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Predicting the temperature dependent viscosity of biodiesel fuels

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ABSTRACT

The purpose of this work was to develop a method for predicting temperature dependent viscosities of biodiesel based on fatty acid ester composition. The Grunberg–Nissan equation combined with a group contribution method was used as the mixing rule to calculate viscosities of mixtures of fatty acid esters. Prediction errors at 25 °C were less than 2.5% for 22 mixtures of fatty acid ethyl esters. Compared with experimentally measured viscosities at 20–100 °C, predicted viscosities of soybean oil and yellow grease methyl esters were within 3%. For coconut, palm and canola oil methyl esters, maximum errors were underestimations at approximately 7%.

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1. Introduction

Biodiesel is a fuel composed of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats. It is an oxygenated fuel that is essentially sulfur-free and biodegradable. Biodiesel is also the only alternative fuel that has passed the Environmental Protection Agency (EPA)-required Tier I and Tier II Health Effects testing requirements of the Clean Air Act Amendments of 1990. In addition, biodiesel is a promising alternative to crude oil-derived diesel fuels because it is renewable, significantly reduces particulate matter, hydrocarbon, carbon monoxide and life cycle net carbon dioxide emissions [1,2] from combustion sources,. It also has the potential to relieve the US dependence on foreign crude oil. Because of these advantages, biodiesel has gained considerable attention in recent years. However, engine manufacturers are concerned about biodiesel's higher viscosity compared with diesel fuel because high viscosity could cause excessive fuel injection pressures during engine warm-up [3]. Viscosity is one of the most important factors affecting the in-cylinder fuel atomization process in direct injection diesel engines. Previous research showed that the higher viscosity of biodiesel could increase fuel penetration in the chamber [4], consequently affecting combustion and emissions from the engine. An increased spray tip penetration and a decreased spray cone angle with biodiesel have been verified using in-cylinder measurement techniques [5].

Some researchers have measured viscosity experimentally for some biodiesel fuels [6] and their diesel blends [3]. These measurements, however, are for specific biodiesel fuels. Because there are numerous biodiesel source materials and the composition of each type of material may vary substantially, it is impractical to determine experimentally the viscosity of fuels produced from each material source. A method of predicting viscosity of biodiesel based on its fatty acid ester composition was first studied by Allen et al. [7], who measured viscosities of some pure fatty acid esters and applied a mixing rule to predict viscosities of biodiesel fuels based on their component composition. This method was reasonably accurate but only applicable to the viscosity at 40 °C. In addition, the viscosities of esters of fatty acids with more than 18 carbon atoms were simplified to be the same as with 18 carbon atoms (C18). This simplification limits application of this method to certain types of biodiesel fuels and excludes fuels that have a high percentage of fatty acids with more than 18 carbon atoms, such as rapeseed oil-derived biodiesel.

Correlative and predictive methods for viscosities have been intensively reviewed by Reid et al. [8] and Monnery et al. [9]. Among these methods, the Vogel [10] equation, Eq. (1), and the van Velzen method [11], Eq. (2), have been widely used in the oil industry to describe the viscosity-temperature relationship:

$$\ln \eta = A + \frac{B}{T + C} \tag{1}$$

$$\log \eta = B\left(\frac{1}{T} - \frac{1}{T_o}\right) \tag{2}$$

In the above equations, η (mPa s) represents the dynamic viscosity of the liquid at temperature T (K). For Eq. (1), A, B, and C are correlation parameters, which can be determined from viscosity measurement at three or more temperatures. For Eq. (2), B and T_o are determined by group contributions on the basis of empirical data

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[11]. Both methods were extensively studied and reported for pure components [8,10,11] but had limited application for fatty acid esters or biodiesel fuels. Considering that experimental data of viscosities of pure fatty acid esters are available, the Vogel equation was regarded as more accurate and simpler to use than the van Velzen method. Therefore, the Vogel equation with some published viscosity data was employed in this study for biodiesel viscosity prediction.

The objectives of this study were to (1) apply the Vogel equation to describe the viscosity-temperature relationship of pure fatty acid methyl esters (FAME) commonly present in biodiesel fuels and (2) estimate the temperature dependent viscosity of some actual biodiesel fuels based on their FAME composition. These objectives were accomplished by correlating or predicting the temperature dependent viscosity of individual FAME and applying appropriate mixing rules for the methyl ester mixtures.

