second generation fuel components could play a role in increasing the biofuel content of blends using gasoline or diesel. However, the implications and effects of blending these components with gasoline or diesel are not fully understood.
Compression ignition (CI) engines have an efficiency advantage over spark ignition (SI) engines, which results in lower carbon dioxide emissions per kilometre. The increased efficiency of CI engines makes them the engine of choice in the haulage industry and their use is likely to continue in the near-term future. Several alternative fuels could be used for this sector such as compressed natural gas, biodiesel, and used cooking oil. However, there is an interest in the development and utilisation of new fuel components to reduce emissions from CI engines. Reducing the emissions from CI engines is becoming a priority for the automotive industry as legislated emissions limits have been reducing with each version of the emissions standards, due to their effects on air quality as well as climate change. The use of cellulosic derived biofuel components could be one route to reduce the emissions from a CI engine.

Diesel fuels sold across Europe must meet the limits for the physical properties set in the European Standard EN 590. The biofuel content of diesel fuel is limited to up to 7% biodiesel and the use of other oxygenated biofuel components results in diesel fuel blends that do not meet EN 590. Thus, amendments to EN 590 or a new standard may be required to allow for the implementation and utilisation of such diesel/biofuel blends. It is therefore important to understand the impact that blending advanced biofuel components and mixtures with diesel may have on the physical and chemical properties of the fuel.

This study investigates the physical properties and blending characteristics of the biofuel components produced from alcoholysis of cellulose when blended with diesel fuels, and as a three-component biofuel blend, including their miscibility, stability, flashpoint and density. The differ-

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ent biofuel components considered in this study are: ethanol, diethyl ether, and ethyl levulinate along with n-butanol, di-n-butyl ether, and n-butyl levulinate. A design of experiments approach was used to generate predictive equations and response surfaces for the measurable properties for the different compositions of the ethyl and butyl based three-component biofuel blends. In these three-component blends the alkyl levulinate was at least 50 vol% of the blend which is favourable from the production point of view.

Blend stability and miscibility of the components were investigated using blends of different volume fractions of diesel and the biofuel components stored at ambient temperature, typically 18 ◦C to 20 ◦C, for a duration of three months. The use of graduated test tubes enabled the quantification of any phase separation. The flash point temperature was determined using a Stanhope Seta Setaflash Series 3 plus small-scale closed cup flash point tester according to ISO 3679. Density was determined according to EN ISO 3838 at 15 ◦C. Both standards are fundamental for fuel safety and utilisation. Having the predictive models enables the composition of the three-component biofuel blend to be tailored for its final application.
The effects of how the different ratios of the three biofuel components when blended at different volume fractions with diesel on the flash points and density of the blends were investigated. Flash points of the blends of ethyl levulinate, ethanol, diethyl ether, and diesel have been found to reduce significantly, due to the high volatility and low flash points of the diethyl ether and ethanol. For the butyl levulinate, n-butanol, di-n-butyl ether, and diesel blends the reduction in the flash points were not as significant. These changes in flash points must be taken into consideration for the storage and handling of the fuel blends and should be reflected in an appropriate standard. The effects of how the components and their blending volumes effect the flashpoints and blend density are discussed.

# Characteristics of flame heat release and soot emissions of methane and ethylene laminar diffusion flames with dimethyl ether addition

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## ABSTRACT

Biofuels could contribute significantly to decarbonisation of the transport and power generation sectors and offer the potential of pollutant emission reduction. In 2018, the World Health Organisation revealed that about 4.2 million deaths around the world are attributed to air pollutions [1]. Prolonged exposure to particles may cause cardiovascular and respiratory illness. Consequently, following the rise in the public's general awareness regarding not only the environmental protection, but more importantly the need for alternate energy sources, decreasing the current levels of greenhouse gas emissions has become the main area of concern, creating a higher demand for relevant research. The utilization of cleaner fuels, such as biofuels, as an alternative to conventional fuels is one of the solutions as it offers similar energy content with fewer emissions. It has been suggested that mixing dimethyl ether (DME) or inert gas with hydrocarbon biofuel reduces the emissions particularly soot [2-4]. However, there is still lack of understanding of biofuel flame structure and the relationship between structure, heat release and emissions.

The objective of this study is to understand the characteristics of soot emissions and flame heat release rate (HRR) for different DME mixtures with hydrocarbon biofuels.

