

Esterification of Crude Palm Oil Using H₂SO₄ and Transesterification Using CaO Catalyst Derived from *Anadara granosa*

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ABSTRACT

In this study biodiesel was produced from crude palm oil through two-step processes, namely esterification reactions using homogeneous H₂SO₄ catalyst and transesterification using the heterogeneous base CaO catalyst derived from *Anadara granosa* shell. Several parameters affecting to the yields of biodiesel were investigated including the amount of the catalysts, the molar ratios of oil to methanol, reaction times and reaction temperatures. The CaO catalyst was prepared by calcining the *A. granosa* shells at the temperatures of 800 and 900 °C for 10 h. The as-synthesized biodiesel was analyzed using GC and its characteristics were determined and the results were compared to Standard National for Biodiesel (SNI 04-7183-2006). The optimum condition for the esterification process (step 1) was as follows: reaction temperature of 65 °C, reaction time of 3 h and mol ratio of oil to methanol 1:24. For the transesterification (step 2) the optimum conditions were attained using the catalyst weight 3%, reaction temperature of 60 °C, reaction time of 3 h, mole ratio of oil/methanol 1:6 and the catalyst calcination time of 10 h with the conversion of 87.17%. This biodiesel yield by the two-step processes was higher (2.7%) than that using only one-step process (transesterification).

Keywords: biodiesel; *Anadara granosa*; esterification; transesterification; crude palm oil

ABSTRAK

Pada penelitian ini biodiesel diproduksi dari minyak sawit mentah melalui dua tahap reaksi yaitu esterifikasi menggunakan katalis homogen H₂SO₄ dan transesterifikasi menggunakan katalis heterogen CaO dari cangkang kerang darah (*Anadara granosa*). Beberapa parameter yang mempengaruhi hasil biodiesel telah dipelajari antara lain jumlah katalis, rasio mol minyak metanol, waktu reaksi dan temperatur reaksi. Katalis CaO disiapkan dengan mengkalsinasi cangkang kerang darah pada suhu 800 dan 900 °C selama 10 jam. Konversi Biodiesel dianalisis menggunakan GC dan biodiesel yang dihasilkan dikarakterisasi dan hasilnya dibandingkan dengan Standar Nasional Biodiesel (SNI 04-7183-2006). Kondisi optimum tahapan esterifikasi diperoleh pada temperatur reaksi 65 °C, waktu raksi 3 jam, rasio mol minyak metanol 1:24. Kondisi optimum untuk tahapan transesterifikasi diperoleh dengan menggunakan katalis 3%, waktu reaksi 3 jam, temperatur reaksi 60 °C dan rasio mol minyak metanol 1:6 dengan hasil konversi yaitu 87,17%. Hasil ini lebih besar 2,7% dibandingkan dengan sintesis hanya satu tahap (transesterifikasi).

Kata Kunci: biodiesel; cangkang kerang darah; esterifikasi, transesterifikasi, minyak sawit mentah

INTRODUCTION

Biodiesel is considered as an alternative energy over fossil fuels as the main source of transportation energy world as it is a renewable and biodegradable fuel. Biodiesel, called as FAME when methanol is used as alcohol source, is also environmentally friendly fuel due to its lower hydrocarbon exhaust emissions than pure diesel, and made from vegetable oils or animal fats. Other advantages of biodiesel include high lubrication effect and high cetane number (>50) so that it can extend the life of the machine [1-2].

Several raw materials can be used for biodiesel production such as sunflower oil, crude palm oil (CPO) and etc [3-4]. Crude palm oil is commonly produced oil palm (*Elaeis guineensis* Jacq) in tropical countries. Data from the Indonesian Palm Oil Association (GAPKI) indicate that the area of Indonesian palm oil plantations in 2013 covered 10,010,824 hectares and increased to 10,210,892 hectares in 2014 [5]. Meanwhile, Indonesia produced 17.37 million tons CPO in 2007 and reached 26 million tons in 2014. One of disadvantages CPO-based feedstock for biodiesel production is its relatively high free fatty acid contents (>5%) [6-7], which interfere

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during reaction. A high content of free fatty acids (>2%) in oil will reduce the yield of biodiesel. These drawbacks occur because the FFAs are saponified by a homogeneous alkaline catalyst, producing excess soap [8].

