

KINETIC MODELING OF A STANDARD JET FUEL OXIDATION IN A FLOW REACTOR

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Abstract

This work analyses, experimentally and numerically, the combustion behavior of a standard jet fuel (Jet-A1). The goal is to demonstrate the ability of a chemical kinetic model to capture the combustion behavior of a representative real jet fuel in a well-controlled experiment. Experimental measurements provided by DLR are used to support and validate the predictions of a chemical kinetic model developed at CRECK Modeling Lab. Jet fuels contain hundreds of components, therefore, a 9 component surrogate blend was formulated by means of detailed compositional information and an in-house optimization tool. This surrogate, together with the kinetic model that describes its combustion chemistry, offers a fundamental tool for the analysis of the performance of the fuel in practical systems.

Flow reactor experiments

Quantitative species profiles have been measured in the DLR high temperature flow reactor [1]. This experimental system is capable for in-depth investigation of the combustion chemistry with respect to main reaction channels and intermediate species formation in the combustion process since most of the relevant species formed during the combustion process can be detected simultaneously. The quantitative species profiles serve as validation targets for the development of surrogates and kinetic models and allow for estimation of the fuel influence on emissions in technical combustors. Since comprehensive recent literature on the applied experimental setup is available [2], [3], only a brief description is given here.

The system can be divided into two segments: i) the high temperature laminar flow reactor including gas supply and vaporizer system; ii) a molecular beam mass spectrometry (MBMS) time-of-flight detection (TOF) system. The reactor exit is positioned to the sampling nozzle of the MBMS-TOF system and gas is sampled directly from the reactor outlet and transferred to the high-vacuum detection system.

The reactor itself features a ceramic tube (40 mm inner diameter, total length of 1497 mm). Premixed laminar flowing gases are fed highly diluted (over 99% Ar) into the reactor to suppress significant heat release and a self-sustaining reaction. Conditions are designed to yield constant carbon flow at slightly rich ($\Phi = 1.2$) and

lean ($\Phi = 0.8$) conditions respectively. The oxidizer (O_2) is adjusted according to the designed stoichiometry. For adjustment of the respective stoichiometry the hydrogen content of the fuels was determined in high precision by low resolution pulsed NMR (ASTM D7171), heteroatoms are neglected and the corresponding carbon content is assumed as the remaining.

The species in the stream exiting the reactor are detected by an electron impact (EI) time-of-flight (TOF) mass spectrometer (Kaesdorf, mass resolution $R = 3000$). The MBMS-TOF system is capable to determine the elemental composition of combustion intermediates within a C/H/O system. To avoid species fragmentation at the ionization process, soft electron energies are applied (10.6eV). Additionally, a residual gas analyzer (RGA), i.e. a quadrupole mass spectrometer, was placed in the ionization chamber (off beam) and operated at a higher electron energy (70 eV) allowing for tracking the major species simultaneously to the MBMS-TOF measurements.

The measurements were performed at constant inlet mass flow with a monotonically decreasing temperature ramp (-200 K/h) applied to the oven. The temperature range is chosen from 600 K to 1200K, to cover the regime from unreacted fuel to full conversion to thermal equilibrium as it occurs in common combustion processes. Flow conditions are in the laminar regime for all temperatures and previous studies have successfully reproduced the experimental results applying a zero dimension (i.e. plug flow) kinetic model calculation [1], [4] using a predefined temperature profile. Axial temperature profiles for any oven temperature passed while ramping the temperature are known from the detailed characterization of the experiment and can be used as boundary condition for the kinetic model.

Quantitative evaluation was performed following well established methods described in previous publications [1], [5], [6] by direct binary (species/Ar) calibration measurements or estimation of the ionization cross section based on the RICS (relative ionization cross section) method.

The fuel model: a surrogate mixture and the associated kinetic model

Jet fuels contain hundreds of components, many of which are not available in well-validated kinetic models currently in use. In order to effectively simulate the behavior of such complex mixtures, surrogate blends with fewer components are generally used. The surrogate represents then the first constituent of a fuel model.

In order to facilitate the formulation of surrogate mixtures for jet fuels of practical interest, the CRECK Modeling Lab developed a fuel surrogate optimization tool. The optimization of the composition of a fuel surrogate is a multi-target multidimensional problem (the number of targets to be match can be in the 10s while the dimensionality is equal to the number of components included in the palette minus 1) with multiple solutions. Different optimization strategies have been proposed in literature for this type of problems (machine learning and genetic algorithms are among them). The optimizer used in this work exploits the

optimization package available in Matlab® and is inspired by previous literature work by Narayanaswamy et al. [7].

