The Specific Gravity Of Biodiesel Fuels And Their Blends With Diesel Fuel

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Abstract

The specific gravity of fuels is used as a precursor for a number of other fuel properties, such as heating value, viscosity and cetane number. Biodiesel fuel has significantly different properties than petroleum-derived diesel fuel. The objectives of this study were to investigate the relationship between the specific gravity and temperature of biodiesel fuels and their blends with No.2 diesel fuel, and to determine whether the ASTM D1250 Petroleum Measurement Tables were applicable to these fuels. Also specific gravity data were provided as a reference for different biodiesel fuels and their blends with No.2 diesel fuel. The specific gravity of three biodiesel fuels, two soybean oil based methyl esters and a yellow grease methyl ester, and their 75, 50 and 25% blends with No.2 diesel fuel were measured in the temperature range from about -5°C or from the onset of crystallization, to 100 °C. The measurements indicated that all the biodiesel fuels and their blends with No.2 diesel fuel had a linear specific gravity-temperature relationship similar to No.2 diesel fuel as expected. The specific gravities of the blends of biodiesel and No.2 diesel were found to be proportional to the mass fraction of the components. This proportionality was used to estimate the specific gravities of the blends of biodiesel and diesel within 0.15% of measured data for all tested fuels from 0°C to 80°C. The estimated results for specific gravity from the ASTM D1250 Petroleum Measurement Tables were compared to measured values and were found to be slightly overestimated at high temperatures while the prediction errors were less than 0.43% for all tested fuels from 0°C to 80°C.

Keywords: Specific gravity; biodiesel; methyl esters; diesel fuel; blends; ASTM D1250

1. Introduction

Biodiesel is described as a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats. It is oxygenated, essentially sulfur-free and biodegradable. The most commonly used biodiesel production method is the base catalyzed transesterification of the oil or fat with alcohol as illustrated by Figure 1 (NBB, 2002). In the reaction in Figure 1, R is the short hydrocarbon chain in the alcohol. The short chain alcohol is usually methanol or ethanol. R_1, R_2, and R_3 are fatty acid chains, which are associated with the oil or fat used. For naturally occurring oils or fats, these fatty acids are largely palmitic, stearic, oleic, linoleic, and linolenic acids (NBB, 2002). The glycerine is removed as a valuable by-product (Howell, 1997).

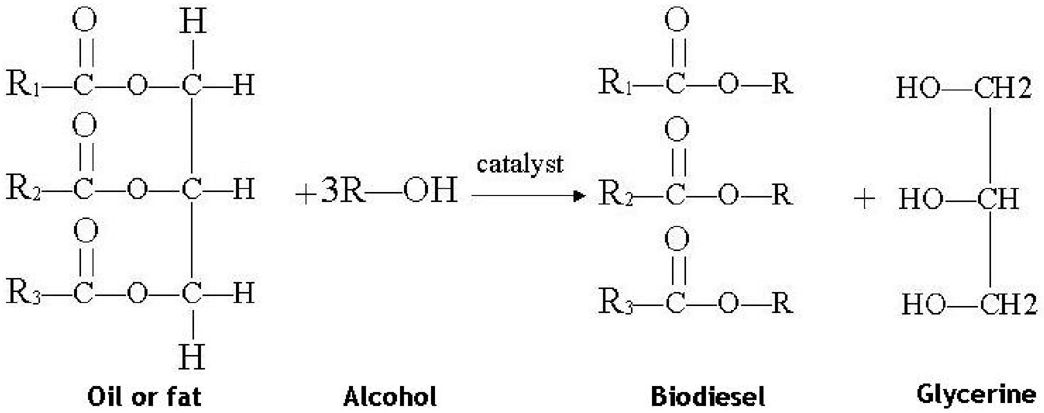

Figure 1 A simplified representation of biodiesel production (NBB, 2002)

Biodiesel is the only alternative fuel that has passed EPA-required Tier I and Tier II Health Effects testing requirements of the Clean Air Act Amendments of 1990. In addition, biodiesel has been shown to be a very promising alternative to crude-oil derived diesel fuels because it is renewable, it significantly reduces particulate matter, hydrogen carbon (HC) and carbon monoxide (CO) emissions (Graboski et al., 1996; McCormick et al., 2001) and the net production of carbon dioxides (CO_2) from combustion sources, and it relieves U.S. dependence on foreign crude oil. Because of these advantages, biodiesel has gained considerable attention in the past few years.

