Physical and Chemical Analysis of Alcohol-to-Jet (ATJ) Fuel and Development of Surrogate Fuel Mixtures

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S Supporting Information

ABSTRACT: In this study, the chemical composition and physical properties of an alcohol-to-jet (ATJ) fuel were used to develop a surrogate mixture containing commercially available hydrocarbons. Analysis of the chemical composition of the ATJ showed a high quantity of two specific branched alkanes (2,2,4,4,6,8,8-heptamethylnonane and 2,2,4,6,6-pentamethylheptane) and a small quantity of other branched alkanes that are isomers of these two alkanes. Surrogate mixtures containing 2,2,4,4,6,8,8-heptamethylnonane and a mixture of isododecane isomers were prepared to determine what composition would match the density, viscosity, speed of sound, bulk modulus, surface tension, and flash point of ATJ. The optimal surrogate contained a 0.25 mass fraction of 2,2,4,4,6,8,8-heptamethylnonane in isododecane isomers. Combustion experiments were then conducted in a Yanmar diesel engine with fuel mixtures containing 70% (by volume) petroleum jet fuel with 30% ATJ, 2,2,4,4,6,8,8-heptamethylnonane, the optimal surrogate mixtures based on physical properties, or the isododecane isomers. The startup performances of the three 30% surrogate mixtures were very similar to that of the 70% JP-5 with 30% ATJ fuel. No significant differences were seen in the engine combustion characteristics of the three 70/30 surrogates, as compared to the base 70% JP-5/ 30% ATJ fuel mixture. These results show that a surrogate mixture has been successfully prepared that matches the physical and chemical properties and combustion behavior of an ATJ fuel.

INTRODUCTION

As nations around the world introduce fuels derived from alternative sources into their commercial pipelines, military forces that refill at various locations need to determine the impact of these new fuels on the combustion process in their engines. Some alternative fuels can be used directly in engines, while others must be mixed with petroleum products for successful use.[1−9] In early 2014, it was reported that the U.S. Army tested a 50/50 mixture of petroleum-based jet fuel and a bio-based jet fuel made from isobutanol (Gevo) in their UH-60 Black Hawk helicopter.[3] This isobutanol-derived fuel is currently called alcohol-to-jet (ATJ) fuel. Jet fuel must also be tested in diesel engines because of the military's single fuel forward policy, which specifies that all equipment use the same fuel when possible.[10] Recent combustion experiments have found that ATJ could be added up to 30% (by volume) to jet fuel before diesel engine start times were adversely affected.[4] In conjunction with the engine tests, numerical modeling efforts strive to understand the combustion process of these fuels. As with many fuels, understanding and modeling the transport and combustion of ATJ can be simplified if a mixture containing only a few compounds, called a surrogate mixture, can be found that matches the ATJ fuel's properties. With fewer components, computational combustion models would require less input on

the properties of each component in the fuel and the relevant chemical kinetic rate constants, reaction pathways, and thermodynamic parameters.[11] Surrogate mixtures can also provide information on what fuel properties are the most important for enhancing engine combustion.

Researchers have developed surrogate mixtures for bio-based fuels such as algal hydrotreated renewable diesel,[8] hydrotreated renewable jet fuel,[9] and biodiesel,[12] as well as for petroleum diesel fuel,[13−16] gasoline,[17,18] aviation fuels,[19−25] coal-derived liquid fuel,[26,27] gas-to-liquid jet fuels,[28] and rocket propellants.[29,30] Edwards and Maurice[30] categorize surrogate mixtures as either "physical surrogates", whose physical properties closely match those of the original fuel, or as "chemical surrogates", whose chemical and combustion characteristics closely match those of the original fuel. In some studies, the chemical kinetic mechanism used in the computer simulations of the combustion process is for the specific compounds in the surrogate mixture, whereas, in other simulations, fewer components or general categories of compounds are used.[12,29,20,24] The properties used in surrogate development have included density, viscosity, speed

of sound, derived cetane number, research octane number, lower heating value, thermal conductivity, flash point, and information from the distillation curve or advanced distillation curve.[8,14,22,23,26,29,31,32] Surrogates have contained between 1 and 14 components. Kim et al.[21] developed two four-component surrogates of conventional jet fuel by minimizing the difference between the surrogate and a jet fuel's cetane number, lower heat value, hydrogen-to-carbon ratio, molecular weight, and density using weighting factors for each component. Luning Prak et al.[8] used composition information and flash point to develop five-component surrogates for algal-based hydrotreated renewable diesel. They then tested the physical properties of the fuel (density, viscosity, surface tension, bulk modulus) and measured combustion behaviors in a diesel engine (start of ignition, start of combustion, ignition delay, maximum heat release, and overall combustion duration).[8]

Surrogate mixtures have been tested and, in some cases, modified based on combustion product composition in jet stirred reactors and in variable-pressure flow reactors,[19,20,24,27,28,33] ignition delay in shock tubes,[12,24,27,28] laminar flame speeds in flame test rigs,[27,28] diffusive extinction limits in a counter flow diffusional flame burner,[19,24] thermal efficiency, combustion phasing, and maximum pressure rise in single cylinder gas engines,[17] heat release rate and start of combustion in a four-stroke direct-injection single cylinder diesel engine,[15] soot in a burner or shock tube,[34−36] ignition delay in a rapid compression machine,[9] and the start of combustion, ignition delay, and combustion duration in a diesel engine.[37] Perez and Boehman[17] developed a five-component surrogate mixture for gasoline by optimizing the combustion metrics including thermal efficiency, crank angle for 50% heat release, and maximum pressure rise in an homogeneous charge compression engine. Other researchers have developed numerical models of the combustion process and compared their predictions for the surrogates with those of real fuels using laboratory data from the literature.[16,38−41]

In the current study, the goal was to develop surrogate mixtures for ATJ that would match the fuel properties that are important for fuel handling, pumping, and safety (density, viscosity, flash point, surface tension, speed of sound, bulk modulus, and flashpoint) and test the surrogates in a military diesel engine. Since recent combustion experiments in diesel engines have found that start times were adversely affected when more than 30% ATJ by volume was added to petroleum jet fuel,[4] the surrogates were tested in mixtures at 30% volume, with the remaining 70% being petroleum JP-5. The method used to develop the surrogate mixture involved determining the major components of the ATJ fuel by chemical analysis and measuring physical properties of the ATJ fuel including density, viscosity, flash point, speed of sound, surface tension, and flash point. The physical properties of petroleum JP-5 were also measured for comparison with the ATJ. Several surrogate mixtures were prepared by varying the amount of the major components found in the ATJ and comparing the physical properties of the surrogate with the ATJ. Several surrogates were mixed with petroleum JP-5 and tested in a military diesel engine.