2. Methods

A correlation method is presented in Section 2.1 to estimate the viscosity of individual FAMEs. The mixing rule is introduced in Section 2.2 and the experimental procedure is discussed in Section 2.3.

2.1. Viscosity of individual fatty acid methyl esters

Published dynamic viscosity data are limited, but kinematic viscosities and densities of methyl esters of fatty acids with less than 20 carbon atoms at low temperatures (20–100 °C) are well documented. Table 1 shows some of the published data.

Densities of pure FAME are required for converting kinematic viscosities to dynamic viscosities. No published data of densities were available for C18:3. However, density-temperature lines of C18:0, C18:1 and C18:2 were observed to be parallel with almost the same displacement of about 0.015 g/ml. Therefore, densities of C18:3 at 20 °C and 37.8 °C were estimated from densities of C18:2 at those temperatures plus 0.015 g/ml. This displacement of 0.015 g/ml was replaced by −0.015, 0, 0.03, and 0.045 g/ml, respectively, in the sensitivity study to determine the effect of the density estimations for C18:3 on viscosity predictions. We believe the corresponding densities at those settings can cover the real density of C18:3 (e.g., the density range investigated in the sensitivity was between 0.875 and 0.935 g/ml at 20 °C). Viscosities of five biodiesel fuels at 20, 40, 60, 80, and 100 °C were predicted at each setting. The Rackett method as modified by Spencer and Danner was recommended for density prediction or correlation of pure hydrocarbons and pure organic liquids [11]. However, this method requires the critical temperature and pressure of the liquid and also an experimentally regressed parameter, which are unknown for fatty acid methyl esters. Therefore, based on the data in Table 1 and estimated densities for C18:3 at 20 °C and 45 °C, a linear correlation method was used to calculate the densities. The correlation equation was formulated as:

$$\rho = mT + b \tag{3}$$

where ρ and T denote density (g/ml) and temperature (K), respectively, and m and b are correlation coefficients. The linear relationship between density and temperature of biodiesel and their diesel fuel blends in the low temperature range has proved sufficiently accurate for combustion modeling [15,16].

The dynamic or kinematic viscosities of methyl esters of C20:0, C22:0 and C24:0 that are also present in some types of biodiesel fuels were not found in any publications. A second order polynomial correlation was extrapolated to estimate dynamic viscosities of these FAME based on the dynamic viscosity calculated for C8:0 to C18:0. For unsaturated FAME, kinematic viscosities of C22:1 were available [13], but densities were not known. Also, viscosities of C20:1 were not available. Therefore, viscosities of C20:1 and C22:1 were estimated based on the assumption that the increase of one double bond would have a similar effect on the viscosity among C18:1/C18:0, C20:1/C20:0 and C22:1/C22:1. The procedure for calculating the viscosity of C20:1 and C22:1 was, first, to determine the relative difference of dynamic viscosity (η_d) of C18:1 ($\eta_{18:0}$) and C18:0 ($\eta_{18:1}$) at a given temperature with the following equation:

$$\eta_d = \frac{\eta_{18:1} - \eta_{18:0}}{\eta_{18:0}} \tag{4}$$

Then, this difference was applied to C16:1/C16:0, C20:1/C20:0 and C22:1/C22:0 at the same temperatures to calculate the viscosities of C16:1, C20:1 and C22:1 from C16:0, C20:0 and C22:0, respectively. In order to determine the effect of the viscosity estimations for C16:1, C20:1 and C22:1 on biodiesel viscosity predictions, η_d was multiplied by −2, −1, 0, and 2, respectively, in the sensitivity study. We believe the corresponding viscosities at those settings can cover the real viscosity of C16:1, C20:1 and C22:1 (e.g., the viscosity range of C20:1 investigated in the sensitivity study was between 3.69 and 8.43 mPa s at 40 °C). Viscosities of five biodiesel fuels at 20, 40, 60, 80 and 100 °C were predicted at each setting. The calculated dynamic viscosities were combined with other reported dynamic viscosity values [7,14] to correlate dynamic viscosity with temperature as described below.

Table 1
Reported kinematic viscosity and density of some methyl esters at various temperatures [12–14].

