

COMPOSITE THERMOPHYSICAL PROPERTY CHARACTERIZATION OF HYDROTREATED RENEWABLE AND FISCHER-TROPSCH SYNTHETIC FUELS

Peter Y. Hsieh, Jason A. Widegren, Tara J. Fortin,
and Thomas J. Bruno*

Applied Chemicals and Materials Division
National Institute of Standards and Technology
325 Broadway
Boulder, CO 80305

*corresponding author: bruno@boulder.nist.gov

Introduction

Second-generation renewable fuels, or advanced biofuels, are produced from non-food biomass such as agricultural byproducts and microalgae.^{1,2} Microalgae, including diatoms and green algae, are photosynthetic microorganisms capable of capturing energy from sunlight and storing it as lipid compounds. They are attractive for energy production because of their high biomass productivity and their ability to grow in brackish or saline environments.³ Cultivation of microalgae does not compete with food crops for land and resources. Oil from microalgae can be converted to chemically stable and energy-dense diesel fuels through hydrotreatment, a chemical process where the algal oil reacts with hot pressurized hydrogen gas in the presence of catalysts to remove oxygen-containing functional groups and to hydrogenate unsaturated olefinic compounds.^{4,5}

Changes in the chemical composition and physical properties of renewable diesel fuel blends can produce significant changes in the atomization and combustion of the fuel, as well as the emissions profile.⁶ The chemical composition and physical properties of second-generation renewable fuels are unlike conventional petroleum distillate fuels or first-generation FAME-based biodiesel fuels. Chemically, algae-based hydrotreated renewable diesel fuel is similar to synthetic fuels produced through the Fischer-Tropsch (F-T) process in that both contain mostly linear and branched alkanes.⁷ Unlike petroleum distillate fuels, neither the algae-based hydrotreated renewable diesel fuel nor F-T synthetic fuels contain significant amounts of aromatic or cycloalkane (naphthenic) compounds. Characterizing the chemical and physical properties of second-generation renewable fuels is important in formulating diesel fuel blends that are compatible with engines and fuel distribution infrastructure in use today.

Experimental

Materials. A sample of algae-based hydrotreated renewable diesel fuel (HRD-76) was provided by the Naval Fuels and Lubricants Cross Function Team at Patuxent River, Maryland. The *n*-hexane solvent used in gas chromatography was purchased from a commercial supplier and determined to be approximately 99 % (mass/mass) pure through gas chromatography with mass spectrometric detection (GC-MS). Deuterated chloroform (CDCl₃) with a stated minimum isotopic purity of 99.8 % used in the nuclear magnetic resonance (NMR) spectroscopy analysis was also purchased from a commercial supplier. The CDCl₃ was used without further purification.

Instrumentation. The reduced-pressure ADC apparatus and sampling method have been described in detail in earlier works,^{8,9} a limited description of the particular steps used in this study is reported here for clarity. The boiling flask (kettle) was filled with 100 mL of HRD-76 fuel from a volumetric pipette. An aluminum heating enclosure was used to increase the fluid temperature uniformly and at a constant rate. The sample temperature was raised slowly under

manual control, using prior distillation data as a guide for the ramp rate. The distillation was performed at ambient pressure (83 kPa in Boulder, Colorado, USA).

Small aliquots (10 μ L) of the distillate were withdrawn at predetermined distillate volume intervals with a standard chromatography syringe in the receiver adapter hammock. The aliquots were dissolved in a fixed quantity of *n*-hexane (approximately 1 mL) inside an autosampler vial. The diluted aliquots were analyzed through temperature-programmed gas chromatography (30 m column with a 250 μ m film of 5 % phenyl-95 % dimethylpolysiloxane, helium carrier gas at 48 kPa or 7 psi inlet pressure, split ratio of 1.17:1, temperature program starting at 75 $^{\circ}$ C for 2 minutes followed by a ramp-up to 300 $^{\circ}$ C at a heating rate of 3 $^{\circ}$ C/min).¹⁰ Mass spectrometric detection was used to quantify and identify compounds present in the distillate.

The HRD-76 fuel was analyzed by both ¹H and ¹³C NMR spectroscopy. A sample for ¹H NMR spectroscopy was prepared by dissolving 20 mg of the fuel in 1 g of CDCl₃; 200 mg of the HRD-76 fuel was dissolved in 1 g of CDCl₃ for ¹³C NMR spectroscopy. We used a commercial 600 MHz NMR spectrometer with a cryoprobe, operated at 150.9 MHz for ¹³C, to obtain the spectra. The samples were maintained at 30 $^{\circ}$ C for all of the NMR measurements. Spectra were referenced to the solvent peak (7.23 ppm for ¹H and 77.0 ppm for ¹³C). A quantitative ¹H NMR spectrum was obtained with a 30 $^{\circ}$ flip angle and a long interpulse delay (9.1 s acquisition time, 10 s relaxation delay). A sweep width of 6,009.62 Hz (0 ppm to 10 ppm) was used. A quantitative ¹³C NMR spectrum was obtained by use of inverse-gated waltz proton decoupling and a long interpulse delay (2.17 s acquisition time, 40 s relaxation delay). A sweep width of 15,121 Hz (-10 ppm to 90 ppm) was used for a total of 1024 scans. Peak assignments were made by comparing this spectrum with the spectra obtained from ¹³C distortionless enhancement by polarization transfer (DEPT)-90 and ¹³C DEPT-135 experiments. For both DEPT experiments, a coupling constant (J_{C-H}) of 125 Hz was used because the sample contains mostly linear and branched alkanes.¹¹ A sweep width of 15,121 Hz (-10 ppm to 90 ppm) was used. Other acquisition parameters for the DEPT experiments included an acquisition time of 2.17 s, a relaxation delay of 10 s, and a total of 256 scans.

