Formulation of 7-Component Surrogate Mixtures for Military Jet Fuel and Testing in Diesel Engine

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ABSTRACT: In this work, military jet fuel JP-5 surrogates were formulated and tested in comparison to a nominal JP-5 fuel. Combustion experiments were conducted in an advanced engine technology (AET) ignition quality tester (IQT) and a Yanmar L100W Tier 4 diesel engine due to the potential use of jet fuel in diesel engines in military situations. The surrogate development process began with determining the fuel chemical composition based on analyses of 256 JP-5 fuel samples. The physical and chemical properties of density, viscosity, flash point, surface tension, speed of sound, and distillation behavior guided the selection of the surrogate components and their composition. JP-5 differs from other aviation fuels in its properties, but most importantly in flash point, which is higher for safety purposes.

Surrogates were prepared from n-dodecane, n-butylbenzene, 1-methylnaphthalene, tetralin, trans-decalin, iso-cetane, and n-butylcyclohexane as representatives of seven of the nine major chemical categories found in jet fuel. The mass fraction of each compound in the surrogates that fell within the range for that chemical class was found in real JP-5 fuels. After optimizing the surrogates for physical and chemical properties, six surrogates were selected for combustion testing in the Yanmar diesel engine, one of which was specifically selected for a low-derived cetane number (DCN). This surrogate performed poorly in the Yanmar engine. Four of the remaining five surrogates performed similarly to the baseline JP-5 in the diesel engine in terms of values and variability of ignition delay, rate of heat release, peak pressure, and the crank angle at which 50% of the fuel is burned. Of the six surrogates tested, the best one in terms of physical properties, chemical properties, and combustion behavior was the one that contained 0.2421, 0.1503, 0.0500, 0.0141, 0.0121, 0.2532, and 0.2782 mass percentages of n-dodecane, n-butylbenzene, 1-methylnaphthalene, tetralin, trans-decalin, iso-cetane, and n-butylcyclohexane, respectively.

1. INTRODUCTION

The use of jet fuel in military diesel engines enables operational fuel flexibility and can streamline the purchasing process. Fuel scientists and engineers often make and test surrogate mixtures with a limited number of components to understand the combustion process of real complex fuels containing hundreds of components.1−31 The combustion process can be broken into the physical processes of injection, spray formation, and evaporation and the chemical reaction kinetics. Researchers have probed the effect of various physical properties on spray behavior and have developed jet fuel surrogates using physical properties.32−34 Huber et al.3 used density, speed of sound, viscosity, thermal conductivity, and advanced distillation curve data to design surrogates for rocket propellants. These properties with the addition of cetane number (CN) were used to formulate surrogates for Jet A.7 Won et al.35 used hydrogen-to-carbon (H/C) molar ratio, derived cetane number (DCN), average molecular weight, and threshold sooting index to formulate surrogates for jet fuel. CN and DCN are diesel engine combustion metrics that capture ignition delay behavior that incorporates both physical and chemical properties of fuels.

A large number of studies have formulated and tested surrogates for commercial aviation jet fuel, Jet A, kerosene, and military jet fuel JP-8,3−9,11,12,14,15,17−19,22,28,31 but fewer studies have focused on Navy jet fuel, JP-5.1,3,13,29 Edwards and Maurice3 reported on studies that had developed different surrogates for the various jet fuels JP-4, JP-5, JP-8, and RP-1. For JP-5, the 11- and 12-component surrogates contained combinations of six linear alkanes, two monocyclohexanes, one dicyclohexane, two monoaromatic, one polyaromatic, and one cycloaromatic compounds.3 Wood et al.2 showed that

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surrogates for JP-4 were not good representatives for JP-5. Allen et al.\textsuperscript{13} reported that Jet A surrogates were not able to capture the complete combustion behavior of JP-5. In an “Overview of the National Jet Fuels Combustion program” in 2017, Colket et al.\textsuperscript{34} summarized some differences between JP-8, Jet A, and JP-5 including their flash points, viscosities, aromatic contents, and distillation curves. For example, the minimum value of flash point for Jet A is 38 °C, which is much lower than JP-5’s minimum requirement of 60 °C.\textsuperscript{53,56} Given that surrogates for other jet fuels do not always capture the behavior of JP-5, this study sought to formulate a surrogate mixture for JP-5.