■ EXPERIMENTAL SECTION

Materials. The pure organic compounds used in the composition analysis of the ATJ fuel included hexane (Aldrich), 4-methyl octane (TCI Chemicals), 3,5-dimethylheptane (ChemSampCo), 3,6-dimethyloctane (ChemSampCo), 2-methyl nonane (Sigma−Aldrich), undecane (Sigma−Aldrich), 3-methylundecane (TCI), dodecane (Sigma−Aldrich, 99+% pure), tridecane (Sigma−Aldrich), 2-methyl tridecane

(MP Chemicals), tetradecane (MP Chemicals), pentadecane (Sigma−Aldrich), 2-methyl pentadecane (MP Chemicals), hexadecane (Sigma−Aldrich, >99% pure), 2-methyl hexadecane (MP Chemicals), 2,2,4,6,6-pentamethylheptane (TCI), and 2,2,4,4,6,8,8-heptamethylnonane (Aldrich, 98% purity). Surrogates were made with 2,2,4,4,6,8,8-heptamethylnonane (isocetane) and isododecane (80% mixture of isomers, Alfa Aesar). The petroleum JP-5 fuel and the alcohol-to-jet fuel (ATJ) were provided by the Naval Fuels and Lubricants Cross Function Team at Patuxent River, MD (PAX River). The ATJ was produced by Gevo using proprietary microorganisms to produce butanol.[42] The butanol was then dehydrated using a catalyst to produce an alkene, and the alkene monomers are oligomerized. Hydrogenation was then used to reduce the number of any remaining double bonds.

Analyses of Chemical and Physical Properties. To determine the composition of the ATJ, GC/MS analysis was conducted and comparisons were made with pure organic compounds. In the analysis, a Shimadzu Model QP2010SE single quadrupole mass spectrometer was used in conjunction with a Shimadzu Model 2010 Plus Gas Chromatograph. The analysis conditions were the same as used in previous studies.[8] Each sample was analyzed using the GC operating at a helium flow rate of 1.5 mL/min and containing a Restek Rxi-5 ms column (30 m, 0.25 mm, 0.25 μm, 5% diphenyl/95% dimethyl polysiloxane). To separate the compounds, a temperature ramping program was used, starting at 60.0 °C and climbing at a rate of 10 °C/min to 250 °C. An electron impact ionization (EI) method was used for the mass spectrometer with an m/z scan from 30 to 600. To prevent the detector from being saturated, all samples analyzed were diluted in n-hexane until the ratio of fuel to n-hexane was less than 1:10 000. The mass spectral analysis was delayed until the solvent peak had passed. The retention times of the various hydrocarbons were determined for comparison with the ATJ. No standards were prepared for quantitative measurements.

The flash point of the fuels and surrogate fuel mixtures was measured using a Setaflash Series 8 closed-cup flash point tester (Model 82000-0, Stanhope-Seta) under temperature ramping settings. This flash point model conforms to ASTM D3828 (gas ignition option), ASTM D1655 (gas ignition option), ASTM D3278, ASTM D7236, and ASTM E502, per the manufacturer's literature, and has been used in past studies of surrogate mixtures and alternative fuels.[8,31,32,43,44] The viscosity of the ATJ and surrogate fuel mixtures was measured using a Model SVM 3000 Stabinger Viscometer (Anton Paar), and the speed of sound was measured using a Model DSA 5000 Density and Sound Analyzer (Anton Paar). Both instruments were used to measured density. NIST-certified and NIST-traceable standards (Standard S3, Cannon Instrument Company) were used to check the accuracy and calibrate each instrument as described in previous work.[43,44] Using Model SVM 3000 Stabinger Viscometer, duplicate samples of each individual liquid or liquid mixture were measured at 10 temperatures between 20 °C and 100 °C. Using the DSA 5000 analyzer, each sample was measured twice at five temperatures between 20 °C and 50 °C. The duplicate measurements for both instruments were used to determine the precision of the measurement. The isentropic bulk modulus (E_v, in units of Pa) was calculated at each temperature and ambient pressure by

$$E_v = c^2 \rho \tag{1}$$

using the density (ρ, given in units of kg m^{-3}) and speed of sound (c, given in units of m s^{-1}) measurements from the DSA 5000 analyzer.

The surface tension of the ATJ and surrogate mixtures was measured via a Kruss Model DS100 axisymmetric drop shape analyzer using procedures reported in previous work.[8,31,32,37,43−47] Briefly, a liquid droplet of the each sample is formed at the tip of a needle in air. An image of the droplet is taken, enlarged, and fit with the Young−LaPlace equation, using input of the densities of the organic phase and air and the diameter of the needle, which was measured using a micrometer.

Analyses of Combustion in Military Diesel Engine. Engine tests were run on mixtures each containing 70% (by volume) JP-5 and the remaining 30% being ATJ or a surrogate of ATJ in a laboratory-installed Yanmar Model L100 V single-cylinder diesel engine coupled to a 6 kW electrical generator. Further tests were also conducted using JP-5, as well

as mixtures of JP-5 with ATJ in the 80/20 and 60/40 blend ratios so that engine sensitivity to fuel composition could be further discerned. The engine-generator test stand was heavily instrumented, including fast in-cylinder and fuel-line pressure sensors as well as conventional flow and temperature sensors. Details of this engine test stand can be found in Arment et al.[48] In order to compare one fuel to another, standard in-cylinder combustion metrics were analyzed from the high-speed experimental data.[49] These include the start of injection, the start of combustion, the ignition delay, the maximum rate of heat release, combustion duration, and combustion phasing (CA50 = crank angle 50% fuel burned location). These combustion metrics are based on an energy conservation analysis of the closed engine cylinder during compression, combustion, and expansion.[50,51] Ignition delay and combustion phasing are the most commonly used metrics to characterize diesel combustion. It is of interest to see how closely the combustion characteristics of surrogate fuel mixtures compare to that of ATJ.

