EXPERIMENTAL INVESTIGATION OF ATOMIZATION AND COMBUSTION PERFORMANCE OF RENEWABLE BIOFUELS  
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This poster presents results from an experimental investigation of the macroscopic and microscopic atomization behavior of B99-biodiesel, ethanol, B99-ethanol blends, methanol, and an F-76-Algae biodiesel blend. In addition, conventional F-76 and Diesel #2 sprays are characterized as a base case to compare with. The experimental spray apparatus consists of a plain air-blast atomizer mounted on a traverse. The breakup characterization of each fuel is conducted under the same air flow conditions in order to simulate use as a drop in source to existing gas turbines with only slight modifications. For this study, a Phase Doppler Particle Analyzer and Laser Doppler Velocimetry system is employed to gain information on drop size, SMD, velocity, and volumetric flux distribution across the spray plume. A Vision Research Phantom high speed camera is used to gather high speed cinematography of the sprays for use in observing breakup characteristics and providing additional insight. The results illustrate how the fuel type impacts the atomization and spray characteristics. A variety of B99-ethanol fuel blends are used which illustrate a tradeoff between lower density, surface tension, and viscosity with a decrease in the air to liquid ratio. Future work will entail swirl stabilized combustion of each fuel in order to compare with non-reacting flow results. Reacting flow measurements will include NOx, SOx, and CO emissions, lean blow out limits, and flame luminosity.

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SPHERICAL FLAME INITIATION AND PROPAGATION IN A LIQUID FUEL MIST WITH FINITE-RATE EVAPORATION  
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Droplet vaporization might have a great impact on fundamental spray combustion processes such as ignition, flame propagation and extinction. In this study, spherical spray flame initiation and propagation through a fuel-rich/lean pre-mixture containing fuel droplet with finite-rate evaporation are analyzed using the large-activation-energy asymptotic method. Thermal-diffusive model with constant density is employed and the spherical flame is assumed to propagate in a quasi-steady state. Analytical correlations describing the change of spherical spray flame propagation speed with flame radius are derived. The droplet vaporization parameters (initial droplet load, δ, and vaporization Damköhler number, Da), Lewis number and ignition power are included in these correlations. Therefore, the present model can predict the evolution of ignition kernel and propagating spherical spray flame. Based on these correlations, spherical spray flame initiation and propagation are investigated and the impact of droplet vaporization on critical ignition condition and spherical flame propagation is assessed.

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SINGULARLY PERTURBED HOMOTOPY ANALYSIS METHOD APPLIED TO THERMAL EXPLOSION OF POLYDISPERSE FUEL SPRAY  
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In this paper we discuss the new Homotopy Perturbation Method (HPM) combined the Homotopy Analysis Method (HAM) and the Method of Invariant Mmanifolds (MIM). The HAM method is used for slow subprocesses only after a decomposition of the original process to slow and fast subprocesses with the help of the MIM method. For a good accuracy we used the first approximation of a corresponding invariant manifold in the sense of a corresponding small parameter. The HAM method was introduced recently by the authors and their collaborators as an attempt to avoid main problems of the HPM method for slow-fast models. With the help of the HAM method we investigate the problem of thermal explosion in two-phase polydisperse combustible mixtures of gas and fuel droplets. The size distribution of the fuel droplets is modeled as a continuous function in the form of an exponential distribution and is found from the solution of the kinetic equation for the probability density function. The system of the polydisperse fuel spray takes into account the effects of the thermal radiation and convection. By applying the HAM, we derived an analytical solution of the system and we compared our results with the numerical solutions.

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EXPERIMENTAL STUDY OF THE INTERACTION BETWEEN AN ETHANOL SPRAY AND A TURBULENT FLAME FRONT  
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The objective of this study is to characterize the direct interaction between a turbulent flame stabilized by a bluff body and the associated spray. This characterization is performed by using a 283.56 nm laser beam to excite the OH radical fluorescence, which marks the reaction zone in the flame, whereas the second harmonic of a Nd:YAG laser is used to generate the Mie scattering signal of the spray droplets. The spray is operated both at the design point and at off design situations by varying the ethanol flow rate. The effect of different air velocities is also investigated. The turbulent Reynolds number is circa 2300 at the bluff body region. The obtained results show that the instantaneous flame front remains mostly continuous, but corrugated by turbulence. The flame front is closed at the vicinity of the bluff body for the smaller flow rates of ethanol. The increase of air velocity increases the flame thickness, which is attributed to a larger
turbulent diffusivity at higher air Reynolds numbers, and is accompanied by higher averaged OH fluorescence intensity. The Mie scattering signal shows that the air velocity influences the geometry when the air flow velocity is increased. All studied cases are shown to lead to strong flame/spray interactions. Indeed, a large number of droplets are found to pass through the flame, indicating that ethanol is not completely evaporated or burned. Thus, the particular regime of combustion obtained seems to be the percolation one, which will be the subject of future studies.

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W3P005 SPARY FLAME STRUCTURE ANALYSIS IN A LAB-SCALE BURNER USING LARGE EDDY SIMULATION AND DISCRETE PARTICLE SIMULATION
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The numerical study of an academic lab-scale spray burner using Large Eddy Simulation (LES) coupled with a Discrete Particle Simulation (DPS) is presented. The objectives of this study are first, to validate subgrid-scale models for two-phase turbulent flow and combustion, and second, to bring new insight on two-phase flame structure in a complex geometry representative of industrial systems. The configuration is an experiment characterized by a strong interaction between the liquid disperse phase and the reaction zone, as is also observed in most industrial combustion chambers. This strong interaction leads to complex spray burning modes that raise additional modeling issues. The comparison with measurements confirms the capability of LES - DPS to reproduce the velocity field in both non-reacting and reacting cases with good quantitative accuracy. Experimental and numerical images of the spray flame are also in good agreement. The detailed analysis of the spray flame shows that both partially premixed and diffusion flames are present, depending on the possible pre-evaporation of the droplets. In addition, and as observed in the experiment, single droplet combustion occurs downstream the main flame front. This combustion mode leads to small diffusion flames around the droplets that can not be resolved in the simulation and require a specific modelling approach. An extended two-phase combustion model that takes into account single droplet combustion is finally presented with first validation tests.

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W3P006 EFFECT OF FUEL-SPRAY OSCILLATIONS AND DROPLET GROUPING IN THE FORMATION OF MULTIPLE FLAMES
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The sensitivity to the vaporization Damkohler number of the behavior of a co-flow laminar spray diffusion flame in an oscillating flow field is investigated. Droplet grouping induced by the host gas flow oscillations is accounted for. The effect of droplet grouping is described through a specially constructed model for the vaporization Damkohler number that responds to the proximity of the droplets as they cluster due to the spray-flow oscillations. A formal analytical solution is developed for Schwab-Zeldovitch parameters through which the dynamics of the spray flame front shapes and thermal fields are deduced. Computed results based on the solutions demonstrate how strongly the vaporization Damkohler number including droplet grouping effects impacts on the type of primary homogeneous flame formed and on the possible existence of multiple flame sheets as a result of dynamic changes from under- to over-ventilated flames as the flow field oscillates. A further subtle, allied phenomenon that produces isolated regions of high fuel vapor concentrations is fuel droplet enrichment that stems from the combination of droplet grouping and the oscillating droplet and host gas flow fields. Such regions also lead to the formation of multiple flames under certain operating conditions. The Burke-Schumann laminar spray flame configuration is considered, in which fuel vapor and droplets flow in an inner duct and air flows in outer duct. Under appropriate operating conditions, after diffusive mixing of the two streams, a laminar spray diffusion flame is maintained. The model and the evolution of the flame with/without the grouping effect of the fuel-droplets, as well as the multi-flame situation will be presented.

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W3P007 PLANAR LASER-INDUCED FLUORESCENCE SPECTROSCOPY AND SIMULATIONS OF IGNITION AND COMBUSTION OF FREELY FALLING ALKANE, ALCOHOL, AND METHYL ESTER DROPLETS
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In emission measurement studies, diesel engines fueled by fatty-acid methyl ester biodiesel often exhibit slightly increased production of oxides of nitrogen (NOx) in comparison to petroleum diesel. A number of explanations for this increase have been proposed by the research community. One theory, which has been supported by optical engine test results, suggests that the presence of oxygen atoms in the methyl ester fuel molecule results in a leaner premixed autoignition zone, thereby increasing in-cylinder temperatures and promoting thermal NOx production. Other experiments have suggested that the unsaturated methyl esters in biodiesel cause an increase in CH radical production (and/or other potential precursors such as C2O) which in turn increases prompt NOx formation.

In the present study, these hypotheses are explored experimentally and computationally by considering the ignition and combustion of single, isolated alkane, alcohol and methyl ester droplets. Experiments were conducted in
which the Planar Laser-induced Fluorescence (PLIF) spectroscopy technique was applied to burning liquid fuel droplets in free-fall. A monodisperse stream of droplets was generated by a piezoelectric device and passed through an electrically heated coil where they autoignited. A pulsed laser beam from a Nd:YAG-pumped dye laser (10 Hz, ~10 ns width) was formed into a sheet and passed through the droplet flame. The dye laser was tuned to excite hydroxyl (OH) at 282.9 nm and Nitric Oxide (NO) at 226.0 nm. The resulting fluorescence was imaged by a Cooke Corporation DiCam Pro ICCD digital camera. Bandpass filters were utilized to reject laser light scattering while admitting fluorescence wavelengths. Due to the small fluorescence signal, many fluorescence images were averaged together to create a useful average image; approximately 250 and 1000 images were averaged for OH and NO spectroscopy, respectively.

Finally, pixel intensities of the averaged fluorescence image were integrated about the droplet center to create radial profiles of OH and NO concentration. Profiles were generated for a number of oxygenated fuels and one pure hydrocarbon: methanol, ethanol, 1-propanol, methyl butanoate, methyl decanoate, and n-heptane.

To quantitatively interpret the contribution of thermal and prompt NOx mechanisms on NOx formation in the vicinity of igniting liquid droplets, simulations were conducted with an independently-developed comprehensive numerical model developed at Princeton University. The transient, spherically symmetric droplet combustion model features detailed gas-phase kinetics, spectrally resolved radiant heat transfer, and multi-component gas transport. Mass and energy conservation is solved in both the gas and liquid phase. The heat transfer within the droplet is of “finite” conduction prescribed by the liquid phase thermal conductivity. Chemical kinetic mechanisms were created by appending NOx chemical kinetics to the respective fuel mechanisms.

The fuels for which simulations have thus far been conducted are: methanol, methyl butanoate, and n-heptane. In the computations, non-oxygenated (heptane) and oxygenated (methyl butanoate, methanol) fuel droplets are introduced into a hot (1150 K) air ambient whereupon the liquid vaporizes, thus producing a stratified fuel/air mixture that thermally autoignites after an ignition delay period. The computational results suggest that NOx formation in stratified fuel/air mixture in the vicinity of a cold liquid droplet is influenced greatly by the detailed full NOx chemistry (prompt, thermal, and N2O) and cannot be fully explained by considering only the thermal NOx route. The computations also suggest, however, that the stoichiometry of the premixed autoignition zone in the laminar gas phase surrounding a spherical droplet differs from that observed in turbulent diesel spray ignition.

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W3P008

SIMULATING FLAME-SPREAD BEHAVIOR OF RANDOMLY DISTRIBUTED DROPLET CLOUDS BASED ON PERCOLATION THEORY AND MICROGRAVITY EXPERIMENT OF DROPLET ARRAY

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It is difficult to conduct the experiment on large-scale droplet cloud combustion because the buoyancy effect is significant in normal gravity. Experiments on the flame-spread characteristics of droplet-array and droplet-cloud elements have been conducted in microgravity, but the findings have not fully elucidated the spray combustion phenomenon because the number of droplets is limited in the experiments. This research presents the numerical simulation of 2-Dimensional (2D) and 3-Dimensional (3D) flame-spread behavior in large scale droplet clouds in which the droplets are distributed randomly. The numerical simulation was calculated using the percolation approach and considering the flame-spread characteristics of droplet array obtained in microgravity experiments, especially the flame-spread-limit distance (Sd0) limit. The Occurrence Probability of Group Combustion (OPGC) was calculated as a function of the mean droplet spacing (Sd0) without and with two-droplet interaction. The results show that OPGC rapidly decreases with increasing (Sd0) m around a specific value and this critical threshold separates the droplet clouds into two types: dilute spray and dense spray. The critical mean droplet spacing (Sd0) critical increases with the two-droplet interaction and is greater for the 3D droplet cloud than for 2D one. (Sd0) critical was also discussed considering the influence of the lattice size (NL/d0), lattice point interval (L/d0).

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W3P009

BURNING CHARACTERISTICS OF BIODIESEL MIXED WITH ALCOHOL IN MICROGRAVITY CONDITION

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By using a drop tower that can support a free-falling process of 0.68s, we have studied combustion characteristics of biodiesel droplets mixed with various alcohols in microgravity environment. By using two hot wires to ignite a droplet with fixed diameter around 535 μm, we have observed various combustion phenomena of fuel droplets made of single and binary components in reduced gravity, including the evolutions of droplet diameter, burning rate, micro-explosion, and extinction. In particular, we studied the propensity to microexplosion of binary fuels containing premixed liquids of biodiesel and ethanol. To minimize experimental uncertainty, we used the powerful built-in function of an image processing software, Matrox Inspector 8.0, to measure the boundaries. It was found that when a droplet of biodiesel mixed with alcohol was deployed onto the cross section of two ceramics fibers, non-uniform sites similar to liquid bubbles occurred. In this situation, whether under the condition of normal gravity or reduced gravity, micro-explosion was always generated while burning. Occurrence of such non-uniform phenomena was related to the relative humidity of the environment. With increasing of relative humidity, the bubble-like sites became bigger. At the same relative humidity, the bubbles became smaller as the carbon number of alcohol increased. Furthermore, with increase of
the alcohol concentration, the size of liquid bubbles became bigger. It was also found that the bubble-like sites inside the droplet diminished with time. After the bubbles vanished, no micro-explosion was ever observed during burning.

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W3P010 LES OF THE SYDNEY SPRAY FLAME SERIES WITH PFGM/ATF AND DIFFERENT SUB-GRID MODELS

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The Sydney spray flame series is investigated by Large Eddy Simulation (LES). Combustion is modeled by the Premixed Flamelet Generated Manifold approach (PFGM), which is combined with the Artificially Thickened Flame Method (ATF). The dilute ethanol and acetone spray flames, stabilised by a coaxial pilot flame, have been experimentally investigated by Masri and coworkers at the University of Sydney. Of the available fuel and mass flow combinations, we have chosen the ethanol flames referred as”EtF3, EtF8 and EtF18”, with the same ethanol mass flow rate but different carrier gas mass flow rates in the central stream.

The simulations are performed with the LES inhouse code PsiPhi. Grids with three different resolutions (from 3 to 24 million cells) are used to investigate the influence of the filter width. The gas and spray phases are described by an Euler/Lagrange approach. The phases are fully coupled by the exchange of mass and momentum. Nicoud’s σ-model is used to determine the turbulent Sub-Grid-Scale (SGS) stresses. One dimensional simulations of premixed freely propagating flames with a detailed reaction mechanism were performed to a priori tabulate the combustion variables as a function of two controlling variables (Φ=f(Z,Y_p)). The Favre filtered mixture fraction (Z) and progress variable (Y_p) are the determining quantities. A thickening factor is applied to the transport equation of the progress variable to resolve the thin reaction zone of the flame (typically ~ 0.1-0.5mm) on the computational grid, and a flame sensor indicates the burning region and determines the use of the thickening factor.

The sub-grid distributions of Z and Y_p are modeled with (a) a presumed beta filtered density function (β-fdf) and (b) a Top-Hat function (TH). In the β-fdf approach, the two-dimensional look-up table (Φ=f(Z,Y_p)) is extended to a third dimension by using either the mixture fraction variance (Z^2) or the progress variable variance (Y_p^2) as a third control variable. Albeit, in the TH approach the two-dimensional look-up table is a priori integrated over a third control variable (Z^2 or Y_p^2), or over a third and fourth control variable (Z^2 and Y_p^2). With the TH approach, the look-up table remains two-dimensional. The variances Z^2 and Y_p^2 are determined with either an algebraic gradient model or with a transport equation model. First, the influence of the mixture fraction variance (Φ=f(Z,Y_p,Z^2)) and the progress variable variance (Φ=f(Z,Y_p,Y_p^2)) on the simulation results is investigated separately. Subsequently, the joint impact of Z^2 and Y_p^2 is investigated with the TH model (Φ=f(Z,Y_p,Z^2,Y_p^2)). The results obtained with the different sub-grid models are compared against the available experimental data and reference simulations without any Sub-Grid Model.

Generally, the particle statistics are in good agreement with the experimental evidence. The results obtained with the TH and the β-fdf model are comparable. It must be stressed that the influence of the sgs models for the mixture fraction and the progress variable was found to be small for the investigated spray flames series. We have therefore set up a more sensitive test case to amplify and show the differences in the models, which are presented in the poster.

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W3P011 OXYGEN LEWIS NUMBER EFFECTS ON REDUCED GRAVITY COMBUSTION OF METHANOL DROPLETS

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Reduced-gravity combustion experiments of individual methanol droplets were conducted on the International Space Station in air/xenon and air/helium environments at 1 atm and 0.7 atm and about 298 K. Droplet diameters were initially in the 2-4mm range. The present study investigates the flammability and extinction of methanol droplets under these conditions. Droplet diameter histories, burning rate histories, and radiometer data are evaluated. The experimental results show that the Limiting Oxygen Index (LOI) for methanol droplets in air/xenon environments is appreciably smaller than in air/helium environments. This discrepancy between the two ambients is due to differences in transport properties and simplified theory for prediction of the LOI is developed in terms of the oxygen Lewis number. Additionally, the radiometer data show fluctuations for methanol droplets with initial diameters greater than 3mm; these fluctuations correlate with flame shape oscillations.

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W3P012 INVESTIGATION OF THE LAMINAR BURNING VELOCITY OF ETHANOL AND HEXANE/AIR AEROSOLS.

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Combustion of droplets is of significant research interest for a wide range of applications such as furnaces, gas turbines or engines. In addition, aerosol explosions represent a hazard in the process industry, with actual methods for preventing the effects of such accidents still qualitative, and rely on correlations used for gas explosions. It is of prime importance to investigate the mechanisms underlying aerosol explosions to evaluate this hazard and develop models to quantify and predict the consequences.

To this end, the presented poster work details an experimental apparatus consisting of a cloud chamber/
Compared to gaseous combustion, spray flames represent a considerably more complex combustion system, which requires the consideration of competing processes between evaporation, mixing and chemical reaction. Because of this complexity, the analysis of spray flames in canonical combustion configurations, such as counterflow flames, represents a viable approach to obtain physical insight into the behavior of these flames.

Laminar gaseous diffusion flames are typically examined in composition space by introducing the mixture fraction $Z_g$ as an independent variable. This quantity is defined with respect to the composition of the gas phase and provides a unique relation to the distance along the flame-normal direction. Such a description allows to obtain a state-space representation of the flame structure that is independent of spatial coordinates. Many turbulent combustion models rely on such a representation, by assuming that a turbulent flame is composed of a collection of laminar flames, called flamelets. Extending this mixture fraction concept to spray flames is desirable to enable the modeling of turbulent spray flames. Unfortunately, the classical mixture fraction definition is not anymore monotonic due to evaporation so that the structure of spray flames cannot be solved in the classical mixture fraction formulation, except for pre-evaporated spray flames. Because of this, spray flames are commonly represented in physical space and then transformed into mixture fraction space, for example by separating the purely gaseous region of the flame from the evaporation zone. Although feasible, this approach introduces undesirable model complexities, thereby preventing the use of analysis tools that have been developed for mixture fraction formulations. Furthermore, this approach does not allow for a theoretically consistent extension of turbulent flamelet combustion models to spray flames.

By addressing these issues, this poster presents recent work on the theoretical development of a spray flamelet formulation that extends the classical flamelet concept for gaseous diffusion systems. The key idea of this approach consists in identifying a unique and monotonic representation of a mixing-describing coordinate for spray flames. This new mixture fraction coordinate, referred to as effective mixture fraction, is then used to extend Peters’ flamelet theory, utilizing the same assumptions that were introduced for gaseous flames. In the absence of a liquid spray phase, this new formulation reduces to the classical mixture fraction definition for gaseous systems, thereby ensuring consistency. The validity of this approach is demonstrated in an application to an axisymmetric mono-disperse counterflow spray flame.

This new formulation represents a theoretical tool for the asymptotic analysis of spray flames in composition space. Moreover, it can be considered as the theoretical basis for one-dimensional spray flamelet formulations.

A detailed numerical investigation of unsupported and fiber supported $n$-heptane droplet combustion in reduced gravity is done in the current study. A compact $n$-heptane mechanism consisting of 20 species and 21 reactions is incorporated to model both high temperature and low temperature reactions. The Volume-Of-Fluid (VOF) method is employed to capture the liquid-gas interface for transient two-phase multidimensional flows. The calculations also include variable thermo-physical properties of the liquid and gas phases.

The reaction mechanism is validated for the ignition delay time. The ignition delay times computed in this study agree the experimental results of Tanabe. Computed burning rates and flame stand-off ratios for both unsupported and fiber-supported droplets have been validated with data from drop tower experiments. The present computational results agree well with the experimental results.

The present study has explored influences of heptane pyrolysis on soot shell locations for the first time with a Computational Fluid Dynamics (CFD) analysis that includes a detailed gas-phase reaction mechanism with high and low temperature chemistry. The results show that soot shells should exist at radial locations where heptane pyrolysis first becomes significant, leading to local variations in the temperature gradient, which determines thermophoretic particle velocities. Calculated soot shell radii compare well with available experimental data.

Autoignition behavior of unsteady spray at relatively low temperature conditions was investigated for the primary reference fuels of $n$-heptane and iso-octane and diesel fuels. The KAUST-research ignition quality tester (KR-IQT, AET
For developing a high performance airblast atomizer, it is important to reveal the atomization behavior. Kerosene model solution is a mixture of liquid and polyvinyl alcohol. Further, the effects of liquid properties on atomization were experimentally investigated from droplet diameters, spray structure and behavior of atomization. In this study, the effects of ambient pressure on atomization process and characteristics of typical type airblast atomizer were experimentally investigated from droplet diameters, spray structure and behavior of atomization. In addition, a two-dimensional atomizer was used to observe detailed atomization process of airblast atomizer, whose structure is simulating an airblast atomizer. Further, the effects of liquid properties on atomization characteristics were also investigated using water and kerosene model solution as a liquid for spray.

A new method in determining SOIgn is introduced and applied in the present study. To isolate the effect of the intermediate heat release, the start of ignition is defined by the point of intersection of two slopes, the first being the maximum slope during which the chamber pressure increases steeply and the other being the slope of the chamber pressure curve at the pressure recovery point, which is defined as the point where the chamber pressure recovers the initial pressure after drop in pressure due to evaporative cooling as liquid fuel is injected. The result clearly demonstrates that the seemingly NTC behavior was due to inaccurate definition of SOIgn for the iso-octane fuel having intermediate heat release behavior.

The high-speed back light imaging was used to observe atomization processes of a typical type airblast atomizer at several pressures between 0.1 MPa and 0.7 MPa. Phase Doppler Particle Analyzer (PDPA) and Particle Imaging Velocimetry (PIV) were performed to measure droplet diameters and spray structure. In the present experiment, air flow velocity and mass Air Liquid Ratio (ALR) set constant. Kerosene model solution is a mixture of liquid and polyvinyl alcohol.

A spray structure was generated in a cone shape which consisted of several regions characterized by air flow. At atmospheric pressure, large recirculation zone was observed inside of the cone (IC) and large high shear zone (high velocity zone) was along the cone. At high pressure of 0.5 MPa, small eddies were inside of the cone and high shear zone became small. These could be explained kinetic viscosity of surrounding air change with increasing pressure.

From PDPA data, pressure dependences of droplet diameters were different in each region. In addition, these tendencies were changed by properties of a liquid for spray. These result indicated that pressure dependence of droplet diameters were strongly affected air flow structure and liquid properties. Therefore, it is required to understand detailed change of air flow structure with increasing pressure and the effects of liquid properties on atomization.
injected into environments of pressure below, around and exceeding its critical value while the temperature was kept far above the critical temperature of the injected liquid.

The research was conducted in a rapid compression machine equipped with piston with transparent crown. N-hexane was chosen as the injectant due to its relatively low critical point parameters and the fact that it remains in liquid form under ambient conditions. N-hexane was injected into environments composed of air. N-hexane was introduced into the RCM by gasoline outward opening pintle injector under pressure of 20 MPa. The injector was mounted centrally on the top of the head.

The ignition data was analyzed in terms of ignition delay. The process of ignition was observed in two ways: by the pressure measurement in the combustion chamber and by visual observation of the combustion chamber by means of high speed camera through transparent window in the piston crown. However, the quantitative analysis was based on monitoring the pressure rise. For monitoring the pressure evolution in the chamber, the AVL IndiCom 621 equipped with piezoelectric sensor was used. The pressure recording frequency was of 5 kHz. The ignition delay was determined by pressure rise according to tangential method. The ignition delay determined that way included both physical delay and chemical delay.

Number of studies already showed that ignition delay is influenced by backpressure due to higher energy entrainment into the fuel jet. However, there arises a question whether there is a change in the energy exchange between the liquid jet and the surrounding air when the conditions become supercritical. This question seems to be important, especially taking into account that physical delay is influenced by atomization, evaporation and fuel vapor-air mixing which are different in supercritical environments than in subcritical ones. The ignition delay in supercritical environments is expected to decrease more than in subcritical ones due to the lack of latent heat and, as a result, lack of evaporation.

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W3P018 LES OF A PARTIALLY PREMIXED SPRAY FLAME USING AN ADAPTATIVE-DYNAMIC ATF MODEL COUPLED TO FGM
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Turbulent spray flames are strongly affected by the unsteady stratification of the reactive mixture, which is originated by the turbulent dispersion of evaporating droplets. This mixture stratification allows the simultaneous appearance of different combustion regimes into the flow, delivering highly complex flame structures. The correct reproduction of these phenomena is indispensable to predict the behaviour of turbulent spray flames through numerical simulations.

To investigate the behaviour of the propagation of partially pre-vaporized spray flames, this work presents an Eulerian-Lagrangian spray module relying on the Artificially Thickened Flame (ATF) framework coupled to the Flamelet Generated Manifold (FGM) chemistry reduction method. The unsteadiness arisen from turbulent dispersion of evaporating droplets are captured by the Large Eddy Simulation (LES) method and an evaporation model based on the non equilibrium approach. In order to avoid the presence of different combustion regimes in the reaction domain, the lean partially pre-vaporized spray flame configuration measured experimentally by Pichard et al., which behaves more like a premixed flame, is used to validate the proposed module.

The modified turbulence-flame interaction created by the ATF is recovered through the usage of the efficiency function proposed by Charlette et al. Modifications due to the presence of the spray are carried out on the computation of this efficiency function. The dynamic thickening approach is used to define where the transported scalar quantities shall be thickened, whereas the grid adaptive method is employed to define the thickening factor. Considering that, to predict the flame propagation, the correct computation of the flame speed shall be done; a detailed n-heptane mechanism including 88 species and 387 elementary reactions is adopted.

The validation of the spray quantities is performed through comparisons with experimental data through radial profiles of: droplets mean velocities and their fluctuations, liquid volumetric fluxes and droplets characteristic diameters. Accordingly, the flame structure is validated through comparisons of mean contour profiles of a reaction progress variable defined experimentally. Qualitative analyzes include the investigation of turbulent flame propagation for two flames with two different global equivalence ratios (0.72 and 0.79), respectively. The effects of the presence of the spray on the efficiency function are also analysed.

The validation process was successfully done. The reaction progress variable contours are reproduced in good agreement with experimental measurement. The spray characteristics e.g. droplet diameters and volume flux show minimal discrepancies compared with measured data. The spray presence on the efficiency function shown to make small influence on the computation of the flame structure. The qualitative analysis show that, as experimentally observed, the increase of the global equivalence ratio reduces the flame length, for lean flames.

Even though some effects were neglected, it is suitable for future investigations to include the SGS dispersion modelling and the evaporative cooling in the chemistry computations.

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W3P019 A COMPUTATIONAL MODELING OF DROPLET EVAPORATION INDUCED BY A LOCALIZED HEAT SOURCE
Droplet evaporation by a localized heat source was numerically investigated as an attempt to understand the mechanism of the fuel vapor jet ejection, which was observed experimentally during the flame spread through a droplet array under microgravity conditions. The phenomenon was believed to be mainly responsible for the enhanced flame spread rate at microgravity conditions. An Eulerian-Lagrangian method was implemented in order to effectively capture the interfacial dynamics between liquid droplet and surrounding air. The numerical algorithm utilizes the stationary Eulerian grids to describe the flow field, and moving Lagrangian surface meshes to treat the phase boundaries. Temperature-dependent surface tension and a new local phase change model were employed for modeling thermocapillary effect and non-uniform droplet evaporation by a local heating. It was found that the temperature difference by a localized heating creates a surface tension gradient along the droplet surface, inducing surface movement. Subsequently, the outer shear flow and internal flow circulation inside the droplet, commonly referred to as the Marangoni convection, are created. The outer shear flow around the droplet transports the fuel vapor to the cold wake region of the droplet, resulting in a fuel vapor ejection. A parametric study demonstrated that, at realistic droplet combustion conditions, the Marangoni effect indeed produces a sufficiently large level of convective flow and following fuel vapor jet, which can enhance flame spread rate by transporting fuel vapor and heat to cold regions. The present study confirmed that the Marangoni effect by a local temperature gradient is the key mechanism to understand the fuel vapor jet ejection observed experimentally.

