Temperature-Dependent Kinematic Viscosity of Selected Biodiesel Fuels and Blends with Diesel Fuel

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ABSTRACT: The kinematic viscosities of four biodiesel fuels two natural soybean oil methyl esters, one genetically modified soybean oil methyl ester, and one yellow grease methyl ester—and their 75, 50, and 25% blends with No. 2 diesel fuel were measured in the temperature range from 20 to 100°C in steps of 20°C. The measurements indicated that all these fuels had viscosity–temperature relationships similar to No. 2 diesel fuel, which followed the Vogel equation as expected. A weighted semilog blending equation was developed in which the mass-based kinematic viscosity of the individual components was used to compute the mixture viscosity. A weight factor of 1.08 was applied to biodiesel fuel to account for its effect on the mixture viscosity. The average absolute deviation achieved with this method was 2.1%, which was better than the uncorrected mass average blending equation that had an average absolute deviation of 4.5%. The relationship between the viscosity and the specific gravity of biodiesel fuels was studied. A method that could estimate the viscosity from the specific gravity of biodiesel fuel was developed. The average absolute deviation for all the samples using this method was 2.7%. The accuracy of this method was comparable to the weighted mass-based semilog blending equation.

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KEY WORDS: Biodiesel, diesel fuel, kinematic viscosity, methyl esters.

Biodiesel is described as a fuel comprising mono-alkyl esters of long-chain FA derived from vegetable oils or animal fats. As an alternative to petroleum-based diesel fuel, biodiesel is renewable and biodegradable. It significantly reduces particulate matter, hydrocarbon, and carbon monoxide emissions (1,2) from combustion. Biodiesel is also the only alternative fuel that has passed the U.S. Environmental Protection Agency-required Tier I and Tier II Health Effects testing requirements of the Clean Air Act Amendments of 1990. Because of these advantages, biodiesel has gained considerable attention in the past few years. Support for biodiesel at the federal and state levels of government in the United States has recently increased considerably through the provision of tax credits and incentives applied to the production and marketing of this fuel. Such support will motivate more widespread use of biodiesel in the United States. However, engine manufacturers have been con-

cerned about biodiesel's higher viscosity compared with diesel fuel since high viscosity could cause excessive fuel injection pressures during engine warmup (3) and affect the in-cylinder fuel atomization process in direct-injection diesel engines, which consequently affects the exhaust emissions from the engine. Since biodiesel is marketed mostly as a blend, such as 20% (B20) with petroleum diesel in diesel engines, a study on how the viscosity of the blends varies with blending level has become urgent.

Although the measurements or predictions of the viscosity of pure biodiesel or blends are not new, they have focused either on a specific type of biodiesel fuel (3) or on pure biodiesel fuels instead of the blends (4,5). At present, no report is available on determining the blending rule for the viscosity of the blends of a general type of biodiesel with petroleum diesel, and no report exists on estimating the viscosity of biodiesel–diesel blends from the specific gravities of pure biodiesel and diesel. The objectives of this work were to address these issues.

MATERIALS AND METHODS

Test fuels. In this study, four 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 natural soybean oil methyl ester (SMEB), a genetically modified soybean oil methyl ester (GMSME), and a yellow grease methyl ester (YGME) were provided by Dr. Jon H. Van Gerpen and Mustafa E. Tat at Iowa State University, Ames, Iowa. It can be seen from the FA profiles of the fuels shown in Table 1 that SMEA and SMEB have slightly different FA compositions from each other, whereas they have significantly different FA profiles from GMSME. The GMSME biodiesel has 82.54% in mass of oleic acid ester and only 8.68% in total of linoleic and linolenic acid esters, which makes it less unsaturated than the other two soybean oil methyl esters. The YGME biodiesel has more fully saturated FA, such as myristic, palmitic, and stearic acids, than other fuels. Therefore, it is even more saturated than the GMSME although the FA chain is somewhat shorter.

A commercial grade No. 2 diesel was used to blend with each biodiesel fuel on a mass basis of 75, 50, and 25% biodiesel in the blends. The names of these blends were defined by the name of the biodiesel fuel 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

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a SMEA, a soybean oil methyl ester (Growmark Inc., Bloomington, IL); measured by Eurofins Woodson-Tenent Laboratories Division (Des Moines, IA). bSMEB, a second natural soybean oil methyl ester; GMSME, a genetically modified soybean oil methyl ester; YGME, a yellow grease methyl ester; provided by Dr. Jon H. Van Gerpen and Mustafa E. Tat, Iowa State University (Ames, IA).

diesel. Selected properties of No. 2 diesel fuel and the biodiesel fuels are listed in Table 2.

