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Research article

Synthesis of methyl esters from palm oil, candlenut oil, and sunflower seed oil and their corrosion phenomena on iron nail

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Abstract: Biodiesel products show corrosive properties. Biodiesel contains components of saturated and unsaturated esters which tend to be unstable, sensitive to light, temperature, and metal ions. Thus, the study aims to synthesize biodiesel from various vegetable oils (palm oil, sunflower seed oil, and candlenut oil), and to analyze its corrosiveness to ferrous nails and characterization of biodiesel. The research stages were: synthesis of methyl ester and its characterization, and corrosion test. The results showed that the methyl ester characteristics of the samples meet requirements with SNI7182 : 2015. In GC-MS results, the largest components of methyl esters from candlenut oil and sunflower seed oil were 35.04% methyl oleate and 46.79% methyl oleate respectively, while in palm oil, the largest components were 41.60% methyl oleate and 41.16%. methyl palmitate. Corrosion test showed that the corrosion rate of ferrous nail in biodiesel at room temperature was lower than 70 °C. Based on GC-MS and SEM results, biodiesel contained high unsaturated fatty acids and had a corrosion rate, i.e., at room temperature, the methyl ester of palm oil, candlenut oil, and sunflower seed oil were 0.006 mpy, 0.011 mpy, and 0.011 mpy respectively, while at 70 °C, they were 0.011 mpy, 0.016 mpy, and 0.017 mpy, respectively. The results corresponded to SEM results at high temperature and significantly high content of unsaturated fatty acids. It was indicated by the formation of pits.

Keywords: palm oil; sunflower seed oil; candlenut oil; methyl ester; corrosiveness; biodiesel

1. Introduction

Consumption of fossil fuels increases rapidly and is categorized as non-renewable fuels [1]. As an impact, there will be an energy crisis in the future [2]. Moreover, fossil fuels cause problems of environment pollution. To reduce fossil fuel usage, researchers have begun exploring alternative fuels [3] that are renewable raw materials in nature and cheap production, such as biodiesel [4].

Biodiesel is a renewable fuel derived from vegetable oils or animal fats. Some of the advantages of biodiesel include higher combustion efficiency and cetane number compared to petroleum-derived diesel fuel, as well as having lower sulphur and aromatic compounds, so that the emission of harmful gases from combustion is lower than petroleum-derived diesel fuel. A common method for the biodiesel synthesis was transesterification [5]. The reaction was a conversion reaction between triglycerides and alcohol to form fatty acid methyl esters and glycerol as a by-product [6]. The synthesis could reduce the viscosity of vegetable oil, so it can be used as fuel for diesel engines [7].

Biodiesel products contained saturated and unsaturated esters which were unstable, sensitive to light, temperature, and metal ions [8]. When compared to diesel fuel, biodiesel contained water vapor, organic acids, aldehydes, peroxides, ketones, and esters that caused corrosion in the fuel combustion system [9]. In addition, several studies have shown that the use of biodiesel was more corrosive than ordinary diesel fuel [8]. The corrosiveness of biodiesel can also be affected by the stability of the biodiesel. The content of biodiesel can affect the stability of biodiesel against oxidation in the air. The stability level of biodiesel will decrease if the linoleic acid content in biodiesel increases [10]. Therefore, this study demonstrates corrosiveness of biodiesel on iron nail surfaces. Because iron nails are local commercial materials that corrosion occurs. This study introduces the demonstration by using an iron nail that is common for alloy based-machine material with low quality.

Three raw materials for biodiesel synthesis were from unique vegetable oils, namely palm oil, candlenut oil, and sunflower seed oil [11]. Palm oil has a relatively high oil content (40%) [12]. Crude palm oil has a higher viscosity coefficient value than diesel fuel, so it cannot be directly used as diesel fuel. Candlenut oil has an iodine number of 136–167 which means it has a high content of unsaturated fatty acids [13]. In addition, there is vegetable oil that can be used as a source of biodiesel, namely sunflower seed oil. Sunflower seeds contain an oil percentage of 45%–50% of the total mass of extracted seeds [14]. So, these three types of vegetable oil will study a composition of the most dominant fatty acids that determine the corrosion activity of ferrous nails. The main difference from various vegetable oils is the type of fatty acid present in the triglyceride molecule, resulting in a different composition of fatty acid methyl esters. These differences can affect the properties of biodiesel fuel. Fatty acid composition can also determine the degree of saturation/unsaturation and molecular weight of vegetable oils [12].

Therefore, the use of biodiesel has a corrosive effect [10]. The research studied: (1) synthesis of methyl esters from various vegetable oils (palm oil, candlenut oil, and sunflower seed oil) by base-catalysed transesterification, (2) characterization of methyl esters from various vegetable oils (palm oil, candlenut oil, and sunflower seed oil) as biodiesel, (3) constituent components of methyl esters from various vegetable oils (palm oil, candlenut oil, and sunflower seed oil), and (4) corrosiveness of methyl esters from various vegetable oils (palm oil, candlenut, and sunflower seed oil). The characteristics of the synthesized methyl ester were studied to contribute toward corrosion phenomena. Therefore, this preliminary study was performed to find the main characteristic contribution on corrosion phenomena.