To help understand the combustion behavior, the derived cetane number was measured using an Advanced Engine Technology Ltd.'s Ignition Quality Tester. These tests were completed in accordance with ASTM D6890 Standard Test Method for Determination of Ignition Delay and Derived Cetane Number (DCN) of Diesel Fuel Oils.[52]

RESULTS AND DISCUSSION

The goal of this surrogate development was to determine the major components of the ATJ and then prepare a hydrocarbon mixture that matches the physical properties as closely as possible. The properties selected in this work to match those of the ATJ were density, viscosity, speed of sound, bulk modulus, surface tension, and flash point.

Property Measurements for ATJ and Petroleum JP-5. Density and viscosity were measured over the range of temperature from 20 °C to 100 °C, as shown in Figures 1 and
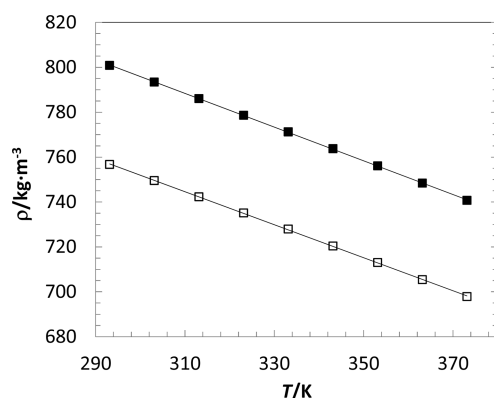

Figure 1. Comparison of the density of petroleum: (■) JP-5 jet fuel and (□) ATJ.

2. The petroleum JP-5 is denser and less viscous than the ATJ. The variation in density with temperature is linear. A least-squares fitting program (Excel, 2010), was used to generate the equations:

$$\text{density (petroleum JP-5, kg m}^{-3})$$
$$= -0.7502\,T(\text{K}) + 1020.9 \qquad (2)$$

$$\text{density (ATJ, kg m}^{-3}) = -0.7353\,T(\text{K}) + 972.5 \qquad (3)$$

The speed of sound, bulk modulus, surface tension, and flash point of the petroleum JP-5 are higher than those of ATJ, as shown in Table 1. The ATJ chemical composition and these
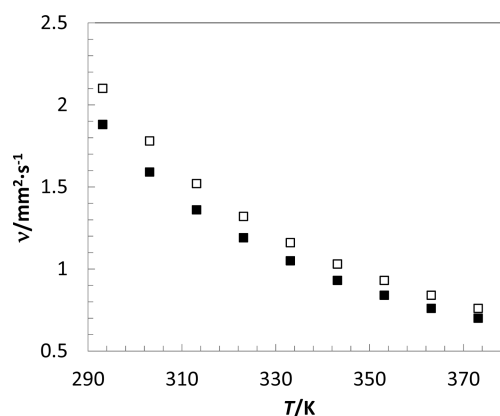

Figure 2. Comparison of the kinematic viscosity of petroleum: (■) JP-5 jet fuel and (□) ATJ.

Table 1. Physical Property Information for Petroleum JP-5 and ATJ

property	temp (K)	ATJ	JP5
density (kg m^{-3})	293.15	756.7	800.9
kinematic viscosity (mm^2 s^{-1})	293.15	2.10	1.88
speed of sound (m s^{-1})	293.15	1229.1	1316.9
bulk modulus (MPa)	293.15	1143	1389
surface tension (mN m^{-1})	294	22.3	26.1
flash point (K)		322	334

physical properties were used to select the composition of the surrogates.

Composition of ATJ. The ATJ has components that span a smaller boiling point range than the petroleum-based JP-5, as shown in the GC/MS scan in Figure 3. The petroleum JP-5 had
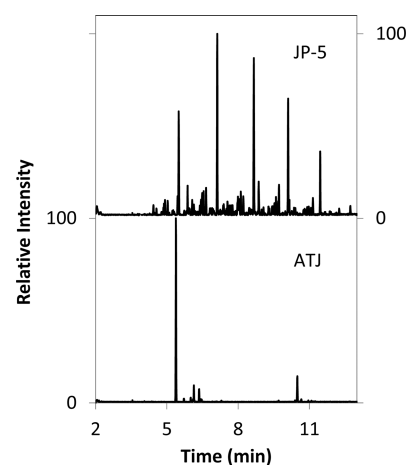

Figure 3. Gas chromatography/mass spectrometry scan of (top) petroleum jet fuel (JP-5) and (bottom) ATJ.

five dominant peaks and many minor peaks, ranging in retention time from 3.5 min to 12.7 min, while the ATJ only had two dominant peaks at 5.37 and 10.48 min with a few other smaller peaks at retention times between them. To determine the potential identity of the components, the retention time and mass spectra of the components in the ATJ were compared with the retention time and mass spectra of commercially available pure component linear and branched alkanes ranging from 9 to 15 carbons in length. As shown in Table 2 and Figure 4, the

Table 2. Physical Property Information and Retention Time Data

organic liquid	formula	boiling point (K)[a]	molar mass	retention time (min)
3,5-dimethylheptane	C_9H_{20}	409	128	3.05
4-methyl octane	C_9H_{20}	415	128	3.39
3,6-dimethyloctane	$C_{10}H_{22}$	433	142	4.53
2-methyl nonane	$C_{10}H_{22}$	440	142	4.91
2,2,4,6,6-pentamethylheptane	$C_{12}H_{24}$	451	170	**5.37**
2-methyldecane	$C_{11}H_{24}$	462	156	6.55
n-undecane	$C_{11}H_{24}$	468	156	7.13
3-methyl undecane	$C_{12}H_{26}$	484 ± 10	170	8.23
n-dodecane	$C_{12}H_{26}$	489	170	8.67
n-tridecane	$C_{13}H_{28}$	507	184	10.11
2,2,4,4,6,8,8-heptamethylnonane	$C_{16}H_{34}$	513	226.4	**10.48**
2-methyl tridecane	$C_{14}H_{30}$	518 ± 3	198	10.98
n-tetradecane	$C_{14}H_{30}$	523	198	11.46
n-pentadecane	$C_{15}H_{32}$	540	212	12.73