When using biodiesel in unmodified diesel engines, one issue that needs to be addressed is that biodiesel fuels have different properties than petroleum diesel, such as higher viscosity, higher cetane number, higher specific gravity and lower heating value (Graboski and McCormick, 1998). These fuel properties may affect the engine performance and emissions considering that the engines were originally optimized with petroleum diesel. Among these properties, specific gravity is one of the most basic and most important properties because some important performance indicators such as cetane number and heating value are correlated with it (Tat and Van Gerpen, 2000). It is also an important parameter in connection with fuel storage and transportation. The objectives of this study were to investigate the relationship between the specific gravity and temperature of biodiesel fuels and their blends with No.2 diesel fuel, and to determine whether the ASTM D1250 Petroleum Measurement Tables (1953) were applicable to these fuels. Another objective of this study was to provide specific gravity data as a reference for different biodiesel fuels and their blends with No.2 diesel fuel.

2. Materials and Methods

2.1 Fuel selection and preparation

In this study, three biodiesel fuels were tested. One sample was a commercially available soybean oil methyl ester (SMEA), which was obtained from Growmark Inc. (Bloomington, IL). A second soybean methyl ester (SMEB) and a yellow grease methyl ester (YGME) were provided by Dr. Van Gerpen and Tat at Iowa State University. The

SMEB ester was selected because it had a slightly different fatty acid profile from SMEA (Table 1) and it exhibited about 8% higher viscosity than SMEA at 40°C. It was expected that they would have different specific gravities and therefore would be worth including in this study. YGME was derived from yellow grease, which had a significantly different fatty acid profile than soybean oil (Table 1).

Table 1 Fatty acid profiles of selected biodiesel fuels

	SMEA[a]	SMEB[b]	YGME[b]
C14:0 (Myristic)	0.08	0	1.27
C16:0 (Palmitic)	10.49	10.81	17.44
C16:1 (Palmitoleic)	0.12	0.11	2.03
C18:0 (Stearic)	4.27	4.54	12.38
C18:1 (Oleic)	24.2	24.96	54.67
C18:2 (Linoleic)	51.36	50.66	7.96
C18:3 (Linolenic)	7.48	7.27	0.69
C20:0 (Arachidic)	0.36	0.37	0.25
C20:1 (Gadoleic)	0.28	0.32	0.52
C22:0 (Behenic)	0.4	0.42	0.21
C22:1 (Erucic)	0.07	0	0
C24:0 (Lignoceric)	0.14	0.12	0

[a] Measured by Eurofins Woodson-Tenent Laboratories Division, Des Moines, IA

[b] Provided by Tat and Van Gerpen (2004)

A commercial grade No.2 diesel was used to blend with each biodiesel fuel at a mass base of 75, 50 and 25 % biodiesel in the blends. The names of these blends were defined by the name of the biodiesel fuels followed by the mass fraction of the biodiesel in the blend. For example, SMEA75 signifies that it is a blend of 75% SMEA and 25% No.2 diesel. The properties of No.2 diesel fuel and the biodiesel fuels are listed in Table 2.

Table 2 Properties of No.2 diesel and biodiesel fuels

	D2	SMEA	SMEB[c]	YGME[c]
Carbon (% mass)[a]	86.97	77.42	77.0	76.66
Hydrogen (% mass)[a]	12.57	12.29	12.18	12.33
Sulfur (% mass)[a]	0.051	<0.005	<0.005	<0.005
Nitrogen (ppm)[a]	122	10	-	-
Ash (% mass)[a]	0.002	0.002	-	-
Oxygen (% mass by difference)	0.39	10.29	10.82	11.01
Gross heat of combustion (Btu/lb)[a]	19573	17103	17183	17252
Net heat of combustion (Btu/lb)[a]	18426	15982	16072	16209
Kinematic viscosity (@40°C, mPas)[b]	2.5566	4.1057	4.4129	5.018
Specific gravity (70/60°F)[a]	0.8454	0.8805	0.8796	0.8722

