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Hydrocarbons for the next generation of jet fuel surrogates

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ABSTRACT

Fuel surrogates are a critical component for the detailed combustion modeling of real transportation fuels. Indeed, the numerical study of engine combustion requires the coupling of computational fluid dynamics and chemical kinetic models, and therefore a limited number of chemical species and reactions can be employed due to current numerical capabilities. As a consequence, surrogates are adopted to simulate the behavior of real fuels. In this study, we evaluate various hydrocarbon molecules that can be employed as next generation surrogate components for conventional and alternative jet fuels. Species considered in this study have smaller number of kinetic data as compared to molecules that are currently used in jet fuel surrogates, but they possess greater physical relevance and the potential to achieve closer emulation of properties when used as jet fuel surrogate components. Using a surrogate optimizer model, we analyze various mixtures that can emulate a petroleum-derived jet fuel (Jet-A POSF-4658) and a coal-derived jet fuel (IPK POSF-5642). The results show that *n*-tetradecane and *n*-dodecane are suitable normal alkane representatives for jet fuels. Also, the use of three C_9 alkylbenzenes (*n*-propyl-, 1,2,4-trimethyl-, 1,3,5-trimethyl-benzene) leads to surrogate mixtures with an aromatic content and a distillation curve that matches the experimental values of Jet-A much better than mixtures that contain toluene or C_{10} alkylbenzenes. In addition, the optimization results with three new branched alkanes for the target IPK show that 2,2,4,6,6-pentamethylheptane is a promising surrogate component for representing low ignition quality highly-branched alkanes in jet fuels. This study highlights the need for experimental studies and further kinetic model development for these molecules, which will benefit the surrogate development for the wide variety of jet fuels in the future.

1. Introduction

Current transportation fuels, such as gasoline, jet fuel, diesel fuel, and even non-petroleum-derived alternative fuels, are very complex mixtures of various classes of hydrocarbons. Despite recent advances in computational power, detailed combustion modeling of these real fuels remains extremely challenging: firstly, it is nearly impossible to identify all the individual molecules present in real fuels as well as their compositions and secondly, detailed information on the combustion modeling of all the constituents is not available. Moreover, the computation time would be prohibitively long when all identified species are included and simulated.

To overcome such challenges, fuel surrogates have been developed and utilized to represent the combustion process of real fuels with a mixture of a few well-characterized pure hydrocarbons. Previous surrogate formulations for transportation fuels have been extensively reviewed in [1–6]. Over the past two decades, several surrogates have been developed for various types of petroleum-derived jet fuels [7–17] and non-petroleum-derived alternative jet fuels [17–23]. While the experimental trial and error method was the primary approach in the past, recent surrogate formulations incorporate model-based optimization methods to determine the surrogate compositions that best matches multiple target properties [13–18].

Works reported by our group [16,17,24–27] has focused on developing jet fuel surrogates that emulate various physical and chemical properties. Since the primary application has been the use of surrogates for reactive CFD simulations, one of the most important criteria for the selection of the components was the availability of matured chemical mechanisms. However, while all the target properties were reasonably emulated, noticeable discrepancies were observed for the matching of molecular weight and distillation curve. This situation was caused by the forced selection of some surrogate components outside the molecular size distribution of the targeted jet fuels due to the limited availability of the chemical mechanisms.

To overcome this issue, in this paper we report on a detailed analysis of hydrocarbon classes to identify new candidates for surrogate

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Table 1
Temperature-independent properties of Jet-A, IPK, and their surrogates [17].

Properties	Jet-A POSF-4658	Jet-A surrogate	IPK POSF-5642	IPK surrogate
DCN[a]	47.3 ± 0.67	46.6 ± 0.68	30.7 ± 0.32	31.9 ± 0.49
LHV (MJ/kg)	42.8 [30]	43.43	44.0 [30]	44.21
H/C ratio	1.957 [30]	1.920	2.119 [30]	2.121
MW (g/mol)	157.5 [29]	150.5	156 [30]	149.6

[a] Derived Cetane Number measured with IQT with ASTM D6890 method.

components for conventional and alternative jet fuels that have the potential to significantly improve the agreement with real fuels. We selected hydrocarbons without considering the availability of kinetic data and performed surrogate optimizations with those new hydrocarbons to assess their feasibility. Still retaining the need for a small number of surrogate components (4 or 5), we provide new formulations for jet-A and IPK fuels that improve on the agreement for two key properties of real fuels: molecular weight and distillation curve. A chemical mechanism that include the new surrogate components are then used to compare ignition delay times of the mixtures containing the new hydrocarbons versus experimental data present in the literature. This study provides guidance on possible directions for future experimental kinetic studies and chemical mechanism development to include these new surrogate components.