In surrogate development, the selection of components for the surrogate is related in some way to the chemical composition of the fuel. In some cases, fuel components are divided into classes and representatives are chosen from those classes to be included in the surrogate. Divisions have included paraffins, monocy cloparaffins, dicycloparaffins, alkylbenzenes, indans and tet ralins, indenes and dihydro naphtalenes, and naphtalenes.\textsuperscript{6} The categories of compounds can be further subdivided by carbon number, and modern two-dimensional gas chromatography (GC × GC) with flame ionization or mass spectrometry greatly facilitates compound identification.\textsuperscript{23,57-40} Greater detail on fuel composition in recent years has led to many successful predictions of fuel properties such as density, volatility, viscosity, flash point, freezing point, and distillation profile.\textsuperscript{38,41} It can also be used to more accurately estimate the molar mass of fuel. Based on compositional information, cost, and commercial availability, a list of prospective compounds for the surrogate is created. Then, specific compounds or hydrocarbon blends are chosen for the surrogate by matching selected physical, chemical, and/or combustion metrics of the surrogate to that of the fuel of interest. Previously used metrics have included DCN, octane number, flash point, total sooting index, lower heating value, thermal conductivity, H/C molar ratio, volatility measurements through a distillation curve, density, speed of sound, and viscosity.\textsuperscript{2,3,5-9,15,16,23,42-48}

In their formulation of Jet A and JP-8 surrogates, Dryer et al.\textsuperscript{18} used either specific compounds, such as 1,3,5-trimethylbenzene, or commercially available hydrocarbon blends like Solvesso Aromatic 100 to prepare surrogates whose TSI, H/C ratio, and DCN matched that of the fuel. In the current study, the surrogates were formulated based on the average GC × GC chemical composition of multiple samples of JP-5 produced over several years, and the combustion of the surrogate was compared to that of a specific production lot of JP-5. The metrics used for surrogate development and selection included density, viscosity, speed of sound, surface tension, flash point, distillation curve information, and DCN. Density, viscosity, and vapor pressure have been shown to be important in direct injection spray and ignition behaviors.\textsuperscript{32} Vapor pressure information can be captured in the flash point and distillation curve information. As mentioned earlier, flash point is a key difference between JP-5 and other aviation fuels, so its inclusion limited the selection of components in the surrogate mixture.\textsuperscript{10}

One factor to consider when choosing compounds for a surrogate is the possibility of chemical kinetic modeling.\textsuperscript{18,19,21,26,28,49-58} For some compounds, there are detailed mechanisms. Westbrook et al.\textsuperscript{50} used over 8000 reactions with more than 2000 chemical species to model the combustion of docedcane. Dagaut and Hadj-Ali\textsuperscript{56} used two kinetic models in their simulation of the oxidation of 2,2,4,4,6,8,8-heptamethyl-nonane (iso-cetane) in a jet-stirred reactor. One model contained 4969 reactions with 174 chemical species, while the other had 1653 reactions with 199 chemical species. Mao et al.\textsuperscript{57} recently developed a surrogate for RP-3 that contained 27.44% n-dodecane, 28.81% isododecane, 26.12% decaln, and 17.63% n-buty1benzene. They modeled the combustion process using 11 898 reactions that included 3065 chemical species. For modeling purposes, there is a balance between including more components to more accurately represent the fuel and using fewer components whose reaction kinetics need to be included in the model.

Most of the combustion and modeling work with jet fuel surrogates have been in aviation-related hardware and test rigs,\textsuperscript{20,22,23,26,59} but there are some studies that have focused on jet fuel combustion in diesel engine applications.\textsuperscript{20,22,23,26,59} The use of military jet fuel in military diesel engine enables fuel flexibility in operational situations. Yu et al.\textsuperscript{59} developed a Jet A surrogate and used a soot model for diesel engines. Kang et al.\textsuperscript{70} measured the carbon monoxide emission, apparent heat release rates, and ignition delay of a Jet A surrogate using (1) a constant volume combustion chamber and (2) a cooperative fuel research (CRF) engine. In the author’s laboratory, a CFR engine was used to measure burn duration, thermal efficiency, maximum rate of heat release (ROHR), and ignition delay for a catalytic hydrothermal conversion jet fuel and its surrogates.\textsuperscript{71} In the current study, the combustion experiments were conducted in an advanced engine technology (AET) ignition quality tester (IQT) to obtain the derived cetane number (DCN) and in a Yanmar L100W Tier 4 diesel engine.

2. MATERIALS AND METHODS

2.1. Methods. The chemical composition of the JP-5 jet fuel was determined using GC × GC techniques reported in previous work.\textsuperscript{30} Other properties measured in this work were flash point, distillation curve, surface tension, density, speed of sound, and viscosity using methods reported previously.\textsuperscript{40,60} In summary, the instruments used were a Stanhope-Seta Setaflash Series 8 closed-cup flash point tester (Model 82000-0) operating at a temperature ramping mode, a Grabner MINIDIS ADXpert automatic distillation apparatus, a Kruss Axisymmetric drop shape analyzer (DS100), an Anton Parr Density and Sound analyzer (DSA 5000), and an Anton Parr Stabinger viscometer (SVM 3000).