In this work, the effects of DME and nitrogen (N2) addition to methane (CH4) and ethylene (C2H4) fuels on combustion characteristics of flame heat release rate, soot emissions and flame temperature were investigated experimentally and numerically in a co-flow non-premixed laminar flame. The co-flow burner used in this work has a similar structure to the Yale co-flow burner [5]. The HRR and soot volume fraction were measured experimentally using CH*, OH* and C2* chemiluminescence and planar two-colour soot pyrometry technique, respectively. The CH*, OH* and C2* were used particularly to find the correlation between their chemiluminescence and HRR as well as to investigate the soot signal's effect on the measurements of HRR. Numerical calculations of all flame conditions were also performed using COSILAB software which was implemented with a detailed chemical kinetic mechanism (Mech_56.54, [6]) comprising of 113 species and 710 reactions to investigate the destruction and production rates of species including OH*, OH, CH*, CH, HRR, CH3, C3H3, C2H2 and flame temperature. The validated mechanism (Mech 56.54) was used because it includes the chemiluminescence reactions, allowing the comparison with the experimental results to further investigate the characteristics of soot emissions and HRR for different DME mixtures. Constant fuel stream volumetric flow rate was maintained throughout all test conditions. The effect of DME on combustion characteristics

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was also studied in flames having equal power output and total stream volumetric flow rate by adding nitrogen N2 (dilution).

It has been observed from the current experimental results (from direct images) that the soot radiation appearance in methane flame became initially stronger with little addition of DME (25%). However, when DME mixture ratio was increased by more than 25%, the soot radiation appearance methane and flame became weaker, indicating either less soot concentration or reduced soot temperature. Whereas, numerical results suggested that C2H2 (soot precursors) peak value was observed to be reduced with 25% DME mixture ratio, nevertheless, the area under C2H2 profile increased. Furthermore, it was noticed numerically that DME/CH4 flame mixture temperature increased by increasing DME mixing ratio, unlike with the CH4/N2 mixture conditions in which the addition of N2 reduced the flame temperature. The addition of DME and/or N2 to methane or ethylene flames were found to decrease the soot concentration and HRR both numerically and experimentally. Numerical results showed that soot concentration and HRR were affected more by the addition of N2 in comparison to the addition of DME to methane or ethylene flames. The addition of N2 to DME/air mixture reduced the HRR, soot concentration and flame temperature significantly. The CH*, OH* and C2* chemiluminescence results of equal power output conditions showed a decrease in their intensities as more DME and N2 are added simultaneously to methane flame, indicating lower HRR and soot concentration. Whereas, numerical results illustrated that the area under curves for all species profiles remained unchanged throughout all flames having similar power output. This study contributes towards collecting and analysing missing data that are related to the relationship between the biofuels flame structure and emissions.

**Keywords:** biofuel, co-flow diffusion flame, dimethyl ether, heat release rate, soot emissions.

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**Reference:** Can be found in the PDF file.

# Numerical investigation of the effects of spatial distribution of CO2 dilution on localised forced ignition of stoichiometric biogas-air mixtures

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As fossil fuel reserves are finite and gradually running out, eco-friendly alternative renewable fuels are becoming ever more important. One such alternative fuel is biogas, which can be used as either a complement or a replacement for existing fossil fuels. Moreover, depending on the production method used, biogas can be a carbon neutral fuel, and due to existing natural gas infrastructure, it can be easily stored and transported whilst also being used in conjunction with natural gas for power generation and transportation [1-6]. Biogas is primarily composed of CH4 and CO2, however production of industrial quantities of biogas with a fixed composition is hard due to its potential biological origins [2]. The composition of biogas is of critical importance, as variations in CO2 content can affect its localised forced ignition (e.g. spark and laser ignition) performance, leading to adverse effects on the subsequent flame propagation [1-6]. Experimental studies of forced ignition of biogas/air mixtures revealed that CO2 acts as a heat sink leading to a higher energy requirement for ignition as well as a slower and cooler flame [1-6]. It has been found that CO2 dilution adversely affects the flame kernel formation and can potentially lead to flame extinction for biogas/air fuelled gas turbines [3,4]. In a recent DNS analysis [7] by the authors, the localised forced ignition of statistically planar mixing layers for different extents of CO2 dilution with CH4-air mixtures was investigated, which demonstrated that an increase in CO2 dilution leads to reductions of burning rate and the probability of obtaining self-sustained combustion once the ignitor is switched off. The analysis which is being proposed will concentrate on the effects of the nature of the spatial distribution of CO2 dilution (i.e. variance and integral length scale of CO2 dilution) has in the case of localised forced ignition of stoichiometric biogas (assumed to be CH4 + CO2)-air mixtures for a range of different turbulence intensities. Thus, the localised forced ignition and subsequent flame propagation for stoichiometric biogas-air mixtures with different spatial distributions of CO2 dilution (i.e. mole fraction of CO2 in CH4/CO2 blend) under different flow conditions (e.g. quiescent laminar condition and different turbulence intensities) have been analysed using three-dimensional Direct Numerical Simulations. The biogas is taken to be a mixture of CH4 and CO2, and a two-step chemical mechanism which has been demonstrated to capture the effects of CO2 dilution on laminar burning velocity with sufficient accuracy has been used for the purposes of the parametric analysis which spans the mean, standard deviation and integral length scale of the initial Gaussian distributions of spatial CO2 dilution in the unburned gas. The CO2 dilution level has not been found not to have any significant influences on the maximum values of temperature and the reaction rate magnitude of CH4. However, CO2 dilution acts to reduce the