[a] Measured by Phoenix Chemical Laboratory, Inc., Chicago, IL

[b] Measured at Agricultural and Biological Engineering Department, University of Illinois at Urbana-Champaign

[c] Provided by Dr. Van Gerpen ant Tat at Iowa State University except the viscosity

2.2 Experimental procedure

Soft glass API gravity hydrometers manufactured by Fisher Scientific Co. (Pittsburgh, PA) were used to measure the gravities of the samples at various temperatures. The thermometers with a temperature range of 10 to 160°F were integrated into these gravity hydrometers. The API gravity range of the hydrometers was 10 to 45 degree. These hydrometers were calibrated at the reference temperature of 60°F (15.56°C) by the manufacturer. Following the ASTM D1298-99e2 standard (2003) in the measurements, the observed hydrometer readings at temperatures other than the reference temperature were corrected to the reference temperature and converted to specific gravity by using the ASTM D1250 Petroleum Measurement Tables (1953). A Brookfield Ex-200 water bath, which had a temperature control precision of ±0.02 °C, was used to control the temperature and to pump constant temperature fluid to a container where a 250 ml KIMAX graduated glass cylinder was placed. The fuel samples were placed in the cylinder. The excess fluid from the container was re-circulated to the water bath to keep the temperature constant. For temperatures higher than 20°C, city water was used as the fluid and measurements were taken at increments of 20°C. From 0-20°C, Ice/water mixture was used as the fluid and specific gravity were measured at steps of 5°C. To reach the temperatures below 0 °C, the samples were placed in a refrigerator to freeze at about –5 °C or until the onset of the crystallization. The measurements were performed in the refrigerator to keep the temperatures stable.

2.3 Correlation and blending models

The measured specific gravity of SMEA, SMEB, YGME and their 75%, 50% and 25% blends with No.2 diesel were correlated as the function of temperature using the linear square method. The linear regression equation was formulated as:

$$SG = mT + b \qquad (1)$$

where SG denotes the specific gravity, T is the temperature in °C, and m and b are correlation constants.

The specific gravity of the blends can also be calculated from the specific gravity of each component by the following equation

$$SG_{blends} = SG_i \times x_i \qquad (2)$$

where SG_{blends} and SG_i represents the specific gravity of the blends and the component *i* respectively. x_i denotes the mass fraction of the component *i*. This equation was first suggested by Clements (1996) and was used by Tat and Van Gerpen (2000) as the blending rule for calculating the specific gravity of biodiesel blends. It was employed in this study to calculate the specific gravities of the blends based on the measured specific gravities of the pure biodiesel fuels and No.2 diesel fuel. The calculated results were compared with measured values to find out if this blending rule was applicable to the tested biodiesel fuels.

2.4 ASTM D1250 Petroleum Measurement Tables method

The specific gravity of the fuels at 15.6 °C was employed to find the specific gravity at other temperatures by using the ASTM D1250 Petroleum Measurement Tables (1953). These tables were originally developed to find the specific gravity of petroleum products at 15.6 °C from the data obtained at other temperatures. Vice versa, the specific gravity of the fuels at 15.6 °C could also be used to find the specific gravity at other temperatures. Tat and Van Gerpen (2000) first used these tables to estimate the specific gravity of a soybean oil methyl ester and found it give accurate estimations at temperatures from the onset of crystallization to 100°C. In this study, we wanted to determine whether these tables would be applicable to other biodiesel fuels by comparing the estimated results from the tables with measured values.

3. Results and Discussion

3.1 Measured specific gravities and regressions

The measured specific gravity as a function of temperature for SMEA, SMEB, YGME and their 75%, 50% and 25% blends with No.2 diesel fuel are shown in Figure 1, Figure 2 and Figure 3 respectively. In these figures, the points are measured values and the lines are linear least square regression lines.

