

PRODUCTION OF ETHYL ESTER BIODIESEL FROM USED COOKING OIL WITH ETHANOL AND ITS QUICK GLYCEROL-BIODIESEL LAYER SEPARATION USING PURE GLYCEROL

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ABSTRACT: In this study, used cooking oil, ethanol and sodium hydroxide (NaOH) were used as raw material and catalyst to produce biodiesel through transesterification reaction. The occurring emulsion from ethanol acts as a surfactant in the reaction mixture make the separation of biodiesel from glycerol layer more difficult. This problem solving was done by adding pure glycerol into the reaction mixture after complete reaction to make quick layer separation between glycerol and biodiesel. The characterization of the produced biodiesel was performed by proton nuclear magnetic resonance (¹H-NMR) and gas chromatography (GC). The result showed that the optimum condition for ethyl ester biodiesel production were 8:1 of ethanol to oil molar ratio, 0.75 %w/w of NaOH amount, 45 min of reaction time and 40 °C of reaction temperature. This condition gave 100% of fatty acid ethyl ester conversion that determined by ¹H-NMR. The result on the optimum condition for layer separation showed that the adding of 2.44% v/v of pure glycerol relation to the total volume of the reaction mixture took 14.38 min for glycerol-biodiesel layer separation. In addition, ethyl ester biodiesel was further analyzed its fuel properties followed ASTM biodiesel standard. The results showed the produced biodiesel met well with the standard.

Keywords: Biodiesel, Glycerol, Surfactant, Transesterification

1. INTRODUCTION

The limited fossil fuel resource along with the need to reduce greenhouse gas emission were a major impulse to the development of alternative fuels. As one result, increased attention has been given to biofuel, such as biodiesel, that can be used as alternative fuel to replace diesel fuel. Its production from renewable resource, such as vegetable oil and animal fat, makes it biodegradable and non-toxic substance. In addition, biodiesel contributes to the reduction of CO₂ emission because it comprises a closed carbon cycle [1]. The choice of vegetable oil as feedstock for making biodiesel rely upon the cost of production, reliability of supply and high yield. Used cooking oil (UCO) was waste that obtained from households, cafeteria and restaurants collection. The UCO offers significant potential source as a low cost raw material for biodiesel production. UCO contained low free fatty acid content, thus it is suitable for making biodiesel via transesterification reaction without any problem caused by soap formation. Furthermore from the waste management viewpoint, using UCO in biodiesel production helps to provide a cleaner way for disposing these wastes [2].

The most common way to produce biodiesel is transesterification reaction that triglycerides react with alcohol to form esters and glycerol as a by-

product. Transesterification consists of a sequence of three consecutive reversible reactions. The first step is the conversion of triglycerides into diglycerides and further into monoglycerides in the second step. The final step, monoglycerides converts into ester and glycerol molecule.

Short-chain alcohol such as methanol and ethanol are the most frequency employed. Methanol is highly reaction and generates satisfactory yields at lower temperatures and reaction time compared with other alcohol [3]. However, methanol presents the disadvantage of higher toxicity compared with ethanol. In our work, ethanol is selected because ethanol can be produced from an agricultural renewable resource such as sugarcane that results in total independence from importing petroleum-based alcohol like methanol [4]. However, as the synthesis progresses through the transesterification reaction, ethanol promotes a more stable dispersion between the ethyl ester biodiesel and glycerol, impeding the layer separation and thus increasing the time required for the production process and lowering the quality of the obtained biodiesel [5]. Pure glycerol is usually used to disperse the layer of ethyl ester biodiesel and glycerol but the amount of adding and the waiting time for separation is not known, so this is the first time to study.

The objective of this work is to determine the optimum condition for the transesterification

reaction between used cooking oil with ethanol using NaOH as alkali catalyst and pure glycerol as dispersing compound for biodiesel-glycerol layer separation. The optimum condition in adding the amount of pure glycerol on the separation of the biodiesel-glycerol layer is also determined. Moreover, the purification ethyl ester biodiesel is further characterized its fuel properties compared with the methyl ester biodiesel standard.

2. MATERIALS AND METHODS

2.1. Material

UCO in this research was obtained from the household collection. The fatty acid composition determined by gas chromatography (GC) consisted of 0.857 %w myristic acid, 36.030 %w palmitic acid, 4.383 %w stearic acid, 43.372 %w oleic acid, 13.606 %w linoleic acid. The calculated average molecular weight of UCO was 852 g/mol and its free fatty acid content was 0.18 %w. Analytical grade ethanol was purchased from Merck (Germany). Methyl heptadecanoate (C₁₇) was obtained from Fluka (Switzerland) and deuterated chloroform was obtained from QReC (New Zealand).

