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# Emulating the Combustion Behavior of Real Jet Aviation Fuels by Surrogate Mixtures of Hydrocarbon Fluid Blends: Implications for Science and Engineering

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**ABSTRACT:** We have demonstrated previously that a (surrogate fuel) mixture of known pure hydrocarbon species that closely matches four combustion property targets (the derived cetane number (DCN), the hydrogen to carbon molar ratio (H/C), the threshold soot index (TSI), and the average molecular weight) of a specific jet fuel, displays fully prevaporized global combustion kinetic behaviors that are closely consistent. Here, we demonstrate a similar result can be obtained by formulating surrogate hydrocarbon fluid mixtures from distillation cuts of molecular class hydrocarbons or even real gas turbine fuels (for which the specific molecular species classes are no more than qualitatively known). Fully prevaporized chemical reactivities of hydrocarbon fluid surrogate mixtures and real jet fuels are compared using a high pressure flow reactor at 12.5 atm pressure, over the temperature range 500–1000 K, at stoichiometric conditions, and for the same fixed molar carbon content. Results are reported for two different real target jet fuels, a global average Jet-A (POSF 4658) used in numerous publications as a reference target fuel, and a military JP-8 (POSF 5699), both of which contain about 25–30% cycloalkanes (by weight). The surrogate mixture to emulate the Jet-A property targets was formulated from three (normal-paraffinic, iso-paraffinic, and alkyl-aromatic) commercial narrow distillation cut hydrocarbon fluids containing few cycloalkanes. The surrogate mixture for the JP-8 sample was formulated using two different (paraffinic, alkyl aromatic) hydrocarbon solvent cuts and a synthetic, iso-alkane jet fuel (IPK POSF 5642). The composition of the paraffinic fluid was nearly half cyclo paraffinic components (by weight) with similar fractions of normal and iso-paraffinic species. Experimental results for the Jet-A surrogate mixture closely parallel the data for the fully prevaporized Jet-A real fuel, as well for prior surrogate mixtures of *n*-decane/*iso*-octane/toluene and *n*-dodecane/*iso*-octane/*n*-propylbenzene/1,3,5-trimethyl benzene, all formulated to share the same combustion property targets. The reactivity comparisons for the JP-8 surrogate mixture and real fuel were of similar quality to the Jet-A comparisons but were improved in the reactivity transition characteristic of hot ignition to chemically branched kinetic conditions. The improvement is hypothesized to be mostly a result of cyclo alkane content differences between the specific surrogate mixtures compared to the real fuels. Sooting properties for the JP-8 hydrocarbon fluid surrogate and fuel are compared in fundamental diffusion flames and a model gas turbine combustor elsewhere.<sup>1</sup> The collective results support that surrogate fuels, each with similar fully prevaporized global combustion behaviors but different physical properties (viscosity, surface tension, class composition, distillation curve) and even different functional class distributions across their distillation curve, can be formulated using mixtures of hydrocarbon fluids. This ability can be used to advantage to investigate experimentally the relative importance of physical and chemical kinetic properties in both fundamental and applied multiphase combustion experiments. Surrogates formulated from varied sources of hydrocarbon fluids of differing molecular classes, and even fractional distillation cuts from fluid streams can facilitate unraveling the fuel property sensitivities of combustion/emissions performance for specific combustor configurations and operating conditions.

## 1. INTRODUCTION

Fuel specification standards for each end-use and certification testing methodologies are essential to ensure that a fuel is fit-for-use, that is, will operate properly, in a specific engine technology.<sup>2</sup> Recently, much effort has been given to extending fuel specification standards to encompass blending of alternative fuel stocks. These include those derived through Fischer–Tropsch processing of natural gas, biomass, and coal, or hydroprocessing of esters and fatty acids (bio-oils) with petroleum derived aircraft gas turbine fuels stocks.<sup>3</sup> A myriad of tests devoted to fuel system and materials compatibility, and substantial rig and full scale engine testing were performed to support evolution of the standards and certification decisions.

Large volumes of candidate alternative fuels have been required for these extensive endeavors, setting a high bar in terms of the minimum volumes of alternative fuel candidates needed for reaching positive indications on their viability as gas turbine fuels. Better rules and tools are needed to relate fuel property effects on critical combustion performance issues, to improve the robustness and efficacy of the alternative fuel screening process and to reduce the full-scale rig and engine testing required to approve a candidate fuel.<sup>2,4</sup>

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The compositional complexity of any real fuel presents severe challenges in terms of defining how to compare different fuels in a scientific manner that quantitatively relates physical and chemical kinetic properties to multiphase combustion behaviors. Data on jet fuel properties collected by the Defense Energy Support Centre (DESC)<sup>5</sup> show that fuels that fall within present certification standard guidelines can have relatively large variability in specific physical properties and chemical compositions. For example, in 2009 the hydrogen content of JP-8's varied from 13.4 to 15.1% by mass, with most lying between 13.8 and 14%. Aromatic fraction varied from 12 to 24%, with most having contents between 16 and 22% by volume. An important question remains: "At what level of detail must these variations be assessed in order to generate a more quantitative understanding of their effects on multi-phase combustion?" Major difficulties reside in what to select as key characterization parameters and how to then emulate the important properties of any particular fuel produced by the interaction of hundreds of molecular structures using numerical combustion models of manageable size (numbers of relevant species, detailed chemistry, and property relations). Integral to developing the needed insights and tools is the concept of "surrogate fuel" formulation.

Surrogate fuels are typically mixtures composed of a handful of defined chemical components that by their combination reasonably replicate the physical, chemical kinetic, or physical/chemical properties of a more complex, real fuel. To replicate detailed physical properties (e.g., distillation curve and vapor dome properties, molecular class distribution over the distillation curve, viscosity, surface tension, density, etc.) generally requires larger numbers of components of varying molecular weight. On the other hand, the selection of large numbers of surrogate species makes the challenge of also replicating chemical kinetic and gas phase transport property parameters significantly more complex. In constructing surrogate fuel mixtures, the key issues are (1) selection of the specific surrogate component(s) to use in formulating mixtures to represent the real fuel; (2) methodologies for defining appropriate mixture(s) that emulate real fuel properties; (3) proofing that the formulated mixtures indeed emulate real fuel behaviors of interest; and finally, (4) developing and validating the physical property<sup>6–10</sup> and detailed kinetic chemical models<sup>11</sup> to predict those behaviors. This paper addresses only emulating the fully prevaporized global combustion behaviors of a real target fuel. Other works in the literature have addressed only emulating the physical properties of a real target fuel, and there are universal interests in determining the combined effects in multiphase combustion environments. The present work is directed toward understanding how best to formulate test fuels to examine the relative importance of chemical and physical properties in multiphase experiments, at both small laboratory and larger, applied scales.

A voluminous literature addressing the fully prevaporized combustion properties of single species, and to a lesser extent, surrogate mixtures of several pure chemical species compared with those of real fuels already exists.<sup>7,8</sup> Most of these works are composed of studies involving only small scale laboratory experiments, where the cost of the surrogate fuel mixtures to be studied is of less concern due to the small quantities of fuels that are required. However, some types of single species components (e.g., weakly branched alkanes, heavier alkyl aromatics, or cycloalkanes) are sometimes prohibitively expensive, even for these small scale tests. A particular concern

of the present work is the much larger volumes of surrogates needed for studies in applied venues such as gas turbine rig combustors. Infrequently, mixtures of commercially available hydrocarbon fluids ("solvents" mixtures, or hydrocarbon "distillation cuts") have been utilized in large scale testing to vary selected physical and chemical properties or to test material compatibilities with fuels. However, methodologies for formulating mixtures of several such materials (or several other real fuels) that would replicate the fully prevaporized global kinetic behavior of a specific real fuel target have received less attention in general and, to our knowledge, no attention in laboratory scale studies. The present paper applies the same formulation concepts discussed in our earlier work<sup>6–10</sup> that used mixtures of a small number of known species to replicate fully prevaporized real fuel global kinetic properties. These concepts are applied here to produce and test surrogate formulations composed of several hydrocarbon fluids, without the necessity of acquiring detailed information regarding their respective chemical compositions. However, chemical class compositions of the materials used in these studies are presented to aid in interpreting results.

In some of the earlier work,<sup>7,8</sup> the surrogate formulation concept was tested experimentally by comparing fully prevaporized real fuel combustion properties with those of the formulated surrogates over a wide range of experimental configurations, equivalence ratios, and pressures. Auto ignition delays in reflected shock and rapid compression machines, as well as laminar premixed and diffusion flame experiments, utilized fuel/air or weakly diluted mixtures, while highly diluted mixtures were studied in single pulse shock tube speciation and flow reactor reactivity experiments. The laminar flame experiments included not only flame speed measurements, but strained flame behaviors in opposed flow configurations, as well as soot laser extinction characterizations in laminar jet diffusion flames.

Here, we report only flow reactor reactivity comparisons at stoichiometric conditions for two target real jet fuels and a hydrocarbon fluid mixture formulated for each fuel. In companion work,<sup>1,12</sup> laser extinction measurements of soot in fundamental laminar jet diffusion flames and a model gas turbine combustor experiments for a real JP-8 fuel and a corresponding surrogate mixture (developed in this work) are also reported. The full experimental range of applying the remainder of experimental venue comparisons made previously<sup>8</sup> were beyond the scope and resources of the present work. However, the prior results<sup>8</sup> suggest that the character of the flow reactor reactivity and sooting behavior results are strong indications of the quality of comparisons to be expected in the other venues and conditions used in initially developing and testing the surrogate formulation concepts applied here.