The fuel palette used in the optimization of the surrogate has been carefully selected cross-referencing the species available in the CRECK kinetic model and compositional information on a Jet A-1 fuel obtained through a GCxGC analysis performed at IFPEN.

The optimization targets used in the process at this stage are cetane number, H/C ratio, distribution within the different family of components, average molecular weight, threshold sooting index, density, distillation curve and liquid viscosity. Additional targets will be added in future works to accommodate more relevant properties. Not all of these targets are strictly related to the kinetics of the oxidation of the fuel but, since the ultimate target is to formulate a surrogate fuel which can be also applied to multi-physics calculations, a general approach has been followed.

	Jet A-1 surrogate composition (% mol)
n-decane	24.1
n-dodecane	16.4
iso-octane	0.3
iso-dodecane	0.0
iso-cetane	7.9
methylcyclohexane	21.6
decalin	10.8
trimethylbenzene	16.9
methylnaphthalene	2.0

Table 1: molar composition of the jet fuel surrogate proposed in this work

The second constituent of a fuel model is the kinetic model describing its chemistry: in this case the CRECK kinetic model.

The kinetic model by CRECK Modeling Lab is based on a reaction mechanism core, which includes a detailed kinetic model for small hydrocarbons, and additional modules for heavier species which can be added depending on the modeling needs. The core model used in the current version of the CRECK model [8] is the Aramco 2.3 [9], [10], a kinetic mechanism published by National University of Ireland – Galway. This model, which includes hydrocarbons up to 3 carbon atoms in size (C₃), is the foundation for additional modules covering larger molecules as in Ranzi et al. [11], [12]. Typically, jet fuels include components having a number of carbons in the C₇-C₁₆ range. Kinetic models for such species require the determination of a large number of reaction rates whose values have not specifically measured or calculated. Analogy rules allow to estimate reaction rates for this molecules. The resulting kinetic model here used covers both high (>1000K) and low temperature (500-1000K) reactions. The comprehensive model includes ~ 460 species and ~14000 reactions.

Thermodynamic properties for all the species in the model have adopted from the active thermochemical tables [13] or from the online repository compiled by Burcat [14].

Modeling Results

The modeling results are shown in Figure 1. Although the flow reactor used in the experiments is a laminar flow reactor with a non-uniform temperature profile, it