2.2. Transesterification Reaction

The transesterification reaction as shown in Eq. (1) was carried out in a laboratory scale setup using a three-necked 100 ml flask equipped with a reflux condenser, a thermometer and a magnetic stirrer. The reaction was conducted with UCO that stirred constantly at 750 rpm with ethanol and NaOH catalyst. The reaction was performed at different amount of NaOH catalyst (0.25-1.25 %w), the different molar ratio of oil to ethanol (4:1-12:1 mole) and different reaction time (15-120 min) with keeping the constant temperature at 40 °C. After the reaction was completed, the mixture was transferred into a separation funnel and 2.44 %v/v of pure glycerol was added into the mixture to separate into two layers that the top layer was biodiesel and the bottom layer was glycerol. The biodiesel was further purified with warm water and dried in an oven. The obtained purified biodiesel was investigated for fatty acid ethyl ester (%FAEE) conversion by ¹H-NMR (varian, inova 400 mhz, USA). The setup of biodiesel production from UCO is shown in figure 1.

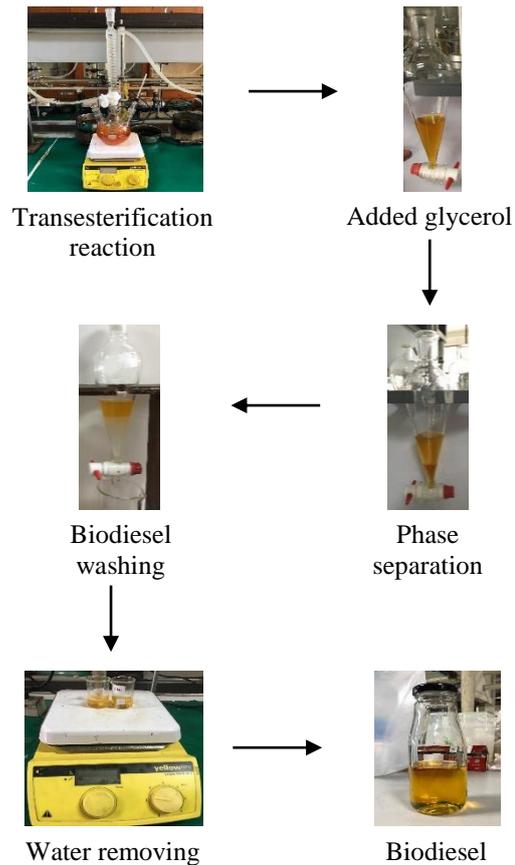
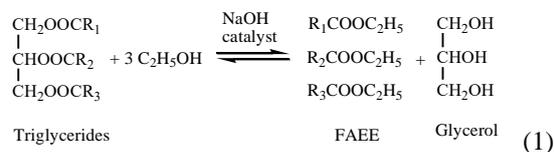


Fig. 1 Flowchart of biodiesel production

2.3. Determination of FAEE

The ¹H-NMR spectra of UCO ethyl ester biodiesel from the ¹H-NMR analysis were obtained for monitoring the transesterification reaction in the form of percentage fatty acid ethyl ester (%FAEE) conversion. The %FAEE conversion was analyzed follow [6]. Briefly, the chemical shift at 4.15 ppm represented the ethyl ester protons and at 3.30 ppm represented the methylene proton (α-CH₂). An equation to calculate the %FAEE conversion is shown in Eq. (2).

$$C = \frac{A_{EE/2}}{A_{\alpha-CH_2/2}} \times 100 \quad (2)$$

Where C is the percentage of FAEE conversion, A_{EE} is the integration value of the protons of the ethyl ester and A_{α-CH₂} is the integration value of the methylene protons. The 2 factor, which divides both integration value, is the normalization factor. This conversion degree was used for determination of the optimum conditions.

2.4. Determination of Properties of UCO

The properties of UCO was determined using standard test methods of the Association of Official

Analytical Chemists (AOAC). The viscosity was determined using Oswald viscometer while the density was measured using a density bottle. The free fatty acid content was estimated by titration of free fatty acids with KOH solution in the presence of phenolphthalein indicator and the free fatty acid content was calculated as the equivalent of oleic acid.

