Chemical functional group descriptor for jet fuel surrogate

Sang Hee Won, University of South Carolina
Francis M. Haas, Rowan University
Stephen Dooley, University of Dublin, Trinity College
Frederick L. Dryer, Princeton University
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Sang Hee Won¹, Francis M. Haas², Stephen Dooley³, Frederick L. Dryer¹,⁴

¹Department of Mechanical Engineering, University of South Carolina, USA
²Mechanical Engineering Department, Rowan University, USA
³School of Physics, Trinity College Dublin, The University of Dublin, Ireland
⁴Department of Mechanical and Aerospace Engineering, Princeton University, USA

*Corresponding Author Email: sanghee@mailbox.sc.edu

Abstract: The global chemical characters of complex chemical fuel mixtures are explicitly determined by evaluating the abundances of chemical functional groups present within it rather by applying molecular species composition. Statistical analyses on the relationships of each chemical functional group and the chemical property targets of the fuel are rigorously developed. The results demonstrate that the four CPTs currently used in surrogate formulation - H/C molar ratio, derived cetane number (DCN), average molecular weight (MW), and smoke point (SP) - effectively constrain the chemical function group distribution of the fuel, hence, the global combustion behaviors of pre-vaporized fuel/air mixtures. Emulating the CPT’s of a target fuel using a mixture of known surrogate components defines an “equivalent” chemical functional group distribution of the target fuel. A successful quantitative structure-property relation (QSPR) regression for DCN is demonstrated using a chemical functional group approach, revealing that the (CH₂)n group, n ≥ 3, plays the most significant role in determining the fuel autoignition propensity, followed by the influences of CH₃ and benzyl-type groups.

Keywords: Combustion property target, DCN, Quantitative structure-property relation

1. Introduction

It has been a theory that the combustion chemistries of both oxidative and pyrolytic kinetics of a fuel are governed by the molecular structural composition of the fuel. In the case of pure components, extensive studies have shown strong relationships between the molecular structure and the global combustion behaviors. However, in the case of real transportation fuels, their combustion chemistries cannot be similarly characterized as a result of the numerous structural variations that exist within each molecular class [1, 2]. This intrinsic ambiguities in defining the chemical character of a real fuel presents fundamental challenges to clarify the relationship of chemical characteristics and experimentally observed behaviors [3-5].

In prior works, we have shown that the global combustion characteristics of a fully vaporized gas turbine fuel can be successfully replicated by a simplified surrogate mixtures that share the same values for a small set of reference indicators that we term “combustion property targets” (CPTs) [6-11]. 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. This paper attempts to provide insights on the fundamental issues that relate fuel composition effects on pre-vaporized behaviors and to establish the foundation for analyzing and integrating chemical and physical property effects in multi-phase combustion situations. 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 [12],
as well as for estimating the physical properties of molecules [13]. 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 [14].

To pursue these objectives, a “Model Fuel” is formulated from twelve pure components with appropriate CPT property targets representative of a “global average” petroleum-derived jet fuel. The effectiveness of the CPT approach to reconstruct this fuel’s chemical structure is statistically analyzed by evaluating the response of a semi-detailed chemical structure, as characterized by key chemical functional groups. In particular, the role of DCN in surrogate formulation is further investigated by constructing a QSPR regression and sensitivity analysis.

2. Methods
The chemical functional group approach utilized here and in our previous papers [7, 15-17] is based on determining the “key” carbon/hydrogen multi-atom functional groups present in the real fuel. Here, six “key” molecular fragments are proposed as the potential chemical functional groups of importance to defining global combustion responses found for mixtures of n-alkanes, iso-alkanes, and aromatics. The molecular fragments considered in the present study are: 1) isolated methylene groups (referred to as CH$_2$); 2) the linearly bonded methylene group ((CH$_2$)$_n$, where “n” indicates the resulting n-alkyl chain length; 3) the methyl group (CH$_3$); 4) the CH group (CH); 5) the C group bonded only to other carbons (C); and 6) the benzyl group (benzyl). Examples of developing functional group assignments on the basis for surrogate compositions and their group constituents are shown in Table 1.

3. Results and Discussion
To demonstrate the effectiveness of the four CPTs in constraining the chemical functional description, a hypothetical, 12 component “Model Fuel” composed of n-/iso-alkanes and aromatics