2. Materials and methods

2.1. Materials

The tools in the study were a set of reflux apparatus, which consisted of reflux condenser, three-neck flask, stative, clamps, thermometer, and magnetic stirrer-hotplate, glassware, pycnometer, Thin-Layer Chromatography (TLC) plate of gel silica GF_{254} type, universal indicator, Ostwald viscosmeter, refractometer, analytical balance, thermostat, Gas Chromatography-Mass Spectrometry (GC-MS) (Shimadzu QP2010 Plus), and Scanning Electron Microscopy (SEM) (FEI Inspect-S50). The materials in the study were palm oil, candlenut oil, sunflower seed oil, anhydrous $MgSO_4$, formic acid p.a. (Sigma Aldrich), diethyl ether p.a. (Sigma Aldrich), n-hexane p.a. (Sigma Aldrich), crystalline iodine, 95% alcohol, phenolphthalein indicator, KOH p.a. (Sigma Aldrich), oxalic acid p.a. (Sigma Aldrich), hydrochloric acid p.a. (Sigma Aldrich), methanol p.a. (Sigma Aldrich), sulfuric acid p.a. (Sigma Aldrich), aquadest, and iron nails from Local material for buildings.

2.2. Synthesis and characterization of methyl ester from candlenut oil, palm oil and sunflower seed oil

2.2.1. Synthesis of methyl ester

Synthesis of Methyl Ester was conducted by two methods: esterification-transesterification for Candlenut Oil, and transesterification for palm oil and sunflower seed oil. Before the synthesis, palm oil, candlenut oil, and sunflower seed oil were characterized by density, viscosity, refractive index, acid number, saponification number, determination of free fatty acid (FFA). The characterization procedure applied Santoso's research [4,15].

The esterification procedures were: oil: methanol mixture with a volume ratio of 1:12 and 3% w/w H_2SO_4 catalyst were mixed into a three-neck flask. The mixture was heated to a constant temperature of 65 °C while stirring for 3 h. After that, the mixture was cooled to room temperature. The mixture was then separated using a separating funnel for 24 h. The top layer contained H_2SO_4 and unreacted methanol, while the bottom layer was a mixture of triglycerides (oil) and fatty acid methyl esters. The bottom layer was washed with warm distilled water. It was then added anhydrous $MgSO_4$ to remove the remaining water. Furthermore, the free fatty acid (FFA) content was tested, if the FFA content in the oil was < 2%, then it was continued with the transesterification process.

The transesterification procedures were: oil: methanol mixture in volume ratio of 6:1 with 1% w/w KOH catalyst was mixed into a three-neck flask. The mixture was heated until a constant temperature of 65 °C with stirring for 4 h. The reaction process was controlled by TLC analysis until a big difference of Rf between the sample node and the synthesis results was obtained. Furthermore, the characterization carried out on the methyl ester included: density, viscosity, refractive index, acid number, saponification number, GC-MS test [16].

2.2.2. Characterization of methyl ester

Characterizations of methyl ester were carried out as follow [4]:

1. Density. The alkyl ester was poured in 10 mL of the pycnometer until it was full and there should be no bubbles. Then the weight was weighed and then the weight of the empty pycnometer flask was reduced. For the calculation of density used the Eq 1:

$$\text{density } (\rho)= \frac{\text{sample mass in pycnometer (g)-mass of pycnometer (g)}}{\text{volume of pycnometer (mL)}} \tag{1}$$

2. Viscosity. The sample was put into an Ostwald viscosmeter tube, and sucked until it passed the two boundary marks. Next, the time noted from the top calibration mark to the bottom calibration mark. Then, it was calculated using the Eq 2:

$$\frac{\eta \text{ aquadest}}{\eta \text{ sample}} = \frac{\rho \text{ aquadest} \times \text{t aquadest}}{\rho \text{ sample} \times \text{t sample}} \tag{2}$$

Which η = viscosity (cSt), ρ = density (g/mL), and t = time (s).

3. Refractive index. Abbe refractometer was used, oil was dripped on the surface of the glass preparation that had been previously cleaned with ethanol. The reading of the refractive index was observed when the bright and dark dividing line was right at the cross of the observation lens. It was performed at a temperature of 26 °C. For the calculation used the Eq 3:

$$n = n' + k(T' - T) \tag{3}$$

Which n = refractive index (25 °C), n′ = refractive index (observed temperature), k = correction factor (0.00045), T = 25 °C), and T′ = observed temperature.

4. Acid number. To test the acid number, 1.00 g of CPO was put into a 100 mL Erlenmeyer and then 5.00 mL of alcohol was added. The mixture was heated in a boiling water bath for 10 min. The mixture was then added to the phenolphthalein indicator and then it was titrated with 0.1 N·KOH (which has been standardized with oxalic acid) until a pink colour was formed. To determine the number of acids used the Eq 4:

$$\text{acid number}= \frac{\left\{\text{volume (mL)} \times \text{Normality (N)} \times \text{molecular weigh } \left(\frac{\text{g}}{\text{mol}}\right)\right\} \text{ of KOH}}{\text{sample mass (g)}} \tag{4}$$

5. Saponification number. 0.5 grams of the synthesized methyl ester was added into 250 mL Erlenmeyer with 5 mL n-hexane and 25 mL KOH 0.5 M. The mixture was stirred until homogeneous. The mixture was then heated to boiling for 30 min. The mixture was then cooled at room temperature. The mixture with 5 drops of Phenolphthalein indicator was titrated with HCl 0.5 M. The titration was also carried out on a blank sample.

$$\text{saponification number} = \frac{(V_2 - V_1) \times M \times \text{molecular weigh } \left(\frac{\text{g}}{\text{mol}}\right) \text{ of KOH}}{\text{sample mass (g)}} \tag{5}$$

In Eq 5, Which V_2 = Volume of HCl for blank titration (mL), V_1 = Volume of HCl for sample titration (mL), and M = molarity of HCl (mol/L).