2.4. Physical-chemical Properties of FAEE Analysis

The physical-chemical properties of FAEE (biodiesel) were analyzed followed these details. Density at 15 °C analyzed followed ASTM D1298, Kinematic viscosity at 40 °C analyzed followed ASTM D445, acid value analyzed followed ASTM D664 and flash point analyzed followed ASTM D93, respectively.

3. RESULTS AND DISCUSSION

3.1. Characterization of UCO

The fatty acid composition of UCO that determined by GC was revealed in Table 1 and Figure 2.

Table 1 Fatty acid composition of UCO

Fatty acid	Molecular formular	Molecular weight	% Area
Octanoic acid	C ₈ H ₁₂ O ₂	144	0.037
Decanoic acid	C ₁₀ H ₂₀ O ₂	172	0.019
Lauric acid	C ₁₂ H ₂₄ O ₂	200	0.320
Myristic acid	C ₁₄ H ₂₈ O ₂	288	0.857
Palmitic acid	C ₁₆ H ₃₂ O ₂	256	36.030
Palmitoleic acid	C ₁₆ H ₃₀ O ₂	254	0.305
Stearic acid	C ₁₈ H ₃₆ O ₂	284	4.383
Oleic acid	C ₁₈ H ₃₄ O ₂	282	43.372
Linoleic acid	C ₁₈ H ₃₂ O ₂	280	13.606
Linolenic acid	C ₁₈ H ₃₀ O ₂	278	0.522
Arachidic acid	C ₂₀ H ₄₀ O ₂	312	0.365
Behenic acid	C ₂₂ H ₄₄ O ₂	340	0.105

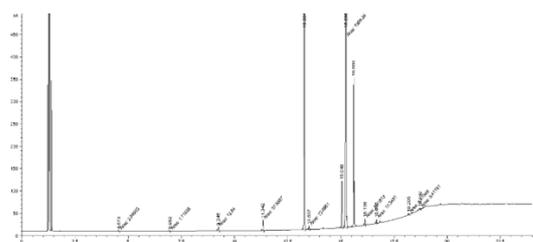


Fig. 2 Chromatogram of a fatty acid composition in UCO

The fatty acid composition showed that oleic acid (43.372%) and palmitic acid (36.030%) are the two major fatty acids, followed by linoleic acid (13.606%), stearic acid (4.383%). The minor fatty acid are octanoic acid (0.037%), decanoic acid (0.019%), lauric acid (0.320%), myristic acid (0.857%), palmitoleic acid (0.305%), linolenic acid (0.522%), arachidic acid (0.365%) and behenic acid (0.105%). The average molecule weight of fatty acid was calculated followed the Eq. (3).

$$\text{Average molecule weight} = \frac{\sum(\% \text{Area} \times \text{Mw})}{100} \quad (3)$$

Where Mw is the molecular weight of each fatty acid

The obtained average molecular weight was 271.33 g/mol that further replaced in the Eq. (4) for the molecular weight of UCO determination.

$$\text{The molecular weight of UCO} = [(3 \times 271.33) - 3] + 41 \quad (4)$$

The average molecular weight of UCO calculated from the Eq. (4) is 852 g/mol. The other UCO properties were shown in Table 2.

Table 2 Properties of UCO

Properties	Amount
Viscosity (cSt)	44.15
Density (kg/m ³)	900
Free fatty acid (% w)	0.18

The result from Table 2 indicated that the low free fatty acid content of UCO (0.18%) made it suitable feedstock for biodiesel production via direct base-catalyzed transesterification reaction.

3.2. ¹H-NMR Spectrum of Ethyl Ester Biodiesel for %FAEE Conversion Calculation

The ¹H-NMR spectrum of the UCO ethyl ester biodiesel obtained after washing and drying is present in Figure 3.

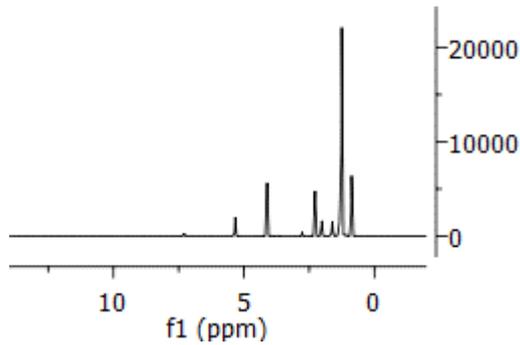


Fig. 3 ¹H-NMR spectra of UCO ethyl ester biodiesel.

