



High-Density Renewable Diesel and Jet Fuels Prepared from Multicyclic Sesquiterpanes and a 1-Hexene-Derived Synthetic Paraffinic Kerosene

Benjamin G. Harvey,* Walter W. Merriman, and Thomas A. Koontz

Chemistry Division, Research Department, Naval Air Warfare Center Weapons Division (NAWCWD), United States Navy, China Lake, California 93555, United States

ABSTRACT: High-density renewable diesel and jet fuels have been generated by blending multicyclic sesquiterpanes with a synthetic paraffinic kerosene (5-methylundecane). The sesquiterpanes impart high density and volumetric net heat of combustion (NHOC) to the blends, while inclusion of the modestly branched paraffin decreases the viscosity and increases the cetane number of the blends. A surrogate diesel fuel comprising 65% sesquiterpanes and 35% 5-methylundecane had a cetane number of 45.7, a density of 0.853 g/mL, and a volumetric NHOC of 134.0 thousand British thermal units (kBtu)/gallon. By increasing the amount of paraffin to 60% by volume, a jet fuel surrogate was prepared with a cetane number of 57.0, a density of 0.806 g/mL, a $-20\text{ }^{\circ}\text{C}$ kinematic viscosity of 8.3 mm²/s, and a NHOC of 124.6 kBtu/gallon. The results show that full-performance and even ultraperformance fuels can be generated by combining bioderived sesquiterpanes and paraffins. The components of the fuel blends studied in this work can be generated from biomass sugars by a combination of fermentation and chemical catalysis, which may allow for their production at industrially relevant scales.

INTRODUCTION

Despite the abundance of gasoline-powered motor vehicles in the U.S., diesel is the workhorse fuel around the globe and is particularly important for heavy trucks and ships. According to the World Bank, worldwide per capita consumption of road sector diesel fuel was 118.8 kg (oil equivalent) in 2011,¹ and a recent study by Exxon suggests that diesel fuel use will exceed that of gasoline by 2020, with demand increasing significantly through 2040.² Diesel engines exhibit 53% higher fuel economy and 27% lower CO₂ emissions compared to comparable gasoline engines,³ and the potential to increase efficiency and significantly reduce greenhouse gas emissions are key factors supporting the increased adoption of diesel-powered vehicles. The benefits of diesel engines have not gone unnoticed by the U.S. Department of Defense. For example, in an effort to increase the range and loiter time of unmanned aerial vehicles (UAVs), the U.S. military is transitioning many of these platforms to diesel engines.

One of the key requirements of diesel fuel is a cetane number (CN) high enough for consistent performance in current commercial engines (>42 in the U.S.). The CN directly relates to the ignition delay of a given fuel, with shorter ignition delays translating to higher CNs.⁴ In general, low-cetane fuels result in higher fuel consumption and increased emissions of unburned hydrocarbons.^{5,6} Longer ignition delays can also result in engine knocking and increased engine wear.⁷ The conventional method for determining the CN of diesel fuels is to combust the fuel in a Cooperative Fuel Research (CFR) engine while changing the compression of the engine to achieve a specific ignition delay. This is then compared to a blend of cetane (*n*-hexadecane; CN = 100) and isocetane (2,2,4,4,6,8,8-heptamethylnonane; CN = 15) that has the same ignition delay under the same compression ratio.⁴ To decrease testing costs while increasing speed and repeatability, ignition quality testing

(IQT) is commonly used to obtain the derived cetane number (DCN) of diesel fuels. IQT measures the ignition delay of the fuel under standard conditions, and the DCN is then calculated from the ignition delay.⁴

The CNs of a variety of hydrocarbons were collected by Murphy et al. in 2004.⁸ Drawing from this work, the CNs of several representative hydrocarbons are listed in Table 1. In general, fuels with long straight chains (paraffins) have high CNs that are proportional to chain length, while highly branched molecules (isoparaffins) and aromatics have low CNs.^{9,10} For example, *n*-dodecane, a 12 carbon linear paraffin,

Table 1. CNs of Selected Hydrocarbons^a

hydrocarbon	formula	structural type	CN
<i>n</i> -decane	C ₁₀ H ₂₂	paraffin	76
<i>n</i> -dodecane	C ₁₂ H ₂₆	paraffin	80
<i>n</i> -hexadecane	C ₁₆ H ₃₄	paraffin	100
2,2,4,6,6-pentamethyl heptane	C ₁₂ H ₂₆	isoparaffin	9
4,5-diethyloctane	C ₁₂ H ₂₆	isoparaffin	20
2,5-dimethylundecane	C ₁₃ H ₂₈	isoparaffin	58
1,3,5-trimethylcyclohexane	C ₉ H ₁₈	naphthene	31
<i>trans</i> -decalin ^b	C ₁₀ H ₁₈	naphthene	32
<i>cis</i> -decalin ^b	C ₁₀ H ₁₈	naphthene	42
<i>n</i> -butylcyclohexane	C ₁₂ H ₂₄	naphthene	36
1,3-diethylbenzene	C ₁₀ H ₁₄	aromatic	9
biphenyl	C ₁₂ H ₁₀	aromatic	21
<i>n</i> -hexylbenzene	C ₁₂ H ₁₈	aromatic	26

^aAll of the CNs except those indicated were taken from ref 8. ^bSee ref 13.