	Temperature (°C)											
	20	37.8	40	60	70	98.9	20	37.8	60	75	80	98.9
FAME[c]	Kinematic viscosity (mm^2/s)						Density (g/ml)					
C8:0	1.590	1.207	1.16	0.911	0.819	0.618	0.8775	0.8615	0.8420	0.8287	0.8240	0.8089
C10:0	2.437	1.765	1.69	1.276	1.13	0.826	0.8730	0.8581	0.8399	0.8271	0.8230	0.8068
C12:0	3.540	2.487	2.28	1.732	1.5	1.072	0.8695	0.8553	0.8376	0.8259	0.8220	0.8068
C14:0	5.201	3.456	3.23	2.323	1.95	1.36	0.8671	0.8534	0.8361	0.8252	0.8210	0.8068
C16:0		4.688	4.32	2.998	2.5	1.703		0.8520	0.8354	0.8247	0.8200	0.807
C18:0		5.881	5.61	3.666	3.11	2.004		0.8524	0.8363	0.8244	0.8210	0.8079
C18:1	7.23		4.45		2.60		0.875[a]	0.860[b]				
C18:2	5.58		3.64		2.25		0.890[a]	0.875[b]				
C18:3	4.84		3.27		2.09							
C22:1	12.50		7.21		3.92							

[a] At 25 °C.
[b] At 45 °C.
[c] The names of the fatty acids are: C8:0 – caprylic acid; C10:0 – capric acid; C12:0 – lauric acid; C14:0 – myristic acid; C16:0 – palmitic acid; C18:0 – stearic acid; C18:1 – oleic acid; C18:2 – linoleic acid; C18:3 – linolenic acid; C22:1 – erucic acid.

The Vogel equation was used to compute dynamic viscosity as a function of temperature. To determine the Vogel equation parameters A, B, and C, initial values of these adjustable parameters were calculated based on three data points that yielded the minimum sum of the deviations squared for dynamic viscosity η in Eq. (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. Variance ranges and computational steps were determined from computational results. When only two data points were available (for C16:1, C20:1 and C22:1), the Vogel equation was simplified to the Andrade equation described by Reid et al. [7] by setting constant C to 0. The Andrade equation is also widely used for describing the viscosity-temperature relationships of liquids [8,17,18]. On the other hand, the concentrations of C16:1, C20:1 and C22:1 in biodiesel fuels are typically very low, therefore, the errors caused by this simplification are expected to be negligible.

2.2. Mixing rule for fatty acid esters

The Grunberg–Nissan equation was evaluated by Reid et al. [8] and Monnery et al. [9]. It was selected as the most suitable equation for computing viscosity of liquid mixtures. The Grunberg–Nissan equation is:

$$\ln \eta_m = \sum_{i=1}^{n} x_i \ln \eta_i + \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1, j\neq i}^{n} x_i x_j G_{ij} \quad (5)$$

where η_m is the liquid mixture viscosity (mPa s), η_i is the viscosity of the ith component (mPa s), x_i and x_j are the molar fractions of the ith and jth components, G_{ij} is the interaction parameter (mPa s), and n is the number of pure components in the mixture. Although biodiesel fuels are non-associated liquids that are composed of mixtures of fatty acid esters with similar structures, interactions among the esters do exist. Our observations showed that when the interaction parameter G_{ij} was neglected, mixture viscosity was always underestimated (see Section 3.2). In this study, G_{ij} was computed by the group contribution method proposed by Isdale et al. [19]. Two modifications were made to apply this method to fatty acid esters as detailed below.

First, in the original method, the component i was determined from a binary mixture of i and j by finding (a) the component with the most carbon atoms, otherwise, (b) the component with the most hydrogen atoms. Once i was determined, the other component was then j. In the mixture of fatty acid esters, for any binary combination of i and j, the only difference of contribution between them is the number of CH_2 groups. However, this priority rule cannot account for components with different carbon numbers and different numbers of double bonds, such as the binary mixtures of C16:0/C18:1 and C18:0/C20:1. For the binary mixture of C16:0/C18:1, C18:1 has the priority with the most carbon atoms, so it is component i. However, when we calculate the contribution, we find that they have exactly the same number of CH_2 groups, so no interaction is taken into account (G_{ij} = 0). Considering that the increase of one double bond causes a decrease of two CH_2 groups, we added double bonds as an independent group into the group contribution table, specifying that one double bond had the same effect as two CH_2 groups. The improvement of this modification on mixture viscosity prediction is discussed in Sections 3.2 and 3.3.

The second modification to the group contribution method was the change of the contribution value of the CH_2 group. The original contribution value for CH_2 of 0.096 used by Isdale et al. [19] was changed to 0.014 based on our observation and experience.

