

Research Paper

## Catalytic Transesterification of Used Cooking Oil to Biodiesel: Effect of Oil-Methanol Molar Ratio and Reaction Time

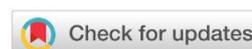
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### Abstract

Used cooking oil has the potential as biodiesel so that it can reduce environmental pollution. Transesterification of triglycerides in used cooking oil with an alcohol to form methyl esters of fatty acids or biodiesel and glycerol. The type of catalyst is one of the determinants of the transesterification reaction and coal fly ash has the potential to be used as a catalyst in the production of biodiesel. Therefore, this study aims to examine the effect of the oil-methanol ratio and the time of the transesterification of used cooking oil to the yield of biodiesel produced using an alkali-activated fly ash catalyst. Transesterification is carried out at 60 °C, the stirring speed is 700 rpm, and the amount of catalyst load is 4%. The result, the highest yield of biodiesel reached almost 89%. This biodiesel consists of 48.86% methyl oleate and 33.86% methyl palmitate and has a density that meets the Indonesian National Standard, which is 0.85 - 0.90 g/cm<sup>3</sup>. Finally, the BET test on the fly ash catalyst shows a catalyst surface area of around 104.106 m<sup>2</sup>/g.

**Key words:** Transesterification; Biodiesel; Heterogeneous catalysts; Fly ash

### Abstrak

Minyak jelantah memiliki potensi sebagai biodiesel untuk mengurangi pencemaran pada lingkungan. Transesterifikasi trigliserida dalam minyak jelantah dengan alkohol membentuk metil ester asam lemak atau biodiesel dan gliserol. Jenis katalis merupakan salah penentu keberhasilan reaksi transesterifikasi. Abu layang batubara (fly ash) berpotensi untuk digunakan sebagai katalis dalam pembuatan biodiesel. Penelitian ini bertujuan untuk mengkaji efek rasio minyak-metanol dan waktu reaksi transesterifikasi minyak jelantah terhadap rendemen biodiesel yang dihasilkan menggunakan katalis abu layang yang diaktifkan dengan alkali. Transesterifikasi dilakukan pada suhu 60 °C, kecepatan pengadukan 700 rpm, dan jumlah muatan katalis 4%. Rendemen biodiesel tertinggi mencapai hampir 89%. Biodiesel ini terdiri dari metil oleat 48,86% dan metil palmitat 33,86% dan memiliki densitas yang telah memenuhi SNI yaitu pada range 0,85-0,90 g/cm<sup>3</sup>. Uji BET terhadap katalis abu layang menunjukkan luas permukaan katalis sekitar 104,106 m<sup>2</sup>/g.

**Kata Kunci:** Transesterifikasi; Biodiesel; Katalis heterogen; Abu layang

### 1. Introduction

Most of the fuel for transportation and industry is sourced from fossil fuels. This energy

source is non-renewable, causes environmental pollution, and its supply continues to decline. Currently, sustainable energy management has



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attracted the attention of developed and developing countries. Biodiesel emerged as one of the candidates to substitute fossil fuels. In Indonesia, the production and use of biodiesel will increase gradually due to the government's policy of increasing diesel oil from B20 in 2016 to B30 in 2025 [1].

Biodiesel is a fuel that can be made from vegetable and animal fats, is renewable, biodegradable, and sustainable. Biodiesel is usually made by transesterification, by reacting fatty acids or triglycerides with alcohols, usually methanol and ethanol, in the presence of a catalyst [2]–[5]. One of the vegetable oils that can be used in making biodiesel is used in cooking oil. Utilization of used cooking oil into biodiesel is an important work in dealing with household waste.

Biodiesel production which always requires conversion and high product selectivity are influenced by the type and amount of catalyst used. This has a continuing impact on the costs of the biodiesel production process. Various types of homogeneous and heterogeneous catalysts have been widely studied such as NaOH/KOH [6], 4-dodecyl benzene sulfonic acid [7],  $\text{La}_2\text{O}_3$  [8], zeolite [9], [10], CaO [11], [12] and still much more. Fly ash has the potential as a catalyst for the manufacture of biodiesel. Fly ash is waste from burning coal in the production of water vapor needs to be used to reduce disposal costs and negative impacts on the environment. It was reported that fly ash has good stability and capability when used as a catalyst in the production of dibenzylidene acetone [13].

Therefore, this study aims to examine the effects of oil-methanol molar ratio and reaction time on the transesterification of used cooking oil, as a source of triglycerides, and methanol. Used cooking oil is chosen because the triglyceride content is still high and is the utilization of household or restaurant waste, thus, it is expected to reduce the effect on the environment.