Formulations of first (*n*-decane/*iso*-octane/toluene) and second generation (*n*-dodecane/*iso*-octane/*n*-propylbenzene/1,3,5 trimethyl benzene) surrogate mixtures that share the same combustion property targets as a specific real fuel and its hydrocarbon fluid surrogate<sup>7,8</sup> can be used to provide detailed and reduced chemical kinetic models to describe the fully prevaporized global combustion behaviors for both the real fuel and its hydrocarbon fluid surrogate.<sup>9</sup> Continuing model development has extended modeling species options to include not only first and second generation components but other *n*-alkanes from C<sub>8</sub>–C<sub>16</sub> and *iso*-cetane. This first step of broadening the range of combustion property targets that can be accommodated is important for integrating both physical

and chemical property emulation, a subject for important future work.

## 2. SURROGATE FORMULATION STRATEGY

An initial focus of a recent United States Air Force Multi University Research Initiative centered at Princeton University<sup>13</sup> was to develop and test (mostly at the laboratory scale) a fundamental methodology for selecting surrogate components, and formulating mixtures of them, that emulate the fully prevaporized combustion behavior of specific real jet fuels. The work concentrated first on emulating fully prevaporized combustion phenomena, with a continuing realization that the approach must eventually encompass physical properties important to the multiphase combustion characteristic of gas turbine applications. Hypotheses were put forward<sup>6</sup> that mixtures of a selected set of pure surrogate component species that closely replicate the same “combustion property targets” as the specific real fuel would share similar global combustion properties. Mixtures composed of several single organic structure components were used to test the formulation strategy by comparing their fully prevaporized combustion properties *experimentally* against those of the subject real fuel.<sup>6–9</sup>

Fundamentally, “combustion property targets” relate specific aspects of the combustion behavior of the surrogate mixture to that of a specific real fuel. Those property targets considered thus far are (1) the specific real fuel hydrogen-to-carbon-ratio (H/C); (2) a measure of the real fuel sooting propensity (the Threshold Sooting Index or TSI); (3) a measure of overall chemical kinetic reaction potential of the real fuel (represented by the Derived Cetane Number or DCN); and (4) the real fuel average molecular weight (MW). These targets were selected because of their relation to real fuel: autoignition, heat release rate, laminar burning rate, adiabatic flame temperature, local mixing-limited stoichiometric constraint, extinction, lean blow-out limit, and sooting. Determining each of these combustion property targets for the surrogate components, surrogate mixtures, and real fuel samples can be accomplished through simple small scale empirical tests, each of which require only small-volume samples. It is well-known that petroleum derived fuels are composed primarily of various fractions of paraffins and alkyl aromatics. With this very basic information, a significant benefit of this approach is that *no quantitative, detailed chemical composition analyses of the real fuel are required to formulate the surrogate mixture*. The chemical structure of the target real fuel is only reflected in the selection of surrogate fuel components that collectively encompass the important distinct functionalities found within it. Through the appropriate mixture of surrogate components, the mixture must also be capable of sharing the same combustion property targets as the target fuel.

The strategy was first tested extensively with two different selections of pure surrogate components: a “first generation” *n*-decane/*iso*-octane/toluene set<sup>7</sup> and “a second generation” *n*-dodecane/*iso*-octane/*n*-propylbenzene/1,3,5-trimethylbenzene set.<sup>8</sup> It was known at the outset that mixtures of the first generation components could not always replicate simultaneously all four selected combustion property constraints found for petroleum-derived jet fuels, especially the TSI and average molecular weight. In ref 7, replication of these two combustion property targets was sacrificed in order to achieve robust kinetic modeling tools to analyze surrogate fuel experimental observations. However, compositions of the second generation surrogate components permit reasonable matching of all of the

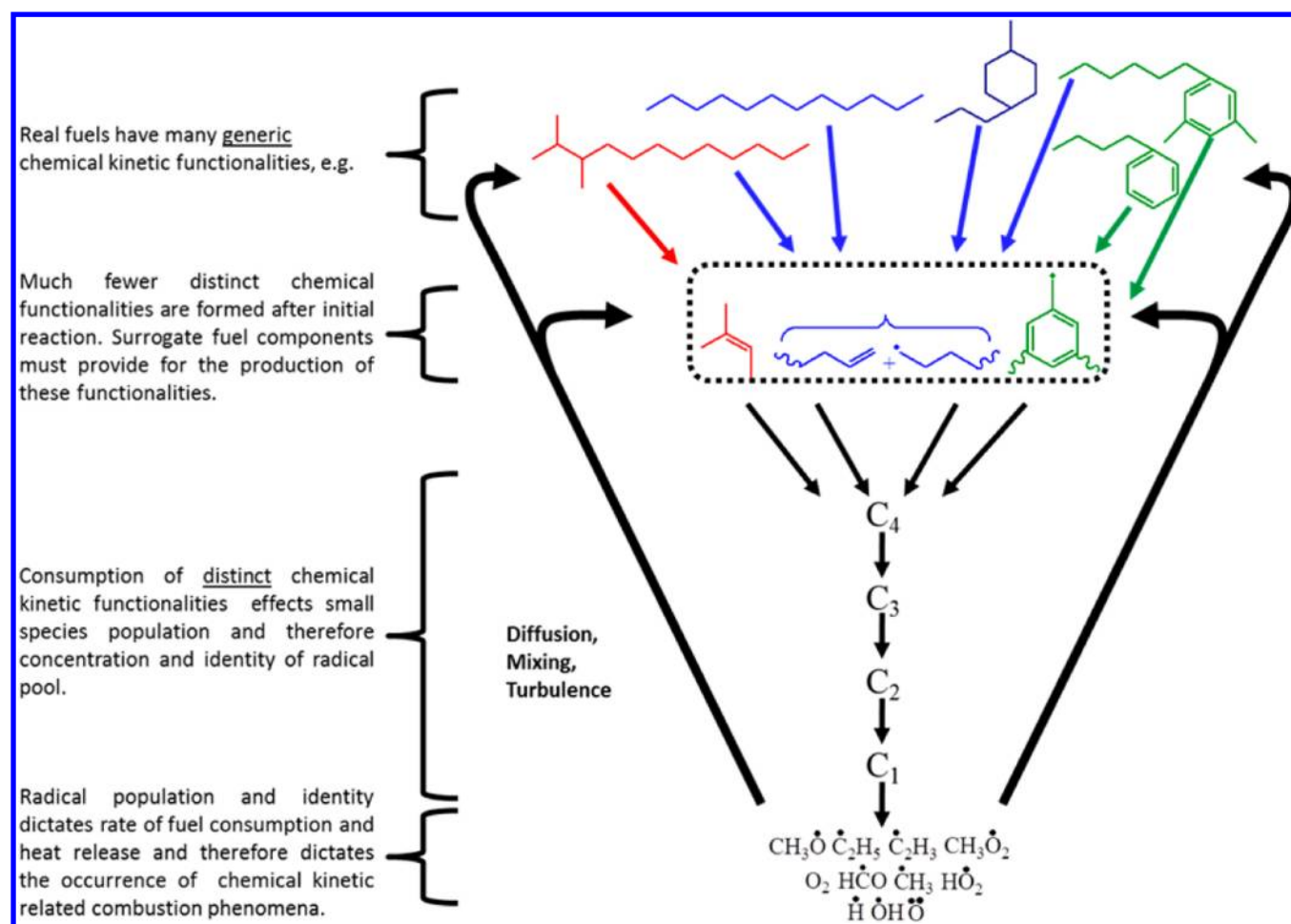
combustion property targets found for any of the jet fuels surveyed within the last several annual DESC data summaries; see for example ref 5, including paraffinic synthetic fuel stocks. Surrogate mixtures based upon both first and second generation components were formulated to replicate combustion property targets of a specific jet fuel sample (Jet-A POSF 4658) obtained from Wright-Patterson Air Force Base and utilized in many other surrogate works appearing in the literature, see for example ref 14.

The combustion performances of the formulated surrogate mixtures and real fuel behaviors were *experimentally* compared directly in a wide range of small scale laboratory experimental venues that encompass: reflected shock ignition delay, single pulse shock species evolution (2nd generation only), rapid compression machine ignition properties, flow reactor reactivity, and fundamental laminar flame phenomena covering premixed burning rate, premixed strained extinction, diffusive strained extinction, and laser extinction measurements of soot within annular jet diffusion flames (2nd generation only). The second generation POSF 4658 surrogate component mixture produced fully prevaporized combustion observations in close agreement to those found for the fully prevaporized real fuel in all of the above fundamental venues with the only exception being for two-stage ignition observations in a rapid compression machine.<sup>8</sup> Typical jet fuels contain no oxygenated species, only limited amounts of multi-ring species, and are principally composed of varying amounts of *n*-alkanes, *iso*-alkanes, *cyclo*-alkanes, and mono-ring alkylated aromatics. These structures, independent of their specific molecular weight distribution within the fuel, essentially present the possibility to form only three *distinct chemical functionalities*, *n*-alkyl, *iso*-alkyl, and benzyl-type functionalities. For fully prevaporized premixed combustion behaviors, the thesis put forth in ref 8 was that as long as the fuel generates the same fractions of these distinct chemical functionalities, the molecular weight distribution (over the range found in jet fuels) of each molecular type is of little significance. In fact, it was found that several different second generation mixtures were capable of reproducing the same real fuel combustion property targets as observed for POSF 4658.<sup>8</sup> The close similarity of the fully prevaporized combustion kinetic behavior of each of the tested POSF 4658 fuel surrogate compositions was shown to be consistent with the fact that each of the alternative second generation molecular mixtures as well as the first generation mixture yielded essentially the same distribution of *distinct chemical functionalities* as measured by the mass fractions of methyl, methylene and benzyl-type molecular groups as present in the chemical structures of each surrogate fuel.