[a]Data taken from refs 53−56.
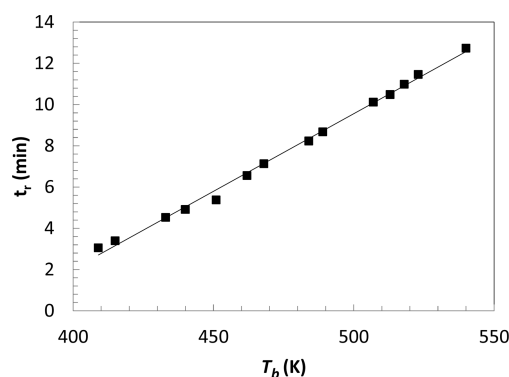
Figure 4. Retention time (t_r) of linear and branched alkanes based on boiling point (T_b). The linear fit to the data is $t_r = 0.0753T_b(K) − 28.078$.

retention times of the linear and branched alkanes increased fairly linearly with increasing boiling point with retention times (t_r's) ranging from 3.05 min to 12.75 min for boiling points (T_b's) ranging from 409 K to 540 K. The linear fit to the data is

$$t_r = 0.0753T_b(K) − 28.078 \qquad (4)$$

This trend suggests that all compounds studied have a similar interaction with the chromatography column.

Since only a few branched alkanes are commercially available, a spectral database search was also conducted for each peak using the NIST library. At a selected retention time, the searching program determines what compounds in its database have fragmentation patterns that match those found in the MS analysis. Seven peaks on the ATJ spectra at retention times of 5.37, 5.72, 6.01, 6.12, 6.36, 10.48, and 10.66 min comprise ∼96% of the total peak area or peak height (Table 3). The top NIST library searches for all peaks are branched alkanes ranging from 9 to 16 carbons, as given in Table 3. For the largest peak that has a retention time of 5.37 min, the mass spectra of this component matches that of the purchased pure compound 2,2,4,6,6-pentamethylheptane ($C_{12}H_{26}$), as shown in Figure 5, and both have the same retention time. The other matches from the NIST database have boiling points that would be predicted to have retention times longer than 6.55 min and shorter than 3.05 min,

based on eq 4. For the second largest peak that has retention time of 10.48 min, the mass spectra of this component matches that of the purchased pure compound 2,2,4,4,6,8,8-heptamethylnonane ($C_{16}H_{34}$), as shown in Figure 6, and both have the same retention times. Several other matches from the NIST database have boiling points of <500 K that would be predicted to have retention times of <9.6 min, based on eq 2. The only other match that is close is 2,2,4,4,5,7,7-octamethyloctane, which has a boiling point of 519 K, which is slightly higher than that of 2,2,4,4,6,8,8-heptamethylnonane (513 K). Based on its boiling point and eq 2,2,2,4,4,5,7,7-octamethyloctane would have a retention time of 11.0 min, which is 0.5 min higher than the peak of interest.

For the five remaining peaks that comprise ∼15% of the peak area, no pure components were available to confirm the compound. For the peaks at 5.72 and 6.01 min, the closest predicted spectral matches were for 2,2-dimethyldecane and 2,2,4,4-tetramethyloctane, respectively. Both of these compounds are dodecane isomers and would likely have retention times near that of the 2,2,4,6,6-pentamethylheptane, which is also a dodecane isomer. For the peaks at 6.12 and 6.36 min, the library search result of 3,6-dimethyloctane is not correct, because a pure component sample of this compound had a retention time of 4.53 min. The tridecane isomers could be possible because their boiling points are above that of the dodecane isomer 2,2,4,6,6-pentamethylheptane. For the peak at 10.66 min, which constitutes only 1% of the total remaining area, the 3,7-dimethylnonane and 3,5-dimethylundecane seem to have boiling points that are too low for this retention time, while the trimethyldodecane isomers seem to have more reasonable boiling points. No definite conclusion can be drawn for this retention time. Based on this analysis, the majority of the compounds present in ATJ were branched isomers of dodecane and hexadecane (2,2,4,4,6,8,8-heptamethylnonane).

Surrogate Mixture Development. Given that the ATJ consisted of ∼74% dodecane isomers and 9.9% 2,2,4,4,6,8,8-heptamethylnonane, four surrogate mixtures were prepared with varying masses of 2,2,4,4,6,8,8-heptamethylnonane in isododecane isomers, using a commercial isomer mix of isododecane, which is significantly less expensive than pure 2,2,4,6,6-pentamethylheptane. The physical properties of these mixtures were compared with ATJ to determine the best surrogate. When comparing the density and viscosity of the surrogate mixtures with those of ATJ at 298.15 K (Figure 7), the mass fraction of 2,2,4,4,6,8,8-heptamethylnonane in isododecane isomers that gives values most similar to those of ATJ is 0.2286 (between 0.2286 and 0.3309 mass fraction). A complete set of density and viscosity data for all temperatures tested can be found in the Supporting Information. The speed of sound and bulk modulus values for ATJ (Figure 8) are matched at mass fractions of 2,2,4,4,6,8,8-heptamethylnonane between 0.2286 and 0.3309. The values for surface tension and flash point do not vary significantly between 0.1759 and 0.3309 mass fractions of 2,2,4,4,6,8,8-heptamethylnonane in isododecane (Table 4), and any of those surrogates could match the ATJ. If a line is fit of the physical properties as a function of mass fraction for the four surrogates only, the "optimal" mass fractions could be estimated to be 0.25 (density), 0.22 (viscosity), 0.26 (speed of sound), and 0.26 (bulk modulus). Based on the physical properties, an optimal surrogate was prepared containing 0.25 mass fraction of 2,2,4,4,6,8,8-heptamethylnonane in isododecane isomers.