DCN was quantified with an advanced engine technology ignition quality tester (IQT) rig-operated according to the ASTM D6890 protocol.\textsuperscript{61} The method has been described in previous studies.\textsuperscript{23,28} A Tier 4 (U.S. EPA Emissions Level) single cylinder Yanmar L100W diesel engine was instrumented for combustion analysis and operated on a small set of surrogate mixtures and the baseline JP-5. This engine has been described in previous work and run with genset at 3600 nominal revolutions per minute (RPM).\textsuperscript{29} The engine was operated under a nominal “light-load” condition of 1.5 kW and a “high-load” condition of 4 kW (approximately 1/4–3/4 of the maximum engine load). These engine metrics were measured using a Kistler 6052C in-cylinder pressure sensor and a Kistler piezo-resistive fuel line pressure sensor for the start of injection (nominally one degree before top center). Engine position was measured with a dual channel BEI shaft encoder on the crankshaft and an ETAS wide-band air-fuel ratio meter in the engine exhaust. The heat release analysis methodology followed a conventional first law of thermodynamic analysis.

2.2. Materials. The compositional analysis provided mass percentages of various categories of compounds subdivided in the number of carbon atoms. The surrogate mixtures were
prepared from compounds that fall within these categories and number of carbon atoms. The surrogate mixtures were prepared from n-decane (99.5% pure, Sigma-Aldrich), n-dodecane (99.6% pure, Alfa Aesar), n-tridecane (99.4% pure, Acros), n-propylcyclohexane (99.7% pure, TCI), n-butylcyclohexane (99.1% pure, TCI), n-hexylcyclohexane (98.8% pure, TCI), 1,2,3,4-tetrahydrodiphenylalanine (tetralin, 98.6% pure, Sigma-Aldrich), 1-methylcyclohexane (99.3% pure, Acros Organics), n-propylbenzene (99.8% pure, TCI), n-butylbenzene (99.1% pure, Acros Organics), n-hexylbenzene (Alfa Aesar, 99.0% pure), trans-decalin (TCI, 99.5% pure), cis-decalin (TCI, 98.2% pure), 2,2,4,4,6,8,8-heptamethylnonane (iso-cetane, 99.7% pure, Acros Organics), and 2,2,4,6,6-pentamethylcyclohexane (isododecane, 99.2% pure, TCI). The JP-5 was supplied by Naval Air Warfare Center Aircraft Division’s (NAWCAD) Fuels Group.

3. RESULTS AND DISCUSSION

3.1. Chemical Composition of JP-5 and Surrogate Compounds to Represent Component Classes in Fuel.

The formulation of the surrogate mixtures was based on the chemical compositions of 256 JP-5 jet fuel samples. The steps of the formulation process are shown in Figure 1. The average mass percentages of n-paraffins, iso-paraffins, monocyclic paraffins, dicyclopentane, tricycloparaffins, aromatics, diaromatic compounds, triaromatic compounds, and cycloaromatic compounds in these fuel samples were 17.31, 23.69, 27.28, 11.62, 1.83, 9.97, 2.08, 0.0011, and 6.54, respectively. This set was reduced to seven categories by eliminating the triaromatics and tricycloparaffins. Using the average compositions and the range of values in each category, 7-component surrogate mixtures were prepared using one or more chemicals to represent each of the categories. The specific compounds were chosen (1) to be among the categories and carbon numbers found in the fuels, (2) to enable the flash point of the mixture to be above 60 °C, and (3) to be commercially available at reasonable costs for preparing large quantities for combustion. As described below, most surrogates contained n-dodecane (n-paraffin), iso-cetane (iso-paraffin), n-butylcyclohexane (monocycloparaffin), trans-decalin (dicyclopentane), n-butylbenzene (aromatic compound), tetralin (cycloaromatic), and 1-methylcyclohexane (diaromatic compound). Other compounds were also examined, and those mixtures are given in the Supporting Information. The composition of the specific JP-5 used in the combustion experiments is given in Table 1.

