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A component library framework for deriving kinetic mechanisms for multi-component fuel surrogates: Application for jet fuel surrogates

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ABSTRACT

Surrogate fuels are often used in place of real fuels in computational combustion studies. However, many different choices of hydrocarbons to make up surrogate mixtures have been reported in the literature, particularly for jet fuels. To identify the best choice of surrogate components, the capabilities of different surrogate mixtures in emulating the combustion kinetic behavior of the real fuel must be examined. To allow extensive assessment of the combustion behavior of these surrogate mixtures against detailed experimental measurements for real fuels, accurate and compact kinetic models are most essential. To realize this goal, a flexible and evolutive *component library framework* is proposed here, which allows mixing and matching between surrogate components to obtain short chemical mechanisms with only the necessary kinetics for the desired surrogate mixtures. The idea is demonstrated using an extensively validated multi-component reaction mechanism developed in stages (Blanquart et al., 2009; Narayanaswamy et al., 2010, 2014, 2015), thanks to its compact size and modular assembly. To display the applicability of the component library framework, (i) a jet fuel surrogate consisting of *n*-dodecane, methylcyclohexane, and *m*-xylene, whose kinetics are described in the multi-component chemical mechanism is defined, (ii) a chemical model for this surrogate mixture is derived from the multi-component chemical mechanism using the component library framework, and (iii) the predictive capabilities of this jet fuel surrogate and the associated chemical model are assessed extensively from low to high temperatures in well studied experimental configurations, such as shock tubes, premixed flames, and flow reactors.

1. Introduction

Transportation fuels, including aviation fuels, represent the largest part of petroleum based fuel consumption. For most civilian and military aviation, kerosene type (Jet-A/Jet A-1/JP-8) jet fuels are used. These jet fuels adhere to the general physical property specifications [1], which include heating value, smoke point, luminosity factor, aromatic content, volatility, viscosity, freezing point, and thermal stability of the fuel, among the properties relevant to the quality of combustion. The important differences between these fuels are that: Jet-A and Jet A-1 have different freezing points (−40 °C for Jet-A and −47 °C for Jet A-1) [2], and JP-8 includes an additive package to Jet A-1 to satisfy military requirements. However, the JP-8 additives have been found to have negligible influence on the fuel reactivity, and the ignition delays of Jet-A and JP-8 fuels show no differences at low to high temperatures [3]. Like typical transportation fuels, jet fuels are mixtures of several hundreds of compounds belonging to different hydrocarbon classes. Their composition is found to vary from one source to another [4,5], and only average fuel properties are known at best.

In computational studies, it is important to incorporate finite rate chemistry to understand the combustion characteristics of the real fuels, address the problem of combustion control, predict emissions, and optimize engine performance. However, the complexity of the real fuels makes it infeasible to simulate their combustion characteristics directly, requiring a simplified fuel representation to circumvent this difficulty. Typically, the real fuels are modeled using a representative *surrogate* mixture, *i.e.* a well-defined mixture comprised of a few components chosen to mimic the desired physical and chemical properties of the real fuel under consideration. These single or multi-component fuels are classified as *physical surrogates* if they have the same physical properties as the real fuel (density, viscosity, boiling and freezing temperatures, distillation curve, thermal conductivity, specific heat, *etc.*), or *chemical surrogates* if they have the same chemical properties (heat release rate and total heat release, fuel ignition, sooting tendencies,

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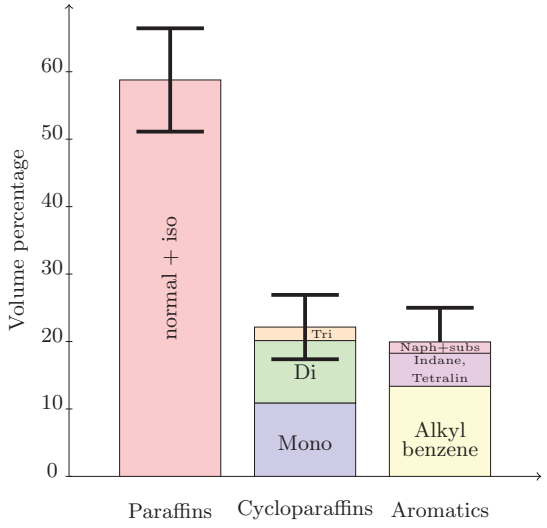

Fig. 1. Average composition of jet fuel from the the World Survey of Jet Fuels [7,8] as summarized in Refs. [9,11].

etc.) as the real fuel [6]. In this work, the interest is towards such a *chemical surrogate* for jet fuels, to represent the gas-phase chemical kinetic phenomena of the real fuel, in particular, heating value, major chemical classes, smoke point, density, average molecular weight, and reactivity.

1.1. Review of jet fuel surrogates and modeling approaches

Surrogates for real fuels are often chosen as mixtures of fuels representing the major hydrocarbon classes found in the real fuel. Chemical analysis [6–10] reveals the different hydrocarbon classes present in jet fuels, whose average composition is provided in Fig. 1. JP-8 fuel contains on average about 18% by volume of aromatics [10], with a maximum of 25%. The volume fraction of paraffins (normal and branched) has a mean value of 58.78%, with a standard deviation of 7.66%, while the mono cycloparaffins have a mean value of 10.89%, with a standard deviation of 4.77% [7–9,11].