JP-5/Surrogate Mixtures Prepared for Engine Combustion. Recent combustion experiments have found that ATJ alone cannot be burned in diesel engines, because the engine will

Table 3. NIST Library Search Top Matches for ATJ Peaks

retention time (min)	percentage of total peak area	percentage of total peak height	top NIST matches	boiling point[a] (K)	
5.37	71.3	70.8	2,2-dimethyldecane	470	$C_{12}H_{26}$
			2,2,4,6,6-pentamethylheptane	451	$C_{12}H_{26}$
			4-ethyl-2,2,6-trimethylheptane	468	$C_{13}H_{28}$
			2,2,9-trimethyldecane	486	$C_{13}H_{28}$
			2,2,4-trimethylhexane	400	C_9H_{20}
5.72	1.3	1.3	2,2,3-trimethylnonane	475	$C_{12}H_{26}$
			2,2-dimethyldecane	470	$C_{12}H_{26}$
			2,2,9-trimethyldecane	486	$C_{13}H_{28}$
			2,2,4-trimethylheptane	420 ± 2	$C_{10}H_{22}$
			3-ethyl-2,2-dimethylheptane	407	C_9H_{22}
6.01	1.6	1.6	2,2,4,4-tetramethyloctane	465 ± 7	$C_{12}H_{26}$
			2,2-dimethyldecane	470	$C_{12}H_{26}$
			2,2-dimethylundecane	493 ± 7	$C_{13}H_{28}$
			2,2,9-trimethyldecane	486	$C_{13}H_{28}$
			2,2,3-trimethylnonane	475	$C_{12}H_{26}$
6.12	6.2	6.8	3,6-dimethyloctane	433	$C_{10}H_{22}$
			2,6,10-trimethyldodecane	525.1	$C_{13}H_{28}$
			2,5,9-trimethyldecane	484.25	$C_{13}H_{28}$
			2,6,7-trimethyldecane	490 ± 7	$C_{13}H_{28}$
			3,5-dimethyloctane	432	$C_{10}H_{22}$
6.36	4.8	4.7	2,5,9-trimethyldecane	484.25	$C_{13}H_{28}$
			3,6-dimethyloctane	433	$C_{10}H_{22}$
			2,6,7-trimethyldecane	490 ± 7	$C_{13}H_{28}$
			2,5,6-trimethyloctane	451 ± 7	$C_{11}H_{24}$
			4,6-dimethylundecane	491 ± 7	$C_{13}H_{28}$
10.48	9.9	10.3	2,2,4,4,6,8,8-heptamethylnonane	513	$C_{16}H_{34}$
			2,2,4,4,5,5,7,7-octamethyloctane	519	$C_{16}H_{34}$
			2,2,4,4-tetramethyloctane	465 ± 7	$C_{12}H_{26}$
			2,5-dimethyldecane	472 ± 7	$C_{12}H_{26}$
			3,6-dimethylundecane	493 ± 7	$C_{13}H_{28}$
10.66	1.0	1.3	2,6,10-trimethyldodecane	525.1	$C_{15}H_{28}$
			3,7-dimethylnonane	456 ± 7	$C_{11}H_{24}$
			3,5-dimethylundecane	493 ± 7	$C_{13}H_{28}$
			2,7,10-trimethyldodecane	522 ± 7	$C_{15}H_{28}$
	96.1	96.8			

[a]Data taken from refs 54 and 57−59, unless noted otherwise.

Figure 5. Mass spectrometry scan of 5.37 min peak on (top) ATJ and (bottom) 2,2,4,6,6-pentamethylheptane gas chromatograms.

not start.[4] ATJ could be added up to 30% (by volume) to jet fuel before diesel engine start times were adversely affected, so a mixture was prepared using 70% (by volume) JP-5 and 30% of the optimal surrogate suggested by the physical property measurements (0.25 mass fraction of 2,2,4,4,6,8,8-heptamethylnonane in isododecane isomers).[4] Additional JP-5/surrogate mixtures were also prepared with 70% (by volume) JP-5 and with 30% 2,2,4,4,6,8,8-heptamethylnonane or the isododecane isomers. Comparison of the physical and chemical properties of these mixtures with those of 70% (by volume) JP-5 and 30% ATJ show that the JP-5 mixture with the optimal surrogate had the closest values for density, viscosity, speed of sound, and bulk modulus to the values for the ATJ mixture (see Table 5). The values are shown in boldface font in Table 5. For the surface tension, flash point, and derived cetane number (DCN), both the optimal surrogate and isododecane isomer mix surrogate had properties similar to those of the ATJ mixture (Table 5). The DCN results for the various 70/30 blends were very close to each other and well within the repeatability of the test, except for the isocetane blend. The 70/30 JP-5/isocetane blend has a lower DCN value than the other 70/30 blends, because of the slightly lower DCN of isocetane (15.4), compared to 16.3 for isododecane and 16.8 for the optimal surrogate.

Combustion in Military Diesel Engine. Startup and steady-state engine testing was performed using a Yanmar diesel
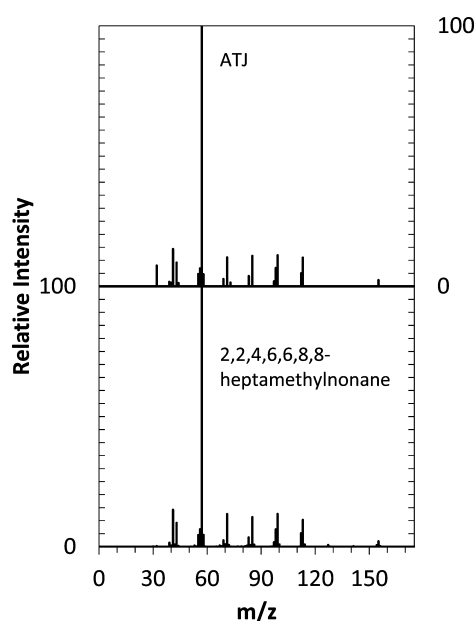
Figure 6. Mass spectrometry scan of 10.48 min peak on (top) ATJ and (bottom) 2,2,4,6,6,8,8-heptamethylnonane gas chromatograms.
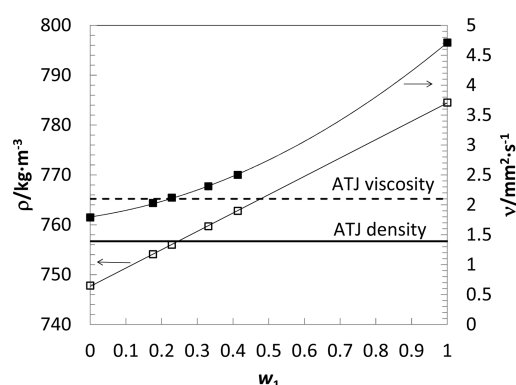