Received: December 11, 2014

Revised: February 18, 2015

Published: February 20, 2015

has a CN of 80, while the highly branched 2,2,4,6,6-pentamethylheptane has a CN of only 9. Lightly branched paraffins, such as 2,5-dimethylundecane, can have CNs far in excess of that required for diesel fuel, but the position of the branching can greatly reduce the CN, as is the case for 4,5-diethyloctane, with a CN of only 20. Aromatics typically have very low CNs because of their excellent stability to oxidation.^{11,12} This property cannot be mitigated by molecular incorporation of even relatively long alkyl chains. For example, *n*-hexylbenzene only has a CN of 26. Cyclic hydrocarbons (naphthenes) often have intermediate CNs, and subtle structural differences can have significant impacts on their ignition delays. As an example, the *trans* isomer of decalin has a CN of only 32, while the *cis* isomer has a CN 10 points higher.¹³

Most of the recent research on full-performance renewable fuels for jet and diesel propulsion has focused on synthetic paraffinic kerosenes (SPKs).^{14–20} These fuels have a number of characteristics that make them attractive for use in both diesel and turbine engines. SPKs burn cleanly and generate little in the way of coke or polyaromatics because of the absence of aromatic compounds in the fuel. The lack of aromatics and naphthenes also has a negative impact, evidenced by the decreased density of the fuel. Further, aromatic compounds are essential to engine integrity in a number of fielded systems because of their ability to swell O-rings and seals. Naphthenes typically account for ~45% of diesel fuel, and aromatics comprise ~25%;^{21a} similarly, jet fuel contains ~35% naphthenes and 20% aromatics.^{21b} The combination of naphthenes, aromatics, and paraffins in conventional diesel fuel results in densities from 0.825 to 0.850 g/mL,^{21a} while petroleum-derived jet fuels have densities of about 0.81 g/mL.^{21b} In contrast, renewable fuels containing purely paraffinic or isoparaffinic hydrocarbons in the C₁₀–C₁₄ range have densities from about 0.73 to 0.76 g/mL,¹⁴ while renewable diesel-range hydrocarbons with their average higher molecular weights have densities of up to ~0.78 g/mL.^{22,23} A potential solution to the low density of these fuels is to blend high-density naphthenes with the paraffins. Terpenoids are particularly compelling sources of renewable naphthenes that can be isolated from pine resin or generated via biosynthetic approaches.²⁴ Toward this end, a number of researchers have been investigating bioderived naphthenes based on monoterpenes,^{25–32} sesquiterpenes,^{33,34} and diterpenes.^{35–38} Some of these molecules have densities as high as 0.94 g/mL, with their viscosities dependent upon their structures and molecular weight.

To overcome the density limitations of renewable SPKs, this paper explores the utility of dense terpenoid hydrocarbons as blendstocks for the preparation of 100% bioderived high-density diesel and jet fuels. The results of this study are then used to prepare renewable fuel blends that have densities and net heats of combustion (NHOCs) higher than petroleum-based fuels while maintaining CNs high enough for use in conventional diesel engines.

■ EXPERIMENTAL SECTION

General. *exo*-Tetrahydrodicyclopentadiene (JP-10) and *exo*-dimethyltetrahydrodicyclopentadienes (RJ-4) were obtained from the fuel supply depot at the China Lake Naval Air Warfare Center and filtered before use. Terpene dimer fuel (TDF),³⁶ hydrogenated limonene dimers,^{35,36} and pinane³⁷ were prepared as previously described. Blends of 5-methylundecane and hydrogenated caryophyllene isomers were prepared by volume. The solutions were then rigorously stirred

for 10 min and allowed to settle before further studies were conducted. DCNs were determined by IQT analysis conducted at Southwest Research Institute using ASTM D6890. Flashpoints were determined by ASTM D7094 on a Grabner Instruments Miniflash FLP. Elemental analysis was performed by Atlantic Microlabs, Norcross, GA.

Preparation of 5-Methylundecane. This hydrocarbon was prepared from 1-hexene as previously described.³⁹ Briefly, 1-hexene was oligomerized with a catalyst prepared from Cp₂ZrCl₂ and methylaluminoxane (MAO). The resulting mixture, which contained ~56% 5-methyleneundecane, was fractionally distilled at atmospheric pressure to yield the dimer in >95% purity. The dimer was then hydrogenated over 10% Pd/C to yield 5-methylundecane. The only significant impurity was ca. 5% 5-methyl-7-butyltridecane.