Other concurrent research<sup>15</sup> hypothesized that petroleum derived diesel fuels (which are also principally composed of molecules classified as aromatic, normal alkyl (~normal-alkanes) and isomerized alkyl (~methylated-alkanes) as the major fractions, with variable amounts of cycloalkanes, alkenes, and polyaromatics) could be replicated by emulating their specific chemical functional group distributions. Using nuclear magnetic resonance, 16 discrete chemical functional entities were experimentally identified to be present in diesel fuels, but preferences as to the relative importance of each group in replicating global combustion properties remained arbitrary.

On the other hand, our continuing efforts on surrogate formulation have suggested that the three molecular fragments mentioned above are very useful (or even adequate) measures





**Figure 1.** Schematic representation of surrogate formulation methodology based upon functional group interactions, adopted from Dooley et al.<sup>8</sup>

of the *distinct chemical functionalities* that define the global combustion properties of fully prevaporized jet fuels. We have further investigated chemical functionality relationships by emulating the global combustion behavior of a synthetic gas turbine fuel feed stock produced from natural gas by Syntroleum,<sup>9</sup> a moderately methylated alkane alternative fuel, 2,6,10 trimethyl dodecane (Farnesane, Amyris Inc.),<sup>10</sup> and the presence of cycloalkanes in petroleum derived Jet-A fuel and its surrogate mixture.<sup>16</sup> We found that any effects of weakly branched alkanes and cycloalkanes on global combustion behavior were sufficiently small such that real fuels containing them could be reasonably emulated by considering only the three distinct chemical functionalities, as measured by the molecular metrics of  $CH_2$  (methylene),  $CH_3$  (methyl), and  $C_6H_5CH_2$  (benzyl) molecular groups. Though in an indirect manner, the results presented in this manuscript give further insights to the significance of cycloalkane presence on surrogate emulation of real fuel behavior.

In summary, the destruction of an initial fuel molecular composition, (however, it occurs) results in a common, smaller dimensional intermediate species distribution that strongly controls the active radical pool evolution during combustion, and thus, the global combustion kinetic behavior of real fuels. Therefore, the central issue in emulating (and in controlling) real fuel chemical kinetic behavior is controlling the distinct chemical functionalities associated with the real fuel initial molecular destruction. This concept is pictorially described in Figure 1.

It can be inferred by these observations that chemical reactions occurring between large molecular weight radical species and fuel components or large molecular weight intermediates are of limited importance in formulating surrogates. The above observations suggest that larger numbers of surrogate fuel initial components, properly blended, can produce the same fully prevaporized chemical kinetic behavior, but can also possess significantly different physical properties, for example, distillation curve, vapor dome, and viscosity. Below, we test this hypothesis experimentally by formulating surrogate mixtures from multicomponent hydrocarbon fluids that have been classified by molecular class structure and distillation cuts as well as by using a real alternative iso-paraffinic fuel.

### 3. EXPERIMENTAL PARAMETERS AND PROCEDURES

Two different types of surrogate mixtures were prepared individually to emulate a global average Jet-A (POSF 4658) and a military JP-8 (POSF 5699) jet fuel. As noted above, Jet-A (POSF 4658) has been used as a bench mark jet fuel in many previous works including our own, since its physical and chemical properties are very similar to the global average of fuels found in the field. Only small quantities of this reference fuel remain at this time, too small an amount for this fuel to serve as a reference in future applied experiments. Instead, JP-8 (POSF 5699) has been used more recently as a reference fuel in such studies, and this fuel was to be employed in model combustor studies conducted at Pennsylvania State University, reported elsewhere.<sup>1</sup> Flow reactor reactivity profile comparisons for the two real fuels also provides an opportunity to demonstrate that real fuels with closely

Table 1. Fuel Class Structure Compositions (Mass %)

	POSF/vendor	<i>n</i> -paraffins	iso-paraffins	cyclo-paraffins	aromatics
Jet-A <sup>a</sup>	4658	19	31	28	21
JP-8 <sup>a</sup>	5699	24	32	24	20
IPK <sup>a</sup>	5642	0.1	99	0.33	0.33
ISOPAR L <sup>a</sup>	Exxon-Mobil	0	94	6	0
EXXSOL D95 <sup>a</sup>	Exxon-Mobil	26	29	44.5	0.5
SOLVESO 100 <sup>a</sup> /150 <sup>b</sup>	Exxon-Mobil	0	0	0	100
NOPAR 12 <sup>b</sup>	Exxon-Mobil	96	4	0	0

<sup>a</sup>From Air Force Research Laboratory GC × GC analyses. <sup>b</sup>From prototypical commercial analyses supplied by Exxon-Mobil Corporation. The data are regarded as semiquantitative and are presented here for the purposes of discussion.

shared combustion property targets have essentially the same fully pre vaporized combustion kinetic behaviors.

Three commercial, narrow distillation cut hydrocarbon fluids were used to produce the Jet-A (POSF 4658) surrogate mixture. Each distillation cut fluid was composed of a well defined carbon number range and molecular class structure that matched relatively well the average molecular weight range of real jet fuels. The commercial reference names for these fluids are (1) NORPAR 12 (NP12), a mixture of >98% (mainly C<sub>11</sub>–C<sub>12</sub>) *n*-alkanes;<sup>17</sup> (2) ISOPAR L (IPL), a mixture of > 99% (mainly C<sub>11</sub>–C<sub>14</sub>) iso-alkanes;<sup>18</sup> and (3) Solvesso Aromatic 150 (A150), a mixture of (primarily C<sub>10</sub>–C<sub>11</sub>) alkyl-benzenes with very small amounts of naphthalenes.<sup>19</sup> The surrogate components used to emulate Jet-A (POSF 4658) contain only small amounts of cyclo-alkanes.

Three different hydrocarbon fluids were used to formulate the surrogate mixture for JP-8 POSF 5699: (1) EXXSOL D95 (D95) a dearomatized fluid, a mixture of normal alkanes (primarily C<sub>12</sub> through C<sub>15</sub>);<sup>20</sup> (2) Solvesso Aromatic 100 (A100), a mixture of C<sub>9</sub>/C<sub>10</sub> alkyl-benzenes;<sup>21</sup> and (3) IPK (POSF 5642), an iso-paraffinic kerosene synthetic jet fuel<sup>4</sup> obtained from the Air Force Research Laboratory, Dayton, Ohio. IPK is a wide distillation range fluid composed entirely of iso-paraffinic components (produced by Sasol). EXXSOL D95, while being composed only of paraffinic components, contains large amounts of cyclo-alkanes, in addition to normal and iso-paraffins. It is to be noted that both Jet-A (POSF 4658) and JP-8 (POSF 5699) also contain small quantities of cyclo aromatics (e.g., indans, tetralins, etc.).

NORPAR, ISOPAR, EXXSOL, and Solvesso alkyl aromatic (A) fluids used in this study are trademarked hydrocarbon distillation cuts produced by Exxon-Mobil Chemical Co. NORPAR dearomatized fluids are no longer available commercially, another factor in utilizing EXXSOL D95 as a paraffinic component in developing the JP-8 (POSF 5699) surrogate.

Table 1 presents the class molecular structure distributions of target fuels and surrogate components used in this study. The data are for the specific materials used. The combustion property targets of the two jet fuels, each of the hydrocarbon fluids and the respective mixtures of these fluids were determined experimentally as described below.

**Derived Cetane Number.** Each DCN measurement was performed in an identical fashion as described in ref 7 using an Ignition Quality Tester (IQT) apparatus.<sup>22,23</sup> The ASTM D 6890<sup>22</sup> procedure for determination of autoignition characteristics of diesel fuels was followed. Each DCN value reported here is the result of an average of thirty-two individual experimental measurements performed on at least three separate samples, that is, the average of a total of 96 individual measurements. The resulting standard deviation in the reported DCN is less than ± 0.6 derived cetane numbers. For determining DCNs of the hydrocarbon fluid mixtures, binary and tertiary mixtures of the fluids used in each surrogate were prepared by mass measurement to delineate the influence of each individual hydrocarbon fluid on the mixture DCN. The DCN is a global indication of a fluid chemically reactive character, while flow reactor reactivity experiments delineate specific reactivity characteristics over a range of reactive temperatures. It deserves mention that a DCN measurement requires only about 20 min, while a flow reactor reactivity experiment characterization requires eight hours or longer.

**Threshold Sooting Index.** The threshold soot index is defined by Calcote and Manos<sup>24</sup> as,

$$TSI = a \left( \frac{\text{Molecular weight}}{\text{Smoke point}} \right) + b$$

where the smoke point is the maximum smoke free laminar diffusion flame height<sup>25</sup> (mm), molecular weight is in g mol<sup>−1</sup>, and *a* (mol mm g<sup>−1</sup>) and *b* (dimensionless) are experimental constants. The hydrocarbon fluid component TSI values utilized in this work were obtained by the smoke point technique,<sup>24–27</sup> as described in ref 27. The TSI values quoted in this study for the hydrocarbon fluids and their mixtures were calculated from the experimentally determined smoke height measurements using the ASTM D 1322<sup>26</sup> methodology and the average molecular weights for each of the surrogate components. The TSI linear mixture rule demonstrated in refs 25 and 27 for the surrogate fuel components has been used in this work.