Figure 7. Comparison of the density (horizontal solid line) and viscosity (horizontal dotted line) of ATJ at 298.15 K with the (□) density and (■) viscosity of the prepared surrogate mixtures containing various mass fractions of 2,2,4,4,6,8,8-heptamethylnonane (w_1) in dodecane isomers.

engine generator set (6 kW). Each fuel was cold-started at least twice in order to confirm consistency. The startup engine speed results are shown in Figure 9. It can be seen that JP-5 (orange line) gives a start time (engine RPM reaches rates speed of 3600 rpm) of 3 s. Next, the 80% JP-5 with 20% ATJ (pink line, 80/20 mixture) shows that the engine is slower to reach rated speed, nominally 9 s, thus much slower with the 20% addition of the low cetane ATJ fuel. The 70% JP-5 with 30% ATJ is shown with the black data line. The start time is delayed with the additional ATJ content, with the engine reaching rated speed after ~18 s. The three 70% JP-5 with 30% surrogate fuels are shown next, with the green line (using the 30% optimal surrogate (mixture of 2,2,4,4,6,8,8-heptamethylnonane and isododecane)), the blue line (using 30% of the isododecane isomer surrogate), and the red line (using 2,2,4,4,6,8,8-heptamethylnonane surrogate). It can be seen that all four 70% (by volume) JP-5 fuel mixtures (70/30 mixtures) produce start times approaching 20 s. From the authors' experience, the repeatability of these start experiments produces a standard deviation of nominally 1 s on start time
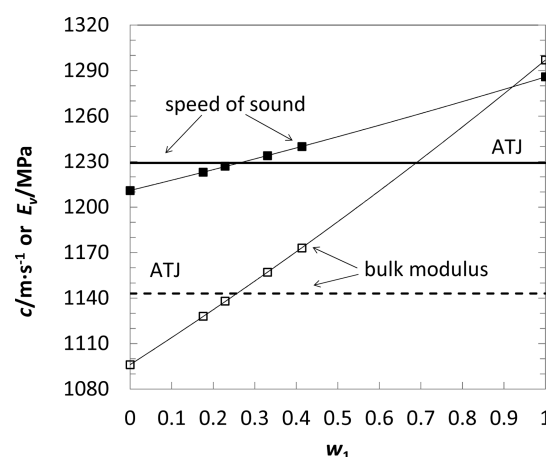

Figure 8. Comparison of the speed of sound (horizontal solid line) and bulk modulus (horizontal dotted line) of ATJ with the (■) speed of sound and (□) bulk modulus of the prepared surrogate mixtures containing various mass fractions of 2,2,4,4,6,8,8-heptamethylnonane (w_1) in dodecane isomers.

when start times are delayed by lower cetane fuel content. Thus, the differences in the four 70/30 start times are not statistically significant; however, the 70/30 surrogates with isocetane show slightly slower engine speed runups late in the range of 3000−3600 rpm. This behavior is consistent with the slightly lower DCN value associated with isocetane mixture. Fuels with lower DCN number have been shown to have longer engine speed run-up times.[4] However, the major similarities in combustion performance may be attributed to other fuel properties, which are compensating for the slightly lower DCN. The 70/30 JP5/isocetane blend has a higher density (and possibly higher heat value) and higher bulk modulus. These two combined may compensate for the slightly lower DCN. Lastly, the yellow data line shows the engine starting speed with 60% JP-5 and 40% ATJ (60/40 mixture). It can be seen that, with 40% ATJ, the engine does not reach rated speed within a data collection time of 30 s. The engine startup results for the 80/20 and 60/40 mixtures also provide an interesting frame of reference for the four 70/30 fuel mixture tests, further confirming that there is very little difference in the four 70/30 fuel blends.

Next, ignition delay (IGD) results are shown in Figure 10 for the four fuels containing 70% JP-5 and 30% of either ATJ, the optimal surrogate (mixture of 2,2,4,4,6,8,8-heptamethylnonane and isododecane), isododecane isomer surrogate, or the 2,2,4,4,6,8,8-heptamethylnonane surrogate. IGD is determined from both the fuel injection pressure signal as well as the in-cylinder pressure sensor. IGD is defined as the time from the start of injection (SOI) to the start of combustion (SOC), as determined using a MIT single zone engine heat release analysis. It can be seen in Figure 10 that all four fuels show significant variability during the first 20 s after the start of cranking. This time period corresponds to the engine run-up period. The erratic IGD results are one reason why the engine run-up to rated speed is so much longer than that observed with JP-5. The data on the x-axis (zero IGD) are all cycles that misfired (no combustion event). The general pattern of misfires was one misfire event followed by a firing event. Since the engine speed is changing during the engine run-up period, the time required for an individual crank angle degree is variable. Next shown in Figure 10b is the IGD data from Figure 10a; however, this time plotted in milliseconds. Generally speaking, it can be seen that IGD

Table 4. Flash Point and Surface Tension at 293.15 K of ATJ Fuel and Surrogate Mixtures[a]

	ATJ	$W_1 = 0.00$	$W_1 = 0.1759$	$W_1 = 0.2286$	$W_1 = 0.3309$	$W_1 = 0.4134$	$W_1 = 1.00$
flash point (K)	322	319	321	323	324	326	367
surface tension (mN m^{-1})	22.3[b]	21.8	22.4(6)	22.4(1)	22.5(4)	22.7	24.0

[a]W_1 is the mass fraction of 2,2,4,6,8,8-heptamethylnonane in isododecane. The error associated with surface tension is 0.1 dyn/cm, and the error associated with the flash point is 1 K. [b]Data taken from ref 4.