Kinematic viscosity measurements. The kinematic viscosities of the four biodiesel fuels and their 75, 50, and 25% blends with No. 2 diesel fuel were measured from 20 to 100°C in steps of 20°C. Cannon–Fenske-type glass capillary viscometers were used to measure the kinematic viscosity of the samples. The ASTM standard D-445 (6) was followed in the measurements. To obtain the kinematic viscosity in mm^2/s by capillary viscometer, the efflux time in seconds was multiplied by the viscometer constant, provided from calibrations by the manufacturer at 40 and 100°C, and could be interpolated or extrapolated to other temperatures. For each sample at each temperature, the measurement was performed three times. Any two of the measurements were required to be within $0.02 \text{ mm}^2/\text{s}$ tolerance, otherwise the three measurements were repeated. A Brookfield EX-200 water bath was used for temperature control. The temperature control stability was $\pm 0.01^{\circ}$ C.

Correlation of viscosity with temperature. The measured viscosities of SMEA, SMEB, GMSME, YGME, and their 75, 50, and 25% blends with No. 2 diesel were correlated as a function of temperature using the Vogel equation, which has been intensively reviewed by Reid *et al.* (7) and Monnery *et al*. (8). It is formulated as:

In Equation 1, v (mm²/s) represents the kinematic viscosity of the liquid at temperature $T(K)$. A, B, and C are correlation parameters, which can be determined from viscosity measurements at three or more temperatures.

The semilog blending model. The semilog blending equation is widely used (3,7,9) to calculate the viscosity of a mixture based on the kinematic viscosity of the components. It is formulated as:

$$
\ln v_{\text{blends}} = f r_1 \times \ln v_1 + f r_2 \times \ln v_2 \tag{2}
$$

where v_{blends} (mm²/s) represents the viscosity of the blends, v_1 and v_2 (mm²/s) denote the viscosity of two components, and fr_1 and fr_2 denote the fraction of the two components, which can be mass-, volume-, or mole-based.

We found that the kinematic viscosities predicted from Equation 2 using the mass fraction were always underpredicted. Since pure biodiesel fuels have higher viscosities with higher densities and larger M.W., if the volume fraction or molar fraction is used, biodiesel fuels will have smaller fractions compared with using a weight fraction, thereby causing the viscosities to be even more underpredicted. Therefore, we selected the mass fraction as the most suitable value for Equation 2 to calculate the mixture viscosity.

The underpredictions led us to hypothesize that components with higher viscosities contributed more than predicted in a mixture using their pure value, thus leading to underpredicted viscosities. This hypothesis was inspired by Allen *et al.* (10), who suggested that components with lower surface tensions should produce less than their 100% effect in a mixture, leading to overpredicted surface tension. The exact mechanism of the more significant effect of the higher-viscosity components on mixture viscosity is unknown. However, it is generally accepted that the interactions between nonassociated components always exist. Therefore, when nonassociated components are mixed, in this case biodiesel and diesel fuel, their interaction makes the internal friction larger than accounted for by Equation 2. This is why the Grunberg–Nissan equation, which considers the interactions among components, is usually used to calculate the viscosity of a mixture $(7,8)$. The Grunberg–

a Measured by Phoenix Chemical Laboratory, Inc. (Chicago, IL).

*^b*Provided by Dr. Jon H. Van Gerpen and Mustafa E. Tat at Iowa State University (Ames, IA). For abbreviations see Table 1.

Nissan equation applies to the kinematic viscosity of the binary mixture and is formulated as:

$$
\ln v_{\text{blends}} = f r_1 \times \ln v_1 + f r_2 \times \ln v_2 + f r_1 \times f r_2 \times G_{12}
$$
 [3]

where G_{12} (mm²/s) denotes the interaction parameter of the two components, with all the other symbols having the same meaning as for Equation 2. Equation 3 accounts for the interaction between nonassociated components; therefore, the predicted viscosity from Equation 3 is larger than from Equation 2. The interaction parameter G_{12} is difficult to specify. For these predictions, a weighted kinematic viscosity was used to compute the mean viscosity of the mixture from:

$$
\ln v_{\text{blends}} = w_1 \times f r_1 \times \ln v_1 + w_2 \times f r_2 \times \ln v_2 \tag{4}
$$

where w_1 and w_2 are weight factors and the other symbols are the same as in Equation 2. To account for the effect of the higherviscosity component, biodiesel, in this study, we used $w_1 = 1.08$ for biodiesel and $w_2 = 1.0$ for diesel. These weight factors were determined empirically by comparing the measured and predicted data to achieve the smallest prediction error.