**Mixture Averaged Molecular Weight.** ASTM methods presently found in the literature for determining the average molecular weight of hydrocarbon mixtures deduce this quantity using empirical correlations of more easily measurable parameters such as mixture boiling point and fluid viscosity. These methods have typical uncertainties of as much as 20 units for the average molecular weight of jet fuels. We have developed an improved method for providing average molecular weight of fuel samples, based upon application of the ideal gas law.<sup>28</sup> The repeatability of the measurements was less than ±1.5 measurement units for the data reported here. The absolute uncertainty of the new measurement method is conservatively estimated to be less than 3% (<5 g/mol, 1 σ). The average molecular weights of each of the jet fuels and hydrocarbon fluid surrogate components were determined using this new method. Some of the values differ from those reported in our earlier publications with the earlier value uncertainties encompassing the present data. The TSI values reported below were determined using the average molecular weights also reported here.

**Hydrogen: Carbon Ratio (H/C).** The H/C molar ratio of each of the jet fuel samples and each of the hydrocarbon fluid surrogate components were determined experimentally using CHN analysis following the methodology of ASTM D 5291.<sup>29</sup>

**Formulating the Surrogate Mixtures.** Tables 2 and 3 summarize the combustion property target data obtained for the surrogate mixture components used to emulate the real target fuels (Jet-A POSF 4658 and JP-8 POSF 5699). The use of a paraffinic surrogate component with high H/C, high DCN, and low TSI (e.g., D95 and NP12) and an aromatic surrogate component with low H/C, low DCN, and high TSI (e.g., A100, A150, IPK) allows for independent control and matching of H/C and TSI of the real fuel but fails to reproduce the DCN of the real fuel. In order to adjust the DCN independently of the H/C and TSI, a surrogate component with lower DCN, but relatively similar H/C and TSI to the paraffinic component, is required. In our pure surrogate component studies,<sup>7,8</sup> this role was fulfilled by *iso*-octane, but this surrogate component is prohibitively expensive in large volumes. As an alternative, we utilized an *iso*-paraffinic hydrocarbon fluid (e.g., IPK, Iso-Par L) to formulate the surrogate mixtures, which share all four combustion property targets of the target real jet fuel and also provide for the replication of

the target fuel molecular structures. The procedure for formulating the specific surrogate mixture to emulate the target jet fuels is described below for the example of Jet-A POSF 4658 as a target fuel. An analogous procedure was applied for developing the reported JP-8 POSF 5699 surrogate mixture.

**Table 2. Combustion Property Target Data for the Jet-A (POSF 4658) Surrogate Components**

hydrocarbon fluid	DCN	H/C	MW [g/mol]	TSI
NORPAR 12 (NP12)	73.8	2.14	156.4	7.9
ISOPAR L (IPL)	31.7	2.19	175.7	13.4
Solvesso 150 (A150)	8.4	1.34	129.8	81.8

**Table 3. Combustion Property Target Data for the JP-8 (POSF 5699) Surrogate Components**

hydrocarbon fluid	DCN	H/C	MW [g/mol]	TSI
EXXSOL D95 (D95)	58.3	2.04	176.7	13.9
IPK (POSF 5642) (IPK)	31.7	2.15	148.5	11.1
Solvesso 100 (A100)	7.9	1.34	116.4	62.5

It is to be noted that the real target fuels both contain significant amounts of cycloalkanes (Table 1). Of the surrogate components, only D95 contains large amounts of cycloalkanes, while all others contain little or no cycloalkanes. In our earlier publications, we have shown that the use of highly branched *iso*-alkanes and no cycloalkane components suffices to emulate the prevaporized combustion behaviors of real fuels that contain weakly branched *iso*-paraffins and cycloalkanes, through the distinct functionality concept. This hypothesis is further tested by the surrogate formulation of Jet-A (POSF 4658), without inclusion of cycloalkanes in the surrogate, and those surrogate formulations for JP-8 (POSF 5699) based upon D95, ~45 mass % cycloalkane, as one of its components.

The combustion property target data as determined using the methods described above were delineated by an extreme vertices matrix to parametrize, in a comprehensive and consistent fashion, the DCN, H/C, MW, and TSI as a function of NP12, IPL, and A150 mol fraction. Several mixtures of NP12, IPL, and A150 that would be suitable as a surrogate fuel mixture for Jet-A (POSF 4658) were computed by a statistical technique described previously.<sup>8</sup> A three-

component mixture that closely shared the DCN, TSI, and H/C of the target fuel was then selected (Table 4). Table 4 also summarizes the combustion property targets and compositions of the Jet-A (POSF 4658) first and second generation surrogates composed of the noted pure components.<sup>7,8</sup>

**3.1. Variable Pressure Flow Reactor Experimental Procedures.** The chemical reactivity behaviors of each fuel and the associated surrogate in terms of low, negative temperature coefficient, hot ignition kinetic, and auto thermal acceleration to high temperature chain branched kinetics can be obtained through reactivity experiments conducted in the Princeton Variable Pressure Flow Reactor. The design, instrumentation, and experimental methodology of this apparatus are described in detail elsewhere,<sup>30–33</sup> and only a brief summary of its configuration and operation for the present experiments is provided here.

Nitrogen carrier gas is heated by electric resistance heaters and homogeneously mixed with oxygen at the entrance to a movable conical shaped mixer/diffuser section that expands from a 2.5 cm diameter mixing region to a 10.2 cm internal diameter quartz test section. The liquid fuel to be tested is volumetrically metered to a liquid evaporator system (0.02 g/s), where it is gas-blast vaporized into a nitrogen flow at 523 K (1.5 g/s). The diluted fuel vapor flows through a central injector tube and is rapidly mixed with a much larger (~12.57 g/s) flow of N<sub>2</sub>/O<sub>2</sub> carrier mixture using a multijet, opposed flow configuration at the entrance to the mixer/diffuser section. The fuel/carrier gas mixture exits the mixer/diffuser section into the constant area test section at Reynolds numbers of about 6000. The mixer/diffuser and reactor sections are surrounded by thermostatted electrical resistance heaters that maintain the reactor wall temperatures at the desired initial gas temperature (without chemical reaction). At each test point in a reactor study, the fuel vapor flow is cycled on only for a period such that all analytical readings achieve steady-state values (~3 min). The fuel vapor flow is then cycled off after acquiring data and the next test point configuration is established.

The benefits of this procedure are 2-fold. First, it allows the initial gas temperature and wall temperatures to reach the desired steady-state temperature without any effect from chemical heat release. Second, any residues remaining in the analytical equipment from the previous sampled condition are purged continuously by the sampled reactor flow without fuel prior to the next sampling of the reaction zone. At each test point, the reacting mixture is sampled at some axial position downstream of the mixer/diffuser using a hot-water cooled, stainless steel sampling probe. The sampled stream is continuously

**Table 4. Combustion Property Targets for the Target JP-8 (POSF 5699) and Jet-A (POSF 4658), Those of the Kerosene Fuel Range, the Previously Reported First<sup>7</sup> and Second<sup>8</sup> Generation Surrogate Fuel Mixtures and the Formulated JP-8 and Jet-A Surrogates of This Work<sup>a</sup>**

fuel			DCN measured	H/C	MW/g mol <sup>-1</sup>	TSI
Jet-A POSF 4658 <sup>7</sup>			47.1	1.95	157.5 ± 2 <sup>b,c</sup>	24.2 <sup>c</sup>
JP-8 POSF 5699			49.3	1.935	153.9 ± 2.7 <sup>c</sup>	22.4 <sup>c</sup>
kerosene fuel range <sup>19</sup>			30–60	1.84–2.07	N/A	15–26
Jet-A POSF 4658 1st generation surrogate (mole %) <sup>7</sup>			47.4	2.01	120.7 <sup>d</sup>	14.1 <sup>d</sup>
<i>n</i> -decane	<i>iso</i> -octane	toluene	48.6	1.96	138.7 <sup>d</sup>	20.4 <sup>d</sup>
42.7	33.0	24.3				
Jet-A POSF 4658 2nd generation surrogate (mole %) <sup>8</sup>			48.6	1.96	138.7 <sup>d</sup>	20.4 <sup>d</sup>
<i>n</i> -dodecane	<i>iso</i> -octane	1,3,5, trimethyl benzene	47.27	2.025	159.8 <sup>d</sup>	24.7 <sup>d</sup>
40.4	29.5	7.3				
Jet-A POSF 4658 surrogate mixture (mole %)			47.27	2.025	159.8 <sup>d</sup>	24.7 <sup>d</sup>
NORPAR 12	ISOPAR L	Solvesso A 150	49.4	1.93	162.6 <sup>d</sup>	21.7 <sup>d</sup>
42.8	40.6	16.6				
JP-8 POSF 5699 surrogate mixture (mole %)			49.4	1.93	162.6 <sup>d</sup>	21.7 <sup>d</sup>
EXXSOL D95	IPK 5642	Solvesso A 100	70.5	13.1	16.4	
70.5	13.1	16.4				

<sup>a</sup>Standard deviations in DCN measurements are typically ±0.6. <sup>b</sup>Originally reported in refs 7 and 8 as 142 ± 20 g/mol based upon less accurate methodology. <sup>c</sup>Direct experimental determinations as described in refs 24, 26, 27, and 29. <sup>d</sup>Calculated by linear-by-mole mixing rule, as demonstrated to be valid in ref 27.



extracted and convectively quenched by wall heat transfer within the sampling probe. The axial temperature of the reacting flow is measured at the same location as the sampling probe tip using silica-coated R-type thermocouples.

