

Densities of Ethyl Esters Produced from Different Vegetable Oils

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Biodiesel density data as a function of temperature is needed to model the combustion process. In this work, the densities of ethyl ester biodiesel obtained from various vegetable oils were measured at various temperatures from (15 to 90) °C. The data obtained were used to validate the method proposed by Spencer and Danner using a modified Rackett equation. The experimental and estimated density values using the modified Rackett equation gave almost identical values with deviations less than (0.21, 0.35, 0.22, 0.15, and 0.24) % for the ethyl esters of palm, soybean, canola, corn, and ricebran oil, respectively. Simple linear equations for density of various vegetable oil ethyl ester biodiesels are also proposed in this work.

Introduction

Biodiesel is a renewable fuel produced from biological oils and fats, which has many characteristics of a promising alternative energy resource. It has properties similar to ordinary diesel fuel made from crude oil and can be used in conventional diesel engines. The most common process for making biodiesel is known as transesterification. This process involves combining any natural oil (vegetable or animal) with alcohol and a catalyst.

Among the applicable oils, virgin vegetable oils and waste vegetable oils are most frequently used in the biodiesel production. Rapeseed, soybean, and palm oils are most commonly used to produce biodiesel, though other crops such as corn, mustard, hemp, jatropha, ricebran, and even algae show great potential as a source of raw materials.

The alcohols that can be used in the transesterification reaction are methanol, ethanol, propanol, butanol, and amyl alcohol. However, methanol and ethanol are used most frequently. Ethanol is preferable because it is derived from agricultural products and is renewable and biologically less objectionable to the environment. Ethanol also has better solvent properties and in the case of ethanolysis mass transfer limitation is less, but the formation of emulsion with oil makes separation of ester very difficult. Engine tests demonstrated that ethyl ester biodiesel has significantly less smoke opacity and exhaust temperature.

Density data are important in numerous chemical engineering unit operations. Biodiesel density data as a function of temperature are needed to model the combustion processes and other applications.

The density of an ethyl ester biodiesel depends on its molecular weight, free fatty acid content, water content, and temperature. As vegetable oil based biodiesel is getting popular as a fuel, a procedure for correcting measured density data will be needed. Results of measurements and predictions of specific biodiesel properties have been reported recently, but ethyl ester biodiesel density measurements and predictions were rarely done. Demirbas¹ prepared density data for the ethyl esters of vegetable oils produced by the noncatalytic supercritical ethanol method. The mathematical relationships were also derived for several properties. In another work, Demirbas² studied the density of ethyl esters obtained from cottonseed oil through transesterification using noncatalytic supercritical fluid.

Densities of fatty acids and biodiesel as a function of temperature were obtained by Liew et al.,³ Tate et al.,⁴ Tat and Van Garpen,⁵ and Nouredini et al.⁶ Yuan et al.⁷ predicted density of biodiesel using the modified Rackett equation. The density of palm oil methyl ester biodiesel was measured and predicted by Baroutian et al.⁸ Benjumea et al.⁹ studied the density of palm oil methyl ester–diesel blends. Demirbas¹⁰ studied the relationship between density and other physical properties of various biodiesel fuels. The density of rapeseed oil methyl esters was measured by Dzida and Prusakiewicz.¹¹ Aparicio et al.¹² determined the rapeseed oil methyl ester density in high pressure.

The specific objective of the research presented in this article was to measure the densities of ethyl ester biodiesel obtained from various vegetable oils as a function of temperature and describe a method of estimating the density based on the chemical composition and structure.

Experimental

Materials. Palm, soybean, canola, corn, and ricebran oil were purchased locally, and absolute ethanol was obtained from Sigma-Aldrich, Malaysia. Pure potassium hydroxide was used as a catalyst and obtained from Sigma-Aldrich, Malaysia. Reference standards such as ethyl oleate, ethyl palmitate, ethyl linoleate, and ethyl stearate of > 99 % purity were supplied from Sigma-Aldrich, Malaysia.