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probability of finding large reaction rate magnitudes of CH4, which also leads to a decreasing trend of burned gas volume with increasing levels of mean CO2 dilution irrespective of flow conditions. Moreover, an increase in turbulence intensity acts to reduce the burned gas volume irrespective of mixture composition due to the enhancement of heat transfer from the hot gas kernel. The initial values of integral length scale and standard deviation of CO2 dilution (i.e. l_{$\psi$}*and*$\sigma$_{*psi*})*havebeenfoundtoaffecttheburnedgasvolumetovaryingdegreesfortheparameterrangeconsi*
*sustainedpropagationwillbeanalysedinthefullpaper.*

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# On the reactivity of carbonate esters examined by weak flames in a micro flow reactor with a controlled temperature profile

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Oxygenated fuels produced from renewable biological resources can be effective solution to the environmental issues caused by the combustion of fossil fuels. Recently, carbonate esters have attracted attention as a combustion additive. Some studies reported that DEC (DiEthyl Carbonate) is easily miscible with diesel without phase separation and is excellent in terms of PM emissions in practical engines. Fundamental ignition and combustion experiments, and kinetic modeling of DEC and DMC (DiMethyl Carbonate) have been conducted. Carbonate esters are extensively used also as a solvent for lithium ion batteries. Unwanted accidents of the lithium ion batteries are an international concern. Fundamental understandings on ignition and combustion characteristics of carbonates esters are indispensable to safety for lithium ion batteries. In this study, the ignition and combustion characteristics of carbonate esters were investigated using a micro flow reactor with a controlled temperature profile (MFR). DMC, EMC (Ethyl Methyl Carbonate) and DEC which are typical solvents for electrolyte of lithium ion batteries were chosen in the present study. They have methyl or ethyl groups with the structure of a carbonate ester (RO-C(=O)-OR').

In MFR, a cylindrical quartz tube is employed as a reactor channel and the inner diameter of the tube is smaller than the ordinary quenching diameter. The tube is heated by an external heat source and a stationary temperature profile along the inner surface of the tube wall is formed in the flow direction. Weak flames were observed at low flow velocities of several cm/s. Theoretical analysis showed that weak flames represent ignition characteristics of test fuels. The reactivity of the mixture can be evaluated by observing the temperature region where flame was formed: higher/lower reactivity fuels make weak flames at lower/higher temperature region. In the present study, a quartz tube with an inner diameter of 2 mm was employed as a reactor channel. H2/air premixed flat-flame burner was used as an external heat source. The maximum wall temperature was set to 1300 K. A stoichiometric mixture with air was introduced to the reactor from the lower temperature side at a flow velocity of 2.0 cm/s to observe weak flame with a digital still camera. The position of the maximum chemiluminescence in the flame image was defined as the weak flame position. Under low flow velocity conditions, flow in MFR can be modeled as a one-dimensional reactive diffusive laminar flow without a boundary layer. Therefore, computations were performed using the steady-state one-dimensional flame code (PREMIX code in the ANSYS Chemkin-pro ver. 19.3) with an additional term of a heat transfer between the reactor wall and the gas in the energy equation. The same wall temperature profile as in the experiments were used in the computations. As detailed chemical kinetic models,

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DMC mechanism developed by LLNL group (257 species, 1563 reactions) and DEC mechanism developed by Tsinghua group (341 species, 1980 reactions) were employed. As no mechanism for EMC has been developed yet, we developed a trial mechanism using rate parameters of EMC reactions modeled by analogy with those of DEC and DMC reactions. The computational conditions were same as the experimental conditions. The maximum peak position of the heat release rate (HRR) was defined as the weak flame position in computations. The computational weak flame positions were compared with the experimental ones.

