



# Biodiesel Production from Waste Frying Oil: Esterification Using $H_2SO_4$ and Transesterification Using CaO Catalyst Derived from *Anadara granosa*

Nurhayati<sup>1\*</sup>, Muhdarina<sup>1</sup>, Amilia Linggawati<sup>1</sup>, Tengku Ariful Amri<sup>1</sup>

<sup>1</sup>Department of Chemistry, Faculty of Mathematics and Natural Science, Riau University  
Kampus Bina Widya Km. 12,5 Simpang baru, Pekanbaru, Indonesia 28293  
Tel./Fax.: +62- 761- 63273 E-mail: [n\\_yatisyam@yahoo.com](mailto:n_yatisyam@yahoo.com)

## ABSTRACT

Biodiesel is one of an environmentally friendly alternative fuels. This study aimed to synthesize biodiesel from waste frying oil by the two step catalytic process, esterification of free fatty acids using sulfuric acid catalyst and transesterification of triglycerides using CaO catalyst derived from blood cockle shells (*anadara granosa*). CaO catalyst was prepared by coarsely grounded cockie shell using a mortar pestle, dried in an oven at 110 °C for overnight and calcined at 900 °C for 10 hours. The optimum conditions of the esterification and transesterification processes was evaluated by varying temperature and time of reaction for both processes. The biodiesel conversion was analyzed by using GC and the biodiesel chacteristics were analized and the results were compared to Standar National for Biodiesel (SNI 04-7183-2006). The maximum yield of biodiesel was 80.04% at reaction conditions of  $H_2SO_4$  catalyst was 3%, the mole ratio of oil: methanol was 1:18, temperature was 70°C, and reaction time was 2 hours, and the transesterification condition were temperature at 60°C, and reaction time for 3 hours. The characteristics of biodiesel were in the range of standar for biodiesel (SNI 04-7183-2006).

**Key words:** Biodiesel, waste frying oil, esterification, transesterification, CaO heterogeneous catalyst

## INTRODUCTION

Biodiesel is an alternative diesel oils which is generally defined as the monoalkyl esters (FAME=fatty acid methyl ester) from plant oils or animal fats. Due to the scarcity of availability of petroleum-based fuels, this biodiesel gives attract attention because it is produced from renewable sources. Moreover, because the content of sulfur and carbon are relatively low so that the use of biodiesel can reduce carbon monoxide and sulfur emissions. Unlike petrodiesel that produce large emissions of carbon and sulfur-emitting fumes, the use of biodiesel do not cause irritation to the eyes. Biodiesel derived from renewable raw materials will reduce the greenhouse effect and global warming that is more friendly to the environment.

Biodiesel is usually obtained from the transesterification reaction between the oil with methanol in an alkaline catalyst (Nurhayati, 2009). But the production value is higher than the value derived from the production of petroleum-based fuels. To lower the price and make biodiesel competitive with petroleum, then the selection of basic materials and catalysts which are cheaper to manufacture biodiesel needs into account.

Waste frying oil (WFO) has the potential in the process of synthesizing biodiesel (Suyin et al. 2010; Nalan et al. 2008). The use of WFO instead of virgin oil to produce biodiesel is an effective way to reduce the raw material cost and help to solve the problem of waste oil disposal. However, WFO contains high concentration of free fatty acid (FFA). Besides harmful to health if it is consumed, the FFA when reacting with alkaline catalyst will produce soap so that the biodiesel production will reduce. Moreover, the soap formed during the reaction prevents glycerol separation from biodiesel (Kondamudi et al. 2011) Thus, to increase the yield of biodiesel

processed from the oil needs to be done by two stage processes, esterification using an acid catalyst and followed by transesterification using base catalyst.

The esterification reaction is conversion process of free fatty acid into methyl ester. The type catalysts often used in the esterification process is derived from strong acids, such as  $H_2SO_4$  (Marchetti and Errazu 2008). Esterification reaction using a homogeneous acid catalyst has the advantage that high activity and selectivity. Transesterification is the reaction process by means of which triglyceride molecules present in animal fats or vegetable oils react with an alcohol, usually methanol in the presence of a catalyst to form esters (fatty acid methyl esters = FAME) and glycerol (Empikul et al. 2010; Birla et al. 2012).