<table>
<thead>
<tr>
<th>Components</th>
<th>Mole fraction</th>
<th>DCN</th>
<th>H/C ratio</th>
<th>MW [g/mol]</th>
<th>TSI</th>
<th>Density at 15 °C [kg/m$^3$]</th>
<th>T10 [°C]</th>
<th>T50 [°C]</th>
<th>T90 [°C]</th>
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<tbody>
<tr>
<td>nC7</td>
<td>0.01</td>
<td>49.2</td>
<td>32.4</td>
<td>52.2</td>
<td>43.2</td>
<td>768.3</td>
<td>168.9</td>
<td>196.3</td>
<td>248.8</td>
</tr>
<tr>
<td>nC8</td>
<td>0.09</td>
<td>2.007</td>
<td>1.857</td>
<td>2.061</td>
<td>1.934</td>
<td>783.4</td>
<td>144.6</td>
<td>169.9</td>
<td>206.5</td>
</tr>
<tr>
<td>nC7</td>
<td>0.11</td>
<td>152.8</td>
<td>132.4</td>
<td>183.7</td>
<td>149.9</td>
<td>833.6</td>
<td>200.9</td>
<td>254.0</td>
<td>285.0</td>
</tr>
<tr>
<td>nC12</td>
<td>0.14</td>
<td>19.6</td>
<td>20.1</td>
<td>23.6</td>
<td>21.3</td>
<td>200.2</td>
<td>170.2</td>
<td>243.2</td>
<td></td>
</tr>
<tr>
<td>nC14</td>
<td>0.10</td>
<td>Density at 15 °C [kg/m$^3$]</td>
<td>768.3</td>
<td>783.4</td>
<td>833.6</td>
<td>799.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>nC16</td>
<td>0.01</td>
<td>168.9</td>
<td>144.6</td>
<td>200.9</td>
<td>170.2</td>
<td>200.2</td>
<td>243.2</td>
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</tr>
<tr>
<td>iC8</td>
<td>0.05</td>
<td>196.3</td>
<td>169.9</td>
<td>254.0</td>
<td>200.2</td>
<td>243.2</td>
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<tr>
<td>iC12</td>
<td>0.19</td>
<td>248.8</td>
<td>206.5</td>
<td>285.0</td>
<td>243.2</td>
<td>243.2</td>
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<tr>
<td>iC16</td>
<td>0.06</td>
<td>2013 PQIS summary report of JP-8 [18]</td>
<td></td>
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<tr>
<td>toluene</td>
<td>0.01</td>
<td>b) Cetane Index is assumed equal to DCN for petroleum-derived jet fuels</td>
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<td></td>
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<tr>
<td>nPB</td>
<td>0.05</td>
<td>c) Calculated from hydrogen content (mass %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>135TMB</td>
<td>0.18</td>
<td>d) Derived from the correlation with density (at 15 °C) and 50% recovering temperature in distillation curve [11]</td>
<td></td>
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</table>

Table 2. Composition and calculated combustion property targets and physical properties of Model Fuel.
is formulated, as described in Table 2. The composition forming the Model Fuel is chosen to match the aromaticity (~ 18%), distillation character, DCN, H/C ratio, and TSI of a typical (global-average) petroleum-derived jet fuel. Density and distillation temperatures are calculated by the methods discussed in [19]. Table 2 also compares the fuel properties to the values summarized in [11]. Below, we proceed to formulate mixtures of the four 2nd generation surrogate components (n-dodecane, iso-octane, n-propylbenzene, and 1,3,5-trimethylbenzene) [7] to emulate various combinations of the four CPT’s of the Model Fuel. The mixtures of the four surrogate components are arbitrarily populated, under the constraint that their mole fractions sum to one. By employing the discrete variation of 0.01 mole fraction changes for each mixture, a total of 176,851 discrete mixtures are populated and the values of CPTs for each composition are calculated. H/C ratio and MW can be simply calculated based upon molar ratios. The values of TSI are calculated by using a linear blending rule with the values of pure components [20]. To account for non-linear behaviors of DCN based on the values of neat components [21], a statistical regression using a Scheffé simplex-polynomial [22] was developed based upon the experimental DCN database [7]. The DCN can be predicted within the uncertainty of 1.8 (3 sigma). Utilizing all of the 176,851 mixtures, the set of mixtures that satisfactorily generate the value(s) of single or combined CPTs can be determined. Our previous measurements [11] showed that the CPT measurement uncertainties are < 0.01 for H/C ratio, < 6 g/mol for MW, < 1 for DCN, and < 1 for TSI. The reported sets of constrained surrogate mixtures are conservatively determined here, based upon imposing an error band for each CPT three times these values. Figure 1 summarizes the number of possible mixtures matching the imposed CPT constraints. In general, the more CPT parameters included in determining the constrained sets, the fewer the number of surrogate mixture solutions. When all four CPTs of the Model Fuel are utilized, the number of possible mixtures is reduced to 673. The significance of the CPT constraints in terms of the distribution of chemical functional groups is shown in Fig. 2, displaying the contributions of each CPT to constraining chemical functional group distributions. Figure 3 shows the comparison of the chemical functional group distributions for the target Model Fuel and two types of surrogate mixtures; one set is extracted by imposing only H/C ratio and the other set by considering all four CPTs. The error bars in the figure represent the span of values determined for each of the chemical functional groups. In general, the surrogates formulated by considering all four CPT’s simultaneously reproduce the known functional group distribution of the Model Fuel reasonably well. However, the surrogate mixtures constrained only by H/C ratio fail to do the same, particularly for important chemical functional groups, such as (CH₂)ₙ and CH₃. The above
results indicate that the chemical properties of a target fuel, that are critical to predicting full pre-vaporized global combustion behaviors, can be accurately captured by simultaneously imposing all four CPTs constraints. The potential impacts of coupled fuel physical and chemical property effects can be investigated by extending the above analyses. We considered five additional fuel physical properties (density, viscosity, surface tension, enthalpy of vaporization, and enthalpy of combustion) utilizing the methods implemented in [19]. Among the five fuel physical properties, the heat of combustion is strongly correlated with H/C ratio [11], while kinematic viscosity strongly correlates with MW, exhibiting a Pearson coefficient of 0.96 in all 176,851 initial mixtures. This result suggests that the chemical properties can be well defined by emulating all four CPTs, while the fuel physical properties can be matched by appropriately choosing the surrogate components utilized in the procedure.

