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Surrogate fuel formulation for oxygenated and hydrocarbon fuels by using the molecular structures and functional groups

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ABSTRACT

A methodology of surrogate fuel formulation by directly using molecular structure and functional groups for both oxygenated and hydrocarbon fuels is proposed and investigated. The novelty of this method is to construct surrogate fuel mixtures by directly matching the molecular structure and the key functional groups instead of using the combustion property targets explicitly. This method is tested by using two different classes of fuels, biodiesel and jet fuel. For biodiesel, by using four functional groups such as CH_3—, —CH_2—, —CH_2—CH=CH—, and —COO—CH_3, a surrogate mixture of methyl-9-decenoate, 1,4-hexadiene and *n*-dodecane is formulated to demonstrate the efficacy of this method by comparing the resulting gas phase combustion targets between the formulated surrogate and biodiesel. For jet fuels, five functional groups such as CH_3, CH_2, CH, C, and phenyl were used to construct the Princeton 1st and 2nd generation surrogate jet fuel mixtures. The simulated results are compared with the experimental data and the results predicted by other surrogate fuel formulation methods. The comparisons show that the present method can formulate surrogated mixtures of both oxygenated and hydrocarbon real fuels and reproduce the combustion characteristics. Therefore, this method can be used not only for biodiesel and jet fuels, but also for other alternative fuels.

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1. Introduction

Detailed chemical kinetic models of real fuels like gasoline, diesel and biodiesel, and jet fuels play important roles in the computational design and optimization of internal combustion engines and propulsion systems by enabling quantitative simulations of combustors. However, real fuels have a large variation in composition and involve hundreds of chemical components with different molecular structures. Consequently, the development of a detailed chemical kinetic model for a real fuel is a big challenge. Alternatively, simplified "surrogate fuels" with only a few component species are regarded as one of the most effective ways for representing the combustion and physical properties of real fuels [1].

Formulating surrogate fuel mixtures that match the conventional fuel performance in engines requires not only matching the combustion properties but also physical properties of the real fuels. Normally, the physical properties of real fuels comprise of density, viscosity, surface tension, heating values, and

diffusion coefficients, etc.; and the chemical properties include auto-ignition delay, flame speed, extinction, speciation, and propensity to the formation pollutants, etc. The more the matching properties are needed, the more a complex surrogate mixture is required.

Surrogate fuels are used to mimic the behavior of a real fuel in various combustion devices, and the definition and complexity of the surrogate fuel formulation depend on the intended applications. Three different types of targets, property targets, development targets, and application targets, have been proposed to quantitatively compare the performance of a surrogate fuel with real diesel [2]. Liang et al. [3] created a diesel surrogate that matched the cetane number, C/H ratio, low heating value, and 50 vol.% distillation temperature. Mueller et al. [4] utilized the state-of-the-art techniques of ^{13}C and ^1H nuclear magnetic resonance (NMR) spectroscopy and the advanced distillation curve to characterize diesel fuel composition and volatility, respectively. Anand et al. [5] proposed a surrogate model using nine basic fuels for studying low-emission, high-efficiency advanced diesel engines. The surrogate composition of the fuels were obtained through the simulation results using KIVA-ERC-CHEMKIN. Pera and Knop [6] proposed a methodology matching the H/C ratio,

O/C ratio, molecular weight, Research Octane Number (RON), and Motor Octane Number (MON) to define proportions of compounds in gasoline surrogates dedicated to auto-ignition modeling in engines. Mehl et al. [7] proposed an alternate method for the formulation of gasoline surrogate mixtures based on limited composition information and chemical kinetic modeling calculations. In recent years, Ahmed et al. [8] developed a regression algorithm to determine the optimal surrogate composition by matching the fuel properties of FACE A and C gasoline, specifically hydrogen/carbon (H/C) ratio, density, distillation characteristics, carbon types, and RON.

Kim et al. [9] built a JP-8 surrogate model by matching eight target properties: cetane number, lower heating value, hydrogen to carbon ratio, molecular weight and temperature dependent density, viscosity, surface tension and distillation characteristics. Dooley et al. [10,11] proposed a systematic methodology to create a surrogate fuel mixture of real jet fuel by matching four combustion property targets: the average fuel molecular weight (MW), hydrogen/carbon molar ratio (H/C), derived cetane number (DCN), and threshold sooting index (TSI). The resulting surrogate fuel mixtures mimicked reasonably well the global targets of ignition, flame speeds, extinction limits, and speciation in flow reactor, except for some discrepancies in the low temperature oxidation region.

In recent years, biodiesel has attracted significant attention around the world [12]. Different from traditional petroleum fuels, biodiesel is an unsaturated and oxygenated fuel, and has a larger molecular size and a unique ester functional group [13–15]. Herbinet et al. [13,16] combined the models of methyl decanoate, methyl-9-decenoate (MD9D), and *n*-heptane to obtain a blended biodiesel surrogate fuel mixtures. However, there are few reports in the literature on how to systematically formulate a surrogate fuel mixture of oxygenated fuels like biodiesel.

