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Experimental and Modeling Study of the Oxidation of Synthetic Jet Fuels

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Abstract

Studies on combustion of synthetic jet fuels is of growing importance because of their potential for addressing security of supply and air transportation sustainability. The oxidation of a 100% naphthenic cut (NC) that fits with typical chemical composition of biomass or coal liquefaction products, gas-to-liquid fuel (GtL), and a GtL–NC mixture were studied in a jet-stirred reactor under the same conditions (550-1150 K; 10 bar; equivalence ratio of 0.5, 1, and 2; initial fuel concentration of 1000 ppm). Surrogate model-fuels were designed based on fuel composition and chemical properties for simulating the kinetics of oxidation of these fuels. We used model-fuels consisting of mixtures of n-decane, decalin, tetralin, 2-methylheptane, 3-methylheptane, n-propyl cyclohexane, and n-propylbenzene. The proposed detailed chemical kinetic reaction mechanism was validated using the full experimental database obtained for the oxidation of pure GtL, GtL–NC mixture, and pure NC. Kinetic reaction pathway analyses and sensitivity analyses were used for interpreting the results.

1 Introduction

The interest for synthetic and bio-derived jet fuels that are considered helpful for reducing dependence of air transportation on petroleum [1-3] is growing. The Fischer-Tropsch (F-T) process allows the production of a jet fuel type from synthesis gas also called syngas. Such synthetic jet fuels are mainly composed of *n*-alkanes, *iso*-alkanes and *cyclo*alkanes [4]. The relative chemical characters (e.g., degree of isomerization or aromaticity) of the fuels are not a function of their raw material source, but rather of the synthesis conditions and fuel specification for use in commercial semi-synthetic jet fuels.

The purpose of this work is to study the kinetics of oxidation of alternative jet fuels (GtL, naphthenic cut, and their mixture) in a JSR under the same conditions. The mass composition of the synthetic jet fuel (GtL) used here was determined by gas chromatography analyses to be: 28.1% *n*-alkanes, 62.8% *iso*-alkanes, 8.8% *cyclo*alkanes, and 0.2% aromatics. The very low concentration of aromatic compounds in GtL causes a reduction in emissions of soot and unburned hydrocarbons [2, 5]. The composition of synthetic jet fuel also allows a decrease in emissions of carbon dioxide [6]. This fuel is a good alternative to conventional oil-derived jet fuels. A naphthenic cut was also considered in this work. Because it is difficult to source a sample that comes from a coal or a biomass liquefaction process, we used a representative commercial solvent that fits with typical chemical composition of product coming from coal or biomass liquefaction. Its mass composition was determined by gas chromatography analyses to be: 4.7% paraffins, 85.2% *cyclo*-paraffins, 9.6% monoaromatics and 0.5% polyaromatics. A mixture of the naphthenic cut and the GtL jet fuel 50:50 v:v was also considered here. This work provides complementary information to our previous measurements and modeling [7, 8] that involved simpler and less representative model-fuels. Here model-fuels were designed to model the oxidation of the GtL, the naphthenic cut, and its mixture with the GtL fuel. A detailed kinetic reaction mechanism was developed and validated by comparison with the JSR experimental results obtained for the oxidation of the GtL, the naphthenic cut, and its mixture with the GtL fuel.

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2 Experimental

The jet-stirred reactor (JSR) used in the current work is similar to that described earlier [8-10]. The reactor JSR consisted of a small sphere of 33 mL in volume made of fused silica to minimize wall catalytic reactions. The JSR was equipped with 4 nozzles of 1 mm diameter, opposite in pairs in order to make the reaction mixture more homogeneous. A nitrogen flow of 100 L/h was used to dilute the fuels. The reactants were preheated before injection in order to minimize temperature gradients inside the reactor. The reaction zone was heated to the desired temperature by two insulated heating elements surrounding the reactor. The liquid fuels (Table 1) were delivered to an atomizer-vaporizer assembly, maintained at ca. 550 K, by a HPLC pump before injection into the JSR.