The sampled gas flow is transferred through heated Teflon lines ( $\sim 405$  K) to a series of analytical instruments that include a Fourier transform infrared (FTIR) spectrometer (Nicolet Model 560) for water ( $\text{H}_2\text{O}$ ), an electrochemical oxygen ( $\text{O}_2$ ) analyzer (Infrared Industries Model 2200), and nondispersive infrared (NDIR) analyzers (Horiba model PIR 2000) for carbon monoxide ( $\text{CO}$ ) and carbon dioxide ( $\text{CO}_2$ ). Full vaporization of the fuel is confirmed by FTIR at the start of each experiment.

The temperature of the flow at the sampling location, with all flows established except the fuel flow, varies by less than  $\pm 1.5$  K (relative uncertainty). The end-to-end-absolute uncertainty in measured temperatures is conservatively estimated as  $\pm 6$  K, independent of the location of the mixer/diffuser in the test section. The initial reaction temperature at the sampling location and all sample analytical readings are allowed to achieve steady state before the data are digitally recorded. Throughout the course of each experiment, all flow rates of carrier, diluents, and reactants are constantly monitored and controlled. The reaction pressure is also held constant.

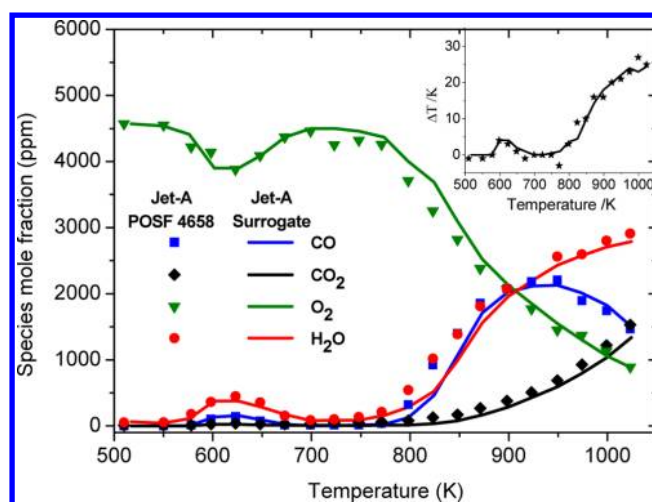
The uncertainties in the reported flow reactor measurements are  $\pm 5\%$  (not less than 30 ppm) in reported species mole fractions. Other estimated measurement uncertainties are  $\pm 0.2$  atm in reported pressures and  $\pm 0.02$  s in the intended residence time for the “reactivity experiments” reported here (1.8 s). In this type of reactor study, the initial temperature of the flow entering the reactor is varied, while the flow rates of each reactant and the carrier gas are all held constant. Reactor wall temperatures are also increased in concert with the increased initial temperatures of the entering flow. The mixer/diffuser is repositioned relative to the sampling location to hold the reaction residence time constant as the initial reaction temperature of the gases is changed. The reaction product distribution and reaction temperature at the sampling location is determined as a function of the initial reaction temperature. The difference between the initial reaction temperature and the sample temperature corresponds to the heat release produced by the reaction over the chemical residence time.

## 4. RESULTS AND DISCUSSION

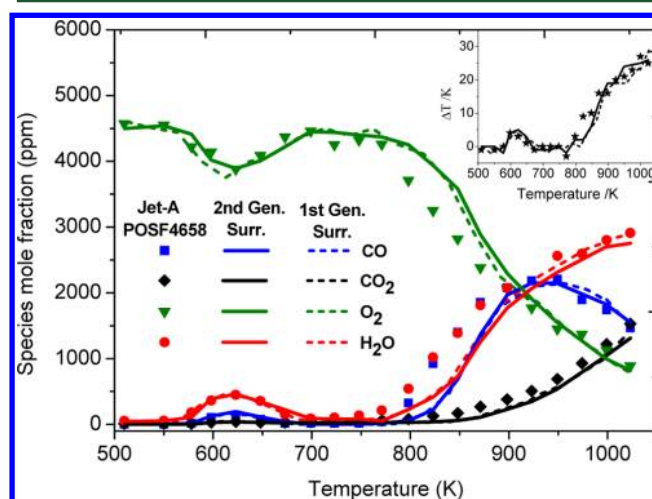
### 4.1. Chemical Reactivity Observations in the Flow Reactor.

**4.1.1. Jet-A (POSF 4658) and Jet-A (POSF 4658) Surrogate Mixture.** The gas-phase chemical kinetic reactivity of the prevaporized Jet-A (POSF 4658) surrogate mixture was determined in the flow reactor over the temperature range, 520–1025 K, to examine if the surrogate emulates the overall reactivity observed for the target Jet-A (POSF 4658) fuel reported previously.<sup>7</sup> Measurements of oxygen ( $\text{O}_2$ ), carbon monoxide ( $\text{CO}$ ), carbon dioxide ( $\text{CO}_2$ ), and water ( $\text{H}_2\text{O}$ ) mole fractions, in addition to heat release ( $\Delta T$ ) were obtained as a function of initial reaction temperature (in  $\sim 25$  K steps). Fuel-dilute conditions with carbon concentrations totaling 0.3 mol % were utilized at stoichiometric reaction conditions for the surrogate fuel. The use of dilute conditions (0.3 mol %) limits axial and radial thermal and concentration gradients within the reactor such that measurements are at essentially adiabatic conditions. The chosen conditions are also identical to those utilized in our prior reactivity studies on Jet-A (POSF 4658) as well as the first generation<sup>7</sup> and second generation<sup>7,8</sup> Jet-A (POSF 4658) surrogate mixtures.

Figure 2 displays flow reactor oxidation data for the Jet-A (POSF 4658) surrogate mixture compared against that determined earlier for the real jet fuel, Jet-A (POSF 4658).<sup>7</sup> For comparison, Figure 3 displays similar chemical reactivity data for the Jet-A (POSF 4658) first and second generation surrogate mixtures along with the chemical reactivity data for



**Figure 2.** Flow reactor chemical reactivity data for conditions of 0.3% molar carbon,  $\phi = 1.0$  at 12.5 atm and 1.8 s for Jet-A POSF 4658<sup>7</sup> (symbols) and the Jet-A POSF 4658 surrogate mixture composed of hydrocarbon fluids (solid lines). Inset: heat release,  $\Delta T$ .



**Figure 3.** Flow reactor chemical reactivity data for conditions of 0.3% molar carbon,  $\phi = 1.0$  at 12.5 atm and 1.8 s for Jet-A POSF 4658 (symbols),<sup>7</sup> the Jet-A POSF 4658 1st generation<sup>7</sup> and 2nd generation<sup>8</sup> surrogate mixtures composed of pure components (lines). See Table 4.

the jet fuel, Jet-A (POSF 4658). All fuels display the chemical kinetic behaviors typical for large alkyl hydrocarbons, that is, low, negative temperature coefficient (NTC), hot ignition followed by autothermal accelerative kinetic transition. Comparisons of the fuel behaviors in each of these regimes are discussed later.

**500–625 K Low Temperature Oxidation.** Figure 2 confirms that the reactivity of the Jet-A (POSF 4658) surrogate mixture is onset at 550–575 K, the rate of oxidation increases until 600–625 K, where turnover and negative-temperature-coefficient (NTC) behavior begins. Within the estimated experimental uncertainties, the magnitude of reactivity for the target real jet fuel and the Jet-A (POSF 4658) surrogate mixture is identical as reflected by the absolute amounts of oxygen consumed and of  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{H}_2\text{O}$  formed by the oxidation of both fuels. In this temperature range, measurements for real and surrogate fuels are consistent to within 5% and the rate of energy release ( $\Delta T$ ) is observed to follow consistently. Figure 3 displays comparable and nearly identical



behavior for both the Jet-A (POSF 4658) first and second generation surrogates. Thus, the global oxidative behaviors of all of the formulated surrogates are essentially indistinguishable from one another in this temperature range.

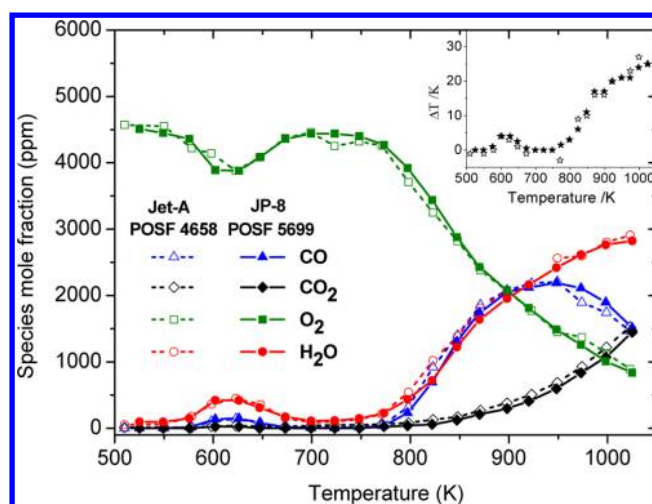
**625–800 K Negative Temperature Coefficient Behavior.** The Jet-A (POSF 4568) surrogate mixture exhibits NTC behavior in the temperature range beginning at 625–650 K and extending to  $\sim 700$  K. Above  $\sim 700$  K the rate of reaction becomes inordinately slow in comparison to the reactor observation time scale such that little or no consumption of molecular oxygen or formation of products is observed. As temperature is increased further, the surrogate mixture displays a low degree of reactivity between 750 and 770 K, transitioning to hot ignition at about 800 K. The observed reactivity for the POSF 4658 surrogate mixture tracks very closely that determined for Jet-A (POSF 4658) in character and magnitude until  $\sim 770$  K. Jet-A POSF (4658) shows a slightly more exaggerated onset of hot ignition, as is evident for example in the quantity of water produced, which is considerably more for the real fuel than for the surrogate. The departure of the onset and character of hot ignition is even more exaggerated for the Jet-A (POSF 4658) first and second generation surrogates<sup>7,8</sup> in comparison to the differences between the hydrocarbon fluid surrogate mixture and the target fuel, Figures 2 and 3.