Ethyl Ester Preparation. Transesterification reactions were performed in a batch reactor. The reaction setup included a 0.5 L jacketed glass vessel equipped with a thermometer and water-cooled condenser. A mechanical stirrer (Kika Werke) fitted with a stainless steel propeller provided the mixing requirement. Reaction temperatures were prepared and controlled by hot water circulation using an RCS and RC6 (LAUDA). The reactor was filled with 125 g of oil. The catalyst, potassium hydroxide (1 %), was dissolved in ethanol and then added to the reactor at the reaction temperature of 50 °C. Agitation was set at a constant speed (1000 rpm) throughout the experiment. The reaction was carried out using 100 % excess ethanol; i.e., the molar ratio of ethanol to oil is 6:1. The mass of 1 mol of oil was determined from the calculated average molecular weight of oil based on the known fatty acid composition of the oil. After the end of the reaction, the mixture was cooled to room

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Table 1. Fatty Acid Mole Fraction x of Vegetable Oil Ethyl Esters

	palm	soybean	canola	corn	ricebran
fatty acid ethyl ester	x	x	x	x	x
C 16:0	0.47	0.14	0.06	0.11	0.19
C 18:0	0.04	0.05	0.02	0.03	0.05
C 18:1	0.38	0.25	0.71	0.29	0.32
C 18:2	0.11	0.56	0.21	0.57	0.44

Table 2. Measured Density ρ of Vegetable Oil Ethyl Esters

	palm	soybean	canola	corn	ricebran
$t/^\circ\text{C}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\rho/\text{g}\cdot\text{cm}^{-3}$
15	0.87380	0.88270	0.88111	0.88162	0.88174
20	0.87004	0.87891	0.87743	0.87817	0.87812
25	0.86642	0.87508	0.87377	0.87489	0.87449
30	0.86276	0.87137	0.87014	0.87134	0.87086
35	0.85907	0.86772	0.86647	0.86774	0.86724
40	0.85527	0.86410	0.86284	0.86409	0.86362
45	0.85158	0.86048	0.85925	0.86042	0.86000
50	0.84797	0.85681	0.85563	0.85684	0.85639
55	0.84430	0.85319	0.85201	0.85321	0.85278
60	0.84059	0.84956	0.84839	0.84956	0.84810
65	0.83698	0.84594	0.84476	0.84593	0.84555
70	0.83333	0.84231	0.84127	0.84231	0.84192
75	0.82971	0.83870	0.83766	0.83869	0.83832
80	0.82608	0.83508	0.83406	0.83506	0.83470
85	0.82245	0.83145	0.83059	0.83144	0.83180
90	0.81882	0.82782	0.82697	0.82782	0.82821

Table 3. Linear Correlation for the Vegetable Oil Ethyl Esters Densities by Means of $\rho/\text{g}\cdot\text{cm}^{-3} = m(t/^\circ\text{C})^2 + n(t/^\circ\text{C}) + q$

ethyl ester	m	n	q	correlation coefficient
palm	$1\cdot 10^{-7}$	-0.0007	0.8850	1.0000
soybean	$2\cdot 10^{-7}$	-0.0007	0.8938	1.0000
canola	$2\cdot 10^{-7}$	-0.0007	0.8922	1.0000
corn	$-2\cdot 10^{-7}$	-0.0007	0.8923	1.0000
ricebran	$4\cdot 10^{-7}$	-0.0007	0.8933	0.9997

temperature and transferred to a separatory funnel. The two layers were separated by sedimentation. The ethyl ester phase was washed with hot distilled water. To avoid the emulsion during the washing step, 0.1 % aqueous tannic acid was used as a washing solution. The excess ethanol was removed on a rotary evaporator at atmospheric pressure.

Fatty Acid Composition Analysis. The compositions of the esters were analyzed by gas chromatography using an HP 6890 series gas chromatograph system equipped with a flame ionization detector and automated split injector (Agilent 7683 automatic sampler). The column was a 60 m \times 0.248 mm \times 0.15 μm DB-23 capillary column (J & W Scientific, USA).

