

Biodiesel Production from Waste Palm Oil Catalyzed by Hierarchical ZSM-5 Supported Calcium Oxide

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ABSTRACT

Biodiesel production from waste palm oil catalyzed by hierarchical ZSM-5 supported calcium oxide was studied. The activity of CaO increased after supported on h-ZSM-5 resulting an increase in conversion from 93.17% to 95.40%. A maximum conversion of 95.40% was achieved at 6 h reaction time, 3 wt.% catalyst amount, 12:1 methanol to oil molar ratio and 65 °C reaction temperature. The waste palm oil showed a high potential as a feedstock in biodiesel production in which there was no significant different in the conversion of fresh and waste palm oil. The properties of the obtained biodiesel required the limits of biodiesel specification according to ASTM D6751-08 and EN 14214 with the methyl ester content of 97.18%, the acid value of 0.24 mg KOH/g, the kinematic viscosity of 4.64 cSt and the density of 869.9 kg/m³.

Keywords: biodiesel; waste palm oil; calcium oxide; hierarchical ZSM-5; conversion

ABSTRAK

Studi produksi biodiesel dari minyak kelapa sawit bekas menggunakan katalis CaO berpendukung ZSM-5 hirarki telah dilakukan. Aktifitas CaO meningkat setelah diimpregnasikan dengan h-ZSM-5 sehingga dihasilkan peningkatan konversi dari 93,17% menjadi 95,40%. Konversi maksimum sebesar 95,40% diperoleh dengan waktu reaksi selama 6 jam menggunakan 3 wt.% katalis dan 12:1 rasio molar methanol terhadap minyak pada suhu 65 °C. Minyak kelapa sawit bekas menunjukkan potensi yang besar untuk digunakan dalam produksi biodiesel dimana tidak ada perbedaan yang signifikan terhadap hasil konversi antara minyak kelapa sawit murni dan minyak kelapa sawit bekas. Karakteristik biodiesel yang dihasilkan telah memenuhi standar spesifikasi biodiesel berdasarkan ASTM D6751-08 dan EN 14214 dengan kandungan metil ester sebesar 97,18%, bilangan asam sebesar 0,24 mg KOH/g, viskositas kinematic sebesar 4,64 cSt dan massa jenis sebesar 869,9 kg/m³.

Kata Kunci: biodiesel; minyak kelapa sawit bekas; kalsium oksida; ZSM-5 hirarki; konversi

INTRODUCTION

Nowadays, fossil fuels generating most of the energy needs in the world. More than 80.3% of the energy needs is accounted by fossil fuels. On the other hand, the consumption of fossil fuels increases every year. The consumption of fossil fuels rose by 100% from 1971 to 2001 and it will increase by 53% in 2030 [1]. The increase in fossil fuels consumption leads to the environmental problems such as larger greenhouse gas (CO₂) due to its combustion which has a big contribution to the global warming. In addition, fossil fuels are derived from non-renewable resources which can be exhausted [2]. According to the prediction of world energy forum, if new oil wells cannot be found, fossil fuels will be run out within 100 years. Due to these facts, the development of alternative fuel for fossil fuels has been stimulated.

In the recent years, biodiesel has been considered as a potential alternative renewable and eco-friendly fuel to replace fossil fuels without engine modifications due to their similar properties [1]. Biodiesel has lower combustion emission which produces 78.5% less carbon dioxide than petroleum-based diesel fuel [3]. As a fuel comprised of mono-alkyl esters of long chain fatty acids, biodiesel resources are renewable (vegetable oils or animal fats). Different vegetable oils have been used as feedstocks for biodiesel production such as sunflower, canola, cotton seed, Jatropha, palm, rapeseed and soybean oil. Among those vegetable oils, palm oil has been considered as a promising feed stock for biodiesel production due to its many advantages [4]. Compared to fossil fuels, the high price of those vegetable oils becomes the main drawback in biodiesel production.

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Hence, non-edible oils like waste palm oil are preferred for biodiesel production to reduce the production cost. By using waste oils, the cost of biodiesel production can be reduced by 60–90% [5]. Furthermore, this is also a way to utilize a waste as a valuable product.