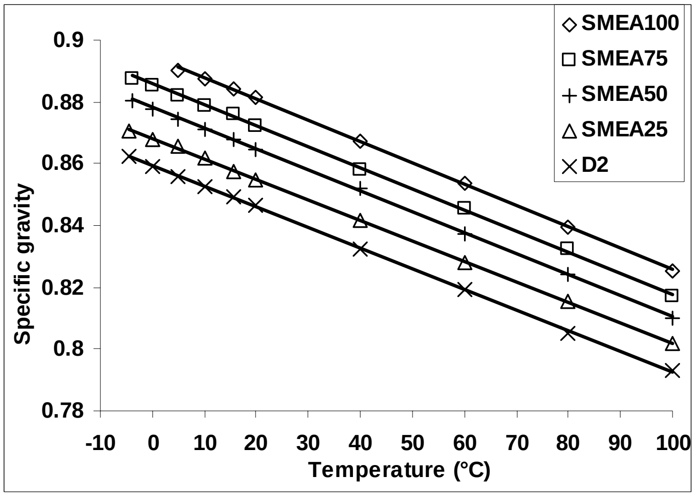

Figure 1 Specific gravity of SMEA and its blends with No.2 diesel

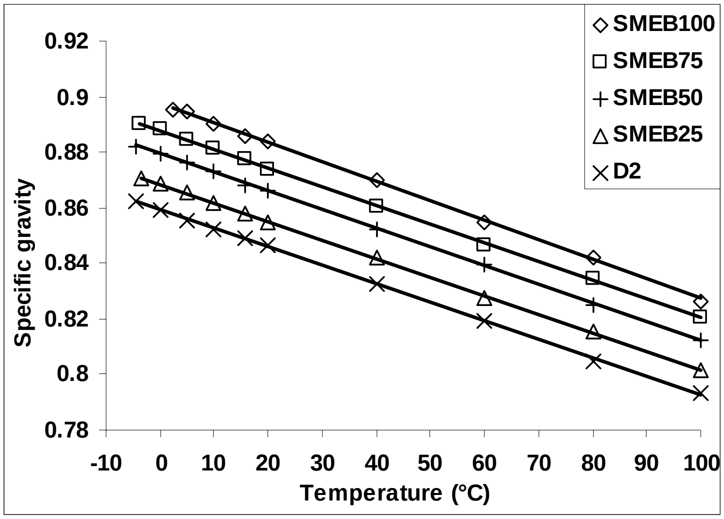

Figure 2 Specific gravity of SMEB and its blends with No.2 diesel

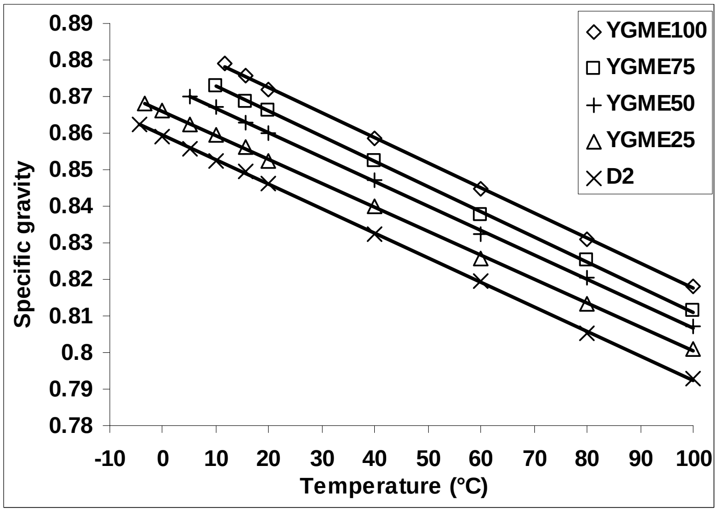

Figure 3 Specific gravity of YGME and its blends with No.2 diesel

Figures 1 to 3 indicate that all the biodiesel fuels and their blends with No.2 diesel fuel have a linear specific gravity-temperature relationship similar to No.2 diesel fuel as was expected. The regression lines closely follow the measured data. The regression coefficients in Equation (1) for the tested fuels are shown in Table 3. The specific gravity of each fuel at various temperatures can be easily calculated by using these coefficients.

