

Density of Palm Oil-Based Methyl Ester

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Biodiesel density data as a function of temperature is needed to model the combustion process. In this work, the density and specific gravity of pure palm oil-based methyl ester biodiesel was measured at various temperatures from (15 to 90) °C. The data obtained was validated with Janarthanan empirical equation and 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 differences less than 0.03 %. The Janarthanan empirical equation performs equally with differences within 0.03 %. A simple linear equation for density is also proposed in this work.

Introduction

Biodiesel or fatty acid alkyl ester is a promising source of energy. It is a renewable and biodegradable diesel fuel with less harmful emissions than petroleum-based diesel fuel and can be used in its pure form or blended with petroleum-based diesel fuel. Biodiesel can be produced by transesterification of fats and vegetable oils. In the transesterification of vegetable oils, triglycerides react with the alcohol in the presence of a strong acid or base, producing a mixture of fatty acids alkyl esters and glycerol.

A variety of vegetable oils can be used to produce biodiesel. These include virgin vegetable oils and waste vegetable oils. Rapeseed, soybean, and palm oils are most commonly used to produce biodiesel, though other crops such as mustard, hemp, jatropha, and even algae show great potential as a source of raw materials. As the world's main palm oil producer and exporter, biodiesel can be produced from this raw material in Malaysia. Palm oil is high in saturated fatty acids (about 50 %). The oil palm gets its name from the 16 carbon saturated fatty acid (called palmitic acid) found in palm oil; monounsaturated oleic acid is also a constituent of palm oil.

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

The density of a methyl ester depends on its molecular weight, free fatty acid content, water content, and temperature. As palm oil biodiesel is getting popular as a fuel, a similar procedure for correcting measured density and specific gravity data will be needed. Results of measurements and predictions of specific biodiesel properties have been reported recently, but palm oil biodiesel density measurements and predictions were rarely or possibly never done.

Densities of fatty acids and biodiesel as a function of temperature were obtained by Liew et al.,¹ Tate et al.,² Tat and Van Garpen,³ and Noureddini et al.⁴ Yuan et al.⁵ predicted the density of biodiesel using a modified Rackett equation.

The specific objective of the research presented in this article was to measure the density of palm methyl ester biodiesel as a function of temperature and describe a method of estimating the density based on the chemical composition and structure.

Experimental Details

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

Methyl 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. The reaction temperature was prepared and controlled by hot water circulation using a RCS and RC6 (LAUDA). The reactor was filled with 250 g of palm oil. The catalyst, potassium hydroxide (1 %), was dissolved in methanol and then added to the reactor at the reaction temperature of 50 °C. Agitation was set at a constant speed (700 rpm) throughout the experiment. The reaction was carried out using 100 % excess methanol, i.e. a molar ratio of methanol to oil of 6:1. The mass of 1 mol of oil was determined from the calculated average molecular weight of palm oil based on the known fatty acid composition of the oil. After the end of the reaction, the mixture was cooled to room temperature and transferred to a separatory funnel. The two layers were separated by sedimentation. The methyl ester phase was washed with hot distilled water. In order to avoid the emulsion during the washing step, 0.1 % aqueous tannic acid was used as a washing solution. The excess methanol was removed on a rotary evaporator at atmospheric pressure.

Fatty Acid Composition Analysis. The composition of the esters was 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 × 0.248 mm × 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 was compared with the corresponding value in the density tables, and the accuracy was ± 0.00003 g·cm⁻³. Methyl ester density

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Table 1. Empirical Constants in Equation 1 Used to Estimate Methyl Ester Density

methyl ester	a_i	b_i
palmitate	$-7.4608 \cdot 10^{-4}$	0.879094
stearate	$-6.9247 \cdot 10^{-4}$	0.877325
oleate	$-6.8563 \cdot 10^{-4}$	0.888357
linoleate	$-7.2226 \cdot 10^{-4}$	0.900981

and specific gravity were measured at temperatures from (15 to 90) °C, measurements were done three times to obtain mean values for each temperature, and the uncertainty was $\pm 0.00001 \text{ g} \cdot \text{cm}^{-3}$.