3.2. Development of JP-5 Surrogate Mixtures and Selection of Surrogates for Combustion Testing.

Surrogate mixtures were prepared using three approaches, as summarized in Figure 1. In the first method, a mixture was prepared with six of the seven components (n-dodecane, n-butylbenzene, 1-methylcyclohexane, tetralin, trans-decalin, iso-cetane, and n-butylcyclohexane) in the same relative proportions of each chemical category found for the average of 256 JP-5 jet fuel samples, which is given in Section 3.1 (mixtures designated A–G) (Table 2). Then, submixtures were made by adding the 7th component at its average (“base case”), minimum, and maximum concentration found in the 256 JP-5 jet fuel samples (mixtures designated with number and letter, like A1) (Table 2). The properties of these mixtures are given in Table 3. In some cases, additional base-case mixtures were prepared with an alternate 7th component that was in the same category of components (see Supporting Information, Table S1). While some of these alternate base-case mixtures had densities closer to that of JP-5 than that of the base-case mixtures, the other parameters were further away (see Supporting Information, Table S2). The remaining discussion only includes surrogate formulations that contain the seven components, as listed in Table 2.

In the second method, surrogates were made to roughly span a range of possible DCN values. Branched and aromatic compounds lower a fuel’s cetane number. A low cetane surrogate was prepared using the highest concentrations of...
Tetralin, trans-aromatic and branched compounds found in the fuels.

Table 2. Mass Fraction of Components in Surrogate Mixtures Containing n-Dodecane, Butylbenzene, 1-Methylnaphthalene, Tetralin, trans-Decalin, iso-Cetane, and Butylcyclohexane

| carbon number | n-paraffin average mass % | iso-paraffin average mass % | monocytoparaffin average mass % | dicycloparaffin, average mass % | tricycloalkanes, average mass % | aromatic compounds, average mass % | cycloaromatics, average mass % | diaromatic compounds, average mass % |
|---------------|---------------------------|-----------------------------|---------------------------------|-------------------------------|---------------------------------|-----------------------------------|----------------------------------|-----------------------------------|
| C7            |                           |                             |                                 |                               |                                 |                                   |                                  |                                   |
| C8            | 0.03                      | 0.02                        | 0.06                            |                               |                                 | 0.01                              |                                 |                                   |
| C9            | 0.32                      | 0.12                        | 0.73                            | 0.20                          | 1.55                            | 0.05                              | 0.08                             | 0.32                              |
| C10           | 3.25                      | 2.06                        | 3.66                            | 1.67                          | 3.03                            | 0.61                              | 0.08                             | 0.51                              |
| C11           | 4.91                      | 5.12                        | 5.46                            | 2.99                          | 0.01                            | 2.42                              | 2.07                             | 0.32                              |
| C12           | 4.34                      | 4.99                        | 5.62                            | 2.98                          | 0.09                            | 1.91                              | 1.79                             | 0.51                              |
| C13           | 3.47                      | 5.03                        | 4.95                            | 2.93                          | 0.16                            | 1.26                              | 1.11                             | 0.13                              |
| C14           | 2.19                      | 4.08                        | 3.22                            | 1.28                          | 0.08                            | 0.77                              | 0.29                             |                                   |
| C15           | 0.70                      | 2.50                        | 1.40                            | 0.21                          |                                 | 0.11                              |                                  |                                   |
| C16           | 0.07                      | 0.86                        | 0.10                            |                               |                                 |                                   |                                  |                                   |
| C17           | 0.02                      | 0.03                        |                                 |                               |                                 |                                   |                                  |                                   |
| C18           | 0.01                      |                             |                                 |                               |                                 |                                   |                                  |                                   |
| total         | 19.31                     | 24.81                       | 25.20                           | 12.26                         | 0.34                            | 11.13                             | 5.92                             | 1.04                              |

aromatic and branched compounds found in the fuels’ survey. Linear and cyclic compounds increase a fuel’s cetane number. A high cetane surrogate was prepared from the highest concentration of linear and cyclic compounds found in the fuels’ survey. Three more surrogates were prepared for DCN values between the high and low cetane surrogates. Their composition was based on pure component values. The average DCN values\(^{62}\) for n-dodecane, n-butylbenzene, tetralin, trans-decalin, iso-cetane, and n-butylcyclohexane are 73.5, 12.5, 13.8, 31.9, 14.5, and 47.8, respectively. The DCN of 1-methylnaph-
Table 3. Properties of 7-Component Surrogate Mixtures and JP-5