Preparation of Caryophyllane Isomers. The mixture of caryophyllane isomers was prepared as previously described.³³ Briefly, commercial caryophyllene was heated to 100 °C with 0.4 g of Nafion SAC-13/100 mL of caryophyllene for 24 h. The resulting isomeric mixture was then hydrogenated over PtO₂ and distilled under vacuum to yield the sesquiterpane blendstock.

Hydrogenation of Limonene. PtO₂ (500 mg, 2.2 mmol) was added to limonene (200 mL, 1.23 mol) in a glass bomb. The atmosphere was exchanged with hydrogen 3 times via pump/pressurize cycles, and the pressure then increased to 40 psi. The reaction flask was then shaken for 36 h at ambient temperature, and the catalyst was removed by filtration.

Viscosity Measurements. The dynamic viscosity of the fuel samples was measured with a Brookfield DV-II+ Pro viscometer equipped with the small sample adapter (SSA). The instrument was calibrated by Brookfield Laboratories, Inc., and ethylene glycol was used as a standard in our laboratory to confirm the accuracy of the instrument. Each sample was placed in the SSA and allowed to equilibrate at a given temperature for a minimum of 20 min prior to the viscosity being measured. The temperature was held to within ±0.05 °C with a constant temperature bath (Brookfield TC-S02). The viscosity was then measured as outlined in ASTM D2983. Each measurement was performed in triplicate, and the reported data are the average of those readings. The error in the measurements is ±1% at the 99.7% confidence level (3σ). Between measurements, the sample adapter and spindle were rinsed several times with hexanes, followed by a water wash and acetone rinse. The components were then dried under a stream of air.

Extrapolation of Dynamic Viscosity. The dynamic viscosities of the fuel blends were extrapolated to –20 °C using the following equation:^{40,41}

$$\log(\log(\mu + c)) = a + b \log T$$

where T is the temperature (K), μ is the dynamic viscosity (mPa s), c is a viscosity correlation factor set at 0.8,⁴⁰ and a and b are coefficients obtained from the experimental data by determining the slope of the line and the y intercept.

Density Measurements and Calculation of Kinematic Viscosity. The densities of the fuel blends were measured using calibrated floats. These measurements were corroborated by filling 10 mL volumetric flasks with the fuel blends and weighing the fuel samples to ±0.1 mg. The error in the density measurements was ±0.001 g/mL. Density at non-ambient temperature (i.e., –20 °C) was calculated using the following equation:

$$\rho_f = \frac{\rho_0}{1 + \beta(T_f - T_0)}$$

where ρ_f is the final density, ρ_0 is the density measured at ambient temperature (T_0 , 20 °C), β is the volumetric temperature expansion coefficient (0.00099/°C), and T_f is the final temperature. Kinematic viscosity at –20 °C was then calculated by dividing the calculated dynamic viscosity by the calculated density.

Heat of Combustion Studies. A monolith of high-purity benzoic acid was cut into cylinders weighing approximately 80 mg. A cylinder was then placed in a platinum capsule and accurately weighed, and then several drops of a given fuel (~30–50 mg) were added to the

monolith. The fuel was allowed to soak into the monolith; the sample was reweighed; and then the capsule was transferred to a Parr 6725 Semimicro Calorimeter. After combustion of the sample under 25–30 atm of O₂, the NHOC was calculated by subtracting the contribution due to benzoic acid from the gross heat of combustion and taking into consideration the hydrogen content [determined by elemental analysis (EA)] and the density of the fuel. NHOC measurements were taken in triplicate and averaged.

RESULTS AND DISCUSSION

As a first step to evaluate the potential for developing a renewable, high-density, high-CN fuel, it was of interest to determine the CN of JP-10 and RJ-4, two high-density multicyclic fuels used for missile propulsion (Figure 1). JP-10

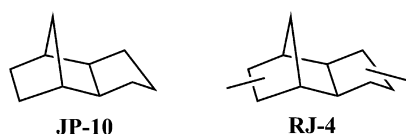


Figure 1. Structures of hydrocarbons present in the high-density fuels JP-10 and RJ-4.

is essentially pure *exo*-tetrahydrodicyclopentadiene and is the gold standard for high-density fuels combining high density (0.935 g/mL), exceptional volumetric NHOC [141.5 thousand British thermal units (kBtu)/gallon], a low freezing point ($T_m = -79\text{ }^{\circ}\text{C}$), and excellent low-temperature viscosity [$8.8\text{ mm}^2\text{ s}^{-1}$ ($-20\text{ }^{\circ}\text{C}$)].⁴² RJ-4 or dimethyl-JP-10 has a similar NHOC value but a slightly higher low-temperature viscosity.^{37,43} A recent paper has shown that bioderived RJ-4 can be synthesized from the terpene alcohol linalool.²⁹ RJ-4 produced in this manner would then be a candidate as a renewable high-density blendstock. Both of the fuels were subjected to IQT analysis to obtain CNs. The tricyclic nature of JP-10 and RJ-4 resulted in poor CNs of 20.4 and 23.5, respectively. This result is not surprising given that JP-10 has four tertiary centers and RJ-4 has six tertiary centers. In light of their very modest CNs, these synthetic hydrocarbons were not considered further as significant components of high-density diesel fuels.