2.3. Experimental procedure

Viscosities of five biodiesel fuels were measured from 20–100 °C in steps of 20 °C and compared with predicted results. One sample was a commercially available soybean oil methyl ester (SME) obtained from Growmark Inc. (Bloomington, IL). Another sample was a yellow grease methyl ester (YGME) provided by Drs. Tat and Van Gerpen at the Iowa State University, Ames, Iowa. The other three samples – a canola oil methyl ester (CME), a palm oil methyl ester (PME) and a coconut oil methyl ester (CCME) – were made in our laboratory at the Kansas State University through a base catalyzed transesterification process. The canola oil used was a commercial food-grade oil, and the virgin palm and coconut oils were obtained from Safari Group Inc. (Buffalo, NY).

Cannon-Fenske type glass capillary viscometers were used to measure kinematic viscosity of the samples following the ASTM Standard D-445 [20]. To obtain kinematic viscosity in mm^2/s by

Table 2
Vogel equation constants (A, B, C) for dynamic viscosity (mPa s) and correlation coefficients (m, b) for density (g/ml) for pure FAME that are commonly present in biodiesel fuels.

	Viscosity				Density		
Esters[d]	A	B	C	AAD (%)[b]	m	b	R^2
C8:0	−3.742	954.946	−58.467	0.35	−8.7487E-04	1.1336	0.9996
C10:0	−3.069	697.193	−110.849	0.28	−8.3722E-04	1.1185	0.9999
C12:0	−3.050	748.201	−113.832	0.77	−7.9320E-04	1.1020	1.0
C14:0	−2.851	709.099	−130.364	0.76	−7.6414E-04	1.0910	0.9999
C16:0	−2.150	507.905	−167.220	0.60	−7.3929E-04	1.0818	0.9994
C16:1	−4.873	1865.661	0[a]	0[a]			
C18:0	−3.503	1091.641	−97.640	0.51	−7.3373E-04	1.0804	0.9993
C18:1	−2.380	627.236	−144.840	0[c]	−7.3373E-04	1.0938	1.0[a]
C18:2	−2.373	633.578	−133.942	0[c]	−7.3373E-04	1.1088	1.0[a]
C18:3	−2.380	652.309	−124.223	0[c]	−7.3373E-04	1.1238	1.0[a]
C20:0	−3.120	968.259	−116.405	0[c]			
C20:1	−5.283	2150.104	0[a]	0[a]			
C22:0	−3.331	1096.881	−108.071	0[c]			
C22:1	−5.788	2387.303	0[a]	0[a]			
C24:0	−3.717	1316.593	−91.202	0[c]			

[a] Only two data points were available.
[b] AAD%: average absolute deviation% = (sum of d)/N, where d = (|exp − calc|)/exp*100, N = the number of points, applicable to all other AAD% in calculations.
[c] Only three data points were available.
[d] The name of the fatty acids that are not listed in Table 1 are: C16:1 – palmitonic acid; C20:0 – arachidic acid; C22:0 –behenatic acid; C20:1 – gadoleatic acid; C24:0 – lignoceratic acid.

capillary viscometer, efflux time in seconds was multiplied by the viscometer constant specified by the manufacturer at 40 °C and 100 °C and could be interpolated or extrapolated to other temperatures. To calculate dynamic viscosity from kinematic viscosity, specific gravities of these fuels (data not shown) were also measured by soft glass API gravity hydrometers (Fisher Scientific Co., Pittsburgh, PA) following the ASTM D1298-99e2 [21]. A Brookfield EX-200 water bath (Middleboro, Massachusetts) was used for temperature control at ±0.01 °C.

3. Results and discussion

3.1. Viscosity of individual FAMEs

Viscosities of FAME commonly present in biodiesel fuels were correlated to temperatures by the Vogel equation. The Vogel equation constants in Eq. (1) for dynamic viscosity and the correlation coefficients in Eq. (3) for density are given in Table 2.

Table 2 shows that the maximum average absolute deviation (AAD) of correlated dynamic viscosities for the methyl esters is 0.77%, indicating the Vogel equation closely represents the relationship between dynamic viscosity and temperature of the methyl esters. The minimum correlation coefficient R^2 for density is 0.9993, which means the densities of methyl esters are linearly related to temperatures as described by Eq. (3).

3.2. Viscosity of ethyl ester mixtures

Viscosities of the binary, ternary and quaternary mixtures of the ethyl esters of C8:0, C10:0, C12:0 and C18:1 at 25 °C were reported by Allen et al. [7]. These values were compared with predicted results to verify the mixing rule. Comparisons are shown in Table 3.