2.3. Corrosion test of methyl ester on iron nails

Corrosion testing was carried out using the immersion test method based on ASTM G-31. Corrosion test procedures were carried out as follows: Iron nails were sanded for 10 min to clean dirt and corrosion crust on the surface. Then, it was rinsed with acetone. After drying, the nails were weighed. Then, each of the nails was dipped in the methyl ester samples in a test tube for 40 d at room temperature and 70 °C. After that, it was dried in an oven to evaporate the remaining methyl ester with a temperature of 200 °C until a constant weight was obtained. Next, it was continued with weighing to determine the amount of mass lost due to corrosion. So, the corrosion rate was measured. In addition, the remaining nails were analysed by Scanning Electron Microscopy (SEM).

Corrosion rate (mpy–millimetre per year) was calculated as Eq 6 [17,18]:

$$\text{corrosion rate (mpy)} = 8.76 \times \frac{\Delta \text{ m}}{(\rho \times t \times A)} \quad (6)$$

Which Δm = final mass (g)−initial mass (g), ρ = density (g/mL), t = dip time (hour), and A = area (m^2).

3. Results

3.1. Synthesis of methyl ester of palm oil, candlenut oil, and sunflower seed oil

Transesterification of palm oil and sunflower seed oil was evaluated by TLC. The TLC test results showed a large difference in Rf between the two nodes (vegetable oil and synthetic product) after 4 h of synthesis (Figure 1). The Rf value can be used as evidence in identifying the compound, if the identification of the Rf value produces the same value, the compound can be said to have the same or similar characteristics. If the Rf value is different, the compound can be said to be a different compound [19,20]. Importantly, the TLC test result did not show 100% formation of methyl ester. It was a qualitative analysis as the indicator of the occurred transesterification. Therefore, it was strongly indicated that a reaction product (methyl ester) has been formed because the Rf of the initial compound (vegetable oil) and the synthesized compound were different.

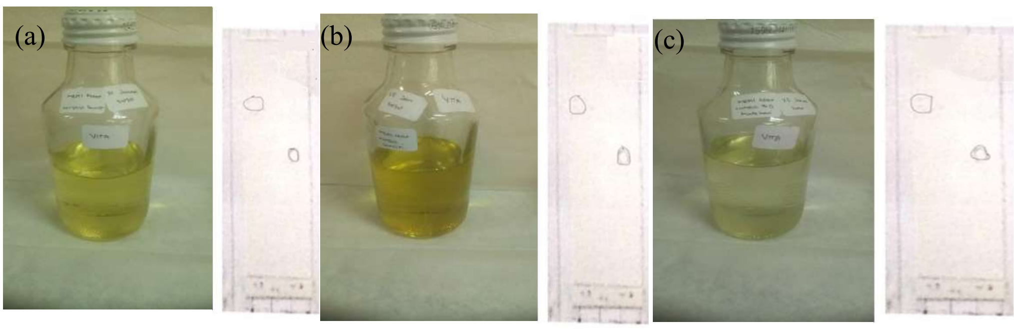

Figure 1. Methyl ssters of: (a) palm oil, (b) candlenut oil, and (c) sunflower seed oil.

The results of the obtained methyl ester can be seen in Figure 1. The yield of methyl ester from palm oil was 74.34%, while the yield of methyl ester from sunflower seed oil was 75.65%. The yield of methyl ester from candlenut oil was 76.40%. The reaction that occurs between triglycerides and 3 moles of methanol with a KOH catalyst produces 3 mol of methyl ester and 1 mol of glycerol in the transesterification process [7]. The reaction can take place completely if an excess of methanol is added to form a product. Also, catalysts are used to speed up the formation of methyl esters.

3.2. Characteristic of methyl ester of palm oil, candlenut oil, and sunflower seed oil

The results of the synthesis of methyl esters of palm oil, candlenut oil, and sunflower seed oil were characterized as shown in Table 1.

Table 1. Characterization of synthesis of methyl esters and oils.

parameter	SNI 7182:2015	Palm		Candlenut		Sunflower Seed	
		methyl ester	Oil	methyl ester	Oil	methyl ester	Oil
density (g/mL)	0.85–0.89	0.879	0.946	0.887	0.957	0.880	0.951
viscosity (cSt)	2.3–6.0	5.88	71.88	4.48	46.93	5.78	71.02
refractive index	1.3–1.45	1.444	1.471	1.445	1.476	1.448	1.472
acid number (mg KOH/g)	max 0.5	0.55	2.65	0.46	5.21	0.49	2.36
saponification number (mg·KOH/g)		184.8	224.0	198.8	254.8	156.8	198.8