After establishing a baseline, the DCNs of several renewable naphthenes, including TDF, pinane, hydrogenated limonene dimers, and limonane, were measured (Table 2). TDF, which is

Table 2. DCNs of Multicyclic Fuels

fuel	DCN
TDF	27.1
JP-10	20.4
hydrogenated α -pinene	23.0
RJ-4	23.5
hydrogenated limonene dimers	23.1
limonane	29.1
caryophyllane	24.5
isomerized caryophyllane	32.5
5-methylundecane	67.0

generated by heterogeneous acid-catalyzed dimerization of gum spirit turpentine,³⁶ has recently been the subject of a number of studies. The combustion of TDF blends with JP-10 and pinane has been explored in a shock tube,⁴⁴ while the composition of TDF, its enthalpy of combustion, and its distillation profile have been analyzed via the advanced distillation method.⁴⁵ The low-temperature viscosity of TDF blended with JP-10, RJ-4, JP-

8, and pinane has also been studied.³⁷ TDF contains dimers derived from α -pinene, camphene, and other terpenes; an example of a typical structure can be found in Figure 2. The

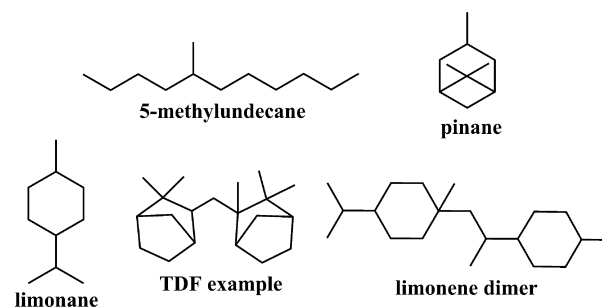


Figure 2. Structures of some multicyclic and branched chain hydrocarbons studied in this work.

mixture of terpene dimers was found to have a moderate CN of 27.1. Although TDF is composed of dozens of isomers,³⁶ it is known that isomerization of α -pinene prior to dimerization results in the presence of a variety of ring-opened structures. These ring-opened structures or perhaps formation of hindered tertiary double bonds that are recalcitrant to hydrogenation likely account for the moderate CN. In contrast, pinane, a bicyclic molecule that can be generated by hydrogenating α - or β -pinene (significant components of pine resin), has three tertiary centers and one quaternary center. This highly branched bicyclic structure resulted in a DCN of just 23.0. Hydrogenated limonene (limonane) with three tertiary carbons had a DCN of 29.1, while dimerization led to a decrease of 6 CNs, perhaps because of the formation of new highly substituted carbons or partial dehydrogenation to yield aromatic structures.

Although this initial set of naphthenic hydrocarbons had low to moderate CNs, it was of interest to evaluate new fuels derived from sesquiterpenes as blendstocks for high-density diesel fuels. β -Caryophyllene can be isomerized and hydrogenated to a fuel mixture (Figure 3) with a density of 0.9 g/mL, NHOC of nearly 138.0 kBtu/gallon, and a DCN of up to 32.5.³³ Solely on the basis of CN, this fuel mixture was the most promising starting point for preparation of a renewable diesel fuel. However, other factors, including density, NHOC, and low-temperature viscosity, were also considered. Although TDF has the highest density (0.94 g/mL) and NHOC (142.0 kBtu/

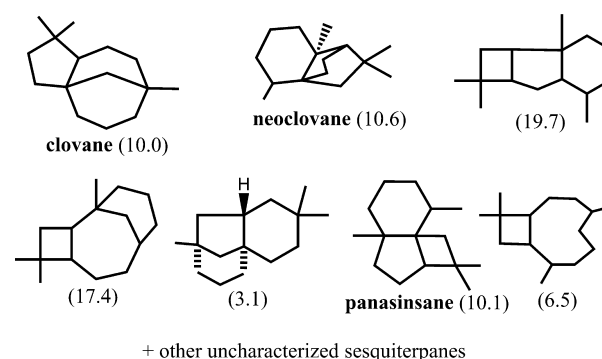


Figure 3. Structures of sesquiterpanes present in the isomerized mixture. The numbers beneath each structure refer to the area percentage obtained from gas chromatography/mass spectrometry (GC/MS).

gallon) of the renewable naphthenes studied in this work,³⁶ its high viscosity at low temperatures reduces the amount that can be incorporated into a fuel blend.³⁷ The monoterpanes (limonane and pinane) have substantially lower viscosities, but their modest densities and NHOCs limit their effectiveness as high-density blendstocks. The caryophyllane isomers, therefore, combine the best properties of the monoterpanes and diterpanes, exhibiting a density and NHOC close to that of TDF but with a $-20\text{ }^{\circ}\text{C}$ viscosity more than 2 orders of magnitude lower.³³