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W3P020 TEMPERATURE IMAGING OF TURBULENT DILUTE ACETONE SPRAY FLAMES USING TWO-LINE ATOMIC FLUORESCENCE
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Diagnostic capabilities in spray flows are gradually evolving but remain limited due to inherent difficulties imposed by the presence of droplets and/or liquid filaments. Dense sprays are extremely hard to probe and techniques such as ballistic imaging and X-ray radiography are just starting to make advances in measuring the structure of the sprays and the mass depletion from the liquid core. Dilute spray flames are relatively easier but still challenging, particularly with respect to measuring details of the mixing and reactive fields. Laser-Induced Fluorescence (LIF) techniques have previously been applied to image selected species such as OH, CH, or fuel vapour. These measurements, while qualitative, reveal interesting information about the structure and evolution of reaction zones. However, measurements of critical parameters such as mixture fraction and temperature remain elusive. This study addresses one of these problems by introducing an approach to measure temperature in turbulent dilute spray flames.

Measurement of temperature in flows laden with solid particles or droplets is very difficult. Standard techniques, such as Rayleigh scattering, are no longer applicable due to corruption by Mie scattering. Coherent Anti-Stokes Raman Spectroscopy (CARS) has established capabilities for accurate measurements of temperature in flames containing soot and more recently in spray flames. Notwithstanding recent developments in CARS, which are yet to be fully exploited, a key limitation of this technique, however, lies in its ability to provide single-point measurements rather than large-scale planar information. Thermometry based on multi-line fluorescence from molecular species such as NO offer capability for two-dimensional imaging, but these methods remain limited to time-averaged measurements. Two-Line Atomic Fluorescence (TLAF) techniques can fill this gap, as demonstrated recently through imaging of instantaneous planar temperature fields in turbulent flames containing soot. The extension of TLAF to the non-linear excitation regime, so called NTLAF, has enabled instantaneous temperature imaging in turbulent non-premixed gaseous flames and flames containing soot. The objective of this study is to extend such capabilities to turbulent dilute spray flames.

With spray flames, there is an opportunity to seed the liquid fuel with indium chloride and thus avoid the need for introducing an additional stream as required for turbulent gaseous flames. Although the NTLAF technique is generally immune from interferences due to soot scattering, it is unclear whether interference from the fuel droplets in spray flames will allow the seeding advantages to be realised. Hence, research is required to determine whether the signal-to-noise ratio is sufficiently high for reliable single-shot data and whether good quality measurement is possible in the region immediately around an evaporating droplet. The aim of the current study is, therefore, to assess, for the first time, the feasibility of conducting instantaneous single-shot temperature imaging in turbulent spray flames using the NTLAF technique.

The liquid-fuel spray flames have been demonstrated to be highly effective for seeding indium required for NTLAF measurements. The detected fluorescence signal is found to be immune to scattering/interference from the spray droplets and vapour. The dilute spray burner is ideally suited to NTLAF thermometry with potential for additional simultaneous measurements via other laser diagnostic techniques. Reliable NTLAF temperature measurements are reported in the reaction zone and these are in excellent agreement with thermocouple measurements.

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W3P021 QUANTIFIED MEASUREMENT OF DROPLET EVAPORATION RATES OF A TWO COMPONENT MIXTURE
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In this work we are using an FTIR to measure the evaporation rate of a suspended binary mixture droplet. The intent here is to devise a method that may be useful to calibrate fuel evaporation models. It is hoped that this information will be used to learn more about distillate fuels injected into small internal combustion engines.

The procedure involves taking a background spectrum using the FTIR (considered the incident light, I0). Next, a droplet is suspended in the instrument beam path beam path and another spectrum is captured (considered as transmitted light, I). The Beer-Lambert law will be applied to determine the path averaged concentration of the evaporated components. Of course beam steering and droplet absorption will be considered. This measurement will be repeated at the scan rate of the instrument to provide a time resolved record of droplet shrinkage.

The components of the droplet will be selected such that their volatilities and absorption spectra are sufficiently different in order to definitely separate the components temporally and optically.

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W3P022 EXTINGUISHMENT OF COOL-FLAMES SUPPORTED BY N-ALKANE DROPLETS IN MICROGRAVITY
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Ongoing droplet-combustion experiments in the International Space Station have shown for the first time that large n-alkane droplets can continue to burn quasi-steadily and subsequently extinguish abruptly, controlled by low-temperature Negative-Temperature-Coefficient (NTC) chemistry, without a visible flame. In this study we report recent experimental observations of n-decane, n-octane, and n-heptane droplets of varying initial droplet sizes burning in microgravity under a range of ambient oxygen and diluent (helium or carbon dioxide) concentrations at 0.5, 1.0 and 2.0 atmospheric pressures. The oxygen concentration in these tests varied in the range of 14% to 30% by volume. It is shown that all three normal alkanes exhibit a quasi-steady “cool-flame” burning mode, followed by cool-flame extinction at a finite droplet diameter. Results for droplet burning rates in both the hot-flame and cool-flame regimes as well as droplet extinction diameters at the end of each stage are presented. An aerosol cloud was found to form in most cases slightly prior to or following the cool-flame extinction, likely by the condensation of unburned fuel vapor that leaks through the cool flame. Time histories of radiant emission from the burning droplet, captured using broadband and narrowband radiometers, help identify the precise time at which cool-flame extinction occurs. It is shown that the measured residence time at cool-flame extinction (extinction diameter squared divided by the burning-rate constant) for all three normal alkanes follow a similar trend, and can be correlated against the oxygen molar concentration, which is inversely proportional to the chemical time in the NTC region. The correlation is based on the idea that the effective unimolecular activation energy for high-temperature alkyl radical removal is about ¾ the unimolecular activation energy for ketohydroperoxide decomposition.

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W3P023 TRANSPORTED PDF MODELING OF AN ETHANOL SPRAY IN HOT-DILUTED COFLOW FLAME
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MILD Combustion, also known as flameless combustion, is attracting wide scientific interest due to its potential of high efficiency and low NOx emission. Delft Spray-in-Hot-Coflow (DSHC) burner has been used to create an experimental database for studying of the fundamental aspects of flameless oxidation of light oils. The hot diluted coflow of the DSHC flame, which is aimed at mimicking the recirculated combustion products in large scale flameless combustion furnace, is generated by secondary burner matrix. This makes the DSHC flame different in many ways from the conventional spray flame. The in-house hybrid finite volume/ transported PDF code 'PDFD' is used to model the DSHC flame. The continuous phase is described by a joint velocity-scalar PDF, and the dispersed phase is described by a joint PDF of droplet position, velocity, temperature, diameter, and the gaseous properties 'seen' by the droplet. Due to the high-dimensionality, the joint PDFs are solved by a Monte Carlo particle method. In contrast with more standard Eulerian-Lagrangian approach, in PDFD, both the gas phase and the dispersed phase are evolution are defined by Lagrangian equations, therefore we refer it as 'Lagrangian-Lagrangian' approach. To overcome the bias error due to the limited number of computational particles in the Monte Carlo method, the mean velocities and Reynolds stresses are calculated using a Finite-Volume (FV) method, in which the Reynolds Averaged Navier Stokes (RANS) equations are solved. A consistent combination of the Generalised Langevin Models (GLM) for Lagrangian particle velocity evolution and Eulerian Reynolds-stress turbulence models is used. The evolution of gas phase composition is described by a Flamelet Generated Manifold (FGM) and IEM micro-mixing model. The detailed ethanol high-temperature oxidation mechanism by Marinov containing 57 species and 383 reactions is used for the generation of an FGM lookup table with 'ChemID' code, which is developed in Eindhoven University of Technology. The droplet heating and evaporation processes are described by 'parabolic temperature profile model' with modified Nusselt and Sherwood numbers taking into account the effect of Stefan flow.

This modeling approach was validated by comparison with experimental measurements. Spray behavior is successfully reproduced, the predicted droplet mean axial and radial velocity profiles for all droplet size classes are in very good agreement with the experimental data at various axial locations. Droplet Sauter Mean Diameter and droplet number density have been accurately predicted comparing to the experiment results. Gas phase velocity and temperature
also match well with experimental data. Though the temperature in the spray region has been slightly over-predicted due to the fact that the absence of enthalpy information in the current 2D FGM table prohibits the consideration of the heat loss by droplet evaporation. Important characteristics of the DSHC flame such as flame lift-off and dual flame front have been successfully captured by the current simulation. Further improvement will be focused on the coupling between dense and dilute spray region as well as better models for local flame structure, such as the spray flamelet.

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W3P024 STOCHASTIC EVAPORATION MODELLING FOR PRESUMED-PDF SPRAY COMBUSTION SIMULATIONS
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The evaporation of liquid fuel sprays determines the distribution of fuel vapour and the mode of combustion in aeronautical gas turbines and direct injection internal combustion engines. Accurate evaporation rate modelling is therefore necessary for useful predictions of combustor performance, including flame stability and pollutant production.

The evaporation rates of individual droplets depend on the temperature, composition and relative velocity that the droplets 'see' in the surrounding fluid. Due to the presence of thin flame fronts in turbulent combustion, the 'seen' temperature, and hence evaporation rate, can vary significantly between similar droplets. However spray combustion models usually compute droplet evaporation rates using an estimate for the local mean gas phase properties. This study develops evaporation modelling which overcomes this limitation.

A new stochastic evaporation model is presented in the context of presumed-pdf modelling. The method samples the composition seen by a given droplet from the presumed joint-pdf of composition at the droplet location. In order to account for possible correlations between progress variable and mixture fraction, the joint-pdf is constructed using a copula from two beta-distributed marginal pdfs for mixture fraction and for normalised progress variable. We use a flamelet generated manifold to relate mixture fraction and progress variable to composition and temperature. The impact of considering the (co-)variances of mixture fraction and progress variable on the evaporation rate, and on global flame structure are analysed in Reynolds-averaged simulations of a laboratory spray flame.

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W3P025 FLAME SPREAD OF A LINEAR N-DECANE DROPLET ARRAY WITH PARTIAL PREVAPORIZATION IN MICROGRAVITY
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In this study, flame spread characteristics of a linear n-decane droplet array with partial prevaporization is investigated in microgravity for obtaining fundamental insight on flame propagation mechanism among partially prevaporized fuel spray. In the experiments, multiple n-decane droplets are generated and sustained at intersections of fine X-shaped SiC fibers (14 micrometer in diameter) simultaneously, by supplying fuel from the tips of fine glass needles. Then, the array is inserted into the combustion chamber which was preheated at a desired high-temperature. In the combustion chamber, activation delay time of the igniter wire at an edge droplet was employed to control the degree of partial prevaporization of the array prior to flame spread. After ignition of the edge droplet, subsequent flame spread behaviors along the array are observed by various cameras. The merit of microgravity environment for the current study is symmetric formation of fuel vapor as well as flame around the axis of the array, even for relatively large diameter droplets. It enables detail observation of the phenomena as well as comparison with numerical simulation. The experimental parameters include initial droplet diameter, droplet interval, ambient temperature, and prevaporization time. In our past research, it was found that flame structure changes with increase of the degree of prevaporization of the array. Occurrence of triple flame structure at the propagating flame front was also recognized. In addition, the relation between the flame travelling speed (flame spread rate) and the degree of prevaporization was obtained.

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W3P026 MODULATION OF TURBULENT PROPERTIES IN A SPRAY FLAME BURNING N-HEPTANE
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The final objective of the current work is to investigate turbulent spray flames at high droplet density, quantifying possible modifications of the turbulent properties. As a first step, the modification of turbulence statistics (kinetic energy, dissipation rate spectrum, the auto-ignition process and the resulting flame structure are investigated in decaying turbulence by Direct Numerical Simulation (DNS) considering n-heptane liquid droplets. The droplets, being smaller than the grid resolution, are modeled as point droplets, while the Navier-Stokes equations are solved in the low-Mach number regime. Detailed models are employed to describe chemical reaction and molecular transport in the gas phase. Existing publications on the subject can be roughly categorized into four groups. First, those investigating in 3D the two-way coupling of a non-reactive turbulent flow with droplets. The second group examined reacting cases but using a single-step reaction mechanism. A third approach takes into account detailed chemistry but only 2D turbulent flows, while, in the last case, both 3D flows and detailed chemistry are considered, like in. However, even with this highest level of detail, the resulting turbulence statistics have never been examined in detail yet. In the current DNS, the continuous (gas) phase is simulated in a standard manner (Eulerian frame) whereas the discontinuous (droplet) phase is tracked in a Lagrangian frame. Two-way coupling interaction between both phases is quantified via the
exchange of mass, momentum and energy. The impact of different parameters is investigated, in particular: initial temperatures, equivalence ratio/droplet mass fraction, droplet size, turbulence level (with a Taylor Reynolds number up to 80). For the figures shown in the uploaded file, n-heptane droplets at 300 K are initially randomly distributed in isotropic turbulence. A fully periodic domain containing hot air at 1000 K is simulated. The Stokes drag force is dominant in the droplet momentum equation, whereas the evaporation process is computed by using a variable Spalding mass transfer number and an infinite conduction model inside the droplet. The in-house 3D DNS solver DINOSSAR is used for all simulations. An implicit time integration scheme is used for the chemistry source term. All kinetic and transport properties are handled in DINOSSAR using Cantera 1.8 and Eglib 3.4. A skeletal mechanism accounting for 29 species and 52 reactions is used for n-heptane combustion. Very complex flame structures are obtained, highlighting the need for powerful analysis tools. The resulting turbulence statistics and the analysis of the data will be shown on the poster.

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W3P027 EFFECTS OF HYDROGEN OR METHANE ADDITION ON THE COUNTERFLOW SPRAY DIFFUSION FLAME: SPRAY-FLAMELET MODEL FOR BIPHASIC AND MULTI-COMPONENT FUEL
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This work presents an extended analysis of the external structure of multi-phase and multi-component fuel counterflow diffusion flame (multi-component spray-flamelet). The model assumes part of the main fuel, ethanol (C₂H₅O) or n-heptane (C₇H₁₈), in liquid phase (droplets) and part in gas phase with addition of methane (CH₄) or hydrogen (H₂). The droplets vaporize completely before the stagnation point and there is no relative velocity between the droplets and the gas phase. The multi-component fuel spray-flamelet is described by means of the Schvab-Zel'dovich-Linan formulation. The model exhibits a more general spray combustion parameter that combines the chemical reaction, flow field and spray properties. The aim of the analysis is to identify how the external structure of the spray-flamelet is affected by addition of a small amount of methane or hydrogen in a spray of ethanol or n-heptane. The droplets are described by a uniform mono-sized distribution. For fixed spray combustion parameter and dimensionless incoming condition, the results point out that by substituting part of the main fuel by methane or hydrogen does not affect significantly the position and temperature of the flame. The small differences are due to the Lewis number. Consequently, the re-scaled species mass fraction of the main fuel and dimensionless temperature show a quasi-universal behavior for the external structure of the spray-flamelet. The description of temperature and fuel mass fraction in terms of the mixture fraction is non linear. To avoid that it is included the gradient of mixture fraction.

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W3P028 A NOVEL APPROACH TO ASSESS DIESEL SPRAY MODELS USING LIQUID-PHASE EXTINCTION AND X-RAY RADIOGRAPHY MEASUREMENTS
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Spray model predictions are a critical component of engine CFD simulations since the spray physics will dictate boundary conditions for fuel-air mixing and subsequent combustion processes. However, given the current capability of spray diagnostics, it is not possible to validate the fundamental mechanisms governing spray breakup under diesel relevant conditions. As a result, there are many different physically-based spray breakup models that have been employed in the literature. Most models are indirectly validated against global spray parameter measurements, such as liquid penetration and vapor penetration. Though some have been validated against quantitative local droplet size measurements, these measurements are limited to the periphery of the spray and have been largely conducted under a limited range ambient density conditions. Due to the lack of high-fidelity quantitative measurements of desired spray parameters, robust validation of spray morphology predictions has not been possible. Questions therefore remain about the ability of current spray models to faithfully represent and predict the correct spray structure over a range of ambient and injection conditions.

Recent advances in spray diagnostics have resulted in a large improvement in quantitative experimental characterization of spray parameters; examples include x-ray radiography measurements, which is an absorption-based technique that quantifies projected mass density throughout the spray, and liquid-phase extinction measurements, which can quantify the optical thickness. Both measurements are coupled functions of droplet size and number density. Although each of these measurements has a coupled dependence on these parameters, simultaneously validating model predictions against these measurements in overlapping regions of the spray shows promise of decoupling their dependencies and providing a more detailed validation of the spray morphology.

In the current work, we explore the use of light propagation and x-ray radiography models in CFD spray simulations to assess spray morphology predictions. Using CONVERGE, we compare predictions of optical thickness and projected mass density against available quantitative liquid-phase extinction and x-ray radiography measurements, respectively, among three different physically-based spray breakup models; Kelvin-Helmholtz (KH), Kelvin-Helmholtz Rayleigh-Taylor (KH-RT), and Kelvin-Helmholtz-Aerodynamics Cavitation Turbulence (KH-ACT). The model predictions of droplet size and number density distributions throughout the spray are compared and spray breakup
statistics and their relative impact on the spray structure is evaluated. Recommendations are then provided for future modeling and experimental endeavors to help guide best modeling practices under diesel-relevant conditions.

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W3P029 INTERMITTENT PRODUCTION OF OH ON A SWIRL-STABILIZED PULSED SPRAY FLAME

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Combustion of fuel droplets in engines and gas-turbines are applied to generate power and, in those systems, instabilities may arise from the interaction between the evaporation, mixing and combustion of the droplets and the surrounding air. In this work, laser diagnostic techniques are applied to analyze combustion instabilities near the burner for an open pulsed ethanol spray flame. Fuel droplet diameter and velocity distributions are acquired by Phase Doppler Interferometry (PDI) across the flame. The interaction between the OH profile, the swirling flow and the spatial evolution of fuel droplets is analyzed by both time resolved Mie scattering and high repetition rate planar Laser Induced Fluorescence of OH. Velocity fields at planes parallel to the exit of the burner are obtained by time resolved Particle Image Velocimetry for the cold flow. The burner, constituted by a swirler mixer and an automotive port fuel injector, was positioned in an open space with quiescent air. The fuel injection frequency was defined as 400Hz, which produces a dilute spray susceptible to the recirculating air. The resulting flame presented a small chemiluminescent region lifted from the burner. The spatial evolution of the OH profile and the velocity field suggest that the lifted behavior is produced by a complex periodic mixing behavior between evaporating droplets and turbulent structures from the swirling flow, which produces regions with intermittent combustion near the burner.

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W3P030 EVAPORATION MODEL OF HYPERGOLIC FUEL DROPLETS

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Bipropellant rocket engines have been used in spacecraft propulsion systems for several decades. These engines have shown high reliability and good achievements in past missions. On the other hand, developments of the bipropellant rocket engines rely mainly on trial-and-error approaches supported by extensive experimental tests. Therefore, it takes a long time and high cost for the experimental tests. From the physics point of view, the mechanisms and interactions occurring in the rocket thrust chamber are manifold and fairly complex. During the first process in the sequence of the phenomena, the fuel and the oxidizer are injected from an injector faceplate, and they collide with each other. After that, primary atomization occurs from the edge of a liquid sheet that is generated by the collision of jets. Some liquid particles of fuel and oxidizer break up again due to secondary atomization. Almost simultaneously, the liquid particles evaporate and generate gaseous fuel and oxidizer. Finally, the gaseous fuel and oxidizer react and are transformed into combustion gas. The characteristics time of the evaporation in these processes significantly affects to the combustion efficiency of the bipropellant rocket engines. Therefore, an accuracy of the evaporation model is very important to predict the thrust performance in the numerical simulation of the bipropellant rocket engine.

In order to support design and optimization of the bipropellant rocket engine, the simulation tools, which is predict thrust and heat load based on three-dimensional combustion simulations with a theoretical atomization model for the unlike doublet impinging jet, has been developed in Japan Aerospace Exploration Agency/JAXA’s Engineering Digital Innovation Center (JAXA/JEDI). This simulation tools include an atomization, a evaporation, a combustion, and a film cooling models. In this study, the evaporation model is evaluated for the experimental data for single droplets.

At first, the two kinds of evaporation models were evaluated for the experimental data of the heptane single droplet evaporation. The evaporation model, which takes into account the non-equilibrium of mass transfer, could reproduce the evaporation rate of the experimental data very well. For the next step, this evaporation model applied for the simulation of the hydrazine and MMH single droplet evaporation, respectively. The hydrazine and MMH have decomposition reactions. Therefore, the reaction model should be taken into account to reproduce the actual evaporation rate. The effect of reaction was clarified for the evaporation rate using the global and the detailed chemical reaction set. In these simulations, the difference for the evaporation rate between the global and the detailed chemical reactions was small because the amount of fuel is a few against for the ambient gas. In the future work, the simulation of the evaporation of the liquid droplet groups will be performed. As a final goal, the applicable evaporation model will be specified for hypergolic fuel spray combustion.

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W3P031 SIMULATIONS OF N-HEPTANE COOL FLAMES IN ZERO GRAVITY

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Numerical simulations of gaseous n-heptane diffusion flames in zero gravity have been performed to study the two-stage combustion leading to a “cool flame”, which has been discovered in the droplet combustion experiment in the International Space Station. The time-dependent, two-dimensional numerical code, which includes a detailed reaction mechanism (127 species and 1130 reactions), diffusive transport, and a gray-gas radiation model, revealed the flame
structure, radiative flame extinction, and subsequent cool-flame formation. N-heptane at boiling point (372 K) issued from an axisymmetric fuel source consisted of (1) a single porous cylinder (4 mm dia. x 2 mm ht.), (2) concentrically superimposed two cylinders (4 mm dia. x 1.33 mm ht. and 1.33 mm dia. x 4 mm ht.), or (3) three cylinders (4 mm dia. x 0.67 mm ht., 2.5 mm dia. x 2 mm ht., and 1 mm dia. x 4 mm ht.). The fuel velocity (0.1 to 1 cm/s) and the pre-ignition injection period were varied. The stoichiometric fuel-air mixture was ignited above and below the fuel source on the axis. The ignition kernel grew and propagated around the fuel source to form a growing spherical flame. The maximum temperature decreased due to the radiative heat loss, and the flame extinction occurred at ~1200 K several seconds after ignition. As the remaining hot zone cooled down, the cool flame with the maximum temperature of 740-780 K became apparent at a closer proximity to the fuel source. The volume of the fuel discharged before ignition plays an important role in the initial flame growth and radiative extinction, leading to the cool flame as a result of the negative temperature coefficient in the low-temperature chemistry.

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W3P032 INVESTIGATION OF GLYCEROL ATOMIZATION IN THE NEAR-FIELD OF A FLOW-BLURRING INJECTOR USING TIME-RESOLVED PIV AND HIGH-SPEED FLOW VISUALIZATION
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Glycerol with its very high viscosity and high vaporization and auto-ignition tendencies has been effectively atomized at room temperature and cleanly combusted by using a novel Flow Blurring (FB) injector without any combustor hardware modification. Present study quantitatively reveals the details of glycerol atomization by the FB injector. Time-resolved Particle Image Velocimetry (PIV) with exposure time of 1 µs and framing rate of 15 kHz is utilized to probe the near injector region of the spray at spatial resolution of 16.83 µm per pixel. PIV results describe the flow structure in terms of the instantaneous and mean velocity fields, turbulent kinetic energy, and histograms of axial velocity. In addition, high-speed imaging (75 kHz) coupled with backside lighting is applied to reveal the glycerol breakup process at exposure time of 1 µs and spatial resolution of 7.16 µm per pixel. Results show that glycerol atomization can be categorized as bubble-explosion atomization and atomization by Rayleigh-Taylor instabilities. FB atomization of glycerol results in a collection of fast-moving droplets and slow-moving streaks at the injector exit. By interacting with the high-velocity atomizing air, the relatively thin long streaks first disintegrate into shorter streaks, and then, into small droplets. Thus, within a short distance downstream of the injector exit, most of the glycerol is atomized into fine droplets with diameter range of about 8 to 21 µm, indicating excellent atomization of glycerol by the FB injector.

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W3P033 EFFECTS OF DROPLET INTERACTION AND AMBIENT-GAS COMPOSITION ON SPONTANEOUS IGNITION OF FUEL DROPLETS
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Spontaneous ignition of fuel droplets in hot ambient gas was experimentally studied. Fuel was n-decane, and initial droplet diameter was 1 mm. First, a suspended droplet pair inserted into hot air was studied in microgravity, and the effect of droplet interaction was examined. Pressure was 0.3 MPa, and air temperature was between 620 K and 700 K. Thus, the ambient conditions were in the range where two-stage ignition, i.e., cool-flame appearance and subsequent hot-flame appearance, occurs. The previous studies with thermocouple measurement showed that the mutual cooling effect of two droplets was dominant before cool-flame appearance, while the effect of duplicated fuel sources was dominant after cool-flame appearance. This is supposed to be related to locations of cool flame and hot flame appearances. In the present study, interferometry was applied to qualitatively observe density field around a droplet pair, and the location of heat release by cool-flame or hot-flame was evaluated. Cool flame appeared on the outer side of the pair, and hot flame appeared on the inner side of the pair. The results indicate that temperature distribution is important before cool-flame appearance, while fuel-concentration distribution is important after cool-flame appearance, which corresponds with the discussion in the previous studies. Next, a suspended isolated droplet inserted into hot ambient gas was studied in normal gravity, and the composition of the gas was varied. Substitution of nitrogen of air by carbon dioxide delayed vaporization and hot-flame appearance in the examined ambient conditions.

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W3P034 CHARACTERISTICS OF LASER-INDUCED BREAKDOWN IGNITION IN DIFFERENT ETHANOL SPRAY CONCENTRATION
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Laser-induced ignition is a new ignition method that employs non-contact ignition. This method has a great potential to improve the thermal efficiency of conventional internal combustion engines because this ignition method is free from both the heat loss to the electrode and the electrode interference to spray. Moreover, an arbitrary ignition position can be selected in the combustion chamber. Numerous researches on laser-induced ignition and breakdown of gaseous fuels have been conducted. There are very limited investigations on the laser-induced breakdown ignition in fuel spray. For an application to spray guided direct injection engines, it is necessary to investigate the characteristics of
laser-induced breakdown ignition in the fuel spray. In this study, we experimentally investigated the effects of the spray concentration on the breakdown and ignition characteristics. The laser ignition characteristics were quantitatively evaluated by using ignition probability.

A laser-induced plasma was generated by focusing the laser beam of 355 nm with energy adjustment. Slightly rich ethanol spray/air mixture was supplied around the focal position. An ultrasonic nebulizer generated the ethanol spray. The number density of droplets in the ethanol spray was controlled by the flow rate of air as the carrier gas for spray. The plasma generation and the flame propagation in ethanol spray were recorded by using a high-speed camera with a Schlieren optics system.

The results show that there is a difference between the energy required for generation of plasma and ignition. The generated plasma does not always contribute to ignition. The probability of the laser-induced breakdown increases with the laser beam energy and the spray concentration. The probability of ignition also increases with the laser beam energy. However, there is an inverse relationship between the ignition probability and the spray concentration. The plasma generated in the spray loses heat by the large heat capacity of the droplet and latent heat of evaporation of the droplet. When the spray concentration is higher, the probability that droplets exist around the plasma is higher, resulting in greater heat loss to droplets and the lower ignition probability. Therefore, the optimal spray concentration possibly exists.

The majority of modern transportation energy is consumed via combustion of liquid hydrocarbon fuels. Manufacturers and consumers are consistently looking for ways to optimize the efficiency of fuel combustion in terms of cost, emissions and consumer safety. Experimental research has shown that the addition of long chained polymers to hydrocarbon fuel imparts non-newtonian characteristics to the emulsified fluid. This results in a suppressed splashing behavior upon spilling over a surface. This has led to a study to not only optimize the emulsion ratio but to characterize the properties of the emulsified fuel (including ignition, extinction and burning rate). This is done to investigate how the modified fuels will impact commercial automotive engines as it relates to their performance and emissions. Experiments are conducted using micro-sized droplets tethered to ceramic fibers. Through a series of synchronous events, droplets are first ignited using electrical hot wire and data is acquired through the use of high speed photography and Schlieren imaging. Time variations regarding droplet diameter and intensity of emitted soot in Schlieren images are used to characterize the sample size. Residual soot aggregates attached to the support fiber are also collected to be analyzed using SEM technique.

As prospective biofuels, long chain alcohols like n-butanol and n-pentanol have a lot of advantages over ethanol, such as higher energy density, better miscibility with practical fuels, lower water absorption, and higher suitability for conventional engines. Compared with n-butanol, the combustion research of n-pentanol is very insufficient. Most previous combustion experiments on n-pentanol were focusing on the measurements of global combustion parameters, such as ignition delay times, laminar flame speeds and engine performances. This work presents the first experimental investigation on the n-pentanol pyrolysis at various pressures and reports a detailed pyrolysis model of n-pentanol.

Synchrotron vacuum ultraviolet photoionization mass spectrometry was used to detect pyrolysis species and measure their mole fraction profiles. Detailed descriptions of the synchrotron beamlines and pyrolysis apparatus used in this work have been reported elsewhere. The pyrolysis of 3% n-pentanol in Ar was investigated from 810 to 1410 K at 30, 150 and 760 Torr. More than 20 pyrolysis species were detected, especially some radicals such as methyl, propargyl and allyl radicals and unstable intermediates like ethenol and 2-propen-1-ol. A detailed pyrolysis model of n-pentanol with 162 species and 1141 reactions was developed and validated against the experimental results, and was used to understand the thermal decomposition processes of n-pentanol. The model was based on our recently reported models of butanol isomers, and the sub-mechanism of n-pentanol was constructed in this work.