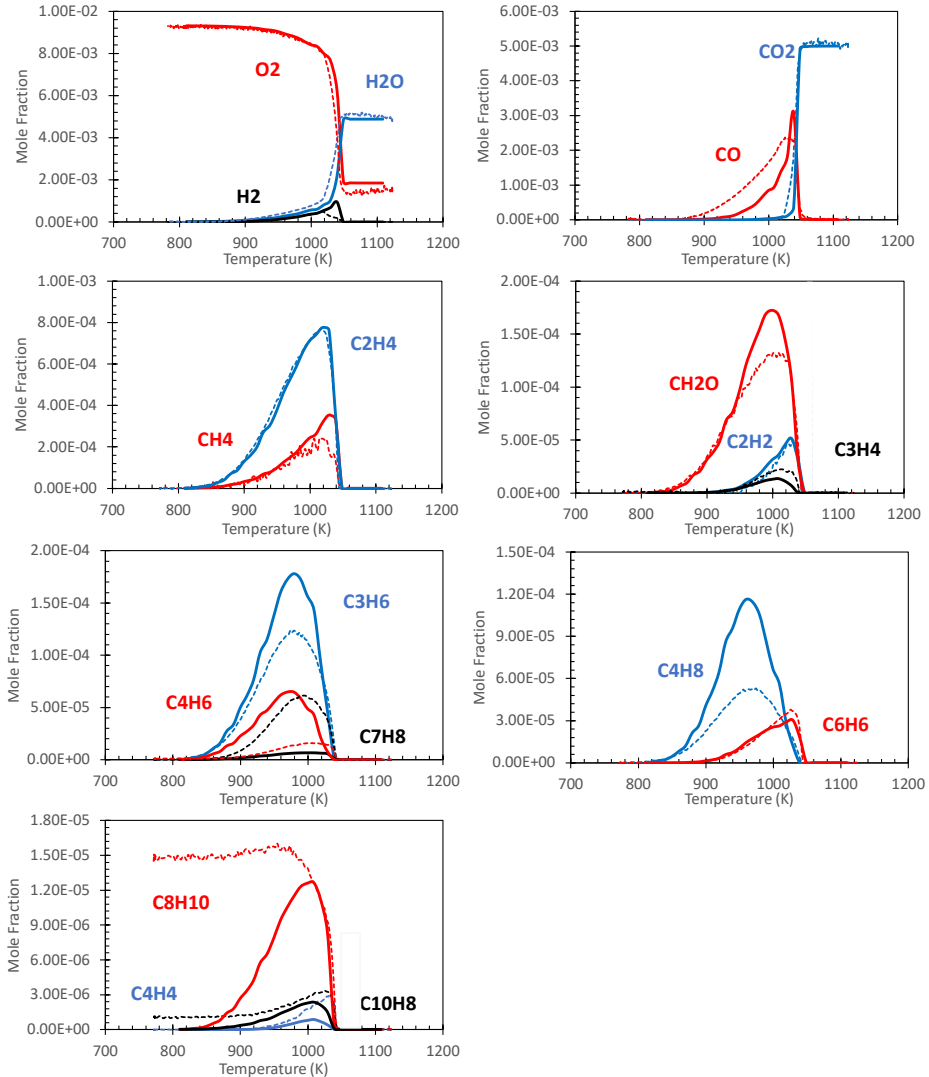


Figure 1: Comparison between measured (dashed lines) and calculated (solid) species profiles in the DLR flow reactor: Jet A-1, $\Phi=0.8$

has been shown previously that the plug flow assumption with an imposed temperature profile allows a quantitative comparison between the data and the simulations [1], [3]. The composition at the exit of the reactor has been calculated for each of the three fuels in the temperature range between 800 and 1150K (nominal temperature) and two equivalence ratios. Since the composition of the initial fuel is not fully resolved, and a surrogate is used to simulate its combustion, it is difficult to compare directly some of the species measured by the experiments. An example is decalin, which can be either a secondary product formed during the combustion and a fuel component. For this reason, in the following comparisons we are focusing on the smaller species that are formed during the decomposition and oxidation of the initial fuel and that may have an impact of the following soot and NO_x formation.

The fuel model (constituted by the combination of the surrogate and the relative kinetic model) is able to predict satisfactorily the formation of major products resulting from the oxidation of the Jet A-1 fuel in the DLR flow reactor, O₂ consumption and H₂O and CO₂ formation are accurately reproduced, while H₂ formation and CO show relatively small discrepancies. Based on the experiments, H₂ concentration should peak at about 1020K, while the model accurately predicts its rate of formation but has a slight delay in the onset of the consumption. CO formation is quantitatively reproduced but slightly delayed, showing a narrower but sharper peak.

More interesting is the comparison with minor species such as ethylene, acetylene and other unsaturated compounds. The agreement with these species is very good, particularly for species up to C₃. The model tends to over-predict C₄H₈ formation and to underpredict C₄H₄. For species like C₈H₁₀ and C₁₀H₈ (xylene and naphthalene) it is evident that the real fuel used in the experiments contain a certain amount of these components while the surrogate used in the calculation does not. Beside the inevitable differences observed at low temperature, where the fuel is not consumed yet, the model captures the timing of naphthalene and xylene formation and their consumption, and the variations shown in the experiments with temperature are correctly captured. Similar observations could be done for the moderately rich conditions tested in the experiments but these are not reported here due to space limitations. The full results will be published in future works.

Conclusions

This paper describes the procedures used to characterize the reactivity of a standard jet fuel from an experimental and modelling perspective.

A Jet A-1 fuel was investigated experimentally using flow reactor experiments and concentration profiled for a number of species involved in the oxidation process of the fuel and in the formation of soot were measured over a wide range of temperatures (800-1150K) and two equivalence ratios ($\Phi=0.8$ and 1.2).

A customized numerical tool was designed and implemented to select suitable mixtures representing the chemical (and physical) properties of jet fuels of interest

and a semi-detailed kinetic model reproducing the oxidation mechanism of a specifically designed fuel surrogate was used to simulate the speciation profile measured in the flow reactor. Comparisons with literature and new experimental data collected by DLR were used to validate the model and support the analysis of the combustion behavior. From the numerical and experimental results it is possible to conclude that the general modelling framework developed by the CRECK Modeling Lab has the potential to capture major combustion characteristics of jet fuels and to reproduce with good accuracy the selectivity towards different intermediates during their oxidation.

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