Characteristics and Stability of Neat and Blended Hydroprocessed Renewable Diesel

2 AUTHORS, INCLUDING:

Jinxia Fu
University of Hawai'i at Mānoa

Characteristics and Stability of Neat and Blended Hydroprocessed Renewable Diesel

Jinxia Fu* and Scott Q. Turn

Hawaii Natural Energy Institute, University of Hawaii, Honolulu, Hawaii 96822, United States

S *Supporting Information*

ABSTRACT: In this study, the physical properties and chemical composition of hydroprocessed renewable diesel derived from algae (HRD-76) were measured. Analysis of HRD-76 showed that the main components are $C_{15}-C_{18}$ n-alkanes and branched monomethyl hexadecanes and heptadecanes. Approximately 50% of HRD-76 is n- and iso-C_{17}. Long-term (ASTM D4625) and accelerated (ASTM D5304) tests were conducted to investigate the storage stability of HRD-76, F-76, and their blends and the effects of long-term storage on the fuel properties. In addition, the ASTM D2274 method was used to test the oxidation stabilities of the neat and blended fuels. HRD-76 has better storage and oxidation stabilities than F-76, and the post-test changes in the fuel properties are influenced by the F-76 fraction in the fuel blend. Extended ASTM D2274 tests were also conducted to investigate the influence of long-term oxidation on the physicochemical properties of the fuel.

■ INTRODUCTION

The development and utilization of alternative fuels have become an ambitious energy goal for industrialized countries striving to decrease reliance on fossil resources. The U.S. military is the largest single energy consumer in America.[1] In keeping with the five energy targets announced by Secretary of the Navy Ray Mabus in October 2009, the U.S. Navy has interest in renewable, drop-in, alternative diesel fuels for blending with NATO F-76. An alternative fuel of particular interest is hydroprocessed renewable diesel derived from algae (HRD-76), and the U.S. Navy has identified a blend of 50% F-76 and 50% HRD-76 to meet the alternative fuel requirements.[2] Combustion system assessment test results indicate that a 50/50 blend performs satisfactorily.[2−5]

Hydroprocessed renewable diesel (HRD) is produced using oil derived from algae and animal fat.[6] Hydroprocessing of these renewable feedstocks has advantages over first-generation transesterification technology for fatty-acid methyl esters as it produces little byproduct and the product can be used in existing refineries and fuel systems without new investments.[7] The process produces a mixture of predominantly linear and branched alkanes ranging from C_{15} to C_{18}, with higher concentrations of n-C_{17} and n-C_{18}.[8,9] The reaction pathway during hydroprocessing of renewable feedstocks generally involves two steps: (i) saturation of the double bonds of the triglycerides and breaking the saturated triglycerides to fatty acids and (ii) conversion of fatty acids into alkanes through hydrogenation or decarboxylation processes.[9,10] World annual vegetable oil production is about 107 Tg, and some of this oil could be used to produce biofuels.[11] Studies have investigated hydroprocessing of different types of vegetable oils, including palm,[12] rapeseed,[10,13−16] sunflower,[17−21] and soybean,[22−24] and waste cooking oil.[25−28] The results indicated that triglyceride conversions can reach 90 wt %[10] and that the resulting biofuel has a high cetane number.[29] Blending of conventional diesel with HRD can significantly increase the renewable fuel lubricity, provide fuel blends with cetane numbers close to

the values of current diesel fuels, and enhance engine performance.[30] The utilization of renewable biofuels can also reduce the impacts of human activities on the environment. Westphal et al.[31] compared the emissions and bacterial mutagenic effects of HRD with fossil diesel fuel, and the results demonstrated that HRD combustion produced smaller amounts of NO_X and polycyclic aromatic hydrocarbons (PAHs) and that HRD showed significant toxicological advantages over fossil diesel fuel and biodiesel produced by esterification. Similar results were also reported by Happonen et al.,[32] Bünger et al.,[33] and Jalava et al.[34] Stamper et al.[35] showed that microbial communities did not develop on selected HRD samples.

The shipboard environment and mixed fuel−seawater ballasting practices on some Navy ships present unique conditions for preserving fuel quality.[36] HRD-76 and its blends must satisfy the specifications identified in MIL-DLT-16884L for NATO F-76, including the evaluation of storage and oxidation stabilities. A number of accelerated methods have been developed for testing the stability of middle-distillate petroleum fuels and renewable biofuels that involve stressing of the fuel samples by combinations of elevated temperature and pressure as well as enhanced oxygen exposure. The most widely accepted methods in the U.S. are American Society of Testing and Materials (ASTM) D4625,[37] ASTM D5304,[38] and ASTM D2274.[39] The standard test method ASTM D4625 is the most widely used test method for assessing the storage stability of middle-distillate petroleum fuels[40−43] and distilled and undistilled biodiesels.[44−50] In this method, the fuel is stored for selected periods of up to 24 weeks at 43 °C, where 1 week of storage is roughly equivalent to a month of storage at normal (environmental) ambient temperature (21 °C).[37] Typically, samples are analyzed to determine the amount of filterable and

adherent insolubles formed every 4 or 6 weeks. Standard test method ASTM D5304 was also developed to study middle-distillate fuel[51] storage stability under elevated temperature and pressure conditions: 90 °C and 800 kPa with pure oxygen. The 16 h test yields approximately the same amount of insolubles as 20 °C storage for 27 months under air at a pressure of 101.325 kPa.[38] As with ASTM D4625, ASTM D5304 has also been employed to study the storage stability of biodiesels.[52−54] Standard test method ASTM D2274 requires an even higher temperature (95 °C) and more oxygen exposure (3L/h) relative to ASTM D4625 and was originally developed to investigate the oxidation stability of distillate fuel oil.[40−42] Although it has not yet been validated for biodiesel, results obtained using this method have been reported for biodiesel and its blends.[46−50,55]

Although a blend of HRD-76 and conventional F-76 has already been used to power U.S. Navy surface ships,[56] the storage and oxidation stabilities of HRD-76 and its blends have not been reported. In this article, the physicochemical properties and chemical composition of HRD-76 were measured. ASTM D4625, D5304, and D2274 tests were conducted to investigate the storage and oxidative stability of HRD-76, F-76, and their blends and the influence of stressing on the fuel sample properties.

■ MATERIALS AND METHODS

Materials. Petroleum F-76 and HRD-76 were provided by the U.S. Navy Supply Center at Patuxent River, MD. The HRD-76 fuel lot was refined by UOP.[5] A "hydrocarbon window defining standard set" containing $n\text{-}C_8$ to $n\text{-}C_{40}$ alkanes in hexane was purchased from AccuStandard, Inc. (New Haven, CT). Individual alkanes had mass fraction purities of >0.98. 4-Methylhexadecane (CAS Reg. No. 25117-26-4, mass fraction purity >0.995), 2-methylheptadecane (CAS Reg. No. 1560-89-0, mass fraction purity >0.873), and 3-methylheptadecane (CAS Reg. No. 6418-44-6, mass fraction purity >0.954) standards were purchased from Chiron AS (Trondheim, Norway). A 2-methylhexadecane standard (CAS Reg. No. 1560-92-5, mass fraction purity >0.99) was purchased from Ultra Scientific (North Kingston, RI). The suite of analytical standards was used to characterize and determine the composition of HRD-76.

