EQUILIBRIUM JOURNAL OF
CHEMICAL ENGINEERING

EJChE
Equilibrium Journal of Chemical Engineering

Density Evaluation of Alkyl Ester from Different Types of Alcohol and Vegetable Oil

Dyah Retno Sawitri*, Khusnul Azzam, Ani Chalwa Isnani, Darryl Al Husein

b*Chemical Engineering Department, Faculty of Industrial Technology, Universitas Islam Indonesia, Yogyakarta, Indonesia 55584*

*Corresponding author: dyah.retno@uii.ac.id

ABSTRACT. Alkyl ester, also known as biodiesel, is an alternative renewable energy source and is produced through the reaction of vegetable oil and alcohol. One of the important characteristics of biodiesel lies in the density value. This study evaluates the density value of alkyl esters from several raw materials. The raw materials used include palm oil and rice bran oil. In comparison, the types of alcohol used include methanol, ethanol, and isopropanol. The density values of palm oil ethyl ester and rice bran oil ethyl ester were measured at $30 - 100°C$. The density measurement results were then compared with the simulation results using ASPEN Plus® software. The density of alkyl esters was measured over a temperature range of 30-100°C. The density measurements were then compared with the simulation results using ASPEN Plus® software. The measurement and simulation results showed that the density was higher in the order ethyl > methyl > isopropyl ester for palm oil. When viewed from the vegetable oil, the density of rice bran oil ethyl ester is higher than that of palm oil ethyl ester. The results of measuring biodiesel from rice bran oil and palm oil at 40°C show that only the isopropyl ester has a density that does not meet the quality requirements of biodiesel as defined by the Indonesian National Standard.

1. INTRODUCTION

As a tropical country, Indonesia has a rich biodiversity that supports research on renewable energy, especially biodiesel. Regarding raw materials, biodiesel can be produced by reacting vegetable oil with alcohol. The most abundant vegetable oil in Indonesia is palm oil. According to the 2024 report on plantations, oil-palm production (45.44 million tons) was far higher than coconut (2.78 million tons) or rubber (2.13 million tons) [1]. On the other hand, other types of vegetable oils also have great potential for development, including rice bran oil. The Indonesian Central Bureau of Statistics reports that in 2024, the harvested area of paddy was ~10.05 million ha and production was ~ 53.14 million tons of dry milled rice [2]. In typical rice milling, about 8–10% of the rice weight becomes bran. That implies — very roughly — an annual potential of ~ 4.4–5.5 million tons of rice bran (8–10% of 54.75 mt) just from one year's production [3]. The potential is large in absolute terms and indicates a substantial raw-material base for rice bran oil. Each type of vegetable oil has fundamental differences in the composition of its constituent fatty acids. Palm oil contains primarily oleic and palmitic acids, while the main composition of rice bran oil consists of palmitic acid, oleic acid, and linoleic acid [4]. From the profile of its constituent fatty acids, palm oil has a balanced proportion of saturated and unsaturated fatty acids, while rice bran oil consists mainly of unsaturated fatty acids.
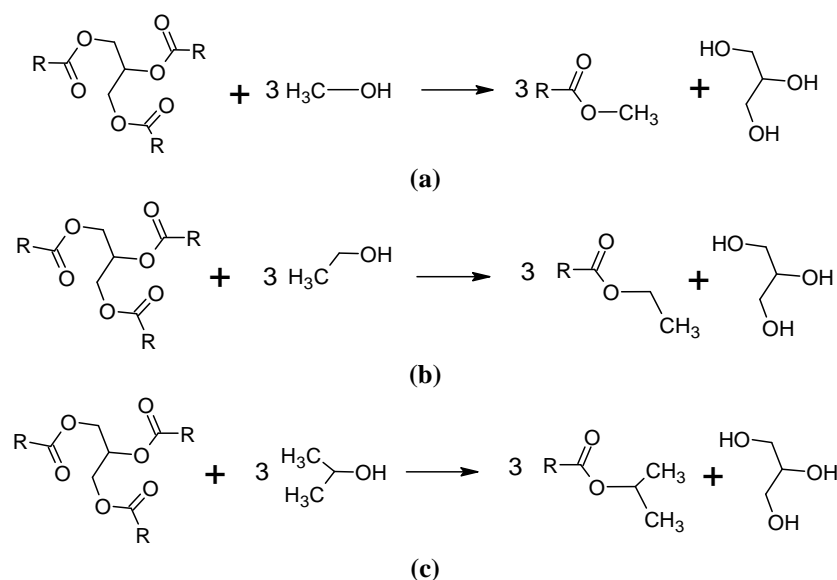
The transesterification reaction to produce biodiesel from vegetable oil can use several types of alcohol. Methanol is the most widely used alcohol because it offers several advantages, including a lower price, higher reaction conversion, and lower product viscosity. However, methanol has a higher level of toxicity when compared to longer-chain alcohols such as ethanol and propanol. In enzyme reactions, ethanol is preferred because methanol can deactivate certain enzymes [5]. Another consideration is the environmental and sustainability aspects. Ethanol can be synthesized through biomass fermentation, making it more environmentally friendly than methanol, which is currently mostly produced from natural gas, a non-renewable resource [6]. Another alternative for longer-chain alcohols is propanol or its isomer (isopropanol). Biodiesel synthesized using isopropanol shows a positive effect on the physical properties of biodiesel at low temperatures [7].