The present model can get reasonable prediction on the mole fraction profiles of n-pentanol and its major pyrolysis products, as shown in Fig. 1. The ROP analysis and sensitivity analysis (Image) demonstrate the importance of unimolecular decomposition reactions and H-atom abstraction reactions by H and OH attack in the primary decomposition of n-pentanol. The unimolecular decomposition reactions have very large sensitivities to the consumption of n-pentanol, because these reactions are the most important chain initiation steps under the investigated conditions. Due to the high carbon fluxes from the H-atom abstraction reactions, C₅H₁₀OH radicals play significant roles in the decomposition processes of n-pentanol. These C₅H₁₀OH radicals mainly decompose through β-scission reactions, especially β-C-C scission reactions. Specific products of most C₅H₁₀OH radicals were observed, such as ethenol, 2-propen-1-ol, 1-butene and propene, which provide validation to the pathways initiated from the H-atom abstraction of n-pentanol. Ethenol also plays a crucial role in the formation of acetaldehyde which is an important oxygenated pollutant.
relevant to alcohol combustion.
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W3P037  UNCERTAINTY ANALYSIS OF VARIOUS THEORETICAL TREATMENTS ON ETHANOL DECOMPOSITION

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The random sampling high dimensional model representation (RS-HDMR) approach was used to reveal the important source and the variation of uncertainty for the rate constants of C-C bond dissociation and H2O elimination of ethanol computed by canonical variational transition state theory. Proper qualitative and quantitative uncertainty evaluation is strongly recommended for theoretically investigation on kinetics of unimolecular decomposition with competing pathways.

7 main parameters (such as the energy parameters, the collisional parameters et al.) were selected for further study according to the test results. The calculations were performed at temperatures (1000-2000 K) and three pressures (0.1 atm, 1 atm, 10 atm) respectively. For each (T, P), we randomly generated 5000 samples and then calculated the corresponding rate constants, where the step number has been checked for convergence. We deduced the uncertainty factors of these two rate constants and the uncertainty source of ethanol decomposition can be divided into three parts: energy parameters, collision parameters and competition relationship.

The uncertainty at high pressure limit is only determined by energy parameters and independent with reaction type. The expression of uncertainty factor was provided quantitatively. The collision parameters are playing an increasingly important role with the decreasing pressure. The rate constant of minor channel shows larger uncertainty than that of major channel at both low and high pressures due to the impact of competing relationship.

The uncertainty propagation of the selected input parameters rate constants provided valid uncertainty information for the sensitivity and uncertainty analysis of chemical model and proper uncertainty evaluation is strongly recommended for theoretically investigation on the temperature and pressure dependent kinetics for complex reaction systems.

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W3P038  AN EXPERIMENTAL AND KINETIC MODELING STUDY OF 2-METHYLBUTANOL COMBUSTION

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The need to reduce emissions in practical engines has spurred the interest in alternative fuels, and the use of bio-derived oxygenated fuels have been considered as potential alternative fuels to reduce fossil fuel consumption and minimize NOx and particulate emissions. However, these oxygenated fuels have different combustion chemistry that needs to be evaluated in practical applications.

Ethanol has been used as fuel extender for petroleum fuels. Due to disadvantages of ethanol such as high O/C ratio, high hygroscopicity and low energy density, the focus of alcohol combustion chemistry research is shifting now to linear and branched C4 and C5 alcohols. Over the last few years, extensive combustion studies on butanol isomers have been conducted, but there have been limited studies on C5 alcohol family including n-pentanol, iso-pentanol (3-methylbutanol), and 2-methylbutanol.

The purpose of the current study is to provide a detailed chemical kinetic model for 2-methylbutanol including high- and low-temperature reactions with new experimental data, including ignition delay times and flame speeds, for a better understanding the combustion characteristics of higher alcohols. The proposed model is based on previous iso-pentanol modeling study and a similar methodology was used to develop a detailed model for 2-methylbutanol.

The present model for the 2-methylbutanol is validated against a wide range of experimental data covering low- and high-temperature oxidation conditions. Ignition delay times were measured for 2-methylbutanol over a temperature range of 800–1300 K, pressures at 20 and 40 atm, and equivalence ratios of 0.5, 1.0 and 2.0 in air using a High Pressure Shock Tube (HPST) at KAUST. The present model is validated against the high-pressure autoignition experimental data by running homogeneous batch reactor simulations. Overall, the proposed model for 2-methylbutanol is in good agreement with the experimental data over the whole temperature region. The present model is also validated against laminar burning velocities. The laminar flame speeds of 2-methylbutanol/air mixtures at 353K and pressures of 1, 2 and 5 atm were measured using the spherically propagating flame in a constant volume chamber at KAUST. The predictions show good agreement with experimental data. In addition, reaction path and temperature A-factor sensitivity analyses were conducted for identifying key reactions in the combustion of 2-methylbutanol.

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W3P039  INVESTIGATION OF THE PERFORMANCE OF SEVERAL METHANOL COMBUSTION MECHANISMS

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Methanol is widely used as an important alternative fuel and feedstock in various industrial processes. Even though substantial efforts have been made to understand its combustion characteristics, large differences in reactivity
predictions of various methanol reaction mechanisms can be observed. While in most experimental and computational studies the agreement between measurements and simulations is characterized by figures, in which the experimental data and the simulation results are plotted together, a quantitative and wide-ranging evaluation with respect to methanol combustion has not yet been performed. The measured values coming from different types of experiments may have different orders of magnitude and different units. Thus, a direct comparison of the deviations corresponding to the different types of experiments would be meaningless. In the present work, a sum-of-squares based objective function suggested by Turányi and co-workers was used that accounts for these difficulties. A MATLAB code was developed which allows for automatic simulations using the CHEMKIN-II and OpenSMOKE++ solver packages. The code also evaluates the value of the objective function for each reaction mechanism to facilitate a direct comparison of the performances of the different mechanisms. A large set of experimental data was accumulated for the combustion of methanol including ignition measurements in shock tubes and RCMs, burning velocity measurements, concentration–time profiles in flow reactors and jet-stirred reactors (~1500 data points in total), covering wide regions of temperature, pressure and mixture composition and measured in different bath gases. All data were encoded in PrIme file format, an XML scheme used for the systematic storage of combustion experiments.

This poster presents the comparison of the performance of 11 recently published methanol combustion mechanisms based on these experimental data. It is a part of a systematic evaluation of kinetic mechanisms for a range of combustion systems, such as hydrogen, syngas and ethanol, and can be considered as an important step towards a better understanding of more complex C/H/O combustion systems.

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W3P040

LAMINAR BURNING VELOCITIES OF C4H8O+O2 IN DIFFERENT BATH GASES AND AN INVESTIGATION OF THE GENERAL PERFORMANCE OF SEVERAL ETHANOL COMBUSTION MECHANISMS
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Ethanol is widely used as a renewable alternative fuel and as a gasoline additive. The combustion characteristics of this fuel were frequently investigated, both in experimental and computational studies. However, the details of the underlying chemistry are still not fully understood and there is a large scatter among the predictions of kinetic mechanisms that were developed to describe ethanol combustion. Due to the lack of experimental data available from literature at particular conditions of interest, new measurements of laminar burning velocities using the heat flux method were carried out. Mixtures of C4H8OH+O2+Ar at initial temperatures ranging from 298 to 348 K were measured at Lund University for different equivalence ratios and various oxygen ratios in the oxidizer mixture (12 to 20 %). At TU Bergakademie Freiberg, C4H8OH+air flames diluted with 5% and 10% H2O were measured at 298 K and 373 K. The comparison of these data with simulations indicated room for substantial improvement of kinetic schemes for ethanol combustion.

The agreement between measurements and simulations is typically characterized by figures, in which the experimental data and the simulation results are plotted together. However, a quantitative measure has to be applied to make these comparisons objective, such as a sum-of-squares objective function based method suggested by Turányi and co-workers. A MATLAB code was written which allows automatic simulations using the CHEMKIN-II and OpenSMOKE++ solver packages and evaluations of the objective function. A large set of experimental data was compiled for the combustion of ethanol, such as burning velocity measurements (including the above presented and further data from the literature), ignition measurements in shock tubes and RCMs, and concentration–time profiles in flow reactors and jet-stirred reactors (~1600 data points in total). This poster presents the comparison of the performance of 14 published ethanol combustion mechanisms based on these experimental data.

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W3P041

RATE CONSTANT CALCULATIONS OF THE H-ATOM ABSTRACTION REACTIONS OF OXYGENATED FUELS WITH HO2 RADICALS
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Oxygenated fuels generated from biomass have received considerable interest in recent years. Alcohols, esters and ketones are among some promising biofuel candidates. Over the last few decades, the combustion community has developed significant knowledge on the fundamental reactions and associated rate constants for hydrocarbon fuels; however, much less is known about oxygenated compounds. High-level theoretical calculations of the H-atom abstraction reactions by OH and HO2 radicals are important in order to predict the reactivity and product formation of these fuels. This work serves to help generate rate constant rules for H-atom abstraction by HO2 radicals from large oxygenated biofuel molecules, and other biofuel candidates, which may be used as possible future fuel for transport and energy generation. High-level ab initio and chemical kinetic calculations have been performed to determine the influence of the functional group of oxygenated species, such as esters1, ethers2, aldehydes, ketones3,4, alcohols5, and acids, on the rate constants for H-atom abstraction by HO2 radicals, under combustion relevant conditions. We have determined that abstraction from the carbon atoms adjacent to the functional group (α'/α) was slower for ketones and esters and faster for alcohols and ethers, when comparing to alkanes. Overall, we found that the further the abstraction occurs from the functional group, the more similar are our calculated rate constants for oxygenated species when
compared to those calculated for alkanes.

Rate constants for abstraction of a hydrogen atom by an HO₂ radical from either side of the functional group on ketones and esters are very similar. However, for ethers the rate constants for abstraction at the α' and α positions are calculated to be faster than for ketones and esters due to the electron lone pair on the oxygen atom being delocalized to the adjacent C–H anti-bonding orbital (α–σ*(CH)). This weakens the adjacent C–H bond which, consequently, lowers the energy required for abstraction.

Abstraction of a hydrogen atom by HO₂ radicals at the α'/α and β'/β positions are the most influenced by the hydrogen bond interactions that occur between the radical and the functional group. At the γ position, abstraction of a H-atom by an HO₂ radical is less influenced by these interactions and only when abstracting a H-atom at the δ position are the rate constants the most similar to alkanes.

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W3P042 THEORETICAL STUDY OF LOW-TEMPERATURE OXIDATION CHEMISTRY OF ISO-BUTANOL
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The efficient use of novel biofuels in internal combustion engines, particularly those relying on compression ignition, critically depends on understanding the fundamental autoignition chemistry. Iso-Butanol is a promising candidate as a next-generation biofuel. Numerous companies, such as Gevo, Inc and Butmax, are already setting up industrial-level production plants, making iso-butanol a viable fuel to enter the marketplace soon. Whereas its high-temperature (T > 1000 K) oxidation is well understood, the low temperature (T < 850 K) oxidation chemistry of iso-butanol remains underexplored. Recent experimental works (Pan et al., Weber et al.) have also indicated that most chemical kinetic models in literature are unable to accurately predict ignition delays in the intermediate-low temperature regime. In the current work, we present detailed insight into the fundamental low-temperature chemistry of iso-butanol. We calculate the relevant stationary points on the potential energy surface for the α-, β-, and γ-iso-hydroxybutyl radicals with O₂ at the CCSD (T) level and perform master-equation calculations on these surfaces. From the master-equation calculations we have obtained (T, P)-dependent product branching ratios for the R+O₂ reactions and compared them with published low temperature, low pressure experimental branching ratios (Welz et al.). Unlike O₂ reacting with alkanes, the predominant reaction for alcohols is α-iso-hydroxybutyl + O₂ yielding HO₂. However, competing channels yielding OH are much more conducive to ignition. We discuss the competition between these channels and its impact on low temperature autoignition of iso-butanol.

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W3P043 EXPERIMENTAL AND KINETIC MODELING STUDY OF TERT-BUTANOL PYROLYSIS
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Using biofuels as alternatives fuels can offset the CO₂ emission and reduce the climatic impact. Butanols are of increasing interest as alternatives to petroleum-based transportation because they offer higher energy density, better miscibility with practical fuels, lower water absorption than ethanol. Tert-Butanol has the most complex branched structure among four butanol isomers, thus it has been used as an octane booster to prevent knock in spark-ignition engines.

In this work, the pyrolysis of tert-butanol in a flow reactor was studied using Synchrotron Vacuum Ultraviolet Photoionization Mass Spectrometry (SVUV-PIMS), which were carried out at the National Synchrotron Radiation Laboratory in Hefei, China. Temperature ranges of 850 – 1550 K at pressures of 5, 30, 150 and 760 Torr were selected to investigate the pyrolysis chemistry of tert-butanol. About 20 species were identified in the experiment and their mole fractions versus temperature and pressure were quantified. A model consisting of 186 species and 1319 reactions was developed base on our previous butanol models. The pyrolysis species profiles measured in the present work are used to validate the model. The simulation was carried out using Plug Flow Reactor module in Chemkin-Pro software. The experimental and simulated results of some selected species were presented in Figure 1. Sensitivity analysis shows that H₂O elimination and C-C scission reactions are very important to the decomposition of tert-butanol. Moreover, the mole fractions of primary products are also very sensitive to rate constants of the unimolecular reactions. For example, the H₂O elimination reaction of tert-butanol is the most sensitive reaction to the mole fractions of tert-butanal at different pressures, as shown in Fig. 2. ROP analysis shows that tert-butanol mainly decomposes through reaction sequence tC₃H₇OH→tC₃H₆OH® tC₃H₆→IC₃H₅→aCC₃H₄→pC₃H₄ at both low and high pressures. The difference is that unimolecular reactions of tert-butanal are more important at low pressure than high pressure. This reaction sequence produces most of the hydrocarbon species in tert-butanol pyrolysis. Moreover, reaction sequence tC₃H₂OH→CH₃COHCH₃→CH₃COCH₃ also contributes approximately 10% of tert-butanal decomposition. The oxygenated species CH₃CO and CO are the follow-up products of this reaction sequence.

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W3P044 EXPERIMENTAL AND NUMERICAL STUDY OF 1-PENTANOL IN A SHOCK TUBE AT HIGH TEMPERATURE
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Due to increase of greenhouse gases and the finite quantity of fossil energies, alternative fuels are the focus of many current research programs. Moreover, European regulation imposes a proportion of 20% of biofuel in conventional fuels. Currently, ethanol is widely used as biofuel but it has several drawbacks such as a low energy density and source of supply. For those reasons, heavier alcohols are foreseen, they are less hygroscopic and have higher energy densities. Among all the heavier alcohols, 1-pentanol seems to be a good candidate. A better understanding of its decomposition at engine like combustion conditions is a requirement, as a first step, in order to construct a detailed kinetic mechanism that will describe its combustion.

In the present study, new experimental data on 1-pentanol in shock tube are provided. The decomposition of 1-pentanol was studied behind a shock wave at high temperature. The implementation of a rapid sampling system on the shock tube was carried out. Previously, the shock tube was characterized at 363K in order to know reaction time and pressure profiles behind a reflected shock wave. The experiments were performed at 10 bars and over a temperature range from 800 to 1600K. The shock tube was initially heated at 363K and the mixture was composed with 100ppm of fuel diluted in argon. Stable species (CH₄, C₂H₆, C₂H₅, C₃H₈, C₅H₁₂, C₃H₆, propadiene, propyne, acetaldehyde, C₅H₈, C₆H₆, 1-C₅H₁₀) from 1-pentanol decomposition were sampled from the shock tube and analyzed by Gas Chromatography. Two detectors were used to identify and quantify the species, respectively a Mass Spectrometer and a Flame Ionization Detector. The species profiles were simulated based on Togbé. Mechanism and present a reasonable agreement with the simulation.

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THEORETICAL INVESTIGATION OF LOW-TEMPERATURE COMBUSTION CHEMISTRY OF THE SOPENTANOL: MASTER EQUATION ANALYSIS OF MULTI-ENERGY WELL REACTIONS OF HYDROXYL ISOPENTYLPEROXY RADICALS
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Isopentanol is potential next generation biofuels for advanced HCCI engines at low temperatures and high pressures. Isopentanol exhibits higher HCCI reactivity over ethanol or gasoline. In spite of lots of theoretical and experimental investigations on the kinetics of the peroxy chemistry of alcohol biofuels, there is no comprehensive report available to the best of our knowledge on theoretical low temperature peroxy chemistry of isopentanol. Present study investigates, detailed potential energy surface of the reactions of a, β, γ and γ-hydroxyisopentyl radicals with O₂ calculated at the B3LYP/cc-pVTZ and CBS-QB3 level of theory for lowest energy conformers, and refined at the CCSD(T)/cc-pVZ//B3LYP/cc-pVTZ levels of theory. All quantum chemical calculations have been performed using the Gaussian 09 suite of programs. Calculations of hindered rotor partition function for low frequency torsional modes were performed employing the 1D Schrödinger equations. Conventional transition state theory calculations have been performed to evaluate the temperature dependent high pressure limit rate constants of all oxidation reaction pathways. Rate constants of barrierless entrance channels were determined at CASPT2 (7e,5o)/aug-cc-pVDZ/UB3LYP/cc-pVTZ level of theory coupled with variational transition state theory. High-level ab initio results were employed in RRKM analysis coupled with steady state master equation analysis with single exponential down model for collisional energy transfer probability and collision frequency using Lennard-Jones model (L-J model) to determine the temperature and pressure dependent rate coefficients in modified Arrhenius form for chemical activation reactions in the 300-2500K temperature and 0.1-100atm pressure range relevant for combustion modeling. Thermochemical parameters of all species involved in elementary reaction channels in complex systems were determined at CBS-QB3 level of theory.

Detailed kinetic model has been developed and optimized on the basis of available reaction mechanisms of isopentanol and further refined for the kinetics of low temperature combustion reactions pertinent to peroxy chemistry calculated from present theoretical and computational analysis. Chemical kinetic simulations have been performed to predict ignition delay times using isothermal batch reactor module as implemented in Chemkin-II software package. Generally, complete model exhibits good agreement for ignition delays times with previously published work in the literature. Present theoretical investigation reveals that high pressure rate coefficients are adequate to explain the low temperature RO₂ chemistry in most ignition conditions. Major objective of the present investigation was to calculate the temperature and pressure dependent rate coefficients of peroxy chemistry of isopentanol and to develop and refine detailed chemical kinetic model to explain its ignition kinetics under low-temperature combustion conditions and validate against literature experimental results. These results will be presented in detail at symposium.

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INVESTIGATION OF THE REACTIVITY OF ENOLS IN THE GAS PHASE BASED ON AB INITIO MO CALCULATION
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Enols have been observed as common intermediates in hydrocarbon oxidation. To reduce the use of fossil fuels, biofuels have attracted considerable attention. Several studies have been performed to elucidate the combustion properties of the butanol isomers and higher alcohols. In our previous work, we studied the pyrolysis of the butanol isomers in a single-pulse shock tube, where acetaldehyde, propionaldehyde and acetone were detected as products. These
aldehydes and ketone were thought to be produced via the tautomerization of enols generated from the pyrolysis of alcohols. To describe the combustion of alcohols accurately, the reaction mechanisms of aldehydes, ketones and enols should be established.

In the present work, we carried out Ab initio MO calculations to estimate the thermochemical properties and kinetic parameters for the tautomerization of enols. The enthalpies of formation estimated based on isodesmic reactions are shown in Table 1 together with those form the NIST database. The enthalpy of formation of isobutyraldehyde estimated in the present work shows good agreement with those in the NIST database. However, discrepancies were confirmed in the case of enols.

Bond Dissociation Energies (BDE) of enols were also estimated, and those of 1-butene-1-ol are shown in Figure 1 as a representative of all enols considered in the present work. The BDE of the O–H bond in n-butanol is 439 kJ mol⁻¹, the BDE of the O–H bond of 1-butene-1-ol (335 kJ mol⁻¹) is much weaker than that of butanol (439 kJ mol⁻¹), because the radical produced in the abstraction of hydrogen atom of O–H bond in enols form resonant structures. The rate constants of tautomerization of enols were also estimated, and it is found that those for the tautomerizations propen-2-ol to acetone and 1-butene-2-ol to 2-butanone are faster than the cases of the other enols due to the relatively lower activation energies of these reactions. Details of the present work will be described in the poster.

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W3P047 KINETICS FOR OH +CH₃OH: ISOTOPIC LABELING STUDIES REVEAL MECHANISTIC FEATURES OF CH₃OH DECOMPOSITION
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Methanol (CH₃OH), the simplest alcohol, is an important molecule in combustion not only because of its potential to be a neat alternative transportation fuel but also it is a prominent intermediate in the combustion of a variety of oxygenated fuels. Due to its implications in combustion, methanol has been the subject of numerous high temperature studies over the past 30-40 years. Despite this, only recent experimental and theoretical studies (from our laboratory) have been instrumental in providing a complete understanding of the mechanistic features related to its high temperature decomposition. While these thermal decompositions act as initiations, subsequent propagation steps that involve H-atom abstractions are often the dominant channels for fuel destruction and also appear as sensitive reactions in ignition.

H-atom abstraction by OH from CH₃OH is one of the important propagation steps of relevance not only in combustion but also in atmospheric chemistry. Measurements of H/D-atoms (using the ARAS technique) that results from shock heating mixtures of deuterated CH₃OH and TBHP (Tert-ButylHydroPeroxide as a thermal source for OH) were used to probe the kinetics of OH + CH₃OD/CD₃OH. H-atom profiles were used to obtain total rate constants for OH + CD₃OH. While kinetics simulations (based on input from ab-initio/theoretical kinetics) for H/D-atoms profiles reveals that site-specific abstraction rate constants at the CH₃ and OH site in CH₃OH are indeterminate in these experiments (because of the sequence of reactions CH₃OH→CH₃O→Products); the H/D-atoms profiles provide some constraints for the abstraction branching ratios in the title reaction. Furthermore the measurements also provide some insights into mechanistic features of CH₃OH decomposition.

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W3P048 KINETIC MODELING STUDY OF PROPANAL OXIDATION AT HIGH TEMPERATURE
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Measurement of ignition delay times were conducted for propanal-O₂ mixtures diluted in argon at temperatures from 1050 to 1800 K, pressures from 1.2 to 16.0 atm, fuel concentrations of 0.5%, 1.25%, 2.0%, and equivalence ratios of 0.5, 1.0 and 2.0. A detailed kinetic model consisting of 250 species and 1479 reactions was developed and validated using the present experimental results and the literature data of shock tube under other conditions. Further validation of the kinetic mechanism was carried out by comparing the simulated results with measured JSR data and laminar flame speeds, and reasonable agreements were achieved under all test conditions. Kinetic analysis was performed using present model to provide an insight into the main reaction pathways and key reactions for the propanal oxidation in both low- and high-pressure.

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W3P049 PYROLYSIS OF CYCLOHEXANONE IN A HEATED MICRO-REACTOR
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Photoionization mass spectrometry has been used to study the initial thermal decomposition products of cyclohexanone using a heated microtubular reactor. Biofuels derived from upgrading bio-oil are important in the development of renewable transportation fuels. There are a number of methods used in upgrading bio-oil that produce cyclic ketones, and understanding the pyrolysis of these compounds is important for incorporation of these fuels into existing petroleum infrastructure. We are currently characterizing the initial thermal products of the pyrolysis of cyclohexanone using Photoionization Mass Spectrometry.
(PIMS) and matrix isolation infrared spectroscopy. Pyrolysis at 1200 K has been carried out at 260 ppm cyclohexanone in H2. The dilute gas mixture was pulsed through a resistively heated silicon carbide tube (1 mm ID). Upon exiting the reactor, the gas entered a vacuum chamber (1 – 10_6 Torr) where it rapidly expanded and cooled, quenching further reaction chemistry. The resulting thermal products were ionized and studied with time-of-flight PIMS (see below). We believe the cyclohexanone is tautomerizing to 1-cyclohexenol and undergoing a retro Diels-Alder reaction to form 1,3-Butadiene-2-ol (CH₂=C(OH)CH=CH₂) and ethylene (H₂C=CH₂). Further work needs to be done to characterize these species in the infrared as a compliment to the PIMS data. Pyrolysis will be carried out in Ar and products will be deposited onto a cryogenically frozen window (C.I, 20 K) and studied with FTIR spectroscopy.

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W3P051

AN EXPERIMENTAL AND KINETIC MODELING STUDY OF NITROETHANE PYROLYSIS AT LOW PRESSURE: COMPETITION REACTIONS IN THE PRIMARY DECOMPOSITION
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The pyrolysis of nitroethane has been investigated over the temperature range of 682-1423 K in a plug flow reactor at low pressure. The major species in the pyrolysis process have been identified and quantified using tunable synchrotron vacuum ultraviolet photoionization mass spectrometry and molecular-beam sampling techniques. From ab initio calculations for nitroethane decomposition, the rate constants for the primary pyrolysis of nitroethane have been generated for the conditions of the present work, and adopted in a detailed chemical kinetic model which contains 118 species and 719 reactions. The model was validated against the experimental results with satisfactory agreement in general. The results indicate that both the concerted molecular elimination and C-N bond rupture are significant in the primary pyrolysis of nitroethane, with the latter channel dominating at high temperatures. The results indicate that decomposition of nitroethane on the reactor wall to form CH₂CHNO and CH₃CNO constitutes a minor consumption pathway, and this step has only a small impact on the overall behavior. Further investigations will be carried out on the pyrolysis of nitroethane at different pressures, too.

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W3P052

LEAN METHANE/PROPANE IGNITION AT HIGH PRESSURES: COMPARISON OF CHEMICAL KINETIC MECHANISMS
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As a result of the importance of CO₂ reduction and worldwide increasing fuel prices, renewable energy sources like biogas, are becoming more and more important. In order to increase the calorific values e.g. propane is added and mixed with the biogas produced. To study the ignition behavior of the propane enriched biogas, two recently published mechanisms were chosen to perform a parameter variation study using COSILAB software. These mechanisms cover C₁-C₃ fuel combustion: NUIG NGM 3, SAN DIEGO.

Simplified chemical kinetic mechanisms play an important role for CFD simulations. To develop a new highly economic engine, e.g. lean biogas-fueled internal combustion engines at high pressure conditions, chemical kinetic simulation tool are inevitable. Due to the fact, commonly published mechanisms are validated only up to 30atm, there is no experience available. For this reason Rapid Compression Machine (RCM) experiments were performed to investigate the simulated ignition behavior at high pressures of 80-120bar, temperatures from 800K to 1000K and an air-to-fuel ratio from 1.9.

Ignition delay times, obtained from a zero - dimensional chemical kinetic simulation, were compared to the measurements. The investigations were adopted at described conditions.

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W3P053

SITE-SPECIFIC RATE CONSTANT MEASUREMENTS FOR PRIMARY AND SECONDARY H- AND D-ABSTRACTION BY OH RADICALS: PROPANE AND N-BUTANE
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The site-specific rate constants for hydrogen (H) and deuterium (D) abstraction by hydroxyl (OH) radicals were determined experimentally by monitoring the reaction of OH with two normal and six deuterated alkanes. The reaction of OH with the propane isotopes: propane (C₃H₈), propane 2,2 D₂ (CH₃CD₂CH₃), propane 1,1,1-3,3,3 D₆ (CD₃CD₂CH₃), and propane D₈ (C₃D₈) and the butane isotopes: n-butane (n-C₄H₁₀), butane 2,2-3,3 D₄ (CH₃CD₂CH₂CD₃), butane 1,1-4,4,4 D₆ (CD₃CH₂CH₂CD₃), and butane D₁₀ (C₄D₁₀) was investigated behind reflected shock waves over 840 – 1470 K and 1.2 – 2.1 atm. Previous low temperature data were combined with the current high temperature measurements to generate three-parameter fits which were then used to determine the site-specific rate constants. Two primary (P₁,H and P₁,D) and four secondary (S₀₀,H, S₀,D, S₁₀,H, and S₁₀,D) H- and D- abstraction rate constants, where the subscripts refer to the number of carbon (C) atoms connected to the Next-Nearest-Neighbor (N-N-N) C atom, are obtained. The modified Arrhenius expressions for the six site-specific abstractions by OH radicals are:

P₁,H=1.90×10⁻¹⁸T²⁺⁰⁰ exp(-340.87 K/T) cm³molecule⁻¹ s⁻¹ (210-1294 K)
P₁,D=2.72×10⁻¹⁷T⁻¹⁺⁶⁰ exp(-895.57 K/T) cm³molecule⁻¹ s⁻¹ (295-1317 K)
INVESTIGATION OF ETHANE PYROLYSIS AND OXIDATION AT HIGH PressURES USING GLOBAL OPTIMIZATION BASED ON SHOCK TUBE DATA

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Tranter et al. conducted a series of experiments of ethane oxidation and pyrolysis covering a wide range of temperature (800 K – 1500 K) and pressure (5 bar – 1000 bar) in a high pressure shock tube. The oxidation and pyrolysis of ethane were carried out behind reflected shock waves, and the concentrations of the reaction products were measured by gas chromatography. The results of these experiments were re-evaluated by optimizing selected rate parameters of the NUIG C5 combustion mechanism. For faster calculations, this mechanism was truncated first by eliminating the reactions of five carbon atom species. Using local sensitivity analysis at the condition of each experiment, 20 reactions steps were selected, which are important for the quantitative reproduction of the experimental results. Direct experimental data and results of theoretical calculations were searched for in the literature for these elementary reactions. A hierarchical optimization strategy was designed based on the sensitivity calculations. Arrhenius parameters (A, n, E) of the selected reaction steps were optimized using not only the experimental data of Tranter et al., but also the results of direct measurements related to these reactions. The obtained mechanism with the optimized rate parameters described the experiments of Tranter et al. much better than the original mechanism. The parameter estimation procedure provided new, temperature dependent uncertainty limits for the rate coefficients of relatively well known reactions, like C₃H₆+H = C₂H₂+H and C₂H₂ + M = C₂H₆ + M, and also gave new recommended Arrhenius parameters and uncertainty estimations for reactions with few previous experimental and theoretical investigations, like the steps C₂H₃ + O₂ = CH₂CHO + O and CH₃ + HO₂ = CH₂O + OH.