A commercial density (ρ) and speed of sound (w) analyzer was used to simultaneously measure these two properties for the HRD-76 fuel over the temperature range 5 to 70 $^{\circ}$ C and at ambient pressure (approximately 83 kPa). Details of the instrument, experimental procedures, and uncertainty analysis have been previously reported,^{12,13} therefore, only a limited description will be provided here. Programmed temperature scans were performed from 70 $^{\circ}$ C to 5 $^{\circ}$ C in 5 $^{\circ}$ C decrements. A fresh aliquot of sample was injected into the instrument prior to each temperature scan and a total of five separate injections/scans were performed.

Results and Discussion

NMR spectroscopy is widely used for the study of hydrocarbon fuels because it simultaneously provides information about the chemical structures and the relative concentrations of individual fuel components.¹¹ The HRD-76 fuel is especially amenable to NMR analysis in that it consists almost entirely of saturated or aliphatic hydrocarbons with no quaternary branching. We collected three ¹³C NMR spectra. First, a quantitative ¹³C NMR spectrum was obtained by use of inverse-gated waltz proton decoupling and a long interpulse delay. Then ¹³C DEPT-90 and ¹³C DEPT-135 spectra were obtained, which allows one to determine the number of protons attached to each type of carbon. The peaks in the quantitative ¹³C NMR spectrum were assigned by comparison with the ¹³C DEPT-90 and ¹³C DEPT-135 spectra. Then the quantitative ¹³C NMR spectrum was integrated to give the relative abundance of CH, CH₂ and CH₃ carbons. The

values obtained, along with the combined expanded uncertainty (U_c) with a coverage factor (k) of 2 are given in **Table 1**. The relative abundance of CH, CH₂ and CH₃ carbons was also calculated using GC-MS data based on peak area and compound identity. The ¹³C NMR and GC-MS data in this study are in good agreement, and are consistent with values reported for hydrotreated algal oil and hydrotreated vegetable oil by Smegala *et al.*⁴

Table 1. Primary, Secondary and Tertiary Carbon Distribution of HRD-76 Fuel Determined by ¹³C NMR and GC-MS.

	¹³ C NMR, %	U_c	GC-MS, %	U_c
CH ₃ (primary)	19.9	1.1	19.1	0.2
CH ₂ (secondary)	72.0	2.3	74.2	0.3
CH (tertiary)	8.1	0.7	6.7	0.1

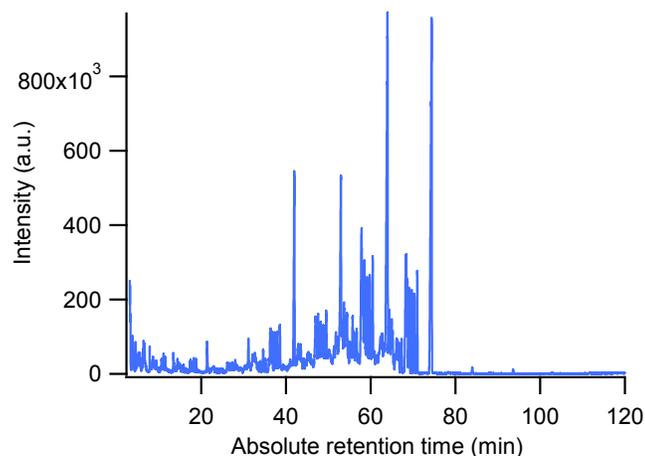


Figure 1. Total ion chromatogram of bulk HRD-76 fuel. Intensity is given in arbitrary units (a.u.).

The chromatogram of bulk HRD-76 fuel is shown in **Figure 1**. GC-MS composition data of distillate fractions over three replicate distillations of HRD-76 fuel were used as the basis for composite property calculation. Critically-evaluated values from the NIST/TRC Web Thermo Tables were used for individual components to the extent permitted by the standard reference database.¹⁴ Quantitative structure property relationship models or statistical estimates were used in instances where no data is available for a given compound or when the identity of the alkane isomer could not be fully resolved. For instance, the Cardozo model was used to estimate the enthalpy of combustion,¹⁵ and the Ozerenko model was used to estimate the speed of sound.¹⁶ Contributions to composite properties from mixing are assumed to be smaller than the uncertainty in the complex fluid composition and uncertainty in the measured or estimated value of the individual component.