Based on the results of the density data in Table 1, the three types of oil showed that the density of methyl esters is lower than the density of vegetable oils, because the molecular weight of methyl esters was lower, so the intermolecular forces on fatty acid methyl esters were smaller than the intermolecular forces molecules in the oil. The greater the intermolecular forces, the more difficult it for the substance to flow, the more viscous the liquid and the greater the viscosity [21]. Based on the results of the viscosity data in Table 1, the three types of oil showed that the viscosity of methyl esters is lower than the viscosity of vegetable oils, because the molecular weight of methyl esters was smaller than that of oil, so the liquid was not thick and it flowed easily. The value of the refractive index aimed to determine the purity of the methyl ester produced. Based on the results of the refractive index data in Table 1, the three types of oil showed that the refractive index of methyl esters is lower than the refractive index of vegetable oils, because the refractive index of a compound will decrease as the carbon chain and double bonds of the compound decrease. Based on the results of the acid number data in Table 1, the three types of oil indicate that the methyl ester acid number is lower than the vegetable oil acid number, because the smaller the acid number, the smaller the free fatty acids contained in the oil. The smaller the saponification number, the longer the alkyl chain attached to the oil. In addition, the smaller the number of saponification, the smaller the number of milligrams and the number of moles of the required KOH, and the large number of mg·KOH indicated the large number of methyl ester molecules. Based on the results of the saponification number data in Table 1, the three types of oil indicated that the saponification number of methyl esters is lower than the saponification number of vegetable oils, because to saponify one molecule of methyl ester it took one molecule of KOH, while one molecule of triglycerides requires three molecules of KOH. The required KOH to saponify methyl esters is less than the required KOH to saponify triglycerides [22].

Finally, the resulting free fatty acid content was 1.39% palm oil and 1.11% sunflower seed oil. The content values have met the requirements for the transesterification process of < 2%. In candlenut oil, the produced free fatty acid content was 2.55%, the value of the content did not meet the requirements for the transesterification process, so it is necessary to carry out an esterification to reduce the value of free fatty acid levels in candlenut oil. High concentrations can interfere with the transesterification reaction, due to the free fatty acids reacting with a base, so that the reaction products produce soap and it inhibits the formation of maximum products.

3.3. Identification of component of the synthesized methyl ester

GC results of palm oil, candlenut oil, and sunflower seed oil showed the number of methyl ester components based on the number of peaks produced as shown in Figure 2.

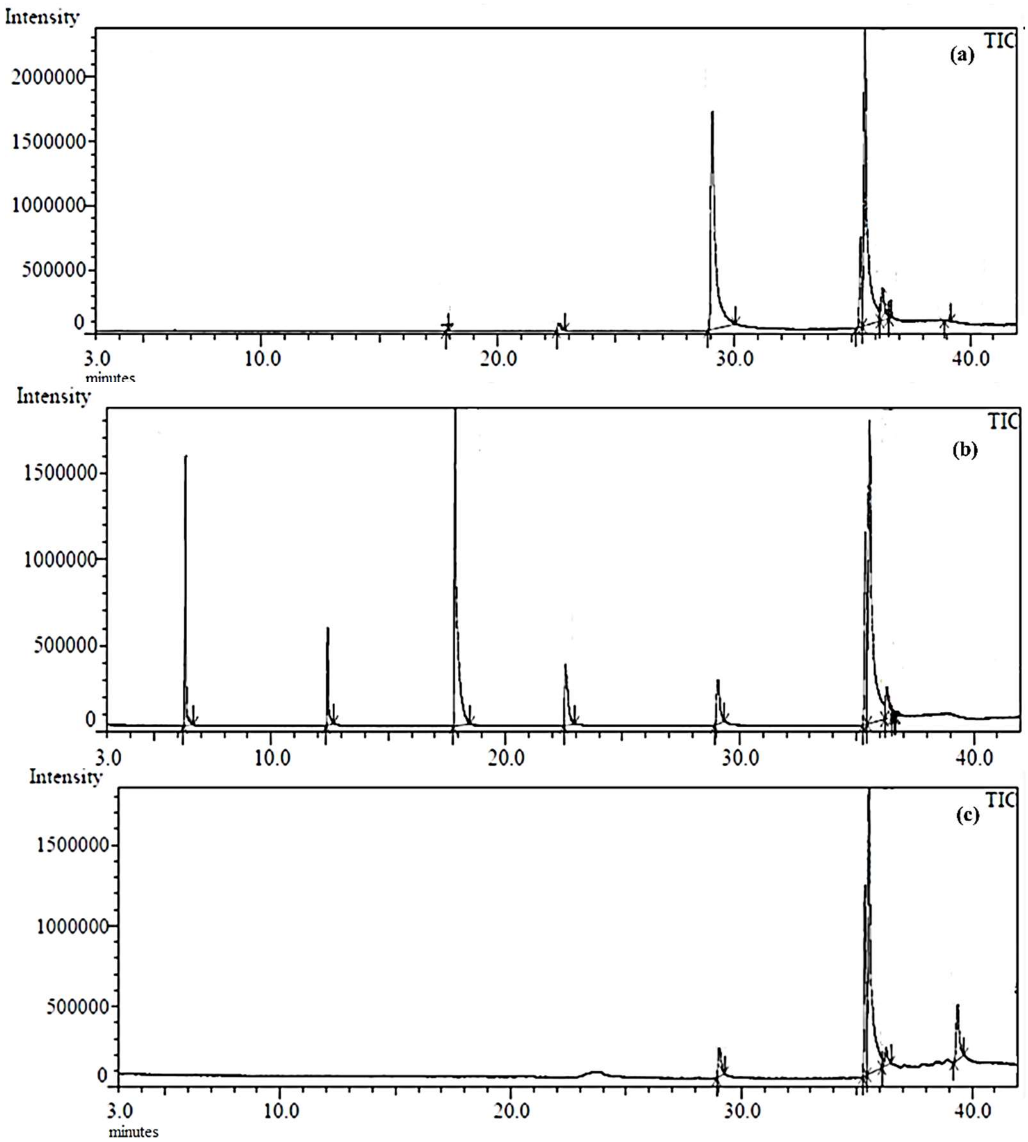

Figure 2. Chromatogram of methyl ester from (a) palm oil, (b) candlenut oil, and (c) sunflower seed oil.