The chemical process by which biodiesel is prepared known as the transesterification reaction, which involves a triglycerin reaction with a short-chain monohydric alcohol normally in the presence of a catalyst at elevated temperature to form fatty acid alkyl esters. The two-step process is usually required for biodiesel production using a base catalyst with a high free fatty acid content. The high free fatty acid concentration commonly encountered in CPO requires esterification process prior to transesterification reaction, which convert free fatty acids into methyl ester (biodiesel). This assists to maximize the biodiesel production. However, the esterification step requires a strong acid catalyst such as HCl, H₂SO₄ (sulfuric acid), other strong acids in the reaction and the study using sulfuric acid shows that the amount of FFA was reduced from 10.684% to 0.54% w/w [9].

The esterification of free fatty acids (FFA) in waste cooking oil has also been done using different ferric sulphate catalyst as a pre-treatment step for biodiesel production by studying the effects of reaction time, methanol to oil ratio, catalyst concentration and temperature on the conversion of FFA. The maximum FFA conversion found 59.2%, when using catalyst concentration of 2 wt.% [10]. Another study was conducted to study the effect of CaO catalyst weight (derived blood clam shell calcined 800 °C) [11] and reaction temperature on the transesterification of CPO. The as-prepared CaO catalyst has surface area of 17.37 m²/g determined via methylene blue-adsorption approach with the biodiesel production of 76.40%, using preparative parameters as follows: 4% CaO catalyst weight for 3 h at ratio mol oil methanol 1:12 and reaction temperature at 65±2 °C.

Calcium oxide (CaO) has been considered as a potential heterogeneous catalyst candidate for biodiesel synthesis because it is readily obtained from decomposition of calcium carbonate (CaCO₃) at elevated temperatures (>800 °C) [12-13]. Apart from a non-toxic catalyst, the use of blood clam (*A. granosa*) shells as a source of CaO catalyst in biodiesel synthesis is to lower the potential for the formation of soap than a homogeneous base catalyst, i.e. NaOH or KOH [14].

The aim of current work was to obtain optimum conditions for biodiesel production using two-step processes, esterification and transesterification processes, to characterize the physicochemical properties of the as-synthesized biodiesel and to compare the as-synthesized biodiesel to the SNI standard biodiesel.

EXPERIMENTAL SECTION

Materials

The materials used in this study were the crude palm oil (CPO) from PT Sumber Sawit Sejahtera (SSS) Pelalawan, the shells of blood clam (*A. granosa*) from the local restaurant, isopropyl alcohol (IPA), indicator phenolphthalein, KOH 0.1 N, H₂SO₄ p.a, potassium hydrogen phthalat, methanol p.a., filter paper Whatman 42, aquabidest, acetone, HCl 0.5 N, CCl₄, reagent Wijs, KI, Na₂S₂O₃, and CH₃COOH.

Instrumentation

Diffraction of gas chromatograph were collected using diffractometer (Philips PW1710 Based), spectrophotometer UV mini-1240 Shimadzu, hotplate magnetic stirrer (Rexim RSH-1DR As One), open cup flash point apparatus.

Procedure

Preparation of CaO catalysts

CaO heterogeneous catalyst was prepared from Blood clam (*A. granosa*) shells. Blood clam shells was first cleaned with water to remove dirt and sand and then rinsed with distilled water to remove any impurities. The cleaned Shells were coarsely ground using a mortar and pestle and calcined at 800 °C and 900 °C for 5, 10 and 20 h. The calcined shells were then crushed and sieved to 200 mesh and stored in a desiccators.

Purification of CPO

Prior to biodiesel synthesis, crude palm oil (CPO) was purified as the procedure below: CPO was first filtered to separate any small particle, and washed with warm distilled water (50 °C) on the separator funnel and finally homogenized. The samples were allowed to stand more or less a day so as to form two layers, the bottom layer was water and the top layer was palm oil that has been washed. The CPO that had been washed, weighed as much as 100 g and heated at 105 °C for ± 1 h and ready to be used for biodiesel synthesis.