Chemical and Physical Property Analyses. The composition of HRD-76 was determined by gas chromatography−mass spectrometry (GC−MS). Fuel samples (1 μL) were dissolved in 1 mL of hexane and analyzed using a Bruker 436-GC gas chromatograph and a SCION-MS select single-quadrupole mass spectrometer. The GC was equipped with an Agilent DB1701 column [low/mid polarity, 60m, (14%-cyanopropyl-phenyl)-methylpolysiloxane] with a 15 m guard column before the back-flush valve and operated at a helium flow rate of 1.5 mL/min. The guard column protects the analytical column by trapping nonvolatile residues and preventing them from getting into the analytical column. The temperature program started at 50 °C for 4 min, then heated to 280 °C at a rate of 10 °C/min, and held at 280 °C for 12 min.

An Anton Paar SVM300 Stabinger viscometer was used to measure the viscosity and density of the neat and blended fuels at given temperatures. The accuracy of the viscometer was tested with a certified viscosity reference standard (Standard S3, Cannon Instrument Company), and the measurement repeatabilities were 0.35% for viscosity, 0.0002 g/cm³ for density, and 0.005 °C for temperature.

Storage and Oxidation Stability. Three ASTM methods, namely, ASTM D4625,[37] ASTM D5304,[38] and ASTM D2274,[39] were used to test the storage and oxidation stabilities of F-76, HRD-76, and their blends. These methods quantify the amounts of insolubles formed under controlled test conditions. The total insolubles include adherent and filterable insolubles. The adherent insolubles are gums formed during storage that remain tightly attached to the walls of the vessel, while the filterable insolubles are solids formed during storage

that can be removed from the fuel by filtration. After it was cooled for 60 ± 5 min in the dark at room temperature, the aged sample was filtered using two Whatman nylon membrane filters (47 mm diameter and 0.8 μm pore size) to obtain filterable insolubles. Adherent insolubles were removed from the oxidation cell/bottle and associated glassware with trisolvent (an equimolar mixture of acetone, methanol, and toluene). Depending on the method, the solvent was evaporated at 135 or 160 °C to obtain the adherent insolubles. MIL-DTL-16884L (2006) identifies maximum allowable total insolubles of 3.0 mg/100 mL for NATO F-76 using the ASTM D4625 analysis method and 1.5 mg/100 mL using the ASTM D2274 analysis method for 40 h instead of the 16 h required by ASTM.

■ RESULTS AND DISCUSSION

Physicochemical Properties of Neat and Blended Fuels. The performance of engines is strongly influenced by the physicochemical properties of the fuels, and density and viscosity are two of the most critical factors that affect fuel quality. MIL-DTL-16884L requires a kinematic viscosity range from 1.7 to 4.3 mm² s⁻¹ at 40 °C and identifies a maximum allowable density of 0.876 g/cm³ at 15 °C for NATO F-76. Figure 1 shows the densities and kinematic viscosities of F-76,
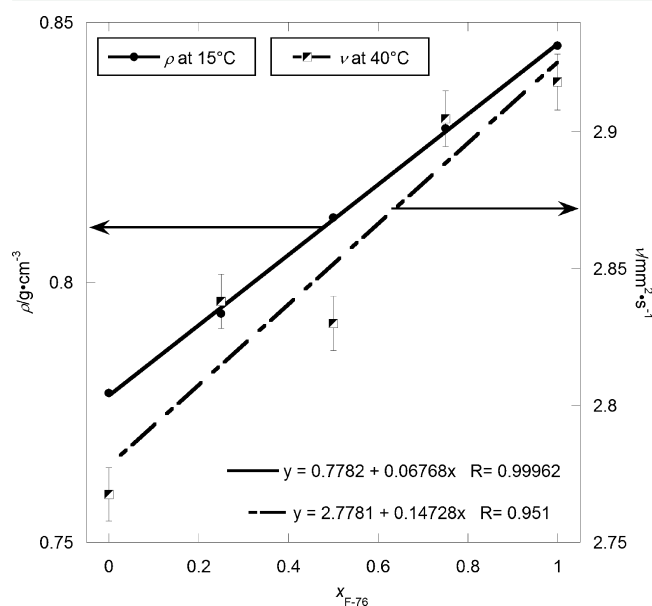

Figure 1. Densities at 15 °C and kinematic viscosities at 40 °C for F-76, HRD-76, and their blends.

HRD-76, and their blends at 15 and 40 °C, respectively. Neat HRD-76 and its blends meet the MIL-DTL-16884L specification, although the conventional petroleum F-76 is denser and more viscous than HRD-76. The density and viscosity of the blend increase linearly with the F-76 fraction, and the relationships of density (ρ) and kinematic viscosity (ν) with the F-76 fraction in the fuel blend ($x_{\text{F-76}}$) are $\rho = 0.7782 + 0.0677x_{\text{F-76}}$ at 15 °C and $\nu = 2.7781 + 0.1473x_{\text{F-76}}$ at 40 °C, respectively. The densities and kinematic viscosities of neat and blended fuels were also measured over the temperature range of 20−100 °C, as shown in the Supporting Information, and the results for F-76 and HRD-76 are in good agreement with those reported by Prak et al.[5]

Characterization of HRD-76. The chemical compositions of F-76 and HRD-76 are qualitatively different (Figure 2). HRD-76 comprises fewer compounds than conventional F-76, and the boiling points of the HRD-76 components span a
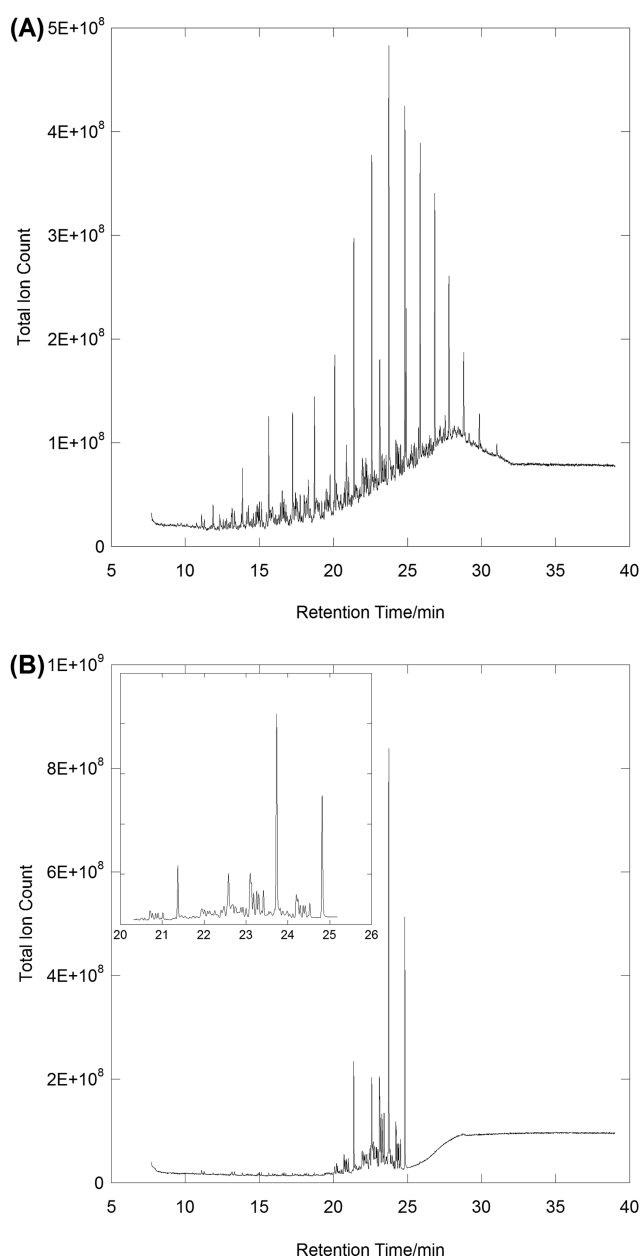
Figure 2. GC/MS chromatograms of F-76 (A) and HRD-76 (B).