Results predicted using the mixing rule presented in Section 2.2 is in close agreement with the measured data (Table 3). The maximum prediction error is less than 2.5% when the interaction parameters are included. Comparisons of results from the mixing rule with and without interactions showed that when interactions

Table 3
Viscosities of binary, ternary and quaternary mixtures of fatty acid ethyl esters at 25 °C.

Sample #	Mass fraction				Viscosity at 25 °C (mPa s)			
					Measured	Predicted (% error)[a]	Predicted (% error)[b]	Predicted (% error)[c]
	C18:1	C12:0	C10:0	C8:0				
1	1				5.5			
2		1			2.88			
3			1		1.99			
4				1	1.37			
5			0.52	0.48	1.67	1.66 (−0.60)	1.64 (−1.80)	1.66 (−0.6)
6		0.5		0.5	1.91	1.98 (3.66)	1.89 (−1.05)	1.92 (0.52)
7		0.5	0.5		2.39	2.39 (0)	2.37 (−0.84)	2.39 (0)
8			0.25	0.75	1.51	1.5 (−0.66)	1.49 (−1.33)	1.5 (−0.66)
9			0.75	0.25	1.82	1.81 (−0.55)	1.79 (−1.65)	1.81 (−0.55)
10		0.25		0.75	1.62	1.65 (1.85)	1.59 (−1.85)	1.61 (−0.62)
11		0.75		0.25	2.32	2.39 (3.02)	2.29 (−1.29)	2.33 (0.43)
12		0.25	0.75		2.19	2.19 (0)	2.16 (−1.37)	2.18 (−0.46)
13		0.74	0.26		2.62	2.62 (0)	2.59 (−1.15)	2.61 (−0.38)
14		0.34	0.33	0.33	1.94	1.99 (2.58)	1.93 (−0.52)	1.98 (2.06)
15		0.25	0.25	0.5	1.77	1.81 (2.26)	1.75 (−1.13)	1.79 (1.13)
16		0.19	0.54	0.27	1.91	1.93 (1.05)	1.88 (−1.57)	1.92 (0.52)
17		0.5	0.25	0.25	2.12	2.18 (2.83)	2.1 (−0.94)	2.16 (1.89)
18	0.25	0.25	0.25	0.25	2.51	2.57 (2.39)	2.31 (−7.97)	2.47 (−1.59)
19	0.52	0.16	0.16	0.16	3.31	3.38 (2.11)	2.95 (−10.88)	3.25 (−1.81)
20	0.16	0.52	0.16	0.16	2.62	2.67 (1.91)	2.49 (−4.96)	2.62 (0)
21	0.16	0.16	0.52	0.16	2.32	2.35 (1.29)	2.18 (−6.03)	2.29 (−1.29)
22	0.16	0.16	0.16	0.52	2.01	2.06 (2.49)	1.86 (−7.46)	1.96 (−2.49)

[a] Predicted results from Allen et al. [7] % error = (predicted value-measured value)/measured value*100, applicable to all other% error in calculations.
[b] Predicted from Eq. (5) without considering interactions ($G_{ij} = 0$).
[c] Predicted from Eq. (5) combined with modified group contribution method presented in Section 2.2.

Table 4
Relative weight composition of fatty acid methyl ester of nine biodiesel fuels.

	SME	SME-A	YGME	CCME	CCME-A	PME	PME-A	CME	CME-A
C8:0	0.0002	0	0	0.092[a]	0.075	0	0	0	0
C10:0	0	0	0	0.064	0.060	0	0	0	0
C12:0	0	0	0	0.487	0.533	0	0.004	0	0
C14:0	0.0008	0	0.0170	0.170	0.171	0	0.013	0	0
C16:0	0.1049	0.058	0.1947	0.077	0.073	0.406	0.481	0.042	0.042
C16:1	0.0012	0.008	0	0	0	0	0.003	0	0.004
C18:0	0.0427	0.016	0.1438	0.022	0.019	0.051	0.04	0.017	0.02
C18:1	0.2420	0.6	0.5467	0.054	0.055	0.428	0.373	0.568	0.574
C18:2	0.5136	0.199	0.0796	0.022	0.014	0.110	0.080	0.217	0.213
C18:3	0.0748	0.096	0.0069	0	0	0.005	0.002	0.157	0.112
C20:0	0.0036	0.007	0.0025	0	0	0	0.003	0	0.012
C20:1	0.0028	0.016	0.0052	0	0	0	0.001	0	0.021
C22:0	0.0040	0	0.0021	0	0	0	0	0	0.001
C22:1	0.0007	0	0	0	0	0	0	0	0
C24:0	0.0014	0	0	0	0	0	0	0	0

