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Biodiesel production process without glycerol by-product with base catalyst: effect of reaction time and type of catalyst on kinetic energy and solubility

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Abstract. Biodiesel is a renewable energy that is very potential to be produced because it has many advantages compared to diesel fuel. The process of making biodiesel which has so far been carried out is a transesterification process with glycerol byproducts. Glycerol has a low economic value and is usually only disposed of as waste. An alternative process for producing biodiesel with more valuable byproducts is interesterification. The by-product of the interesterification reaction is triacetin which is widely used in the chemical, food and pharmaceutical industries. From the analysis and calculation, the highest FAME yield was 87.18% at reaction temperature 60°C, the molar ratio of palm oil: methyl acetate = 1: 6, reaction time 1 hour, NaOH catalyst, stirring speed of 400 rpm and catalyst mass of 0.5% wt. oil. From the calculation of ChemDraw software for the triglyceride + methyl acetate + NaOH system had an energy kinetic of 2930.8062 kcal/kmol and a dipole moment of 12582.9333 debye, whereas the triglyceride + methyl acetate + KOH system had a kinetic energy of 3140.9573 kcal/kmol and a dipole moment of 9630.3735 debye so that the NaOH catalyst is superior in solubility and the KOH catalyst is superior in reactivity. Biodiesel produced had an acid value of 0.224 mg KOH/g and meets ASTM D664 for a maximum acid value of 0.5 mg KOH/g, and a density of 0.888 g/ml so that meets ASTM D1298 for a density between 0.86 – 0.89 g/ml.

1. Introduction

Currently, the need for fuel oil is increasing along with the increasing population and the development of technology, however, petroleum reserves derived from fossils are dwindling because of their non-renewable nature. Therefore, many efforts have been made to find alternative energy sources that can be renewed (renewable). One of the alternative energy sources that are currently being developed is fatty acid methyl ester (FAME) which is commonly known as Biodiesel. Biodiesel is a promising alternative fuel that can be made from waste cooking oil, animal fat or vegetable oil which is converted into methyl esters by transesterification with alcohol. When compared to diesel fuel, biodiesel is more environmentally friendly, renewable, biodegradable, has lubricating properties for piston engines because it belongs to the non-drying oil group, capable of eliminating the effect greenhouse, and the guaranteed availability of its raw materials. Biodiesel is environmentally friendly because it produces



exhaust emissions that are far better than diesel fuel, which is sulfur-free, low smoke number, and cetane number ranging from 57-62 so that combustion efficiency is better, burning perfect (clean burning) and does not produce toxins (nontoxic).

The general process for making biodiesel is the transesterification process with alcohol (methanol) which functions to supply alkyl (methyl) groups. In this process, a glycerol byproduct is produced, which is a relatively difficult separation process. The presence of glycerol in biodiesel disrupts engine performance. The new method that will be developed is to change the reaction route from using alcohol to a reaction route that does not use alcohol. The non-alcoholic reaction route can be done by replacing alcohol with an alkyl acetate which both functions as an alkyl supply. In the non-alcohol route of biodiesel synthesis, methanol can be replaced with methyl acetate as a supplier of methyl groups. In the interesterification process, the resulting by-product is triacetin which can be used as an additive in biodiesel to reduce knocking in car engines and reduce emissions [1]. The addition of 9% triacetin to biodiesel still provides results that meet biodiesel quality standards [2]. Triacetin can be used as a plasticizer, polymer and as a fuel bioadditive [3, 4].

Several studies on the interesterification process using homogeneous catalysts have been carried out. The homogeneous catalyst has the advantage that the reaction rate is faster [5]. Casas et al. [6] conducted interesterification of sunflower oil with CH_3OK catalyst and obtained 40% FAME mass fraction at 10 minutes reaction time. Kusumaningtyas et al. [7] obtained 9% yield in the interesterification of castor oil at 60°C , the molar ratio of oil: ethyl acetate = 1:6 and reaction time of 8 hours. Chuepeng and Komintarachat [8] obtained 50% yield on the interesterification of waste cooking oil with CH_3COOH catalyst at a reaction temperature of 80°C , the molar ratio of oil: ethyl acetate = 1:30, and a reaction time of 3 hours. Packaged palm oil has an initial % FFA (0.124%) and a moisture content (0.0496%) [9]. In the esterification process, palm oil has the highest yield compared to *Calophyllum inophyllum* oil, castor oil and waste cooking oil [10]. In transesterification of used cooking oil from palm oil with Fresnel solar concentrator, obtained biodiesel with physical properties as FFA (0.14%), density (0.871 g/cm^3) and kinematic viscosity ($3.9 \text{ mm}^2/\text{sec}$) [11].