narrower range than those of F-76. The characteristics of petroleum F-76 were identified previously, and F-76 generally is

composed of approximately 25% aromatics and 73% saturates (alkanes and cycloalkanes) with small amounts of olefins (alkenes, cycloalkenes, and some dienes).[57] HRD-76 has approximately 16 dominant GC peaks with retention times ranging from 21 to 25 min. A mixture with $n\text{-}C_8\text{-}C_{40}$ alkanes was used to identify the HRD-76 GC peaks, and the results indicate that HRD-76 mainly consists of $C_{15}\text{-}C_{18}$ alkanes. The unknown dominant peaks between $n\text{-}C_{16}$ and $n\text{-}C_{17}$ and between $n\text{-}C_{17}$ and $n\text{-}C_{18}$ could be identified using the retention index (RI) system first developed by Kovats[58] to identify the peaks between a series of n-alkanes. With a linear temperature program, the Kovats RI was calculated using direct retention times according to the following equation:

$$\text{RI} = 100c + 100\frac{(t'_R)_x - (t'_R)_c}{(t'_R)_{c+1} - (t'_R)_c} \tag{1}$$

where t'_R denotes a standard or analyte retention time corrected for the dead time, c is the carbon number of the n-alkane, and x is the analyte interpolation between two alkanes (i.e., c and $c + 1$).

Table 1 lists the chemicals estimated by matching the calculated RIs based on the retention times and the corresponding RIs reported by Krkosova et al.[59] 2-Methylhexadecane, 4-methylhexadecane, 2-methylheptadecane, and 3-methylheptadecane standards were purchased for peak identification and assumption verification. The RIs for 2-methylhexadecane and 4-methylhexadecane are 1662.69 and 1658.34, which are both slightly lower than the values reported by Krkosova et al.[59] A similar trend was also found for 2-methylheptadecane and 3-methylheptadecane, indicating that the RI values of isoparaffins under this measurement method are all lower than those reported by Krkosova et al.[59] This method could be used to identify all of the dominant GC peaks except for the three peaks with retention times at 24.202 min. These are tentatively identified as 9-, 8-, and 7-methylheptadecane, but the peaks and associated RI values are too close together to distinguish between them.

The composition of each compound was calculated using the response factor determined from the calibration of the n-alkane with the same carbon number, that is, the concentrations of the branched monomethyl hexadecanes and heptadecanes were calculated using the response factors of n-heptadecane and n-octadecane, respectively. Approximately 50% of HRD-76 consists of n-heptadecane and isoheptadecane. HRD-76 is mainly composed of $C_{15}\text{-}C_{18}$ n-alkanes and branched monomethyl C_{16} and C_{17} alkanes, and the mole percentages were estimated to be 11% for n-pentadecane, 9% for n-hexadecane, 22% for n-heptadecane, 25% for isoheptadecane,

Table 1. Retention Index (RI) values for Branched Monomethyl Hexadecanes and Heptadecanes

compound	RI lit.[a]	RI this work[b]	compound	RI lit.[a]	RI this work[b]
8-methylhexadecane	1646.96	1644.86	9-methylheptadecane	1745.40	1743.04
7-methylhexadecane	1647.63		8-methylheptadecane	1745.55	
6-methylhexadecane	1650.07	1647.30	7-methylheptadecane	1746.93	
5-methylhexadecane	1653.97	1651.82	6-methylheptadecane	1749.71	1746.91
4-methylhexadecane	1659.91	1658.34	5-methylheptadecane	1753.65	1751.24
2-methylhexadecane	1665.35	1662.69	4-methylheptadecane	1759.94	1758.16
3-methylhexadecane	1672.99	1672.52	2-methylheptadecane	1765.29	1762.58
			3-methylheptadecane	1773.21	1772.72

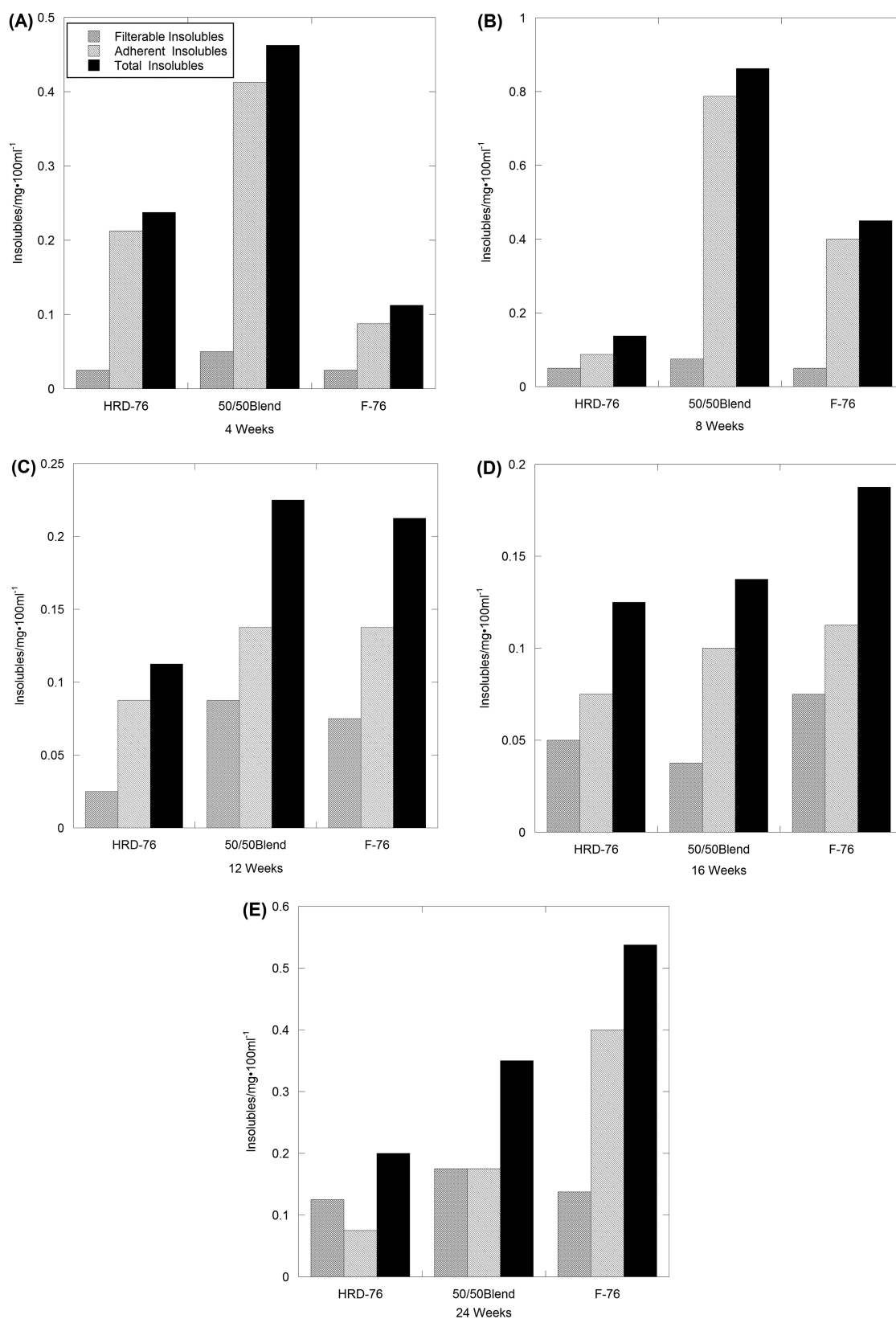[a]From Krkosova et al. 2008.[59] [b]Calculated using eq 1.