**800–1025 K Intermediate Transition to High Temperature Chemistry.** Figures 2 and 3 show that the auto thermal accelerative reactivity with increasing initial reaction temperature of the Jet-A (POSF 4658) surrogate mixture is somewhat greater than that of the Jet-A (POSF 4658) first and second generation surrogate mixtures and somewhat more closely follows that of the real fuel. At the onset of the region, 800–900 K, the chemical reactivity profiles for the hydrocarbon fluid surrogate continue to show some departure from the real fuel profiles, similar to those observed for the Jet-A first and second generation surrogate mixtures.

A direct comparison of the heat release and the extent of each fuel's reactivity (shown in the insets in Figures 2 and 3) display only minor differences above  $\sim 900$  K, suggesting that the net reactivity (radical producing/consuming abilities) of the intermediates formed by both fuels are approximately equal in the temperature range 900–1025 K at the tested residence time.

**4.1.2. Comparison of Jet-A (POSF 4658) and JP-8 (POSF 5699) Reactivity.** Figure 4 presents profiles of chemical reactivity of the JP-8 (POSF 5699) fuel obtained in the flow reactor at identical conditions, a constant residence time of 1.8 s, 12.5 atm pressure, and carbon concentrations of 0.3 mol % corresponding to an oxygen concentration of 0.445 mol % to achieve stoichiometric reaction conditions. Also exhibited in Figure 4 are profiles of Jet-A POSF (4658) reactivity (discussed in section 4.1.1) requiring a very similar oxygen concentration for stoichiometric conditions, Table 4. Figure 4 shows that the oxidation characteristics of the JP-8 fuel and the Jet-A fuel are closely shared. Both fuels exhibit the three regimes of reactivity typical for large alkyl hydrocarbons. Given the estimated experimental uncertainties, the extent of reactivity as reflected by the chemical heat release ( $\Delta T$ ), in addition to the amount of major products formed, and of  $O_2$  consumed, are all extremely similar. These observations give some measure of the effects of the comparable, but small differences in the combustion property targets for the two fuels on observations (Table 4).

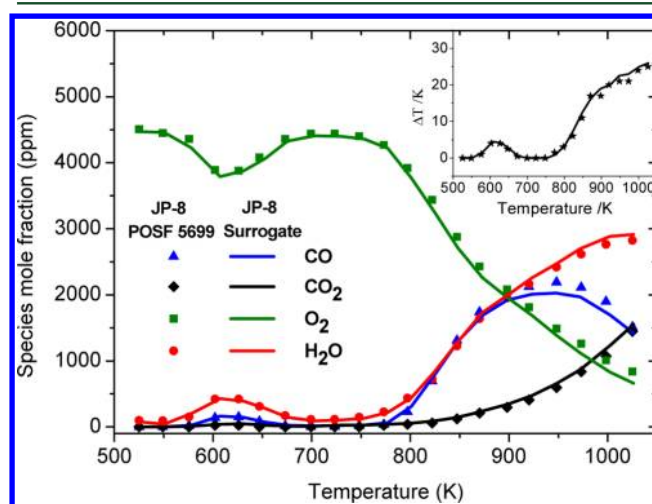
**4.1.3. JP-8 (POSF 5699) Fuel and JP-8 (POSF 5699) Surrogate Mixture.** As described above, a separate JP-8 (POSF



**Figure 4.** Flow reactor chemical reactivity data for conditions of 0.3% molar carbon,  $\phi = 1.0$  at 12.5 atm and 1.8 s for Jet-A POSF 4658<sup>7</sup> (open symbols/dashed lines) and JP-8 POSF 5699 (closed symbols/solid lines). Inset: heat release,  $\Delta T$ .

5699) surrogate mixture was formulated from different hydrocarbon fluids to further test the validity of the combustion property matching methodology (Table 4). In complementary work, two additional JP-8 (POSF 5699) hydrocarbon fluid surrogate mixtures composed of different components were also formulated similarly and their sooting behaviors are discussed elsewhere, along with those of the present surrogate mixture.<sup>1,12</sup>

Figure 5 shows a comparison of the flow reactor chemical reactivity of the JP-8 (POSF 5699) fuel and the JP-8 (POSF



**Figure 5.** Flow reactor chemical reactivity data for conditions of 0.3% molar carbon,  $\phi = 1.0$  at 12.5 atm and 1.8 s for JP-8 POSF 5699 (symbols) and the JP-8 POSF 5699 surrogate mixture composed of hydrocarbon fluids (lines). Inset: heat release,  $\Delta T$ .

5699) surrogate mixture at 525–1025 K, 1.8 s, and 12.5 atm. It is apparent that the temperature dependent reactivity exhibited by JP-8 (POSF 5699) fuel at these conditions is closely emulated by the surrogate mixture. The onset of low temperature oxidation at  $\sim 550$  K, negative temperature dependence at  $\sim 625$  K, transition to hot ignition between  $\sim 750$ – $775$  K are all very closely shared between the two fuels. The heat releases as a function of extent of reaction for the fuel

and its surrogate shown in the inset of Figure 5 are also essentially the same. Notably, the emulation of the target JP-8 fuel at the onset of the high temperature oxidation mechanism, 800–900 K, and thereafter is also very well reproduced by the JP-8 (POSF 5699) hydrocarbon fluid surrogate. Minimal disparity between the chemical reactivity profiles is observed, contrary to the case for the Jet-A (POSF 4658) and those for the Jet-A (POSF 4658) surrogate and the Jet-A (POSF 4658) first and second generation surrogate mixtures. In fact, since the reactivity properties of the two target fuels are very similar (Figure 4), the JP-8 (POSF 5699) hydrocarbon fluid surrogate will also reproduce very closely the reactivity characteristics of the Jet-A (POSF 4658) fuel.

The D95 paraffinic fluid stream used in formulating the JP-8 (POSF 5699) surrogate mixture contains large amounts of cycloalkanes, similar to the target fuel. In another recent paper,<sup>16</sup> we investigated experimentally and numerically, the addition of methyl cyclohexane to the first generation surrogate components, *n*-decane, *iso*-octane, and toluene. The four component surrogate mixture was formulated to reproduce the combustion property targets of the Jet-A (POSF 4658) target fuel with an imposed content of ~25 mol % cycloalkane. The reactivity characteristics of this alternative surrogate, or model fuel, were experimentally compared with those of the target fuel and its first generation surrogate. The reactivities of both surrogate mixtures were also computationally predicted using appropriate detailed kinetic models. Better agreement of the cycloalkane model fuel to the real fuel in the kinetic regime marking the onset of hot ignition was again observed, in both the experimental and computational results. These results strongly suggest the cycloalkane functional group to behave distinctly when being oxidized in a complex mixture of normal paraffin, branched paraffin, and aromatic functionalities. However, the impact of this uniqueness is isolated to one kinetic regime, the onset of hot ignition, where it amounts to an approximate 25% acceleration in reactivity.

The IPK component used in formulating the JP-8 (POSF 5699) surrogate mixture also has a broad distillation range and thus a wider range of molecular weights than other hydrocarbon fluids used in prior experiments.<sup>7,8</sup> The richer palette of chemical functional groups associated with the IPK as compared to other hydrocarbon fluids may in part be responsible for the better agreement found between the JP-8 (POSF 5699) real fuel and its surrogate mixture reactivities in the temperature range ~750–900 K. However, it is important to note the chemical composition information of Table 1, where large quantities of cycloalkanes are present in the JP-8 surrogate component EXXSOL D95 (~45% cycloalkane). This information with the deductions presented in ref 16 are consistent with the presence of a cycloalkane fraction as the most probable reason for the better degree of emulation observed for the JP-8 surrogate composition relative to the Jet-A surrogate compositions which are cycloalkane free.

In conclusion on the matter, both here and in the associated study,<sup>16</sup> the presence/absence of cycloalkanes in a surrogate composition produces little difference in reactivity characteristics of the low and high temperature regimes but does marginally advance the rate of oxidation in the hot ignition and subsequent transition to chemically branched, high temperature kinetic behavior.

**4.2. Implications of the Experimental Results.** The flow reactor chemical reactivity data for the Jet-A (POSF 4658) and JP-8 (POSF 5699) surrogate mixtures provides further evidence

that it is not the specific molecular identities of the initial surrogate mixture that are important in determining the noted, fully prevaporized kinetic behavior, but the collective interactions of the distribution of distinct functional groups represented by them.