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IGNITION DELAY TIME MEASUREMENTS AND MODELING OF PENTANE ISOMERS

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Pentane isomers (n-pentane, iso-pentane (2-methyl-butane), and neo-pentane (2,2, dimethyl-propane) combustion chemistry is of interest because pentanes are components of gas-turbine and gasoline engine fuels and are intermediate species in the oxidation of higher-order hydrocarbons. Although the combustion of pentanes was examined in several studies in Rapid Compression Machine (RCM), shock-tube, well-stirred reactor, and an annular flow reactor, some conditions remain unexplored.

The present study expands on the current knowledge of n-pentane, iso-pentane, and neo-pentane combustion by investigating conditions not reported in the literature and which may be of interest to engine designers. Ignition delay time data from mixtures of the various pentanes in air were collected experimentally via shock tube and RCM for mixtures over wide ranges of equivalence ratios, pressures (1, 10, and 20 atm), and temperatures (640-1550 K). Shock-tube experiments were performed on the high-pressure shock tube at Texas A&M University, and all RCM experiments were performed at the National University of Ireland Galway’s Combustion Chemistry Centre (NUIG). These data were used to improve the detailed kinetics mechanism developed at NUIG. The purpose of this study was to verify and adjust the chemical kinetic mechanism based on experimental results.

Experimentally, the pentane isomers present similar ignition delay times at high temperature. Noticeable differences are however visible for intermediate (in the Negative Temperature Coefficient (NTC) region) and low temperatures, where the branched isomers showed longer ignition delay times than n-pentane. The ignition delay time decreases as pressure increases for all isomers. Ignition delay times were well predicted for all isomers throughout the temperature range.

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AN EXPERIMENTAL STUDY OF ISOBUTENE AND 1,3-BUTADIENE IGNITION DELAY TIME AT ELEVATED PRESSURES

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Isobutene is an important intermediate of the pyrolysis and oxidation of branched alkanes such as iso-octane. The oxidation or combustion of Ethyl Tert-Butyl Ether (ETBE) and Ethyl Tert-Butyl Ether (ETBE), which are used as octane enhancer worldwide, also produce significant amount of isobutene. While 1,3-butadiene is also an intermediate in the combustion of higher order hydrocarbons, and is emitted to the environment from the exhaust of automotive engines, biomass combustion and industrial on-site uses, which is involved in the formation of polycyclic aromatic hydrocarbons,
soot, and tropospheric ozone. Therefore, it is necessary to study the oxidation of isobutene and 1,3-butadiene to build their chemical kinetic model. Despite these importance, there is a lack of experimental data available in the literature for both of them at low and intermediate temperatures (700-1200K) and high pressures (≥10atm). In this study, Rapid Compression Machine (RCM) and Shock Tube (ST) ignition delay time measurements were performed for both isobutene and 1,3-butadiene fuel/air mixtures at equivalence ratios of 0.3, 0.5, 1.0, and 2.0. The wide range of experimental conditions included temperatures from 760 to 1500 K at pressures of approximately 10, 30, and 50 atm. Experimental results of these 2 fuels were compared based on different equivalence ratios and different pressures respectively.

As to the results of isobutene ignition delay time measurement, for several pressures and equivalence ratios, the ST and RCM meet at nearly coincident temperatures, with remarkable agreement between the two techniques, and all results got from RCM showed an excellent coalescence with those from ST which were quite linear. As to the effect of pressure on ignition, it is apparent that reactivity increases with increasing pressure, as a decrease in ignition delay time with an increase in pressure at constant temperature was observed. NTC behavior wasn’t pointed out along with temperature increasing. As to the effect of equivalence ratio on ignition, at these particular high pressures (30 and 50atm) and relatively low temperature conditions (≤950K), fuel-rich mixtures are most reactive while fuel-lean mixtures are slowest to ignite at constant temperature. While at relatively high temperature conditions (≤1000K), there appears to be a lesser dependence of ignition delay time on equivalence ratio. Moreover, under the pressure condition of 10atm and relatively high temperature conditions (≥1100K), there appears to be no dependence on equivalence ratio with all mixtures igniting at about the same time when at the same temperature and pressure. These experimental results above will be used to validate detailed chemical kinetic models of them.

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W3P059 KINETICS OF HOMOALLYLIC/HOMOBENZYLIC REARRANGEMENTS REACTIONS UNDER COMBUSTION CONDITIONS
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Homoallylic/homobenzyl radicals refer to typical radicals with the radical site located at the β position from the vinyl/phenyl group and are largely involved in combustion systems[1], such as the pyrolysis or oxidation of alkenes, cycloalkanes and aromatics. Therefore, it’s significant to carry out investigations of Homoallylic/homobenzyl radical.

The homoallylic/homobenyl rearrangement, called 1,2-vinyl/phenyl migration, is a peculiar reaction type for homoallylic/homobenzylic radicals. The 1,2-vinyl migration is regarded as taking place by a two-step sequence: (1) ring closure of an allylic radical to form a cyclopropylcarbiny radical, and (2) ring opening of the formed radical to yield an allylic radical of rearranged structure. With the help of rate constant calculations, the competitions between this reaction mechanism and other possible reaction pathways under combustion temperatures (500-2000 K) were evaluated. The 1,2 vinyl/phenyl migration is the most favored reaction channel for R1/R2 compared with other competing reactions at least under 1500K due to its low energy barrier and it still has ~20% contribution even at 2000 K.

Analogous rearrangements, like 1,3 and 1,4 vinyl/phenyl migrations are also evaluated with the help of rate constant calculations of elementary reactions. Results indicate that the reaction mechanisms of 1,3- or 1,4-vinyl/phenyl migration for radicals with similar structures are not favored under combustion temperatures.

Our studies suggest that the homoallylic/homobenzylic rearrangements have great influence on the unimolecular reaction of such radicals with homoallylic/homobenzylic structures, which are extremely needed in the kinetic models of combustion systems involving such homoallylic/homobenzylic radicals.

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W3P060 THERMAL DECOMPOSITION OF STYRENE: AN AB INITIO/MASTER EQUATION STUDY
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Styrene is a key intermediate formed during the combustion of the xylene compounds, a type of aromatic compound found in gasoline. Styrene itself can undergo further decomposition at high temperatures, with experimental studies showing that it predominantly decomposes to benzene and acetylene ($C_6H_6 + C_2H_2$). Although mechanisms have been proposed in order to explain the decomposition process, this following work is the first of its kind to use ab initio quantum chemistry methods to elucidate the decomposition mechanism of styrene.

The Gaussian-4 (G4) composite method was used to determine structures and energies for each of the intermediates and transition states involved in the decomposition mechanism. It was found that there exist three distinct decomposition channels, each of which contributes under combustion-relevant conditions. The most energetically favourable pathway was the dissociation to benzene and vinylidene, the latter being a carbene isomer of acetylene. This pathway was found to have a barrier height of 84.9 kcal/mol and consists of a series of ring opening/closing steps that involve the formation of a seven-membered ring structure. It was also discovered that styrene can surmount a 94.7 kcal/mol barrier to produce phenylacetylene plus molecular hydrogen ($C_6H_6 + H_2$) via a two-step hydrogen migration/elimination process. Furthermore, styrene can also isomerise to o-xylene and benzocyclobutene before dissociating to benzene and ethene ($C_6H_6 + C_2H_4$) after overcoming a 95.6 kcal/mol energy barrier.

The constructed mechanism was then used to conduct an RRKM/Master Equation study in order to examine the kinetics of styrene decomposition. According to the simulations, negligible decomposition of styrene was observed to
The fulvenallenyl radical (C$_{7}$H$_{5}$) is a Resonance Stabilised Radical (RSR) which is present in appreciable quantities during the combustion of aromatic fuels. By virtue of its structural similarity to the propargyl (C$_{3}$H$_{3}$) and cyclopentadienyl (C$_{5}$H$_{5}$) radicals, it has been postulated that the fulvenallenyl radical can undergo reactions with other RSRs, and thus contribute to the formation of Polycyclic Aromatic Hydrocarbon (PAH) molecules during aromatic fuel combustion. Although a recent kinetic study has incorporated several such reactions in their model, uncertainties abound in the rate expressions for these reactions since these are estimations based on the kinetics for the self-addition of propargyl radicals. This study examines the kinetics of the reaction between the fulvenallenyl and propargyl radical to form naphthalene by first investigating the reaction mechanism using ab initio quantum chemistry methods. Both the M06-2X and G$_{2}$X-K methods were used in calculations. It was found that only two out of the eight possible addition sites between the two radicals directly lead to subsequent isomerisation and formation of naphthalene and the naphthyl radicals. The first involves direct addition of the acetylenic end of the propargyl radical to the β-carbon on the CCH$_{2}$ side chain, followed by isomerisation to naphthalene via fulvalene. The acetylenic end of the propargyl radical can also add to the ring on the carbon atom adjacent to the CCH$_{2}$ side chain, followed by a series of H-transfer and ring closing/opening steps to form naphthalene via azulene, another bicyclic PAH molecule. Once formed, naphthalene can then lose a hydrogen at either the α or β site to form the corresponding naphthyl radical. A total of three different formation mechanisms with a barrier height below the initial entrance channel were found, with the fulvalene pathway being the most energetically favourable (25.0 kcal/mol below the entrance channel). The two other pathways that take place via azulene have barriers of 8.8 and 13.2 kcal/mol below the entrance channel respectively.

An RRKM/Master Equation study was then performed on the resulting mechanism to determine the kinetics of the reaction between 300-2000K and 0.01-100 atm. At low temperatures, quenching of the initial adduct dominates due to the high-pressure limit being attained, even at the lower end of pressures examined in this study. At high temperatures, the formation of naphthalene and the naphthyl radicals was found to compete with dissociation back to the original radical reactants. A three-parameter Arrhenius fit was used to determine separate rate expressions for the formation of naphthalene, naphthyl radicals and fulvalene as well as the dissociation to form the original reactants.

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The generated models have been validated by simulating experimental results obtained in a jet-stirred reactor for butylbenzene and hexylbenzene and a a priori prediction of the reactivity of decylbenzene has been given.

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Self-reactions of hydrocarbon radicals are important steps in the pyrolysis and combustion of hydrocarbon fuels. At the same time, such reactions are difficult to study experimentally and reliable information on their kinetics available in the literature is rather sparse.

In the current work in progress, the kinetics of the self-reaction of cyclopentadienyl radicals is being studied experimentally over the temperature interval 298 – 600 K and at bath gas (He) densities of (3 - 12)×10^16 molecule cm^{-3} by the Laser Photolysis / Photoionization Mass Spectrometry technique. Cyclopentadienyl radicals are produced by 248-nm laser photolysis of cyclopentadiene. Initial concentrations of the cyclopentadienyl radicals are determined using the measured fraction of cyclopentadiene decomposed during the photolysis. The kinetics of cyc-C_{5}H_{5} decay is monitored in real time and the values of the rate constant of the self-reaction reaction are determined from the [cyc-C_{5}H_{5}] temporal profiles.

Preliminary results indicate that the values of the rate constant obtained in the experiments are rather large compared with those of the self-reactions of alkyl radicals, similar to the value of the collision frequency. C_{10}H_{10} is observed as the recombination product.

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W3P064 EXPERIMENTAL AND KINETIC MODELING STUDY OF DIMETHYL CARBONATE
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Dimethyl carbonate (CH_{3}COOC_{2}H_{5}, DMC) is an attractive oxygenated fuel because of its very high weight percent of oxygen. Diesel engine studies have shown that dimethyl carbonate addition to the fuel can significantly reduce smoke emissions. However, the chemical mechanism responsible for this decrease is still not well understood. Ignition delay times of dimethyl carbonate were measured in a shock tube for the first time at T =1100-1600 K, p =1,2-10,0 atm, fuel concentration=0.5-2.0%, and f =0.5-2.0. A chemical kinetic model was developed and can well predict measured ignition delay times. Further validation of the proposed kinetic model was made on the basis of the opposed flow diffusion flame data. Reasonable agreements were also achieved under the literature conditions. Reaction pathway analysis shows that the DMC molecule is primarily consumed through the H-abstraction. Sensitivity analysis provides some key fuel-species reactions at high temperature ignition.

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W3P065 A HIGH-PRESSURE AUTO-IGNITION STUDY OF METHANE IN A HIGH-PRESSURE SHOCK TUBE
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Fundamental data such as ignition delay times and species profiles at practical conditions are invaluable for the improvement and extension of chemical kinetics models to engine applications. High pressure shock tubes are ideal to study such measurements and have been used during last decade. A major challenge for kinetic modeling is pressure dependence of branching fractions for the most sensitive reactions; it is why more experimental results are needed at high pressure. A 9m long high-pressure shock tube with an inner diameter of 50 mm has been designed and validated during this study. The shock tube is designed to reach 40 bar after the reflected shock wave and can be heated up to 473 K. A double-diaphragm section divides the tube into a 4 m long driver section and a 5 m driven section.

The shock tube has been validated by reproducing previously published experimental results on methane by Zhang et al. and results show a very good agreement. The experimental study extends the ignition delay time results to pressure up to 40 bar. The experiments were performed using a lean mixture with an equivalence ratio of 0.5. All gases used for the experiments had a purity of 99.9 % or higher. The ignition delay times recorded show a strong dependence on the compressed pressure. The ignition delays decrease with increasing pressure. The temperature both impacts the ignition delay which reduces with increasing temperature.

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W3P066 SHOCK-TUBE STUDY OF THE IGNITION OF FUEL-RICH CH_{4}/AIR AND CH_{4}/ADDITIVE/AIR MIXTURES OVER A WIDE TEMPERATURE RANGE AT HIGH PRESSURE
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Flexibility between the conversion and storage of energy will be an important aspect in future energy systems, especially when considering the fluctuating availability of renewable energies. In times of low demand but high availability of energy, an interesting concept is the use of external mechanical or electrical energy in Internal Combustion Engines (ICEs) to convert “cheap” chemicals (e.g., natural gas) into higher-value chemicals so that most of the energy of the cheap fuels is stored. This production of chemicals typically proceeds at fuel-rich conditions, far away from current operating regimes of ICEs. A fundamental understanding of the chemical kinetics under these conditions and the availability of validated reaction mechanisms for these fuel-rich conditions are essential for the successful implementation of such processes. However, most of the reaction mechanisms published in the literature are validated preferentially for lean and stoichiometric mixtures, because these conditions are important in ICEs and gas turbines.

To test the performance of existing reaction mechanisms under fuel-rich conditions, we measured the ignition delay times of CH_{4}/air and CH_{4}/additive/air mixtures at fuel-rich (F = 2) and engine-typical conditions (p = 30 bar) and
compared the results with the predictions of literature mechanisms. A very good agreement was found using the mechanisms of Herzler and Naumann and Yasunaga. Additives (ethanol, dimethyl ether, propene) were used to reduce the ignition delay times of CH₄ so that engines can be used in the HCCI mode without preheating the reactants.

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PARTIAL OXIDATION OF METHANE AT ELEVATED PressURES AND EFFECTS OF PROPENE AND ETHANE AS ADDITIVE
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Partial homogeneous oxidation of methane within stationary engines may be one concept for conversion of available energy to alternatively mechanical energy, heat, and additional useful chemicals like syngas, formaldehyde, methanol or higher hydrocarbons (e.g. ethene).

These thermochemical conversion reactions are investigated experimentally using a flow reactor. Methane oxidation is studied under fuel-rich conditions (stoichiometry=20) at high pressures (6 bar) and high temperatures (Tmax = 1030K) for long residence times in a tubular reactor. The gas composition after passage through the reactor is determined by time-of-flight mass spectrometric analysis for different reactor temperatures. Through variation of reactor temperature an overview of the maximum mole fractions of target chemicals, the temperature of observed reaction onset and the optimal temperature to increase target yields can be determined.

The experimental results are compared to kinetic simulations of neat methane conversion in the reactor setup using two literature mechanisms to assess how well the data are reproduced for these uncommon reaction conditions. Both mechanisms have not been optimized for this use and the simulation deviate significantly in the predicted initiation temperature and absolute species mole fractions. The experimentally observed initiation temperatures fall between the simulation results. Absolute mole fractions exhibit differences between experiment and simulation that are as large as the deviations between the two mechanisms. In summary, the comparisons of experimental data and the results of the simulation of the experiment with these two mechanisms identify a need for further improvements of the experiments as well as the reaction mechanisms.

Given the low reactivity of methane at temperatures below 1000K the addition of additives to the gas mixture seems to be a viable way to reduce the initiation temperatures and make partial oxidation reactions more attractive for the production of base chemicals. The potential for activating the conversion reactions with ethane and propene as additives is investigated. Methanol is chosen as one target compound. Its yield is improved by both additives. In addition, propene as additive reduces the temperature of reaction onset in the experiments. Simulations of these experiments capture general trends correctly, e.g. lower initiation temperature with use of propene additive, but reproduce absolute mole fractions values poorly. This work emphasizes the need for better chemical models and accurate validation data to progress model based planning of thermochemical conversion reactions and to develop the ability to predict target chemical yields.

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MODELING THE MULTIPLE-WELL, MULTIPLE-PATH UNIMOLECULAR DECOMPOSITION OF SMALL RADICAL INTERMEDIATES – A COMPARISON BETWEEN CANTHERM, MULTIWELL, AND VARIFLEX
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Three commonly utilized rate theory packages (Rice–Ramsperger–Kassel–Marcus (RRKM) theory and Master Equation solvers) are used to investigate the unimolecular decomposition of CH₂OH, CH₂O, CH₃CHOH, and C₂H₅O. These systems, with varying possibilities for isomerization and dissociation to bimolecular products, also have pressure-dependent kinetics. In the cases of methoxy and ethoxy, comparisons of simulation results are made with available experimental data over a wide range of pressures. Comparisons between analogous high-pressure limit rate coefficients, density of states, microcanonical rate coefficients, rates in the falloff regime, and product branching fractions reveal an array of differences between Cantherm, Multiwell, and Variflex predictions. In some cases, absolute differences in species properties (e.g., the density of states) between the three packages can be large, but the consequences of these differences can be reduced due to error cancellation in computed rate coefficients. Because focus of this work is to compare simulation results with equal input parameters, the rigid rotor harmonic oscillator assumption is used to describe molecular internal degrees of freedom. However, differences in and consequences of how internal hindered rotors are treated across the three packages is also highlighted. This work is part of an ongoing effort to delineate differences across rate theory packages for atmospheric and combustion-related kinetics.

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CLOUDFLAME: A HYBRID CLOUD SYSTEM FOR COMBUSTION KINETICS SIMULATION
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The kinetics and combustion communities use various computational simulation applications (e.g., CHEMKIN, Cantera, OpenSMOKE) and platforms (Windows, Linux, Macintosh). Some problems hindering the sharing of scientific results for collaboration among researchers in the community are the lack of standardized input data (kinetics
Realistic numerical simulations of combustion phenomena necessarily require not only accurate, detailed modeling of fluid dynamic aspects, but also a detailed characterization of the chemical reactions and the physical and chemical properties of the species involved. In recent years many efforts were devoted to the development of very complex kinetic mechanisms, consisting of thousands of reactions and species, with a very high level of accuracy and excellent predictive capabilities. However, the computational cost of simulations performed using such large mechanisms can be prohibitive, even for ideal systems (batch, plug-flow, perfectly-stirred reactors, etc.) or one-dimensional laminar flames (flat premixed flames, counter-flow diffusion flames, etc.). Moreover, the huge number of species and reactions makes very difficult and complicated to recognize the main chemical paths and to interpret the numerical results from a kinetic point of view.

The considerations reported above suggest the need of computational tools able to manage large kinetic schemes, with the following features:

1. Efficiency: the calculations have to be fast, i.e. proper numerical technique have to be adopted to reduce the computational cost, without loss of accuracy;
2. User-friendly interface: i.e. the user must be able to easily incorporate them in new or existing numerical codes, to perform also complex operations (reduction of species, stiffness analysis, etc.)
3. Availability of tools to perform kinetic analyses: Reaction Path Analysis, Sensitivity Analysis, Rate Production Analysis, etc. in order to better understand the results of the numerical simulations. This work describes a suite of numerical tools, known as OpenSMOKE++, designed to provide a flexible, extensible framework for numerical simulations involving thermodynamics, transport processes, and chemical kinetics. The proposed framework is specifically conceived to manage very large detailed kinetic mechanisms (thousands of species and reactions). The OpenSMOKE++ framework strong relies on the Computation Cost Minimization (CCM) techniques, i.e. a set of strategies that expedite the numerical simulations with little or no accuracy loss through optimization of the computation sequence. Moreover, since it is based on the most modern features of C++ (template- and meta- programming, polymorphism, policies, etc.), the OpenSMOKE++ framework can be easily incorporated in new or existing numerical codes to efficiently evaluate thermodynamic properties, transport properties, and homogeneous and heterogeneous kinetics rates. In order to better show the generality and the potential applications of the proposed framework, a series of illustrative examples is presented, with particular emphasis about the numerical performances with respect to existing tools currently used by the combustion community.

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of chemical kinetics has exploded over the past two decades, leading to the development of ever growing detailed kinetic schemes for a wide range of molecular species pyrolysis and oxidation, mostly for combustion applications. With more accurate rate rules and improved mechanistic considerations, some of the latest published mechanisms are approaching 104 species and as many reactions. However, these advances in chemical kinetics and detailed model development have to be integrated with Computational Fluid Dynamics (CFD) tools to fully realize their potential in terms of improved understanding and optimization of practical energy conversion devices. The real challenge then is to maximize the level of chemical detail that can be afforded in CFD so that meaningful and reliable data are obtained for advanced design purposes.

In this work, we propose and assess the performance of a novel adaptive chemistry strategy specifically designed for LES/particle PDF simulations of non-premixed turbulent flames. For a given reactive flow configuration, thermodynamic conditions can vary widely in space and time, and in any small range of temperature and compositions, many species have negligible concentration, and only a few are chemically active. The short-term trajectories, in composition space, of the particles used to sample the local gas mixture can therefore be described using many fewer species and reactions than the original, comprehensive model.

Our approach relies on an a priori partitioning of the composition space into a user-specified number of regions, over which suitable reduced chemical representations and chemical models are identified. A computational particle in the LES/PDF simulation evolves according to, and carries only the variables present in, the reduced representation corresponding to the composition space region it belongs to. This region is identified using a low-dimensional binary tree search algorithm, thereby keeping the run-time overhead associated with the adaptive approach to a minimum. An overview of the adaptive strategy is presented, with details being provided for the major components of the algorithm. The adaptive treatment of the chemistry is then implemented within the ISAT/RCCE framework validated previously by Hiremath et al. [Hiremath, Ren & Pope, Combust. Flame, 2011]. A proof-of-concept of the combined adaptive chemistry and tabulation strategy is presented in different configurations, including the simpler partially stirred reactor (PaSR) with pair-wise mixing configuration. Even in the stringent PaSR case, results indicate that for a similar overall computational cost, using a set of reduced models adaptively using the proposed strategy increases accuracy by up to an order of magnitude compared to a non-adaptive approach that is, using a single reduced chemical model valid over the entire composition space.

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W3P072 STRATEGIES FOR ACCELERATING COMBUSTION SIMULATIONS WITH GPUs
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Combustion simulations with detailed chemical kinetics require the integration of a large number of ordinary Differential Equations (ODEs), with at least one ODE system per spatial location solved every time step. This task is well-suited to the massively parallel processing capabilities of Graphics Processing Units (GPUs), where individual GPU threads concurrently integrate independent ODE systems for different spatial locations. However, the typical high-order implicit algorithms used in combustion modeling applications (e.g., VODE, LSODE) to handle stiffness involve complex logical flow that causes severe thread divergence when implemented on GPUs, thus limiting the performance. Alternate algorithms are therefore needed.

We will demonstrate that standard explicit integrators such as the fifth-order Runge–Kutta–Cash–Karp (RKCK) algorithm can be used in the case of nonstiff chemical kinetics. When implemented on GPUs, we demonstrate a performance speedup of up to 126 times over the same algorithm executed on a single CPU with a nine-species hydrogen oxidation mechanism. In the case of moderate stiffness, the second-order stabilized Runge–Kutta–Chebyshev (RKC) method can be used. The GPU-based RKC algorithm performed 64 times faster than the same algorithm executed a CPU for an ethanol oxidation mechanism with 57 species; in addition, GPU-RKC outperformed a six-core parallel CPU version of VODE by a factor of 57 with the well-known GRI-Mech 3.0 methane oxidation mechanism (53 species). However, in the case of more severe stiffness, the performance of GPU-RKC degraded below that of VODE on six CPUs, demonstrating the need for a stiff integrator appropriate for GPU acceleration. Pending results, we will also demonstrate that specialized GPU-based stiff integrators can replace standard implicit algorithms even in the case of severe stiffness.

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W3P073 RMG-PY : THE PYTHON VERSION OF REACTION MECHANISM GENERATOR
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The open-source software project Reaction Mechanism Generator (RMG) has been generating detailed kinetic models for hydrocarbon combustion since its launch in 2003, with continued development over the decade adding many new features. In recent years a new version has been written, in the Python programming language, with the design aims of facilitating future development. RMG-Py has new capabilities, and an interactive website allowing easy estimation of thermochemical and kinetic parameters, interrogation and modification of the databases, and visualization of results.

RMG-Py is an open source project developed collaboratively on GitHub. Current features include: rate-based
model expansion; thermodynamics estimation using group additivity or, optionally, on-the-fly semi-empirical quantum chemistry calculations; extensible libraries, to allow model expansion from a known seed mechanism, or inclusion of trusted thermodynamic and kinetic data; kinetics estimates via functional-group interpolation or group-additive estimates; pressure-dependent reaction network master-equation calculations based on Modified Strong Collision or Reservoir State methods; simultaneous mechanism generation for several conditions of interest; transport properties estimation; pruning of minor species to keep memory requirements in check.

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W3P074

EXPERIMENTAL AND MODELING INVESTIGATION OF THE OXIDATION OF DIMETHYL ETHER IN A JET-STIRRED REACTOR WITH CRDS DIAGNOSTIC

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Due to the current issue concerning the growing primary energy demand, not to mention a general interest in sustainable development, bio-fuels became very fashionable in recent years. They are subject to a lot of research on combustion with the characterization of the reactivity and pollutant emissions. The molecule of Dimethyl Ether (DME) has led to a strong interest in the field of combustion. Corresponding to the simplest linear ether (\(\text{CH}_3\text{O-CH}_3\)), it has a high cetane value (55-60) and a low toxicity. Promising studies have highlighted key-strengths of this molecule as an additive agent or even an alternative diesel fuel. Among these advantages, we find a particularly significant decrease in the formation of soot and NO\(_x\) particles. Several experimental and theoretical studies have investigated the combustion of DME, using various equipments (jet-stirred reactor, shock-tube, counterflow diffusion flame, variable-pressure flow reactor) and under different conditions. Even if they bring essential information, they are unable to predict a single valid model for all circumstances. The objective of this study is to investigate DME oxidation with a different approach in order to complete existing experimental data sets, and subsequently better understand its reaction chemistry.

This was done with several experiments carried out in a jet-stirred reactor operating at 800 Torr, 500-1100 K, and at different equivalence ratios: 0.25, 1 and 2. Reaction products have been analyzed using two complementary methods: Gas Chromatography (GC) and Cavity Ring-Down Spectroscopy (CRDS). GC is efficient in separating compounds and allows to analyse a wide range of products like CO, CO\(_2\), hydrocarbons, CH\(_2\)CHO and CH\(_2\)OCHO ; while CRDS is an absorption spectroscopic technique which allows to analyze species such as CH\(_2\)O, H\(_2\)O and H\(_2\)O\(_2\) (undetectable by GC).

Significant differences were observed when comparing experimental results to data computed with a model from the literature, especially at low-temperature (500-750 K) where the reactivity was over-predicted. A new model was developed and quantum mechanics calculations have been performed to improve the set of kinetic parameters used in this new model.

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W3P075

HIGH AND LOW TEMPERATURE OXIDATION OF METHYL-STEARATE, –OLEATE AND –LINOLEATE IN JSR

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The attention towards biodiesel combustion is increasing worldwide due to the interest in renewable energy. The five major components of typical biodiesel fuels are both saturated and unsaturated methyl-esters, specifically methyl-palmitate, -stearate, -oleate, -linoleate and -linolenate. The degree of unsaturation of these molecules has a noticeable influence on the combustion characteristics and emissions. The combustion of large saturated methyl-esters is very similar to the one of methyl-decanoate, while large unsaturated methyl esters are significantly less reactive at low and intermediate temperatures. The ignition times of the four methyl esters in the NTC region follow the same order as their cetane numbers. In this work, we present new experimental data on the oxidation of large methyl-esters at high and low temperature. The experiments, performed in a Jet Stirred Reactor (JSR) at 800 Torr and temperatures 500-1050 K, refer to mixtures of benzene (92% mol) and methyl-esters (8%), such as stearate, olete, linoleate. The residence time is 2 s and the initial total fuel mole fraction is 0.5%. The reactivity of benzene can be considered negligible below 900 K under these conditions.

Due to the size and complexity of the molecules, the detailed kinetic mechanism of Westbrook et al., able to describe the high and low temperature reactivity of the five components biodiesel fuels, contains more than 4800 species and ~20,000 reactions. Saggese at al. developed a model of these biodiesel fuels starting from the POLIMI kinetic mechanism by introducing new ~60 lumped species and ~2000 reactions. The limited dimension of the overall kinetic scheme, involving ~420 species, allows an easier application of the model for practical applications. Due to the lack of experimental data, Saggese et al. only theoretically showed that large differences in the ignition delay times of biodiesel fuels components exist at low and intermediate temperatures and that the lumped and detailed mechanisms predicted the same trends, but with a larger effect of the presence of unsaturations in the case of the detailed model. The new experimental measurements presented in this work, which include a detailed analysis of the intermediate products, are compared to the lumped POLIMI_1311 kinetic mechanism (http://creckmodeling.chem.polimi.it).
The comparison showed that the lumped model is able to correctly characterize the effect of the different degree of unsaturation on the low temperature oxidation of methyl-esters. Nevertheless, the comparisons showed that this kinetic model overestimates the reactivity at very low temperatures. For this reason we revised the model in order to improve the predictions of the low temperature reactivity of the system. The revision of the kinetic scheme was performed adopting proper simplifications in order to maintain the lumped structure of the mechanism and limit the total number of species. The model was also further validated using recent experimental data, such as the ignition delay times of methyl-esters at 7 atm, and the oxidation of stoichiometric mixtures of n-decane with methyl-palmitate methyl-oleate at ~1 atm.