Density Measurements. Density measurements were carried out using a DMA 4500 density/specific gravity meter (Anton Paar, Austria). The adjustment of the density meter was checked using degassed bidistilled water. The measured value at 25 $^\circ\text{C}$ was compared with the corresponding value in the density tables,¹³ and the difference was $\pm 0.00003 \text{ g}\cdot\text{cm}^{-3}$. Ethyl ester densities were measured at temperatures from (15 to 90) $^\circ\text{C}$, and measurements were done three times to obtain mean values for each temperature. The density repeatability precision was $\pm 0.00001 \text{ g}\cdot\text{cm}^{-3}$, and the temperature repeatability precision was $\pm 0.01 \text{ }^\circ\text{C}$.

Estimations

Spencer and Danner Method. The critical properties of biodiesel are an important starting point to estimate the liquid density. Poling et al.¹⁴ recommended the method of Joback¹⁵ to compute the critical properties of each pure constituent and to achieve high accuracy in the estimation of the mixture

properties. The earlier methods such as Ambrose^{16,17} and Lydersen's method¹⁸ do not appear to be as accurate as this method.¹⁴

In the Joback method, the three critical properties T_c , P_c , and V_c are estimated by the following relations

$$T_c/\text{K} = T_b/\text{K} \left[0.584 + 0.965 \left\{ \sum_k N_k(tck) \right\} - \left\{ \sum_k N_k(tck) \right\}^2 \right]^{-1} \quad (1)$$

$$P_c/\text{bar} = \left[0.113 + 0.0032 N_{\text{atoms}} - \sum_k N_k(pck) \right]^{-2} \quad (2)$$

$$V_c/\text{cm}^3 \cdot \text{mol}^{-1} = 17.5 + \sum_k N_k(vck) \quad (3)$$

T_b is the normal boiling point, and tck , pck , and vck are contribution values given in Table C-1 of Poling et al.¹⁴

The normal boiling point is one of the key properties for the estimation of the critical properties. Meissner¹⁹ proposed an approximation method to calculate normal boiling point

$$T_b/\text{K} = [637 \cdot (R_D/\text{m}^3 \cdot \text{mol}^{-1})^{1.47} + B] \cdot (P/N^4 \cdot \text{kg}^{-1} \cdot \text{m}^{-7})^{-1} \quad (4)$$

where R_D is a molar refraction; P is the parachor; and B is a constant dependent on the functional group or moiety. Molar refraction is the defined constant in the Lorentz–Lorenz equation and can be calculated using the Eisenlohr method where the characteristic values to each atom and bond are summed up for the compound.²⁰ The parachor defined by Sugden²¹ may be estimated.

To determine the mixture critical properties, the Lee–Kesler mixing rules recommended by Knapp et al.^{22,23} were used. The equations are

$$T_{\text{cm}} = \frac{1}{V_{\text{cm}}^{1/4}} \sum_i \sum_j x_i x_j V_{cij}^{1/4} T_{cij} \quad (5)$$

$$P_{\text{cm}} = (0.29050 - 0.085 \omega_m) RT_{\text{cm}} / V_{\text{cm}} \quad (6)$$

$$V_{\text{cm}} = \sum_i \sum_j x_i x_j V_{cij} \quad (7)$$

where

$$T_{cij} = (T_{ci} T_{cj})^{1/2} k'_{ij} \quad (8)$$

$$\omega_m = \sum_i x_i \omega_i \quad (9)$$

$$V_{cij} = \frac{1}{8} (V_{ci}^{1/3} + V_{cj}^{1/3})^3 \quad (10)$$

In this work, binary parameters k'_{ij} were simplified to be unit because no published data are available. The pure component acentric factor (ω_i) was computed by²⁴