Research on biodiesel as a renewable, environmentally friendly fuel alternative has experienced rapid development in raw materials, processes, and catalyst types [5]. Aspects related to biodiesel synthesis have been widely studied. A study on the prediction of biodiesel density and viscosity has also been conducted by several authors [8–10]; however, factors associated with the density characterization of biodiesel derived from different types of alcohol and vegetable oil fatty acid profiles remain rare. This study aims to determine the density characteristics of biodiesel produced from various raw materials. Empirical studies confirm that biodiesel fuels and blends exhibit higher density than conventional diesel, as a consequence of their molecular composition (fatty-acid methyl/ethyl esters), which reduces compressibility and increases droplet mass in sprays [8,9]. The higher density of biodiesel compared to petroleum-derived diesel poses a significant challenge for diesel-engine combustion optimization [10]. Because diesel-fuel injection systems meter fuel on a volumetric basis, a denser fuel delivers a higher mass per injection for the same volume, potentially upsetting the designed air–fuel ratio and affecting combustion quality [11]. Biodiesel is a mixture of fatty acid alkyl esters, so the density of biodiesel is determined from the density of the mixture of its constituent alkyl esters [12]. The standard biodiesel density in Indonesia is specified in the Indonesian National Standard (SNI) 7182:2015, with a density requirement of 850–890 kg/m³ at 40°C [13].

In this study, measurements and analyses of biodiesel density were carried out based on the fatty acid profiles of vegetable oils (palm oil and rice bran oil) and the type of alcohol used (methanol, ethanol, or isopropanol). Density measurements were also carried out at various temperatures to determine the correlation of density as a function of temperature. Apart from being needed for combustion process optimization, density data is also required for large-scale process simulation and design [14].

2. MATERIALS AND METHODS

Commercial edible-grade palm cooking oil (Bimoli, PT Salim Ivomas Pratama Tbk., Jakarta, Indonesia) and commercial rice bran oil (Oryza Grace rice bran oil, imported and distributed in Indonesia by PT Hero Intiputra, Jakarta, Indonesia) were purchased from a local supermarket and used as the feedstock. Methanol, ethanol, isopropanol, and potassium hydroxide (KOH) were obtained from Merck.

Figure 1. The reaction scheme for the synthesis of (a) Fatty Acid Methyl Esters; (b) Fatty Acid Ethyl Esters; (c) Fatty Acid Isopropyl Esters

Biodiesel was produced via transesterification of vegetable oil with alcohol, using KOH as a catalyst. The molar ratio of vegetable oil to alcohol was 1:6, with KOH at 1% of the oil weight. The reaction temperature was maintained at 60°C for 2 hours [5]. The transesterified biodiesel was purified through washing and evaporation, and its density was measured using an Anton Paar model DMA 4100M densitometer. When palm oil was used, biodiesel was synthesized using all three alcohols, yielding palm oil methyl ester (PME), palm oil ethyl ester (PEE), and palm oil isopropyl ester (PIE). For rice bran oil, only ethanol was used, yielding rice bran oil ethyl ester (REE). The reaction scheme is shown in Fig. 1. Density measurements were conducted over a 30–100°C

temperature range in 10°C increments. The density measurements at various temperatures were then compared with simulation data using Aspen Plus® software (V.14). The simulation used the Non-Random Two-Liquid (NRTL) thermodynamic model.