Figure 3. Insolubles formed as determined using the ASTM D4625 test method. Each bar represents the average of two samples.

15% for *n*-octadecane, and 18% for isooctadecane. Similar results were also reported by Robota et al.,[8] Huber et al.,[9] and Hsieh et al.[60]

Storage Stability. The aromatic content, sulfur content, and fuel oxidative and thermal stability affect the fuel storage stability. F-76, HRD-76, and their 50/50 blend were selected for long-term storage tests (i.e., ASTM D4625 for 24 weeks),

and the samples were analyzed 0, 4, 8, 12, 16, and 24 weeks (i.e., every 4 weeks except for 20 weeks) after being stressed in the oven at 43 ± 1 °C. Figure 3 displays the amount of total insolubles measured after each test period, and the values shown are averages of two samples obtained by the same operator with the same apparatus under constant operating conditions on identical test material. No significant linear relationships between the amount of total insolubles formed and the storage time were found. Generally, the amounts of adherent insolubles formed after aging were greater than the amounts of filterable insolubles, except for the HRD-76 and 50/50 blend analyzed at 24 weeks, indicating that adherent insolubles form more readily than filterable insolubles. The amounts of filterable and adherent insolubles formed in HRD-76 samples are almost all lower than those of F-76 samples, demonstrating that HRD-76 is more stable than F-76 and has fewer unstable precursors. It should be noted that the 4, 8, and 12 week sample analyses (Figure 3A−C) found more total insolubles in the 50/50 blend than in neat F-76.

The influence of long-term storage on fuel physicochemical properties was also investigated in this study. Figure 4A,B displays the changes in kinematic viscosity and density, respectively, with time after the fuel samples were stressed. Although the fuels became more viscous after aging, the kinematic viscosities of the neat and blended fuels still met the MIL-DTL-16884L specification. The densities of the fuel samples increased neglibly with storage time.

The oxygen overpressure method, ASTM D5304, was also employed to study the storage stability of neat and blended fuels. The advantage of this test method compared with ASTM D4625 is the greatly reduced testing time (16 h vs 24 weeks). To achieve this reduction, ASTM D5304 uses pure oxygen at 800 kPa and a temperature of 90 °C. The 16 h ASTM D5304 test yields approximately the same amount of insolubles as a 27 month storage test using air at atmospheric pressure at 20 °C.[38] Figure 5 displays the amounts of insolubles formed in the neat and blended fuel samples. As expected, the amount of insolubles formed in the F-76 samples is more than 1 mg/100 mL greater than that formed in the HRD-76 samples, indicating that HRD-76 has better storage stability than F-76 under pure oxygen and high-pressure conditions. The amount of insolubles formed in the fuel sample is correlated with the F-76 content, with higher F-76 content inducing greater insolubles formation, which is consistent with the results obtained in the ASTM D4625 tests after 16 weeks. The slopes of the trend lines indicate that the amount of filterable insolubles increases faster than the amount of adherent insolubles with increasing F-76 content. The viscosity and density changes in this test were also investigated, as shown in Figure 6. Trends similar to those for the ASTM D4625 test (Figure 4) were observed. The kinematic viscosity and density stayed the same or slightly increased after the test but still met the MIL-DTL-16884L specification. It should be noted that the increase in the densities of these fuel samples is less than 0.0004 g/cm^3 and has little influence on the fuel properties.

Oxidation Stability. Formation of insolubles in 0/100, 25/75, 50/50, 75/25, 100/0 F-76/HRD-76 percentage blends was tested using the ASTM D2274 method for 16 and 40 h (Figure 7A,B, respectively). MIL-DTL-16884L requires an oxidation time of 40 h and specifies that the total insolubles formed must be less than 1.5 mg/100 mL for NATO F-76, and this standard would likely be applied to HRD-76 blends as well. As indicated by the ASTM D4625 and ASTM D5304 test results, HRD-76
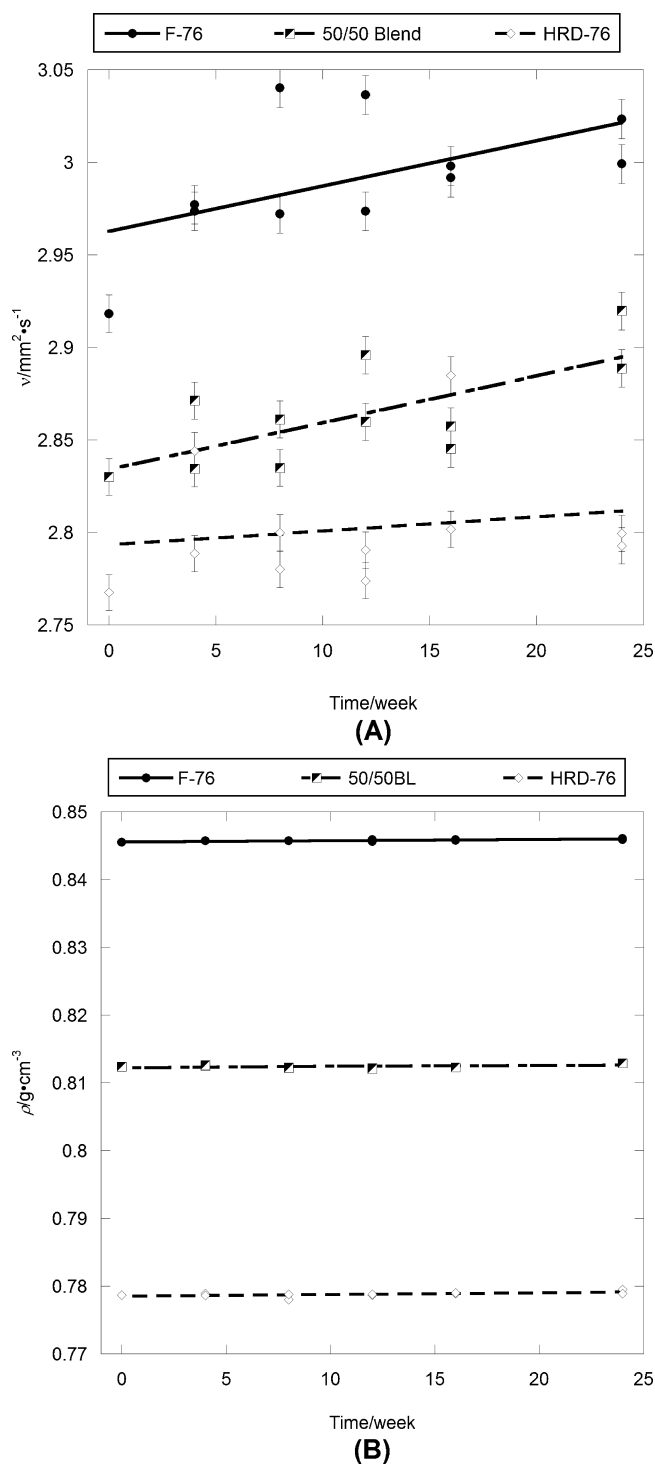

Figure 4. Change in (A) kinematic viscosity at 40 °C and (B) density at 15 °C for the fuels after the ASTM D4625 test.