[a] Include 1.1% C6:0.

are not considered, predicted results are always underestimated. For samples 18 to 22 that include C18:1, errors are relatively large without considering the interactions. This is because C18:1 has many more carbon atoms than the other components; therefore, its interaction effect on the viscosity cannot be neglected. Because the effect of interaction is the greatest for sample 19, which has the highest percentage of C18:1, the error without considering this interaction is the largest. This result follows the principles in the mixing rule that interactions between components do exist and cannot be ignored, especially when carbon numbers of components vary significantly. Allen et al. [7] used the mass fraction instead of the molar fraction of the components to calculate mixture viscosity, which overestimates the effect of the components with higher molecular weights. Because fatty acid esters with higher molecular weights normally have higher viscosities, the viscosities predicted with the method of Allen et al. [7] are higher than the measured data for most samples. The effect of interaction can also be seen in the Allen et al. [7] method. For samples 6 and 19, prediction errors are large because differences in carbon numbers are significant.

The effect of double bonds on viscosities can be seen from the comparisons. For samples 18 to 22, C18:1 appears in the mixture. If the effect of the double bond is not considered, predicted viscosities are underestimated further. As discussed in Section 2.2, this effect will be greater if the mixture has more C16:0/C18:1 or C18:0/C20:1 groups.

3.3. Viscosity of biodiesel fuels

Viscosities of nine actual biodiesel fuels were predicted. The FAME compositions of these fuels are listed in Table 4. Composition of SME was analyzed at Woodson–Tenent Laboratories (Des Moines, IA). The YGME composition was provided by Drs. Tat and Van Gerpen at Iowa State University, Ames, IA. The CCME, PME and CME were analyzed by American Analytical Chemistry Laboratories (Champaign, IL). Fatty acid profiles of SME-A (soybean methyl ester), CCME-A (coconut oil methyl ester), PME-A (palm oil methyl ester) and CME-A (canola oil methyl ester) were reported by Allen et al. [7].

Predicted viscosities of these seven biodiesel fuels were correlated with temperature using the Vogel equation. Vogel equation constants are listed in Table 5. The AAD based on nine data points from 20 to 100 °C are almost zero, which indicates that the predicted viscosity-temperature relationship of biodiesel fuels follows the Vogel equation closely. Using these constants, viscosities of these fuels at a given temperature can be easily calculated.

Predicted viscosities of SME, YGME, CCME, PME and CME were compared with measured values from 20 to 100 °C (Table 6). Predicted values for SME and YGME are in close agreement with the measured data, with prediction errors of less than 3% in the temperature range of 20–100 °C. However, for the other three biodiesel fuels, maximum errors were underestimations of around 7.2% at 20 °C.

Table 5
Vogel equation constants of biodiesel fuels.

Fuel	A	B	C	AAD (%)
SME	−2.36068	633.36971	−138.93663	0.004
SME-A	−2.40090	640.98345	−140.07045	0.004
YGME	−2.45982	663.47653	−140.63377	0.010
CCME	−2.97941	750.58798	−113.94236	0.034
CCME-A	−2.89808	720.31377	−118.713701	0.005
PME	−2.28046	582.22917	−153.29997	0.054
PME-A	−2.24381	575.59185	−154.24726	0.006
CME	−2.35359	621.69779	−141.59977	0.117
CME-A	−2.41542	648.45888	−138.68064	0.005

Table 6
Comparison of predicted and measured viscosities (mPa s) of biodiesel fuels from 20 to 100 °C.