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A DETAILED KINETIC MODEL FOR METHYL BUTANOATE OXIDATION
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2nd generation biofuel, mainly originated from non food lignocellulosic materials, could potentially be an interesting solution for supplying a non negligible amount of biofuel (e.g. biooil or biodiesel) to replace crude oil derivatives. Unsaturated or saturated methyl and ethyl esters are potential future biodiesel but their higher oxygen content impacts their reactivity. Therefore, investigating these new species that differ from the current diesel structure is a challenge but necessary. New pollutants can be emitted and combustion characteristics may be different. The objective here is to obtain an oxidation mechanism for methyl levulinate. Because of the lack of experimental results, methyl butanoate has been chosen for testing the capabilities of a mechanism generator (RMG, in development at MIT) that could help developing levulinate mechanisms. Methyl butanoate may present the same reactivity due to the ester function and many experimental studies are available for testing the mechanism generated. In order to test the sub-mechanism, the methyl propenoate and methyl formate, two intermediate species from the methyl butanoate oxidation, have been chosen. New experimental data for methyl butanoate and methyl propenoate measured in a jet stirred reactor at 10 bar and for different equivalence ratios will also be compared to the model. The detailed kinetic model generated includes 11890 reactions and 272 species. Initial model did not predict well the different sets of data and refinement based on sensitivity analysis and rates of production lead to about 30 rates replacement with existing data or slight adjustments within the existing uncertainty factor when existing. In addition, five reactions were added to better simulate methyl formate ignition delays. The final mechanism successfully models several set of data of lean and rich compositions and in different conditions (1-10 bar, ~700 - 1900 K) for three molecules, namely methyl butanoate, propenoate and formate. Two examples are given in Figure 1. A first mechanism is also generated for methyl levulinate based on the changes required to generate a methyl butanoate oxidation model.

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EXPERIMENTAL AND KINETIC MODELING STUDY OF 2-METHYLFURAN PYROLYSIS AT VARIOUS PRESSURES
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As a new kind of biofuels, furan and its derivatives, such as 2-methylfuran (MF) and 2,5-dimethylfuran (DMF), have received more and more attentions because of the rapid consumption of fossil fuels and the novel production methods from biomass. Understanding the combustion chemistry of furan and its derivatives is crucial for their practical utilization, and requires thorough detection of their combustion products which can provide solid validation for their combustion models. This work presents a new experimental study of MF pyrolysis at 30, 150 and 760 Torr using synchrotron vacuum ultraviolet photoionization mass spectrometry, and reports a modified pyrolysis model of MF.

The experimental work was performed at National Synchrotron Radiation Laboratory, Hefei, China. Rate constants of several radical attack reactions of MF and some reactions of small hydrocarbons in the MF model developed by Somers were updated according to the validation against the present and previous pyrolysis data of MF. The simulation was carried out using Plug Flow Reactor module in Chemkin-Pro software.

Based on the Rate Of Production (ROP) and sensitivity analyses, main pathways in the decomposition of MF and the growth of aromatics are determined. The unimolecular decomposition to produce 1-butene + CO and acetyl + propargyl, H-atom abstraction to produce 2-furanmethyl radical, ipso-substitution by H to produce furan, and H-atom attack to produce CH2CHCHCO + CH3 and CH2H2 + CO are concluded to dominate the primary decomposition of MF. Further decomposition of 2-furanmethyl radical leads to great production of vinylacetylene. Many large aromatic hydrocarbons, including benzene, benzyl radical, toluene, phenylacetylene, styrene, indenyl radical, indene, naphthalene, and so on, are also detected. It is observed that at the same conversion of fuels, the concentrations of benzene and toluene in the pyrolysis of MF is slightly higher than those in the pyrolysis of DMF. Based on the ROP analysis, it is concluded that the higher concentrations of benzene and toluene in the MF pyrolysis than in the DMF pyrolysis under the similar conditions mainly result from the greater formation of propargyl radical and 1,3-butadiene.

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UNCERTAINTY PROPAGATION AND GLOBAL SENSITIVITY ANALYSIS FOR THE EVALUATION OF
Cleaner combustion devices based on the utilization of oxygenated fuels provide promising options for the development of lower carbon strategies in the transportation and energy sectors in the near future. The high heating value, high cetane number and the ability of Dimethyl Ether (DME) to provide low gaseous and particulate emissions makes it a suitable substitute for most existing direct injection diesel engines. NOx emissions when using DME may also be lower than with diesel since ignition delays are shorter. The ability of combustion models to predict emissions properties and ignition delays is therefore critical to designing practical combustion devices in order to use DME optimally. This relies on the availability of accurate and robust detailed chemical kinetic models for DME oxidation. Several DME oxidation mechanisms have recently been proposed that could potentially fulfil this purpose1-3, although the mechanisms may display either mechanistic, or parametric differences. It is therefore useful to perform an evaluation of such mechanisms, to explore any major differences between them, and to evaluate how inherent uncertainties in their input data may impact on their predictive capability with respect to available target experimental data. Liu et al. for example highlight the over-prediction of key intermediates HO2 and H2O2 by current schemes and suggest that large uncertainties may be present at high pressure3. In this work we perform a global uncertainty propagation of errors within input rate parameterisations for several DME oxidation mechanisms1-3 in order to assess their ability to predict key experimental targets such as oxygenated products within a low temperature atmospheric pressure flow reactor4, as well as ignition delays based on recent data obtained within a high pressure Rapid Compression Machine (RCM), within the temperature range (550 K – 700 K). The uncertainty propagation is based on a quasi-random sampling approach where input rate constants are varied based on a uniform distribution in log (k) space within their uncertainty bounds and sample sizes of up to 4096 are utilized to generate predicted target output distributions. A new Graphical User Interface (GUI) has been designed to facilitate global sampling based uncertainty/sensitivity studies within the Cantera software suite and will be illustrated.

Based on current uncertainties within the mechanisms, it is shown that the predicted distributions of key targets for a single experimental target can be wide. Predicted concentrations of CH2O, CH3CHO and H2O2 as well as ignition delays may vary over several orders of magnitude for some conditions. However, in all cases the experimental target data is encompassed by the 75th percentile of the predicted output distributions, indicating that the mechanistic formulation of the models is likely to be sound, but that better quantification of key rate data is required. A global sensitivity analysis is then performed in order to highlight the main sources of predictive uncertainty within the schemes. Sensitivities to the key reactions will be demonstrated and we show that the isomerisation step CH3OCH2O2 = CH3OCH2O2H strongly influences the formation of all species at the 550 K as well as ignition delays and methyl formate production over the whole temperature range. At higher temperatures the competition between 2nd O2 addition to CH3OCH2O2H and its decomposition to OH+CH2O dominate uncertainties in H2O2 predictions, whereas CH2O prediction is dominated by reactions of OH with DME and CH2O above 650 K. There are some minor differences between the key product channels between the schemes. Most of the sensitivities are highly nonlinear across the uncertainty range and significant 2nd order interactions between parameters were found. Finally, the impact of new data from a combined experimental/theoretical study6 of CH3OCH2O2 on the prediction of key targets will be explored.

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GLOBAL UNCERTAINTY PROPAGATION AND SENSITIVITY ANALYSIS IN THE CH3OCH2 + O2 SYSTEM: COMBINING EXPERIMENT AND THEORY TO CONSTRAIN KEY RATE COEFFICIENTS IN DME COMBUSTION.

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Theoretical calculations provide a useful way of estimating rate coefficients for systems over wide ranges of temperatures and pressures, not all of which are accessible from experiments. However, several studies have recently demonstrated that errors in calculated transition state energies, for example, can lead to substantial uncertainties in predicted rate coefficients. These have been suggested to be from a factor of 2 for simple abstraction reactions, up to 5-10 for complex multi-well systems, even when using high levels of theory. When experimental data are available for a system, these can be used to substantially reduce the uncertainties in predicted rate coefficients by constraining the ab initio parameters. In this work the CH3OCH2 + O2 system, of relevance to the low temperature combustion of DME, is used to illustrate this point. The input parameters for master equation calculations and their uncertainties are first derived from theory and then subsequently refined through fitting to experimental data using a Levenburg Marquardt algorithm available within the MESMER code. Uncertainties in predicted yields and overall and elementary rate constants are compared for the two approaches. At each stage, a global sensitivity analysis is also performed in order to first demonstrate how particular experiments can help to constrain the input parameters to the master equation, and secondly to explore the causes of remaining uncertainties following the fitting process. The uncertainty and sensitivity analyses are performed both for the conditions of existing experiments, and for conditions under which no experimental data are available, allowing the investigation of conditions relevant to practical combustion devices. Correlations between input parameters, present due to the fitting procedures, are taken into account. For reactions of importance to low temperature
DME oxidation, the uncertainties from the system constrained by experiment are predicted to be between factors of 2-3. However, substantial differences are found between predicted elementary rate constants in this work and those used within currently available mechanisms, suggesting that such parameters should be updated, thereby reducing overall uncertainties within low temperature DME oxidation models.

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W3P080 EXPERIMENTS AND MODELING OF A LARGE OXYGENATED MOLECULE: TRI-PROPYLENE GLYCOL MONOMETHYL ETHER (TPGME)
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TPGME is being considered as a fuel additive due to its soot reduction capabilities. It has been compared previously to a selection of other oxygenated soot reducing compounds and showed favourable trends. These results have led to interest in studying the combustion chemistry of this molecule. From a kinetic modeling point of view its structure provides an interesting challenge. It has primary, secondary and tertiary hydrogen atoms, it has both alcoholic and ether functional groups and it has a high oxygen to carbon ratio.

Ignition delay time measurements behind reflected shock waves were recorded in order to provide validation targets for a lumped kinetic model. No previous experimental data was available for TPGME. Its low vapour pressure is prohibitive when attempting to study it practically, but using a heated shock tube and laser absorption measurements ignition delay times were measured for 0.25% TPGME at φ = 0.5, 1.0 and 2.0 and pressures of 10 and 20 atm covering a temperature range of 990 – 1540 K.

(Image) A lumped approach was taken to building a model for TPGME’s oxidation. There are 8 structural isomers of TPGME. Isomer #1 (Image) was chosen to represent of all isomers in order to simplify our modeling efforts. Rate constants were assigned via analogies to similar chemical environments. This initial modeling effort was capable of predicting the experimental data very well.

Further experimental data is needed to continue development of this chemical kinetic model. Low-temperature oxidation and high-temperature pyrolysis data would allow further validation of this model in order to improve its predictive capabilities.

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W3P081 OXIDATION PATHWAYS OF CINEOLE
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Recently, direct decomposition of cellulose biomass by fungi was found to produce significant quantities of cineole (1,3,3-trimethyl-2-oxabicyclo[2,2,2]octane), a saturated cyclic ether and monoterpenoid. This has prompted researchers to consider cineole as a prospective biofuel for use in advanced engines. However, little is known about cineole’s fundamental oxidation chemistry and viability as a fuel. In this work, the low temperature (550 – 650 K) oxidation pathways of cineole were explored using a combination of experiment and theory. Chlorine-initiated oxidation using Multiplexed Photoionization Time-Of-Flight Mass Spectrometry (MPIMS) was used to identify products as a function of time, mass, and photoionization energy. Theoretical quantum calculations at the CBS-QB3 level were performed to elucidate the potential energy surfaces associated with key species and expected pathways. These calculations were incorporated into the Reaction Mechanism Generator (RMG) software package to generate a detailed reaction network for cineole.

The generated model predicts the major products found in experiment and demonstrates similar temperature dependencies in product distribution. Under the studied conditions, cineole's decomposition is initiated by hydrogen abstractions by Cl radical. The resulting alkyl radicals (m/z = 153) can add O₂ to form RO₂ or thermally decompose, mainly to acetone (m/z = 58) and C₅H₁₁ radicals (m/z = 95). One important general oxidation pathway is intramolecular hydrogen abstraction of RO₂ to form a carbon-centered radical, QOOH. These QOOH can undergo ring closure upon ejection of OH to form a cyclic ether moiety, a chain-propagating channel. This cyclic ether formation channel leads to a plethora of products with atomic masses that are 15 amu higher than the primary intermediate radicals, mainly C₅H₃O (m/z = 110) and C₁₀H₁₆O₂ (m/z = 168).

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W3P082 LOW-TEMPERATURE IGNITION OF DME/AIR MIXTURE AT ATMOSPHERIC PRESSURE: ON THE TRANSITION FROM COOL FLAME TO HOT FLAME
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Dimethyl Ether (DME: CH₃OCH₃) has been considered as a promising alternative fuel due to its merits of favorable compression ignition property and little soot formation in combustion field. A deep understanding of low-temperature ignition of DME is important in two engineering aspects: the design of engine and the safety for preventing accidental explosions. The ignition of DME exhibits a two-stage mode, which shows complexity due to the existence of
the Negative Temperature Coefficient (NTC) effect. The objective of this study is to clarify the ignition characteristics of DME, and special attention is given to the transition from a cool flame to a hot flame.

Low-temperature (< 550 K) ignition regime of DME/air mixture is experimentally investigated in a laminar flow reactor, which is updated from our previous work. The ignition limit is depicted in the temperature-equivalence ratio (TR, ex - ϕ) plane. It is found that the equivalence ratio has a dramatic impact on the ignition regime: at a specific equivalence ratio (ϕ = 1.6), cool flames transit to hot flames; while as equivalence ratio increases, the transition is significantly suppressed, resulting in weak flames. To investigate the ignition kinetics, computation is then performed using the plug-flow model based on the latest detailed kinetics by Zhao et al. The Zhao model predicts well the ignition limit, however, fails to predict the transition from a cool flame to a hot flame. Reaction pathway analyses suggest that the competition between the β-scission reaction and the molecular oxygen addition reaction of the methoxy-methyl radical (CH₃OCH₂) could strongly influence the transition. This influence is further investigated via a slight modification of the activation energy of the β-scission reaction of the CH₃OCH₂ radical. Depending on this modification, both the ignition limit and the ignition regimes against equivalence ratio are well predicted: a two-stage ignition regime corresponds to a hot flame in the experiments, and a transition suppressed ignition regime corresponds to a weak flame in the experiments, respectively. In addition, the kinetics model with this modification shows reasonable agreement with shock tube ignition delay results. It is indicated that the modification strongly influences the reactivity in the NTC region, therefore influences the transition to a hot flame. Further investigations determining the rate constants of the reactions of the CH₃OCH₂ radical may be needed to improve the DME oxidation kinetics.

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W3P083 THERMAL DECOMPOSITION MECHANISM OF 2-METHOXYFURAN
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Substituted furans including furanic ethers derived from nonedible biomass have been proposed as second-generation biofuels. In order to use these molecules as fuels it is important to understand how they break apart thermally. In this work a series of experiments were conducted to study the unimolecular and low-pressure bimolecular decomposition mechanisms of the smallest furanic ether, 2-methoxyfuran. CBS-QB3 calculations indicate this substituted furan has an unusually weak O–CH₃ bond, approximately 45 kcal mol⁻¹, thus the first reaction is bond scission resulting in CH₃ and 2-furanyloxy radicals. Final products from the ring opening of the furanyloxy radical include CO, CH₂=CHCH₂ and H. The decomposition of this molecule was studied over a range of concentrations (0.0025–0.1%) in helium or argon in a heated Silicon Carbide (SiC) microtubular flow reactor (0.66–1 mm i.d, 2.5–3.5 cm long) over a range of reactor wall temperatures from 300 to 1300 K. Inlet pressures are 150 to 300 Torr and the gas mixture emerges as a skimmed molecular beam at a pressure of approximately 10 µTorr. Products formed at early pyrolysis times (50–200 µs) are detected by 118.2 nm (10.487 eV) Photoionization Mass Spectrometry (PIMS), tunable synchrotron VUV PIMS and matrix infrared absorption spectroscopy. Secondary products resulting from H or CH₃ addition to the parent and radical reactions with 2-furanyloxy include CH₂=CH-CHO, CH₃=CH-CHO, CH₃CO-CH=CH₂ and furanones; at the conditions in the reactor we estimate these reactions contribute to at most 1-3% of total methoxyfuran decomposition. This work also includes characterization of the 2-furanyloxy radical by the assignment of several intense vibrational bands in an Ar matrix and a low-resolution estimate of the ionization threshold and photoionization efficiency curve of this allylic lactone.

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W3P084 KINETIC STUDY OF LOW- AND INTERMEDIATE-TEMPERATURE OXIDATION OF 2-METHYLFURAN AND 2-METHYLFURAN-PRIMARY REFERENCE FUEL BLENDS
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Recently, furan and its derivatives such as 2-methylfuran (MF) and 2,5-DiMethylFuran (DMF) have been produced from residual or nonfood biomass by a catalytic strategy. In addition to offering a novel production process, furans provide certain advantages in terms of their physicochemical properties over ethanol, the chief biofuel in the current market. However, more fundamental studies are required to utilize MF and DMF as alternative fuels. Besides the investigations of MF and DMF combustion charaterers, it is necessary to evaluate the effects of MF or DMF addition on the ignition delay times of Primary Reference fuel (PRF). Because the blended fuels of gasoline or diesel with biofuels are already being utilized. In this study, the autoignition characteristics of MF and MF-PRF blends were studied using a rapid compression machine at an equivalence ratio of 1.0 with an oxygen concentration of 4.1% and 16.4% in nitrogen and argon or nitrogen and carbon dioxide, in the temperature range 694–1063 K and pressure range 21.0–30.1 atm, respectively. The measured ignition delays were simulated using a detailed kinetic model of DMF constructed by Somers et al., which included the MF oxidation mechanism and a detailed kinetic model of MF-PRF blends.

As a result, in the intermediate temperature range, the ignition delays of MF are shorter than those of PRF. The ignition delays of MF-PRF₀₉₀⁰ blends become slightly shorter than those of PRF₀₉₀, which indicates that the MF promotes the ignition in this temperature range. On the other hand, in the low temperature range, the ignition delays of MF are longer than those of PRF₀₉₀. In the case of MF, ignition does not occur below 846 K. The ignition delays of MF-PRF₀₉₀
blends become drastically longer than those of PRF₉₀. In the low-temperature range, MF is found to inhibit the PRF₉₀ oxidation. Simulated ignition delays using the existing MF model and MF-PRF model, which is constructed in this study, are in reasonably agreement of those of experiments in the low temperature range. Rate-of-product analysis indicates that the ring-opening reactions of MF followed by H abstraction reactions from MF by radicals, and radical addition reactions to MF are considered to be the key reactions in the MF oxidation mechanism. In the intermediate temperature range, the model does not predict the experimental results well; therefore, further improvement is required.

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W3P085 REVISITING THE LOW TEMPERATURE COMBUSTION OF DIMETHYL ETHER
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The combustion of dimethyl ether has been extensively studied due to its ability to act as an ignition enhancer and emissions reducer when blended with fossil fuels, and due to its promise as a neat biofuel. In turn, there are numerous chemical kinetic models in the literature which describe its combustion in flow/stirred reactors, flames, shock tubes etc.

However, in order to reproduce the experiments against which they were validated, the kinetic and thermodynamic parameters applied in current mechanisms can vary significantly from one another, and from experimental/theoretically derived recommendations.

Surprisingly, despite the many DME mechanisms which have arisen since the late 90’s, none have attempted to incorporate the theoretical rate constants of Yamada et al. (Int. J. Chem. Kin 32 (7) (2000), 435–452.) for DME low-temperature combustion from early 2000, relying instead on rate constants estimated based on Evans-Polanyi correlations and analogy to alkanes (whose kinetics are also still open to debate). Effectively all the mechanisms in the literature require unreasonable alterations to the rate constant recommended by for the decomposition of O=CH-CH₂-OCH₂OOH to an alkoxy and a hydroxyl radical. Virtually all current mechanisms have had to alter the rate constant recommended for the decomposition of CH₃OCH₂ from Li et al. (J. Phys. Chem. A., 108 (11) (2004) 2014–2019.) in order to predict low-temperature/NTC data accurately. These reactions form the cornerstone of any model which aims to predict the low-temperature combustion of DME, yet there is still no consensus on what kinetic parameters are representative of the physical truth.

So despite the mechanism of DME oxidation being well-known, and despite over a decade passing since the still popular Curran/Fischer (Int. J. Chem. Kin 32 (12) (2000), (a) 713–740 (b) 741–759.) mechanism was described, there are still inconsistencies between the mechanisms which are currently in wide-spread use, and the literature rate constants which perhaps best describe the elementary kinetics of low-temperature DME combustion.

Here we present an updated chemical kinetic mechanism for DME pyrolysis and oxidation where the most recent experimental and/or theoretical determinations of elementary reaction kinetics are adopted, where available, into an existing C₉–C₂ chemistry set (AramcoMech 1.3). Whilst initially these updates had a deleterious impact on the predictive capability of the mechanism, minimal alterations were ultimately required to reproduce literature data, which we ultimately attribute to a pressure-dependent treatment of the low temperature combustion kinetics of CH₃OCH₂ radical and its derivatives.

The unimolecular decomposition of the CH₃OCH₂ radical and corresponding low-temperature reactions of RO₂ and QOOH species have been treated as pressure-dependent via QRRK/MSC computations. Non-negligible fall-off is observed in the rate constants for CH₃OCH₂ and CH₃OCH₂OOH radical β-scission reactions, which are of importance in predicting low-temperature combustion properties. RRKM/ME calculations on the decomposition of CH₃OCH₂ radical were also carried out to assess the validity of the QRRK/MSC results, with the two methods diverging by a factor of ~2 in the worst instances. The current work highlights the value which high-level quantum chemistry coupled with RRKM/ME computations would have in removing (a) the remaining uncertainty in the kinetics of the low-temperature oxidation pathways of DME, and (b) the many disparities which exist in current kinetic mechanisms for this supposedly well-understood fuel.

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W3P086 RELATIONSHIP BETWEEN OCTANE NUMBER, CETANE NUMBER, AND METHANE NUMBER: ANALYSIS OF CONSTANT VOLUME COMBUSTION CHAMBER AND VARIABLE COMPRESSION RATIO ENGINE RESULTS
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The Octane Number (ON), Cetane Number (CN), and Methane Number (MN) metrics have historically been used to characterize the relative reactivity of fuels used in spark ignited and compression ignition engines. The relationship between ON and CN has previously been reported to approximate an inverse proportionality, but a fundamental relationship between the two metrics has yet to be developed. In this study, a phenomenological relationship between these two fuel reactivity scales is presented. The relationship is then compared against experimental results from 18 different liquid fuel blends tested in a Waukesha Fuel Ignition Tester (FIT), a device typically used to measure Derived Cetane Number (DCN), and a Cooperative Fuels Research (CFR) engine. Fuel blends of Primary Reference Fuels (PRFs), toluene/n-heptane, ethanol/n-heptane, and n-butanol/n-heptane are examined and the results reveal different reactivity trends for the alcohol fuels compared to the hydrocarbon fuels. Chemical kinetic modeling suggests that differences in the observed alcohol reactivity trends are due in large part to the relatively higher rates of H abstraction by
OH radicals from alcohols compared to traditional fuels. Additionally, a new parameter called knock length is proposed as a more fundamental metric to examine fuels in Spark Ignited (SI) engines as well as a way to investigate results that cannot be explained by either ON or MN scales. The knock length parameter can be calculated directly from 0-D homogeneous ignition delay and 1-D steady laminar flame speed computations using full detailed chemical kinetic mechanisms. As part of the knock length portion of this work, 5 different methane/hydrogen fuel blends were tested in a CFR engine and the experimental results were interpreted using knock length computations using CHEMKIN. The results of this study suggest the potential to use knock length for comparing the reactivity of real fuels across various engine platforms without the use of reference fuels. For example, knock length could be used to compare reactivity differences between liquid and gaseous fuels and could potentially be extended beyond SI engines to dual-fuel applications.

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W3P087
A COMPUTATIONAL APPROACH FOR GASOLINE SURROGATE FUEL FORMULATION TO EMULATE PHYSICAL AND CHEMICAL KINETIC PROPERTIES
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Gasoline is the most widely used fuel for light duty automobile transportation. Due to its complex nature, studying the fundamental combustion properties of real gasoline fuels is intractable. Therefore, surrogates with simpler molecular composition that represent real fuel behavior in one or more aspects are needed to enable experimental and computational combustion research. This study presents a novel computational approach combining regression modeling with physical and chemical kinetics simulations to formulate surrogates for FACE (Fuels for Advanced Combustion Engines) gasoline A and C. The computational methodology links various simulations executed across software platforms. The regression algorithm implemented in MatLab is linked to Refprop for simulation of distillation curves and calculation of physical properties. The MatLab code generates surrogate compositions at each iteration, which are then automatically inputted to CHEMKIN input files and submitted to homogenous batch reactor simulations for prediction of Research Octane Number (RON). The regression algorithm determines the optimal surrogate composition to match the FACE A and C fuel properties, specifically H/C ratio, density, distillation behavior, carbon types and RON. The palette species and carbon types are selected based on Detailed Hydrocarbon Analysis (DHA) of FACE A and C. The surrogate-fuel properties were compared to the measured real-fuel properties, and a good agreement was observed.

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W3P088
A COMPARATIVE STUDY OF THE OXIDATION CHARACTERISTICS OF TWO GASOLINE FUELS AND AN N-HEPTANE/ISO-OCTANE SURROGATE MIXTURE
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Energy is considered to be the driving force and lifeline for modern economies. World energy consumption is projected to grow by 56 % through 2040 and approximately 80% of this demand will be met by fossil sources (coal, oil, gas) [US EIA 2013]. The demand for petroleum-based liquid fuels and other alternative/renewable liquid fuels is also increasing rapidly to fulfill the requirements of growing transportation sector. Recently, advanced engine concepts (HCCI, PCCI, RCCI etc.) have received special attention due to their promise of decreasing transportation related emissions and increasing engine efficiency. The performance and control of these new engine concepts is closely linked to the chemical kinetics phenomena.

Gasoline is most widely used light duty transportation fuel. Ignition delay times and CO, H2O, OH and CO2 species time-histories were measured for two FACE (Fuels for Advanced Combustion Engines) gasoline fuels and one PRF (Primary Reference Fuel) blend behind reflected shock waves. Using these data, it was possible to compare the behavior of the various species for different gasolines and PRF blend. The FACE gasolines chosen for this work are primarily paraffinic and have the same octane rating (RON 84), but contain widely varying amounts of iso- /n-paraffins and aromatics. Species time-histories and ignition delay times were measured using laser absorption methods over a temperature range of 1350 – 1550 K and pressures near 2 atm. The species time-histories and ignition delay times of the PRF surrogate reasonably duplicated the trends found in measured speciation profiles and ignition delay times of the two widely different FACE fuels. However, when compared to recent gasoline surrogate mechanisms, the simulations did not capture some of the kinetic trends found in the species time-history profiles. To our knowledge, these data provide some of the first shock tube time-history data for gasoline fuels and PRF surrogates and should enable further improvements in detailed gasoline kinetic mechanisms.

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W3P089
EFFECTS OF CHEMICAL ADDITIVES ON THEIGNITION DELAY OF ISO-OCTANE IN THE RAPID COMPRESSION MACHINE
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Concerns about global warming due to the increasing amount of CO2 and lack of fossil fuels are increasing. Transportation sector has a significant impact on the CO2 and energy consumption. Therefore, engines with high
efficiency and low emissions are gaining more and more attention.

The Homogeneous Charge Compression Ignition (HCCI) engine uses premixed homogeneous charge of the Spark Ignition (SI) engine and compression ignition of the Compression Ignition (CI) engine. It has an advantage of low NOx and PM emission, and high thermal efficiency. However, controlling combustion timing is hard because it does not have a direct controlling device such as a spark plug or an injector. The ignition delay change of iso-octane by chemical additives such as hydrogen, Di-Tert-Butyl Peroxide (DTBP), and 2-Ethylhexyl Nitrate (2EHN) was investigated. Homogeneous charge was made by using the fuel mixing vessel with the magnetic stirrer, and the ignition delay was measured by Rapid Compression Machine (RCM) experiment.

As a result, the ignition delay was increased with hydrogen addition, and decreased with DTBP and 2EHN addition. In the case of hydrogen addition, most of added hydrogen molecules consumed OH radicals by OH+H2=H+H2O reaction, so the rate of hydrogen abstraction was decreased due to the smaller amount of OH radical, and ignition delay was increased. DTBP was divided into two tertiary butoxy radicals, and then increased the rate of hydrogen abstraction. Thus, auto-ignition process became slow and ignition delay was decreased. Similarly, 2EHN was divided into NO2 and alkox radical, and this radical makes the overall reaction rate fast. Therefore, the possibility of changing ignition delay by chemical additives was confirmed.

Other species with various chemical additives will also be tested, and chemical kinetic analysis and optical diagnostics will also be conducted to figure out detailed reaction paths.