2. Surrogate formulation methodology

2.1. Surrogate optimizer

The surrogate optimizer, previously developed by our group [16,17], was used to formulate surrogates in this study. The optimizer includes various models and correlations to estimate the properties of the test mixtures during the iterative optimization process. The mixture properties that the optimizer is capable of predicting are Derived Cetane Number (DCN), Lower Heating Value (LHV), Hydrogen/Carbon ratio (H/C), Molecular Weight (MW), temperature-dependent density, viscosity, specific heat, and distillation curve. Thus, the surrogate optimizer determines the composition of given surrogate components that best matches these eight target properties. While all the details of the surrogate optimizer and the methods for mixture property prediction can be found in [16,17], a brief description of the DCN estimation method and the distillation curve calculation are given here.

The primary DCN prediction method for the optimizer is the non-linear regression model developed for the six-component surrogate palette which consist of *n*-dodecane/*n*-decane/iso-cetane/iso-octane/decalin/toluene [17]. The regression model was generated by fitting a non-linear expression to DCN measurements of 76 mixtures within the six-component surrogate palette, and was shown to provide significantly more accurate predictions than the commonly-used volume fraction average method [17]. However, this regression model was specifically generated for the six-component palette and cannot be used for the new surrogate components. Thus, the optimizer was modified for this study to selectively use the non-linear regression method for the portion of the mixture containing the six-component, and the volume fraction average method for the overall mixture including hydrocarbons outside the six-component palette. For example, DCN of a mixture that contains *n*-dodecane/iso-octane/2,2,5-trimethylhexane/*n*-butylbenzene is estimated as follows. First, the non-linear regression model is used to estimate DCN of *n*-dodecane/iso-octane portion of the mixture. Then, the mixture is treated as a 3-component mixture with (the six-component part)/2,2,5-trimethylhexane/*n*-butylbenzene and the volume fraction average is used to estimate the overall mixture DCN.

The distillation curve for the test mixtures is calculated by discretizing the distillation curve into 100 volume steps and solving the liquid-vapor equilibrium at the liquid-vapor interface with Raoult's law at each volume step. The model is calibrated to match the experimentally measured distillation curves using the Advanced Distillation Curve metrology from NIST [18]. It is also validated against measured distillation curves of 75/25 and 50/50 mixtures of *n*-decane/*n*-tetradecane [16] and various surrogate mixtures in [28], which can be found in Supplementary Material.

2.2. Target fuels and original surrogates

Two jet fuels, Jet-A POSF-4658 and IPK POSF-5642, were investigated in this study. Key properties of these fuels are summarized in Table 1 and Fig. 1, together with the values of their corresponding surrogates developed by Kim et al. [17]. Jet-A POSF-4658 is a petroleum-derived conventional jet fuel. The properties of Jet-A POSF-4658 are regarded as the nominal values for conventional jet fuels [16,29]. IPK (Iso-Paraffinic Kerosene) POSF-5642 is a coal-derived alternative jet fuel, which has considerably lower ignition quality (or lower cetane number) than typical petroleum-derived jet fuels [17]. While Jet-A is a complex mixture of normal alkanes, branched alkanes, cyclic alkanes,

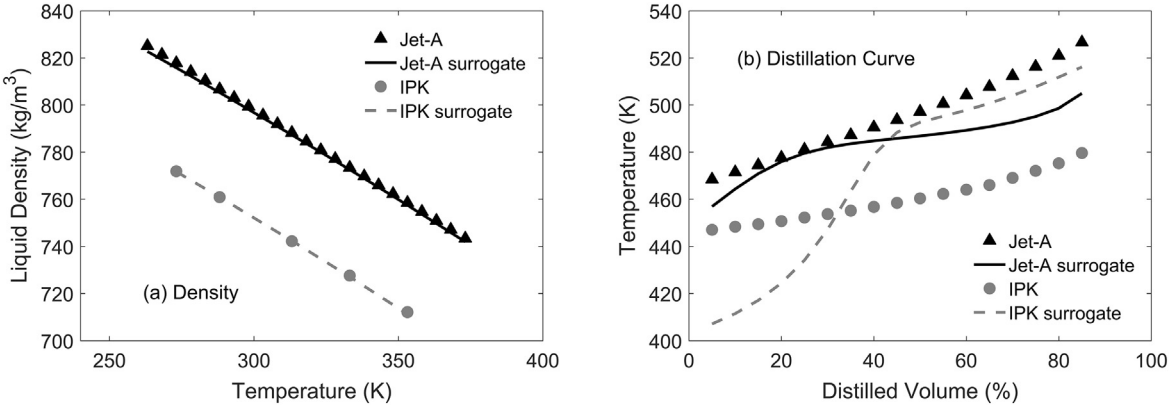

Fig. 1. (a) Temperature-dependent liquid densities and (b) distillation curves of Jet-A, IPK, and their surrogates. Properties of the target fuels are experimentally measured [31–34], while properties of the surrogates are estimated using the surrogate optimizer [16,17].