| fuel or surrogate mixture | density at 15 °C (g/mL) | viscosity at -20 °C (mm²/s) | flash point (°C) | speed of sound at 20 °C (m/s) | surface tension (mN/m) (°C) | Distillation curve temperatures (°C) |
|---------------------------|--------------------------|-----------------------------|-----------------|-----------------------------|----------------------------|----------------------------------|
| jet fuel spec              | 0.788–0.845              | <7                          | >60             |                             |                            |                                  |
| JP-5                      | 0.80549                  | 5.00                        | 63.5            | 1318.7                      | 25.9 at 21.2               | 205 max                          |
| A                         | 0.82956                  | 5.10                        | 59.0            | 1336.6                      | 26.7 at 21.4               | 191.9                            |
| A1                        | 0.82642                  | 5.07                        | 59.0            | 1336.3                      | 26.5 at 21.6               | 190.95                           |
| A2                        | 0.81454                  | 4.96                        | 61.0            | 1328.9                      | 26.4 at 21.4               | 193.25                           |
| A3                        | 0.81274                  | 4.96                        | 62.0            | 1327.8                      | 26.3 at 21.6               | 195.45                           |
| A4                        | 0.80193                  | 4.91                        | 64.0            | 1312.5                      | 25.9 at 21.5               | 190.35                           |
| B                         | 0.80964                  | 5.70                        | 62.0            | 1329.3                      | 26.1 at 21.1               | 191.05                           |
| B1                        | 0.81153                  | 5.37                        | 62.0            | 1328.5                      | 26.2 at 21.8               | 191.05                           |
| B2                        | 0.81717                  | 4.71                        | 60.0            | 1329.4                      | 26.8 at 21.3               | 191.05                           |
| C                         | 0.81265                  | 4.96                        | 60.0            | 1327.3                      | 26.2 at 21.0               | 191.05                           |
| C1                        | 0.82175                  | 5.03                        | 62.0            | 1335.0                      | 26.7 at 21.3               | 191.05                           |
| D                         | 0.80514                  | 4.98                        | 59.5            | 1320.1                      | 26.1 at 21.3               | 189.25                           |
| D1                        | 0.80625                  | 4.98                        | 60.1            | 1321.1                      | 26.1 at 21.5               | 196.5                            |
| D2                        | 0.82510                  | 4.99                        | 61.5            | 1339.8                      | 26.7 at 21.3               | 225.8                            |
| E                         | 0.80704                  | 4.92                        | 62.2            | 1320.7                      | 25.9 at 20.9               | 226.1                            |
| E1                        | 0.80769                  | 4.92                        | 62.2            | 1321.3                      | 26.0 at 21.5               | 226.1                            |
| E2                        | 0.82254                  | 5.16                        | 59.5            | 1337.8                      | 26.7 at 21.9               | 226.1                            |
| F                         | 0.82345                  | 3.93                        | 58.0            | 1342.5                      | 27.3 at 21.0               | 226.1                            |
| F1                        | 0.81724                  | 4.61                        | 60.0            | 1333.0                      | 26.4 at 21.0               | 226.1                            |
| F2                        | 0.80542                  | 6.84                        | 66.0            | 1314.7                      | 25.6 at 21.2               | 226.1                            |
| G                         | 0.81924                  | 5.73                        | 68.0            | 1330.0                      | nm                         | 226.1                            |
| G1                        | 0.81665                  | 5.27                        | 63.0            | 1329.3                      | 26.5 at 21.3               | 226.1                            |
| G2                        | 0.81368                  | 4.91                        | 60.0            | 1328.9                      | 26.2 at 21.3               | 226.1                            |
| H1                        | 0.82944                  | 6.28                        | 66.0            | 1332.2                      | 25.7 at 21.3               | 226.1                            |
| H2                        | 0.79676                  | 5.01                        | 61.0            | 1320.2                      | 25.9 at 20.9               | 226.1                            |
| H3                        | 0.81826                  | 6.16                        | 66.5            | 1326.5                      | 25.9 at 20.9               | 219.76                           |
| H4                        | 0.80561                  | 5.48                        | 63.0            | 1318.5                      | 25.9 at 21.2               | 219.76                           |
| H5                        | 0.82533                  | 4.92                        | 61.3            | 1342.4                      | 26.9 at 21.5               | 219.76                           |
| I1                        | 0.80561                  | 4.73                        | 61.0            | 1318.9                      | 26.1 at 21.2               | 219.76                           |
| I2                        | 0.80759                  | 4.80                        | 64.0            | 1325.9                      | 26.3 at 21.1               | 219.76                           |
| I3                        | 0.81130                  | 4.89                        | 59.0            | 1322.2                      | 26.0 at 21.2               | 219.76                           |
| I4                        | 0.80562                  | 4.83                        | 63.0            | 1318.9                      | 26.0 at 20.7               | 219.76                           |
| I5                        | 0.80532                  | 4.70                        | 61.0            | 1318.7                      | 26.0 at 20.8               | 219.76                           |

"na," no reporting requirement for DCN; Cetane Index is a report-only requirement. "nm," not measured.