Estimations

Janarthanan Empirical Method. A simple method for estimating the density of methyl esters of fatty acids is to use the empirical relation developed by Janarthanan et al.⁶

$$\rho/\text{g} \cdot \text{cm}^{-3} = a_i(t/^\circ\text{C}) + b_i \quad (1)$$

where t is the temperature and the component dependent empirical constants a_i and b_i are reported in Table 1.

The density of palm methyl esters which is a mixture of these components can be estimated using a simple linear mixing rule, as shown in eq 2.

$$\rho_{\text{m}}/\text{g} \cdot \text{cm}^{-3} = \sum x_i(a_i(t/^\circ\text{C}) + b_i) \quad (2)$$

where, x_i is the mole fraction of fatty acid methyl esters.

Spencer and Danner Method. The critical properties of biodiesel are an important starting point to estimate the liquid density. Reid et al.⁷ recommended two different methods to compute the critical properties of each pure constituent and to achieve high accuracy in the estimation of the mixture properties.

The first method is Ambrose's method.^{8,9} In this method, the three critical properties T_c , P_c , and V_c are estimated by the following relations:

$$T_c/K = T_b/K [1 + (1.242 + \sum \Delta_T)^{-1}] \quad (3)$$

$$P_c/\text{bar} = M(0.339 + \sum \Delta_P)^{-2} \quad (4)$$

$$V_c/\text{cm}^3 \cdot \text{mol}^{-1} = 40 + \sum \Delta_V \quad (5)$$

Δ_T , Δ_P , and Δ_V are constants for Ambrose's method given in Table 2-1 in the work of Reid et al.⁷

The second method is the Joback modification of Lydersen's method.¹⁰ The proposed relations for critical properties are the following:

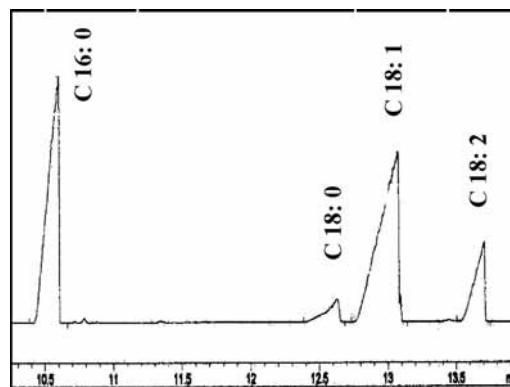
$$T_c/K = T_b/K [0.584 + 0.965 \sum \Delta_T' - (\sum \Delta_T')^2]^{-1} \quad (6)$$

$$P_c/\text{bar} = (0.113 + 0.0032n_A - \sum \Delta_P')^{-2} \quad (7)$$

$$V_c/\text{cm}^3 \cdot \text{mol}^{-1} = 17.5 + \sum \Delta_V' \quad (8)$$

Δ_T' , Δ_P' , and Δ_V' are given in Table 2-2 in the work of Reid et al.,⁷ which was based on approximately 400 fuels.

Reid et al.⁷ concluded that Ambrose's method was more accurate for estimation of critical temperature and critical pressure while the Joback modification of Lydersen's method yielded higher accuracy in the estimation of critical volume. For that reason, in this study Ambrose's method was employed to estimate T_c and P_c and the Joback modification of Lydersen's method was used for V_c .

**Figure 1.** GC-FID chromatograms of palm oil methyl esters.**Table 2. Fatty Acid Mole Fraction x of Palm Oil Methyl Esters**

fatty acid	x
C 16:0	0.43
C 18:0	0.04
C 18:1	0.43
C 18:2	0.10

To determine the mixture critical properties, the Lee–Kesler mixing rules recommended by Knapp et al.^{11,12} were used.