The wall temperatures at the weak flame positions obtained in the experiments were 1149–1183 K for DMC, 1128–1162 K for EMC, and 1142–1154 K for DEC: in the computations, 1177 K for DMC, 1140 K for both EMC and DEC. In both experiments and computations, a weak flame of DMC was stabilized at higher temperature compared to those of the other samples, which means lower reactivity of DMC. EMC and DEC exhibited almost the same reactivity with each other. To investigate the difference in the reactivity, the weak flame structures of DMC with methyl groups and DEC with ethyl groups were compared. DEC had a negative heat release rate around 970 K where in the upstream of the main heat release took place and it was found that the decomposition of DEC is a major pathway of DEC consumption. On the other hand, most of the initial DMC were consumed by H-abstraction reactions. This is probably because the molecular structure of DMC is stronger than that of DEC. It is considered that the DEC decomposed at low temperature because of the low bond energy of ethyl group on DEC. Focusing on the profiles of fuel mole fractions, DEC was completely consumed on 1050 K, while DMC remained up to 1165 K. It is considered that the difference in the initial reaction between DMC and DEC leads to the difference in the reactivity. EMC also had a similar tendency to DEC, suggesting that the presence of the ethyl group would control the reactivity.

# Combustion and emission characteristics of next generation biofuels – kinetic modelling analysis of dimethyl-ether/heptane flames

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The use of biofuels dates back to the conception of humanity. The invention of electricity initiated the utilization of biofuels for power generation, which eventually shifted to fossil fuels following the discovery and eventually, cheap supply of petroleum. However, climate change and the increased insecurity in the oil market considering hikes in oil price and depleting reserves, has once again sparked global interest in biofuel utilization for power generation and transportation. In order to transition towards low-emission fuels, it is important to understand the technicalities of biofuel utilization; combustion characteristics, energy content and emission levels, and these factors are not well understood. The objective is to study the combustion reaction mechanisms responsible for the formation of particulate matter and NOx for biofuels such as bioethanol, biodiesel, synthesis gas, as well as the effect of different lean or rich blends of selected biofuels on said emissions.

Through kinetic modelling, the effect of fuel-lean to rich equivalence ratios of selected fuel blends on the flame speed/structure, heat release, combustion characteristics and soot and NOx emissions are analysed to produce information on how these fuels can be utilized in transport engines.
This research focuses on various blend compositions of Dimethyl Ether (DME) with Methane, and more interestingly, DME with Heptane (C7H16) fuel, providing new understanding of the flame structure, soot formation and NOx emissions of the key biofuel combustion.

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# Ignition and kernel to flame transition in a non-premixed CH4/CO2/air planar turbulent jet

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Localised forced ignition (spark, laser) of flammable mixture is a topic of fundamental importance in combustion science. A thorough knowledge of ignition is needed for safety standards as well as in the design of efficient and reliable Spark ignition and Direct Injection engines, in which misfire causes inef fective combustion, but also for the relight of gas turbine at altitude. The ignition of turbulent flammable mixtures is not only influenced by the minimum ignition energy or the critical flame radius, but it also is strongly dependent on the local properties of the energy deposition region (turbulence characteristics, scalar gradients, mixture composition, etc.) and of the overall flow field [1–3].

Furthermore, the flammable mixture resulting from the dilution of methane with carbon dioxide is generally referred to as ”biogas” and has been identified as a carbon neutral fuel when originating from anaerobic digestion of organic matter by living organisms [4]. It is also widely accepted as a sustainable fuel that can be used either as a complement or a replacement in applications such as power generation or within the transport sector [5, 6]. However, to date, limited effort has been directed to the understanding of its ignition, and the uncertain combustion behaviours arising from the various amount of methane and CO2 on the ignition process are yet to be analysed in detail. In particular, the ignition of biogas in inhomogeneous mixtures and in the presence of shear has not been studied.

The ignition of a simple canonical turbulent round methane jet in ambient air has been extensively studied by both experimental and numerical means [3, 7–10]. Building on previous numerical studies of methane/air ignition [1, 3], three-dimensional compressible Direct Numerical Simulations (DNS) have been carried out to investigate the ignition of a biogas planar jet. A two-step mechanism involving incomplete oxidation of CH4 to CO and H2O and an equilibrium between the CO oxidation and the CO2 dissociation has been used [2]. This two-step mechanism captures the variation of the unstrained laminar flame speed with equivalence ratio and CO2 dilution with sufficient accuracy when compared with detailed chemistry results. The study focuses on the three stages of flame evolution, i.e., (i) flame kernel growth, (ii) downstream flame expansion and radial propagation, and (iii) potential upstream flame propagation which relies on edge flame propagation. The flame expansion spans different combustion modes, from premixed to non-premixed in the presence of edge flames. The addition of CO2 in the fuel stream affects significantly the flame kernel development and the subsequent flame behaviour by reducing the unstrained laminar flame speed and the heat release rate.