The chromatogram showed that there were components of the sample. Then, the main components of fatty acid methyl esters were analysed by MS based on their fragmentation. Mass spectrum analysis has been referred as the WILEY8.LIB library and analysis of fragmentation patterns (data not shown here). The retention time and area of the main components of fatty acid methyl esters were shown in Table 2.

Table 2. Retention time and area of main components of methyl ester of palm oil, candlenut oil, and sunflower seed oil.

Peak to	Retention Time (min)	Area	Content (%)	Compound
Palm Oil				
3	29.089	22662901	41.16	methyl palmitate
4	35.360	4384965	7.96	methyl linoleate
5	35.549	22902966	41.60	methyl oleate
6	36.283	2443446	4.44	methyl stearate
Candlenut Oil				
1	6.3330	5095971	9.19	methyl caprylate
2	12.412	2091120	3.77	methyl caprate
3	17.846	13146807	23.71	methyl laurate
4	22.562	3269184	5.90	methyl myristate
5	29.086	2457367	4.43	methyl palmitate
6	35.369	6683214	12.05	methyl linoleate
7	35.554	19431707	35.04	methyl oleate
8	36.287	1894515	3.42	methyl stearate
Sunflower Seed Oil				
1	29.049	1659589	4.73	methyl palmitate
2	35.355	654953	18.67	methyl linoleate
3	35.532	16413036	46.79	methyl oleate
4	36.275	1103121	3.14	methyl stearate

Based on the results of the GC-MS test, it can be stated that the synthesis of palm oil was a methyl ester compound. The largest methyl ester content was methyl oleate at 41.60%, so the components of the methyl ester indicated that biodiesel from palm oil contained high amounts of unsaturated fatty acids. However, palm oil also contained a fairly high amount of saturated fatty acids, namely methyl palmitate of 41.16%. The largest methyl ester from candlenut oil was methyl oleate about 35.04%. The largest methyl ester from sunflower seed oil was methyl oleate about 46.79%, so that the constituent components of the methyl ester indicated that biodiesel from sunflower seed oil contained high amounts of unsaturated fatty acids.

4. Discussion

The characteristic of the synthesized methyl ester was clear. For more study, the synthesized methyl ester was tested about corrosiveness properties. As a preliminary study, the corrosiveness properties were performed by corrosion phenomena in iron nails.

Differences in the raw materials used for biodiesel production will produce biodiesel with varying properties. Biodiesel contains components of saturated esters and unsaturated esters which tend to be unstable, sensitive to light, temperature, and metal ions [8]. The content of biodiesel can affect the stability of biodiesel against oxidation by oxygen in the air. The high content of unsaturated fatty acids (methyl oleic and methyl linoleic) tends to cause biodiesel to be easily oxidized by air to form free radicals that lead to the formation of corrosive organic compounds [23] or also leads to reactions that form new products such as aldehydes, ketones, lactones, formic acid, acetic acid, and propionic acid [24], especially such as defect/unknown product [25].

The corrosion test was shown in Figure 3. The corrosion test showed that the corrosion rate of the nail immersed in biodiesel was affected by temperature, and the test was carried out at room temperature and temperature of 70 °C. It was carried out for 40 d, because the corrosion effect did not show after 10, 20, 30 d significantly.

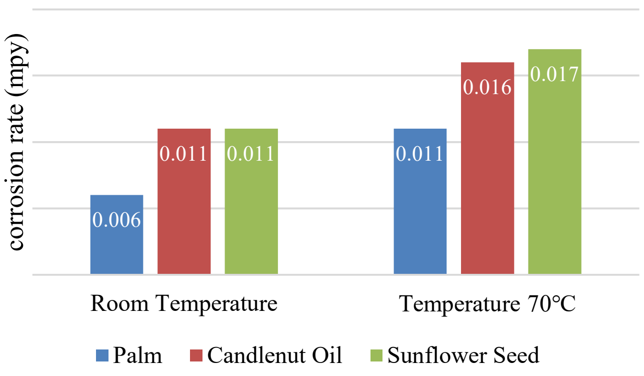

Figure 3. Corrosion rate of iron nails in methyl esters from palm oil, candlenut oil, and sunflower seed oil.

The data in Figure 3 showed that the corrosion rate of the immersed ferrous nail in biodiesel was affected by temperature. Corrosion test results showed that increasing the temperature of biodiesel will tend to increase the corrosion rate of ferrous nails because increasing the temperature of biodiesel will increase the kinetic energy of molecules so the interaction of molecules will increase, including the amount of the absorbed oxygen [18]. On the other hand, the figure showed that the various oil feedstock used to produce biodiesel could also affect its corrosive properties [10]. For previous study, the corrosion phenomena listed in Table 3. The two types of biodiesels, namely methyl esters of candlenut oil and sunflower seed oil, had components containing unsaturated fatty acids with more carbon double bonds and less hydrogen, so it was susceptible to oxidation. The oxidation of biodiesel can reduce the quality of fuel for the engine due to the formation of oxidation products such as aldehydes, alcohols, short chain carboxylic acids, and sediments [26]. However, methyl ester of palm oil has the opposite result, because it has a component containing a fairly high content of unsaturated fatty acids, and a high content of saturated fatty acids. According to previous study [27], composition of fatty acids was strongly linear related to the corrosion rate in gray cast iron. Besides, higher content of unsaturated fatty acids in biodiesel, greater effect on the corrosion in gray cast iron [10,27]. So, this demonstration work showed different corrosion rates because of the difference in chemical compounds and characteristics of the synthesized methyl esters.