The viscosity–specific gravity relationship and blending model. The following empirical equation, which describes the relationship between the dynamic viscosity and density of vegetable oils, was proposed by Rodenbush *et al.* (11):

$$
\rho = A + \frac{B}{\eta^{1/2}}
$$
 [5]

where ρ and η denote the density (kg/m³) and dynamic viscosity (cP), respectively, and *A* = −513 and *B* = 2405 for vegetable oils. Rodenbush *et al.* (11) reported that the absolute average deviation for 117 data points of 12 types of vegetable oils from Equation 5 was 14.6%. However, this method has never been applied to biodiesel. Equation 5 can be reformulated as Equations 6–9 for application to biodiesel and diesel blends:

$$
SG = A + \frac{B}{v^{1/2}}
$$
 [6]

where SG and ν represent the specific gravity and kinematic viscosity $\text{(mm}^2\text{/s)}$, respectively, of pure biodiesel or diesel fuel, and *A* and *B* are correlation parameters that are dependent on different biodiesel fuels.

For mixtures of biodiesel and diesel, the following equations were applied:

$$
SG_{\text{mix}} = A_{\text{mix}} + \frac{B_{\text{mix}}}{v_{\text{mix}}^{1/2}}
$$
 [7]

$$
A_{\text{mix}} = A_{b100} \times fr_{b100} + A_d \times \text{fr}_d \tag{8}
$$

$$
B_{\text{mix}} = B_{b100} \times fr_{b100} + B_d \times \text{fr}_d \tag{9}
$$

where *A* and *B* have the same meaning as in Equation 6 with subscripts mix, *b*100, and *d* representing the mixture, pure biodiesel, and diesel fuel, respectively. The fraction fr in this method was mass-based for simplicity. The advantage of this method is that it can estimate viscosity based on the specific gravity of the biodiesel, which is usually easier to measure once the correlation parameters *A* and *B* are known.

RESULTS AND DISCUSSION

Measured kinematic viscosities and correlations. The measured kinematic viscosity at temperatures from 20 to 100°C for steps of 20°C for SMEA, SMEB, GMSME, and YGME and their 75, 50, and 25% blends with No. 2 diesel fuel are shown in Table 3.

Table 3 indicates that all the biodiesel fuels have higher viscosities than No. 2 diesel fuel. The lower the blending level was, the lower the viscosities were, as was expected. The two natural soybean oil biodiesel fuels showed similar viscosities, although SMEB was slightly higher. Bearing in mind that the longer-chain FA esters with the same saturation degree and the more saturated FA esters with the same length of hydrocarbon chain typically have higher viscosities (12), the genetically modified soybean oil biodiesel fuel had higher viscosities than the other two soybean oil biodiesel fuels because it was less unsaturated. The yellow grease biodiesel had even higher viscosities than the GMSME, owing to the presence of a greater quantity of highly saturated FA. The higher saturation of YGME had a greater effect on viscosity than its shorter FA chain lengths compared with GMSME.

The Vogel equation (Eq. 1) was used to compute the viscosity as a function of temperature. To determine the Vogel equation parameters *A*, *B*, and *C*, the initial values of these adjustable parameters were calculated based on three data points that yielded the minimum sum of the deviations squared for kinematic viscosity ν in Equation 1. Then *A*, *B*, and *C* were varied from −0.5 to 0.5, −10.0 to 10.0, and −5.0 to 5.0, respectively, relative to the initial values using computational steps of 0.01, 1.0, and 0.1, respectively. These variances were applied to optimize the curve to fit all data points while achieving the least square of deviations. The variance ranges and computational steps were determined from computational results. The computed Vogel equation parameters and the average absolute deviations, AAD%, are shown in Table 4.

It can be seen from Table 4 that the average absolute deviations are less than 0.41%, which indicates that the Vogel equation can represent very closely the relationship between viscosity and temperature. With these parameters, the viscosities of these fuels can be calculated easily at any temperature between 20 and 100°C using Equation 1.

Predicted viscosity from the semilog blending models. The measured kinematic viscosities of the four pure biodiesel fuels and No. 2 diesel were used to calculate the viscosities of their 75, 50, and 25% blends using both Equations 2 and 4. The predicted results are provided in Table 5.

Table 5 shows that the viscosities from Equation 2 are always underpredicted compared with the measured data in Table 3. As we expected, the predicted viscosities from Equation 4 are larger than from Equation 2 and are closer to the measured data. For all 12 blends at temperatures from 20 to 100°C, the

	Kinematic viscosity (mm^2/s)							
20° C	40° C	60° C	80° C	100° C				
6.45	4.10	2.87	2.15	1.68				
5.98	3.78	2.65	1.97	1.54				
5.41	3.41	2.41	1.79	1.40				
4.84	3.11	2.16	1.63	1.26				
7.07	4.41	3.05	2.24	1.76				
6.53	4.07	2.81	2.08	1.62				
5.83	3.60	2.51	1.87	1.46				
4.91	3.10	2.17	1.63	1.28				
7.95	4.87	3.33	2.45	1.88				
6.74	4.18	2.88	2.14	1.66				
5.88	3.66	2.55	1.89	1.47				
4.93	3.11	2.18	1.64	1.28				
8.34	5.02	3.36	2.42	1.86				
7.26	4.41	2.99	2.20	1.68				
6.08	3.72	2.57	1.89	1.46				
5.19	3.23	2.24	1.67	1.31				
3.94	2.56	1.82	1.35	1.09				