3. RESULTS AND DISCUSSION

Historically, vegetable oil has been used directly as fuel in diesel engines. However, experience has shown that vegetable oil causes several problems, including pumping difficulties, injector fouling, excessive engine wear, and carbon deposits in some engine parts. These problems are likely caused by their high viscosity and density, low volatility, and high iodine number. The density of some types of vegetable oil is 910–930 kg/m³, much higher than the density of petroleum-based diesel fuel, which is 850 kg/m³ [15]. Transesterification is one way to overcome these problems. The transesterification reaction of vegetable oil with alcohol produces a mixture of various alkyl esters, depending on the fatty acid composition of the vegetable oil and the type of alcohol used as the raw material. The diversity of the fatty acid composition of the oil and the type of alcohol used also indirectly affects the density of the resulting biodiesel. The fatty acid compositions of palm oil and rice bran oil are shown in Table 1.

Table 1. Fatty acid composition of palm oil [16] and rice bran oil [4]
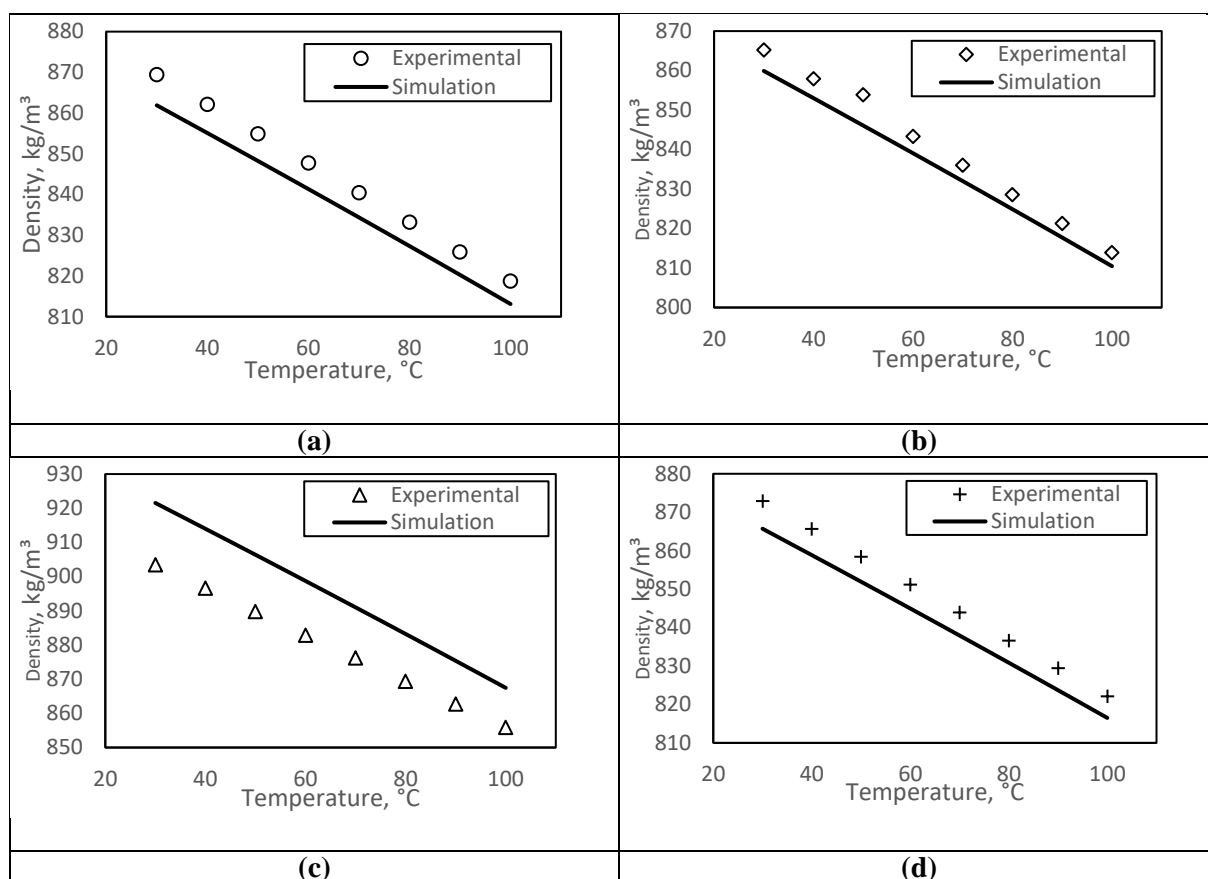
	Palm oil	Rice bran oil
Component	Composition (%mol)	Composition (%mol)
Lauric acid	0.10	-
Myristic acid	1.00	0.31
Palmitic acid	44.00	18.30
Palmitoleic acid	0.10	0.20
Stearic acid	5.00	2.41
Oleic acid	41.20	41.19
Linoleic acid	8.00	34.16
Linolenic acid	0.50	2.31
Arachidic acid	0.10	1.00