$$\omega_i = \frac{\alpha_i}{\beta_i} \quad (11)$$

where

$$\alpha_i = -\ln P_{ci} - 5.97214 + 6.09648 \theta_i^{-1} + 1.28862 \ln \theta_i - 0.169347 \theta_i^6 \quad (12)$$

$$\beta_i = 15.2518 - 15.6875 \theta_i^{-1} - 13.4721 \ln \theta_i + 0.43577 \theta_i^6 \quad (13)$$

$$\theta_i = \frac{T_{bi}}{T_{ci}} \quad (14)$$

The Rackett equation is modified by Spencer and Danner²³ to estimate liquid density

$$\rho = \frac{\rho_R}{Z_{RA}^\phi} \quad (15)$$

where

$$\phi = \left(1 - \frac{T}{T_c}\right)^{27} - \left(1 - \frac{T_R}{T_c}\right)^{27} \quad (16)$$

ρ_R and T_R in eqs 15 and 16 are reference density and temperature, respectively. Z_{RA} is the Rackett compressibility factor and can be determined for biodiesel using measured densities and applying eq 15.

Results and Discussion

Fatty Acid Composition. The compositions of esters were detected by GC-FID. The fatty acid composition of the ethyl esters are presented in Table 1.

Density Measurements. Densities were determined from (15 to 90) °C at 5 °C intervals. The results are shown in Table 2. The results indicate that ethyl ester biodiesels obtained from vegetable oils demonstrate temperature-dependent behavior, and liquid density of ethyl esters decreases linearly with the increase in temperature.

The accuracy of the density data were further evaluated by correlating them with temperature by means of eq 17

$$\rho/\text{g}\cdot\text{cm}^{-3} = m(t/^\circ\text{C})^2 + n(t/^\circ\text{C}) + q \quad (17)$$

Good correlations were obtained, and the values of m , n , and q and the correlation coefficients are shown in Table 3.

Figure 1 compares the density of palm oil ethyl esters with the palm oil methyl ester density from our previous work.⁸ As can be seen, the density of palm methyl esters is higher than

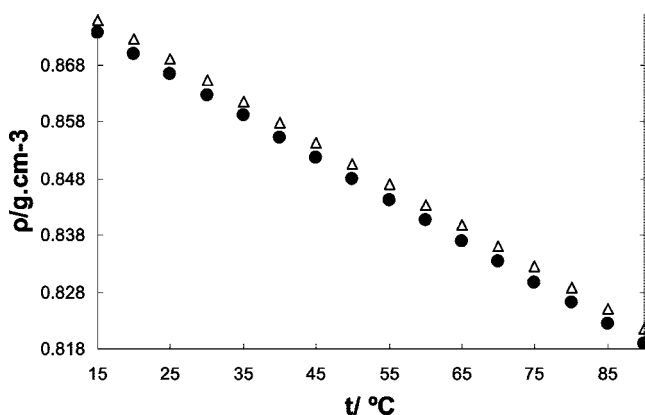


Figure 1. Comparison between densities ρ of palm oil ethyl and methyl esters at various temperatures t . ●, palm ethyl esters; △, palm methyl esters.

Table 4. Estimated Properties of the Fatty Acid Ethyl Esters, T_b Obtained Using Meissner's Method, and T_c , P_c , and V_c Obtained Using Joback's Method

	C16:0	C18:0	C18:1	C18:2
T_b/K	749.05	776.70	784.20	792.2
P_c/bar	11.56	10.19	10.53	10.89
$V_c/\text{cm}^3\cdot\text{mol}^{-1}$	1069.50	1181.50	1161.50	1141.50
MW	270.46	298.50	296.49	294.47
T_i/K	600.55	628.81	633.17	637.67

Table 5. Estimated Critical Properties of the Mixtures of Fatty Acids Ethyl Esters, T_{cm} , P_{cm} , and V_{cm} , Obtained Using Lee–Kesler Mixing Rules

ethyl ester	T_{cm}/K	P_{cm}/bar	$V_{cm}/\text{cm}^3\cdot\text{mol}^{-1}$
palm	768.18	12.07	1116.55
soybean	783.33	12.08	1138.28
canola	783.59	11.94	1152.10
corn	784.62	12.08	1140.47
ricebran	780.60	12.06	1136.04