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 by⁷

$$\omega_i = \frac{\alpha_i}{\beta_i} \quad (9)$$

where

$$\alpha_i = -\ln P_{ci} - 5.97214 + 6.09648\theta_i + 1.28862 \ln \theta_i - 0.169347\theta_i \quad (10)$$

$$\beta_i = 15.2518 - 15.6875\theta_i - 13.4721 \ln \theta_i + 0.43577\theta_i \quad (11)$$

$$\theta_i = \frac{T_{bi}}{T_{ci}} \quad (12)$$

The Rackett equation modified by Spencer and Danner¹² to estimate liquid density is the following:

$$\rho/\text{g} \cdot \text{cm}^{-3} = \frac{\rho_R/\text{g} \cdot \text{cm}^{-3}}{Z_{RA}^\phi} \quad (13)$$

where

$$\phi = \left(\frac{1 - T/K}{T_c/K} \right)^{2/7} - \left(\frac{1 - T_R/K}{T_c/K} \right)^{2/7} \quad (14)$$

Z_{RA} is Rackett compressibility factor and can be determined for biodiesel using measured densities and applying eq 13.

Results and Discussion

Fatty Acid Composition. The compositions of esters were detected by GC-FID. Figure 1 shows GC-FID chromatograms of methyl esters. The fatty acid composition of the methyl esters is presented in Table 2.

Density Measurements. Densities were determined from (14 to 90) °C at 1 °C intervals. Measurements were done three times, and the uncertainty was $\pm 0.00001 \text{ g} \cdot \text{cm}^{-3}$. The results are shown in Table 3. The results indicate that biodiesel demonstrates temperature-dependent behavior: the liquid density of

Table 3. Density ρ of Palm Methyl Ester

$t/^\circ\text{C}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$t/^\circ\text{C}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$t/^\circ\text{C}$	$\rho/\text{g}\cdot\text{cm}^{-3}$
15	0.8759	40	0.8578	66	0.8390
16	0.8755	41	0.8571	67	0.8382
17	0.8748	42	0.8564	68	0.8375
18	0.8741	43	0.8557	69	0.8367
19	0.8733	44	0.8549	70	0.8360
20	0.8726	45	0.8542	71	0.8353
21	0.8718	46	0.8535	72	0.8346
22	0.8711	47	0.8528	73	0.8338
23	0.8704	48	0.8521	74	0.8331
24	0.8697	49	0.8513	75	0.8324
25	0.8689	50	0.8506	76	0.8317
26	0.8682	51	0.8499	77	0.8309
27	0.8674	52	0.8492	78	0.8302
28	0.8667	53	0.8484	79	0.8295
29	0.8659	54	0.8477	80	0.8288
30	0.8652	55	0.8470	81	0.8280
31	0.8645	56	0.8462	82	0.8273
32	0.8638	58	0.8448	83	0.8266
33	0.8630	59	0.8440	84	0.8258
34	0.8623	60	0.8433	85	0.8251
35	0.8615	61	0.8426	86	0.8244
36	0.8608	62	0.8419	87	0.8236
37	0.8601	63	0.8411	88	0.8229
38	0.8593	64	0.8404	89	0.8222
39	0.8586	65	0.8397	90	0.8215

biodiesel decreases linearly at the lower temperatures. The accuracy of the density data was further evaluated by correlating them with temperature by means of eq 15:

$$\rho/\text{g}\cdot\text{cm}^{-3} = n + m(t/^\circ\text{C}) \quad (15)$$

The values of n and m are 0.8827 and -0.0007 , respectively. Good correlations were obtained, and the correlation coefficient is 1.

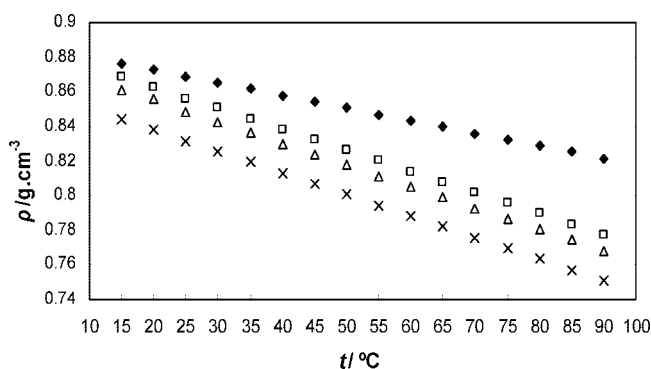


Figure 2. Density comparison of palm, canola, soy, and fish oil methyl esters:² \blacklozenge , palm methyl ester; \square , canola methyl ester; \triangle , soy methyl ester; \times , fish-oil methyl ester.