Table 5. Comparison of Physical Property Information of Mixtures Containing 70% JP-5 and 30% of the Surrogates or the ATJ[a]

property	temperature (K)	ATJ	JP5	30% ATJ	30% optimal surrogate[b]	30% isocetane[c]	30% isododecane
density (kg m^{-3})	293.15	756.7	800.9	**787.5**	**787.4**	795.9	785.0
kinematic viscosity (mm^2 s^{-1})	293.15	2.10	1.88	**1.91**	**1.93**	2.31	1.82
speed of sound (m s^{-1})	293.15	1229.1	1316.9	**1291.9**	**1291.1**	1308.2	1286.7
bulk modulus (MPa)	293.15	1143	1389	**1314.7**	**1312.5**	1362.1	1299.8
surface tension (mN m^{-1})	294 ± 1	22.3[d]	26.1	**24.5**	**24.6**	25.3	**24.5**
flash point (K)		322	334	**329**	**330**	340	**328**
derived cetane number		18[d]	45[d]	**40.4**	**40.2**	39.1	**40.6**

[a]The errors in the measurements are 0.02 kg m^{-3}, 0.06 mm^2 s^{-1}, 0.4 m s^{-1}, 0.5 MPa, 0.1 mN m^{-1}, 1 K for density, viscosity, speed of sound, bulk modulus, surface tension, and flash point, respectively. [b]The optimal surrogate contains 0.25 mass fraction of 2,2,4,6,8,8-heptamethylnonane in isododecane isomers. [c]Isocetane = 2,2,4,6,8,8-heptamethylnonane. [d]Data taken from ref 4.
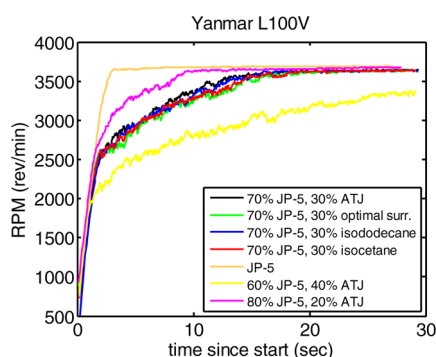

Figure 9. Engine speed (data given in revolutions per minute (RPM)) during a cold engine start with the various tested fuels: JP-5, 60% JP-5 with ATJ, 80% JP-5 with ATJ, 70% JP-5 with ATJ, 70% JP-5 with either the optimal surrogate, isododecane, or 2,2,4,6,8,8-heptamethylnonane (isocetane).

becomes shorter as the time increases (e.g., increasing engine speed). This effect is believed to be both due to the increased turbulence at higher engine speeds, as well as the increasing thermal state of the engine, because of progressive combustion events.

In order to get a better sense of the average nature of the IGD for each fuel during the first 30 s after the start of crank, a sixth-order MATLAB curve fit was applied to each dataset, excluding the misfire cases. Figure 11 shows these fits for the 70/30 mixtures as well as those for the 80% JP-5 with 20% ATJ fuel and the 60% JP-5 with 40% ATJ fuel. The four 70% JP-5 data lines are all reasonably similar to one another, and again as with engine RPM, are not statistically significantly different. Generally, IGD increases (in crank angle degrees) with time since the start over the first 10 s. This lengthening is due to the engine speed increasing, thus crank angle degrees are occurring faster in real time. Once the maximum in IGD (in crank angle degrees) is reached, then IGD begins to shorten again. This later effect is believed due to the fuel-air ratio leaning out from the mechanical governor as the rated speed is approached. It is important to keep in mind that as shown in Figure 10b, when IGD is measured on a time basis, it steadily shortens with increasing time since the start of cranking.

Finally, the location in degrees after top dead center (TDC) in the engine where 50% of the fuel has burned is shown in Figure 12 for the four fuels containing 70% JP-5 and 30% of either the ATJ, optimal surrogate (mixture of 2,2,4,6,8,8-heptamethylnonane and isododecane), isododecane isomer surrogate, or the
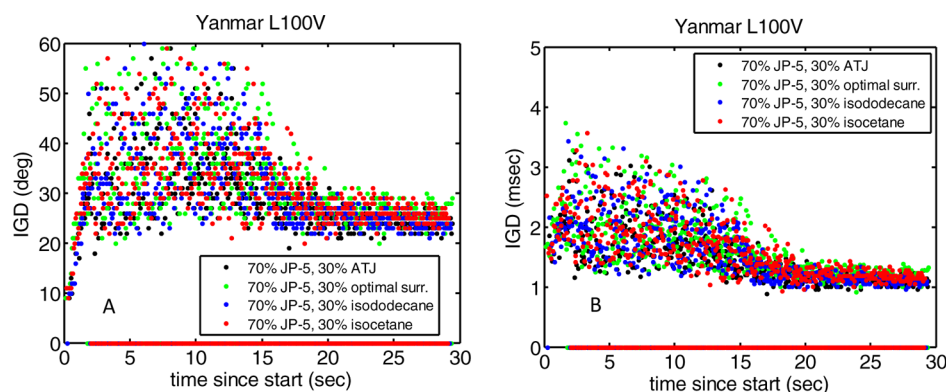

