



Reconstruction of chemical structure of real fuel by surrogate formulation based upon combustion property targets



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ABSTRACT

The global chemical character of complex chemical fuel mixtures is explicitly determined by evaluating the abundances of chemical functional groups present within them rather than by applying a traditional interpretation based upon molecular species composition. Statistical analyses of the relationships among each chemical functional group and specific combustion property targets (CPTs) of the fuel are rigorously developed. The results demonstrate that the four CPTs currently used in aviation kerosene surrogate formulation - H/C molar ratio, derived cetane number (DCN), average molecular weight (MW), and threshold sooting index (TSI) - effectively constrain the chemical functional group distribution of the fuel, and, hence, the global combustion behaviors of pre-vaporized fuel/air mixtures. Successful emulation of the CPTs for a target real fuel involves developing a surrogate mixture that defines an “equivalent” chemical functional group distribution to that of the target fuel. Among the CPTs used for real fuel surrogate development, DCN does not abide by a linear blending rule, which generally frustrates development of surrogates. However, a quantitative structure–property relation (QSPR) regression for DCN is demonstrated here using the chemical functional group approach. Results of the regression reveal that the $(\text{CH}_2)_n$ group plays the most significant role in determining the fuel autoignition propensity, followed by the influences of CH_3 and benzyl-type groups. The QSPR functional group approach extends to provide a powerful tool to address potential preferential vaporization effects dictated by fuel distillation characteristics. Further analysis of fuel chemical property variation (DCN and H/C ratio) over the distillation curve (and other physical properties) provides a foundation for understanding the complex combustion behaviors of multi-phase and multi-component fuels relevant to real gas turbine engine applications.

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1. Introduction

Extensive study supports the theory that both oxidative and pyrolytic combustion chemistries of a fuel are governed by the molecular structure of the fuel. In the case of pure components (a single molecular structure), strong relationships between the molecular structure and the global combustion behaviors have been observed in various canonical experimental configurations, including measurements of laminar flame speed [1–4], autoignition [5,6], flame extinction [7–10], soot formation [11–14], etc. However, the combustion chemistries of real transportation fuels cannot be similarly characterized from their complex molecular composition as a result of the numerous structural variations that exist within

each molecular class [15–17]. The resulting intrinsic ambiguities in defining the chemical character of a real fuel based upon molecular composition have been a fundamental challenge, therefore obscure the relationship of chemical characteristics and experimentally observed behaviors such as near-limit global combustion properties in gas turbine combustors (e.g., lean blow off and relight) [18–21]. To overcome the intrinsic ambiguities presented by real fuel composition, combinations of fuel “reference” indicators are frequently used to certify a particular fuel to be fit-for-use in a particular type of energy conversion device [22]. Both chemical and physical properties of real fuels need to be considered in forecasting the effects of fuel properties on multi-phase combustion performance and emissions.

In prior works, we have shown that the global combustion characteristics of a fully pre-vaporized gas turbine fuel can be successfully replicated by a relatively simple mixture of components (a

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“surrogate”) that shares the same values for a small set of reference indicators that we term “combustion property targets” (CPTs) [23–29]. Four CPTs - hydrogen to carbon molar ratio (H/C ratio), derived cetane number (DCN), average molecular weight (MW), and threshold sooting index (TSI) - have been utilized as targets to be matched in a surrogate formulation to replicate the behavior of a particular fuel. These specific CPTs were chosen based upon empirical (but fundamentally supported) understanding of how various combustion behaviors might relate to each CPT [22]. The effectiveness of the surrogate formulation method based upon CPTs has been extensively demonstrated over a wide range of canonical experimental platforms for pre-vaporized fuel/air mixtures, measuring fundamental combustion behaviors, such as laminar flame speed, premixed and non-premixed flame extinctions, ignition delays, and oxidative speciation profiles [23–29]. It has been also shown that the CPTs can be used to evaluate the global combustion behaviors of emerging alternative jet fuels and their blends with petroleum-derived jet products [28].

Considering the complex interactions of fuel chemical and physical properties in multi-phase combustion, it is important to expand the surrogate approach to incorporate fuel physical properties, which play central roles in determining spray dynamics of liquid fuel atomization [30,31]. Some efforts have previously included fuel physical properties as additional combustion property targets in surrogate formulation (e.g. [32–35]). The fidelity of a surrogate mixture in emulating both physical and chemical properties of a target fuel can be achieved by considering a larger number of constraining property targets, but also typically requires larger numbers of surrogate components (e.g. [25,33]). The dimensionality of computations rapidly becomes limiting with the increased number of components. On the other hand, if the number of surrogate components is too constrained, the optimal solution yields poor fidelity (e.g. [36]) in approximating the more complex detail. Thus, it is important to determine which fuel properties need to be more precisely replicated as different engine configurations are considered [37,38]. Regardless of classification as either pre-vaporized property or physical property, some CPTs may be strongly correlated with others [28] or their values may not be determined with sufficiently low uncertainties by existing methodologies [28,39] to constrain surrogate formulation sufficiently. The resulting ambiguities may be, in part, addressed by weighting the optimization among CPT constraints [25,32]. These technical challenges primarily originate from the inability to define *a priori*, rather than *posteriori*, the relationships between fuel properties and combustion behaviors.