This research aimed to find the optimum condition of mass NaOH catalyst and reaction time in the interesterification process of palm oil into methyl ester and triacetin. Also, to compare the performance of NaOH and KOH catalysts in the interesterification process in terms of their role as a solvent in accelerating the reaction.

2. Material and Methods

2.1. Material

The materials used are palm oil, aqua dest, oxalic acid, KOH (Riedel-de Haen, 99%), NaOH (Riedel-de Haen, 99%), methyl acetate (Sigma Aldrich, 99.9%), indicator PP, acetone (Merck, 99.8%), CH_3COOH (Sigma Aldrich, 99.7%).

2.2. Raw material preparation

Palm oil was analyzed for FFA concentration and water content. If the FFA concentration is $< 3\%$ and the water content is $\leq 0.6\%$, it can be directly used for the interesterification reaction. If the FFA concentration is $> 3\%$, an esterification reaction is carried out and if the water content is $> 0.6\%$, evaporation is carried out in an oven at 110°C until the mass is constant.

2.3. Interesterification reaction with the base catalyst

Palm oil (250 g), methyl acetate (molar ratio of oil: methyl acetate = 1: 6) and NaOH catalyst (0.25; 0.5; 0.75% oil mass) were weighed according to the research variables. Palm oil was put into a three-neck flask, methyl acetate and catalyst were put into a separate Erlenmeyer, then each material was heated at 60°C . After the reaction temperature of 60°C was reached, the methyl acetate and catalyst were put into a three-neck flask containing palm oil which has been heated to 60°C with a hot plate. After all the ingredients were put in a three-neck flask equipped with a condenser for reflux, stirring was carried out with a magnetic stirrer with a stirring speed of 400 rpm and the calculation of the reaction time was started according to the research variables (15, 30, 45, 60 and 75 minutes). After the reaction time has

been reached, 20 g of the sample from the reaction was taken for separation and purification processes. The optimum conditions for the interesterification reaction time with NaOH catalyst were used for variable interesterification reactions with KOH catalysts with variations in the mass of the catalyst (0.25; 0.5; 0.75% oil mass). The other operating conditions are the same as the interesterification reaction with NaOH catalyst.

2.4. Separation and purification

The sample resulting from the reaction was then added with hot water at 60°C as much as 50% of the sample volume and also 0.03% acetic acid of the sample volume. The mixture was then stirred with a magnetic stirrer at 300 rpm for 20 minutes. The sample was then put in a separating funnel for 1 hour to separate the washing product and the methyl ester. In the separating funnel, 2 layers will be formed, namely, the top layer is a non-polar compound, namely methyl ester, methyl acetate and oil from the reaction. While the bottom layer is a polar compound, namely triacetin, water and the result of the catalyst neutralization reaction. Washing was repeated until the water was clear and pH neutral [12]. After the washing water was clear and pH neutral, the top layer was then distilled at 105°C to separate the methyl acetate and the rest of the washing water. Distillation was carried out until no distillate drips [13]. The residue from distillation, namely methyl ester and the residual oil of the reaction was weighed as the mass of the product. Calculating the yield with equation (1):

$$\text{Yield (\%)} = \frac{\text{mass of product}}{\text{mass of initial oil}} \times 100\% \quad (1)$$

2.5. Analysis

2.5.1. Density analysis

An empty pycnometer was weighed and its mass recorded. The sample was inserted into the pycnometer and its mass recorded. Density was calculated by equation (2):

$$\text{Density} = \frac{\text{mass of pycnometer fill} - \text{mass of pycnometer empty}}{\text{volume of pycnometer}} \quad (2)$$

2.5.2. Acid number analysis [14]

0.5-g sample was put into Erlenmeyer and 50 ml acetone was added. The sample was then added with 3 drops of PP indicator and titrated with 0.1 M KOH solution until it was pink. The pink colour should last for at least 15 seconds. The acid number was calculated by equation (3):

$$\text{Acid number} = \frac{(56.1 \times \text{volume of KOH} \times M \text{ KOH})}{\text{mass of sample}} \quad (3)$$