Typical saturated fatty acids include: lauric, myristic, palmitic, stearic, and arachidic acids; monounsaturated fatty acids include: palmitoleic and oleic; polyunsaturated fatty acids include: linoleic and linolenic acid. Table 1 shows that palm oil has a relatively balanced composition of saturated and monounsaturated fatty acids. In contrast, rice bran oil contains three main components, with monounsaturated and polyunsaturated fatty acids much greater than saturated fatty acids. The density measurements for alkyl esters produced from the various raw materials used in this study at several temperatures are shown in Table 2.

Table 2. Experimental density

Temperature, °C	Density, kg/m³			
	PME	PEE	PIE	REE
30	869.4	865.2	903.5	872.9
40	862.1	857.9	896.6	865.7
50	854.9	853.9	889.8	858.4
60	847.7	843.3	882.9	851.2
70	840.4	836.0	876.2	843.9
80	833.2	828.6	869.4	836.6
90	825.9	821.3	862.7	829.4
100	818.7	813.9	855.9	822.1

Table 2 shows that for all alkyl esters, the higher the temperature, the lower the density. Regarding SNI, the density values for PME, PEE, and REE are within the standard range, but for PIE, the density value is above the established standard. Density is the mass value divided by volume. The higher the temperature, the greater the distance between molecules, resulting in expansion. This expansion increases volume for the same mass amount, resulting in a lower density. The next trend to observe is the density of alkyl esters for different types of alcohol. The density value of PIE is higher than that of PME and PEE. However, the density of PEE is lower than that of PME. It shows that the density value is not directly correlated with the number of carbon atoms in the type of alcohol used. The same was also found in the study by Pratas et al. [17]. The cause of this tendency lies in the molecular structure of vegetable oil ethyl esters, where adding CH_2 groups increases molecular density.

Figure 2. Density comparison between experimental and simulation results for: (a) PME; (b) PEE; (c) PIE; and (d) REE.

From the perspective of the feedstock oil, palm oil ethyl esters tend to exhibit lower density values than rice bran oil ethyl esters. This tendency is influenced by differences in the fatty acid profiles of the two oils, which govern the molecular structure of the resulting alkyl esters [17]. In general, the density of fatty acid alkyl esters decreases as the carbon chain length increases, because longer chains reduce molecular packing efficiency [21]. At a constant carbon chain length, density increases with increasing saturation due to the ability of saturated molecules to pack more tightly in the liquid phase [18].

However, the overall density of a complex mixture such as vegetable oil ethyl esters is not determined solely by saturation, but by the combined effects of chain-length distribution, degree of unsaturation, and the relative abundance of each fatty acid [19]. Rice bran oil contains significant amounts of long-chain unsaturated fatty acids—particularly oleic (C18:1) and linoleic acids (C18:2)—which produce ethyl esters with inherently higher molecular weights than those dominant in palm oil [4]. Although unsaturation generally lowers density at a given carbon number, the higher proportion of C18-based esters in rice bran oil can result in a higher overall density than palm oil ethyl esters, which contain more C16-based saturated esters such as palmitic acid. As a result, the combined effect of chain length and unsaturation in rice bran oil results in ethyl esters with slightly higher densities, consistent with the observed tendency.