Synthesis biodiesel

Biodiesel was synthesized with a two-stage reaction namely esterification using sulfuric acid catalyst (H₂SO₄), and transesterification using CaO catalyst derived from blood clam (*A. granosa*) shells. The both esterification and transesterification reactions were performed in a 500 mL of three-necked batch reactor equipped with a thermometer, a magnetic stirrer

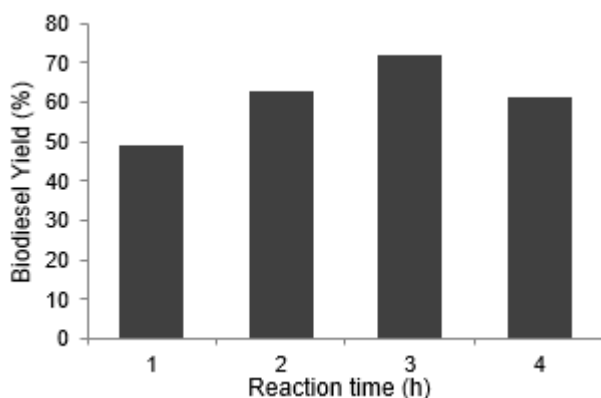


Fig 1. Effect of esterification reaction time on biodiesel yield using H_2SO_4 catalyst

and a reflux condenser.

Esterification of CPO using H_2SO_4 catalyst.

Esterification reactions were carried out with the variation of reaction times (1, 2, 3 and 4 h) and reaction temperatures (60, 65, 70 and 75 °C). A mixture of 2 g of concentrated H_2SO_4 catalyst and methanol (ratio oil to methanol 1:24) was added to a three neck flask which already contains the CPO (100 g). The mixture was then refluxed under a magnetic stirring for 3 h with the reaction temperature of 70 ± 2 °C. After reaction, the mixture was placed into a separating funnel and washed with warm distilled water (50-60 °C). The mixture was then shaken and then allowed to stand ± 10 min to form two layers. The bottom of the washing water was discarded and the upper part was inserted into the glass beaker for further the transesterification process.

Transesterification CPO using CaO catalyst derived from blood clam shells. Transesterification reaction was initiated by reacting 4 g CaO catalyst (derived from blood clam shells) and methanol with molar ratio oil/methanol was 1:6 for 30 min under a magnetic stirring in a three-neck flask. The oil resulted from esterification was heated above the boiling point of water at a temperature of 105 °C for ± 1 h and at lower temperature to 50 °C. The oil was mixed with the catalyst and methanol mixture and stirred for 3 hours at the reaction temperature 60 ± 2 °C [15]. After the reaction completed, the flask was dipped into cold water, and then the mixture was put into a separator funnel and leave at room temperature overnight to form two layers. The bottom layer was glycerol and the upper was crude biodiesel. Biodiesel raw formed, was put into separating funnel and washed with warm distilled water (50-60 °C) with a weight ratio of biodiesel and distilled water 1:1. The same procedure was repeated with the variation of catalyst weight, reaction time and temperature, oil to methanol molar ratio and time of catalyst calcination. Yield of biodiesel was calculated according to equation 1 [15].

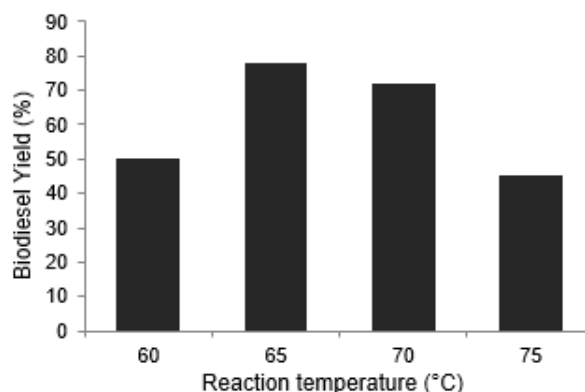


Fig 2. Effect of esterification reaction temperature on biodiesel yield using H_2SO_4 catalyst

$$\text{Yield}(\%) = \frac{\text{Weight of biodiesel found}}{\text{Weight of CPO used}} \times 100\% \quad (1)$$

Characterization of biodiesel

The Biodiesel characteristics was characterized through the determination of water content (ASTM D-2709), density (ASTM D-1298), viscosity (ASTM D-445), flash point (ASTM D-93), acid number (ASTM D-664), iodine number (AOCS Cd 1-25) and cetane number (ASTM D-613).