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W3P090

UNCERTAINTY OF THE RATE PARAMETERS OF SEVERAL IMPORTANT ELEMENTARY REACTIONS OF THE H2 AND WET CO COMBUSTION SYSTEMS

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Data bases of elementary combustion reactions characterize the uncertainty limits of the rate coefficients with uncertainty parameter f. Re-evaluation of the temperature-dependent uncertainty parameter f(T) is proposed by considering all available direct measurements and theoretical calculations. A procedure is presented for making function f(T) consistent with the recommended Arrhenius expression. It is shown that the corresponding uncertainty domain of the Arrhenius parameters is convex and centrally symmetric around the recommended parameter set. The f(T) function can be stored efficiently using the covariance matrix of the Arrhenius parameters. The calculation of the uncertainty of a reverse rate coefficient from the uncertainty of the forward rate coefficient and the uncertainty of the thermodynamic data is discussed. For the rate coefficients of several hundred elementary reactions, a large number of experimental and theoretical determinations is available, and a normal distribution can be assumed for the uncertainty of ln k. If little information is available for the rate coefficient, equal probability of the Arrhenius parameters within their domain of uncertainty can be assumed. Algorithms are provided for sampling the Arrhenius parameters with either normal or uniform distributions. A suite of computer codes is presented that allows the straightforward application of these methods. For twenty-one important elementary reactions of the H2 and wet CO combustion systems, the Arrhenius parameters and 3rd body collision efficiencies were collected from experimental, theoretical and review publications. For each elementary reaction, kmin and kmax limits were determined at several temperatures within a defined range of temperature. These rate coefficient limits are used to obtain a consistent uncertainty function f(T) and to calculate the covariance matrix of the Arrhenius parameters. Uncertainty ranges for the 3rd body collision efficiencies are also recommended.

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W3P091

EXPERIMENTAL AND MODELING STUDY ON EFFECT OF DILUENT GASES ON AUTO-IGNITION OF HYDROGEN BEHIND REFLECTED SHOCK WAVE

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Dilution strategy is important to control the auto-ignition in Homogeneous Charge Compression Ignition (HCCI) engine, improve the combustion and emissions in Internal Combustion Engine (ICE) with Exhaust Gas Recirculation (EGR) and validate the kinetic mechanisms. In this study, new ignition delay times were measured for hydrogen with diluent gases (Ar, N2 and CO2) behind reflected shock conditions: at temperatures of 850 – 1350 K, pressures of 1.2 – 16.5 atm, and equivalence ratios of 0.5, 1.0 and 2.0. Both NUIG H2-CO Mech and USC 2.0 Mech were evaluated against the measured ignition times, with poor agreement in the cases of N2 and CO2 dilutions and fair agreement in the case of Ar dilution. Effects of diluent gases on the shock-pressures and ignition times were then examined through the comparison between simulations and experiments. Thermal and kinetic effects of dilution gases on the auto-ignition of hydrogen were quantified. Results revealed that thermal effects were negligible at high temperature, but it becomes significant with the decrease in temperature. Differences between model predictions and measurements are mainly resulted from the uncertainties of third-body collision efficiencies of reactions H + O2 (+M) = HO2 (+M) and H2O2 (+M) = OH + OH (+M), especially in the case of CO2 and N2 dilutions.

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COMBUSTION PROPERTIES OF H₂/CO MIXTURES: CONSISTENT CHEMICAL MECHANISM FROM COLLABORATIVE DATA PROCESSING
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A revision of the DLR H₂/CO kinetic model and related experimental data is presented. The new development employed numerical algorithms and tools of the Bound-to-Bound Data Collaboration (B₃B-DC) module of an automated data-centric infrastructure, Process Informatics Model (PrIMe). The uncertainty-quantification framework of B₃B-DC establishes consistency or inconsistency of a data-and-model system, when model parameters and experimental observations used for model validation are known within their respective uncertainties. Applying this to the DLR H₂/CO kinetic model, the influence of parameter and experiment uncertainties on the optimal solution were examined and experimental targets that are most difficult to match as well as model parameter values that are likely to be questionable were identified. Over 100 experimental observations (targets) of H₂/CO ignition delays and laminar flame speeds along with their respective bounding uncertainties were collected from literature and included in the B₃B-DC dataset. After the B₃B-DC analysis of consistency, the H₂/CO data-mode system was subjected to model-parameter optimization over the feasible region of the parameter space. Considering the experimental uncertainties along with the parameter uncertainties, the rate coefficients of 12 most influential reactions were optimized. The approach to optimizing combustion models by constraining the optimization not only to parameter uncertainties but also to the uncertainties in experimental data promises the best-fit solution. The predictions calculated with such a model deviate the least from the experimental targets while remaining within their experimental uncertainties. It is anticipated that developed in this way reaction model may offer more reliable predictions for combustion at arbitrary conditions of interest.

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DEVELOPMENT OF A SYNGAS COMBUSTION MECHANISM BASED ON A HIERARCHICAL OPTIMIZATION APPROACH
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An optimized syngas combustion mechanism has been developed using a large set of indirect experimental data, consisting of ignition measurements in shock tubes and rapid compression machines, and flame velocity measurements, covering wide ranges of temperature, pressure, equivalence ratio and H₂/CO ratio. The performance of the mechanism was also tested against concentration profiles measured in flow reactors and jet-stirred reactors.

The starting point of development was the hydrogen and syngas combustion mechanism of Kéromnès, which was recently optimized for hydrogen combustion (Image). According to the sensitivity analysis carried out at each experimental data point, the rate coefficients of 16 elementary reaction steps could be optimized and estimated with acceptable accuracy. 10 of these reaction rates have been determined in, and the previously obtained reaction rates and uncertainties have been utilized in the current optimization. Direct measurements of the 6 new important reactions (H+H+M=H₂+M; CO+O₂=CO₂+O; CO+OH=CO₂+H; HCO+M=H+CO+M; HCO+O₂=HO₂+CO; HCO+H=CO+H₂) were collected and their prior uncertainty ranges were determined based on the literature data.

We used the optimization methodology described in detail by Turányi et al. coupled with a hierarchical optimization strategy using both the indirect and direct experimental data measurements as optimization targets. As a result of optimization, a new syngas combustion mechanism was obtained that is also consistent with the hydrogen combustion experimental data. The performance of the optimized mechanism was compared to those of various recently published syngas combustion mechanisms.

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SHOCK TUBE STUDY ON THE THERMAL DECOMPOSITION OF HYDROFLUOROCARBONS USING IR LASER ABSORPTION DETECTION OF HF
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The global production and consumption of HydroFluroCarbons (HFCs) is dramatically increasing. Because some of HFCs, particularly those having low global warming potential, are flammable, elucidation of their combustion properties and chemistry is critical to ensure their safe use. Thermal decomposition of HFCs is important initiation reactions in combustion of HFCs, but the kinetic of HFC decomposition is still sparsely understood. In the present study, the rate constants for the thermal unimolecular decomposition of some HFCs have been measured by using a shock tube / laser absorption spectroscopy. The experiment was performed using a double piston-actuated shock tube. The rate constants for the thermal decomposition of HFCs diluted in Ar were measured behind reflected shock waves by monitoring the formation of HF. HF was detected by the IR absorption of R (1) line in the 1-0 fundamental vibrational band near 2476 nm using a distributed feedback laser. The HF concentration was determined using the known line intensity and the line shape parameter determined by monitoring the HF generated from C₂H₃F decomposition. The rate constants for the decomposition of HFCs were determined from the time-concentration profiles of the HF produced. The results for the selected HFCs, including C₂H₃F (HFC-161), CH₂CF₂ (HFC-143a), and CH₂=CFCF₃ (HFO-1234yt) are presented.

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THE IGNITION OF GAS MIXTURE \( \text{CH}_3\text{Cl} + \text{Cl}_2 \) AFTER BRIEF EXPOSURE TO UV – LIGHT

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Under the action of UV radiation on the mixture \( (\text{CH}_3\text{Cl} + \text{Cl}_2) \) as a result of photodissociation of chlorine molecules there are formed initial reaction centers- chlorine atoms. In isothermal conditions within a short time, the concentration of chlorine atoms in the system becomes quasi-stationary. Since during the chlorination \( \text{CH}_3\text{Cl} \) chains are not ramified

\[
[\text{Cl}]_i = (W_i/k[M])^{1/2} = \frac{W_i}{k[M]}
\]

where \( W_i \) – thy rate of initiation, and \( k \) – rate constant of the reaction \( \text{Cl} + \text{Cl} + M \rightarrow \text{Cl}_2 + M \).

After the cessation of initiation the concentration of active particles decreases

\[
[\text{Cl}] = [\text{Cl}]_i e^{-[k[\text{Cl}]i]^{1/2}} + [k[\text{Cl}]]^{1/2} = \frac{W_i}{1/2} + [k[\text{Cl}]i]^{1/2} - 1
\]

The experimental studies of temperature fields in photochemical reactions were conducted in a steel cylindrical vessel with a diameter of 0.05 m and a length of 0.89 m. The \( \text{CH}_3\text{Cl} + \text{Cl}_2 \) mixture contained in atmospheric pressure and room temperature, was irradiated with a mercury lamp UV-radiation of 1 kW through the quartz glass installed in the end of the vessel. Irradiance was register at \( 2 \cdot 10^{21} \text{ quantum/m}^2\text{s} \). The temperature in the vessel was measured by thermocouples \( (d = 20 \cdot 10^{-6} \text{ m}) \), placed at the distances \( 1 \), \( 0.03 \), \( 2 \), \( 0.07 \), \( 3 \), \( 0.1 \), \( 4 \), \( 0.15 \), \( 5 \), \( 0.225 \), \( 6 \), \( 0.795 \) m along the axis of the vessel.

In \( (0.14\text{CH}_3\text{Cl} + 0.86\text{Cl}_2) \) and \( (0.59\text{CH}_3\text{Cl} + 0.41\text{Cl}_2) \) mixtures photoignition occurs approximately 0.1 s after the cessation of initiation. In a rich mixture the photosensor disposed near the quartz glass outside of reaction vessel captures the radiation of arising flame.

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THE INFLUENCE OF THE GAS MIXTURE \( (\text{CH}_3\text{Cl} + \text{Cl}_2) \) COMPOSITION ON SPEED AND TEMPERATURE OF THE FLAME

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The spread of the flame was explored in a cylindrical stainless steel vessel with a diameter of 0.05 m and a length of 0.05 m. To initiate the ignition of \( (\text{CH}_3\text{Cl} + \text{Cl}_2) \) mixture contained in \( T_0 = 293 \text{ K} \) and \( P = 101 \text{ kPa} \), it was irradiated with a mercury lamp radiation of 1 kW through the quartz glass installed in the end of the vessel. The flame propagation was monitored by microthermocouples \( (d = 20 \cdot 10^{-6} \text{ m}) \) placed at various distances along the axis of the vessel. According to the indications of thermocouples the relationship \( x = f (\tau) \) was plot, and using it the instantaneous rate of flame propagation was calculated.

The highest speed is typical of \( (0.33 \text{CH}_3\text{Cl} + 0.67 \text{Cl}_2) \) mixture, which is stoichiometric under the condition of substituting two hydrogen atoms by chlorine in molecule of chloromethane. The high speed in the initial sections are due to propagation of photoignition wave. Mixtures containing 14 and 59 % vol. \text{CH}_3\text{Cl} are ultimate. Dependence of maximum values of temperature (fixed by thermocouples placed at distances \( 1 \), \( 0.035 \), \( 2 \), \( 0.105 \), \( 3 \), \( 0.155 \), \( 4 \), \( 0.235 \), \( 5 \), \( 0.38 \), \( 6 \), \( 0.585 \), \( 7 \), \( 0.805 \text{ m} \)) on the concentration of chloromethane has been received. In near thermocouples \( (1-4 \) ), maximum values are also fixed in the mixture \( (0.33 \text{CH}_3\text{Cl} + 0.67 \text{Cl}_2) \). At the distal thermocouple \( (7) \), all the indications are higher, and the maximum value is observed in a mixture of \( (0.5 \text{CH}_3\text{Cl} + 0.5 \text{Cl}_2) \) which is stoichiometric when one of hydrogen atom is substitute by chlorine. Maximum heating of the same mixture was observed previously in its photoignition in a short vessel \( (l = 0.05 \text{ m}) \).

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THE LOCATION AND SIZE OF CORE OF PHOTOIGNITION IN MIXTURES \( (\text{CH}_3\text{Cl} + \text{Cl}_2) \)

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The photodissociation of chlorine molecules occurs under the action of UV light on the gas mixtures with formation of the initial reaction centers

\[
\text{Cl}_2 + \text{hv} \rightarrow 2\text{Cl}
\]

The rate of initiation of the photochemical reaction \( (W_i) \) decreases in the direction of the light flux due to radiation attenuation in an absorbing medium in accordance with the equation

\[
W_i = 2I_0E C_{\text{Cl}}\text{e}^{-\chi}-E C_{\text{Cl}}\text{e}^{-\chi}
\]

The photoignition occurs in the region of space where \( W > W_i^{\text{crit}} \). The photoignition zone size will be estimated by the dependence \( W_i(x) \). We have previously established critical values of the rate of initiation in mixtures of different composition at \( P_0 = 101 \text{ kPa} \) and \( T_0 = 293 \text{ K} \). From the dependence of \( W_i(x) \) the distance at which the initiation rate is reduced to the critical values was estimated. Depending on the mixture composition the distance varies from \( 2.5 \cdot 10^{-2} \) to \( 8.8 \cdot 10^{-2} \text{ m} \).

The experimental studies of temperature fields in photochemical reactions were conducted in a steel cylindrical vessel.

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vessel with a diameter of 0.05 m and a length of 0.89 m. To initiate the reaction, the CH$_3$Cl + Cl$_2$ mixture, placed in a box at atmospheric pressure and room temperature, was irradiated with a mercury lamp of 1 kW through quartz glass set in the back of the vessel. Incident intensity ($I_0$) was $2 \times 10^{11}$ quantum/m's. The temperature in the vessel was measured by thermocouples ($d = 20 \times 10^{-6}$ m), placed at different distances along the axis of the vessel.

In a mixture with chloromethane of 14 and 25 % vol. concentration the photoignition source due to heat transfer in quartz glass is formed at some distance from it. Primarily, the core is placed at a distance from 3 - 10$^{-2}$ to 10$^{-2}$ m. Higher concentration of chlorine in the mixture makes the area of the initial ignition narrower. The dimensions of source are significantly bigger than the calculated values estimated without account of thermal expansion of the reaction mixture.

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W3P099  
A COMPREHENSIVE REACTION MODEL FOR THE Si-H-Cl-C CHEMICAL SYSTEM  
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Silicon-based compounds, such as silicon hydrides, silicon halides, and silicon hydridohalides, are widely used as a source of silicon atoms in a number of industrial processes. A large variety of materials, including SiC, Si$_3$N$_4$ and SiO$_2$, can be produced from chemical vapor deposition and combustion-based processes. For example, SiH$_3$Cl and SiH$_2$C$_2$ can be employed to create epitaxial layer onto electronic devices. Because of a wide range of applications, a deep understanding of the high-temperature kinetics of the Si-H-Cl-C chemical system is required to improve and optimize industrial fabrication processes. The aim of the present study is to develop a comprehensive reaction model able to reproduce available high-temperature data for gaseous mixtures containing Si-H-Cl-C atoms.

Experimental time-resolved profiles of Si, H and Cl obtained during the pyrolysis of different mixtures containing one or several components among Si$_2$H$_6$, SiH$_4$, SiC$_3$H$_4$, SiHC$_3$, HC$_3$, CH$_3$, CH$_2$I, CH$_3$Cl and CH$_2$I, have been collected as a validation database. These experimental data come from Roth's group and have been obtained using the shock-tube technique within the following ranges: $X_{reactant}=0.2-20$ ppm; $T=1137-4525$ K; $P=72-172$ kPa. The proposed reaction model includes 311 elementary reactions and 87 chemical species. Silane pyrolysis kinetics was taken from Petersen study and hydrocarbon pyrolysis reactions were taken from Konnov's reaction model. Halogen and silicon hydridohalides reactions, and halogen-hydrocarbon as well as halogen-silicon interactions were compiled from various studies from the literature.

The figures below present typical results obtained in the present study. The proposed reaction model allows to reproduce satisfactorily most of the experimental data available in the literature. In all cases, the main trends are captured by the model. The largest discrepancies were observed for hydrogen atom profiles. In some cases, the concentration is over-estimated by a factor of two. Typical error for silicon and chlorine atoms is on the order of 30%. This seems to indicate that some rate constants relevant for hydrogen atom kinetics might need reappraisal.

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W3P100  
EXPERIMENTAL AND MODELING INVESTIGATION OF N-DECANE PYROLYSIS AT SUPERCRITICAL PRESSURES  
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The pyrolysis kinetics of fuels under supercritical conditions is an important concern for developing regenerative cooling technology of advanced aircraft using hydrocarbon fuels as the primary coolant. N-Decane as a component of some jet fuels was studied at the temperature range from 773 to 943 K in a flow reactor under the pressure of 3, 4 and 5 MPa. GC-MS was used to analyze the pyrolysis products, which were mainly alkanes from C$_1$-C$_9$ and alkenes from C$_2$-C$_9$. A kinetic model containing 138 species and 697 reactions has been developed and validated by the experimental results including the distribution of products and the chemical heat sink of fuel. The decomposition pathways of n-decane were illustrated through the reaction flux analysis. It is concluded that the C$_8$-C$_9$ alkanes are mainly generated by the recombinations of alkyls, while the small alkanes (C$_1$-C$_3$) are formed by H-abstraction reactions by C$_1$-C$_3$ alkyl radicals. The applicability at supercritical pressure and high fuel concentration condition of previous models was discussed, the performance of the present model in reproducing the experimental data is reasonably well.

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W3P101  
EXPERIMENTAL AND KINETIC MODELING STUDY OF N-TETRADECANE PYROLYSIS  
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Long chain normal alkanes with 10 and more carbon atoms are important components in commercial transportation fuels such as gasoline, diesel, kerosene and jet fuels. They are also widely used as major components of surrogate fuels. Compared with n-decane and n-dodecane, the combustion studies of n-tetradecane were very limited and completely focused on the global parameters such as laminar flame speeds and ignition delay times. No measurement on the mole fraction profiles in the gas phase pyrolysis and oxidation of n-tetradecane has been performed. The targets of this work are to report the first investigation on the chemical structure of n-tetradecane pyrolysis at low and atmospheric pressures and develop a kinetic model of n-tetradecane pyrolysis.

The experimental work was performed at National Synchrotron Radiation Laboratory, Hefei, China. Detailed
descriptions of the two beamlines and pyrolysis apparatus used in this work have been reported elsewhere. The pyrolysis of 2% n-tetradecane in Ar was investigated from 830 to 1300 K at 30 and 760 Torr. Synchrotron vacuum ultraviolet photoionization mass spectrometry was used to detect the pyrolysis species. Dozens of pyrolysis products of n-tetradecane were detected, including alkanes, 1-alkenes, 2-alkenes, dialkenes, alkynes, and free radicals such as methyl radical (CH₃), propargyl radical (C₃H₅) and allyl radical (aC₃H₅) and so on. And their mole fractions were evaluated as functions of temperature. A new pyrolysis model of n-tetradecane with 184 species and 925 reactions was developed to reproduce the experimental results. The simulation was carried out using Plug Flow Reactor module in Chemkin-Pro software.

The present model can get reasonable prediction on the profiles of n-C₁₄H₃₀ and its major pyrolysis products. Rate of production analysis shows that the consumption of n-C₁₄H₃₀ is dominated by unimolecular C-C bond dissociation reactions and H-atom abstraction reactions. Based on the sensitivity analysis of n-C₁₄H₃₀ at 30 Torr, 1163 K and 760 Torr, 1017 K, the C-C bond dissociation reactions have the highest sensitivities to the decomposition of n-C₁₄H₃₀ among all types of primary decomposition reactions of n-C₁₄H₃₀ at both 30 Torr and 760 Torr, mainly due to their crucial roles in both the consumption of n-C₁₄H₃₀ and the production of free radicals. Among all H-atom abstraction reactions, the H-atom abstraction reactions by H and CH₃ have the greatest contributions to the consumption of n-C₁₄H₃₀ and are also the major formation source of H₂ and CH₄. The C₂ and larger alkyl radicals mainly suffer β-scission reactions to produce 1-alkenes (e.g. 1-C₃H₅), the subsequent decomposition reactions of C₄ and larger 1-alkenes will lead to the production of smaller radicals (e.g. aC₃H₅), alkenes and dialkenes.

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W3P102

EXPERIMENTAL AND KINETIC MODELING STUDY OF N-PROPYLECYCLOHEXANE COMBUSTION
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Cycloalkanes are an important component family in the gasoline, diesel oils and jet fuels, as well as their surrogates. Thus, their combustion kinetics is crucial for the development of kinetic models of real fuels. As a further step of the systemic study on the combustion of cycloalkanes, the pyrolysis of N-PropylCycloHexane (PCH) at 30, 150 and 760 Torr were investigated in a flow reactor using synchrotron vacuum ultraviolet photoionization mass spectrometry. Mole fraction profiles of more than 40 species were quantified, providing new validation data for the kinetic models of PCH.

A detailed kinetic model of PCH combustion was developed and validated against the pyrolysis data in the present work. The developed kinetic model can reproduce the consumption of PCH and the formation of pyrolysis products. Under the pyrolysis conditions of this work, PCH is consumed via both unimolecular decomposition and H-abstraction reactions. The dominant unimolecular decomposition pathway is the loss of n-propyl radical to cyclohexyl radical. The contribution of this reaction to PCH consumption decreases as the pressure increases. Products from the ring-opening isomerization of PCH and the dissociation of C₅H₁₇ and cyclohexyl radicals constitute the product pool in the PCH pyrolysis.

Furthermore, mole fraction profiles of species measured in the Jet-Stirred Reactor (JSR) oxidation and lean premixed flame of PCH reported in the literature were used for further validation of the present model. Under these oxidation conditions, PCH is mainly consumed by the H-abstraction reactions by OH attack, while the unimolecular reactions of PCH only have little contributions.

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W3P103

DEVELOPMENT OF RATE RULES FOR THE LOW-TEMPERATURE OXIDATION OF ALKANES
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Ignition delay times of fuel-‘air’ n-pentane, iso-pentane and neo-pentane mixtures were measured in a Rapid Compression Machine (RCM). The experimental data were then used to improve the current chemical kinetic models of the isomers. The present study shows ignition delay time data at equivalence ratios of 0.3, 0.5, 1.0 and 2.0 at pressures near 10 and 20 atm across temperatures ranging from 640 to 1020 K.

Rate rules for reaction classes important to low-temperature oxidation, including those related to the Negative Temperature Coefficient (NTC) region and to first-stage ignition, have been updated based on recent quantum-chemically derived rate coefficients from the literature. There have been a variety of systematic studies which have used various computational quantum chemical methods for rate coefficient calculations for reactions relevant to the low-temperature oxidation of alkanes. These studies have calculated high-pressure limit rate coefficients for sets of training reactions with the aim that they can be used directly in chemical kinetic mechanisms for combustion relevant applications. In this work, the rate coefficients from these studies are compared and applied to the mechanisms of the isomers of pentane. Several reaction classes have also been included, and pressure dependency of rate coefficients has also been investigated. Updates to the thermochemistry of the species important in the low-temperature oxidation of hydrocarbons have also been made based on a thorough literature review. The work in this study will provide a systematic evaluation of the rate rules in the literature and their suitability for application to mechanisms for the low temperature oxidation of straight-chain, branched and highly-branched alkanes, and new rate rules are developed which will form the basis for efficient mechanism construction for larger alkanes. This will be particularly important for the
When compared to the chemical kinetic models, in general, ignition delay times were well predicted for all of the isomers over all ranges of temperature, pressure and mixture composition. To the authors' knowledge, this study covers compositions and conditions not yet present in the literature, and will expand fundamental knowledge of the combustion kinetics of alkanes.

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PARAMETRIC STUDY OF THE LOW TEMPERATURE OXIDATION OF HEXANE IN A FLOW REACTOR
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The goal of the present study is to characterize in detail the low-temperature oxidation process of a kerosene surrogate over a wide range of conditions, in order to accurately evaluate the effectiveness of alternative inerting strategies for flammable atmospheres in aircraft fuel tanks.

The experimental facility is a flow reactor composed of three parts: an inlet, a quartz reactor and an outlet. The residence time within the reactor is controlled by a mass ow controller from Omega. The quartz tube is located in an oven and has an inner diameter of 2.54 cm and a length of 25 cm. The inlet and outlet are made of stainless steel and have a width of 5.08 cm. The inlet is used to feed the gaseous mixture into the flow reactor and check the initial composition using infrared laser absorption measurements through sapphire windows. At the outlet, sampling and spectroscopic measurements of water and fuel are performed. Both the pressure and the temperature are monitored along the inlet-reactor-outlet assembly. Gaseous samples are analyzed using a gas chromatograph with identification and calibration performed for 26 chemical species.

The evolution of the gas phase composition at the flow reactor exit as a function of temperature was investigated for n-hexane based mixtures over the following ranges: φ=0.7-1.5; T=450-1000 K; P=40-100 kPa; τ =2-30 s. The figures below illustrate the effect of residence time and pressure on the oxidation regimes. The cool ame region shifts from 600 K to 500 K as the residence time is changed from 2 to 30 s. In the Negative Temperature Coecient, NTC, region, between 700 and 800 K, significant consumption of the fuel occurs essentially through pyrolysis as demonstrated by the large amounts of non-oxidized species formed. As the pressure is decreased from 100 to 40 kPa, the cool ame region shifts from 500 K to 550-575 K. The NTC region, within T=650-750 K, appears more pronounced at 40 kPa than at 100 kPa. The peak production of hydrogen, alkanes and alkenes is shifted from 800 to 900 K. The temperature at which total oxidation is achieved is shifted from 900 K to above 950 K.

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THERMAL STABILITY OF N-HEXANE-OXYGEN MIXTURES
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Accidental combustion events in fuel tanks and flammable leakage zone are a major concerns in aviation safety. In order to mitigate this risk and fulfill safety regulations, some commercial aircraft use an inerting strategy based on hollow fiber membranes that exhibit selective permeability so that a nitrogen-enriched environment is created in the fuel tank. Although effective, this approach has limitations. The present study examine the alternative strategy of a long duration thermal process close to but below the auto-ignition temperature to create an inert mixture through slow oxidation.

Experiments were performed in a 1.14 L cylindrical cell made of stainless steel. Two 5 cm in diameter, 5 mm thick ZnSn windows are located opposite to each other for optical access. A Frontier Perkin-Elmer Mid-IR FTIR spectrometer is employed to monitor in real-time the evolution of the gas-phase composition. For all experiments, resolution was 1 cm⁻¹ and the scanning rate was 0.17 Hz with averaging of three consecutive spectra. The test cell is equipped with 3 pneumatic valves for rapid filling, gas sampling and evacuation. The temperature and pressure inside the cell are monitored with a shielded K-type thermocouple and a pressure transducer. Mica foil-heaters and a heated magnetic stirrer plate are used along with temperature controllers to heat the vessel and maintain the temperature constant. Prior to experiments, the test cell is evacuated to below 2 Pa and heated to the desired temperature. The gas mixture, prepared from research-grade liquid n-hexane and gaseous oxygen and nitrogen, is introduced from a 5 L glass into the test cell. Homogeneity of the mixture is ensured by active mixing with a quartz coated magnetic stirrer. Infra-red spectra, temperature and pressure are recorded over 7200s. Experiments were performed for fuel-O₂ mixtures diluted with 89% and 78% nitrogen and an equivalence ratio between 0.67 and 1.35. The temperature and pressure were varied between 420 and 500 K and between 37 and 147 kPa, respectively. The figures below show the evolution of the IR spectrum as a function of time as well as the evolution of CO₂ as a function of temperature. For all conditions studied, no ignition was observed but significant amounts of CO₂ and H₂O were formed. At low temperature, the chemical activity is characterized by a slow and constant reaction rate. At high temperature, the reaction proceeds in two-phases. Initially, rapid production of CO₂, CO and CH₂O is observed followed by a period of slower production of CO₂ and H₂O.

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EXPERIMENTAL COMBUSTION STUDY OF LARGE LINEAR AND BRANCHED HYDROCARBONS USING NOVEL MOLECULAR BEAM MASS SPECTROMETRY TECHNIQUES

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Linear and branched hydrocarbons with chain lengths from C₆ to C₁₄ as prototype Fischer-Tropsch fuels from coal, gas or biomass have become the main target for applications as alternative fuels in aviation as well as mid-term energy storage solutions. Long-term goals include the application of numerical CFD based methods as flexible design tools for fuels or storage media. The CFD approach includes the combination of fluid dynamics with chemical processes, provided by implementation of kinetic models. However, for the development of those chemistry models, experimental data for validation is strongly needed based on the new demands. Molecular Beam Mass Spectrometry (MBMS) has proven to be a reliable and versatile technique in obtaining a vast, quantitative overview of species related information in complex kinetic processes.

Here, we present two novel MBMS approaches to provide quantitative experimental species information for large hydrocarbons from C₆ to C₁₀₀: the first part deals with a high-temperature flow reactor with coupled MBMS-ToF detection operating at atmospheric conditions, currently under close characterization at the DLR in Stuttgart to provide species profiles as a function of temperature. Initial experimental results from gaseous species (methane) are presented to demonstrate the potential for the first time together with preliminary studies for large hydrocarbons such as n-nonane. The second part involves a new approach at the iPEPICO experiment of the Swiss Light Source (SLS) at the Paul Scherrer Institut in Villigen, Switzerland. This powerful tool is a new diagnostic method allowing the investigation of complex chemistry reaction pathways. In the present work, the potential of the iPEPICO system is demonstrated for a premixed low pressure (40 mbar) iso-butane/O₂/Ar-flame, stabilized on a McKenna type burner. Experimental results for large hydrocarbons, e.g. n-nonane doped into a premixed low pressure (30 mbar) H₂/O₂/Ar-flame at a total equivalence ratio of Φ = 1.5 are presented and discussed.