There is some precedence for the idea of using high-density naphthenes as blendstocks in diesel fuels. For example, the combustion of neat decalin and blends with cyclohexane or hexane have been studied in a diesel engine.⁴⁶ In addition, work by Heyne et al.¹³ on JP-900 (a coal-based fuel) has shown the utility of blending fuels rich in fused bicyclic hydrocarbons (decalins) with SPKs, biodiesel, or nitrate esters to generate fuels with high CNs. In a similar manner, blends of a renewable SPK with the caryophyllane isomers would be expected to generate high-density fuels with CNs high enough for diesel propulsion. Advantageously, we recently developed SPK fuels that can be generated from ethanol via 1-hexene³⁹ (Figure 4). A

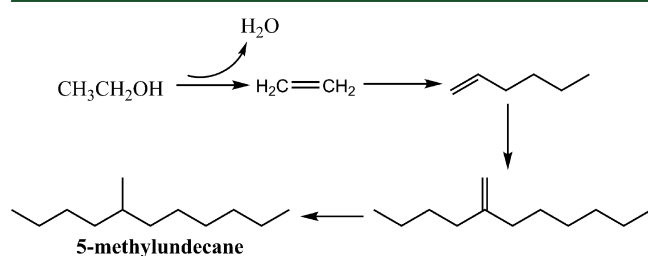


Figure 4. Synthesis of 5-methylundecane from ethanol.

C_{12} molecule produced by this approach (5-methylundecane) has a remarkable CN of 67.0 while maintaining excellent low-temperature properties. With both the sesquiterpane mixture and modestly branched SPK in hand, it seemed likely that both a high-density renewable diesel fuel and jet fuel surrogate could be created by blending the two components.

To achieve these goals, three different fuel blends were prepared with different ratios of caryophyllane isomers and 5-methylundecane. The dynamic viscosities of these blends were then measured between -14 and $40\text{ }^{\circ}\text{C}$ (Figure 5). The target was a fuel that would meet the specifications for both JP-5⁴⁷ and F-76,⁴⁸ high-flashpoint U.S. Navy jet and diesel fuel,

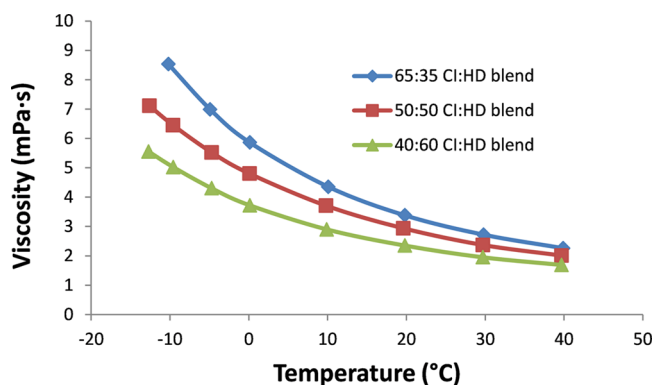


Figure 5. Dynamic viscosity data for caryophyllane isomers/5-methylundecane blends.

respectively. In particular, this would require a fuel with an acceptable low-temperature kinematic viscosity ($<8.5\text{ mm}^2/\text{s}$ at $-20\text{ }^{\circ}\text{C}$) for jet aircraft and a suitable high-temperature kinematic viscosity for diesel applications ($>1.7\text{ mm}^2/\text{s}$ at $40\text{ }^{\circ}\text{C}$). The first fuel examined was a 50:50 blend of sesquiterpane isomers and 5-methylundecane. Extrapolation of the viscosity data led to a calculated kinematic viscosity of $10.8\text{ mm}^2/\text{s}$ at $-20\text{ }^{\circ}\text{C}$. The $40\text{ }^{\circ}\text{C}$ kinematic viscosity was $2.5\text{ mm}^2/\text{s}$, well within the viscosity specification for F-76.⁴⁸ This fuel could then be considered a potential diesel fuel surrogate and jet fuel blendstock because of its moderate viscosity while having a density higher than either JP-5 or JP-8²¹ (Table 3). With this result in hand, it became of interest to maximize the density while still maintaining a high enough CN for use in conventional diesel engines. Using a simple, linear approach and assuming that the CN of the sesquiterpane blendstock is ~ 30 , a blend comprising 65% caryophyllane isomers and 35% hexene dimer was expected to yield a fuel with a CN in excess of 42 while maintaining the highest density possible. The CN of this blend was 45.7, well within the range for conventional diesel fuel. The blend had an extrapolated kinematic viscosity of $14.0\text{ mm}^2/\text{s}$ at $-20\text{ }^{\circ}\text{C}$ and a $40\text{ }^{\circ}\text{C}$ kinematic viscosity of $2.7\text{ mm}^2/\text{s}$ with a density of 0.853 g/mL , with the final value being higher than conventional F-76.