In a parallel work by the coauthors,<sup>1,12</sup> comparisons of sooting behavior in wick flames and a multiphase, high pressure gas turbine combustor were made using the JP-8 (POSF 5699) fuel and three surrogate hydrocarbon fluid mixtures for emulating its behavior, including the JP-8 POSF (5699) hydrocarbon fluid surrogate mixture discussed here (identified as Surrogate #3, or “IPK surrogate” in refs 1 and 12). The comparison of laser extinction measurements as a function of radius at equivalent flame axial positions for the JP-8 POSF 5699 fuel and these surrogates were in very good agreement. Moreover, comparisons of soot laser extinction as a function of overall equivalence ratio in a high pressure multiphase model gas turbine combustor were also in reasonable agreement in comparison to the precision of those tests, at approximately  $\pm 15\%$ . Agreement was not as good as in the fully prevaporized burner experiments and varied with the surrogate mixture used, perhaps indicating differences related to physical property effects. Along with similar wick burner experiments presented in Dooley et al.,<sup>8</sup> these results suggest that gross sooting behavior (e.g., soot volume fraction) of real fuels can be further studied using combustion property target surrogate formulation concepts and varied types of hydrocarbon fluids as surrogate fuel components to investigate chemical and physical property parameter influences.

The central observation of this work is the consistency of the Jet-A (POSF 4658) surrogate reactivity results with those of the Jet-A (POSF 4658) first and second generation surrogate mixtures and the real (POSF 4658) jet fuel. The simple functional group analysis described by Dooley et al.<sup>8</sup> showed that the Jet-A (POSF 4658) first and second generation surrogate fuel mixtures are composed of common molecular fragments. The combustion behaviors of these surrogates, the real fuels, and the hydrocarbon fluid surrogates of this study have been measured to be essentially equivalent. The logical deduction from this is that similar key functional group compositions should exist for the much more complicated compositions of the studied Jet-A (POSF 4658), JP-8 (POSF 5699), and their surrogate mixtures composed of multispecies hydrocarbon fluids. This consistency strongly supports that the molecular mixture of a real fuel may be regarded as a complex but generic composition, the combustion kinetics of which are defined by the ability of the fuel to populate a limited number of intermediate chemical functional groups that react in a distinct manner.<sup>8</sup> Thus, it is asserted that the identity and proportion of these distinct functional groups are the fundamental targets for surrogate fuel formulations.

It is well-known that ignition quality measures such as Cetane and Octane number can be empirically described accurately by considering the interactions of unique molecular structural fragments found in a real fuel.<sup>34,35</sup> Similarly, the TSI can be correlated with molecular structural fragments, though different fragments are considered in these correlations than those for autoignition.<sup>36,37</sup> Many more physical and chemical properties can be predicted accurately with correlations based on chemical structure.<sup>38</sup> DCN and TSI simply represent experimentally determined correlation functions. These empirical correlation determinations adequately quantify autoignition and diffusive sooting properties of real fuels and

surrogate mixtures, more simply than can be achieved by correlations that require assigning molecular compositions of the fuels.

In this context it is fundamentally important to comment on the notion of reproducing the complete initial chemical structural composition of some real fuel with a surrogate composition by more quantitative determination and classification of all of the real fuel generic chemical functionalities and their distribution using complex analyses such as nuclear magnetic resonance methods.<sup>15</sup> Replicating the entire functional group complexity of the real fuel would lead to significant complexity and analytical uncertainty in replicating global combustion properties and developing surrogate fuel kinetic models. The combustion property target approach has apparently identified a small subset of distinct functional groups that most affect the fully prevaporized global combustion properties of the real fuel by emulating them with well defined mixtures such as the first and second generation surrogates. The further ranking of other distinct functionalities can be investigated by adding well considered additional components to these simple pallets.<sup>16</sup>

The surrogate fuel formulation concepts and results presented here offer considerable promise in guiding methodologies to simplify the formulation of surrogate mixtures that emulate both physical and chemical properties of specific real fuel compositions. This promise will yield opportunities to experimentally investigate the relative importance of such properties in the multiphase combustion environments of realistic combustion systems, such as gas turbines and reciprocating engines. Specifically, relatively inexpensive surrogate formulations using narrow distillation cuts of hydrocarbon fluids (e.g., IPK) can be formulated to match the fully vaporized combustion properties of real fuels. Subsequently, the combustion properties of these surrogates can be compared with those of real fuels in fully prevaporized applied experiments, initially to further investigate their robustness in replicating fully prevaporized combustion behavior of real fuels. In parallel, pure component surrogate mixtures (e.g., Jet-A second generation surrogate) that emulate the same combustion property target parameters as the real fuel can be determined to produce the appropriate composition input for chemical kinetic/transport composite models that are of proven accuracy for mixtures of the pure components in wide ranges of fundamental venues.

A substantial inference from the above findings is that surrogate mixtures of hydrocarbon fluids can be formulated such that the mixtures emulate the combustion property targets of any other specific fuel. Using these techniques surrogate mixtures can be formulated that each have the same fully prevaporized combustion property targets, but have different physical properties, including different distillation and vapor dome properties, and as importantly, even different molecular class distributions over their distillation curve. These hydrocarbon fluid surrogate mixtures can be used experimentally in both laboratory scale model combustors and applied rig combustors to yield further understanding of the relative importance of specific physical properties to combustion observations in multiphase combustion environments.

## 5. CONCLUSIONS

Comparisons of fully prevaporized experimental combustion behaviors of surrogate mixtures of multispecies hydrocarbon fluids formulated to replicate key combustion property targets

of *specific* real fuels are shown here to result in similar combustion kinetic behaviors in variable pressure flow reactor reactivity experiments as their targeted real fuels. Results showing that similar sooting behaviors are also yielded for real fuels and hydrocarbon fluid mixtures are presented in a companion publication.<sup>1</sup>

The principal conclusions of this work are as follows:

- Surrogate mixtures of hydrocarbon fluids from narrow distillation cuts of discrete molecular class structure (i.e., NOPAR 12 (linear alkanes); ISOPAR L (iso-paraffinic alkanes); Aromatic 150 (alkylbenzenes)) can be used to formulate mixtures with combustion property targets (DCN, TSI, H/C molar ratio, and average molecular weight) that emulate well a majority of fully prevaporized global combustion behaviors of a *specific* target jet aviation fuel, without detailed knowledge of its chemical species composition.
- Surrogate mixtures of hydrocarbon fluids composed of narrow distillation cuts, pure components, and even full blend fuels or distillation cuts from full blend fuels in a similar manner can also be formulated to emulate the combustion property targets of a specific jet fuel.
- The chemical kinetic reactivity of the fully prevaporized surrogate mixture so formulated closely emulates that of the real fuel. Results presented elsewhere show similar emulation of sooting behaviors in both fundamental jet diffusion flame and model gas turbine combustor experiments.<sup>1</sup> It is inferred from prior work,<sup>8</sup> that combustion behaviors at other reactant concentrations, equivalence ratios, and pressures will be similarly reproduced well. Unfortunately experimental confirmation of this inference is beyond the scope of the present effort. The promise of the technique supports the need for further work to confirm these matters.
- The chemical reactivities of two real jet fuels sharing nearly the same combustion property targets were shown to be essentially the same, further demonstrating the validity of the combustion property matching methodology for analyzing fuels.
- Surrogate mixtures formed from hydrocarbon fluids containing cycloalkanes in addition to normal alkanes and iso-alkanes and aromatics improve the reactivity behavioral agreement of the surrogate mixture with a specific target fuel containing significant cycloalkanes. The improvement in agreement is principally at reactivity conditions at the onset of hot ignition and subsequently as the reactivity is accelerated auto thermally (~750–900 K in the present work). Little changes in behavior in other kinetic regimes result from including cycloalkanes in the surrogate mixture pallet.
- More generally, the choice of surrogate components and class composition can differ significantly from those of the real fuel without degrading the quality of predictions as long as the surrogate mixture composition reproduces the combustion property targets of the target fuel. The guiding principle active is to maintain a reasonable emulation of the distribution of the key *distinct functional groups* represented by the real fuel component selection and mixture composition, and not necessarily in approximating the original fuel molecular structure or structural class distribution.



- Hydrocarbon fluid surrogate mixtures, which are much less expensive than single molecular structural pure components, can yield close replication of fully prevaporized global combustion properties of a real fuel, provided the surrogate formulation emulates well the real fuel combustion property target values.

Finally, we have discussed how the ability to formulate hydrocarbon fluid surrogate blends to emulate real fuel behavior might be applied to bridge the present experimental knowledge base developed on surrogate fuel science to applied combustion research aimed at simplifying the integration of emerging alternative fuel feed stocks into the aircraft transportation sector. This is an important aspect of the present work, since formulating mixtures with essentially the same fully prevaporized combustion property targets but different distillation characteristics or other physical properties can be useful in investigating the relative effects of physical and chemical kinetic properties on multiphase, multidimensional combustion performance and emissions parameters at rig scale and larger test configurations. The concepts discussed here can also be applied to advance future combustion systems designs having improved performance and emissions.

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### Notes

The authors declare no competing financial interest.

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## REFERENCES

- (1) Iyer, V.; Iyer, S.; Linevsky, M.; Litzinger, T.; Santoro, R. J.; Dooley, S.; Dryer, F. L.; Mordaunt, C. J. Simulating the sooting propensity of JP-8 with surrogate fuels from hydrocarbon fluids. *J. Propulsion Power* **2014**, in press.
- (2) Edwards, T.; Dryer, F. L.; Moses, C. A. Evaluation of combustion performance of alternative aviation fuels. *46th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit*, 25–28 July 2010, Nashville, TN, Paper No. AIAA-2010-7155, 2012.
- (3) ASTM D7566.14S86601, *Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons*; ASTM International: West Conshohocken, PA, 2013.