Table 1. Properties of the fuels oxidized experimentally

Properties	GtL	NC	NC/GtL
Chemical formula	$C_{10.45}H_{23.06}$	$C_{12.64}H_{23.64}$	$C_{11.54}H_{23.35}$
M (g mol^{-1})	148.44	175.32	161.83
Density (g L^{-1})	737.7	863.1	800.3
H/C atomic ratio	2.20	1.87	2.02
DCN, ASTM D7668	58.0	39.3	45.8

The reactants were diluted with nitrogen (<5 ppm of H_2, <50 ppm of O_2, and <1000 ppm of Ar) and mixed before admission into the injectors. High purity oxygen (99.995% pure) was used in these experiments. The sampling system assembly includes a low-pressure fused-silica sonic probe coupled to a mobile thermocouple (0.1 mm, Pt/Pt-Rh inside a thin-wall fused silica tube) which allows taking samples and measuring the temperature along the vertical axis of the reactor. Temperature measurements showed a good thermal homogeneity along the vertical axis of the JSR (gradient < 3 K/cm). The sampling (≤ 50 mbar) was carried out at steady temperature and residence time in order to freeze the reactions. Thereafter, the samples were analyzed online by Gas Chromatography-Mass Spectrometry (GC-MS) and Fourier Transformed Infrared Spectrometry (FTIR) and offline by GC after collection and storage at low pressure (ca. 40 mbar) in 1 L Pyrex bulbs. The

low-vapor-pressure species were analyzed online, whereas high-vapor-pressure chemicals and permanent gases were analyzed offline. For the offline analyses, we measured the species by gas chromatographs (Varian) equipped with capillary columns (Al_2O_3/KCl, DB-5ms, DB-624, Carboplot-P7), a flame ionization detector (FID), and a thermal conductivity detector (TCD). H_2O, CO, CO_2, CH_2O, CH_4, C_2H_2, and C_2H_4 were quantified by FTIR analyses online (Nicolet Magna 560, 0.5 cm^{-1} resolution). For these measurements, the sampling probe was connected to a temperature controlled (413 K) gas cell (2 m path length, 500 mbar) via a 6.35 mm outer diameter deactivated stainless-steel heated line (473 K). A good repeatability of the measurements and a reasonably good carbon balance (typically 100 ± 10%) were obtained. No oxygen balance could be computed because many oxygenated intermediates could not be quantified. The experiments in the JSR were performed at high pressure (P = 10 ± 0.1 bar), at temperatures ranging from 550 to 1150 K, at a constant mean residence time of 1 ± 0.05 s, at φ = 0.5, 1, and 2. Species concentration profiles of reactants, stable intermediates and final products were measured versus temperature at 3 equivalence ratios for the oxidation of the two fuels.

3 Modeling

The CHEMKIN package [11] and the PSR (Perfectly Stirred Reactor) computer code [12] were used for the kinetic modeling of the oxidation of the fuels herein studied. PSR computes species concentrations from the balance between the net rate of production of each species by chemical reactions and the difference between the input and output flow rates of species. Model-fuels (also called surrogates) were used for the kinetic modeling. Their composition was defined to match the fuel chemical composition, the fuel molecular weight, the H/C ratio affecting soot production, and DCN which is a global parameter related to ignition properties of the fuel. In the present study, the synthetic kerosene GtL was represented by a mixture of *n*-decane, 2-methylheptane, 3-methylheptane and decalin (28.1%, 30%, 33.1%, and 8.8% in mass, respectively).

Table 2. GtL 4-component model-fuel used in computations ($C_{10.45}H_{23.06}$; H/C=2.20; DCN=57.94; M= 148.46 g mol^{-1}; 1.209×$C_{8.64}H_{18.97}$ since we used 1209 ppm of model-fuel to represent 1000 ppm of fuel; DCN computed from [20, 21]).