Table 3 Linear square regression constants and regression coefficients for the fuels

Fuel	m	b	R^2
SMEA100	-6.90148E-04	0.89468	0.9990
SMEA75	-6.78611E-04	0.88581	0.9993
SMEA50	-6.77397E-04	0.87811	0.9998
SMEA25	-6.65446E-04	0.86822	0.9997
SMEB100	-7.01565E-04	0.89753	0.9990
SMEB75	-6.76946E-04	0.88791	0.9996
SMEB50	-6.71785E-04	0.87927	0.9997
SMEB25	-6.69692E-04	0.86856	0.9997
YGME100	-6.82948E-04	0.88607	0.9995
YGME75	-6.83173E-04	0.87951	0.9998
YGME50	-6.67609E-04	0.87349	0.9996
YGME25	-6.57082E-04	0.86587	0.9997
D2	-6.66676E-04	0.85917	0.9996

It can be seen from Table 3 that the lowest regression coefficient R^2 is 0.999, which indicates that the linear least square regression can represent very closely the relationship between specific gravity and temperature.

3.2 Specific gravities from blending model and ASTM D1250 tables

The measured specific gravities of the three pure biodiesel fuels and No.2 diesel were employed to calculate the specific gravities of their 75%, 50% and 25% blends using Equation (2). Also, the measured specific gravities of each fuel at 60°F (15. 6°C) were used to find the specific gravities at other temperatures by using ASTM D1250 Petroleum Measurement Tables. The results from these two methods along with measured values are shown in Figures 4 to 6. The temperatures shown are below 80°C because the Petroleum Measurement Tables only have data up to this point for the specific range applied.

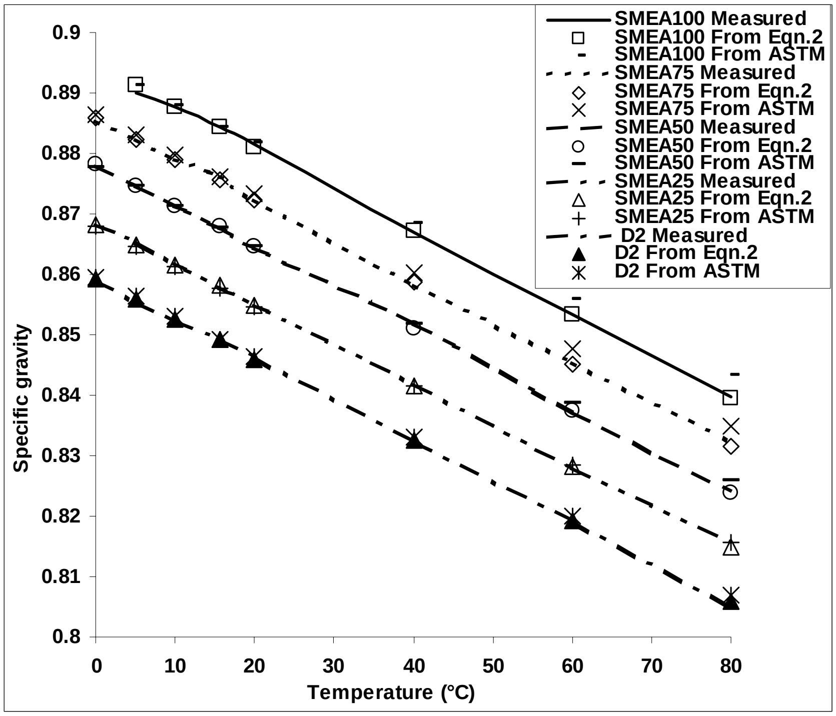

Figure 4 Measured and predicted specific gravity of SMEA and its blends with No.2 diesel