Table 2. Composite Density (ρ), Speed of Sound (w) and Enthalpy of Combustion (ΔH_c°) for HRD-76 Fuel at 20 °C.

ρ , g/cm ³	$U_c(\rho)$, g/cm ³	w , m/s	$U_c(w)$, m/s	ΔH_c° , kJ/mol	$U_c(\Delta H_c^\circ)$, kJ/mol
0.744	0.038	1301	64	-9991	500

Table 2 summarizes the composite density, speed of sound and enthalpy of combustion for bulk HRD-76 fuel. The combined expanded uncertainties of the bulk composite properties are approximately 5 % of the calculated values. The composite values for

fuel density and speed of sound in the HRD-76 fuel are lower than values measured with the density and sound speed analyzer (see **Table 3**); however, the differences in the two values are not statistically significant at a 95 % confidence interval. The composite thermophysical properties approach appears promising and may be used to estimate other parameters for HRD-76 fuel and other second-generation renewable fuels under higher pressures and temperatures.

Table 3. Density (ρ), Speed of Sound (w) and Derived Isentropic Compressibility (κ_s) of HRD-76 fuel measured in the density and sound speed analyzer.

ρ , g/cm ³	$U_c(\rho)$, g/cm ³	w , m/s	$U_c(w)$, m/s	κ_s , TPa ⁻¹	$U_c(\kappa_s)$, TPa ⁻¹
0.7769	0.0003	1342	1	714.9	0.7

Conclusions

We analyzed the composition of HRD-76 fuel through NMR spectroscopy and GC-MS analysis. Differences in the CH, CH₂ and CH₃ carbon ratios based on NMR and GC-MS data were found to be statistically insignificant. Composite values of density, speed of sound and enthalpy of combustion for bulk HRD-76 fuel were calculated using composition and a combination of critically-evaluated thermophysical properties and quantitative structure property relationship models. The composite density and speed of sound values were within 5 % of bulk fluid values measured with a density and sound speed analyzer.

This work is significant in showing that NMR and GC-MS compositional data can be coupled with critically evaluated thermodynamic data and quantitative structure property relationship models to estimate fluid properties such as enthalpy of combustion, density and speed of sound with reasonable accuracy.

Acknowledgement. This research was performed while Peter Y. Hsieh held a National Research Council Research Associateship Award at NIST.

References

- Sims, R. E. H.; Mabee, W.; Saddler, J. N.; Taylor, M. *Bioresource Technology* **2010**, *101*, 1570.
- Schenk, P.; Thomas-Hall, S.; Stephens, E.; Marx, U.; Mussgnug, J.; Posten, C.; Kruse, O.; Hankamer, B. *Bioenerg. Res.* **2008**, *1*, 20.
- Sheehan, J.; Dunahay, T.; Benemann, J.; Roessler, P. *A Look Back at the U.S. Department of Energy's Aquatic Species Program - Biodiesel from Algae*, National Renewable Energy Laboratory, 1998.
- Smagala, T. G.; Christensen, E.; Christison, K. M.; Mohler, R. E.; Gjersing, E.; McCormick, R. L. *Energy & Fuels* **2013**, *27*, 237.
- Robota, H. J.; Alger, J. C.; Shafer, L. *Energy & Fuels* **2013**, *27*, 985.
- Lee, C. S.; Park, S. W.; Kwon, S. I. *Energy & Fuels* **2005**, *19*, 2201.
- Leckel, D. *Energy & Fuels* **2009**, *23*, 2342.
- Bruno, T. J. *Industrial & Engineering Chemistry Research* **2006**, *45*, 4371.
- Windom, B. C.; Bruno, T. J. *Industrial & Engineering Chemistry Research* **2011**, *50*, 1115.
- Bruno, T. J.; Svoronos, P. D. N. *Handbook of Basic Tables for Chemical Analysis*; 3rd ed.; Taylor & Francis: Boca Raton, 2011.
- Petrakis, L.; Allen, D. *NMR for Liquid Fossil Fuels*; Elsevier, 1987.
- Fortin, T. J.; Laesecke, A.; Freund, M.; Outcalt, S. *J Chem Thermodyn* **2013**, *57*, 276.
- Laesecke, A.; Fortin, T. J.; Splett, J. D. *Energy & Fuels* **2012**, *26*, 1844.
- Kazakov, A. F.; Muzny, C. D.; Chirico, R. D.; Diky, V.; Frenkel, M.; 2-2012-1-Pro ed.; Standard Reference Data Program Gaithersburg, MD, 2012.
- Cardozo, R. L. *AIChE J* **1986**, *32*, 844.
- Ozerenko, A. A.; Gyl'maliev, A. M.; Gagarin, S. G. *Coke Chem.* **2007**, *50*, 392.