has fewer oxidation precursors than F-76. The amount of insolubles formed in F-76 is greater than that in HRD-76, as HRD-76 mainly consists of saturated hydrocarbons. As seen in the results obtained from the ASTM D4625 and ASTM D5304 tests, the amount of insolubles formed in the fuel blend samples was influenced by the oxidation time and the F-76 fraction in the fuel, with longer oxidation times and higher F-76 fractions producing larger amounts of insolubles. The trend lines indicate that more adherent insolubles than filterable insolubles were formed in all of the fuel samples in the 16 and 40 h tests,
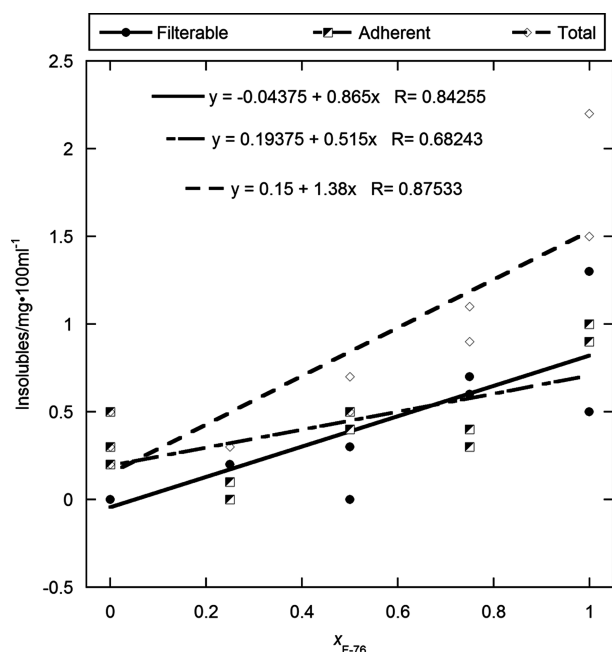
Figure 5. Insolubles formed in HRD and F-76 blends using the ASTM D5304 test method. x_{F-76} is the fraction of F-76 in the sample.
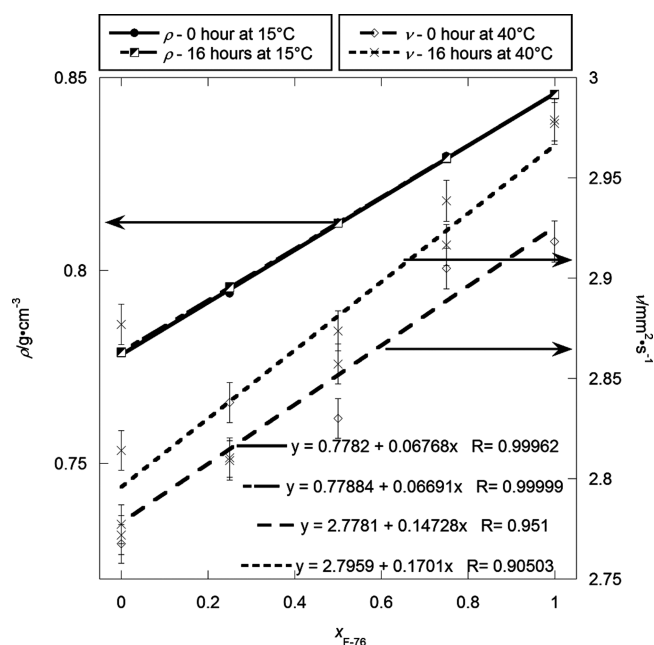

Figure 6. Kinematic viscosity and density changes for the fuels after the ASTM D5304 test at 40 and 15 °C, respectively. The error bars for the density data points are ±0.0002 g/cm³.

Figure 7. Insolubles formed using the ASTM D2274 test method for (A) 16 h and (B) 40 h.

differing from the results observed in the ASTM 5304 test. The trend lines in Figure 7 indicate that increasing the F-76 fraction in the blended samples resulted in greater increases in adherent insolubles compared with filterable insolubles. The former could be correlated with fuel tank cleaning requirements after long-term air storage of fuel. It is also important to note that the insolubles formed in F-76 samples approach the limit of the MIL-DTL-16884L specification, and blending with HRD-76 increases the oxidative stability of the fuel blend. The influence of fuel oxidation on the fuel properties was also investigated. Figure 8 shows the kinematic viscosity and density changes for
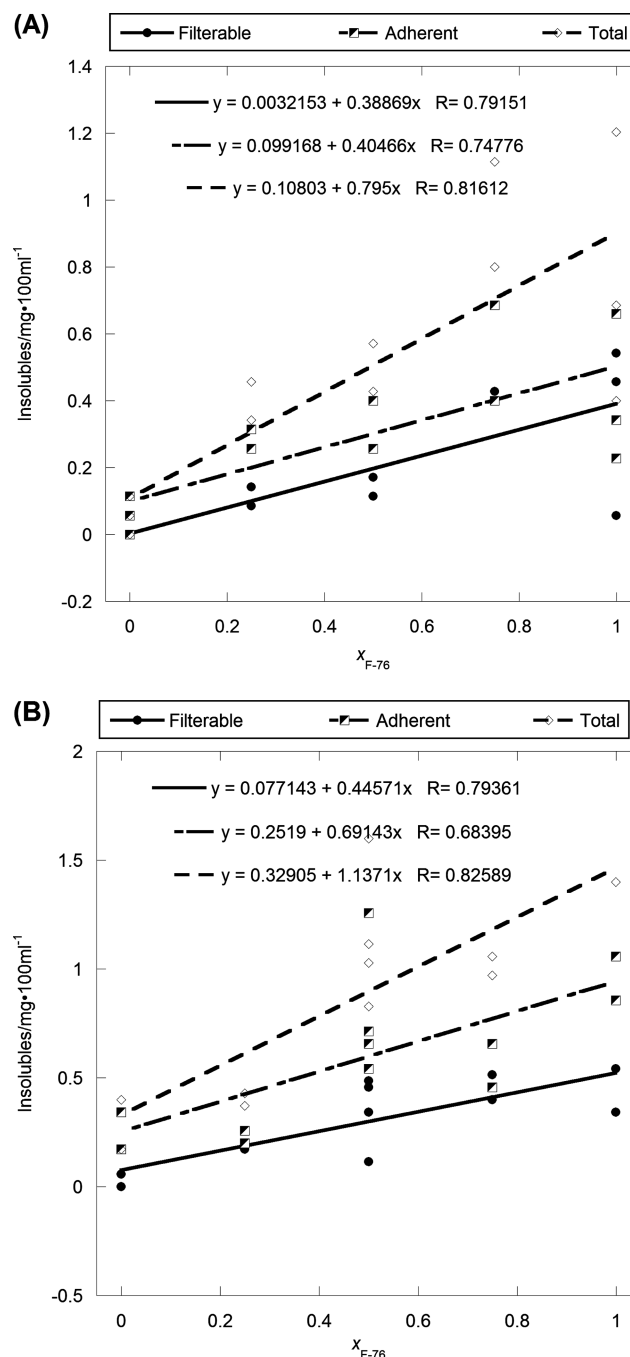
the fuel samples after 16 and 40 h of oxidation. As expected, both the viscosity and density stayed the same or slightly increased with the oxidation time and F-76 fraction, but the density increase was negligible.