Several groups have proposed surrogates involving two, three, or more components for kerosene fuels and developed kinetic models to describe their oxidation. An extensive review of the kinetic modeling efforts for jet fuels until 2006 is available from Dagaut and Cathonnet [12]. Early studies modeled kerosene oxidation via quasi-global models [13,14] for the surrogate mixture. With the increase in computing capabilities, reduced and detailed mechanisms for the surrogates began to be proposed in place of global reaction models, for instance, in Refs. [15–20]. The kinetic models were validated for kerosene oxidation against the available ignition delay data at high temperatures [21,22], species profile data in jet-stirred reactors [15,17], and premixed flames [23].

There is a large variation in composition of kerosene surrogates due to the wide variety of jet fuel applications [2]. The similarities between reactivities and product species profiles in *n*-decane and kerosene oxidation observed in experiments [15,23] motivated many studies to include *n*-decane as the alkane class representative in their surrogate mixtures, for instance, in Refs. [15–17,19]. Normal dodecane was also used to represent the alkane class, since *n*-dodecane has physical properties similar to JP-7 and JP-8/Jet A [6], for instance, in Refs. [18–20]. In addition, small amounts of iso-octane or iso-cetane were included as surrogate components to represent the iso-alkanes in the real fuel, such as in Refs. [18,20].

A number of studies compared various aromatic compounds in surrogates and concluded that alkyl-substituted aromatics were the best aromatic components [16,24–29]. Xylenes, *n*-propylbenzene, *n*-butyl benzene, and α-methyl naphthalene have all been considered as representatives of the aromatic class, for instance, in Refs. [18–20,30,31]. In addition to paraffins and aromatics, Dagaut et al. [17,32] observed that including a cycloalkane representative in the surrogate led to better agreement in aromatics profiles between jet stirred reactor experimental results and the model. Naphthenes such as methylcyclohexane, *n*-propylcyclohexane, and decalin have been used as cycloalkane representatives in several surrogate mixtures, for instance, in Refs. [17,18,20,30,33–35].

In most of the studies mentioned above, surrogates were defined such that average amount of the major chemical classes in the jet fuel, given by 79% alkanes, 10% cycloalkanes, and 11% aromatics (by mole) [23,36], was matched. In contrast, Violi et al. [18] proposed a strategy for surrogate formulation based on matching volatility, sooting tendency, as well as combustion properties between the surrogate and the real fuel. Following the recommendations of Colket et al. [2], the surrogate definition procedure for gas-phase combustion applications was subsequently refined in many later studies (for instance, Refs. [37–40]) to additionally reproduce *targets* such as hydrogen-to-carbon ratio, density, cetane number, threshold sooting index, and average molecular mass between the surrogate and the real fuel. A non-exhaustive summary of the recent surrogate formulation and kinetic modeling efforts is discussed in the following. Some of these studies have utilized a much wider experimental database [3,39–52], which has become available in recent years, to validate their kinetic models for kerosene fuel oxidation.

Recently, Dooley et al. [39] proposed a surrogate for a specific Jet-A fuel (labeled POSF 4658) for gas-phase applications, made up of *n*-decane, iso-octane, and toluene, to reproduce the aforementioned combustion targets, except that they considered derived cetane number over the conventional cetane number. The real fuel as well as the surrogate mixture were investigated experimentally in several configurations and found to show similar extents of chemical reactivities. They also proposed a kinetic model to represent their surrogate, compared against their experimental data, and observed that the chemical reactivity of the surrogate is strongly dependent on the kinetics of its *n*-alkane component. Since this surrogate had a lower molecular weight and TSI compared to the real fuel, Dooley et al. [40] proposed a second surrogate comprised of *n*-dodecane, iso-octane, *n*-propylbenzene, and 1, 3, 5-trimethyl benzene, which better matched the target Jet-A fuel. Their choice of surrogate components did not include every chemical class present in the real fuel, but rather only those necessary to form intermediate species of markedly different potential for radical production and consumption.

This surrogate was studied experimentally, and found to exhibit essentially the same global combustion kinetic behavior as the real fuel. They also observed similar chemical reactivities between the different surrogate fuels proposed in Refs. [39,40] in flow reactors and shock tubes, which were traced back to equivalence in integrated pool of functionalities between the two surrogates. Based on these observations, Dooley et al. [40] conceptualized a *functional group based approach* to define surrogates with minimal complexity, knowing the average chemical structure and functionalities of the real fuel.

Malewicki et al. [52] developed a chemical model for this surrogate using the Dooley et al. [39] model as the base model and adding sub-models for *n*-propylbenzene and 1,3,5-trimethylbenzene, and predicted mole fractions of CO, CO_2, C_1–C_3 intermediate species and the decay of the surrogate fuel and oxygen in their shock tube experiments satisfactorily. Flow reactor simulations using their surrogate model captured the overall trends of the decay of O_2 and the formation of CO, CO_2, and H_2O. The computed ignition delays (above 750 K) predicted shock tube data within a factor of two.

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