Density of palm oil-based methyl ester

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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., Tate et al., Tat and Van Garpen, and Noureddini et al. 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.

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

<table>
<thead>
<tr>
<th>methyl ester</th>
<th>( a_i )</th>
<th>( b_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>palmitate</td>
<td>(-7.4688 \times 10^{-4})</td>
<td>0.879994</td>
</tr>
<tr>
<td>stearate</td>
<td>(-6.9247 \times 10^{-4})</td>
<td>0.877325</td>
</tr>
<tr>
<td>oleate</td>
<td>(-6.8563 \times 10^{-4})</td>
<td>0.888357</td>
</tr>
<tr>
<td>linoleate</td>
<td>(-7.2226 \times 10^{-4})</td>
<td>0.900981</td>
</tr>
</tbody>
</table>

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 ± 0.00001 g·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

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

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

\[
\rho/\text{g} \cdot \text{cm}^{-3} = \sum x_i(a_i(t^\circ \text{C}) + b_i)
\]

(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.¹ 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. In this method, the three critical properties \( T_c, \rho_c, \) and \( V_c \) are estimated by the following relations:

\[
T_c/K = T_v/K[1 + (1.242 + \sum \Delta \gamma_i)^{-1}]
\]

(3)

\[
P_c/\text{bar} = M(0.339 + \sum \Delta \gamma_i)^{1.9}
\]

(4)

\[
V_c/\text{cm}^3 \cdot \text{mol}^{-1} = 40 + \sum \Delta \gamma_i
\]

(5)

\( \Delta \gamma_i, \Delta \rho_c \) and \( \Delta V_c \) are constants for Ambrose’s method given in Table 2-1 in the work of Reid et al.³

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

\[
T_c/K = T_v/K[0.584 + 0.965 \sum \Delta \gamma_i - (\sum \Delta \gamma_i)^2]^{-1}
\]

(6)

\[
P_c/\text{bar} = (0.113 + 0.00324M - \sum \Delta \gamma_i)^2
\]

(7)

\[
V_c/\text{cm}^3 \cdot \text{mol}^{-1} = 17.5 + \sum \Delta \gamma_i
\]

(8)

\( \Delta \gamma_i, \Delta \rho_c, \) and \( \Delta V_c \) are given in Table 2-2 in the work of Reid et al.³ which was based on approximately 400 fuels.

Reid et al.³ 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

<table>
<thead>
<tr>
<th>fatty acid</th>
<th>( x )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 16:0</td>
<td>0.43</td>
</tr>
<tr>
<td>C 18:0</td>
<td>0.04</td>
</tr>
<tr>
<td>C 18:1</td>
<td>0.43</td>
</tr>
<tr>
<td>C 18:2</td>
<td>0.10</td>
</tr>
</tbody>
</table>

To determine the mixture critical properties, the Lee–Kesler mixing rules recommended by Knapp et al.¹¹ were used. In this work, binary parameters \( k_{ij} \) were simplified to unit because no published data is available. The pure componentacentric factor \( (\omega_i) \) was computed by

\[
\omega_i = \frac{\alpha_i}{\beta_i}
\]

(9)

where

\[
\alpha_i = -\ln P_i - 5.97214 + 6.09648 \theta_i + 1.28862 \ln \theta_i - 0.169347 \theta_i
\]

(10)

\[
\beta_i = 15.2518 - 15.6875 \theta_i - 13.4721 \ln \theta_i + 0.43577 \theta_i
\]

(11)

\[
\theta_i = \frac{T_N}{T_c}
\]

(12)

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

\[
\rho/\text{g} \cdot \text{cm}^{-3} = \frac{\rho \rho_c}{Z_{RA}^{-3/2}}
\]

(13)

where

\[
\phi = \left[1 - \frac{T_c}{T_c/K}\right]^{3/2} - \left[1 - \frac{T_c}{T_c/K}\right]^{5/2}
\]

(14)

\( Z_{RA} \) is Racket 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 ± 0.00001 g·cm⁻³. The results are shown in Table 3. The results indicate that biodiesel demonstrates temperature-dependent behavior: the liquid density of

Full text is available at :

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