2.5.3. Methyl ester analysis

FAME composition analysis using Gas Chromatography (GC) of the Shimadzu brand with the following data:

- Column: BPX5 0.25 μ m, 12 m x 0.53 mm ID
- Initial temp: 100 C, 0.5 min
- Rate 1: 50 C / min
- Temp: 280 C
- Rate 2: 10 C / min
- Final temp: 360 C, 5 min
- Carrier gas: He, 5 min
- Detector: FID
- Injection mode: on column (OCI-5)
- Injection volume: 1 μ l

3. Result and Discussion

3.1. Raw material preparation

From the results of the initial analysis, it was found that the water content of oil was 0.015% and FFA 0.15% so that the oil could be used directly in the transesterification reaction.

3.2. Transesterification reaction with the base catalyst

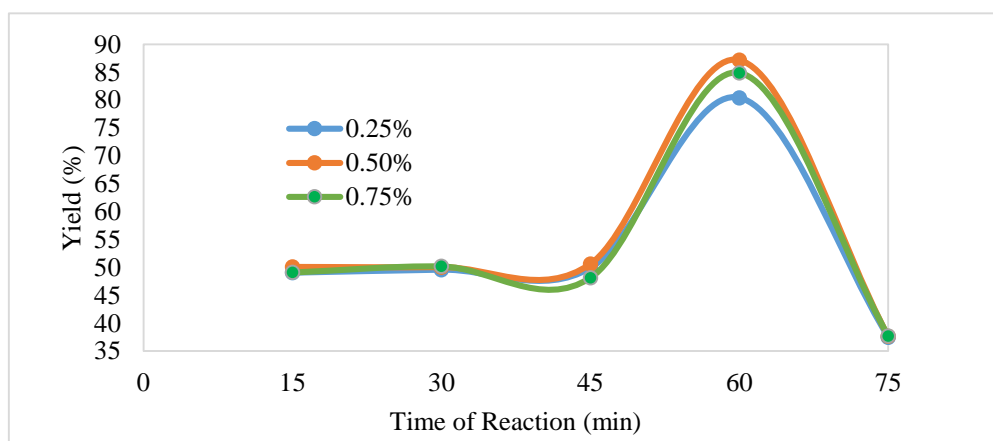


Figure 1. The relationship between reaction time (minutes) and yield (%) with variations in the mass of NaOH catalyst (%) at a reaction temperature of 60°C, the molar ratio of oil: methyl acetate = 1: 6 and stirring speed of 400 rpm

In Figure 1, it can be seen that for all reaction time variables, the highest yield of methyl ester is found in the mass of NaOH catalyst 0.5% wt. oil. The optimum conditions of the study were obtained at 0.5% wt. oil of mass NaOH catalyst and reaction time of 60 minutes with a yield of 87.18%. This is because with the reaction time of 60 minutes the transesterification reaction has reached equilibrium so that if the reaction time is increased it will shift the equilibrium reaction towards the reactants because the transesterification reaction is reversible. At the reaction time of 15 minutes, the resulting methyl ester yield was still low, because the materials were not completely mixed so that the reaction had not yet reached equilibrium. The highest methyl ester yield was obtained at 0.5% wt. oil of mass NaOH catalyst. This is because the amount of NaOH catalyst is 0.5% wt. oil sufficient to meet the needs of the reaction catalyst to achieve equilibrium. Kusumaningtyas et al. [7] obtained the highest yield on the mass of 0.5% wt. oil of KOH catalyst with a reaction time of 8 hours. Casas et al. [6] obtained a FAME mass fraction of 20% with a molar ratio of CH_3OK catalyst: oil = 0.2 and a reaction time of 15 minutes. Chuepeng and Komintarachat [8] obtained a yield of 72% with the molar ratio of NaOH catalyst: WCO = 0.015 at a reaction time of 3 hours.

