**W5P094: SURROGATE MODEL DESIGN FOR GTL KEROSENE**

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Rising costs of fossil fuels in combination with tighter emission limits require either new type of engines (non-drop-in fuels), or new synthetic kerosene (drop-in fuels). The new type of engines has to be able to provide the required services with mixtures of crude oil based kerosene and alternative fuels like GTL-fuel, while lowering fuel consumption and minimizing emissions. The new type of kerosene has to satisfy the specification for crude-oil based aviation kerosene for a number of reasons such as atomization, evaporation, combustion, safety and etc.

The focus of this study is on the combustion modeling of synthetic Gas-To-Liquid (GTL) kerosene produced via the Fischer-Tropsch synthesis route from Natural Gas. The input formula of surrogate (IFS) is determined from the optimization of a set of criteria on physical and chemical properties of the fuel. The specified set of criteria are formation enthalpy, density, H/C ratio, iso - / normal paraffin ratio, viscosity, Threshold Sooting Index, two phase diagram, distillation curve, boiling temperature, ignition delay, laminar flame speed and Cetane Number. This way the optimal composition of IFS is obtained as “full” GTL Surrogate consisting of 17% of 2,7-di-methyl-octane(i-C10H22), 32% of 2-methyl-decane(i-C11H24), 15% of n-propyl-cyclohexane(cy-C9H18) and 36% of n-decane (n-C10H22).

Due to the lack of thermochemical data for 2,7-di-methyl-octane and 2-methyl-decane, a simplified surrogate namely, SPK Surrogate - 1 (composed of n-decane, n-propyl-cyclohexane, iso-octane) has been suggested as a reference surrogate model.

Furthermore, a reaction model for mono iso-paraffin, 2-methyl-decane(i-C11H24) and branched iso-paraffin 2,7-di-methyl-octane(i-C10H22) has been developed and validated based on the experimental data for ignition delay times of iso-octane, 2-methyl-nonane(i-C9H20), and 2,7-di-methyl-octane(i-C10H22).

The experimental data for ignition delay times and laminar flame speed of GTL kerosene have been modeled using the two simplified and the “full” surrogates and results have been compared. The influence of branched paraffines on the ignition delay times of blends has been investigated. The sensitivity of the blend components and its functions to chemical and physical properties are analyzed.

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**W5P095: A DETAILED CHEMICAL REACTION MECHANISM FOR FUEL MIXTURES AND OXYGENATED SPECIES EXTENDED TO C4 CHEMISTRY.**

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The interest in biofuels has increased in the last years. A comprehensive fuel model can be used to simulate mixtures of biofuels, hydrocarbons and to predict emissions from oxygenated fuels. Such mechanism can be the base for oxidation models of larger hydrocarbons.

A comprehensive mechanism that is able to describe the oxidation of hydrocarbon fuels from C1 to C4, oxygenated species and aromatic fuels has been developed. The model is based on a previous study which has been updated in a recent work. Methanol, ethanol and propanol are included as oxygenated species; toluene and xylene as aromatic fuels. DME and its decomposition pathways were added to enhance the capability of the mechanism.

Ignition delay time of hydrocarbon-oxygen mixtures (CH4-, C2H6-, C3H8-, n-C4H10, CH4 + C2H6-, C2H4-, C3H6-, CH3OH-, C2H5OH-O2) with a pressure range of 2 atm to 10 atm and a temperatures from 1100 K–2000 K are well predicted by the model.

Flame velocities of laminar premixed flames (CH4-, C2H6-, C3H8-, n-C4H10, C2H4-, C3H6-, CH3OH- and C2H5OH-air) at 1 atm, different ambient temperatures and equivalence ratios from 0.5 to 2.6, showed a good agreement with respect to the experimental points.

Special attention was paid to C4 species, optimizing the model with the help of experimental measurements of premixed, laminar low-pressure flames (40mbar) for propene, butane isomers (n-butane and iso-butane) and butene isomers (1-butene, 2-butene and iso-butene). Concentration profiles for major and intermediate species were well predicted by the model. With this comprehensive investigation we believe that we could demonstrate how existing chemical models can be expanded and improved to describe a large range of fuels and combustion conditions.

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**W5P096: OXIDATION OF DIMETHOXYMETHANE IN A FLOW REACTOR**
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The dimethoxymethane, a liquid compound which can be blended with diesel fuel, has been proposed as one of the possible oxygenated additives in order to reduce the diesel emissions of particulate matter (soot) and NOx. In this context, the objective of this study is to investigate the oxidation of dimethoxymethane in a flow reactor at atmospheric pressure and its ability for reducing soot and NOx emissions. Different experiments are planned in order to study the influence of the stoichiometry and the temperature on the gas-phase dimethoxymethane oxidation, which include pyrolytic, lean, stoichiometric and rich oxygen conditions, at temperatures between 375 and 1475 K and atmospheric pressure. The initial dimethoxymethane concentration is 700 ppm and the total gas flow rate is 1000 mL/min (STP). The experimental results are interpreted in terms of a detailed chemical kinetic model developed in our group, to which a subset for DMM reaction taken from literature has been added. Rate of production analysis and sensitivity analysis are used to obtain the main reaction pathways and the most important reactions for dimethoxymethane conversion. The effect of the presence of dimethoxymethane on the reduction of NO and particulate matter will be also studied. To study the ability of dimethoxymethane to reduce NO emissions, experiments with an initial NO concentration of 500 ppm will be carried out at the same conditions as in the gas-phase dimethoxymethane oxidation experiences. To know the capacity of the dimethoxymethane to produce soot, experiments with a high initial dimethoxymethane concentration (30000 ppm) will be made in a flow reactor with a soot collection system.

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W5P097: DIRECT HIGH TEMPERATURE MEASUREMENTS OF THE REACTIONS NCN + O2 AND NCN + H2
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Nitrogen oxides, NOx, are major atmospheric pollutants formed by different reaction mechanisms in combustion processes. NO formation initiated by the reactions of small hydrocarbon radicals with molecular nitrogen stemming from the combustion air is termed prompt-NO formation. As a major modification of the original Fenimore mechanism, it has been theoretically predicted and experimentally proven that the corresponding key initiation reaction CH + N2 yields the products NCN (cyanonitrene) and H atoms instead of the formerly assumed products HCN and N atoms. Therefore, consistent models of prompt-NO formation in flames need to account for the high temperature kinetics of the NCN radical. As NCN high temperature rate constant data are scarcely available, current implementations have to rely on estimated or theoretically derived rate expressions. Taking the reaction NCN + O2 as an example, several orders of magnitude diverging rate constant values are assumed in different combustion mechanisms. Using the thermal decomposition of NCN3 as a suitable and quantitative source of NCN radicals, we were able to directly measure the rate constants of several NCN reactions at temperatures between 700 K and 3200 K for the first time. Concentration-time profiles of NCN in its triplet electronic ground state can be monitored by time-resolved laser absorption spectroscopy at a wavelength of λ = 329.1302 nm behind shock waves. Here, our most recent results for the high temperature rate constants of the reactions NCN + H2 and NCN + O2 will be presented. Whereas the reaction with molecular hydrogen could be studied under pseudo-first order reaction conditions, the determination of the rate constant of NCN + O2 required a detailed kinetic modeling of the experimental concentration-time profiles. Most importantly, the overall reaction turned out to be rather slow. Hence, for a reliable rate constant estimate, high concentration reaction gas mixtures with initial mole fractions of up to 17% O2 had to be used in these experiments and resulting thermal effects stemming from the vibrational relaxation of O2 behind the shock waves had to be properly taken into account.

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