The conversion of the triglyceride to monoalkyl ester is clearly observed in the ¹H-spectra by the appearance of the quartet at 4.15 ppm which related to the ethyl ester CH₂ group. From the chemical shift at 4.15 ppm and at 2.30 ppm of the CH₂ group adjacent to the carbonyl group, both chemical shifts were used to calculate the percentage conversion of fatty acid ethyl ester (%FAEE) followed Equation 2.

3.3. Optimum Condition in Biodiesel Production by Transesterification

3.3.1. Influence of the amount of catalyst on the percentage of fatty acid ethyl ester conversion (%FAEE)

The influence of the NaOH amount of catalyst on the %FAEE conversion is examined in Figure 4.

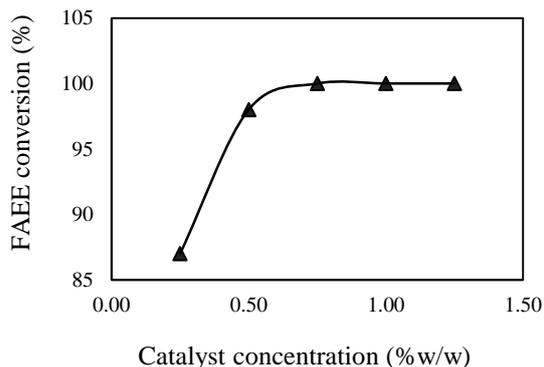


Fig. 4 Influence of the amount of NaOH catalyst on %FAEE conversion. Transesterification condition: reaction temperature = 40 °C, molar ratio of ethanol to UCO = 10:1, reaction time = 90 min at 750 rpm of constant stirring.

The amount of NaOH catalyst varies from 0.25 %w/w to 1.25 %w/w. The %FAEE conversion using NaOH catalyst increases rapidly from 0.25 %w/w to 0.50 %w/w after that the %FAEE increases gradually from 0.50 %w/w to 0.75 %w/w. The %FAEE conversion reaches a maximum of 100% at 0.75 %w/w. Further increase in the amount of NaOH catalyst up to 1.25 %w/w cannot promote the conversion. So, the selected optimum amount of NaOH catalyst was 0.75 %w/w.

3.3.2. Influence of molar ratio of ethanol to UCO on the percentage of ethyl ester conversion (%FAEE)

Figure 5 describes the influence of the mole ratio of ethanol to UCO on the %FAEE conversion.

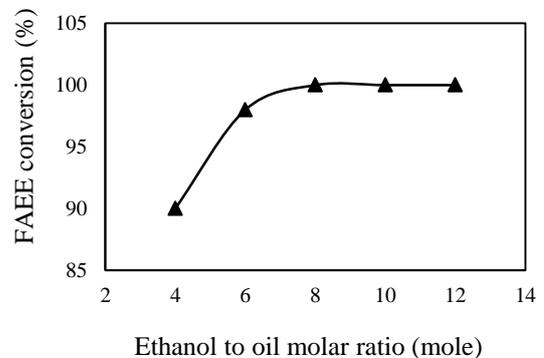


Fig. 5 Influence of molar ratio of ethanol to UCO on %FAEE conversion. Transesterification condition: reaction temperature = 40 °C, amount of NaOH catalyst = 0.75%, reaction time = 90 min at 750 rpm of constant stirring.

The molar ratio of ethanol to UCO is one of the most important parameters affecting the transesterification conversion. Although the stoichiometric ratio requires three moles of ethanol for each mole of UCO, in practice, the mole ratio should be higher to shift the equilibrium towards the direction of the ethyl ester formation.

It can be found that the %FAEE conversion increases rapidly from 4:1 to 6:1 of molar ratio after that the %FAEE increases gradually from 6:1 to 8:1 of molar ratio. The maximum of 100% FAEE conversion obtained at 8:1 of molar ratio and a further increase in the molar ratio from 8:1 to 12:1 gave the same %FAEE conversion.

3.3.3. Influence of reaction time on the percentage of ethyl ester conversion (%FAEE)

The influence of reaction time on the %FAEE conversion is studied and depicted in Figure 6.