Fuel component	Initial mole fraction (ppm)
3-methylheptane	431
2-methylheptane	390
n-decane	294
decalin	94

This corresponds well with the GtL jet fuel composition (GtL%/surrogate% in mass: 28.1/28.1, 62.8/63.1, 8.8/8.8 in mass of n-alkanes, *iso*-alkanes, and naphthenes, respectively). The global formula of the GtL surrogate was $C_{8.64}H_{18.97}$ with a molar weight of 122.65 g mol^{-1}. The naphthenic cut was represented by a mixture of decalin, tetralin, *n*-propylcyclohexane, *n*-propylbenzene, 2-methyl heptane, and 3-methylheptane (27.6%, 12%, 10.3%, 12.1%, 25%, and 13% in mass, respectively). This is in line with the naphthenic cut composition (fuel%/surrogate% in mass: 89.9/87.9 of paraffins + cycloparaffins and 10.1/12.1 of aromatics). The global formula of the naphthenic cut surrogate was $C_{8.95}H_{16.57}$ with a molar weight of 123.97 g mol^{-1}. Sub-models for surrogate components were taken from our previous modeling efforts [13-19]. The compositions of the model-fuels used in the kinetic modeling are given in Tables 2, 3, and 4.

Table 3. Composition of the NC model-fuel ($C_{12.64}H_{23.41}$; H/C=1.85; DCN= 36.2; M=174.74 g mol^{-1}; 1.4127× $C_{8.95}H_{16.57}$ since we used 1413 ppm of model fuel to represent 1000 ppm of naphthenic cut; DCN computed from [20, 21]).

Fuel component	Initial mole fraction (ppm)
2-methylheptane	383.8
decalin	350
3-methylheptane	200
n-propylbenzene	177.1
tetralin	159.4
n-propylcyclohexane	142.4

The chemical kinetic reaction mechanism proposed here contained 2384 species and 10370 reversible reactions. It describes both the low and high temperature chemistry, according to previously proposed kinetic models [7, 8, 22]. Experimental data obtained in a JSR were compared to simulated results in order to validate the chemical kinetic mechanism.

Table 4. Model-fuel composition for the GtL/NC mixture ($C_{11.547}H_{23.18}$; H/C=2.01; DCN=47.1; M= 161.74 g mol^{-1}; 1.311× $C_{8.806}H_{16.57}$ since we used 1311 ppm of model fuel to represent 1000 ppm of GtL/NC mixture; DCN computed from [20, 21]).

Fuel component	Initial mole fraction (ppm)
2-methylheptane	387
3-methylheptane	316
decalin	222
n-decane	147
n-propylbenzene	88.5
tetralin	79.6
n-propylcyclohexane	71.2

4 Results and Discussion

A JSR was used to study the oxidation of a GtL jet fuel, the naphthenic cut and the GtL/NC fuel mixture at 10 bar, over the temperature range 550-1150 K, at a constant residence time of 1 s, and at equivalence ratios of 0.5, 1, and 2. The concentration profiles of major species formed during the oxidation of the fuels were measured as a function of temperature. The fuels are composed of hundreds of constituents which prevented their quantification. The species identified and quantified by FTIR and gas chromatography were H_2, H_2O, O_2, CO, CO_2, CH_2O, CH_4, C_2H_2, C_2H_4, C_2H_6, acetaldehyde, C_3H_6, 1-C_4H_8, cis and trans 2-C_4H_8, *iso*-C_4H_8, 1,3-C_4H_6, 1-C_5H_{10}, 1-hexene, benzene, and cyclohexene. Among the hydrocarbons formed as intermediates, the most abundant are ethylene (600-1000 ppm), methane (400-500 ppm), and propene (100-200 ppm), by decreasing order of importance. They are followed by C_4 olefins which have concentrations about 10 times less than propene. The data showed 3 regimes of oxidation: the cool flame regime (T <750 K), the negative temperature coefficient (~640-750 K) and the high-temperature oxidation regime (>750 K).