Table 3. Corrosion phenomena on iron based-alloys of methyl esters.

methyl ester from	sample	Conditions	Time (h)	Corrosion rate (mpy)	Ref.
sun flower	gray cast iron (93.41% Fe)	T = 18 °C, P = 74.46 kPa	450	0.0028	[27]
soybean				0.0019	
lard				0.0016	
tallow				0.0013	
coconut				0.0011	
moringa	mild steel (98.8% Fe)	T = 60 °C	1100	0.0005	[28]
palm	gray cast iron (94.2% Fe)	T = 25 °C	1200	0.0020	[29]
palm	gray cast iron (94.2% Fe)	T = 25 °C	2880	0.0028	[30]
rapeseed	mild steel (22.71% Fe)	T = 43 °C	1440	0.01819	[17]

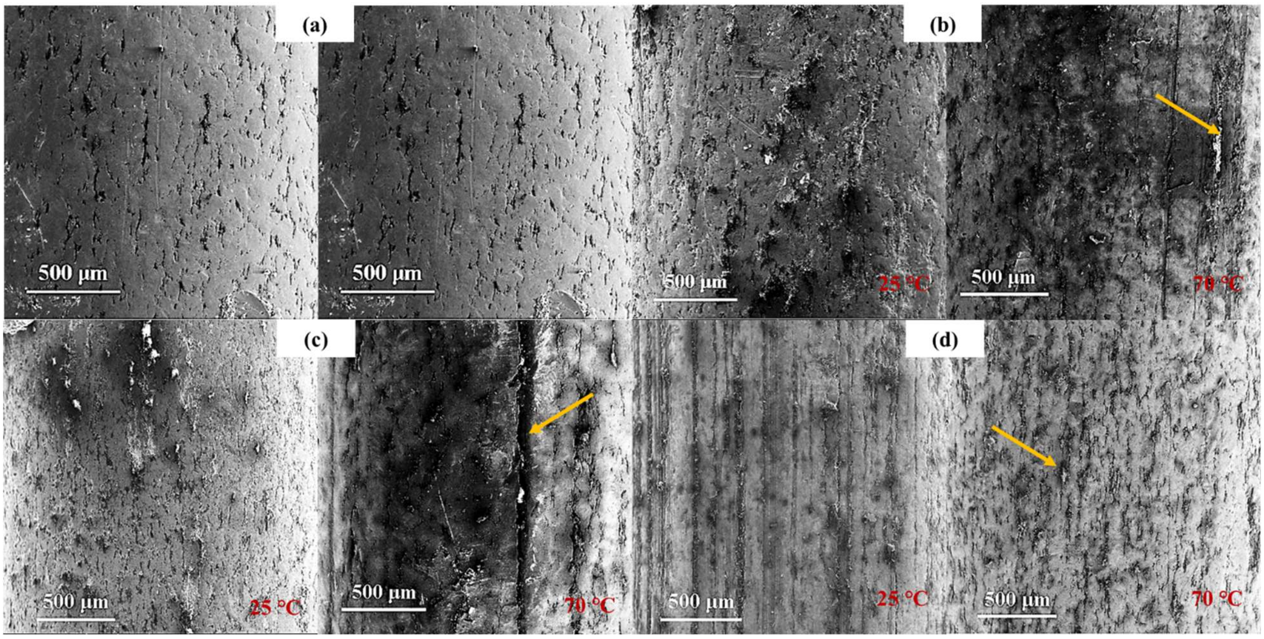

Figure 4. SEM of: (a) ferrous nail before immersion test and after immersion test in biodiesel from: (b) palm oil, (c) candlenut oil, and (d) sunflower seed oil.

The SEM results in Figure 4 showed that the corrosion was spread on the ferrous surface marked by the formation of dark coloured pits, also obtained in the previous study [17,31,32]. The increasing temperature will lead to an increase in the size of the hole (pit) and will spread evenly on the iron nail. This was because the corrosion rate of iron increases with increasing temperature. The nail surface in contact showed the damage, due to corrosion in biodiesel. These nails were very reactive to organic acids formed due to the degradation process in biodiesel. According to previous study [17], elemental composition of corrosion phenomenon on mild steel by XPS results (at%: atomic percentage of metal element) were C (26.28%), O (51.01%), Fe (22.71%) before corrosion and C (42.7%), O (43.55%), and Fe (13.75%) after corrosion. Compared with this demonstration study, it was correlated that Fe content of iron nail reduces after immersion test.

The chemical reactions describing the corrosion mechanism of iron-based alloys in biodiesel are presented in Eqs 7–11 [33]. In this work, iron may be oxidized as an oxide compound and methyl ester may be produced hydrocarbon derivatives.

$$4Fe + 3O_2 \rightarrow 2Fe_2O_3 \quad (7)$$

$$2Fe + O_2 + H_2O \rightarrow 2Fe(OH)_2 \quad (8)$$

$$4Fe(OH)_2 + O_2 \rightarrow 2Fe_2O_3{\cdot}H_2O + 2H_2O \quad (9)$$

$$RCOOR_1 \rightarrow RCOO^* + R_1^* \quad (10)$$

$$2RCOO^* + Fe \rightarrow FeCO_3 + R - R + CO \quad (11)$$

Based on Figure 4, it is possible that the nail weight will be reduced after the immersion test. The presence of dissolved nails in biodiesel can accelerate the catalytic reaction of the biodiesel degradation process, because nails can directly react with fatty acids to produce fatty acid alkyl radicals [34]. During the oxidation process of biodiesel by oxygen in the air, methyl esters from biodiesel formed free radicals and double bonds that form new products such as aldehydes, ketones, lactones, formic acid, acetic acid, and propionic acid [24]. Biodiesel is hygroscopic because it easily absorbs moisture and water, so that it can form dew on nail surfaces that have the potential to cause corrosion [26].