RESULT AND DISCUSSION

Optimization of Esterification Step

Effect of reaction time and temperature on biodiesel yield

Prior to the synthesis of the biodiesel, the CPO samples were first analyzed for the amounts of water content and free fatty acids (FFA). The samples containing high water content and FFA could cause formation of emulsion and saponification. Data from the previous work [6] indicated that the samples contained the water and FFA of 0.052 and 5.595% respectively, which exceed the required values.

The optimum condition for the esterification reaction was achieved by manipulating the reaction times and temperatures of the process from 1 to 4 h and 60 to 75 °C respectively (Fig. 1 and 2), which was followed by transesterification process using catalyst CaO from *A. granosa* calcined 800 °C for 10 h. In theory, the longer the reaction time, the greater the possibility of contact between substances, thus produce a substantial conversion. However, when an equilibrium has been reached, the rise reaction time will not have a considerable influence on the results obtained. The experimental data showed that during the period of 1 to 3 h of reactions, the products continued to rise, but decrease during of 3 to 4 h of

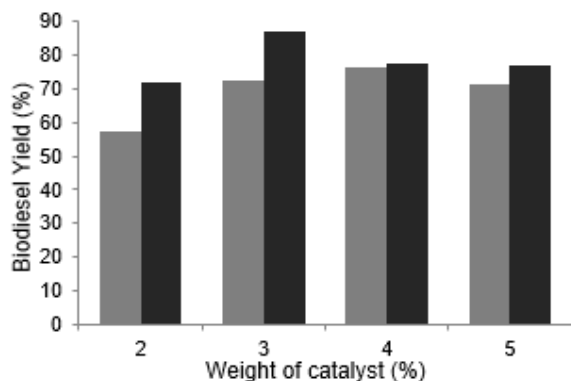


Fig 3. Effect of catalysts weight in the transesterification step on biodiesel yield using CaO catalyst calcined 10 h at 800 °C (□) and 900 °C (■)

reaction times (Fig. 1) due to the formation of reaction equilibrium within 3 h.

To study the effects of reaction temperatures during esterification process on the biodiesel yields, the reaction was carried out by varying the reaction temperatures (60, 65, 70 and 75 °C), keeping other variables constant such as the reaction time (3 h), with molar ratio oil to methanol (1:24) and H₂SO₄ catalyst concentration (2% w/w). Fig. 2 shows the maximum biodiesel yield was 2% w/w at a temperature of 65 °C. Nurhayati et al. [6] produced biodiesel from CPO and gain the maximum yield was 84.89% by transesterification process using catalyst derived from *A. granosa*. Biodiesel yield in this study was lowered than reported, and that to maximize the biodiesel yield some factors affecting the transesterification stage will be studied.

Optimization of Transesterification Stage on the Biodiesel Yield

The optimum conditions for the transesterification process was achieved using the differences of the catalyst weights, reaction times, reaction temperatures and mole ratio of oil/methanol, catalyst calcination times using catalyst CaO (*A. granosa*) calcined at 800 and 900 °C.

Effect of catalyst weights

The effect of catalyst weight on transesterification was performed with the variation weight (2, 3, 4, and 5% w/w), at a reaction time of 3 h, reaction temperature of 65 °C and the molar ratio of oil to methanol (1:6). In theory, the more catalyst weights are added the more products are produced and the results are consistent with the theory as shown in Fig. 3. Fig. 3 shows that the optimum yield of biodiesel obtained was 76.40% at 4% (w/w) of the catalyst using catalyst CaO calcined 800 °C. However, when catalyst calcined 900 °C the yield

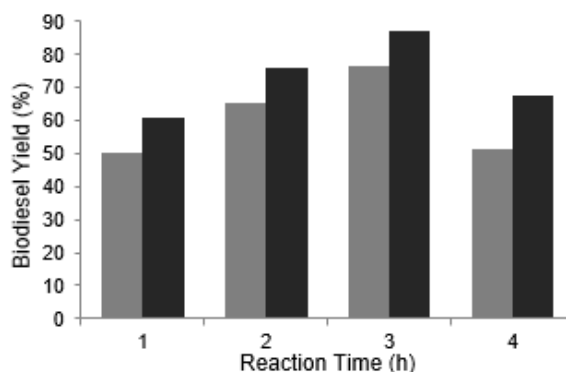


Fig 4. Effect of Reaction time in the transesterification step on biodiesel yield using CaO catalyst calcined 10 h at 800 °C (□) and 900 °C (■)

biodiesel produced was 79.23% at 3% (w/w) of catalyst. The addition of catalyst after reaching a maximum condition causing the conversion of biodiesel decreased. This is because excessive use of catalyst causes the formation emulsion resulting from saponification reaction.