Finally, the data from the first two sets of surrogates were used to create linear correlations of density, speed of sound, viscosity, and flash point. When modeling flash point using the Liaw-type model, with the Antoine equation and coefficients for vapor pressure, the predictions were low by 1 K. Since the flash point range was small, this model was not used. To weight these properties evenly, the units for density, viscosity, and speed of sound were converted to g/mL, km/s, and 10⁻¹ mm²/s, respectively. The correlations were used to predict the density (P_surrogate), viscosity (P_surrogate), and speed of sound (P_surrogate) of a surrogate based on the amount of each component in the surrogate. The amount of each compound was constrained within its minimum and maximum for the category based on the fuel survey. Surrogates were then designed by minimizing the difference between the sum of three predicted physical properties of the surrogate and their target values for the jet fuel (eq 1)

\[ \sum_{i=1}^{3} (P_{surrogate} - P_{JP-5})^2 \]  

(1)
The GRC nonlinear solver in Excel was used to optimize the surrogate composition. The composition and properties of these “I” mixtures are given in Tables 2 and 3, respectively. All of the surrogates prepared had viscosities and densities that fall within that specification. Some of the surrogates had flash points that are below a minimum value of 60 °C. The DCN and distillation curve data were measured for a subset of surrogates (Table 3).

Six surrogate fuel mixtures were selected for engine testing, A3, E1, H2, H3, I2, and I4. The A3 surrogate had a composition that matched the average of the referenced JP-5 samples, and E1 had properties in the first round that were close to JP-5 and a DCN at the military specification limit for diesel fuel, F-76, of 42.\(^{19}\) Surrogate H2 was the surrogate with a high concentration of high DCN compounds, and surrogate H3 was the surrogate with the highest amounts of low DCN components. Note that H1 had an even lower DCN than H3, but it would not have combusted because the DCN is too low, so it was not used. Surrogates I2 and I4 had DCN values closest to the JP-5. The best surrogate in terms of properties was I4. The percentage differences between the surrogate property value and that of JP-5 were calculated by

\[
\text{% difference} = 100 \times \left( \frac{\text{value for JP-5} - \text{value for surrogate}}{\text{value for JP-5}} \right)
\]

(2)

The percentage differences between JP-5 and surrogate I4 were of 0.016% for density, 3.4% for viscosity, 0.79% for flash point, 0.015% for speed of sound, 0.39% for surface tension, 0.42% for T10, 2.7% for T50 and 2.9% for T90, and 1.5% for average molar mass. The DCN matched within the error of the measurements, being 0.3 lower than the JP-5 (Tables 3 and 4).

### 3.3. Combustion Testing

The combustion behavior of the JP-5 and six surrogate mixtures in the Yanmar Tier IV diesel engine was quantified using the following engine metrics: ignition delay, maximum rate of heat release, and peak pressure location, and crank angle location of when 50% of the fuel was burned. The ignition delay (from the start of injection to 10% of the fuel burned) engine results at both engine loads are shown in Figure 2. In general, the trends are as expected with higher DCN fuels leading to more reactive shorter IGDs. Also, high-load IGDs are shorter due to the hotter thermal state of the engine (faster overall chemical kinetics). The reference JP-5 used in this study has a nominal DCN of 44.5. The final two developed surrogate candidates, I2 and I4, are the two surrogates that bound the JP-5 “x” data points with slightly lower and higher DCN values. Considering the 95% confidence interval results, the four surrogates whose DCN values range from 44.2 to 48.8 have IGDs that agree with the baseline JP-5 at both high and light engine loads. The large error bars for the lowest cetane fuel are caused by erratic combustion, which is not consistent with the behavior of the JP-5. In general, the IGD behavior of the five surrogates with DCN > 40 is very similar (statistically) to the baseline JP-5.