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The effect of CO2 dilution on the mixture fraction field will be discussed and it will be shown that an increase in CO2 content may lead to more favourable regions for the flame development closer to the jet nozzle. The different flame development stages reported experimentally have also been captured irrespective of the CO2 dilution level, starting from the initial growth and downstream convection of the kernel to the final upstream propagation and stabilisation of the flame through the radial expansion and downstream propagation stage. The flame structure arising from the kernel growth appears tribrachial in which a triple point propagates along the stoichiometric mixture fraction iso-surface. The stabilisation of the flame was found to primarily rely on the propensity of the triple point to locally propagate faster than the streamwise flow velocity, allowing the lifted height of the flame to decrease slowly in time until an equilibrium with the streamwise velocity is found. The CO2 dilution was found to alter this height relatively long after the energy deposition has ended, when the edge flame speed becomes the main parameter driving the flame movement, as this speed decreases with an increase in dilution.

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# High-throughput fuel screening tool toward advanced combustion concepts using machine learning QSPR and chemical kinetic

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A high-throughput fuel screening tool is developed to accelerate the property-oriented fuel design and identify fuel blendstocks with desirable physicochemical properties to realize the full potential of advanced combustion concepts. Tier 1 screening examines volatility, atomization, energy density, sooting tendency, ignitability which cover 15 physicochemical properties. A fuel property database, molecular descriptor QSPR-UOB 3.0 and 15 machine learning QSPR (quantitative structure-property relationship) models are constructed. Tier 2 screening explores the chemical kinetic properties of ignition delay time, -sensitivity and laminar flame speed. Tier 1 screening preselects 166 and 129 blendstock candidates for boosted SI (spark ignition) and CI (compression ignition) engines. The design rules of high antiknock, low sooting tendency gasoline blendstocks are: (1) constructing highly compact, branched structure, (2) adding oxygenic functional group, (3) introducing unsaturated, cyclic structure and moving toward a central position of molecule, (4) absence of aromatic structure. The design rules of high reactivity and low soot emission diesel blendstock are: (1) lengthening average chain length and decreasing primary C-H bonds; (2) adding acyclic or cyclic ether group; (3) moving unsaturated bond, oxygenated group (except ether) toward the edge of the molecule if available; (4) avoiding unsaturated, cyclic structures; (5) discarding aromatic structure. 16 selected blendstocks rank in order of priority as: (a) for SI engine: diisobutylene > iso-octane > ethanol > cyclopentanone > cyclopentanol > 2,5-dimethylfuran > toluene > 2-methylfuran; (b) for CI engine: dibutyl ether > n-heptane > n-octane > 2-butyltetrahydrofuran > butylcyclohexane > 1-octanol > PODE3 > PODE4.

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# Identifying potential lignocellulosic octane boosters through co-oxidation studies with isooctane

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Despite continuous efforts towards extending the range of batteries, the application of full-electric vehicles to long-range transport remains challenging, therefore calling for extensive research in alternative fuels with low carbon impact. Among the current production routes, synthesis of fuels from lignocellulosic biomass is an interesting option, leading to a variety of products. The operability of such biofuels is however strongly dependent on their reactivity towards the low-temperature combustion regime, which is in turn strongly linked to the octane rating.

It has been demonstrated that a pure compound can display high resistance to knock, and therefore high octane number, but be very reactive when blended inside a fuel. This is mostly due to co-oxidation, where a reactive moiety of the fuel produces radicals that can in turn trigger the reactivity of the unreactive counterpart. In order to detect such behaviour for biofuel candidates, co-oxidation studies must be performed inside a controlled laboratory environment.

Ignition delays of mixtures of four biofuel candidates -anisole, orto-cresol, cyclopentanone and prenol- inside mixtures with isooctane have therefore been measured inside a Rapid Compression Machine at the University of Lille. These show the very different impact that the addition of such biofuels has on the reactivity of this SI fuel surrogate. These help discussing the most important reaction pathways during the oxidation of these potential biofuels.

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