After successfully preparing a high-density diesel fuel, an attempt was made to generate a jet fuel surrogate. To maintain the highest density possible while lowering the viscosity to an acceptable level, a 40:60 caryophyllane isomer/hexene dimer mixture was prepared. This resulted in a fuel with a density of 0.806 g/mL and an extrapolated $-20\text{ }^{\circ}\text{C}$ kinematic viscosity of $8.3\text{ mm}^2/\text{s}$, which meets the specification for JP-5 ($<8.5\text{ mm}^2/\text{s}$ at $-20\text{ }^{\circ}\text{C}$).⁴⁷ Because of the high concentration of 5-methylundecane in this blend, the DCN was 57. This high DCN is not required for JP-5 but would allow this blend to be used in diesel engines.

To further characterize the fuel blends, the volumetric NHOCs were measured. The NHOC varied from 134.0 kBTU/gallon for the highest density fuel to 124.6 kBTU/gallon for the lowest density fuel. These numbers can be compared to F-76 ($\sim 129\text{ kBTU/gallon}$) and JP-5 ($\sim 125\text{ kBTU/gallon}$).²⁰ The NHOC data are quite remarkable for renewable fuel blends, as evidenced by the fact that the highest density fuel tested in this work had a NHOC approximately 13% higher than conventional biodiesel.⁵⁰ In addition to the NHOC, the amount of hydrogen in the fuels was determined by elemental analysis and the flashpoints of the fuels were measured. Despite the significant concentration of naphthenes in the blends, all of the fuels had higher hydrogen contents than required by the military fuel specifications (Table 3). In addition, the flashpoints of all of the fuels were higher than that required for JP-5 and F-76 ($>60\text{ }^{\circ}\text{C}$) for use onboard naval vessels.

CONCLUSION

High-density renewable fuel blends comprising a synthetic paraffinic kerosene combined with a complex multicyclic sesquiterpane mixture have been prepared and characterized. These fuels have excellent CNs ranging between 45 and 57 and can be formulated to have densities higher than petroleum-derived diesel fuel. Through targeted blending, the viscosity was tuned between 8.3 and $14.0\text{ mm}^2/\text{s}$ at $-20\text{ }^{\circ}\text{C}$, showing that these fuels have applications for both jet and diesel propulsion. The ability to synthesize renewable fuels that outperform petroleum-derived fuels is an emerging trend in biofuel

Table 3. Key Properties of Renewable Fuel Blends and Conventional Petroleum Fuels

fuel	−20 °C viscosity (mm ² /s)	40 °C viscosity (mm ² /s)	DCN ^a	density (g/mL)	EA (%)	FP	NHOC (kBtu/gallon) ^b
65:35 CI/HD ^c	14.0	2.7	45.7 (1.1)	0.853	C, 86.11; H, 13.89	89	134.0 (1.6)
50:50 CI/HD ^c	10.8	2.5	52.6 (1.1)	0.826	C, 85.81; H, 14.13	84	128.1 (2.2)
40:60 CI/HD ^c	8.3	2.1	57.0 (1.1)	0.806	C, 85.25; H, 14.29	82	124.6 (1.5)
JP-5 ^d	<8.5	NA		~0.81	>13.4% H	>60	~125
JP-8 ^e	<8.0	NA		~0.81	>13.4% H	>38	~125
F-76 ^f	NA	1.7–4.3	>42	~0.84	>12.5% H	>60	~129

^aNumbers in parentheses are the standard deviation for the IQT measurement. ^bNumbers in parentheses are the uncertainty in the measurements.

^cCI stands for caryophyllane isomers, and HD stands for the hexene dimer (5-methylundecane). ^dSpecifications taken from ref 47. ^eSpecifications taken from ref 49. ^fSpecifications taken from ref 48.

development. Virtually all full-performance biofuels are generated via direct biosynthesis or some combination of biosynthesis and chemical catalysis. This provides the opportunity to improve the performance of renewable fuels through custom design of fuel composition. In addition to their utility in high-performance fuel blends, the individual components studied in this work can be used to upgrade the properties of other biofuels as well as conventional jet and diesel fuels. Both components of the fuel blends studied in this work can be derived from biomass sugars by combining fermentation processes with chemical catalysis. This suggests that fuels of this type could potentially be generated on a scale that would make them practical for widespread military or commercial use.

AUTHOR INFORMATION

Corresponding Author

*E-mail: benjamin.g.harvey@navy.mil.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank the Office of Naval Research for supporting Thomas Koontz with a Naval Research Enterprise Intern Program (NREIP) fellowship. Support for Walter Merriman from the Power Systems Science and Technology Initiative (PSSTI) at NAWCWD is also greatly appreciated.