This particular paper provides new insights on the fundamental issues that relate fuel composition effects on pre-vaporized combustion behaviors and establishes a foundation for analyzing and integrating chemical and physical property effects in multi-phase combustion situations. Here, the chemical functional group approach, inspired by the works of Benson and colleagues [40–42] among others [43,44], is further explored as a means of relating observed global combustion behaviors with the chemical structural characteristics of both single- and multi-component mixtures [24,45–49]. The global chemical structure is examined by investigating the chemical functional group distribution represented by the fuel. Similar approaches have been widely utilized to estimate thermochemical properties critical for kinetic research [40–42,50], as well as for estimating the physical properties of molecules [51], e.g., as in the UNIFAC model series [52]. The chemical functional group approach adopted here can be also regarded as similar to the structure-oriented lumping approach [43,44], which has been utilized for describing pyrolytic refining processes for heavy crude fractions with very detailed description for molecular structures. The approach here specifically targets jet fuel components and their chemical functionalities, thus resulting

in comparatively simplified chemical functional group descriptors based on our previous results.

For combustion kinetic behaviors, we have used the chemical functional group concept to explain similarities of CPTs among multiple surrogate mixtures (and real fuels) by a hypothesis of a commonality of key kinetically-constraining molecular fragments, namely methylene (CH_2), methyl (CH_3), and benzyl-type groups [24]. In the case of weakly and significantly branched alkanes, we have shown that the behaviors of these molecules are controlled by the abundances of CH_2 and CH_3 groups [45,46]. Defining a chemical structure of a fuel via key chemical functional groups provides a basis for predicting particular combustion responses to specific chemical functionalities through quantitative structure–property relationship (QSPR) regressions [22], such as demonstrated for reflected shock ignition delays [47], derived cetane numbers [48,49], and threshold sooting index [14].

Chemical functional group distributions can be experimentally determined by nuclear magnetic resonance spectroscopy (NMR) [47,53–55] or, in principal, by other spectroscopic and/or chromatographic methods. We speculate that significant analytical and predictive capabilities toward relating chemical characteristics to the combustion of real fuels can be realized using a chemical functional group methodology and QSPR [22]. Accordingly, the objectives of this study are to:

- 1) Investigate the applicability of the chemical functional group approach for defining the chemical structure of complex fuel mixtures.
- 2) Elucidate the (relative) role of each CPT in constraining and reconstructing the important chemical-structural characteristics in surrogate mixture formulation.
- 3) Evaluate the surrogate approach to capture both fuel chemical and physical properties.

To pursue these objectives, a “Model Fuel” is formulated from twelve pure components, typical of the molecular classes found in petroleum-derived jet fuels. The Model Fuel has CPTs that are representative of a “global average” petroleum-derived jet fuel [21] to test our CPT ↔ chemical functional group hypothesis. The ability of commonly employed CPTs to define surrogates that themselves also reconstruct the chemical structure of this Model Fuel is statistically analyzed by evaluating the response of key chemical functional groups to single and/or multiple CPTs imposed as constraints. In particular, the role of DCN as a surrogate formulation CPT is further investigated by constructing a QSPR regression and performing a sensitivity analysis. Based upon the results of these analyses, fuel physical properties are also incorporated to formulate four surrogate mixtures targeting the “average” petroleum-derived jet fuel, Jet-A POSF 10,325 [21]. Finally, the potential impact of preferential vaporization on combustion behaviors is demonstrated based upon the variations of the CPTs over the calculated distillation curve of the real fuel.

2. Methodology - description of chemical structure

It is well known that the character of a chemical reaction depends upon the molecular structural features of the participating molecules (and molecular fragments) in question. These critical features can be represented by molecular fragments, termed “chemical functional groups” [56]. A functional group may be an atom or a group of atoms that yield similar chemical character wherever they occur as part of the structure of a molecule. The important fundamental premise applied here is that the identity and population of “key” functional groups participating in chemical or physical interactions define the chemical or physical properties of the substance in question. The notion of chemical functionality can be applied at the atomic level by considering each

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