Although HRD-76 has been proved to be a reliable blendstock for F-76,[3,4] a paucity of data on HRD-76 properties is available. Because of the short reaction time, no clear relationship between the oxidation time and HRD-76 stability in the ASTM D5304 and ASTM D2274 tests was observed that could contribute to understanding the long-term properties of HRD-76. Additional tests using longer oxidation times were conducted using the ASTM D2274 test method. Figures 9 and 10 show the effect of oxidation time on the HRD-76 oxidation
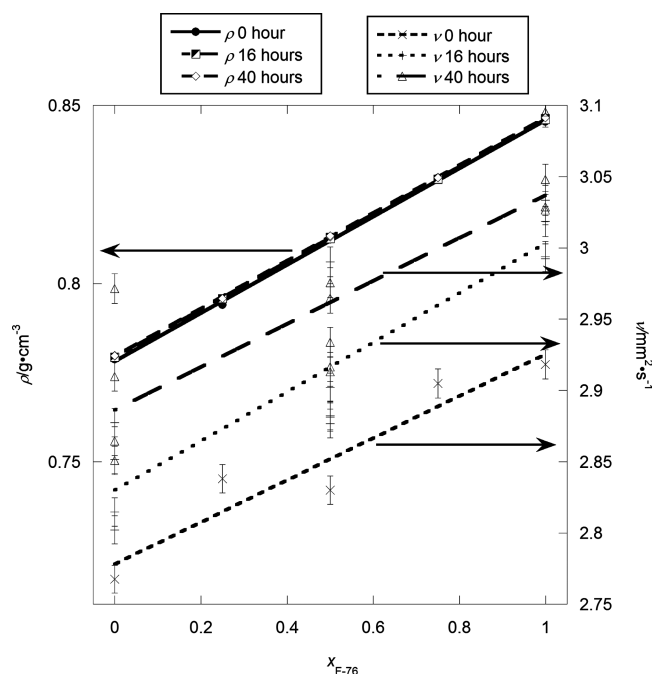
Figure 8. Kinematic viscosity at 40 °C and density at 15 °C for the fuels after the ASTM D2274 test for 16 and 40 h.
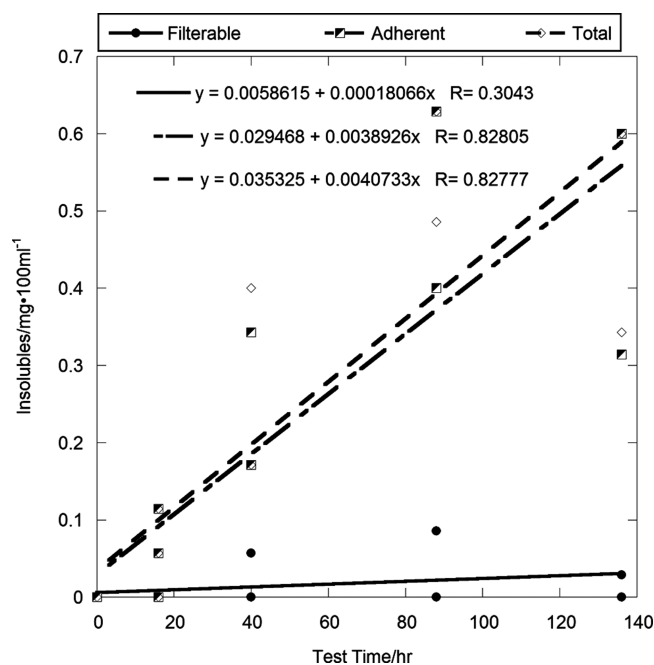

Figure 9. Insolubles formed in the extended-time ASTM D2274 test.

stability, viscosity, and density. Although the HRD-76 mainly comprises saturated $C_{15}-C_{18}$ paraffins, these paraffins can be oxidized with longer exposure to oxidative conditions. The amount of total insolubles formed in the HRD-76 samples increased with oxidation time, consisting almost exclusively of adherent insolubles. The amount of filterable insolubles is weakly correlated with the oxidation time, as illustrated by the low correlation coefficient (R). The kinematic viscosity and density of HRD-76 both increased with oxidation time. A density increase of 0.0018 g/cm^3 was observed after 136 h. The amount of insolubles formed in HRD-76 oxidized for 136 h ($\sim$0.6 mg/100 mL) is much less than that in F-76 oxidized for

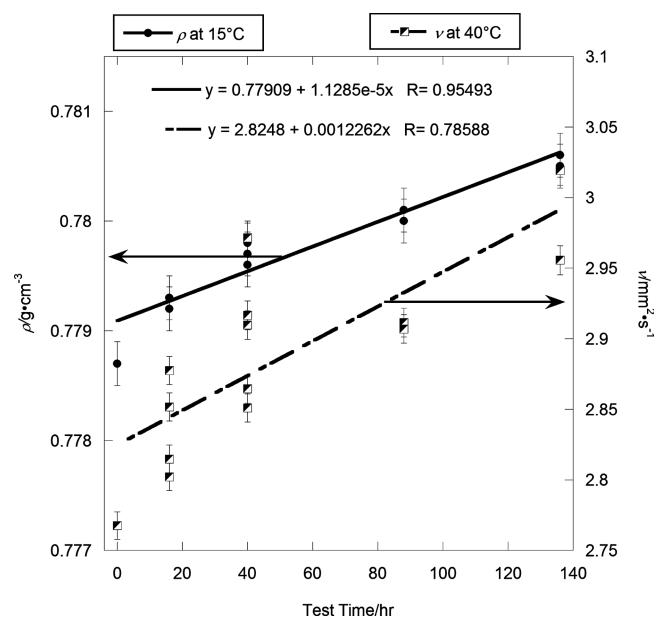**Figure 10.** Kinematic viscosity at 40 °C and density at 15 °C for fuels after the extended-time ASTM D2274 test.

40 h ($\sim$1.5 mg/100 mL), demonstrating that HRD-76 can contribute to improved stability in blends with NATO F-76.

Hydroprocessed renewable diesel is currently made from a variety of different oil sources (e.g., vegetable and animal fats). The applicability of the current test results to fuels derived from a wider range of feedstocks should be explored.

■ CONCLUSION

The influence of long-term storage and oxidation on the properties of neat and blended HRD-76 and F-76 fuels was investigated. Their effects were characterized by monitoring the formation of insolubles, the kinematic viscosity, and the density. Different from the well-characterized F-76, HRD-76 comprises fewer compounds, mainly $C_{15}-C_{18}$ n-alkanes and branched monomethyl C_{16} and C_{17} alkanes. The ASTM storage stability tests (D4625 and D5304) produced similar trends of increasing kinematic viscosity and density over the test duration, but these properties still met the MIL-DTL-16884L specification for F-76. For these two test methods, the amounts of insolubles formed in the HRD-76 samples were generally less than those in F-76, indicating that HRD-76 has better storage stability. The results of the oxidative stability test (ASTM D2274) illustrated that the amounts of insolubles formed in the fuel blend samples and their density and viscosity all increased with the oxidation time and F-76 fraction in the fuel blends. The extended oxidation tests of HRD-76 also demonstrated that the kinematic viscosity and density are highly correlated with oxidation time and that HRD-76 is more stable than F-76 and the fuel blends.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional kinematic viscosity and density data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Telephone: 808-956-8508. Fax: 808-956-2336. E-mail: JinxiaFu@hawaii.edu.

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Holland, A.; Cunningham, N. *DoD's Biofuels Program*; American Security Project: Washington, DC, 2013.

(2) Turgeon, R.; Williams, S.; Kamin, R.; Leung, R.; Eldridge, G. In *Overview of U.S. Navy's Ship Renewable Fuels Evaluation, 2011*; International Association for Stability, Handling and Use of Liquid Fuels: Atlanta, GA, 2011; pp manoharan1/1−manoharan1/26.

(3) MacKinnon, M. T.; Shaw, J. D.; Quiñones, M. Combustion Assessment of a 50% Algae-Based HRD76 Fuel and 50% Conventional F76 Military Diesel Fuel Blend. *J. Eng. Gas Turbines Power* **2012**, *134* (12), No. 121501.