The maximum rate of heat release (ROHR) results from the Yanmar engine testing are shown in Figure 3. The general trend is that the maximum ROHR falls off for both low DCN and high DCN fuels. In the case of low DCN fuels, combustion occurs very late (after engine top dead center) with relatively large cylinder volumes leading to lower overall combustion pressures. While for high DCN fuels, IGD is short leading to very little fuel–air premixing, followed by longer lower-intensity combustion events. From the statistical perspective (confidence interval, CI 95%, based on the cycle-to-cycle engine variations), five of the surrogates (with higher DCNs) have the same maxROHRs

| surrogate | density | viscosity | flash point | speed of sound | surface tension | DCN  |
|-----------|---------|-----------|-------------|----------------|----------------|------|
| A3        | 0.90    | 0.80      | 2.4         | 0.69           | 1.5            | 9.7  |
| E1        | 0.27    | 1.6       | 2.1         | 0.20           | 0.39           | 6.3  |
| H2        | 1.1     | 0.20      | 4.0         | 0.11           | 0.00           | 9.0  |
| H3        | 1.6     | 23        | 4.7         | 0.59           | 0.39           | 18   |
| I2        | 0.26    | 4.0       | 0.79        | 0.55           | 1.5            | 1.4  |
| I4        | 0.016   | 3.4       | 0.79        | 0.015          | 0.39           | 0.67 |

Previous work\(^{18}\) had mole fractions of the components in this surrogate mixture were 0.25, 0.40, 0.15, and 0.20 for n-dodecane, n-butyloxohexane, n-butylbenzene, and iso-cetane, respectively. \(^{18}\) A previously formulated surrogate using four compounds is included for comparison.

\(*\) The mole fractions of the components in this surrogate mixture were 0.19, 4.82, 4.52, 0.94, 1.54, 0.86, 0.42, 3.92, 4.52, 3.1

Figure 2. Ignition delay in Yanmar Tier 4 engine for JP-5 (designed by an “x”) and six surrogate mixtures. Surrogates on the order of DCN: H3 (DCN = 36.6), E1 (DCN = 41.7), I4 (DCN = 44.2), I2 (DCN = 45.1), H2 (DCN = 48.5), and A3 (DCN = 48.8).

Figure 3. Maximum rate of heat release (ROHR) results from the Yanmar engine testing are shown in Figure 3. The general trend
as the reference JP-5. The variabilities in their measurements are similar also.

The peak pressure location (PPLOC) experimental results from the Yanmar engine testing are shown in Figure 4. The very low DCN results show peak pressure results close to the piston top center (0°). This effect is due to the very late combustion with very low in-cylinder pressures that are not detectable by the MATLAB peak detection logic. There is a lot of variability in these data due to incomplete combustion events. In moving from DCN 41.7 to higher cetane levels, a modest advancing occurs due to the shorter IGDs and earlier overall combustion. At DCN 41.7, the variability in peak pressure location is much greater than that of JP-5, suggesting that the behavior of this surrogate is different. As with IGD, the surrogates with DCN values of 44.2–48.8 have peak pressure locations that agree with the JP-5 at both high and light engine loads and the combustion variations are similar.

The engine crankshaft location where 50% of the fuel has burned is shown next in Figure 5. This combustion metric is also referred to as CAD50 or a crank angle degree of 50% fuel burned. It is seen that the CAD50 for the lowest DCN fuel is very late from 35 to 40 crank angle degrees after engine top center. This result supports the very low max ROHR results for the lowest DCN fuel in Figure 3. It also further explains the location of the peak pressure in Figure 4 for the lowest DCN. As DCN increases above 40, it is evident that this mid-burn CAD50 combustion phasing is more conventional. Increasing DCN through the 40s range shows the CAD50 advancing from 18 degATC to nominally 13 degATC with little sensitivity to engine load. As with the other combustion properties, the surrogates with DCN values of 44.2–48.8 have CAD50s that agree with the JP-5 at both high and light engine loads and the combustion variations are similar.

3.4. Discussion. JP-5 surrogates were formulated in this experimental work in the context of a diesel engine, which has been done in only a few cases for jet fuel, 20,22,3,25,39 Recent past surrogates prepared in the author’s laboratory 29,40 for JP-5 had four components and were tested in a diesel engine. The surrogate development process in the current study differs from that of past work. For the past work, the density, viscosity, speed of sound, surface tension, and flash point (physical properties only) were measured for more than 70 surrogate samples containing butylbenzene, butylcyclohexane, dodecane, and isocetane and then compared to one specific JP-5 sample to determine which mixtures would be the best surrogates. 40 The current study additionally used the chemical compositions of 256 jet fuel samples to set the average and limits to the concentration of each type of chemical class used in the surrogate. Three more chemical classes were included in the current surrogate to better fit the properties. The properties of fewer surrogates were measured in the present study, and preliminary measurements led to rough correlations that could be used to formulate mixtures that were closest to the JP-5 fuel sample and were within the bounds of real JP-5. It is important to develop a surrogate specifically for JP-5 because surrogates for other jet fuels do not always capture the behavior of JP-5.