5. Conclusions

The study has resulted in the following conclusions: (1) synthesis of methyl esters by base-catalysed transesterification (KOH) can be carried out on palm oil, candlenut oil and sunflower seed oil, but esterification was carried out first to reduce free fatty acid levels in candlenut oil, (2) the characteristics of the synthesized methyl esters from various vegetable oils (palm oil, candlenut oil, and sunflower seed oil) were carried out with the parameters of density, viscosity, refractive index, and acid number, and met requirements of the biodiesel standards of SNI7182 : 2015, (3) the components of the methyl esters from candlenut oil and sunflower seed oil contained high amounts of unsaturated fatty acids, while the components of methyl esters from palm oil contained a fairly high content of unsaturated fatty acids, and a high content of saturated fatty acids, and (4) the unsaturated fatty acid content of the three types of vegetable oil caused biodiesel to be easily oxidized by oxygen in the air. Corrosion rates of the methyl ester of palm oil, candlenut oil, and sunflower seed oil were 0.006 mpy, 0.011 mpy, and 0.011 mpy respectively at room temperature, and also 0.011 mpy, 0.016 mpy, and 0.017 mpy, respectively at 70 °C. Therefore, biodiesel from candlenut oil and sunflower seed oil was more corrosive than palm oil based on SEM results. It was indicated by the formation of pits. The corrosiveness problem will be a challenge regarding the produced by-products and their effects.

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Conflict of interest

The authors declare no conflict of interest.

References

1. Silalahi FTR, Simatupang TM, Siallagan MP (2020) Biodiesel produced from palm oil in Indonesia: Current status and opportunities. *AIMS Energy* 8: 81–101. https://doi.org/10.3934/energy.2020.1.81
2. Abas N, Kalair A, Khan N (2015) Review of fossil fuels and future energy technologies. *Futures* 69: 31–49. https://doi.org/10.1016/j.futures.2015.03.003
3. Santoso A, Sumari, Joharmawan R, et al. (2019) Catalytic cracking of waste frying oil using Ni-Fe/activated zeolite catalyst as a source of renewable energy. *IOP Conf Ser: Mater Sci Eng* 509: 12009. https://doi.org/10.1088/1757-899X/509/1/012009
4. Santoso A, Rizky M, Sumari S, et al. (2021) Pengaruh jenis alkohol pada sintesis alkil ester dari CPO melalui reaksi transesterifikasi menggunakan katalis heterogen CaO-MgO. *RBAET J* 5: 1–9. https://rbaet.ub.ac.id/index.php/rbaet/article/view/86
5. Santoso A, Sumari, Salim A, et al. (2018) Synthesis of methyl ester from chicken oil and methanol using heterogeneous catalyst of CaO-MgO as well as characterization its potential as a biodiesel fuel. *J Phys Conf Ser* 1093: 12035. https://doi.org/10.1088/1742-6596/1093/1/012035
6. Sumari, Murti M, Santoso A, et al. (2022) Sono-Transesterification of Kapok seed oil with CaO: BaO-(x:y)/active natural zeolite catalyst. *J Renew Mater* 10: 3659–3670. https://doi.org/10.32604/jrm.2022.022995
7. Sumari S, Santoso A, Asrori MR (2021) A review: Synthesis of biodiesel from low/off grade crude palm oil on pretreatment, transesterification, and characteristics. *Orbital: Electron J Chem* 13: 385–391. http://dx.doi.org/10.17807/orbital.v13i4.1632
8. Jin D, Zhou X, Wu P, et al. (2015) Corrosion behavior of ASTM 1045 mild steel in palm biodiesel. *Renew Energ* 81: 457–463. https://doi.org/10.1016/j.renene.2015.03.022
9. Fazal MA, Jakeria MR, Haseeb ASMA (2014) Effect of copper and mild steel on the stability of palm biodiesel properties: A comparative study. *Ind Crops Prod* 58: 8–14. https://doi.org/10.1016/j.indcrop.2014.03.019
10. Hoang AT, Tabatabaei M, Aghbashlo M (2020) A review of the effect of biodiesel on the corrosion behavior of metals/alloys in diesel engines. *Energ Source Part A* 42: 2923–2943. https://doi.org/10.1080/15567036.2019.1623346
11. Shaah MAH, Hossain MS, Allafi FAS, et al. (2021) A review on non-edible oil as a potential feedstock for biodiesel: physicochemical properties and production technologies. *RSC Adv* 11: 25018–25037. http://dx.doi.org/10.1039/D1RA04311K
12. Issariyakul T, Dalai AK (2014) Biodiesel from vegetable oils. *Renew Sust Energ Rev* 31: 446–471. https://doi.org/10.1016/j.rser.2013.11.001
13. Tambun R, Tambun JOA, Tarigan IAA, et al. (2020) Activating lipase enzyme in the candlenut seed to produce fatty acid directly from candlenut seed. *J Phys: Conf Ser* 1542: 12006. http://dx.doi.org/10.1088/1742-6596/1542/1/012006
14. Rashid U, Anwar F, Moser BR, et al. (2008) Production of sunflower oil methyl esters by optimized alkali-catalyzed methanolysis. *Biomass Bioenergy* 32: 1202–1205. https://doi.org/10.1016/j.biombioe.2008.03.001