Table 6. Rackett Compressibility Factor Z_{RA} for Vegetable Oil Based Ethyl Ester Biodiesel Obtained Using the Spencer and Danner Method

ethyl ester	Rackett compressibility factor Z_{RA}
palm	0.198
soybean	0.186
canola	0.195
corn	0.216
ricebran	0.199

that of ethyl esters. It can be attributed to the higher molecular weight of fatty acid ethyl ester. As mentioned before, the liquid density depends on molecular weight, and density increases with a decrease in molecular weight.

Density Estimations. The fatty acids of ethyl ester critical properties and normal boiling points are listed in Table 4. The results of applying critical properties T_{ci} , P_{ci} , and V_{ci} from Table 4 in the mixing rules for the Lee–Kesler equation are presented in Table 5.

These values were used in the predictions of palm, soybean, canola, corn, and ricebran oil ethyl ester density. By selecting $T_R = 288.15$ K and corresponding densities and solving eq 15 for the experimental density at $T = 303.15$ K, the prediction equations for densities of ethyl esters is obtained. The calculated Rackett compressibility factors Z_{RA} for the vegetable oil ethyl esters are listed in Table 6.

It was found that the average absolute percent deviations (AAPD) between estimated values and experimental data for the ethyl esters of palm, soybean, canola, corn, and ricebran oil were (0.06, 0.12, 0.06, 0.08, and 0.06) %, respectively. The average absolute percent deviations (AAPD) were calculated according to the expression

$$\text{AAPD} = \frac{1}{N} \sum_{i=1}^N \left| \left(\frac{\rho(\text{exptl}) - \rho(\text{calcd})}{\rho(\text{exptl})} \right)_i \right| \cdot 100 \quad (18)$$

In Figure 2, estimation absolute deviation percentages for the ethyl esters of vegetable oils are compared. As seen from Fig-

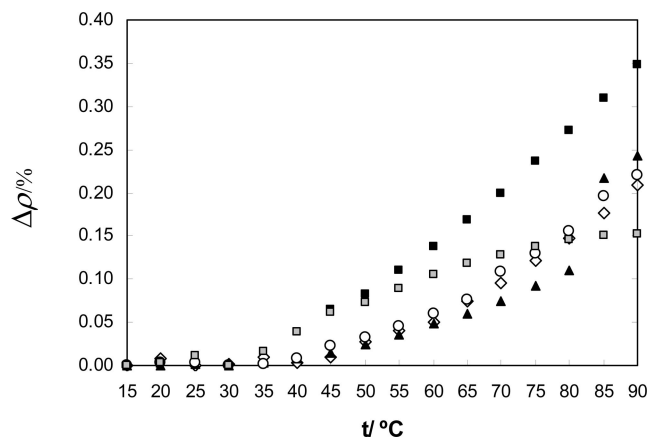


Figure 2. Comparison of the experimental ethyl ester density measurements from estimated data $\Delta\rho$ at different temperatures t . ■, soybean; ▲, ricebran; ○, canola; gray square, corn; ◇, palm.

ure 2, the accuracy of the estimations is reasonably good, and this method of estimation is more accurate at lower temperatures.

Conclusion

Densities of various vegetable oil based ethyl esters were measured as a function of temperature. The critical properties of a vegetable oil based ethyl ester biodiesel were estimated using a widely used Joback modification of Lydersen's method.¹⁵

The results of this method were employed to represent the properties of the pure components, and the mixing rules for the Lee–Kesler equation^{22,23} were employed to compute the critical properties of the mixtures. The Rackett equation modified by Spencer and Danner²³ was used to predict the densities, and the average errors of (0.06, 0.12, 0.06, 0.08, and 0.06) % for the ethyl esters of palm, soybean, canola, corn, and ricebran oil, respectively, show very good agreement.

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