## 2. Method

This research consists of several stages such as catalyst preparation, transesterification process and continued with the process of purification of

biodiesel produced. Used cooking oil is collected from the rest of the household, while fly ash is obtained from PT Indo Acidatama in Karanganyar, Central Java. Sulfuric acid and methanol were purchased from Merck.

### 2.1. Catalyst preparation

Coal fly ash is neutralized with  $\text{H}_2\text{SO}_4$  with a ratio of 50 grams of coal fly ash: 100 mL  $\text{H}_2\text{SO}_4$ , then stirred for 24 hours until 2 layers are formed. The top layer is removed and the bottom layer is neutralized by the distilled water, then dried with an oven. The neutralized coal fly ash is calcined with NaOH in the furnace for 4 hours at 700 °C. Then, it was added to distilled water and stirred for 24 hours, and then filtered. The filtrate obtained is oven-dried.

The surface area and pore size were determined by the application of gravimetric nitrogen surface analysis Brunauer-Emmett-Teller (BET). To find out the components and crystallinity of fly ash, XRD Philips-Binary Xpert MPD is used. The diffraction results are obtained with Cu-K radiation in the range of  $2\theta$  10-90°. Phase identification is carried out with the help of data from JCPDS available in the Match application.

### 2.2. Transesterification

The transesterification reaction is done by varying two factors, i.e. reaction time (60, 120 and 180 minutes) and oil-methanol molar ratio (1: 8; 1:10; 1:12). This reaction is carried out at a constant temperature of 60 °C, the amount of catalyst 4% of the mass of oil, and the magnetic stirring speed of 700 rpm.

Used cooking oil used in this research without pre-treatment. The oil is reacted with methanol at 60 °C. The transesterification product is put into a separating funnel to separate the methyl ester and glycerol. The lower layer in the separating funnel is glycerol and the upper layer is methyl ester. The methyl ester is then rotary-evaporated at 50 – 60 °C. The results of the rotary-evaporator are cooled at room temperature and then weighed. Finally, testing with GC-MS is carried out to determine the components and composition of biodiesel.

### 3. Result and Discussion

#### 3.1. XRD test

To determine the content of coal fly ash, XRD analysis was performed. The results of the analysis are presented in Figure 1. Based on the graph, it can be seen that the coal fly ash before the alkali fusion process showed diffraction peaks at  $2\theta$  around 21, 27, 31, 33, 35, 37, 39, 40, 41, 43 and 50 degrees. The peak of diffraction shows the presence of quartz crystals at  $2\theta$  is around 21, 27 and 37 degrees, while the mullite crystals at degrees are around 31, 33, 35, 39, 40, 41 and 43 degrees. After alkaline fusion, there are new peaks around 18, 29, 34 and 39 degrees, which may indicate the presence of alkali in the catalyst. Besides, the alkaline fusion process has changed the structure of quartz crystals and the disappearance of several diffraction peaks of mullite crystals. It was reported that coal fly ash is a compound dominated by aluminum and silicon [14]. By using Match software, the presence of  $Al_2Na_{2.28}O_8Si_2$ , berlinite  $AlO_4P$ , and  $SiO_2$  quartz was detected.

#### 3.2. BET test

To find out the active surface area of coal fly ash before and after the alkaline fusion process, BET analysis was performed with the results

presented in Table 1. It shows an increase in surface area of more than 100% after alkaline fusion, which is around  $104\text{ m}^2/\text{g}$ .

Table 1. The BET analysis of coal fly ash

Parameters	After alkaline fusion	Before alkaline fusion
Slope	30.330	55.071
Intercept	3.122e+00	2.022e+01
The correlation coefficient, r	0.999599	0.999745
C constant	10.714	3.723
Surface Area	104.106 $\text{m}^2/\text{g}$	46.252 $\text{m}^2/\text{g}$

#### 3.3. Biodiesel yield

After the fly ash catalyst is obtained, then the transesterification process is carried out to produce biodiesel by varying the molar ratio of oil: methanol and the reaction time, the biodiesel yields are presented in Table 2.

Table 2. Biodiesel yield for various treatments

The molar ratio of oil-methanol	Times (hour)		
	1	2	3
1:8	82,17	73,17	53,43
1:10	82,90	78,55	70,32
1:12	83,32	84,91	88,79