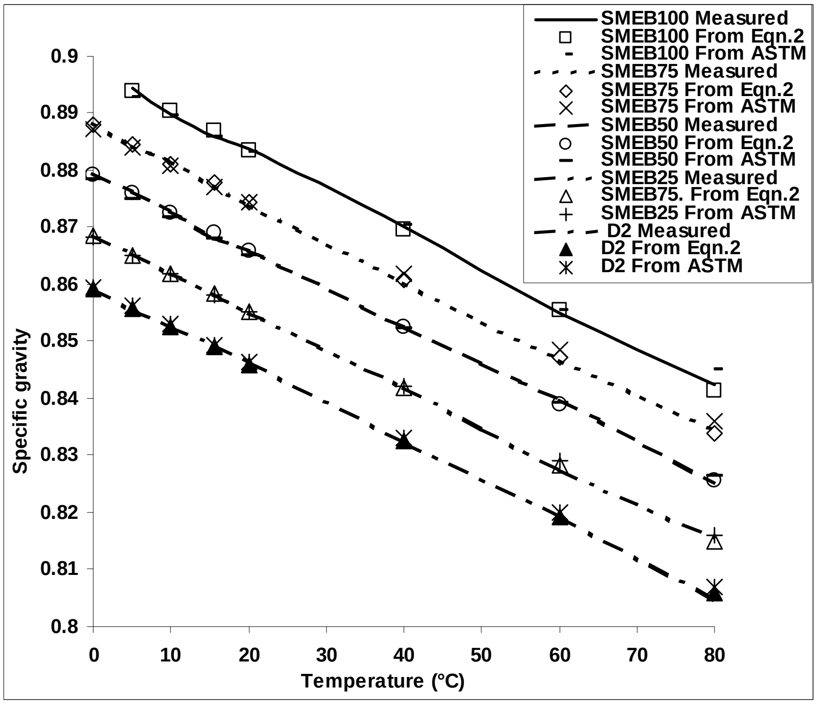

Figure 5 Measured and predicted specific gravity of SMEB and its blends with No.2 diesel

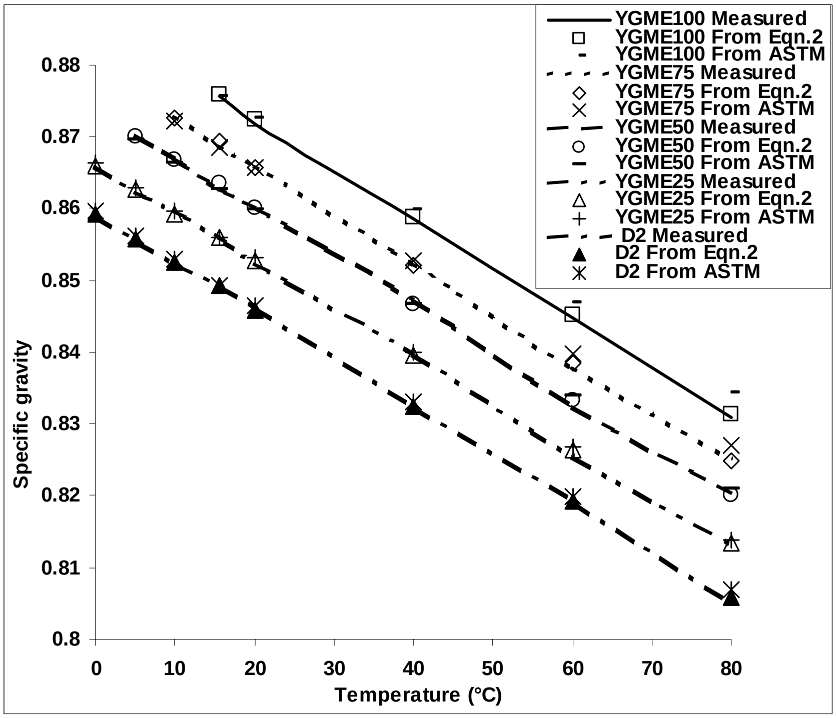

Figure 6 Measured and predicted specific gravity of YGME and its blends with No.2 diesel

Figures 4 to 6 show that the predicted results from Equation (2) are very close to the measured values, while the estimated results from the ASTM D1250 tables at high temperatures are overestimated. This finding is different than the conclusion of Tat and Van Gerpen (2000) that the results from ASTM D1250 tables were underestimated at high temperatures. It must be noted that Tat and Van Gerpen (2000) used a specific gravity balance, not a glass hydrometer in their measurements to obtain the specific gravities of the fuels. However, all tables in ASTM D1250 involving reduction of gravity to a standard temperature assume that the measurement has been made by means of a glass hydrometer, and correction for the thermal expansion of a standard glass has been incorporated (ASTM-IP, 1953). This is probably the main reason for the different conclusions. Comparisons of the prediction errors from both Equation (2) and ASTM D1250 tables are shown in Table 4.