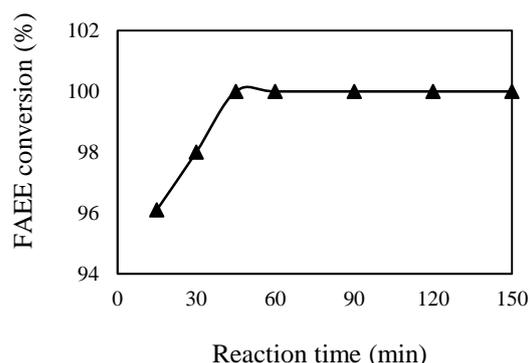


Fig. 6 Influence of reaction time on %FAEE conversion. Transesterification condition: reaction temperature = 40 °C, amount of NaOH catalyst = 0.75%, molar ratio of ethanol to UCO = 8:1 at 750 rpm of constant stirring.

It can be seen that %FAEE increased rapidly from 15 min to 45 min after that the %FAEE became almost constant. The optimum time obtained from the study was 45 min that gave 100% of FAEE conversion.

3.3.4. Influence of adding pure glycerol on the waiting time for layer separation

The influence of pure glycerol addition percentage on the waiting time for layer separation of biodiesel and glycerol is shown in Figure 7. Pure glycerol addition percentage varies from 2.44%, 4.76%, 6.98%, 9.09% and 11.11% v/v related to the total volume of the biodiesel and glycerol mixture.

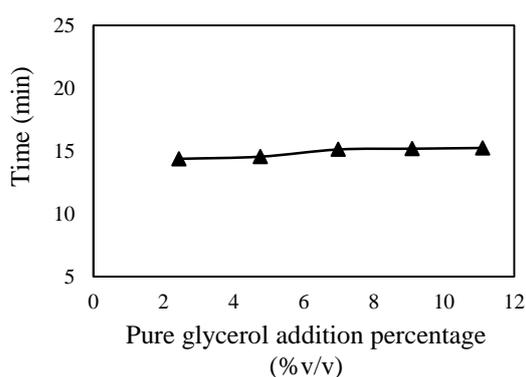


Fig. 7 Influence of adding pure glycerol on the waiting time for layer separation. Transesterification condition: reaction temperature = 40 °C, molar ratio of ethanol to UCO = 8:1, reaction time = 45 min at 750 rpm of constant stirring.

The result indicated that more pure glycerol addition percentage from 2.44% to 11.11% v/v gave

the constant waiting time at 14.38 min for layer separation. Therefore, the selected optimum amount of adding pure glycerol was considered 2.44% v/v. The reason for adding a low quantity of pure glycerol provokes a rapid separation of the two-layer can be understood by the formation of hydrogen bonds between ethanol and pure glycerol that are stronger than the van der Waals forces between ethanol and biodiesel.

3.4. Physical-chemical properties of ethyl ester biodiesel

The physical-chemical properties of ethyl ester biodiesel were compared with the methyl ester biodiesel standard that followed the USA (ASTM standard). The results were exhibited in Table 3.

Table 3 Physical-chemical properties of ethyl ester biodiesel

Physical-chemical properties	Test method	Ethyl ester biodiesel	Methyl ester biodiesel (ASTM)
Density at 15 °C (kg/m ³)	ASTM D1298	863	860-900
Kinematic viscosity at 40 °C (cSt)	ASTM D445	4.94	1.9-6.0
Acid Value (mg KOH/g)	ASTM D664	0.36	0.50 max
Flash point (°C)	ASTM D93	216	120 min

The result revealed that all physical-chemical properties of the produced ethyl ester biodiesel meet well with methyl ester biodiesel standard. In addition, this result implied that ethyl alcohol can replace methyl alcohol for biodiesel production.

4. CONCLUSION

In this study, the transesterification of UCO with ethanol in the presence of NaOH catalyst shows a favorable reaction. A high FAEE conversion (100%) was achieved by optimizing variable effects. The optimum conditions on %FAEE determined by ¹H-NMR during transesterification were 0.75 %w/w of NaOH catalyst, 8:1 of the molar ratio of UCO to ethanol, 45 min of reaction time, 40 °C of reaction temperature, 750 rpm of stirring. The separation of glycerol and biodiesel layer is optimized by adding a different amount of pure glycerol into the mixture of glycerol and biodiesel product. The result showed that 2.44 %v/v of adding pure glycerol can accelerate the waiting time

for layer separation. It took 14.38 min for optimum time for separation. Additionally, the physical-chemical properties of the ethyl ester biodiesel met well with the ASTM methyl ester biodiesel standard.

5. ACKNOWLEDGMENTS

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