(4) Quiñones, M.; Leung, R.; Williams, S. Algae Based Hydroprocessed Fuel Use on a Marine Gas Turbine. *J. Eng. Gas Turbines Power* **2012**, *134* (12), No. 122201.

(5) Prak, D. J. L.; Cowart, J. S.; Hamilton, L. J.; Hoang, D. T.; Brown, E. K.; Trulove, P. C. Development of a Surrogate Mixture for Algal-Based Hydrotreated Renewable Diesel. *Energy Fuels* **2013**, *27* (2), 954−961.

(6) Knothe, G. Biodiesel and renewable diesel: A comparison. *Prog. Energy Combust. Sci.* **2010**, *36* (3), 364−373.

(7) Bezergianni, S.; Dimitriadis, A. Comparison between different types of renewable diesel. *Renewable Sustainable Energy Rev.* **2013**, *21*, 110−116.

(8) Robota, H. J.; Alger, J. C.; Shafer, L. Converting Algal Triglycerides to Diesel and HEFA Jet Fuel Fractions. *Energy Fuels* **2013**, *27* (2), 985−996.

(9) Huber, G. W.; O'Connor, P.; Corma, A. Processing biomass in conventional oil refineries: Production of high quality diesel by hydrotreating vegetable oils in heavy vacuum oil mixtures. *Appl. Catal., A* **2007**, *329*, 120−129.

(10) Kubicka, D.; Kaluza, L. Deoxygenation of vegetable oils over sulfided Ni, Mo and NiMo catalysts. *Appl. Catal., A* **2010**, *372* (2), 199−208.

(11) Demirbas, A. New Biorenewable Fuels from Vegetable Oils. *Energy Sources, Part A* **2010**, *32* (7), 628−636.

(12) Guzman, A.; Torres, J. E.; Prada, L. P.; Nunez, M. L. Hydroprocessing of crude palm oil at pilot plant scale. *Catal. Today* **2010**, *156* (1−2), 38−43.

(13) Kubicka, D.; Horacek, J. Deactivation of HDS catalysts in deoxygenation of vegetable oils. *Appl. Catal., A* **2011**, *394* (1−2), 9−17.

(14) Simacek, P.; Kubicka, D.; Sebor, G.; Pospisil, M. Hydroprocessed rapeseed oil as a source of hydrocarbon-based biodiesel. *Fuel* **2009**, *88* (3), 456−460.

(15) Simacek, P.; Kubicka, D.; Sebor, G.; Pospisil, M. Fuel properties of hydroprocessed rapeseed oil. *Fuel* **2010**, *89* (3), 611−615.

(16) Priecel, P.; Kubicka, D.; Capek, L.; Bastl, Z.; Rysanek, P. The role of Ni species in the deoxygenation of rapeseed oil over NiMo−alumina catalysts. *Appl. Catal., A* **2011**, *397* (1−2), 127−137.

(17) Kovács, S.; Kasza, T.; Thernesz, A.; Horváth, I. W.; Hancsók, J. Fuel production by hydrotreating of triglycerides on NiMo/Al$_2$O$_3$/F catalyst. *Chem. Eng. J.* **2011**, *176*, 237−243.

(18) Hancsók, J.; Krár, M.; Magyar, S.; Boda, L.; Holló, A.; Kalló, D. Investigation of the production of high cetane number bio gas oil from pre-hydrogenated vegetable oils over Pt/HZSM-22/Al$_2$O$_3$. *Microporous Mesoporous Mater.* **2007**, *101* (1−2), 148−152.

(19) Krár, M.; Kovács, S.; Kalló, D.; Hancsók, J. Fuel purpose hydrotreating of sunflower oil on CoMo/Al$_2$O$_3$ catalyst. *Bioresour. Technol.* **2010**, *101* (23), 9287−9293.

(20) Kikhtyanin, O. V.; Rubanov, A. E.; Ayupov, A. B.; Echevsky, G. V. Hydroconversion of sunflower oil on Pd/SAPO-31 catalyst. *Fuel* **2010**, *89* (10), 3085−3092.

(21) Simacek, P.; Kubicka, D.; Kubickova, I.; Homola, F.; Pospisil, M.; Chudoba, J. Premium quality renewable diesel fuel by hydroprocessing of sunflower oil. *Fuel* **2011**, *90* (7), 2473−2479.

(22) Gusmão, J.; Brodzki, D.; Djéga-Mariadassou, G.; Frety, R. Utilization of vegetable oils as an alternative source for diesel-type fuel: Hydrocracking on reduced Ni/SiO$_2$ and sulphided Ni-Mo/γ-Al$_2$O$_3$. *Catal. Today* **1989**, *5* (4), 533−544.

(23) Darocha, G. N.; Brodzki, D.; Djegamariadassou, G. Formation of Alkanes, Alkylcycloalkanes and Alkylbenzenes during the Catalytic Hydrocracking of Vegetable-Oils. *Fuel* **1993**, *72* (4), 543−549.

(24) Veriansyah, B.; Han, J. Y.; Kim, S. K.; Hong, S. A.; Kim, Y. J.; Lim, J. S.; Shu, Y. W.; Oh, S. G.; Kim, J. Production of renewable diesel by hydroprocessing of soybean oil: Effect of catalysts. *Fuel* **2012**, *94* (1), 578−585.

(25) Bezergianni, S.; Dimitriadis, A.; Kalogianni, A.; Pilavachi, P. A. Hydrotreating of waste cooking oil for biodiesel production. Part I: Effect of temperature on product yields and heteroatom removal. *Bioresour. Technol.* **2010**, *101* (17), 6651−6656.

(26) Bezergianni, S.; Dimitriadis, A.; Sfetsas, T.; Kalogianni, A. Hydrotreating of waste cooking oil for biodiesel production. Part II: Effect of temperature on hydrocarbon composition. *Bioresour. Technol.* **2010**, *101* (19), 7658−7660.

(27) Toba, M.; Abe, Y.; Kuramochi, H.; Osako, M.; Mochizuki, T.; Yoshimura, Y. Hydrodeoxygenation of waste vegetable oil over sulfide catalysts. *Catal. Today* **2011**, *164* (1), 533−537.

(28) Bezergianni, S.; Kalogianni, A. Hydrocracking of used cooking oil for biofuels production. *Bioresour. Technol.* **2009**, *100* (17), 3927−3932.

(29) Al-Sabawi, M.; Chen, J. W. Hydroprocessing of Biomass-Derived Oils and Their Blends with Petroleum Feedstocks: A Review. *Energy Fuels* **2012**, *26* (9), 5373−5399.

(30) Lapuerta, M.; Rodríguez-Fernández, J.; Agudelo, J. R.; Boehman, A. L. Blending scenarios for soybean oil derived biofuels with conventional diesel. *Biomass Bioenergy* **2013**, *49*, 74−85.

(31) Westphal, G. A.; Krahl, J.; Munack, A.; Rosenkranz, N.; Schröder, O.; Schaak, J.; Pabst, C.; Brüning, T.; Bünger, J. Combustion of Hydrotreated Vegetable Oil and Jatropha Methyl Ester in a Heavy Duty Engine: Emissions and Bacterial Mutagenicity. *Environ. Sci. Technol.* **2013**, *47* (11), 6038−6046.

(32) Happonen, M.; Heikkila, J.; Aakko-Saksa, P.; Murtonen, T.; Lehto, K.; Rostedt, A.; Sarjovaara, T.; Larmi, M.; Keskinen, J.; Virtanen, A. Diesel exhaust emissions and particle hygroscopicity with HVO fuel−oxygenate blend. *Fuel* **2013**, *103*, 380−386.