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W3P107 AN INVESTIGATION OF PHASE-CHANGE BEHAVIOR IN RCM EXPERIMENTS WITH LARGE MOLECULAR WEIGHT FUELS
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Rapid Compression Machines (RCMs) are well-suited for acquiring validation targets for chemical kinetic models at the operating conditions of current and future internal combustion engines. These laboratory devices are able to provide empirical access to the low- to intermediate-temperature (e.g., T = 600–1000 K) kinetics of transportation-relevant fuels at elevated pressure (e.g., p = 10–80 bar), under non-dilute conditions. However, probing the gas-phase chemistry of large molecular weight fuels (e.g., MW > 140) in these devices has historically been challenging due to the in-volatility of constituent or surrogate species, and full boiling range fuels. This challenge has been addressed via heating the apparatus and accompanying pre-mixing tank, while experiments utilizing fuel aerosols have also been suggested as a viable approach. The effect of phase change during experiments with these large molecular weight fuels using either fuel loading method, on the well-defined “adiabatic core” of the reaction chamber has not been previously assessed. This study attempts to do so where a computational approach is utilized and several representative conditions are investigated. A reduced-order model is extended to facilitate this study, where the multi-phase species and energy transport are taken into account. Simulated stratification profiles are presented for mixtures containing two non-reacting, aerosol-loaded diesel surrogates, n-dodecane and n-hexadecane. For the conditions explored here, it is found that a thermally and compositionally well-defined “adiabatic core” can be maintained throughout the duration of a typical experiment, e.g., 100 ms. The simulation results presented here also indicate that fuel condensation within the cooler thermal boundary layer may be beneficial during RCM experiments, where condensive heating reduces the boundary thickness and stabilizes the core gas temperature.

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W3P108 QUASI-GLOBAL KINETIC MODELING OF DIFFERENT ALKANE AND ALCOHOL FUELS
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Within the Cluster of Excellence „Tailor Made Fuel from Biomass” at RWTH Aachen University novel synthesis and production routes for bio-based fuels are investigated. Detail understanding of combustion chemistry of such tailor-made fuels plays an important role in combustion research area. However, detailed kinetic modeling usually needs a significant amount of effort and time and is not suitable for screening of many bio-fuel candidates within short time. Furthermore, CFD simulation of e.g. combustion engines with full kinetic models cost computational effort. For this reason kinetic models with a small number of reactants and reactions are desirable.

These aspects motivate to develop a quasi-global kinetic model for describing the auto-ignition of various fuels. The approach is based on the idea to combine a C0 base mechanism with some characteristic fuel reactions. In principle this idea has already been described by Westbrook and Dryer for modelling laminar flame speeds but according to the authors knowledge this approach hasn’t been applied for autoignition studies. The focus of the present study is the low temperature autoignition of fuels based on the reactions described by Curran et al. as the major pathway towards low temperature chain branching (RH => R => RO₂ QOOH O₂QOOH => Ketone + OH => Decomposition Products + OH). Although this reaction scheme has been reported first for alkane fuels recent studies of biofuels, e.g. butanol, have shown
that this reaction pathway plays a dominant role in the low temperature chemistry also of these fuels. Consequently, this scheme has been implemented as base mechanism for the low temperature kinetic of all fuels of interest focusing in a first step on alkane and alcohol fuels. One of the main differences compared to other global mechanisms is the fact that the proposed model directly includes the most important radicals OH and HO$_2$ as reactants which play major role in low temperature chemistry. Preliminary results for n-heptane-air mixtures show a very good agreement between the proposed quasi-global model and results from experiment and from a detailed kinetic model.

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W3P109 IDENTIFICATION AND COMPARISON OF DETAILED CHEMICAL MECHANISMS
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We are developing tools to facilitate identification of chemical species in a kinetic model “Chemkin file”, and then to allow comparison of the models. The tools, built on top of the Python version of Reaction Mechanism Generator software (RMG-Py), will also enable error identification, self-consistency checking, model merging, gap-filling, and facilitate model validation and updating. In recent decades, detailed kinetic models have become integral to combustion research. Progress has been significant and the latest models can explain many complicated combustion phenomena, and allow increasingly accurate engine simulations.

These models can be very large (eg. the LLNL model for 2-methylalkanes has over 7,000 species and 30,000 reactions) and there are now dozens of large published models. Unfortunately, these ever-proliferating detailed kinetic models are incompatible and inconsistent, are seldom compared directly, and often contain undetected mistakes.

Adoption of collaborative optimization, solution mapping, and data curation projects is low, and the preferred publication format remains a “Chemkin file”. This Chemkin format, devised in the 1970’s when input was limited by the width of 80-column punch-cards, forces model-builders to abbreviate species’ names, thereby losing their chemical identity, and to discard other metadata. The main challenge in comparing these models is in recognizing, for example, that the name “C$\text{$_1$$\text{$_2$$\text{$_2$$\text{$_1$$$_2$KET}}$}$_1$$$_2$” in one model represents 1-hydroperoxypropan-2-one, which another research group may have named “CH$_3$COCH$_2$OH” in a different model.

We are using our tool to import all the models published in supplementary material to the Proceedings of the 34th Combustion Symposium into a unified and cross-referenceable database, and to analyze them to reveal agreements, disagreements, consistencies, and areas for the combustion kinetics community to focus on in the future. If the proceedings are published in time, we will also analyze the current 35th symposium.

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W3P110 COMBUSTION CHEMISTRY MODEL OF FOUNDATIONAL FUELS
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Because of the hierarchical nature of hydrocarbon fuels high-temperature oxidation, a reliable foundational fuel chemistry model is crucial to the accuracy of any reaction chemistry model of fuel combustion. The current effort centers on providing a detailed chemical kinetic model with well-quantified and minimized uncertainty for use as a foundation for the combustion of all hydrocarbon fuels at high temperatures. This foundation model describes the combustion kinetics of hydrogen, carbon monoxide, and C$_1$-4H$_x$O$_y$ species. The current version is consisted of 291 elementary reactions of 33 species.

The model development effort takes the following steps with an emphasis on uncertainty quantification, propagation and minimization: trial model compilation in which the reaction pathways were analyzed and updated and their rate constants evaluated, validation against experimental targets, rate constant re-evaluation, and constrained rate parameter optimization with uncertainty quantification and minimization. A total of 148 targets were selected for model optimization, including laminar flame speed, shock tube ignition delay and species profile of H$_2$, H$_2$O$_2$, CO, CH$_4$, CH$_2$O and C$_3$H$_6$ oxidation. Model optimization and uncertainty minimization uses the Method of Uncertainty Minimization by Polynomial Chaos Expansion (MUM-PCE), with response surfaces generated from Sensitivity Analysis-Based (SAB) method as well as Monte Carlo sampling and factorial design. Experimental targets were carefully evaluated with a special attention placed on an assessment of the uncertainties in the initial conditions and their impact on the simulation of flow reactor and shock tube experiments.

This poster will present validation results of the trial and the optimized model and an assessment of the initial conditions and their impact on the simulation of flow reactor and shock tube experiments.

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W3P111 APPROXIMATE TRAJECTORY OPTIMIZATION ALGORITHM FOR MECHANISM REDUCTION OF N-HEPTANE OXIDATION
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In this work, a novel Approximate Trajectory Optimization Algorithm (ATOA) to generate skeletal mechanisms is presented and validated. To produce a skeletal mechanism with combustion trajectory closely resemble that of the detailed mechanism, we require the relative error of the global species production rate to be smaller than a preset threshold on a set of representative state points. A trajectory approaching process which minimizes global species production rate error is proposed to fulfill this requirement. Many skeletal mechanisms can be generated in this way and iterative improvement algorithm is further adopted to optimize the obtained skeletal mechanism systematically. In the iterative improvement process, a skeletal mechanism is first perturbed and new skeletal mechanism will be achieved based on the trajectory approaching process. Lots of skeletal mechanisms can be produced and the one with minimum number of species and simulation error bellow a given accuracy criteria will be chosen as the optimal skeletal mechanism. This algorithm has been applied to reduce a detailed n-heptane oxidation mechanism with 561 species and a 75-species skeletal mechanism has been obtained. This skeletal mechanism is shown to be able to reproduce combustion trajectory of the detailed mechanism under a wide range of parameters and configurations.

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W3P112 IMPROVING DETAILED KINETIC MODELS OF BIO-OIL GASIFICATION VIA RATE RULE CALCULATIONS
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The major challenge in modeling thermal conversion and combustion of biofuels is the presence of a wide range of cyclic oxygenated species and in particular, more attention should be paid to specific reaction classes like primary ring-opening isomerization that can take place through direct C–C or C–O bond breaking. Since manually generating detailed chemical models is effortful and error-prone, it is preferable to use computers instead. In this study, Reaction Mechanism Generator (RMG), an open-source software, has been used to study the main kinetic features of bio-oil pyrolysis and gasification. RMG’s kinetics database contains various type of reaction families with relevant reaction recipes to generate an extensive set of elementary reactions. Electronic structure calculations can be used to estimate Arrhenius rate parameters and fill the kinetics database. However, the number of reactions in each reaction family is massive, and applying high-level electronic structure calculations, especially for biofuels molecules that are quite large, would be prohibitively expensive. Alternatively, rate calculations can be performed for a smaller set of reactants belonging to the particular reaction class and, if it is transferable, it can be applied to the whole target reaction class. In order to identify the transferability of the rate rule in a specific reaction class, the role of the different functional groups should be deliberated.

A detailed kinetic model for bio-oil gasification was built in RMG and comparison with experimental data shows that the RMG-built model couldn’t predict CO and CO$_2$ formation properly. Testing the RMG-built model against the wide range of literature data revealed that RMG missed some important primary ring-opening pathways for cyclic oxygenated molecules, via either C–C or C–O bond breaking and simultaneous H-migration. For mechanism generating purposes, new reaction classes for cyclic oxygenated molecules were added into the current RMG database and associated kinetic parameters were determined. In order to investigate if the rate rule can be generalized to the reaction class or not, kinetic parameters of specific reaction groups belong to each reaction class were calculated using the CBS-QB3 quantum calculations and Transition State Theory (TST). Rate rule calculations were started from xylan, the most relevant component of hemicellulose, whose C–O bond breaking reactions have significant impact on model prediction because of H$_2$O and CO$_2$ formation. From literature, proposed transition state geometry of ring opening reaction of xylopyranose, a monomer of xylan, was used as an initial guess for transition state optimization of the rest relevant reactions. There are some significant differences in simulation results between RMG-built models before and after updating the database, specifically in CO and CO$_2$ predictions. Discrepancies in the models show the important role of specific reaction families and their relevant kinetics parameters when studying thermal conversion and combustion of biofuels.

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W3P113 A GROUP ADDITIVE APPROACH FOR HIGH-THROUGHPUT TRANSITION STATE ESTIMATION
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We propose an automated procedure to locate transition state geometries using molecular group contributions. Important combustion parameters, such as ignition delay, are very sensitive to the chemistry, and detailed chemical reaction networks help understand such processes. The detailed models are built with automated network generators, such as Reaction Mechanism Generator (RMG), due to their size and complexity. Ideally, trusted thermodynamic and kinetic parameters are used to complete the model, but these are sparse in comparison to the number required. As a result, correlation based estimates are used, but they can be quite approximate. In an effort to improve the thermochemistry, an automated procedure has been implemented in RMG to calculate thermodynamic parameters using semi-empirical quantum calculations (Magoon & Green, 2012). Known bond lengths are used to position the atoms in three-dimensional space using distance geometry, then the geometry is optimized by a quantum chemistry package.
which also returns molecular properties. While this has reduced the thermodynamic errors in RMG, the kinetic errors remain.

Kinetic parameters can be calculated via transition state theory, but this first requires location of a transition state geometry. Distance geometry can only be used if interatomic distances at the transition state are known, but they are not; we can now estimate these distances using a group additive approach. The only interatomic distances that undergo appreciable change during a reaction are the ones between the active atoms. By organizing these key distances for known transition states into a tree structure, group values can be determined and used to estimate the distances for unknown transition state geometries. In this poster we demonstrate the ability of this procedure to automatically find unknown transition states.

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W3P114 RELIABLE FORMATION ENTHALPIES FROM A COMBINATION OF COMPOUND METHODATOMISATION ENERGIES
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Mid/high-level quantum chemical methods are recognized as an indispensable tool in determining formation enthalpies ($\Delta H^f$) of stable and radical molecules due to their decreasing expense, their ability to study experimentally inaccessible molecules, and most importantly, their increasing ability to approach chemical accuracy. Typically, very high-level determinations using CCSDT, Wn, HEAT, or other such methods, are feasible only for systems containing a small number ($\Delta H^f$) are known, in order to determine $\Delta H^f$ in instances where ‘gold standard’ methods cannot be employed. If the working reactions and standard $\Delta H^f$ are well chosen, the uncertainties in the computed $\Delta H^f$ can rival high-level methods. The atomisation method is also frequently used to determine $\Delta H^f$, but due to the inherent lack of error-cancellation, uncertainties can be large unless very high-level methods are used.

We recently applied (J. Chem. Thermo., 58 (2013) 117–128.) the isodesmic reaction method to determine formation enthalpies of 40+ stable polyoxymethylene furans of interest as platform chemicals and biofuels, using the CBS-QB3, CBS-APNO and G3 methods. Comparison with experiment showed agreement in the majority of instances, giving credence to the thermochemical networks which were hierarchically built. Atomisation energies were also computed which agreed surprisingly well with the isodesmically derived values. We have re-visited the data to rationalize the agreement between the isodesmic and atomisation results, benchmarking the latter against the former, with some interesting trends arising. The computed atomisation formation enthalpies could be correlated by isodesmic enthalpies via $\Delta H^f$ (Atomisation) = $\Delta H^f$ (Isodesmic) +0.24 kJ/mol, with $R^2 = 0.99$. Despite this remarkable correlation, if a single molecule were considered, the uncertainty (2σ) in the formation enthalpy of any given compound was much greater in the atomisation $\Delta H^f$ than the isodesmic $\Delta H^f$ - up to 26 kJ/mol for the former but only 6 kJ/mol for the latter in the worst instances. The uncertainty in the atomisation results seems to be somewhat overestimated however, certainly in light of the above correlation.

When methods were considered in isolation, atomisation calculations from the CBS-QB3 and G3 methods tended to slightly over-predict the isodesmic formation enthalpies by 0.16±4.4 and 4.17±2.4 kJ/mol respectively, and the CBS-APNO method tended to under-predict by −5.57 ± 4.9 kJ/mol. On average the combination of these three methods tended to agree with the isodesmic values within -0.41±2.2 kJ/mol at 2σ uncertainty—significantly less than the 26 kJ/mol extreme highlighted above. The excellent linearity observed appears to be the result of an error-cancellation effect introduced by using a combination of the CBS-QB3, CBS-APNO and G3 methods, which overcomes the lack of error-cancellation when only a single method was used—some methods tended to consistently over-predict $\Delta H^0$, others under-predicted $\Delta H^0$, but the methods tended to compensate well for each others deficiencies. Future studies should assess the applicability of a combination of these, or similar, methods for determining accurate but cost-effective formation enthalpies, by benchmarking their performance against a test-set of well-known (e.g. ATcT, 3rd Millenium Database) stable and radical species.

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W3P115 COMPARATIVE ANALYSIS OF COMBUSTION CHEMISTRY MODELS USING THE ALTERNATE SPECIES ELIMINATION APPROACH
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In recent years, numerous chemical kinetic models have been developed for computational analysis of various combustion processes. Different modeling approaches are taken, sometimes leading to large deviations in model prediction of combustion properties from experimental measurements, as well as deviations among the various models. Comparative analysis of these models is complicated since typical models consist of hundreds of species and thousands of reactions. Identifying specific sub chemistry models that lead to these differences is challenging. A promising approach to identify key kinetic differences appears to be the use of reduced models which retain the predictive ability of their original versions. These reduced models can also be independently employed in further computational analysis of combustion phenomena. In this work, we use the Alternate Species Elimination (ASE) method to derive and compare reduced models for propane and syngas combustion based on selected detailed models from the literature. Chemical species are systematically eliminated and reinstated while changes in a specific combustion property, ignition delay in this case, are recorded. The simulations for this process are carried out in CANTERA and MATLAB. The importance of
a chemical species is revealed through a high ranking of the normalized change in ignition delay time caused by the elimination of the said species. A reduced model is obtained by imposing a reasonable normalized change threshold, below which all species and their reactions are eliminated. Results show a normalized change threshold of 10−4 retains good predictive ability for both ignition delay and flame speed. In most cases the model is reduced to at least half of the original number of species and at least a third the number of reactions. The average deviation for each reduced model from original simulation results was within 5%. A comparison of the various skeletal models based on the relative rankings and normalized changes reveal underlying differences in modeling approaches and the extent of chemical reactivity of key species. The results show that the approach is useful in revealing differences in chemical kinetic modeling strategies and kinetic parameter assignment.

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W3P116 FIRST HIGH-TEMPERATURE MEASUREMENT OF THE HNO + O₂ REACTION RATE CONSTANT BEHIND SHOCK WAVES
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Strategies for reducing NOₓ emissions from fossil fuel burning rely on a detailed knowledge of the reaction kinetics of the underlying elementary gas phase reactions. HNO (nitroxy1) represents an important flame species and its intermediate concentrations are closely linked to the resulting NO levels in the exhaust gas. Depending on the combustion conditions, HNO equilibrium reactions such as HNO → H + NO, HNO + OH → NO + H₂O, and H + HNO → NO + H₂ can either increase or reduce NO formation. As most HNO reaction rates have not been measured at combustion temperatures so far, estimated or theoretical values have to be used in NO formation models. These estimates vary strongly depending on the fuel type and the applied kinetic mechanism, respectively. For example, for the reaction HNO + O₂ → NO + HO₂, which acts as a major NO source under certain combustion conditions, reported literature data differ by several orders of magnitude.

Here, the first detection of HNO behind shock waves and the first rate constant measurements for the reaction HNO + O₂ at temperatures between 750 K > T > 1370 K will be presented. The obtained overall rate expression reveals that the reaction is astonishingly fast, even when compared with the highest literature data. This result underlines the high uncertainties of HNO chemistry implementations in current flame models.

We directly observed the reaction HNO + O₂ behind shock waves by applying the very sensitive absorption based Frequency Modulation (FM) spectroscopy. FM spectra of the electronic A'A'' - X'A' HNO transition and concentration-time profiles of HNO have been detected at three different wavelengths around 618 nm and 625 nm. HNO mole fractions of about 200 ppm behind reflected shock waves have been generated from the 193 nm UV photolysis of glyoxal/NO₂ mixtures. Glyoxal photolysis provides HCO radicals in high yields whereas HNO is formed by the fast consecutive reaction HCO + NO → HNO + CO. By simultaneous modeling of corresponding HNO and HCO concentration-time profiles, which were obtained under similar reaction conditions, the temperature dependent absorption cross section of HNO could be determined as well.

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W3P117 KINETICS OF NO₂ + NH₃ RADICAL-RADICAL REACTION: THEORETICAL AND EXPERIMENTAL STUDIES
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The Air Force Research Laboratory is developing new hypergolic fuels which will provide enhanced performance capabilities as well as improved affordability and efficiency. Furthermore, handling of these new hypergolic fuels is expected to have a much smaller logistical footprint due to the fact that they are being designed to be environmentally benign. However, practical realization of these hypergols in spacecraft propulsion systems will only come after attaining a satisfactory understanding of how to optimize their combustion characteristics in relevant operating environments.

The state-of-the-art hypergol combination currently used in the US for many space propulsion applications consists of monomethyl hydrazine, as the fuel, and nitrogen tetroxide, as the oxidizer. Here we report theoretical and experimental results obtained on a prototypical NO₂-radical reaction with N₂H₃. The potential energy surface was investigated by *ab initio* multi-reference second-order perturbation, density functional, quadratic configuration interactions, and coupled-cluster theories. The reaction proceeds via a complex mechanism with submerged energy barriers and relatively large exothermicities. It was found that direct NO₂ addition to the NH site in N₂H₃ forms two isomeric adducts with energy of 38.12 kcal/mol lower than that of the N₂H₃ + NO₂ entrance channel, which is set as a zero energy reference. The isomeric adducts undergo decomposition to trans-HONO + trans-NH=NH and trans-HONO + cis-NH=NH with energy barriers of -9.56 and -4.65 kcal/mol, respectively. Furthermore, the addition adducts undergo decomposition to NO, NNH and H₂O via several steps involving isomerization and molecular elimination. It was also found that the NO₂ can add to the NH₂ site in N₂H₃ to form an unstable adduct which undergoes isomerization to form the NH₂NHO radical. The NH₂NHO isomer has energy of -19.94 kcal/mol and further isomerizes before dissociating to smaller products. Important reaction channels for the NH₂NHO isomers involve dissociation to NO + NH₂NO radical products with energy barriers ranging from 5.2 to 13.8 kcal/mol. Dilute mixtures of N₂H₃/NO₂ in nitrogen carrier gas, maintained at 2 Torr and 298 K, were subjected to 193-nm laser photolysis in a flow-tube reactor coupled to an electron-impact ionization mass spectrometer to study the reaction kinetics of N₂H₃ radicals in excess NO₂. Upon photolysis, the reacting gas was mass spectrometrically sampled using a skimmer as the mixture escaped via
a pin-hole inside the flow-tube reactor. The temporal profile of the product, HONO, was determined by direct detection of the ion signal at m/z = 47. For each chosen [NO2], the observed [HONO] trace could be fitted to a bi-exponential kinetics expression, which yielded a value for the pseudo-first-order rate coefficient, k', for the reaction of N2H2 with NO2. A value for the bimolecular rate coefficient, k = (1.03 ± 0.29) × 10^{-11} cm^3 molecule^{-1} s^{-1}, for this reaction was obtained from the slope of a plot of k' versus [NO2]. Pressure-dependent rate coefficients of the N2H3 + NO2 reaction system were determined by Rice–Ramsperger–Kassel–Marcus (RRKM) theory with multi-well master equation simulations. With the energy transfer probability approximated by DE_{down} = 100 × (T/300)^{0.85} cm^{-1}, excellent agreement was observed between the measured value and the computed overall rate coefficient at 298 K and 2 Torr of N2. The negative energy barriers and large exothermicities for the various product channels suggest a significant role of this reaction in the early stages of hypergolic ignition of hydrazine and its derivatives.

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W3P118

AB INITIO KINETICS AND THERMAL DECOMPOSITION MECHANISM OF MONONITROBUTIURET AND 1,5-DINITROBUTIURET

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Mononitrobiuret (MNB) and 1,5-Dinitrobiuret (DNB) are, tetrazole-free, nitrogen-rich compounds that have been reported as powerful new explosives. A new ignition mechanism for the thermal decomposition of MNB and DNB is proposed herein. Ignition of MNB and DNB occurs through a multistep reaction process, in which the thermal decomposition of MNB and DNB is initiated by intramolecular H-atom transfer from the central NH group to an adjacent nitro oxygen of the NO2 group to eliminate an unstable HNNOH intermediate that rapidly dissociates to OH, HNNO, NH2, NO2, N2O, and H2O. The radicals produced from HNNOH decomposition react further with MNB and DNB via H-abstraction reactions to produce MNB and DNB radicals, which subsequently decompose and oxidize to low-molecular weight intermediates and then final products.

In this work, the potential energy surface for thermal decomposition of the HNNOH intermediate was investigated at the RCCSD(T)/cc-pV\(\infty\)Z/CASPT2/aug-cc-pVDZ level of theory, and pressure-dependent rate coefficients were determined by Rice–Ramsperger–Kassel–Marcus (RRKM) theory with multi-well master equation simulations at the E, J resolved level. Isomerization of HNNOH to NH2NO2 isomer occurs with an energy barrier of 28.87 kcal/mol, which then dissociates to NH2 + NO2 radicals, while inversion of the amineylene-H has an energy barrier of 30.11 kcal/mol to form another HNNOH isomer, which undergoes \(\cdot\)OH bond fission to form OH and trans-HNNO radicals. Furthermore, it also undergoes migration of the amineylene-H to the hydroxyl-O which results in H2O elimination with an energy barrier of 30.73 kcal/mol and reaction exothermicity of 50.4 kcal/mol. At atmospheric pressure, the result shows that decomposition to NH2 + NO2 is competitive with decomposition to OH + trans-HNNO at all temperatures. At ~700 K and above, formation of thermodynamically stable products, N2O + H2O, becomes less competitive to the radical channels, and decreases with increasing temperature.

Abstraction of H-atoms from different positions in MNB generates three different MNB radicals, for which the bond dissociation energies for the amine-H in terminal NH group, central NH group and terminal NH2 group, were respectively computed to be 109.72, 119.51, and 116.59 kcal/mol by CCSD(T)/cc-pV\(\infty\)Z/B3LYP/6-311++G(d,p) calculations. The energy barriers for the OH radical to abstract each of the different H-atoms in MNB were found to be 10.49, 13.04, 12.30, and 8.85 kcal/mol, which are consistent with the corresponding bond dissociation energies calculated above. The bimolecular rate coefficients for H-abstraction in MNB by OH radicals were also determined in the range 300-2500 K. The H-atoms in DNB have the same bonding environments as that in MNB except for the central amine-H, which is shielded by two -C(O)NHNHO2 groups. It was found that the abstraction of the central amine-H of DNB occurs once one of the surrounding groups rotates away and makes its bonding moiety the same as that of MNB. This implies that the rate coefficients of DNB + OH are similar as those of MMB + OH.

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W3P119

IGNITION DELAY TIME AND KINETIC MODELING OF NITROMETHANE-OXYGEN-ARGON MIXTURES

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Energetic materials such as nitrogen-containing molecules, commonly used as fuel, fuel additives and propellants, are mainly studied for their capability of releasing large amount of energy. Nitro-alkanes are relatively simple model fuels to study the gas phase combustion kinetics of these compounds. Gas phase detonations in nitro-alkanes exhibit a double cellular structure under certain conditions. Although nitro-methane is the most studied nitro-alkane, there is a limited amount of experimental data in the high-temperature range. The present study aims at providing a comprehensive set of auto-ignition delay time for nitro-methane-oxygen mixtures.

The shock-tube is composed of three parts separated by two diaphragms and is made of stainless steel. The driver section and the driven section are 6.19- and 11.28-m-long, respectively, (i.d. 15.24 cm). The test section is 2.44-m-long (i.d. 7.62 cm) and is linked to a 2.03-m-long cookie-cutter. The driver gas was nitrogen. The test section is equipped with 4 pressure transducers, for shock velocity measurements, and two quartz optical window mounted at 13 mm from the tube end. Two optical fibers are used to collect emission. One of the optical fibers is linked to a single-photomultiplier (Hamamatsu) equipped with a 306+5 nm band-pass filter for detecting the OH* radicals. The second fiber is linked to a
dual-photomultiplier (Thorlabs) equipped with a quartz beam splitter and two band-pass filters centered at 410±5 nm and 430±5 nm for detecting the CO$_2^*$ and CH* emission, respectively. Emission and pressure histories of CH$_3$NO$_2$:O$_2$-Ar mixtures with $\phi$=0.75-1.5 were measured behind reflected shock wave in the temperature and pressure ranges 1076-1509 K, 340-410 kPa, respectively. The argon dilution was 97% in all cases. The figures below display an example of experimental signals a) and the evolution of the delay-time with reciprocal temperature b) and c). Delay-times in b) come from Guirguis et al. and were derived on pressure signals. For all equivalence ratios and temperatures, the oxidation of nitro-methane is characterized by two distinct exothermic steps. The first one is taking place very shortly after the reflected shock heating and exhibits a low activation energy whereas the second one has a large activation energy. A comprehensive reaction model has been built and validated against data from the literature. It can reproduce the main trends observed in the present study.

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W3P120

CHEMICAL KINETICS OF SILANE-NITROUS OXIDE MIXTURES AT TEMPERATURE BELOW 1700 K

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Silane-nitrous oxide mixtures are widely used as a source of silicon atom in the semi-conductors industry to produce thin solid layers of SiO$_2$. Chemical Vapor Deposition, CVD, processes can be employed to form these protective and/or insulative layers onto the device surface. The utilization of SiH$_4$ based mixtures is potentially hazardous and can lead to significant material destruction as well as human fatalities. The specific kinetic properties of silane are also relevant to propulsion applications. Despite a number of application of silane-based mixtures, there is a lack of experimental data for these systems. Especially, elementary reaction rate parameters are missing for a large number of reactions. The purpose of the present study is to obtain additional experimental data for reflected shock heated SiH$_4$-N$_2$O-Ar mixtures at temperature below 1700 K.

Mixtures were prepared from a mixture containing 1% of SiH$_4$ in argon. High purity gases, 99.998% and above, were employed. The shock tube used was a 78 mm internal diameter stainless-steel pressure-driven shock tube with a 5.5-m-long driven section and a 3.5-m-long driver section. A turbomolecular pump evacuated the test section to less than 2.10-4 Pa. The optical detection technique for measuring O atom concentration was an emission line absorption method. A microwave-excited discharge lamp that contained a flowing mixture of 1% O$_2$ in He maintained at a pressure of 1.4 kPa was used as light source. A vacuum ultraviolet monochromator was used to isolate the O triplet wavelength, 130.5 nm, and a solar blind photo-multiplier was used to convert vacuum UV photons.

The dynamics of oxygen atom in reflected shock-heated silane-nitrous oxide-argon mixtures was investigated at temperatures between 1353-1885 K and pressures from 212 to 373 kPa. In the 1450-1700 K temperature range, the absorption profiles exhibit unusual complex shapes characterized by an initial rapid rise, a plateau and a second rise. This complex behaviour was attributed to the reaction of disilyne with oxygen atom: Si$_2$H$_4$+O=Si$_2$H$_2$+OH. The rate constant of this reaction has been determined by fitting the experimental absorption profiles with computed ones, as illustrated in the figures below.

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W3P121

THERMAL DECOMPOSITION OF ORGANOPHOSPHORUS AGENTS

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Organophosphorus compounds are involved in toxic compounds such as pesticides or chemical warfare agents. The understanding of their thermal decomposition and oxidation chemistry is largely limited by the scarcity of thermochemical and kinetic data due to the extreme difficulty to perform experiments with these highly toxic molecules. Literature studies on the decomposition of nerve agent surrogates such as DIMP showed that the preponderant decomposition channels of these molecules occur through pericyclic molecular reactions. Therefore, an accurate determination of the rate parameters of these reactions is critical to describe their thermal decomposition.