Figure 10. Ignition delay (IGD) in terms of (A) crank angle (degrees) and (B) time (milliseconds) for the 70/30 fuels tested during the first 30 s after the start of cranking. The 70/30 fuels are 70% JP-5 with 30% of ATJ, the optimal surrogate, isododecane, or 2,2,4,6,8,8-heptamethylnonane (isocetane).
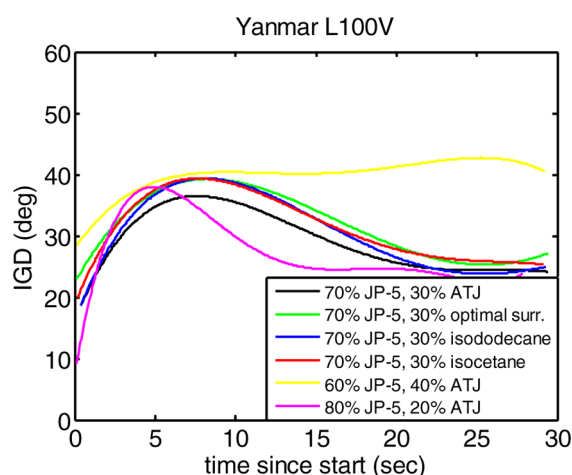
Figure 11. Ignition delay (IGC) curve fit data lines during the first 30 s after the start of cranking for the various fuels tested: 60% JP-5 with ATJ, 80% JP-5 with ATJ, 70% JP-5 with ATJ, 70% JP-5 with either the optimal surrogate, isododecane, or 2,2,4,4,6,8,8-heptamethylnonane (isocetane).
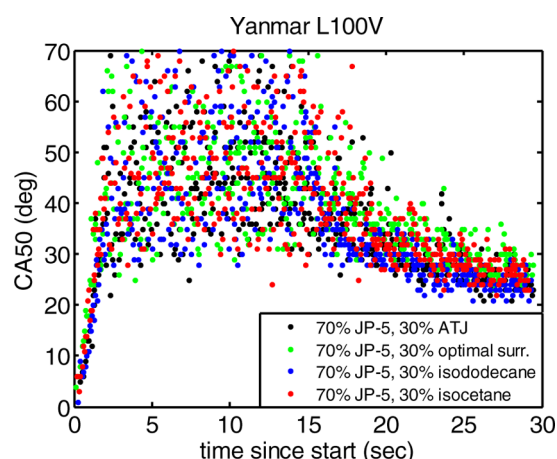

Figure 12. Location of 50% fuel burned (CA50) for the 70/30 fuels tested during the first 30 s after the start of cranking. The 70/30 fuels are 70% JP-5 with 30% of either ATJ, the optimal surrogate, isododecane, or 2,2,4,4,6,8,8-heptamethylnonane (isocetane).

2,2,4,4,6,8,8-heptamethylnonane surrogate. As with IGD, there is significant variability during the first 20 s after the start of cranking, as the engine is accelerating toward its rated speed. As noted above, a sixth-order curve fit was applied to these 70/30 mixtures as well as those for the 80% JP-5 with 20% ATJ fuel and the 60% JP-5 with 40% ATJ fuel for comparison purposes. These curve fits of the data are shown next in Figure 13. The general trend is that CA50 (crank angle of 50% fuel burned) delays to later crank angle degrees during the engine runup. This effect is due to the engine speed increasing as well as IGD lengthening as seen above. As the engine warms up and IGD begins to shorten then the CA50 point advances back toward TDC. The four 70−30 blends show similar behavior that is not statistically different. For reference, the 80% JP-5 with 20% ATJ is shown with the pink data line. This engine start to run-up occurs in one-half the time that the 70−30 blends take. The lower cetane 60% JP-5 with 40% ATJ shows very late CA50 results due to the long IGDs associated with this fuel blend.

   In this work, the approach for developing a surrogate mixture was to determine the major components of the fuel, use physical
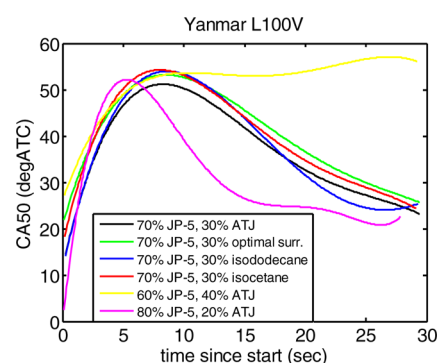

Figure 13. Location of 50% fuel burned (CA50) curve fit data lines for the fuel tested: 60% JP-5 with ATJ, 80% JP-5 with ATJ, 70% JP-5 with ATJ, and 70% JP-5 with either the optimal surrogate, isododecane, or 2,2,4,4,6,8,8-heptamethylnonane (isocetane).

and chemical properties to determine the surrogate mixture composition, and then test the mixture in an engine. The success of this approach in the current work and other past experiments shows that it can be used for other fuel mixtures.[8] For fuel mixtures containing a very large number of components, some researchers select representative compounds from the categories of compounds found in the fuel (aromatic, alicyclic, unsaturated, linear, and branched organic compounds) and use correlations to predict the properties of the multicomponent systems.[13,14,22,23,26,29,60] Using their method, the mixture composition can be optimized to match as many of the fuel properties as desired. In some of these cases, researchers have tested these mixtures in engines.[25] Other researchers have focused solely on engine metrics for surrogate component selection and have not used the physical and chemical properties as a guide. They usually begin with a mixture composition that is representative of the fuel being tested.[36] The dominant strategy for surrogate mixture development begins with information on the chemical composition of the fuel.

4. CONCLUSIONS

In this study, the chemical composition and physical properties of an alcohol-to-jet (ATJ) fuel were used to develop a surrogate mixture containing commercially available hydrocarbons, and the combustion of a subset of surrogates mixed with JP-5 was tested in a Yanmar engine. Analysis of the chemical composition of the ATJ showed that it is primarily composed of branched isomers of dodecane and hexadecane. Using pure 2,2,4,4,6,8,8-heptamethylnonane and commercially available isododecane isomers, several surrogate mixtures were prepared and their physical properties were compared to those of ATJ to determine the best match. The optimal composition of the surrogate based on the physical properties was 0.25 mass fraction of 2,2,4,4,6,8,8-heptamethylnonane in the isododecane isomers. Engine tests were then run on four mixtures that contained 70% (by volume) JP-5 and 30% of either ATJ, the optimal surrogate mixture, 2,2,4,4,6,8,8-heptamethylnonane, or isododecane isomers. The engine results showed that all three surrogates had similar combustion behavior to the 70% (by volume) JP-5 with 30% ATJ fuel, with no significant differences discerned from the engine data. Overall, these results show that surrogate mixtures were successfully designed to match the physical properties and combustion behavior of ATJ and JP-5 mixtures in a diesel engine. These data can be used for future studies that numerically

simulate the combustion behavior of mixtures that contain long-chain branched hydrocarbons.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Additional density, viscosity, speed of sound, and bulk modulus data can be found in the Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.5b00668.

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Notes

The authors declare no competing financial interest.

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