4.1 Kinetic modeling of the GtL fuel oxidation

The oxidation of the GtL jet fuel in a JSR has been performed earlier [8]. These data are used here to verify the performance of the proposed kinetic model and the new surrogate formulation. Mole fraction profiles of some of the main stable intermediates and the final products are presented in Fig. 1. As can be seen from that figure, the kinetic model gives a very good representation of the oxidation of the GtL jet fuel under

the considered JSR conditions. The use of lightly branched *iso*-paraffins and naphthenes in the surrogate fuel strongly improved the modeling (especially in predicting ethylene and *iso*-butene) when compared to the simpler surrogate used in [8]. Therefore, the proposed kinetic mechanism was used for the other simulations presented in the next paragraphs. By comparing the results obtained for the JSR oxidation of the GtL and NC fuels, one can note that they have very similar rates of oxidation at high temperature. However, the GtL fuel is more reactive at low temperature (cool flame) which is expected based on their respective DCN (58 vs. 39.3). The GtL fuel produces more ethylene and less methane that the NC which must be due to the large differences of n-alkanes and naphthenes concentrations in these fuels.

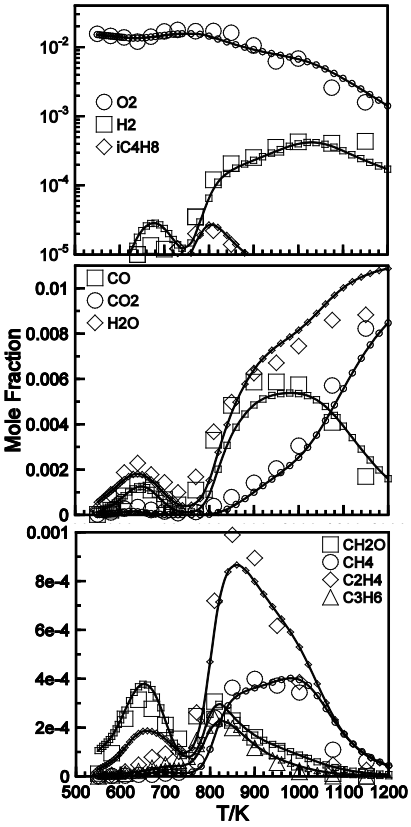

Figure 1. Comparison of experimental [8] and computed concentrations profiles obtained from the oxidation of 1000 ppm of the GtL fuel with 16215 ppm of O_2 in a JSR at 10 bar, τ=1 s, and φ=1 (experimental data: large symbols; computations: lines and small symbols; dilution by N_2).

4.2 Kinetic modeling of the NC fuel oxidation

The oxidation of the naphthenic cut was carried out in a JSR. Concentration profiles of some of the main stable intermediates and final products are presented in Fig. 2. The proposed detailed chemical kinetic reaction mechanism represents fairly well the measured concentration profiles over the entire range of temperatures covering the cool flame, NTC and high temperature oxidation regimes. Similar results were obtained for the oxidation of this fuel at φ of 0.5 and 2. Thus, the proposed kinetic model should be appropriate for modeling the oxidation of the naphthenic cut/GtL mixture.