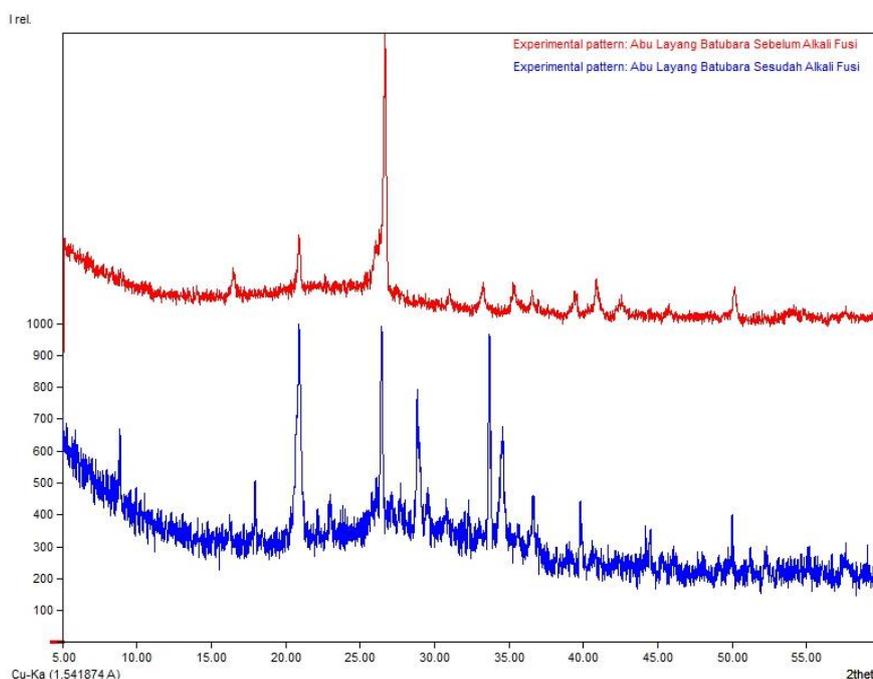


Figure 1. The XRD analysis of coal fly ash before and after alkaline fusion

Increasing the reaction time at the oil-methanol ratio of 1: 8 and 1:12 decrease the yield of biodiesel. However, at a ratio of 1:12, there was an increase in yield. The amount of methanol in the reagents might cause a shift of equilibrium towards the formation of the product.

The increase of methanol in the reaction system causes an increase in the yield of biodiesel produced. The increase in yield is quite significant when the reaction time is extended from 1 to 2 and 3 hours. Other studies report that to increase the speed of transesterification reaction with heterogeneous catalysts is done by increasing the reaction temperature (373-523K), the amount of catalyst (3-10% w/w), and the molar ratio of oil: methanol (1:10 - 1:25) [15]. An important factor in biodiesel production is the use of heterogeneous catalysts. Heterogeneous catalysts can be used optimally if they have high stability, strong active groups, large pores, large hydrophobic surface area, good recycling capability, and economical. Besides, factors affecting biodiesel production such as temperature, pressure, reactant molar ratio, methanol vapor feed rate, the active surface area of methanol vapor bubbles, and contact time or residence time of methanol vapor in oil [16].

### 3.4. The GC-MS analysis

Table 3 shows the composition of biodiesel as a result of reaction with catalyst fused fly ash. The main components of biodiesel consist of methyl palmitate (34%) and methyl oleate (49%). The type and number of components of biodiesel are very dependent on the type of oil used. For used cooking oil, the quality of used cooking oil determines the quality of biodiesel produced.

To be used as fuel, biodiesel must meet national standards. Therefore, it is necessary to do some standard measurements such as density and free fatty acid content. A comparison of the Indonesian National Standard (SNI) with biodiesel from this study is presented in Table 4. The results of the measurement of density and acid numbers indicate that the Indonesian National Standard has been fulfilled. However, it is necessary to test other standards to ensure that

biodiesel from waste cooking oil meets the requirements as a commercial fuel.

**Table 3.** The GC-MS analysis of biodiesel produced

No.	Compound	Content (%)
1.	Methyl laurate	0.98
2.	Methyl myristate	1.71
3.	Methyl palmitoleate	0.55
4.	Methyl palmitate	33.86
5.	Methyl oleate	48.86
6.	Methyl stearate	2.61
7.	Methyl elaidate	0.76
8.	Dipalmitin	2.92
9.	Methyl hexadecadienoate	2.51
10.	Methyl arachate	1.40
11.	Methyl eicosatetraenoate	0.37
12.	Olealdehyde	3.48

**Table 4.** Density and acid number of biodiesel produced compared with SNI

Compound	Sample	SNI
Density	0.8615	0.85 - 0.89
Acid number	0.71	Max. 0.8

## 4. Conclusion

Based on the results of the research conducted, we found that the molar ratio of oil-methanol affects the yield of biodiesel produced. Increasing the amount of methanol in reagents increases biodiesel products. The highest yield of 83.2167% was obtained in the ratio of 1:12 and a reaction time of 3 hours. Transesterification reaction time also affects the yield of biodiesel produced. In conclusion, there is an interaction between the oil-methanol molar ratio and the reaction time.

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