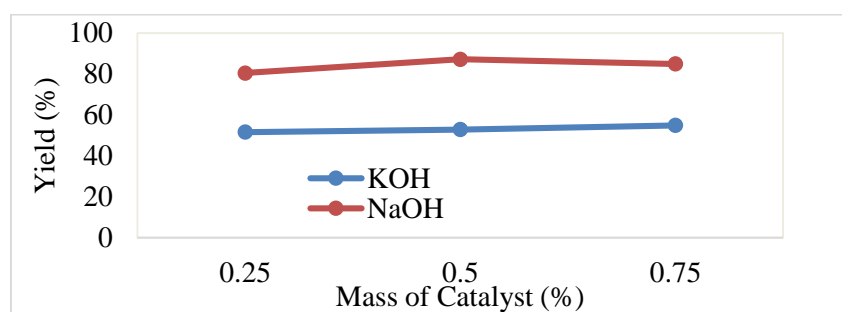


Figure 2. The relationship between catalyst mass (%) and yield (%) with variations in the type of catalyst at stirring speed of 400 rpm, reaction temperature of 60°C, the molar ratio of oil: methyl acetate = 1: 6 and reaction time of 1 hour

In Figure 2, it can be seen that the highest yield is obtained on the NaOH catalyst. At the KOH catalyst, the highest yield was 54.87%, which was obtained at 0.75% wt. oil of mass catalyst. The optimum condition has not been achieved, because it is possible that if the amount of KOH catalyst is increased, the yield will also increase. In contrast to the NaOH catalyst, the optimum methyl ester yield was 87.18% which was obtained at 0.5% wt. oil of mass NaOH catalyst. This is because the amount of NaOH catalyst is 0.5% wt. oil sufficient to meet the needs of the reaction catalyst to achieve equilibrium. If the amount of catalyst is increased, it will shift the reaction equilibrium towards the reactants because of the nature of the reversible reaction. The function of the catalyst in accelerating the reaction and as a solvent is very important for the reaction to occur.

Table 1. Calculation of Total Energy and Dipole Moment in Components with ChemDraw

Components	E potential (kcal/kmol)	E kinetic (kcal/kmol)	E total (kcal/kmol)	Dipole Moment (debye)
Triglycerides+methyl acetate+NaOH	-2930.8062	2930.8062	0	12582.9333
Triglycerides+methyl acetate+KOH	-3140.9573	3140.9573	0	9630.3735

From Table 1, it can be seen that the addition of a KOH catalyst produces greater kinetic energy than the NaOH catalyst. The greater the kinetic energy, the more active the molecule moves [15]. When viewed from the dipole moment, it can be seen that the addition of NaOH catalyst produces a dipole moment that is greater than the KOH catalyst. The greater the dipole moment, the greater the solubility of the material [16]. So it can be said that triglycerides and methyl acetate are more soluble with NaOH catalysts than with KOH catalysts. The more easily dissolved triglycerides and methyl acetate will accelerate the interesterification reaction.

3.3. Analysis

Table 2. Data of density and acid number of methyl ester resulting from interesterification with NaOH catalyst.

Mass of NaOH (% wt. oil)	Reaction Time (min)	Density (g/ml)	Acid Number (mg KOH/g sample)
0.25	15	0.835	0.393
	30	0.858	0.449
	45	0.856	0.449
	60	0.873	0.337
	75	0.882	0.393
0.5	15	0.871	0.449
	30	0.870	0.337
	45	0.890	0.281
	60	0.888	0.224
	75	0.863	0.561
0.75	15	0.875	0.449
	30	0.878	0.449
	45	0.880	0.393
	60	0.850	0.449
	75	0.887	0.561

In Table 2, it can be seen that the density of the methyl ester is between 0.856-0.890 g/ml. This value meets ASTM D1298, namely the biodiesel density between 0.86-0.89 gr / ml [12]. In the mass of 0.25% NaOH catalyst with a reaction time of 15 minutes, the density value of 0.835 g/ml was obtained which did not meet the standard, this was because there were still impurities involved in the biodiesel product.

For the value of the acid number that does not meet the standard is the variable mass of the KOH catalyst 0.5% wt. oil and at the KOH catalyst mass variable 0.75% wt. oil with a reaction time of 75 minutes, namely 0.561 mg KOH/g sample. Based on ASTM D664, the acid number of biodiesel is a maximum of 0.5 mg KOH/g sample [17]. This is because the longer the reaction time allows the formation of free fatty acids.