When comparing how close the properties were to the fuel, the percentage differences between the property value for the fuel and that of the surrogate mixture were calculated. For the previously developed 4-component surrogate that best matched the combustion of the baseline JP-5, the percentage differences in density, viscosity, flash point, and speed of sound were higher than for surrogates A3, E1, H2, I2, and I4 (Table 4). For surface tension, the % difference for the 4-component surrogate was the same or higher than the current surrogates. There was no consistent pattern for the volatility. The DCN for the 4-component surrogate matched that of its JP-5 within the error of the measurements, being only 0.4 higher than the JP-5 sample. 29 It is important to note that the percentage composition of the linear, branched, aromatic, and cyclic compounds in the “best” 4-component JP-5 surrogate in those studies did fall within the bounds of the category of components from the current surrogate study when grouping together all aromatic and cyclic compounds and not including cycloaromatic compounds like tetralin.

The JP-5 surrogates developed herein have components with flash points greater than 50 °C. When the mass fraction of components with flash points less than 60 °C exceeded 53.7%, the flash point of the surrogate fell below the 60 °C military minimum requirement. Jet fuel surrogates, such as those for Jet A, that do not have this flash point (FP) requirement have been prepared from components with flash points below the compounds used herein. Jet A, JP-8, and kerosene surrogates 14,16,11,13,15,19,24,66,68,69 have contained benzene (~11 °C FP), iso-octane (~12 °C FP), methylcyclohexane (~4 °C FP), toluene (4 °C FP), meta-xylene (27 °C), propylenebenzene (30 °C FP), ortho-xylene (32 °C FP), 1,2,4-trimethylbenzene (44 °C FP), and 1,3,5-trimethylbenzene (50 °C FP). 70 Two JP-8
surrogates contained three components with flash points below 60 °C, butylbenzene, butylcyclohexane, and n-decane (51 °C FP). The optimal surrogate developed in the current study has a flash point of 63 °C.

Diesel combustion experiments on five 4-component JP-5 surrogates showed that DCN is an important metric for predicting the performance of a diesel engine. The ensuing discussion highlighted the importance of measuring DCN and how difficult it is to predict DCN from mixture composition because studies have shown both linear and nonlinear relationships between DCN and composition. This difficulty in predicting DCN is further supported by Figure 6, which shows that DCN is not well predicted when using either a simple mole fraction or mass fraction weighting of the DCN of the individual components. More advanced prediction is beyond the scope of this paper, and many researchers are seeking ways to predict the DCN of individual compounds and mixtures. Researchers have sought various approaches to predicting CN or predicting the DCN of individual compounds and mixtures. More advanced prediction is beyond simple mole fraction or mass fraction weighting of the individual component DCN values.

4. CONCLUSIONS
In this study, six JP-5 surrogates composed of seven pure fuel components were formulated and tested in comparison to a nominal JP-5 fuel. The physical properties of five of the surrogates were very similar to that of the JP-5 and were within the military specifications. A key metric here was flash point, which is required to be above 60 °C, and makes this surrogate differ from those previously formulated for JP-8 and Jet A. The similarity in density, viscosity, and surface tension helps ensure comparable spray patterns in the engine. The similarity in distillation temperature helps ensure comparable volatilization behavior of the fuel. Surrogate I4 developed last had the closest physical properties to those of JP-5 and its DCN values within 1 DCN of JP-5. In the combustion experiments, several of the surrogates were able to match the combustion IGD, peak pressure, max heat release, and CAD50 of JP-5 in terms of the engine’s cycle by cycle average values and variability. The lowest DCN surrogate designed and tested contained a higher amount of lower cetane compounds (Mix H3) leading to erratic combustion behavior, similar to that seen in previous low cetane JP-5 surrogates. Of the six surrogates tested, the best one in terms of physical properties, chemical properties, and combustion behavior was the one that contained 0.2421, 0.1503, 0.0500, 0.0141, 0.0121, 0.2532, and 0.2782 mass percentages of n-dodecane, n-butylbenzene, 1-methylnaphthalene, tetralin, trans-decalin, iso-cetane, and n-butylcyclohexane, respectively. These are good components to have in a surrogate mixture because chemical kinetic models have been established or are currently being researched for these compounds. Lawrence Livermore Laboratory has developed kinetic models for dodecane, iso-cetane, and butylbenzene and is working to developing kinetics models for butylcyclohexane, tetralin, 1-methylnaphthalene, and trans-decalin.

Figure 6. Prediction of DCN using a mole fraction and mass fraction weighting of the individual component DCN values.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c05904.

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Notes
The authors declare no competing financial interest.

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