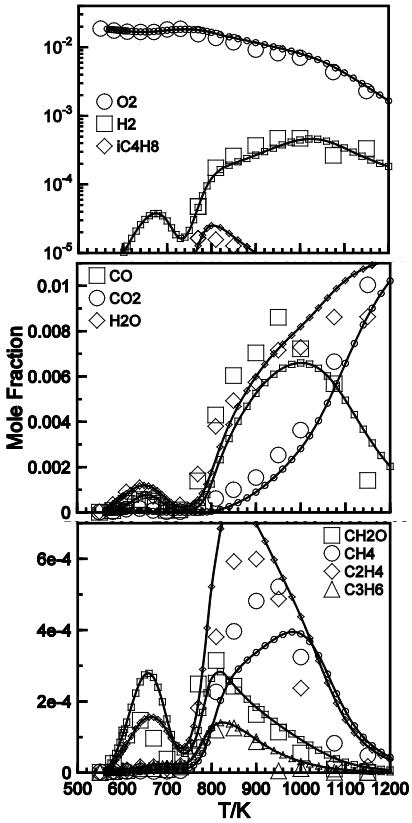

Figure 2. Computed and experimental mole fractions obtained by oxidation of 1000 ppm of the NC with 18570 ppm of O_2 in a JSR at 10 bar, τ=1 s, and φ=1.

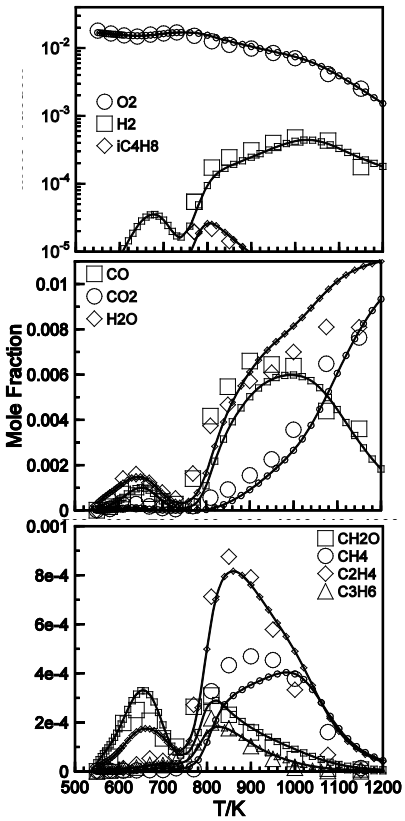

Figure 3. Computed and experimental mole fractions obtained by oxidation of 1000 ppm of the NC/GtL fuel mixture with 17378 ppm of O_2 in a JSR at 10 bar, τ =1 s and φ=1.

4.3 Kinetic modeling of the NC-GtL fuel oxidation

The oxidation of the naphthenic cut/GtL fuel mixture was carried out in a JSR. Concentration profiles of the final products and some of the main stable intermediates are displayed in Fig. 3. The present model adequately captures the oxidation of the naphthenic cut/GtL fuel mixture under the present JSR conditions. Similar agreement was obtained in fuel-rich and fuel-lean conditions. These results rationalize the modeling approach based on the definition of model-fuels that are representative of the complex fuels composition in terms of DCN, H/C ratio, and global chemical formula. Moreover, they also confirm the validity of the kinetic scheme to mimic the oxidation of the model-fuel components, complex fuels, and their mixtures.

4 Conclusions

The kinetics of oxidation of synthetic fuels (GtL, naphthenic cut, NC-GtL) were studied in a JSR at 10 bar, at a constant mean residence time of 1 s, at 550 –1150 K, and at equivalence ratios of 0.5–2. Gas chromatography and FTIR analyses allowed identifying many stable intermediates. Mole fractions of stable intermediates and final products were measured versus temperature for all fuels. A kinetic reaction mechanism involving 2384 species and 10370 reversible reactions was proposed. Relatively complex model-fuels were designed to model the oxidation of the synthetic fuels. They were composed of n-decane, 2-methylheptane, 3-methylheptane, decalin, tetralin, n-propylcyclohexane, and n-propylbenzene. The model was able to accurately simulate the oxidation of 3 fuels (a GtL, a naphthenic cut, and a GtL/naphthenic cut mixture) which supports the validity of the procedure followed and the kinetic mechanism for simulating the oxidation of synthetic jet fuels. The substitution of *iso*-octane by lightly branched paraffins and the addition of naphthenes in model [8] resulted in an improved agreement between computations and data for the JSR oxidation of synthetic jet fuels.

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