REFERENCES

- (1) World Bank. *Road Sector Diesel Fuel Consumption Per Capita (kg of Oil Equivalent)*; World Bank: Washington, D.C., 2014; http://data.worldbank.org/indicator/IS.ROD.DESL.PC/countries/1W?order=wbapi_data_value_2010%20wbapi_data_value%20wbapi_data_value_first&sort=asc&display=default (accessed Nov 12, 2014).
- (2) Exxon Mobil Cooperation. *The Outlook for Energy: A View to 2040*; Exxon Mobil Cooperation: Irving, TX, 2014; cdn.exxonmobil.com/.../Outlook%20For%20Energy/.../2014-Outlook-for-Energy.pdf (accessed Oct 31, 2014).
- (3) Sullivan, J. L.; Baker, R. E.; Boyer, B. A.; Hammerle, R. H.; Kenney, T. E.; Muniz, L.; Wallington, T. J. *Environ. Sci. Technol.* **2004**, *38*, 3217–3223.
- (4) Ghosh, P.; Jaffe, S. B. *Ind. Eng. Chem. Res.* **2006**, *45*, 346–351.
- (5) Yang, C.; Kidoguchi, Y.; Kato, R.; Miwa, K. *Bull. Mech. Eng. Sci. J.* **2000**, *28*, 55–62.
- (6) Kidoguchi, Y.; Yang, C.; Kato, R.; Miwa, K. *JSAE Rev.* **2000**, *21*, 469–475.
- (7) Hashimoto, K.; Ikeda, M.; Arai, M.; Tamura, M. *Energy Fuels* **1996**, *10*, 1147–1149.
- (8) Murphy, M. J.; Taylor, J. D.; McCormick, R. L. *Compendium of Experimental Cetane Number Data*; National Renewable Energy Laboratory (NREL): Golden, CO, 2004; NREL/SR-540-36805.

- (9) O'Connor, C. T.; Forrester, R. D.; Scurrall, M. S. *Fuel* **1992**, *71*, 1323–1327.
- (10) Heck, S. M.; Pritchard, H. O.; Griffiths, J. F. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 1725–1727.
- (11) Ghosh, P. *Energy Fuels* **2008**, *22*, 1073–1079.
- (12) Burger, J. L.; Lovestead, T. M.; Gough, R. V.; Bruno, T. J. *Energy Fuels* **2014**, *28*, 2437–2445.
- (13) Heyne, J. S.; Boehman, A. L.; Kirby, S. *Energy Fuels* **2009**, *23*, 5879–5885.
- (14) Corporan, E.; Edwards, T.; Shafer, L.; DeWitt, M. J.; Klingshirn, C.; Zabarnick, S.; West, Z.; Striebich, R.; Graham, J.; Klein, J. *Energy Fuels* **2011**, *25*, 955–966.
- (15) Rahmes, T. F.; Kinder, J. D.; Henry, T. M.; Crenfeldt, G.; LeDuc, G. F.; Zombanakis, G. P.; Abe, Y.; Lambert, D. M.; Lewis, C.; Juenger, J. A.; Andac, M. G.; Reilly, K. R.; Holmgren, J. R.; McCall, M. J.; Bozzano, A. G. Sustainable bio-derived synthetic paraffinic kerosene (Bio-SPK) jet fuel flights and engine tests program results. *Proceedings of the 9th AIAA Aviation Technology, Integration, and Operations Conference (ATIO)*; Hilton Head Island, SC, Sept 21–23, 2009.
- (16) Edwards, T.; Moses, C.; Dryer, F. Evaluation of combustion performance of alternative aviation fuels. *Proceedings of the 46th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit*; Nashville, TN, July 25–28, 2010; AIAA 2010-7155.
- (17) Carter, N. A.; Stratton, R. W.; Bredehoeft, M. K.; Hileman, J. I. Energy and environmental viability of select alternative jet fuel pathways. *Proceedings of the 47th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit*; San Diego, CA, July 31–Aug 3, 2011; AIAA 2011-5968.
- (18) Wright, M. E.; Harvey, B. G.; Quintana, R. L. *Energy Fuels* **2008**, *22*, 3299–3302.
- (19) Harvey, B. G.; Quintana, R. L. *Energy Environ. Sci.* **2010**, *3*, 352–357.
- (20) Harvey, B. G.; Meylemans, H. A. *J. Chem. Technol. Biotechnol.* **2011**, *86*, 2–9.
- (21) (a) National Academy of Sciences (NAS). *Petroleum in the Marine Environment*; NAS: Washington, D.C., 1973; p 43. (b) Edwards, T. J. *Propul Power* **2003**, *19*, 1089–1107.
- (22) Hsieh, P. Y.; Widegren, J. A.; Fortin, T. J.; Bruno, T. J. *Energy Fuels* **2014**, *28*, 3192–3205.
- (23) Prak, D. J. L.; Trulove, P. C.; Cowart, J. S. *J. Chem. Eng. Data* **2013**, *58*, 920–926.
- (24) Fortman, J. L.; Chhabra, S.; Mukhopadhyay, A.; Chou, H.; Lee, T. S.; Steen, E.; Keasling, J. D. *Trends Biotechnol.* **2008**, *26*, 375–381.
- (25) Sarria, S.; Wong, B.; Martin, H. G.; Keasling, J. D.; Peralta-Yahya, P. *ACS Synth. Biol.* **2014**, *3*, 466–475.
- (26) Bruno, T. J.; Baibourine, E. *Energy Fuels* **2011**, *25*, 1847–1858.
- (27) Renninger, N. S.; Ryder, J. A.; Fisher, K. J. Jet fuel compositions and methods of making and using same. WO Patent 2008130492, 2008.
- (28) Meylemans, H. A.; Quintana, R. L.; Rex, M. L.; Harvey, B. G. *J. Chem. Technol. Biotechnol.* **2014**, *89*, 957–962.
- (29) Meylemans, H. A.; Quintana, R. L.; Goldsmith, B. R.; Harvey, B. G. *ChemSusChem* **2011**, *4*, 465–469.