The alkyl ester density measurements were then compared with simulation results obtained with Aspen Plus. In the simulation, the ethyl ester composition of rice bran and palm oil was adjusted to the fatty acid composition in Table 1. The NRTL thermodynamic model was used in the simulation because it is applicable to non-ideal systems and can be used for esterification and transesterification reactions in biodiesel production [20]. The comparison of ethyl ester density values for rice bran oil and palm oil, based on measurement and simulation results, is shown in Fig. 2. The simulation results show the same trend as the measurement results: density decreases with increasing temperature. However, there are differences between the measurement results and the simulation results. In general, the simulation results show a lower density than the measurement results, except for PIE. When viewed from the vegetable oil raw materials used, the simulation results closely match the measurement results, with the density of rice bran oil ethyl ester higher than that of palm oil ethyl ester. The relative errors

between the simulation and measurement results at each temperature, along with the average relative error, are shown in Table 3.

Table 3. Relative error of simulation density results compared to measurement results

Temperature, °C	Relative error, %			
	PME	PEE	PIE	REE
30	0.862	0.611	1.997	0.824
40	0.811	0.569	1.940	0.792
50	0.778	0.917	1.864	0.754
60	0.750	0.502	1.792	0.733
70	0.717	0.477	1.689	0.707
80	0.702	0.447	1.589	0.687
90	0.683	0.437	1.469	0.686
100	0.683	0.421	1.350	0.681
Average	0.748	0.548	1.711	0.733

Table 3 shows that the average relative error across all alkyl ester types is quite low, indicating that the simulation results are not significantly different from the measurement results. The lowest average relative error value was obtained in the PEE data, at 0.548%. The correlation between density and temperature can be approximated by a straight-line equation [12] as shown in Equation 1.

$$\rho = bT + a \tag{1}$$

where ρ is the density in $kg \cdot m^{-3}$, T is the temperature in K, b and a are constants. By performing linear regression using the least-squares method and statistical analysis, the constant value and the 95% confidence interval for each constant are obtained, summarised in Table 4.

From Table 4, it can be seen that the constant values b and a are in a range that is not much different for all data, both simulation and measurement results. The fairly large standard deviation observed in the PEE data is likely due to the measurement at 50°C. In addition to the correlation with a straight line equation, density data with temperature can also be approximated by the expansivity coefficient at constant pressure (α_P) with Equation 2. The calculation results are shown in Table 5.

$$\alpha_P = -\left(\frac{\partial \ln \rho}{\partial T}\right)_P \tag{2}$$

Table 4. Density correlation constants and corresponding 95% confidence limit.

Alkyl ester	Data source	b ($kg \cdot m^{-3} \cdot K^{-1}$)	±	$t \cdot s_b$	a ($kg \cdot m^{-3}$)	±	$t \cdot s_a$
PME	Simulation	-0.7062	±	0.0059	1073.4	±	2.0
	Experimental	-0.7242	±	0.0012	1088.9	±	0.4
PEE	Simulation	-0.7062	±	0.0058	1074.2	±	2.0
	Experimental	-0.7444	±	0.0464	1091.7	±	15.7
PIE	Simulation	-0.7725	±	0.0061	1155.9	±	2.1
	Experimental	-0.6793	±	0.0028	1109.3	±	0.9
REE	Simulation	-0.7028	±	0.0057	1079.0	±	1.9
	Experimental	-0.7260	±	0.0012	1093.0	±	0.4

$t \cdot s_b$: standard deviation for b

$t \cdot s_a$: standard deviation for a

Table 5. The coefficient of expansivity at constant pressure

Alkyl ester	$\alpha_P \times 10^3$, K^{-1}	
	Simulation	Experimental
PME	0.8330	0.8585
PEE	0.8463	0.8986
PIE	0.8644	0.7753
REE	0.8363	0.8566

The calculated data in Table 5 show that the expansivity coefficient values at constant pressure for all types of alkyl esters are within a narrow range. Based on the results of similar research [17], the expansivity coefficient value is influenced by the saturation level of the fatty acid chain, where the higher the saturation, the lower the expansivity coefficient. Thus, it can be concluded that both the measurement data and the simulation data show the same tendency, where the α_P value for REE is lower when compared to the α_P value for PEE.

4. CONCLUSION

Based on the density measurements for several types of alkyl esters, it can be concluded that the density values of the alkyl esters produced from this study mostly meet the standards set in SNI 7182:2015. The simulation results with ASPEN Plus show a trend that aligns with the measurement results. In general, the lowest density of palm oil raw materials is for ethyl esters, followed by methyl and isopropyl esters. The change in density with temperature for all alkyl esters follows a linear equation. It has an expansivity coefficient that aligns with the fatty acid saturation profile.

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