Effect of reaction time

The effect of reaction times (1, 2, 3 and 4 h) at reaction temperature of 60 °C and the mole ratio of oil and methanol (1:6) on biodiesel yields during the transesterification reaction was studied and shown in Fig. 4. The optimum time required for producing maximum biodiesel yield was 3 h, with the yields of biodiesel obtained were 76.40% and 87.17% using catalyst calcined 10 h at 800 °C and 900 °C respectively. The results suggest that the reaction equilibrium was reached within ± 3 h and the yields remain constant at longer reaction times. On the other hand, the length of reaction time depends on the reaction conditions oil used. Oils with a large free fatty acid and water content takes longer reaction than oil which has a free fatty acid and water content smaller.

Effect of molar ratio oil to methanol

Stoichiometrically, the transesterification process requires 3 moles of methanol to convert 1 mole of triglycerides to 3 moles of methyl ester and 1 mole of glycerol. In the transesterification process, methanol has a dual role as a solvent in the extraction process triglycerides and as a reagent in the transesterification process. Therefore, the excess methanol is required as it can increase the reaction rate of methanolysis. High amount of methanol facilitates the formation of methoxy species on the surface of CaO, causing a shift in the equilibrium towards the product [15-16]. Therefore, the influence of molar ratios oil/methanol (1:6, 1:15) on the biodiesel yield is studied by keeping the other variables

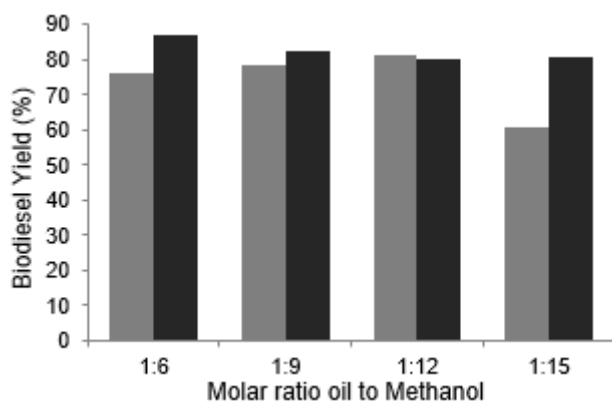


Fig 5. Effect of oil to methanol molar ratio in the transesterification step on biodiesel yield using CaO catalyst calcined 10h at 800 °C (□) and 900 °C (■)

constant such as (3% w/w) CaO catalyst weight, reaction time of 3 h, and reaction temperature of 60 °C.

Fig. 5 shows the results of the acquisition of biodiesel on a variety of moles of oil and methanol. The maximum yields of biodiesel were 81.56% with the molar oil/methanol of 1:12 for catalyst calcined 800 °C and 87.17% with the molar ratio oil/methanol of 1:6 for catalyst calcined 900 °C. The conversion drops with a further increase of oil/methanol molar ratio. The results suggest that glycerol dissolved with excess methanol and then will inhibit the reaction of methanol to the reactants and catalysts, thereby disrupting the separation of the glycerol as it will largely soluble in excessive methanol and will reduce the conversion by shifting the equilibrium towards the opposite. In addition, the excessive amount of methanol will require high energy and consequently will increase the production cost of biodiesel [17].

Effect of catalyst calcination time

The CaO catalyst used in this current work was produced from the decomposition of CaCO_3 from the shells of blood clam, which has been calcined at temperatures of 800 and 900 °C. The calcination, which was heating a material at high temperatures above 500 °C, aims to remove organic compounds and decompose calcium carbonate (CaCO_3) in the blood clam shells into carbon dioxide (CO_2) and calcium oxide (CaO). Several factors affecting the decomposition of calcium carbonate, one of which was the time of calcination. The effects of the calcination times (5, 10 and 20 h) on the CaO crystal structure and its catalytic activities during the transesterification was investigated by maintaining other variables constant. The biodiesel yields for different CaO calcinations times were shown in Fig. 6, which clearly indicates that the yields are greatly affected by the calcination time.