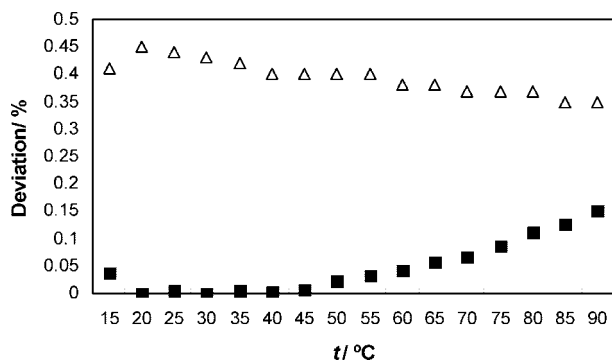


Figure 3. Comparison of density estimation deviations from experimental data: \blacksquare , modified Rackett method; \triangle , Janarthanan empirical method.

Table 4. Estimated Critical Properties of the Fatty Acids, T_c and P_c Obtained Using Ambrose's Method and V_c Using Lydersen's Method

	C16:0	C18:0	C18:1	C18:2
T_c/K	767.1	774.2	772.3	795.3
P_c/bar	12.50	11.46	11.68	11.91
$V_c/\text{cm}^3\cdot\text{mol}^{-1}$	1013.5	1125.5	1105.5	1085.5
MW	270.46	298.50	296.49	294.47
T_b/K	611	625	622	639

The measured densities of palm oil methyl ester were compared with the methyl esters of canola, soy, and fish oil from the work of Tate et al.² The comparison is shown in Figure 2, and the density of palm oil methyl ester is higher than those of other methyl esters.

Density Estimations. The results of using the empirical method proposed by Janarthanan to estimate methyl esters densities are shown in Figure 3. It was found that the maximum deviation between estimated values and experimental data was 0.45 %. As seen from Figure 3, the accuracy of the estimates is reasonably good.

The critical properties of fatty acids of methyl esters 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 were the following:

$$T_{cm} = 772.2375 \text{ K}$$

$$P_{cm} = 12.5840 \text{ bar}$$

$$V_{cm} = 1063.0717 \text{ cm}^3 \cdot \text{mol}^{-1}$$

These values were used in the predictions of palm oil methyl ester density. By selecting $T_R = 14^\circ\text{C}$ and $\rho_R = 0.87697 \text{ g}\cdot\text{cm}^{-3}$ and solving eq 16 for the experimental density at $T = 30^\circ\text{C}$, the prediction equation for density becomes the following:

$$\rho/\text{g}\cdot\text{cm}^{-3} = \frac{0.87697}{0.2004^{[(1 - T/\text{K})/(772.2375)]^{0.2857} - 0.8755]}} \quad (16)$$

The predicted densities of methyl ester biodiesel from (15 to 90) $^\circ\text{C}$ using the Rackett equation modified by Spencer and Danner are shown in the Figure 3. The maximum difference between estimated values using the modified Rackett equation and experimental data was 0.15 %, and this method of estimation is more accurate than the Janarthanan empirical method.

Conclusion

Biodiesel density data as a function of temperature is needed to model the combustion process. Densities and specific gravities of palm methyl esters were measured as a function of temperature. The critical properties of a palm oil-based methyl ester biodiesel were estimated using two widely used methods: Ambrose's method^{8,9} and the Joback modification of Lydersen's method.¹⁰

The results of these two methods were employed to represent the properties of the pure components, and the mixing rules for the Lee–Kesler equation¹¹ were employed to compute the critical properties of the mixture. The Rackett equation modified by Spencer and Danner was used to predict the density, and the average deviation of 0.03 % shows very good agreement.

An empirical estimation method⁶ was employed to predict biodiesel density, and the results were absolutely good.

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