TABLE 3 Measured Kinematic Viscosities of Biodiesel, Diesel Fuel, And Blends*^a*

a A commercial grade No. 2 diesel was used to blend with each biodiesel fuel on a mass basis of 75,

50, and 25% biodisel in the blends. For example, SMEA75 signifies a blend of 75% SMEA and 25% No. 2 diesel. For abbreviations see Table 1.

maximum absolute deviation from Equation 2 is 9.4% compared with 5.5% from Equation 4, and the average absolute deviation is 4.5% from Equation 2 and 2.1% from Equation 4. Equation 4 achieved higher accuracy than Equation 2. However, it can be seen that almost all the predicted viscosities from Equation 4 are still less than the measured values except for GMSME25, suggesting that the weight factor for most biodiesel fuels could be larger than 1.08, and for each type of biodiesel, it could be different. This study comprised biodiesel fuels derived from a few key source materials, and the objective was to determine a weight factor that provided the smallest prediction error in its application to all the biodiesel fuels in this study. The analysis of fuel samples from other source ma-

terials will allow this factor to be optimized to achieve even higher prediction accuracy from this method.

Predicted viscosity from the specific gravity. The specific gravities of the samples from 20 to 80°C at steps of 20°C were measured in a previous study (13). These reported data were used to calculate the correlation parameters *A* and *B* of Equation 6 for the pure biodiesel fuels and No. 2 diesel fuel. The correlation parameters and R^2 of Equation 6 and predicted viscosities of the mixtures from Equations 7–9 are shown in Table 6.

It can be seen from Table 6 that the predicted viscosities from this method are close to the measured data. The maximum absolute average deviation for all blends is 9.6%, and the average absolute deviation is 2.7%. The accuracy of this method is

 $a^aAAD%$: average absolute deviation % = (sum of *d*)/*N*, where $d = 100*$ ($|exp - calc|$)/exp, exp = experimental result, calc = calculated result, N = the number of points. For abbreviations see Table 1.

	From Equation 2				From Equation 4					
	20° C	40° C	60° C	80° C	100° C	20° C	40° C	60° C	80° C	100° C
SMEA75	5.71	3.64	2.56	1.92	1.51	5.86	3.71	2.59	1.93	1.51
SMEA50	5.05	3.24	2.28	1.71	1.35	5.33	3.36	2.34	1.73	1.36
SMEA25	4.46	2.88	2.04	1.52	1.22	4.84	3.04	2.11	1.55	1.22
SMEB75	6.11	3.85	2.68	1.97	1.56	6.28	3.92	2.71	1.99	1.56
SMEB50	5.28	3.36	2.35	1.74	1.39	5.58	3.49	2.41	1.76	1.39
SMEB ₂₅	4.56	2.93	2.07	1.54	1.23	4.96	3.10	2.14	1.56	1.24
GMSME75	6.67	4.15	2.86	2.11	1.64	6.86	4.23	2.90	2.13	1.64
GMSME50	5.60	3.53	2.46	1.82	1.43	5.92	3.66	2.52	1.84	1.44
GMSME25	4.70	3.00	2.11	1.57	1.25	5.10	3.18	2.19	1.60	1.26
YGME75	6.92	4.24	2.88	2.09	1.63	7.11	4.32	2.92	2.11	1.63
YGME50	5.74	3.58	2.47	1.81	1.43	6.06	3.72	2.53	1.83	1.43
YGME25	4.76	3.03	2.12	1.57	1.25	5.16	3.20	2.19	1.59	1.25

TABLE 5 Predicted Viscosities (mm²/s) for Biodiesel–Diesel Blends from the Semilog Blending Models^a

a For abbreviations see Table 1.

comparable to Equation 4 and is better than Equation 2.

One potential problem of this method is that we need to find the correlation parameter for every specific biodiesel fuel. However, it can be seen from Table 6 that the two natural soybean oil biodiesel fuels from different producers have very close parameters although they have a 7.6% difference in viscosity at 40°C. Therefore, it should be possible to find general correlation parameters for natural soybean oil biodiesel fuels regardless of the different sources of soybeans, which makes feasible the prediction of the viscosity of natural soybean oil methyl esters based on their specific gravity. More types of biodiesel fuels are needed to optimize the correlation parameters.

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