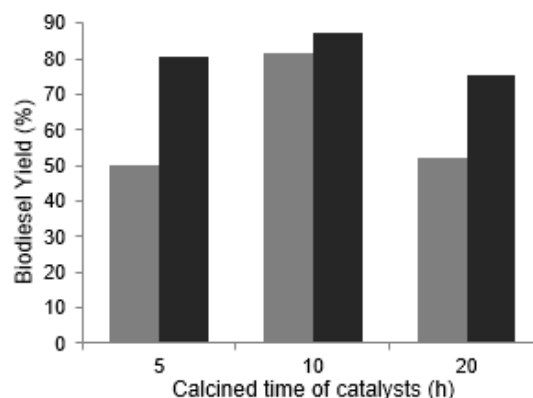


Fig 6. Effect of catalyst calcination time in the transesterification step on biodiesel yield using CaO catalyst calcined at 800 °C (□) and 900 °C (■)

The CaO catalyst calcined at 900 °C with different calcination times (5 and 10 h) improved the biodiesel yields from 80.67% to 87.17% respectively. However, longer calcination time (20 h) dropped the yields significantly (75.25%). The similar results were also observed using catalyst calcined at 800 °C. The data from [13] the surface area indicated that of the catalyst calcined at 10 h posses the greater surface area than that of the catalyst calcined at 5 and 20 h. High surface area of the catalyst, of course, can provide more active sites for the reactants to be adsorbed and participated in the reaction.

In Summary, the biodiesel yields with CaO calcined at 900 °C were higher than those calcined at 800 °C. The data suggest that higher temperature may produced more crystalline and pure CaO, which is clearly indicated by XRD results. The maximum biodiesel yield found in this study was 87.17% which was around 3% more than biodiesel produced when using only one stage process namely transesterification [6].

Characteristics Product Biodiesel

The as-synthesized Biodiesel characteristics must fulfill the government regulation prior to be implemented on a vehicle's engine. The Indonesian government has been issued the biodiesel standard based on Standard Nasional Indonesia (SNI) 04-7182-2006, which includes water content, density, viscosity, flash point, carbon residue, acid number, iodine number and cetane number. The characteristics of biodiesel produced in this study can be seen in Table 1. The results are as follows: the water content of 0.04 and 0.02%, a density of 867 and 872 kg m^{-3} , the viscosity of 3.45 and 2.78 $\text{mm}^2 \text{S}^{-1}$, a flash point 170 and 250 °C, acid number 0.36 and 0.26 mg KOH g^{-1} , iodine number 56.49 and 58.76 $\text{g-I}_2/100 \text{g}$, and cetane

Table 1. Characteristic biodiesel results and comparison with Standard National Indonesia for Biodiesel SNI-04-7182-2006

No	Parameter	Biodiesel this study		Standard Biodiesel
		CaO 800 °C	CaO 900 °C	
1	Water content, %-Vol	0.04	0.02	0.05 (max)
2	Density at 40 °C, kg/m ³	867	872	850-890
3	Viscosity at 40 °C, mm ² /s	3.45	2.98	2.3-6.0
4	Flash point, °C	170	250	100 (min)
5	Acid number, mg-KOH/g	0.36	0.26	0.8 (max)
6	Iodine number, g -I ₂ /100g	56.49	58.76	115 (max)
7	Cetane number	59.50	64.61	51 (min)

number of 59.50 and 64.61 with CaO catalyst calcined 800 and 900 °C respectively. The characteristics of as-synthesized biodiesel generated in this study fulfill the biodiesel quality standards SNI 04-7182-2006.

CONCLUSION

Biodiesel can be produced from raw materials crude palm oil (CPO) in two stages, namely stage esterification reaction with H₂SO₄ catalyst and transesterification reaction with CaO catalyst derived from shells blood clam (*Anadara granosa*) shells calcination at 800 and 900 °C. The maximum biodiesel yield found in this study was 87.17% which was produced at optimum esterification reaction for 3 h at a temperature of 65 °C, while the transesterification using catalyst CaO calcined at 900 °C for 10 h. This biodiesel result was around 3% more than biodiesel produced when using only one stage process (transesterification). All the characteristics of biodiesel generated in this study were in the range of the biodiesel quality standard SNI 04-7182-2006.

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