15. Santoso A, Putri DEK, Rusdi M, et al. (2021) The effect of basic catalyst concentration on tobacco oil transesterification (Voor-Oogst) using ultra-sonic wave and its potential as renewable energy. *AIP Conf Proc* 2330: 070008. https://doi.org/10.1063/5.0043406
16. Santoso A, Wijaya AR, Purwaningtyas CF, et al. (2020) The effect of K_2O concentration in K_2O/Al_2O_3 catalyst on methyl ester (biodiesel) synthesis from CPO off grade with ultrasonic wave. *IOP Conf Ser: Mater Sci Eng* 833: 012043. https://doi.org/10.1088/1757-899X/833/1/012043
17. Hu E, Xu Y, Hu X, et al. (2012) Corrosion behaviors of metals in biodiesel from rapeseed oil and methanol. *Renew Energ* 37: 371–378. https://doi.org/10.1016/j.renene.2011.07.010
18. Setiawan A, Nugroho A (2016) Analisis korosivitas biodiesel yang diproduksi dari minyak goreng bekas terhadap material baja karbon. *Seminar MASTER* 1.
19. Fontana JD, Zagonel G, Vechiatto WW, et al. (2009) Simple TLC-screening of acylglycerol levels in biodiesel as an alternative to GC determination. *J Chromatogr Sci* 47: 844–846. https://doi.org/10.1093/chromsci/47.9.844
20. Fedosov SN, Brask J, Xu X (2011) Analysis of biodiesel conversion using thin layer chromatography and nonlinear calibration curves. *J Chromatogr A* 1218: 2785–2792. https://doi.org/10.1016/j.chroma.2011.01.067
21. Atabani AE, Silitonga AS, Badruddin IA, et al. (2012) A comprehensive review on biodiesel as an alternative energy resource and its characteristics. *Renew Sust Energ Rev* 16: 2070–2093. https://doi.org/10.1016/j.rser.2012.01.003
22. Kumar H, Sarma AK, Kumar P (2020) A comprehensive review on preparation, characterization, and combustion characteristics of microemulsion based hybrid biofuels. *Renew Sust Energ Rev* 117: 109498. https://doi.org/10.1016/j.rser.2019.109498
23. Wang W, Li F, Li Y (2020) Effect of biodiesel ester structure optimization on low temperature performance and oxidation stability. *J Mater Res Technol* 9: 2727–2736. https://doi.org/10.1016/j.jmrt.2020.01.005
24. Sarin A, Arora R, Singh NP, et al. (2009) Influence of metal contaminants on oxidation stability of Jatropha biodiesel. *Energy* 34: 1271–1275. https://doi.org/10.1016/j.energy.2009.05.018
25. Asrori MR, Santoso A, Sumari S (2022) Initial defect product on immiscible mixture of palm oil: Ethanol by amphiphilic chitosan/Zeolite LTA as optimization of microemulsion fuel. *Ind Crops Prod* 180: 114727. https://doi.org/10.1016/j.indcrop.2022.114727
26. Pullen J, Saeed K (2012) An overview of biodiesel oxidation stability. *Renew Sust Energ Rev* 16: 5924–5950. https://doi.org/10.1016/j.rser.2012.06.024
27. Castro JD, Piamba OE, Olaya JJ (2016) Corrosiveness of biodiesel obtained from different raw materials on gray cast iron. *CT F-Cienc Tecn Fut* 6: 79–88. https://doi.org/10.29047/01225383.05
28. How HG, Hwang JWS, Teoh YH (2020) Investigation of the corrosion metals in moringa biodiesel fuel. *J Adv Res Fluid Mech Therm Sci* 75: 94–103. https://doi.org/10.37934/arfmts.75.1.94103
29. Fazal MA, Haseeb ASMA, Masjuki HH (2011) Effect of different corrosion inhibitors on the corrosion of cast iron in palm biodiesel. *Fuel Process Technol* 92: 2154–2159. http://dx.doi.org/10.1016/j.fuproc.2011.06.012
30. Fazal MA, Haseeb ASMA, Masjuki HH (2012) Degradation of automotive materials in palm biodiesel. *Energy* 40: 76–83. https://doi.org/10.1016/j.energy.2012.02.026
31. Jakeria MR, Fazal MA, Haseeb ASMA (2015) Effect of corrosion inhibitors on corrosiveness of palm biodiesel. *Corros Eng Sci Technol* 50: 56–62. https://doi.org/10.1179/1743278214Y.0000000208

32. El Hawary M, Khachani M, Benhiba F, et al. (2022) Investigation of the corrosion of stainless steel, copper and aluminium in sunflower biodiesel solution: Experimental and theoretical approaches. *Chem Data Collect* 40: 100870. https://doi.org/10.1016/j.cdc.2022.100870
33. Cursaru DL, Brănoiu G, Ramadan I, et al. (2014) Degradation of automotive materials upon exposure to sunflower biodiesel. *Ind Crops Prod* 54: 149–158. https://doi.org/10.1016/j.indcrop.2014.01.032
34. Squissato AL, Neri TS, Coelho NMM, et al. (2018) In situ electrochemical determination of free Cu(II) ions in biodiesel using screen-printed electrodes: Direct correlation with oxidation stability. *Fuel* 234: 1452–1458. https://doi.org/10.1016/j.fuel.2018.08.027