The statistical analyses shown above indicate that applying DCN in analyzing fuel combustion behaviors leads to significant constraints as to the chemical functional distribution represented by a complex fuel mixture. To consider integrating physical and chemical property emulation cases, a wider set of surrogate components is required, especially for emulating preferential vaporization (distillation curve) effects. Thus, we constructed a QSPR regression based on our DCN database [6, 7, 23] and some of pure component values [17, 24]. The objective of our QSPR regression exercise is to analyze the response of DCN to the specific chemical functional groups, rather than to establish a comprehensive QSPR regression. For simplicity, cross-correlation terms amongst those groups considered are ignored, see Eq. 1.

\[
DCN_{predicted} = DCN_{ref} \times \sum_{i} a_i \left(\frac{n_i}{n_{i,ref}}\right)^m_i
\]  
(Equation 1)

Here, \(a\) and \(m\) are the constants subjected to regression, and \(i\) represents each chemical functional group shown in Table 1. \(n\) is the number density of chemical functional group in the mixture, derived from multiplying the number of chemical functional group with the mole fraction of each component in case of mixtures. The 2\(^{nd}\) generation surrogate mixture [7] is used as a reference (\(DCN_{ref} = 48.5\)). Figure 4 shows the comparison between the measured DCN and the predicted DCN values yielded from the multivariate regression. The DCN value of a mixture can be predicted within the uncertainty of 3.5, defined as standard deviation between the measured and predicted values. Although the uncertainty from the regression results are found to be slightly larger than typical measurement repeatability (~ 1 DCN), it remains sufficient to constrain the chemical functional distribution of a surrogate formulation as discussed above.

Figure 5 shows the sensitivity analysis for DCN of the target Model Fuel to each of the key chemical functional groups. The logarithmic sensitivities are derived by perturbing individual chemical functional group abundance and monitoring the response of DCN. As clearly shown in Fig. 5, the DCN is primarily sensitive to changes in the \((\text{CH}_2)_n\) group abundance, with some additional more moderate sensitivities the \(\text{CH}_2, \text{CH}_3, \) and benzyl-type group abundances. Considering the test conditions of DCN determination in an IQT, a strong sensitivity to the \((\text{CH}_2)_n\) group abundance can be attributed to the chemical kinetic potential of such groups to promote low...
temperature chain branching reactions. However, it is also noteworthy that the \((\text{CH}_2)_n\) group contribution also reflects the propensity of thermal decomposition of fuel and fuel radicals to form relatively small hydrocarbon species at higher temperatures. The \(\text{CH}_2\) group mainly exists in alkyl benzene, demonstrating a moderate role of promoting the DCN value. In the case of \(\text{CH}_3\) and benzyl-type groups, they are yielded primarily by H abstraction reactions, consuming active radical species in the oxidation of molecule containing these structures. Thus, their contributions correlate negatively with the DCN value.

In addition to providing important insights as to the roles of each functional group structure to the DCN of a particular mixture, the QSPR regression provides the ability to now consider the variation of surrogate component selection along with CPT emulation to consider both physical and chemical property effects on multiphase combustion behavior. Our future work will apply this approach to offer methodologies that can be applied in multi-phase experiments to decipher the coupled roles of physical and chemical properties on combustion observations.

4. Conclusions
A methodology to simulate the chemical structure of complex chemical mixtures such as real aviation fuel has been investigated based on chemical functional group representation of a fuel. A total of six chemical functional groups, 1) \(\text{CH}_2\), 2) \((\text{CH}_2)_n\), 3) \(\text{CH}_3\), 4) \(\text{C}\), 5) \(\text{CH}\), and 6) benzyl groups were considered and their relationships to the CPT constraints were statistically analyzed with a Model Fuel, composed of twelve components. Statistical analysis reveals that matching all four CPTs constrains the chemical functional group distribution in surrogate formulation. Based on a statistical analysis revealing the strong relationship of chemical structure and DCN, a quantitative structure-property relation (QSPR) regression has been performed using a DCN database. A sensitivity analysis of DCN QSPR regression shows that the DCN is strongly influenced by the abundance of \((\text{CH}_2)_n\) groups, followed by \(\text{CH}_2\), \(\text{CH}_3\), and benzyl groups, whereas \(\text{C}\) and \(\text{CH}\) groups are of little influence.

5. Acknowledgements
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6. References
Sub Topic: Internal Combustion and Gas Turbine Engines