A theoretical study of the initial concerted reactions in the decomposition of a series of organophosphorus compounds (sarin, soman, tabun, VX) was performed by means of quantum chemical calculations at the CBS-QB3 level of theory. For each organophosphorous compound, the potential energy surface of 4-, 5- and 6-centered concerted eliminations were investigated. Based on the calculation of the electronic structures, canonical transition state theory was used to evaluate rate constants. The contributions of hindered internal rotations were corrected in the harmonic vibrational partition functions with the tabulations of Pitzer and Gwinn. The characteristics of internal rotor potentials were determined using scans performed at the B3LYP/6-31+G(d,p) level of theory.

Theoretical results show that 6-centered eliminations generally face energy barriers of ~40 kcal/mol. Such low activation energies should favor molecular decomposition routes over radical initiation pathways that involve much higher bond dissociation energies. To confirm the critical role of molecular eliminations, a comprehensive chemical kinetic model, including molecular and radical reactions, was developed for the pyrolysis of the toxics. Simulations showed that 6-centered eliminations in these compounds are preponderant over a wide range of conditions.

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MICROWAVE INTERFEROMETER FOR IONIZATION KINETICS

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The electrical aspects of flames have attracted much interest and study over the years, but there remains considerable uncertainty regarding the processes fundamentally responsible for the various observed phenomena. Detailed physical models will be crucial in developing a clear understanding of these effects, but they must be supported by experimental measurements. Specifically, determination of the chemical kinetics responsible for ionization in flames is necessary. Free electrons, the primary negative charge carrier in flames, have proven difficult to measure accurately and unobtrusively. In this work, we present a Microwave Interferometer (MWI) as a means to measure the number density of electrons in a shock tube for the evaluation of reaction kinetics.

The MWI is fundamentally equivalent to the familiar optical techniques used in combustion. A coherent wave is generated at 94 GHz and then split into a test and reference signal to be sent through and around, respectively, the test section of a shock tube. Subsequent comparison of the two signals resolves the relative phase shift and attenuation of the test signal, from which index of refraction and absorptivity can be determined. Free electrons have the uncommon property of exhibiting an index of refraction below unity and absorptivity that increases non-linearly with their concentration. Both of these effects are increased at low frequency, making microwave systems significantly more sensitive than optical wavelengths. This high sensitivity is critical for combustion experiments due to the low electron densities produced by chemionization.

The present work begins with detailed characterization of the in situ spatial response of the MWI in the shock tube by measurement known physical structures (e.g. non-reacting shocks). From those data, signal deconvolution tools are developed to improve spatial resolution beyond apparent limitations imposed by the long wavelengths (~3 mm) and quasi-optical properties of microwave antennae. Ultimately, the MWI is used to measure the formation and decay of electrons in the combustion of various hydrocarbon fuels over a range of equivalence ratios, pressures and temperatures. These results, coupled with simultaneous optical emission and absorption measurements provide a dataset against which proposed ion chemistry mechanisms can be validated and calibrated.

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A NEW SHOCK-TUBE FACILITY FOR THE STUDY OF HIGH-TEMPERATURE CHEMICAL KINETICS

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A new stainless steel shock-tube facility designed for the study of chemical kinetics at elevated temperatures and pressures is described. It consists of a helium-driven, single-pulse shock tube capable of using both lexan diaphragms and die-scored aluminum disks of up to 4 mm in thickness. It has a relatively large driven-section inner diameter of 16.2 cm to minimize non-ideal boundary layer effects. Test times around 3 milliseconds are achievable at conditions ranging from temperatures between 600 and 4000 K and pressures between 1 and 100 atm behind the reflected shock wave. The facility includes a new high-vacuum system capable of achieving ultimate pressures on the order of 1x10^-6 torr, a new gas-delivery system, a shock velocity-measurement scheme, a computer-based data acquisition system and the capability of implementing several optical diagnostics. Applications of the new facility include ignition delay time measurements, measurement of reaction rates coefficients and high-temperature spectroscopy, among others.

Additionally, an overall description of the set up and operation of the facility along with details on the characterization procedure of the shock tube will be provided. These include pressure behavior, vacuum integrity, turnaround times and a thorough study on the velocity behavior of the shock to maximize the accuracy of calculated experimental conditions. Also, in order to validate the facility, demonstrated behavior of standard diluted methane-air and hydrogen-air mixtures will be shown. The first set of new data obtained with the new shock tube for acetylene-air ignition delay times will also be presented.

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COMPARING PREDICTIONS AND EXPERIMENTAL DATA FOR FLOW REACTOR STUDIES: COMPUTATIONAL RE-INITIALIZATION

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Flow reactor experiments are frequently modeled as plug flow phenomena. Typically, comparison of the computational predictions with experimental data requires careful considerations and reflection of the experimental conditions upstream of the diagnostic region. The manner in which these upstream conditions are reflected in comparison to the experimental reality introduces uncertainties in terms of utilizing the data for kinetic model development and validation. Moreover, the reaction region itself may be neither adiabatic nor isothermal, requiring experimental characterization of the axial temperature distribution. Flow reactor modeling approaches, including various approximation methods, have recently been discussed in detail. One of the methods, referred to as “computational re-initialization”, avoids the need of considering the impacts of upstream experimental conditions and bypasses the requirement of defining an absolute time scale for comparing predictions and experimental data. The general philosophy of this approach is to utilize measured data at some axial location within the region where plug flow
assumptions are well approximated to estimate concentrations of the remaining species for which the measurements are not available. This provides the complete model initialization for comparing predictions and further experimental data downstream of the initialization location and reaction time scale in the region of interest. This technique has been applied in several specific flow reactor studies previously. High dilution was employed in these experiments, thus eliminating the need to consider changes in the diluent mole fraction and closure in experimental atom conservation consistent with the initial reactor chemical composition supplied to the reactor.

In this poster, we will present a more robust methodology for applying computational re-initialization, and demonstrate the method for reaction systems that are neither adiabatic nor isothermal. Applications will be presented involving the pyrolysis of iso-propanol and the oxidation of several fuels, including hydrogen and methane. Uncertainties arising from computational re-initialization, model size, and the importance of adding additional initialization species data will be examined.

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W3P125
IMPROVED SEMICLASSICAL TUNNELING FORMULA AND ITS APPLICATION TO DEEP TUNNELING
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The analytic multidimensional semiclassical tunneling formula of Miller is qualitatively incorrect for deep tunneling at energies well below the top of the barrier. The origin of this deficiency is that the formula uses an effective barrier weakly related to the true energetics but correctly adjusted to reproduce the harmonic description and anharmonic corrections of the reaction path at the saddle point as determined by second order Vibrational Perturbation Theory (VPT2). We have developed an analytic improved semiclassical formula that correctly includes energetic information and allows a qualitatively correct representation of deep tunneling. This involves constructing of a three segment composite Eckart potential that is continuous everywhere in both value and derivative. This composite potential has an analytic barrier penetration integral from which the semiclassical action can be derived and then used to define the semiclassical tunneling probability. The middle segment of the composite potential by itself is superior to the original formula of Miller et al. because it incorporates the asymmetry of the reaction barrier produced by the known reaction exoergicity.

Recent experimental studies by the Continenti group have concluded that the barrier between HOCO and the dissociated products H+CO is considerably narrower than that represented in a previously available Potential Energy Surface (PES). We apply the original and improved semiclassical formulas to this PES, two recent PESs, and a partial PES specific to this project. As seen in the figure, the original formula is qualitatively incorrect on three of the four PESs. The improved formula produces tunneling probabilities that, with one exception, are quite similar to POLYRATE and in qualitative agreement with the experimental studies. Unlike many methods that require the calculation of a reaction path, semiclassical tunneling requires only VPT2 calculations at the saddle point that can be readily parallelized and are options in popular electronic structure code packages. For existing PESs, we have a code soon to be distributed that samples a user PES to construct a VPT2 description of a saddle point and thereby enables semiclassical tunneling approaches.

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W3P126
SIMULATIONS OF INTERNALLY EXCITED MOLECULES IN DENSE GASES
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At low pressures, the relaxation of vibrationally and rotationally excited molecules by a thermal bath gas is characterized by rates that are directly proportional to pressure because each collision can be considered an isolated event. At higher pressures, collisions are no longer isolated, collision frequencies are not directly proportional to pressure, and the relaxation rates are overestimated by linear extrapolations derived from low pressures results. In order to better understand at what pressures this over-estimation becomes important and what mechanisms might be responsible, we have started a series of molecular dynamics simulations in which diatomic, triatomic, and polyatomic molecules are excited in an argon bath gas at different pressures and the system is followed to times where full thermalization has almost been reached (up to 1000 ps). All Ar atoms and the molecule are explicitly followed and the simulations are contained with either periodic boundary conditions or cell techniques. This approach, while computationally expensive, avoids the isolated binary collision approximation of single collision studies and the assumption of full IVR relaxation between collisions of the successive collisions approximation. In our simulations, the intramolecular potential for the molecules are taken from the literature and pairwise additive potentials are used to represent Ar-Ar and Ar-molecule interactions. Preliminary representative decay curves, on a semi-log scale, are shown in the figure where CH$_3$NO$_2$ is excited to approximately 40 kcal/mol above thermal energy in room temperature argon. The results in the figure are normalized to the excess vibrational energy above thermal at t = 0. One can see that the vibrational relaxation rate increases with pressure. However, between 75 atm and 150 atm, the rates increase by noticeably less than a factor of two. Furthermore, since two of these decay curves are not linear on a log plot, it is clear that multi-rate relaxation becomes apparent at the higher pressures. Mechanisms for this behavior are being investigated. At the highest pressures, van der Waals clusters of Ar and of CH$_3$NO$_2$-Ar become important. Related results with similar methods have been seen by others for C$_6$F$_6$ in a N$_2$ bath.
GLOBAL SENSITIVITY ANALYSIS WITH SMALL SAMPLE SIZES
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A new algorithm for Global Sensitivity Analysis (GSA) has been developed for small sample sizes. It relies on the use of sparse regression, specifically the lasso. Results for butanol speciation and ignition will be presented, as well as extensive tests of the algorithm on ignition of n-heptane/methyl butanoate mixtures at low temperatures and high pressures. An example of the accuracy for butanol ignition is presented in the Table where column 2 shows the ranking of the sensitivity of reactions using a sample size of 800 runs with the sparse algorithm versus a full regression with 10,000 runs (column 3). This table demonstrates that the method finds the most sensitive reactions with good accuracy, particularly for sensitivity coefficients greater than 0.01. The mechanism used for the butanol calculations had 1446 reactions, indicating that the sparse GSA can use sample sizes smaller than brute-force local sensitivity analysis, which generally is undertaken with two computer runs per reaction. We have also made comparisons of the sparse GSA with our new algorithm for brute-force local sensitivity analysis which generally requires ~ 1.2 computer runs per reaction.

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USING DIFFERENTIAL ENTROPY AS A DATA DISCRIMINATION TOOL AT THE DEVELOPMENT OF DETAILED REACTION MECHANISMS
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Development of detailed reaction mechanisms is traditionally based on using rate parameters that had been measured directly or determined in theoretical calculations, and comparing the simulation results based on the obtained mechanism with the outcomes of indirect experiments, like concentration measurements in reactors or flame velocity determinations. At the testing of reaction mechanisms, an important question is the relative weighting of the available experimental data. An alternative approach for mechanism development is the optimization of a detailed reaction mechanism. In this context, weighting of the experimental data used is also an important issue.

To determine the importance of data points, we implemented the approach of Sheen et al, which is based on differential entropy. Differential entropy indicates how much the calculated uncertainty of a rate parameter is affected by the reduction of the experimental error of a given data point. Its calculated from the sensitivity of Shannon entropy with respect to data uncertainty. This approach is conceptually related to Bayesian experimental design, which commonly minimizes Shannon entropy, and hence the model prediction uncertainty, during parameter optimization.

Our calculations were based on the optimized version of the hydrogen combustion mechanism of Kéromnès et al. The analysis included flame velocity data, and ignition delay time data measured in shock tubes and rapid compression machines. Weighting was assigned to the data points according to their information content for the improvement of the hydrogen combustion mechanism. The impact of the differential entropy based data discrimination on parameter estimation results was also investigated.

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GENERATION OF SKELETAL KINETIC MECHANISMS THROUGH REACTING FLUX ANALYSIS AND SENSITIVITY ANALYSIS
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The use of detailed kinetic mechanisms in multidimensional applications is often limited by the significant computing load, resulting from the high number of involved species and reactions: in particular, when mixtures including large hydrocarbon molecules are concerned, their use in CFD codes is practically impossible with the current available technology. Therefore, reduction techniques have been developed in order to obtain proper skeletal models with the right trade-off between mechanism size and accuracy.

In this work, a two-step procedure to reduce a detailed mechanism to an affordable size for CFD applications is presented. Two different approaches are coupled to this purpose: an analysis of reacting fluxes (RFA) in ideal, plug flow reactors to first cut out the unnecessary species and reactions from the original model, and a sensitivity analysis of the retained reactions with respect to some key species, through which the importance of the remaining species is assessed. Following this methodology, several reduced mechanisms were successfully developed for different starting fuels and fuel surrogates, with a “design” criterion of a maximum 15% error on the ignition delay time in the operating range of temperature, pressure and equivalence ratio. The effectiveness of the proposed approach was validated through a multi-scale benchmark. Starting from laminar flame speed evaluations and species formation in ideal reactors, the comparison between the skeletal models and original mechanisms was carried out in more complex case studies, too, like a quasi-dimensional, multi-zone model of a HCCI engine and a two-dimensional CFD model of a laminar coflow flame. In all the cases, the results proved that the reduced models can be used in place of the original ones without significant errors in the provided output. Finally, the computational benchmarks quantified the time savings in using the reduced models, thus showing the practical advantages in the use of skeletal mechanisms even in the simplest simulations.

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MONTE CARLO SIMULATIONS FOR UNCERTAINTY ANALYSIS IN MODELING SINGLE PULSE SHOCK TUBE DATA

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When modeling speciation data, such as those from single pulse shock tube experiments, agreement between chemical kinetic models and the data is often only described qualitatively. The models developed are typically adjusted manually, where individual reaction rate constants are adjusted within their known error bounds based on sensitivity analysis. Targets used for model development and refinement are typically only the experimentally measured magnitudes of stable intermediate species and their measured reactivity. The experimental target data, within their bounds of uncertainty, can be readily compared with the nominal model predictions. Unlike the uncertainty bounds on experimental data, error bounds for chemical kinetic models used to simulate the experimental data are difficult to determine due to the large number of rate constants with finite uncertainties that are included in the models.

In this study, simple Monte Carlo simulations were performed in order to sample the range of uncertainty of an automatically generated chemical kinetic model when simulating high pressure single pulse shock tube data. Two simple test cases were examined for uncertainty in the rate constants; ±30% and a factor of 2 uncertainties were applied to all of the Arrhenius pre-exponential factors (A), representing minimum and more reasonable estimates in uncertainty, respectively. Approximately 1000 samples were simulated at each uncertainty level, and the results showed a strong central tendency. It was found that the range of probable outputs of the model at the higher temperatures of the experiments were significantly larger than the estimated systematic error in the experimental results. This leads to the possibility of using single pulse shock tube data in constraining larger chemical kinetic models in order to reduce uncertainty. In addition, it is demonstrated how this simple to apply technique provides a quantitatively meaningful way to evaluate the agreement between single pulse shock tube experiments and chemical kinetic models.

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A SEGMENTED KINETIC INVESTIGATION ON SULFATION OF CONDENSED POTASSIUM CHLORIDE IN SO2/O2/H2O AT 523K-1023K

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The sulfation of condensed alkali chloride has significant implications for deposition and corrosion on heat transfer surfaces in biomass combustion. In the present work, an investigation on the heterogeneous sulfation of condensed KCl (100-200 μm) was conducted in a fixed bed reactor at 523-1023 K with levels of 0.1%-2% SO2, 2.5%-10% O2 and 5%-15% water vapor. The sulfation rate was determined by measuring the formation of HCl in gas and the content sulfur in solid residues. Results show that the sulfation product is only K2SO4, not other potassium sulfates, and the sulfation rate of KCl within temperature range of 523-1023 K can be divided into three stages: 1) a slow increase of sulfation rate below 723 K, 2) a slight decline at 723-773 K, 3) a rapid increase over 823 K. It should be noted that a transformation in sulfation mechanism takes place between 723 K and 823 K, and the further investigations on the reactions of reactant SO2, O2 and water vapor at temperature 723 K and 923 K further proved this changing on reaction mechanism. A reason for this phenomena is that a mixture of KCl and the reaction products K2SO4 may form a eutectic at higher temperatures, which was confirmed by the results of SEM and TGA. Based on the experimental results, the kinetic calculation has been performed, and the sulfation reaction rate of condensed potassium chloride can be described by the expression dX/dt=5.32×10^0 exp(-2120/T)(1-X)^2/3 (CO2)^0.27(CSO2)^0.27(CH3O)^0.42 at 523-723 K, and dX/dt=1.20×10^4 exp(-14180/T)(1-X)^2/3(CO2)^0.92(CSO2)^0.39(CH3O)^0.12 at 823-1023 K.

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ESTABLISHMENT OF KINETIC PARAMETERS OF PARTICLE REACTION FROM A PERFECTLY STIRRED FLUIDIZED BED REACTOR

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A Perfectly Stirred Reactor (PSR) ideally provides homogenous, controlled conditions for process and reaction analysis. Therefore, it forms a basis for model development and validation. A novel method for an experimental study of gas-particle reaction, based on realizing a perfectly stirred reactor as a small scale fluidized bed is presented. The reactor enables high heating rates (~ 10,000 K/s), high temperatures (T=1073K-1553K), long timescale observation (up to several hours), operation with small fuel particles (~100 micron), and accurate control of reaction conditions. Char reaction rates are established from real-time gas products analysis by FTIR spectroscopy, through a detailed data-analysis procedure. For rapid reactions, this iterative procedure employs a particle surface-evolution model, while accounting for sampling system signal attenuation. The validity of the perfectly stirred conditions has been experimentally established, by performing temperature and concentration measurements at different heights inside the bed. The method is employed here for char gasification – the Boudouard reaction. The results are highly consistent for over a wide range of conditions (T=1073K-1553K, CO2=0-76%), enabling the reliable establishment of kinetic parameters. The activation energy as well as order of reaction are comparable to the values found in literature. Hence, the
perfectly stirred fluidized bed reactor presented here, provides a novel method to quantitatively study heterogeneous reaction.

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W3P134 | INITIAL STAGES OF THE PYROLYSIS OF POLYETHYLENE

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Combustion and flammability of plastics are important topics of practical interest directly related to fire safety and recycling of polymeric materials; pyrolysis of the solid is the initial step of its combustion. Mechanistic modeling of combustion and pyrolysis of polymers is considerably hindered by the lack of kinetic data necessary for the modeling. In virtually all existing models of polymer pyrolysis the majority of kinetic parameters used are derived from the data on chemically similar but smaller species in the gas phase. The use of gas phase rate constants is, generally, not justified without an experimental support for the values used.

In the current work, the kinetics of the formation of liquid phase and gas phase products of polyethylene pyrolysis was studied experimentally in the 400 – 440 K temperature range. Gas Chromatography was used to determine the yields of volatile products and Nuclear Magnetic Resonance spectroscopy was employed to determine the kinetics of the formation of three types of carbon-carbon double bonds and terminal –CH₃ groups in the liquid polymer melt phase. Experimental conditions were selected to limit the conversion of polyethylene to less than 1% and thus isolate for study only the initial stages of the overall process, where secondary reactions of pyrolysis products are unimportant.

The results were modeled with a simple mechanism consisting of a limited number of reaction types: C-C bond scission, beta-scission of alkyl radicals, hydrogen atom transfer via abstraction, addition of alkyl radicals to double bonds, and radical recombination. Values and temperature dependences of the rate constants of key reactions were determined and compared to the constants of similar reactions of smaller molecules in the gas phase.

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W3P135 | COMPUTATIONAL FLUID DYNAMICS ANALYSIS OF DIFFERENT GEOMETRIES FOR A JET STIRRED REACTOR FOR BIOFUEL RESEARCH

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Most biofuels are derived from alcohols obtained from biomass fermentation and esters produced from the transesterification of vegetable oils. Their use is growing, from the blending with conventional petroleum-based fuels in amounts up to 20%, to the development of new formulations and additives. While real fuels are very complex mixtures, surrogates offer simpler alternatives that emulate physical and combustion properties, and, as such, have become important research tools. The components of surrogates of biofuels include alcohols, methyl esters, acyclic and cyclic ethers. The development of the chemical kinetics mechanisms for surrogates relies on measurements of important combustion parameters for the pure species and their combinations, under the many different conditions of temperature, pressure and concentrations. This is a very active area of research but, still, few chemical kinetics mechanisms for the oxidation of the pure components are available and the set of available measurements is far from covering the range of conditions found in the applications. This work reports an ongoing effort to develop surrogates for aviation biofuels. Among the target experiments being developed, the jet stirred reactor appear as a very flexible and practical tool for chemical kinetics research. The design idealized by P. Dagaut and co-workers is the most well known. It employs four jets to achieve homogeneous turbulent-mixing within a spherical crystal reactor. In this work, several geometric variations on Dagaut’s design were numerically studied to assess the homogeneity of the distribution of temperature and concentration of chemical species across the reactor. Full multicomponent-transport and a RANS turbulent model were used in ANSYS Fluent™. The computational domain was divided from 12 to 25 million tetrahedral volumes. The numerical results revealed the main features of the flow within the feeding system and reactor evidencing the high pressure drop in the jet orifice and flow impingement on the reactor’s rear wall in some alternative configurations. The nozzle diameter and angle were found to be the critical factors to ensure mixing. From the simulations, a 7 cm³ spherical crystal reactor was designed and manufactured. The experiment is scheduled to be operational in 2015.

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W3P136 | APPLICATION OF BIOMASS-COAL CO-COMBUSTION FOR ELECTRIC GENERATION IN CHINA

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Purpose of the work: There is abundant of biomass resource in China which however is not properly used, large amounts of biomass such as agricultural and forestry waste are frequently simply burned and rot away in the land, causing severe pollution problems and energy wastage. One most typical way of utilizing biomass is to burn it in blends with coal or alone for electric generation and this technique has been tested in many areas in China. In this article, we aim at telling the combustion feature; ash characteristics; chlorine derived corrosion and pollutants status of burning several types of typical local biomass with coal, trying to give an advice on the application of biomass-coal co-combustion in domestic power market.
Approach: In our experiment, biomass samples (cotton stalk, rice husk, sawdust) is mixed with huangling bituminous coal at the ratio of 0%, 10%, 20% and 30% and each group is combusted at the temperature of 10500C and 13000C in TG-DTG and drop tube furnace. Firstly, a thermogravimetry analysis is made to analyze the overall combustion feature. During the combustion in drop tube furnace, The excess air coefficient is 1.2 and 1.4 and the feeding speed is 0.3g/min. Then, an infrared gas analyzer is used to detect the gas emissions (CO₂, NO, SO₂, HCl, HF) on line and the concentration of O₂ is also measured by a portable flue gas analyzer. Later, an XRD and SEM-EDX test is made of the ash. A numerical simulation is conducted on a trial running coal and biomass co-combustion power plant to estimate the combustion and pollution status.

Results & Conclusions: A synergy obviously occurs when co-combusting biomass and coal and it facilitates the process of coal combustion. But apparently, the promotion degree depends on the different kinds of coal and biomass. Rice husk has a higher concentration of ash content and alkali metal, in comparison with cotton stalk and sawdust. It advised mix ratio for Rice husk is no more than 10% and the ratio for cotton stalk and sawdust is no more than 20% in co-combustion. With a higher proportion of biomass mixed in coal, the production of NO₂ reduce in both high and low temperature zone, indicating that a lower NO₂ emission may be approached with the designed condition and the co-combustion of biomass and coal. As demonstrated in the simulation, with a higher proportion of biomass mixed in coal, the production of NO₂ reduce in both high and low temperature zone, indicating that a lower NO₂ emission may be approached with the designed condition and the co-combustion of biomass and coal. And also, a weakened tube erosive wear could be seen.

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W3P137 EFFECTS OF FLUE GAS ADDITION ON THE PREMIXED OXY-METHANE FLAMES IN ATMOSPHERIC CONDITION
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This numerical study investigates the flame characteristics of premixed methane with various inert gas dilutions in order to simulate oxy-combustion of hydrocarbon fuels with flue gas recirculation system. In general, a flue gas consists of high concentration CO₂/H₂O and high gas temperature. The diluent gas in oxy-combustion has been changed compared with air-combustion, so that the flame behavior and combustion characteristics of oxy-fuel must be influenced. The effect of laminar burning velocity and adiabatic flame temperature on inert gas dilution is discussed via using Chemkin-pro simulation. By observing the resultant flame temperature and species concentration profiles one can identify that the flame location shifts, and the concentration profile of major chemical reaction radicals varies, indicating the change of flame structure and flame chemical reaction paths. The dominant initial consumption reaction step of methane shifts from R53 (H+CH₄→CH₃+H₂) to R98 (OH+CH₄→CH₃+H₂O) when nitrogen is replaced by the recirculated gases. It is because the chemical effects of the recirculated gases changes the flame reaction pathway, and further affect reaction rate, species and radical concentrations.

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W3P138 STRUCTURE OF PREMIXED AMMONIA/AIR FLAMES AT ATMOSPHERIC PRESSURE - LASER DIAGNOSTICS AND KINETIC MODELLING
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Ammonia (NH₃) flame structure has been the subject of many studies. However, previous studies employed oxidizers (O₂/N₂, O₂/Ar, N₂/Ar) with composition significantly different from that of air, in order to facilitate flame stabilization. Thus, there is a lack of flame structure data for ammonia/air combustion. Therefore, the goal of the present work was to acquire experimental profiles of temperature as well as concentration of O₂ and important intermediates, NH, NO, and OH, in lean, stoichiometric, and rich ammonia/air flames at atmospheric pressure using laser diagnostic methods. Measurements were made on a water-cooled stainless steel porous-plug burner for ammonia/air flames of equivalence ratio (ф) of 0.9, 1 and 1.2. Radical species were monitored by Laser-Induced Fluorescence (LIF) whereas profiles of temperature and O₂ concentration were acquired using rotational Coherent Anti-Stokes Raman Spectroscopy (CARS). Fluorescence measurements were made under signal saturation conditions or combined with absorption measurements in order to allow for evaluation of quantitative radical concentrations.

Three mechanisms were compared with the new experimental data: the model of Duyunslaeger et al., the model of Shmakov et al., and the mechanism of Mendia and Glarborg. The impact of uncertainties in equivalence ratio, inlet flow rates and temperatures was evaluated by re-runs of the models, which allowed for estimations of total uncertainties in radical concentrations and flame front positions.

The stoichiometric flame showed a maximum temperature of around 1800 K while the lean and rich flames reached maximum temperatures around 2000 K. Only the model of Mendia and Glarborg was able to reproduce flames detached from the burner when solving the energy equation. The shapes of the temperature and O₂ profiles were very well reproduced by this model for all flames with good agreement in terms of absolute values and flame front position. In addition, the shape of experimental radical profiles in general showed good agreement with this model. Regarding radical concentration prediction, the performance of models of Mendia and Glarborg and Shmakov et al. was found to
be similar whereas the model of Duynslaegher et al. showed larger discrepancy with the experiments and the two other models in most cases. For OH and NO prediction, the best agreement with experimental data was observed for the model of Mendiara and Glarborg in the stoichiometric flame. In the lean and rich flames all three models showed a considerable discrepancy for one or both of these radicals and variations of individual rate constants did not improve the agreement sufficiently. Thus, further investigations to determine the accuracy of experimental data, in particular for NO but also NH, are currently in progress in order to clarify whether some structural modifications of the mechanisms are necessary.

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W3P139

IMPROVED KINETIC MODEL AND HCCI ENGINE SIMULATIONS OF DIISOPROPYL KETONE IGNITION
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DiIsoPropyl Ketone (DIPK) is considered as a promising biofuel candidate, which is produced using endophytic fungal conversion. In the current study, modeling of DIPK HCCI engine experiments from Sandia is conducted with single-zone engine and multi-zone models using CHEMKIN PRO. Both adiabatic and non-adiabatic single-zone HCCI models are explored. The non-adiabatic model employs the Woschni correlation to account for heat transfer from the Sandia HCCI engine with the coefficients determined by matching the motored pressure trace of the engine. In order for the single-zone model to give accurate compressed-gas pressures and temperatures, the published DIPK kinetic model is improved. The modifications have been done by adding important intermediate species and radical reactions which were not considered in the original reaction mechanism. The corresponding thermodynamic properties for the new species were calculated using the THERM program and rates were either estimated in comparison with similar molecules or calculated using the RMG program. In addition, zero dimensional simulation has been conducted to obtain ignition delay time for the temperature range of 500-1000 K which showed better agreement with the available shock tube experimental data. For the single zone model of HCCI engine, the updated model provides better agreement from BDC to TDC, however, it over predicts the pressure peak as expected. Brute force sensitivity analyses revealed that the most sensitive reaction in which DIPK participates is the H-abstraction reaction from the fuel by HO_2. Discussion is provided on the validity of the DIPK model in comparison with the parametric engine data over a range of temperature, pressure, equivalence ratio, and engine speed. Although ignition timing can be investigated using the single-zone model, heat release rates in HCCI engines is largely controlled by charge non-uniformities. Since the charge in the Sandia HCCI engine was well premixed for these experiments, the heat-release rate is mainly affected by temperature non-uniformities resulting from heat transfer and turbulent convection. Heat release results from multi-zone modeling of the current experiments showed good agreement with the Sandia experimental trends.

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