- (4) Moses, C. A. *Comparative Evaluation of Semi-Synthetic Jet Fuels*; Final Report, CRC Project No. AV-2-04a; Defense Technical Information Center, 8725 John J. Kingman Road, Suite 0944, Fort Belvoir, VA 22060-6218; [www.dtic.mil/dtic/tr/fulltext/u2/a578384.pdf](http://www.dtic.mil/dtic/tr/fulltext/u2/a578384.pdf); Coordinating Research Council: Alpharetta, GA, 2008.

- (5) *2009 Petroleum Quality Information Systems (PQIS) Annual Report*; Petroleum Quality Information System, Petroleum Quality Information System Defense Energy Support Center: Belvoir, VA, 2010.

- (6) Xu, H.; Yang, Z.; Chaos, M.; Dryer, F. L. Surrogate jet fuel mixture formulation and development of experimental databases. *JANNAF 42nd Combustion Joint Sub-Committee Meeting Modeling and Data For Combustion Simulation*, Boston Marriott Newton, Hanscom AF Base, Newton, MA, May 12–16, 2008.

- (7) Dooley, S.; Won, S. H.; Chaos, M.; Heyne, J.; Ju, Y.; Dryer, F. L.; Kumar, K.; Sung, C.-J.; Wang, H.; Oehlschlaeger, M. A.; Santoro, R. J.; Litzinger, T. A. A jet fuel surrogate formulated by real fuel properties. *Combust. Flame* **2010**, *157* (12), 2333–2339.

- (8) Dooley, S.; Won, S. H.; Heyne, J.; Farouk, T. I.; Ju, Y.; Dryer, F. L.; Kumar, K.; Hui, X.; Sung, C.-J.; Wang, H.; Oehlschlaeger, M. A.; Iyer, V.; Iyer, S.; Litzinger, T. A.; Santoro, R. J.; Malewicki, T.; Brezinsky, K. The experimental evaluation of a methodology for surrogate fuel formulation to emulate gas phase combustion kinetic phenomena. *Combust. Flame* **2012**, *159* (4), 1444–1466.

- (9) Dooley, S.; Won, S. H.; Jahangirian, S.; Ju, Y.; Dryer, F. L.; Wang, H.; Oehlschlaeger, M. A. The combustion kinetics of a synthetic paraffinic jet aviation fuel and a fundamentally formulated, experimentally validated surrogate fuel. *Combust. Flame* **2012**, *159* (10), 3014–3020.

- (10) Won, S. H.; Veloo, P. S.; Santner, J.; Ju, Y.; Dryer, F. L. Comparative evaluation of global combustion properties of alternative jet fuels. In *51st AIAA Aerospace Sciences Meeting*, Grapevine, TX, Jan. 7–10, 2013; AIAA ASM 2013-0156.

- (11) Dooley, S.; Dryer, F. L.; Farouk, T. I.; Ju, Y.; Won, S. H. Reduced kinetic models for the combustion of jet propulsion fuels. In *51st AIAA Aerospace Sciences Meeting*, Grapevine, TX, Jan. 7–10, 2013; AIAA ASM 2013-0158.

- (12) Iyer, V. R.; Iyer, S. A.; Litzinger, T. A.; Santoro, R. J.; Dooley, S.; Dryer, F. L.; Mordaunt, C. J. Emulating the sooting propensity of JP-8 with surrogate fuels from solvent mixtures. In *50th Annual Aerospace Sciences Meeting*, Nashville, TN, Jan. 9–12, 2012; AIAA-2012-621.

- (13) Dryer, F. L.; Ju, Y.; Sung, C.-J.; Brezinsky, K.; Santoro, R. J.; Litzinger, T. A.; *Science-Based Design of Fuel-Flexible Chemical Propulsion/Energy: Generation of Comprehensive Surrogate Kinetic Models and Validation Databases for Simulating Large Molecular Weight Hydrocarbon Fuels*; AF Office of Scientific Research Final Report, Grant No. FA9550-07-1-0515; October 1, 2012.

- (14) Widegren, J. A.; Bruno, T. J. Thermal decomposition kinetics of the aviation turbine fuel Jet-A. *Ind. Eng. Chem. Res.* **2008**, *47* (13), 4342–4348.

- (15) Mueller, C. J.; Cannella, W. J.; Bruno, T. J.; Bunting, B.; Dettman, H. D.; Franz, J. A.; Huber, M. L.; Natarajan, M.; Pitz, W. J.; Ratcliff, M. A.; Wright, K. Methodology for formulating diesel surrogate fuels with accurate compositional, ignition-quality, and volatility characteristics. *Energy Fuels* **2012**, *26* (6), 3284–3303.

- (16) Dooley, S.; Dryer, F. L.; Heyne, J.; Won, S. H.; Dievart, P.; Ju, Y. On the importance of a cycloalkane functionality in the oxidation of a real fuel. *Energy Fuels* **2014**, submitted.

- (17) NORPAR 12 Hydrocarbon Fluid, Materials Safety Data Sheet, Product Code 133598, Exxon Company, Houston, TX. Issue Date 01/21/00. 2000.

- (18) ISOPAR-L Hydrocarbon Fluid, Materials Safety Data Sheet, Product Code 133465, Exxon Company, Houston TX. Issue Date 01/21/00. 2000.

- (19) AROMATIC 150 Product Safety Summary, ExxonMobil Chemical Company, Houston, TX. Updated June 2009.

- (20) EXXSOL D95 Fluid Product Summary. ExxonMobil Chemical Company, Houston, TX. Updated August 2013.

- (21) AROMATIC 100 Product Safety Summary, ExxonMobil Chemical Company, Houston, TX. Updated June 2009.
- (22) ASTM D6890-09, *Standard Test Method for Determination of Ignition Delay and Derived Cetane Number (DCN) of Diesel Fuel Oils by Combustion in a Constant Volume Chamber*; ASTM International: West Conshohocken, PA, 2009.
- (23) Allard, L. N.; Hole, N. J.; Webster, G. D.; Ryan, T. W. I.; Ott, D.; Beregszazy, A.; Fairbridge, C. W.; Cooley, J.; Mitchell, K.; Richardson, E. K.; Elliot, N. G.; Rickeard, D. J. *SAE Tech. Pap.* **1997**, No. 1997, 971636.
- (24) Calcote, H. F.; Manos, D. M. Effect of molecular structure on incipient soot formation. *Combust. Flame* **1983**, *49* (1–3), 289–304.
- (25) Olson, D. B.; Pickens, J. C.; Gill, R. J. The effects of molecular structure on soot formation II. Diffusion flames. *Combust. Flame* **1985**, *62* (1), 43–60.
- (26) ASTM D1322, *Standard Test Method for Smoke Point of Kerosine and Aviation Turbine Fuel*; ASTM International: West Conshohocken, PA, 2008.
- (27) Mensch, A.; Santoro, R. J.; Litzinger, T. A.; Lee, S. Y. Sooting characteristics of surrogates for jet fuels. *Combust. Flame* **2010**, *157* (6), 1097–1105.
- (28) Dryer, F. L.; Won, S. H.; Dooley, S. A *Measurement Process for the Determination of the Mixture Averaged Molecular Weight of Complex Mixtures*, Provisional Patent Disclosure; Princeton University: Princeton, NJ, Feb. 17, 2012; 08544.
- (29) ASTM D5291-10, *Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants*; ASTM International: West Conshohocken, PA, 2010.
- (30) Held, T. J.; Dryer, F. L. A comprehensive mechanism for methanol oxidation. *Int. J. Chem. Kinet.* **1998**, *30* (11), 805–830.
- (31) Zhao, Z.; Chaos, M.; Kazakov, A.; Dryer, F. L. Thermal decomposition reaction and a comprehensive kinetic model of dimethyl ether. *Int. J. Chem. Kinet.* **2008**, *40* (1), 1–18.
- (32) Dooley, S.; Burke, M. P.; Chaos, M.; Stein, Y.; Dryer, F. L.; Zhukov, V. P.; Finch, O.; Simmie, J. M.; Curran, H. J. Methyl formate oxidation: Speciation data, laminar burning velocities, ignition delay times, and a validated chemical kinetic model. *Int. J. Chem. Kinet.* **2010**, *42* (9), 527–549.
- (33) Jahangirian, S.; Dooley, S.; Haas, F. M.; Dryer, F. L. A detailed experimental and kinetic modeling study of *n*-decane oxidation at elevated pressures. *Combust. Flame* **2012**, *159* (1), 30–43.
- (34) Ghosh, P.; Hickey, K. J.; Jaffe, S. B. Development of a detailed gasoline composition-based octane model. *Ind. Eng. Chem. Res.* **2005**, *45* (1), 337–345.
- (35) Ghosh, P.; Jaffe, S. B. Detailed composition-based model for predicting the cetane number of diesel fuels. *Ind. Eng. Chem. Res.* **2005**, *45* (1), 346–351.
- (36) Yan, S.; Eddings, E. G.; Palotas, A. B.; Pugmire, R. J.; Sarofim, A. F. Prediction of sooting tendency for hydrocarbon liquids in diffusion flames. *Energy Fuels* **2005**, *19* (6), 2408–2415.
- (37) Pepiot-Desjardins, P.; Pitsch, H.; Malhotra, R.; Kirby, S. R.; Boehman, A. L. Structural group analysis for soot reduction tendency of oxygenated fuels. *Combust. Flame* **2008**, *154* (1–2), 191–205.
- (38) Katritzky, A. R.; Kuanar, M.; Slavov, S.; Hall, C. D.; Karelson, M.; Kahn, I.; Dobchev, D. A. Quantitative correlation of physical and chemical properties with chemical structure: Utility for prediction. *Chem. Rev.* **2010**, *110* (10), 5714–5789.