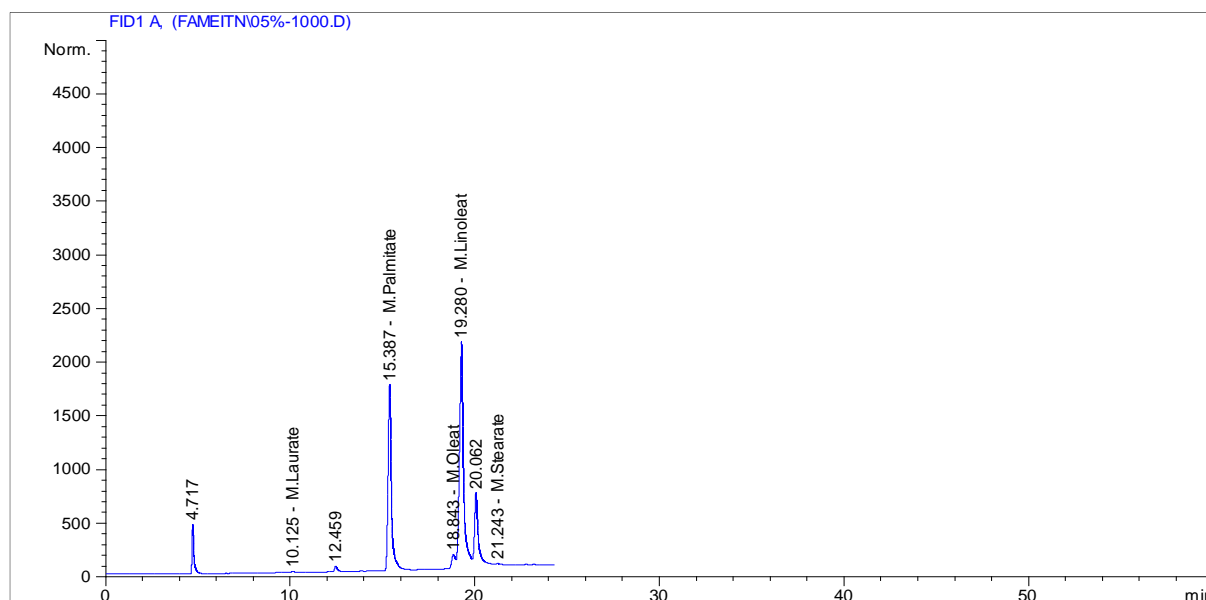


Figure 3. FAME chromatogram on 0.5% wt. oil of mass NaOH catalyst, stirring speed 400 rpm, reaction temperature 60°C, the molar ratio of oil: methyl acetate = 1: 6 and reaction time 1 hour

Table 3. Composition of FAME results from GC analysis on 0.5% wt. oil of mass NaOH catalyst, stirring speed 400 rpm, reaction temperature 60°C, the molar ratio of oil: methyl acetate = 1: 6 and reaction time 1 hour

FAME (Fatty Acid Methyl Esters)	Composition (%)
Methyl Laurate	0.8166
Methyl Palmitate	67.9093
Methyl Oleate	5.4639
Methyl Linoleate	25.7583
Methyl Stearate	0.0520

The results of the GC chromatogram for FAME were the results of the transesterification reaction of triglycerides and methyl acetate on 0.5% wt. oil of mass NaOH catalyst, stirring speed of 400 rpm, reaction temperature of 60°C, the molar ratio of oil: methyl acetate = 1: 6 and reaction time of 1 hour are presented in Figure 4. Whereas the composition of FAME results from the transesterification reaction of triglycerides and methyl acetate on 0.5% wt. oil of mass NaOH catalyst, stirring speed 400 rpm, reaction temperature 60°C, the molar ratio of oil: methyl acetate = 1: 6 and 1 hour reaction time are presented in Table 3. The largest composition of FAME is methyl palmitate 67.9093% according to the largest composition of palm oil, namely palmitic acid 44 % [18].

4. Conclusions

The reaction time, the mass of the catalyst and the type of catalyst are the factors that determine the success of the transesterification reaction between triglycerides and methyl acetate to produce methyl esters and triacetin. From the analysis and calculation results, the highest FAME yield was 87.18% at a reaction temperature of 60°C, the molar ratio of palm oil: methyl acetate = 1: 6, 1 hour reaction time, NaOH catalyst, stirring speed 400 rpm and 0.5% wt. oil of catalyst mass. From the simulation results of ChemDraw software, it was found that the NaOH catalyst was superior to the KOH catalyst, which had

a greater solubility of triglycerides and methyl acetate. It is known that the dipole moment is higher than the KOH catalyst. From the analysis, the biodiesel product at optimum conditions has a density of 0.888 g/ml and meets ASTM D1298, which is the biodiesel density between 0.86-0.89 g/ml. The acid number is 0.224 mg KOH/g and meets ASTM D664 for a maximum acid number of 0.5 mg KOH/g.

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