- (30) Brennan, T. C. R.; Turner, C. D.; Krömer, J. O.; Nielsen, L. K. *Biotechnol. Bioeng.* **2012**, *109*, 2513–2522.
- (31) Zhang, F.; Rodriguez, S.; Keasling, J. D. *Curr. Opin. Biotechnol.* **2011**, *22*, 775–783.
- (32) Rude, M. A.; Schirmer, A. *Curr. Opin. Microbiol.* **2009**, *12*, 274–281.
- (33) Harvey, B. G.; Meylemans, H. A.; Gough, R. V.; Quintana, R. L.; Garrison, M. D.; Bruno, T. J. *Phys. Chem. Chem. Phys.* **2014**, *16*, 9448–9457.
- (34) Peralta-Yahya, P. P.; Ouellet, M.; Chan, R.; Mukhopadhyay, A.; Keasling, J. D.; Lee, T. S. *Nat. Commun.* **2011**, *2*, 483.
- (35) Harvey, B. G.; Wright, M. E.; Quintana, R. L. *Energy Fuels* **2010**, *24*, 267–273.
- (36) Meylemans, H. A.; Quintana, R. L.; Harvey, B. G. *Fuel* **2012**, *97*, 560–568.
- (37) Meylemans, H. A.; Baldwin, L. C.; Harvey, B. G. *Energy Fuels* **2013**, *27*, 883–888.
- (38) Zou, J.-J.; Chang, N.; Zhang, X.; Wang, L. *ChemCatChem* **2012**, *4*, 1289–1297.
- (39) Harvey, B. G.; Meylemans, H. A. *Green Chem.* **2014**, *16*, 770–776.
- (40) Daučík, P.; Višňovský, J.; Ambro, J.; Hájeková, E. *Acta Chim. Slovaca* **2008**, *1*, 43–57.
- (41) Merlotra, K. A. *Can. J. Chem. Eng.* **1990**, *68*, 839.
- (42) Bruno, T. J.; Huber, M. L.; Laesecke, A.; Lemmon, E. W.; Perkins, R. A. *Thermochemical and Thermophysical Properties of JP-10*; National Institute of Standards and Technology (NIST): Boulder, CO, 2006; NISTIR 6640.
- (43) Burdette, G. W.; Schneider, A. I. High density, low viscosity airbreather fuel (RJ-4-I) U.S. Patent 4,398,978, 1982.
- (44) Zhu, Y.; Li, S.; Davidson, D. F.; Hanson, R. K. *Proc. Combust. Inst.* **2015**, *35*, 241–248.
- (45) Gough, R. V.; Bruno, T. J. *Energy Fuels* **2013**, *27*, 294–302.
- (46) Ogawa, H.; Ibuki, T.; Minematsu, T.; Miyamoto, N. *Energy Fuels* **2007**, *21*, 1517–1521.
- (47) Fuels and Lubricants Division, Naval Air Systems Command. *MIL-DTL-5624U Detail Specification Turbine Fuel, Aviation Grades JP-4 and JP-5*; Fuels and Lubricants Division, Naval Air Systems Command: Patuxent River, MD, 2004.
- (48) Naval Sea Systems Command. *MIL-DTL-16884M Detail Specification Fuel, Naval Distillate*; Naval Sea Systems Command: Washington Navy Yard, D.C., 2012.
- (49) Air Force Petroleum Agency (AFPA). *MIL-DTL-83133H Detail Specification Turbine Fuel, Aviation, Kerosene Type, JP-8 (NATO F-34), Nato F-35, and JP-8 + 100 (NATO F-37)*; AFPA: Wright-Patterson Air Force Base, OH, 2013.
- (50) This calculation assumes a NHOC of 118 kBtu/gal for biodiesel (see ref 20).