Fuel	20 °C	40 °C	60 °C	80 °C	100 °C
SME-measured	5.73	3.56	2.43	1.80	1.38
SME-predicted	5.74	3.58	2.46	1.82	1.41
% error	0	0.57	1.45	1.16	2.54
YGME-measured	7.10	4.31	2.83	2.00	1.51
YGME-predicted	6.71	4.03	2. 70	1.95	1.49
% error	−1.83	−3.02	−1.06	1.00	2.65
CCME-measured	3.61	2.35	1.63	1.18	0.90
CCME-predicted	3.39	2.22	1.57	1.18	0.92
% error	−7.20	−6.38	−4.07	−0.43	1.95
PME-measured	7.03	4.17	2.73	1.91	1.41
PME-predicted	6.52	3.88	2.59	1.88	1.44
% error	−7.25	−6.90	−5.21	−1.76	2.30
CME-measured	6.19	3.81	2.56	1.81	1.35
CME-predicted	5.75	3.56	2.44	1.80	1.39
% error	−7.11	−6.55	−4.52	−0.80	3.04

Viscosities of SME-A, CCME-A, PME-A and CME-A were reported by Allen et al. [7] and were available only at 40 °C. Comparisons of predicted results and reported data are shown in Table 7.

It can be calculated from Table 6 that the average absolute prediction error of viscosities for these four biodiesel fuels is 1.78%. The CCME-A viscosity was underestimated by 3.45%. Allen et al. [7] measured purities of these four biodiesel fuels using thin layer chromatography-flame ionization detector and found that the CCME-A had only 95% methyl esters with the remaining 5% being one or a combination of mono-glycerides, di-glycerides, sterols or polar lipids. These impurities were attributed to the increased viscosity of biodiesel fuels [7], which, consequently, increased the prediction error. The other three biodiesel fuels contained more than 98% methyl esters, and the prediction errors were relatively smaller. As can be seen from Table 6, the pattern of prediction errors shows that viscosities of CCME, PME and CME between 20–80 °C were also all underestimated, suggesting a similar impurity problem as found for CCME-A. Although CME, PME and CCME have similar fatty acid profiles as CME-A, PME-A and CCME-A (Table 4), respectively, our measured viscosities of CME (3.81 mPa s at 40 °C) and PME (4.17 mPa s at 40 °C) were much higher than those reported by Allen et al. [7] (3.7 and 3.87 mPa s at 40 °C for CME-A and PME-A, respectively). Our measured viscosity of CCME at 40 °C (2.35 mPa s) was close to that reported by Allen et al. [7] (2.32 mPa s) for CCME-A, which had 5% impurities. It is likely that a certain amount of mono- glycerides, di-glycerides, sterols or polar lipids presented in these samples, which boosted the viscosities of these fuels and caused higher prediction errors.

3.4. Sensitivity analysis

A sensitivity study was carried out to determine the effect of density estimations for C18:3 and viscosity estimations for C16:1, C20:1 and C22:1 on biodiesel viscosity predictions as men-

Table 7
Comparison of predicted and reported viscosities of biodiesel fuels at 40 °C (mPa s).

Fuel	Reported	Predicted (% error)[a]	Predicted (% error)[b]	Predicted (% error)[c]
SME-A	3.67	3.62 (−1.36)	3.63 (−1.09)	3.68 (0.27)
CCME-A	2.32	2.19 (−5.60)	2.09 (−7.93)	2.24 (−3.45)
PME-A	3.87	3.76 (−2.84)	3.75 (−3.1)	3.97 (2.58)
CME-A	3.7	3.61 (−2.43)	3.63 (−1.89)	3.67 (−0.81)

[a] Predicted results from Allen et al. [7].
[b] Predicted from Eq. (5) without considering interactions ($G_{ij} = 0$).
[c] Predicted from Eq. (5) combined with modified group contribution method presented in Section 2.2.

tioned previously. In the case of C18:3 as can be seen from Table 8, the effect on YGME and PME was not noticeable because C18:3 concentrations in these fuels are very low. CCME was not listed because it does not contain C18:3. The effects on SME and CME were detectable, but were minimal and negligible.

In order to determine the effect of the viscosity estimations of C16:1, C20:1 and C22:1 on viscosity predictions, η_d in Eq. (4) was multiplied by −2, −1, 0, and 2 in the sensitivity study as mentioned previously. Since CME, CCME and PME do not contain C16:1, C20:1 or C22:1, the estimations had no effect on their viscosities. For SME and YGME, the effects are negligible as can be seen from Table 9.

The sensitivity analysis indicated that the effect on biodiesel viscosities of the density estimations for C18:3 and the viscosity estimations for C16:1, C20:1 and C22:1 are negligible, mainly because the concentrations of these components in biodiesel fuels are relatively low.