From various alkaline solid catalyst that has been used for the synthesis of biodiesel (Leung et al. 2010; Peng et al. 2011), CaO has been investigated have high activity in the transesterification of triglycerides with alcohol (Peng et al. 2011; Fanny et al. 2012). The use of CaO catalyst for biodiesel synthesis besides not too toxic, the potential for the formation of soap is also very small compared to using base catalyst, i.e. NaOH or KOH (Lee et al. 2009). Blood cockle (*Anadara granosa*) shells have a good potential to be used as heterogeneous catalysts in the manufacture of biodiesel because it contains calcium carbonate ( $CaCO_3$ ) that will decompose to CaO at high temperature ( $>800^\circ C$ ) (Birla et al. 2011; Nurhayati et al. 2013).

Previous work was synthesized biodiesel from WFO by two stages process, esterification followed by transesterification by studying the effect of catalyst weight ( $H_2SO_4$ ) and ratio molar oil to methanol in the esterification stage (Sartika et al. 2015). The maximum yield of biodiesel found was 70.36% using 3 g of catalyst ( $H_2SO_4$ ) and ratio molar oil to methanol was 1:18, while the condition for transesterification was fixed. This biodiesel result was still low and it could be increased by varying the transesterification process.

The aim of this study is the synthesis of biodiesel from WFO with a variety of conditions at the stage of esterification and transesterification, in order to obtain the optimum conditions Biodiesel production. Physico-chemical properties of biodiesel produced were characterized and the results will be compared to the SNI standard biodiesel.

## MATERIAL AND METHODS

### Materials

WFO samples were collected from households and cafeteria near campus, all of which were then homogeneously mixed. The oil was filtered out to remove small food particle and then it was heated to remove its moisture. Before synthesis biodiesel, FFA and water content was measured. Blood cockle shells were collected from cafeteria. The chemicals used in this study were methanol (99.8% purity, Sigma Aldrich), potassium hydroxide (KOH) solution prepared to 0.1 N using KOH pellets (99.99% purity, Sigma Aldrich), iso-propanol (99% purity, Merck), phenolphthalein indicator, potassium hydrogen phthalate, sulfuric acid (98%) as acid catalyst and distilled water. All the chemicals and reagents were of analytical grade.

### Preparation of CaO catalysts

CaO used in this study comes from the shells waste of blood cockle (*Anadara granosa*). Blood cockle shells was cleaned using water to remove dirt and sand that remains. Then, the shells was washed using distilled water until clean, coarsely grounded and dried in an oven at a temperature of  $110^\circ C$  for 24 hours. Then, the shells were covered and calcined at a temperature of  $900^\circ C$  for 10 hours.

### Synthesis Biodiesel

Esterification and transesterification reactions were performed in a three-necked batch reactor equipped with a thermometer and a reflux condenser. Esterification reactions were carried out in the temperature range of  $60-75^\circ C$  and reaction time from 1-4 h. 100 g of WCO was heated at a temperature of  $105^\circ C$  for  $\pm 1$  hour while stirring in a three-neck flask, then the temperature of the oil was lowered to  $50^\circ C$ . 3 g of  $H_2SO_4$  (99.8%) catalyst and methanol (molar ratio oil to methanol was 1:18) were added into the flask. The mixture was refluxed at a





Hak Cipta Dilindungi Undang-Undang

1. Dilarang mengutip sebagian atau seluruh karya tulis ini tanpa mencantumkan sumber:

a. Pengutipan hanya untuk kepentingan pendidikan, penelitian, penulisan karya ilmiah, penyusunan laporan, penulisan kritik atau tinjauan suatu masalah.  
b. Pengutipan tidak merugikan kepentingan Universitas Riau.