(33) Bünger, J.; Krahl, J.; Schröder, O.; Schmidt, L.; Westphal, G. A. Potential hazards associated with combustion of bio-derived versus petroleum-derived diesel fuel. *Crit. Rev. Toxicol.* **2012**, *42* (9), 732−750.

(34) Jalava, P. I.; Aakko-Saksa, P.; Murtonen, T.; Happo, M. S.; Markkanen, A.; Yli-Pirila, P.; Hakulinen, P.; Hillamo, R.; Maki-Paakkanen, J.; Salonen, R. O.; Jokiniemi, J.; Hirvonen, M. R. Toxicological properties of emission particles from heavy duty engines powered by conventional and bio-based diesel fuels and compressed natural gas. *Part. Fibre Toxicol.* **2012**, *9*, No. 37.

(35) Stamper, D. M.; Morris, R. E.; Montgomery, M. T. Depletion of Lubricity Improvers from Hydrotreated Renewable and Ultralow-Sulfur Petroleum Diesels by Marine Microbiota. *Energy Fuels* **2012**, *26* (11), 6854−6862.

(36) Compensated Fuel Ballast: Nature of Discharge. In *Phase I Final Rule and Technical Development Document of Uniform National Discharge Standards (UNDS)*; U.S. Environmental Protection Agency: Washington, DC, 1999; Appendix A, pp 1−20.

(37) *ASTM 4625: Standard Test Method for Distillate Fuel Storage Stability at 43°C (110°F)*; ASTM International: West Conshohocken, PA, 2009.

(38) *ASTM D5304: Standard Test Method for Assessing Middle Distillate Fuel Storage Stability by Oxygen Overpressure*; ASTM International: West Conshohocken, PA, 2010.

(39) *ASTM D2274: Standard Test Method for Oxidation Stability of Distillate Fuel Oil (Accelerated Method)*; ASTM International: West Conshohocken, PA, 2010.

(40) Marshman, S. J. A rapid colorimetric method for predicting the storage stability of middle distillate fuels. In *Proceedings of the 5th International Conference on Stability and Handling of Liquid Fuels*; National Technical Information Service: Alexandria, VA, 1995; pp 377−389.

(41) Waynick, J. A.; Taskila, S. M. A comparison of low and high sulfur middle distillate fuels in the United States. In *Proceedings of the 5th International Conference on Stability and Handling of Liquid Fuels*; National Technical Information Service: Alexandria, VA, 1995; pp 697−723.

(42) White, E. W. A bit of history—The development of storage stability tests for middle distillate fuels since World War II. In *Proceedings of the 6th International Conference on Stability and Handling of Liquid Fuels*; National Technical Information Service: Alexandria, VA, 1998; pp 717−730.

(43) Muzikova, Z.; Prochaska, F.; Pospisil, M. Storage stability of FCC light cycle oil. *Fuel* **2010**, *89* (11), 3534−3539.

(44) Obadiah, A.; Kannan, R.; Ramasubbu, A.; Kumar, S. V. Studies on the effect of antioxidants on the long-term storage and oxidation stability of *Pongamia pinnata* (L.) Pierre biodiesel. *Fuel Process. Technol.* **2012**, *99*, 56−63.

(45) Bondioli, P.; Gasparoli, A.; della Bella, L.; Tagliabue, S.; Lacoste, F.; Lagardere, L. The prediction of biodiesel storage stability. Proposal for a quick test. *Eur. J. Lipid Sci. Technol.* **2004**, *106* (12), 822−830.

(46) Bondioli, P.; Gasparoli, A.; Della Bella, L.; Tagliabue, S. Evaluation of biodiesel storage stability using reference methods. *Eur. J. Lipid Sci. Technol.* **2002**, *104* (12), 777−784.

(47) Westbrook, S. R.; Stavinoha, L. L. Biodiesel and B20 Blends: Stability Test Methods and Stability Characteristics. In *Proceedings of the 8th International Conference on Stability and Handling of Liquid Fuels*; International Association for Stability, Handling and Use of Liquid Fuels: Atlanta, GA, 2003; pp 271−298.

(48) Waynick, J. A. Evaluation of the stability, lubricity, and cold flow properties of biodiesel fuel. In *Proceedings of the 6th International Conference on Stability and Handling of Liquid Fuels*; National Technical Information Service: Alexandria, VA, 1998; pp 805−829.

(49) McCormick, R. L.; Westbrook, S. R. Storage Stability of Biodiesel and Biodiesel Blends. *Energy Fuels* **2010**, *24* (1), 690−698.

(50) Dinkov, R.; Hristov, G.; Stratiev, D.; Aldayri, V. B. Effect of commercially available antioxidants over biodiesel/diesel blends stability. *Fuel* **2009**, *88* (4), 732−737.

(51) Aksoy, P.; Gul, O.; Cetiner, R.; Fonseca, D. A.; Sobkowiak, M.; Falcone-Miller, S.; Miller, B. G.; Beaver, B. Insight into the Mechanisms of Middle Distillate Fuel Oxidative Degradation. Part 2: On the Relationship between Jet Fuel Thermal Oxidative Deposit, Soluble Macromolecular Oxidatively Reactive Species, and Smoke Point. *Energy Fuels* **2009**, *23* (4), 2047−2051.

(52) Mushrush, G. W.; Willauer, H. D.; Wynne, J. H.; Lloyd, C. T.; Bauserman, J. W. Storage Tank Stability of Soybean-Derived Biodiesel. *Energy Sources, Part A* **2011**, *33* (24), 2303−2308.

(53) Mushrush, G. W.; Beal, E. J.; Hughes, J. M.; Wynne, J. H.; Sakran, J. V.; Hardy, D. R. Biodiesel fuels: Use of soy oil as a blending stock for middle distillate petroleum fuels. *Ind. Eng. Chem. Res.* **2000**, *39* (10), 3945−3948.

(54) Hilten, R. N.; Das, K. C. Comparison of three accelerated aging procedures to assess bio-oil stability. *Fuel* **2010**, *89* (10), 2741−2749.

(55) McCormick, R. L.; Ratcliff, M.; Moens, L.; Lawrence, R. Several factors affecting the stability of biodiesel in standard accelerated tests. *Fuel Process. Technol.* **2007**, *88* (7), 651−657.

(56) Fact Sheet: Great Green Fleet. http://greenfleet.dodlive.mil/files/2012/12/20121203_Great-Green-Fleet-Factsheet.pdf (accessed March 9, 2014).

(57) Waynick, J. A.; Giannini, R. M. Effect of Refining Severity on the Lubricity of NATO F-76 fuel. In *Proceedings of the 8th International Conference on Stability and Handling of Liquid Fuels*; International Association for Stability, Handling and Use of Liquid Fuels: Atlanta, GA, 2003; pp 804−833.

(58) Hübschmann, H.-J. Evaluation of GC/MS Analyses. In *Handbook of GC/MS*; Wiley-VCH: Weinheim, Germany, 2008; pp 293−420.

(59) Krkosova, Z.; Kubinec, R.; Sojak, L.; Amann, A. Temperature-programmed gas chromatography linear retention indices of all C-4−C-30 monomethylalkanes on methylsilicone OV-1 stationary phase—Contribution towards a better understanding of volatile organic compounds in exhaled breath. *J. Chromatogr., A* **2008**, *1179* (1), 59−68.

(60) Hsieh, P. Y.; Widegren, J. A.; Fortin, T. J.; Bruno, T. J. Chemical and Thermophysical Characterization of an Algae-Based Hydrotreated Renewable Diesel Fuel. *Energy Fuels* **2014**, DOI: 10.1021/ef500237t.