Table 4 Prediction errors of Equation (2) and ASTM D1250 tables

	From Equation (2)		From ASTM tables	
	AAD%[a]	MAD%[b]	AAD%[a]	MAD%[b]
SMEA100	0.044	0.146	0.157	0.429
SMEA75	0.045	0.108	0.153	0.312
SMEA50	0.032	0.106	0.061	0.231
SMEA25	0.038	0.074	0.037	0.092
SMEB100	0.062	0.113	0.085	0.321
SMEB75	0.052	0.070	0.109	0.213
SMEB50	0.047	0.127	0.093	0.170
SMEB25	0.039	0.109	0.043	0.193
YGME100	0.040	0.069	0.180	0.397
YGME75	0.043	0.084	0.105	0.242
YGME50	0.047	0.120	0.069	0.180
YGME25	0.033	0.097	0.057	0.157
D2	0.033	0.112	0.083	0.261

AAD%[a]: average absolute deviation% = (sum of d)/N, where d =100* (|exp – calc|)/exp, N = the number of points

MAD%[b]: Maximum absolute deviation% = Maximum of d, where d = 100* (|exp – calc|)/exp

Table 4 shows that the maximum absolute deviation for Equation (2) is about 0.15%, and 0.43% for ASTM D1250 tables. The prediction errors from the ASTM D1250 tables seem to be higher than from Equation (2), although both of these two methods have very small errors. The prediction errors are proportional to the percentages of biodiesel in the blends for both of these two methods. The higher the percentage, the larger the error is. This is probably because the tables were originally developed for petroleum fuels.

Conclusions

1. The specific gravity of three biodiesel fuels and their 75, 50 and 25% blends with No.2 diesel fuel were measured at various temperatures. All the biodiesel fuels and their blends with No.2 diesel fuel had a linear specific gravity-temperature relationship similar to No.2 diesel fuel as was expected.
2. The specific gravities of the blends of biodiesel and No.2 diesel were proportional to the mass fraction of the components, which could be used to estimate the specific gravities of the blends of biodiesel and diesel within 0.15% of measured data for all tested fuels from 0°C to 80°C.
3. The ASTM D1250 tables could be used to estimate the specific gravity of biodiesel fuels as well as petroleum products. The predicted results were slightly overestimated at high temperatures. The predicted results were within 0.43% of measured data for all tested fuels from 0°C to 80°C.

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References

ASTM-IP Petroleum Measurement Tables. 1953. Prepared jointly by American Society for Testing Materials [and] the Institute of Petroleum. ASTM Designation: D1250, IP Designation: 200.

ASTM D1298-99e2. 2003. Standard Test Method for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method.

Clements, D.L. 1996. Blending rules for formulating biodiesel fuel. *Liquid Fuels and Industrial Products from Renewable Resources-Proceedings of the Third Liquid Fuel Confersnce*, Nashville, TN, pp. 44-53.

Graboski, M.S., J.D. Ross, and R.L. McCormick. 1996. Transient emissions from No.2 diesel and biodiesel blends in a DDC series 60 engine. SAE technical paper 961166.

Graboski, M.S. and R.L. McCormick. 1998. Combustion of fat and vegetable oil derived fuels in diesel engines. *Prog. Energy Combust. Sc.* 24:125-164.

Howell, Steve. 1997. U.S. biodiesel standards – an update of current activities. SAE technical paper 971687.

McCormick, R.L., M.S. Graboski, A.M. Herring and T.L. Alleman. 2001. Impact of biodiesel source material and chemical structure on emissions of criteria pollutants from a heavy-duty engine. *Environmental Science & Technology*. 35(9):1742-1747.

NBB. 2002. Biodiesel production and quality. Available online at http://www.biodiesel.org/pdf_files/prod_quality.pdf. Accessed 20 Oct. 2003.

Tat, M.E. and J.H.Van Gerpen 2000. The specific gravity of biodiesel and its blends with diesel fuel. *J. Am. Oil Chem. Soc.* 77(2):115-119.