2. Dilarang mengumumkan dan memperbanyak sebagian atau seluruh karya tulis ini dalam bentuk apapun tanpa izin Universitas Riau.

temperature and time specified. After the esterification reaction, the flask was dipped into cold water, and then the mixture was put into a separator funnel and washed with warm water. Washing water at bottom part of separating funnel was discharged and the upper part was inserted into the three-neck flask for transesterification process.

While the esterification reaction took place, a mixture of 4.0 g of CaO catalyst from blood cockle shells and methanol (molar ratio oil:methanol was 1:6) was stirred by magnetic stirrer for 30 min. The oil results after esterification was heated above the boiling point of water at a temperature of 105°C for ± 1 hour. After lowering temperature to 50°C, the mixture of CaO catalyst and methanol was added in to the flask and stirred for 3 hours and the reaction temperature of 60°C. After the reaction completed, the flask was dipped into cold water, and then the mixture was put into a separator funnel and kept at room temperature overnight so that it will form two layers. The next day, the glycerol was removed from the separator funnel. Crude biodiesel was formed, collected and washed with warm water. Yield of biodiesel was calculated according to equation below:

$$\text{Yield} = \frac{\text{Weight of biodiesel found}}{\text{weight of WFO used}} \times 100 \%$$

## RESULTS

### FFA analysis of WFO

Free fatty acid (FFA) contained in WFO was determined by titrating WFO with KOH solution using phenolphthalein indicator and the result was 4.25%. After esterification the FFA reduced to 0.68% (reduced around 84%). It believed that during esterification the FFA converted to methyl ester using methanol and acid catalyst.

### Biodiesel yield

reaction temperature and time of the esterification and transesterification reaction on biodiesel yield were performed, and the result can be seen in Figure 1.

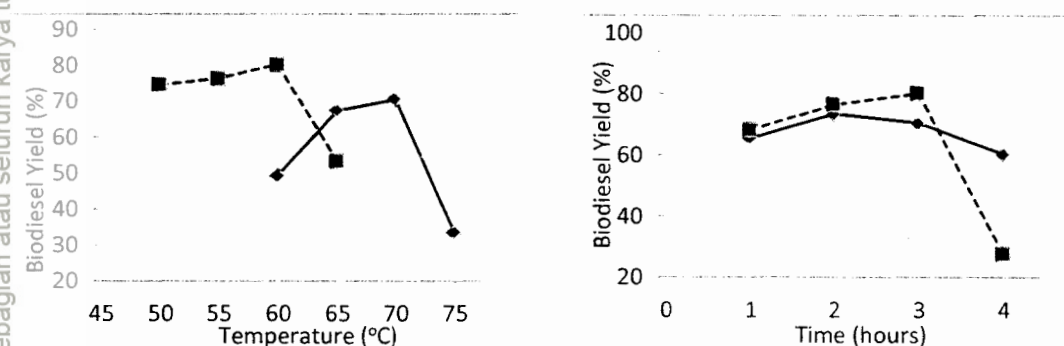


Figure 1. Graphs the effect of temperature (a) and reaction time (b) in the esterification ( —●— ) and transesterification ( - -■ - - ) reaction on biodiesel yield.

### Characteristics biodiesel

Table 1. Characteristic of Biodiesel and comparison with the SNI Biodiesel (SNI-04-7182-2006)

No	Parameter	Characteristic Biodiesel this study	SNI Biodiesel
1	Water content (%v)	0,046	Max. 0,05
2	Density at 40°C (kg/m <sup>3</sup> )	876	850-890
3	Viscosity at 40°C (mm <sup>2</sup> /s)	4,590	2,3-6,0
4	Flash point (°C)	218	Min. 100
6	Acid number (mg KOH/g)	0,142	Maks. 0,8
9	Cetane number	54,60	Min. 51