From the above discussion, it is obvious that the formulation of a surrogate fuel mixture for real fuel is still highly empirical and an engineering art. The choice of surrogate fuel components still has high subjective randomness. Most of the surrogate fuel property targets such as MW, H/C, DCN, TSI, and distillation curves are macroscopic and phenomenological quantities. Although these phenomenological methodologies for surrogate fuel model construction are intuitively to understand and simple to use, they still have some disadvantages in requiring personal experience and difficulty to be applied to fuels with unknown combustion properties.

The goal of this study is to develop and validate a more universal and rigorous methodology for surrogate fuel formation of fuels without knowing their physical and chemical properties. The method is applied to both biodiesel and jet fuels by using the representative fuel molecular structures and functional groups. For biodiesel, a new surrogate mixture was formulated and the kinetic model was assembled to help interpret experimental observations. For jet fuels, this method was used to construct new formulations for the Princeton 1st and 2nd generation surrogates.

2. Theoretical foundation and methodology

2.1. Theoretical foundation

A functional group is a portion of a molecule that is a recognizable/classified group of bound atoms. In organic chemistry it is very common to see molecules comprised mainly of a carbon backbone with functional groups attached to the chain. Basically, the thermochemical, physical, and combustion properties of a fuel are the summed results of the fuel molecular structures and functional groups. Rossini and co-workers [17–20] have developed a theory of group additivity scheme to predict the heat of formation of hydrocarbons. Benson and co-workers [21,22] demonstrated the wide applicability of group additivity rules for the estimation of thermochemical properties. Quann and Jaffe [23] provided an effective method, called structure-oriented lumping (SOL), for describing the composition, reactions, and properties of complex hydrocarbon mixtures.

The functional group additivity scheme can also be used for correlation of the partial molar volumes, compressibilities, heat capacities, hydration enthalpies, and hydration Gibbs energies at infinite dilution of aqueous organic electrolytes and non-electrolytes [24]. The group additivity enables one to predict the thermochemical properties of a molecule in terms of the characteristic properties imparted by the functional groups and molecular structures and to identify the presence of a given group through the same characteristic properties [25].

Moreover, not only the functional group additivity scheme can predict the thermochemical properties of a molecule, but also can estimate its reaction rates with alkyl and free radical molecular classes [25–28]. In combination with Benson's group additivity tables, Sumathi et al. [27] predicted the reaction rates for 15 sets of reactions, which can be used as reasonable estimates in constructing large kinetic models. Mehl et al. [29] also developed the reaction mechanisms of high molecular weight fuels by using a functional group approach.

Yan et al. [30] proposed a theoretical method, based on a structural group contribution approach for predicting the smoke point of pure hydrocarbon liquids. Pepiot-Desjardins et al. [31] proposed a structural group contribution approach to interpret experimental observations on the effect of oxygenated additives on the sooting propensities of hydrocarbon fuels. Barrientos et al. [32] indicated that molecular structure has an important influence on the sooting tendency of fuels. Different functional groups resulted in different sooting tendencies. In their study, a structural group contribution approach based on group additivity is proposed to interpret experimental observations on the effect of oxygen functional groups on the sooting tendency of fuels using the example of C-5 oxygenated fuels. Recently, Won et al. [33] reported that the methylene to methyl ratio globally correlates the low temperature alkylperoxy radical reactivity for large paraffinic fuels and suggested the metric of $\frac{CH_2}{CH_3} \times [CH_2 + CH_3]$ as an additional combustion property target. Besides, Won et al. have also studied the universal correlation of extinction limit to molecular structure. [34].

The goal of a surrogate fuel mixture is to match certain physical and combustion properties of a target fuel by using a small number of relatively well-studied pure compounds. Based on the successful applications of group additivity in predicting sooting tendency, elementary rate constants, and thermochemical properties discussed above, it is therefore reasonable to infer that if the molecular structure of a target fuel is known and that one can match the collective or summed molecular structure and functional groups between the surrogate fuel mixtures and the target fuel, the chemical, physical, and combustion properties will likely to be matched without knowing the global combustion properties. Although a similar viewpoint was hinted or mentioned in literature [10,11], there are no surrogate mixtures have been constructed and validated using this approach until now.

2.2. Methodology for surrogate fuel formulation using molecular structure and functional group

In this study, we propose a method to match the collective or summed functional groups of a real fuel by using a surrogate fuel mixture. All the fuel molecules will be represented by a summation of a few representative functional groups. The main principle of choosing surrogate components is that the surrogate components can provide the same base functional groups as and have compara-