Although only nine actual biodiesel fuels were tested, the method presented in this study can be extended to any type of methyl ester biodiesel fuel with known ester composition. The applicable temperature of this method can be extended up to the reduced temperature of 0.7 of the fuels because of the limitation of the Vogel equation [8]. Below 20 °C, this method should be used with caution when the temperature is reduced down to the cloud point of the fuel, depending on the components.

Table 8
The effect of density uncertainty of C18:3 on biodiesel viscosity predictions.

Fuel	Density adjustment (g/ml)	Predicted viscosity (mPa s)				
		20 °C	40 °C	60 °C	80 °C	100 °C
SME	−0.015	5.73	3.57	2.46	1.81	1.41
	0	5.73	3.58	2.46	1.81	1.41
	0.015	5.74	3.58	2.46	1.82	1.41
	0.03	5.75	3.59	2.47	1.82	1.41
	0.045	5.76	3.60	2.47	1.82	1.41
YGME	−0.015	6.71	4.03	2.70	1.95	1.49
	0	6.71	4.03	2.70	1.95	1.49
	0.015	6.71	4.03	2. 70	1.95	1.49
	0.03	6.71	4.03	2.70	1.95	1.49
	0.045	6.71	4.03	2.70	1.95	1.49
PME	−0.015	6.52	3.88	2.59	1.88	1.44
	0	6.52	3.88	2.59	1.88	1.44
	0.015	6.52	3.88	2.59	1.88	1.44
	0.03	6.52	3.88	2.59	1.88	1.44
	0.045	6.52	3.88	2.59	1.88	1.44
CME	−0.015	5.71	3.54	2.43	1.79	1.38
	0	5.73	3.55	2.43	1.79	1.39
	0.015	5.75	3.56	2.44	1.80	1.39
	0.03	5.76	3.57	2.45	1.80	1.40
	0.045	5.77	3.58	2.46	1.80	1.40

Table 9
The effect of viscosity uncertainty of C16:1, C20:1 and C22:1 on biodiesel viscosity predictions.

Fuel	η_d adjustment	Predicted viscosity (mPa s)				
		20 °C	40 °C	60 °C	80 °C	100 °C
SME	−2	5.75	3.59	2.47	1.82	1.41
	−1	5.73	3.59	2.47	1.82	1.41
	0	5.75	3.58	2.46	1.82	1.41
	1	5.74	3.58	2.46	1.82	1.41
	2	5.73	3.58	2.46	1.81	1.41
YGME	−2	6.74	4.04	2.71	1.95	1.49
	−1	6.73	4.04	2.70	1.95	1.49
	0	6.72	4.04	2.70	1.95	1.49
	1	6.71	4.03	2. 70	1.95	1.49
	2	6.70	4.03	2.69	1.95	1.49

4. Conclusions

1. Vogel equation constants for dynamic viscosity and correlation coefficients for density applied to pure fatty acid methyl esters that are commonly present in biodiesel fuels were determined. The maximum average absolute deviation of correlated dynamic viscosities for the methyl esters was 0.77%, indicating that the Vogel equation closely represented the relationship between dynamic viscosity and temperature of the methyl esters. The minimum correlation coefficient R^2 for density was 0.9993, which confirmed that the densities of methyl esters were linearly related to temperature.
2. The Grunberg-Nissan equation was used as the mixing rule to calculate the mixture viscosity of biodiesel fuels. Two modifications were made to the group contribution method to calculate the interactions between individual components. The modified method was used to predict viscosities of binary, ternary and quaternary mixtures of the ethyl esters of C8:0, C10:0, C12:0 and C18:1 at 25 °C, and prediction errors were less than 2.5%.
3. Viscosities of nine biodiesel fuels were predicted. Compared with experimentally measured viscosities in the range of 20–100 °C, predicted viscosities of a soybean oil methyl ester and yellow grease methyl ester were within 3% of the measured data. For coconut oil, palm oil and canola oil methyl esters, maximum errors were underestimated at around 7.2% for a temperature of 20 °C. The density estimations for C18:3 and viscosity estimations for C16:1, C20:1 and C22:1 were found to have no significant effect on biodiesel viscosity predictions based on the sensitivity study performed.
4. The method presented in this study accounts for a broad range of both saturated and unsaturated esters with varying carbon chain lengths, and therefore it can be extended to any type of methyl ester biodiesel fuel with known ester composition. However, impurities were not considered in the model developed in this study since the model was for mixtures of fatty acid methyl esters only. If the biodiesel samples contained large amount of impurities, for example above 5%, the model would have generated higher prediction errors.

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