## DISCUSSION

### Optimization esterification Stage

Variables that affect the yield of biodiesel results during the biodiesel esterification process are weight of catalyst ( $H_2SO_4$ ), molar ratio of oil to methanol, reaction temperature and reaction time. This study will find the temperature and time of reaction optimum in the esterification stage in order to obtain maximum biodiesel yield for the esterification stage. The influence of the reaction temperature on the biodiesel yield was carried out using the optimum conditions which have been obtained by the weight of 3 grams of catalyst, the mole ratio of oil : methanol 1:18. Variation of the reaction temperature used here was 60, 65, 70 and  $75^\circ C$  and the results of the study can be seen in Figure 1 (a). It can be seen from the graph that the optimum temperature of the esterification reaction in this research was at  $70^\circ C$ , with the yield of biodiesel was 70.35 %. It is clear that the higher the reaction temperature, then the greater the conversion of methyl ester. This happens because as the temperature increases, the collision between particles become larger so that the reaction will be faster and the reaction constants be greater.

Effect of reaction time in the esterification stage was performed using the optimum conditions that have been obtained from previous experiments (weight of acid catalyst 3 g, the mole ratio of oil to methanol 1:18, and the reaction temperature  $70^\circ C$ ). Figure 1 (b) shows effect reaction time of esterification on biodiesel yield. During the period of 1 to 2 hours the reaction conversion results continue to rise, but at 3 and 4 hours of reaction the conversion declined. This is because the reaction equilibrium is reached within approximately 2 hours and that a longer time than it would not be beneficial, because it does not increase results.

### Optimization of Transesterification Stage

Transesterification stage was performed directly after the esterification stage finish. In this study, the weight of the catalyst of shells blood cockle (*Anadara granosa*) was 3 % (w/w), with a mole ratio of oil to methanol was 1 : 6. Temperature variations reaction used for the synthesis of biodiesel was 50, 55, 60 and  $65^\circ C$ . As the temperature increased, the yield of biodiesel also increased until maximum biodiesel yield (80.04%) at a temperature of  $60^\circ C$ . The increase in temperature afterward does not increase the acquisition of biodiesel but will decrease biodiesel results by 53.17 % (Figure 1a ). This is because when temperature is too high, it can lead to evaporate or loss of methanol in which the range of the boiling point of methanol at a temperature of  $64.5^\circ C$ . If the reaction temperature used less or in excess of the normal boiling point of methanol, then the biodiesel produced will be low. According Prihandana et al. (2006 ), the reaction temperature is maintained at a temperature around the boiling point of methanol (  $64.5^\circ C$  ), if the temperature  $< 50^\circ C$  will lead to high viscosity of biodiesel

In addition to reaction temperature, the effect of reaction time on the biodiesel yield was also studied. The reaction time studied were 1, 2, 3 and 4 hours. Biodiesel optimum results obtained with a reaction time of 3 hours is equal to 80.04 % with a weight condition the catalyst was 3 % (w/w), reaction temperature of  $60^\circ C$ , and the mole ratio of oil / methanol 1 : 6 (Figure 1.b).

The maximum result was obtained at the reaction time of 3 hours and a decline for a longer time. According Huaping et al. (2006) reaction time is too long will result in the formation of glycerol and emulsions in the product, thereby increasing the viscosity and affect the yield of biodiesel. In the early stages of the transesterification reaction, biodiesel production was fast, and then the speed decreased and eventually reached equilibrium in approximately 3 hours. This can be explained that the transesterification reaction between the oil and the alcohol is reversible, when the reaction time is quite long.

## CONCLUSION

Based on the research results, it can be concluded that the maximum biodiesel yield in this study was 80.04% that was gained on the condition of esterification reaction at temperature of  $70^\circ C$ , and a reaction time of 2 hours using a sulfuric acid catalyst, and transesterification temperature of  $60^\circ C$  with a reaction time of 3 hours using catalyst of *anadara granosa* shell. Characteristics of





Hak Cipta Dilindungi Undang-Undang

1. Dilarang mengutip sebagian atau seluruh karya tulis ini tanpa mencantumkan sumber:

- Pengutipan hanya untuk kepentingan pendidikan, penelitian, penulisan karya ilmiah, penyusunan laporan, penulisan kritik atau tinjauan suatu masalah.
- Pengutipan tidak merugikan kepentingan Universitas Riau.

2. Dilarang mengumumkan dan memperbanyak sebagian atau seluruh karya tulis ini dalam bentuk apapun tanpa izin Universitas Riau

biodiesel obtained were water content 0.046, density value 876 kg/m<sup>3</sup>, viscosity 4.59 mm<sup>2</sup>/s, flash point 218°C, acid number 0.142 mg KOH/g, and cetane number 54.60. All the values obtained were within the range of values biodiesel standards set by SNI-04-7182-2006.

## ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support of Riau University under PUPT Grant 2015

## REFERENCES

- Birla A, Singh B, Upadhyay SN, Sharma YC. 2012. Kinetics studies of synthesis of biodiesel from waste frying oil using a heterogeneous catalyst derived from snail shell, *Bioresource Technology*, 106: 95–100.
- Empikul NV, Krasae P, Puttasawat B, Yoosuk B, Chollacoop N, Faungnawakij K. 2010. Waste shells of mollusk and egg as biodiesel production catalysts, *Bioresource Technology*, 101: 3765–3767.
- Fanny WA, Subagio, Tirta T. 2012. Pengembangan Katalis Kalsium Oksida untuk sintesis Biodiesel, *Jurnal Teknik Kimia Indonesia*, 11: 66-73.
- Huaping Z, Zongbin W, Yuanxiong C, Ping Z, Shijie D, Xiaohua L, Zonqiang M. 2006. Preparation of Biodiesel Catalyzed by Solid Super Base of Calcium Oxide and Its Refining Process. *Chinese Journal of Catalysis*. 27(5): 391-396.
- Kondamudi N, Mohapatra SK, Misra M. 2011. Quintinite as a bifunctional heterogeneous catalyst for biodiesel synthesis. *Applied Catalysis A: General* 393:36–43.
- Lee D, Park Y, Lee K. 2009. Heterogenous base catalysts for transesterification in biodiesel synthesis. *Catalysis Surveys from Asia*, 13: 63 – 77.
- Leung DY, Wu X, Leung MKH. 2010. A review on biodiesel production using catalyzed transesterification. *Appl. Energy*, 87: 1083–1095.
- Marchetti JM, Errazu AF. 2008. Esterification of free fatty acids using sulfuric acid as catalyst in the presence of triglycerides, *Biomass and Bioenergy*, 32: 892 – 895.
- Nalan O, Nuray O, Alper NT. 2008. Esterification of free fatty acids in waste cooking oils (WCO): Role of ion-exchange resins, *Fuel* 87: 1789–1798.
- Nurhayati. 2009. Comparative study on the Use of Acid and Base Catalyst for the Synthesis of Biodiesel from Waste Cooking Oil, *Prosiding SEMIRATA BKS Barat di UNRI, Pekanbaru, Mei 2008*
- Nurhayati, Muhdarina, Utami W. 2013. Mollusk shell of *Anadara Granosa* as a Heterogeneous Catalyst for the Production of Biodiesel. *Prosiding Seminar Nasional Kimia UGM 2013. Yogyakarta*
- Peng LB, Gaanty PM, Shafida AH. 2011. Performance of calcium oxide as a heterogeneous catalyst in biodiesel production: A review. *Chemical Engineering Journal* 168: 15–22.
- Prihandana R, Hendroko R, Nuramin M. 2006. Menghasilkan biodiesel murah, mengatasi polusi dan kelangkaan BBM. *Agromedia Pustaka, Jakarta*.
- Partika A, Nurhayati, Muhdarina. 2015. Esterifikasi Minyak Goreng Bekas dengan Katalis H<sub>2</sub>SO<sub>4</sub> dan Transesterifikasi dengan Katalis CaO dari Cangkang Kerang Darah: Variasi Kondisi Esterifikasi. *Jurnal Online mahasiswa FMIPA*, 2 (1): 178-185.
- Suyin G, Hoon KN, Chun WO, Nafisa OM, and Mohd AFI. 2010. Ferric sulphate catalysed esterification of free fatty acids in waste cooking oil, *Bioresource Technology*, 101: 7338–7343.