Several methods have been used to produce biodiesel including blending, pyrolysis, microemulsification and transesterification. Transesterification becomes the best method due to its simplicity to produce high quality biodiesel [6]. Transesterification is a reaction between triglycerides (oil) and alcohol which produces methyl ester and glycerol. In the transesterification reaction, methanol is commonly alcohol used due to its low price and it is suitable with mostly vegetable oils to produce a high yield of biodiesel. Since the natural reaction is slow, the transesterification reaction is catalyzed by acid, base or enzyme [7]. Generally, transesterification reaction is catalyzed by homogeneous acids and bases such as H_2SO_4 , HCl, NaOH and KOH. Because of the high activity of the catalysts, the reaction can be performed in mild conditions resulting in high yield of biodiesel in a short time. However, homogeneous catalyzed biodiesel production process needs a difficult and expensive purification step to separate the catalyst with the products since the catalyst soluble in the reaction medium. High amount of wastewater containing high basicity or acidity liquids is generated in this process resulting in a problem to the environment [1]. In addition, those catalysts cannot be reused resulting the high cost of biodiesel production. Especially for homogeneous base catalysts, their reactivity with free fatty acid which lead the soap formation via saponification reaction become an important problem since it reduces biodiesel yield and consumes catalyst [1]. To solve those drawbacks related with homogeneous catalysts, the use of heterogeneous catalysts becomes a favorable solution.

Among the researched heterogeneous catalysts, CaO has been considered as a promising heterogeneous base catalyst in the transesterification reaction. As a heterogeneous catalysts, CaO is not dissolved or consumed in the reaction resulting easy separation from the product, able to be reused leading a cheaper production cost, able to be used in mild reaction conditions, inexpensive (obtainable from waste shells) and environmental friendly [8]. CaO also has high alkalinity, activity and tolerance in FFA allowing the use of waste oils and low methanol solubility [9].

CaO has been supported on high surface area materials such as alumina, silica and zeolite in order to increase the activity of the catalyst. These support materials allow a good dispersion of the metal oxide and thus increasing the active surface. Zeolite exhibits low activity for transesterification reaction, but when loaded

with CaO, it can increase the activity of the main catalyst [10]. Wu et al. [10] in their study examined the biodiesel production from soybean oil using CaO and CaO/NaY catalyst. The supported catalyst was found to be more active than pure CaO with a biodiesel yield of 95%. Another type of zeolite, hierarchical ZSM-5 (h-ZSM-5) with its high surface area due to its bimodal porosity (micropores and mesopores) was used in the transesterification of *Nannochloropsis* microalga oil resulting in a biodiesel yield of 4% using 2 wt.% catalyst and 100:1 methanol to oil molar ratio at 115 °C for 4 h [11]. Since the activity of the zeolite was very low, in this study, h-ZSM-5 was used as a support catalyst for CaO resulting CaO/h-ZSM-5 catalyst in the transesterification of waste palm.

EXPERIMENTAL SECTION

Materials

Refined palm oil was obtained from market. Waste palm oil was prepared by using the refined palm oil in potato stick frying at 200 °C for 15 min. Hierarchical ZSM-5 was obtained from Institut Teknologi Sepuluh Nopember, Indonesia. Calcium oxide (96%) was purchased from AJAX Finechem while calcium acetate monohydrate (98%) was purchased from POCH. Methyl heptadecanoate as an internal standard (99%) was purchased from Sigma Aldrich. Other chemicals such as methanol (99.8%) was purchased from J.T. Baker while sulfuric acid (95–97%) and sodium hydroxide (98%) were purchased from Merck.

Instrumentation

The methyl esters composition determination of the obtained biodiesel was performed using a gas chromatography-mass spectrometry (GC-MS, Shimadzu) equipped with a J&W 122-7032DB-Wax column (30 m × 250 µm × 0.25 mm).

Procedure

Preparation of catalyst

CaO/h-ZSM-5 was prepared using impregnation method with 50 wt.% CaO loading. 6.3 g calcium acetate monohydrate was dissolved in 20 mL distilled water. 2 g h-ZSM-5 was added in calcium acetate solution and the mixture was stirred at 80 °C for 40 min. The obtained slurry was dried at 105 °C for 12 h to obtain the solid catalyst. Before used in the reaction, pure CaO and CaO/h-ZSM-5 was activated through calcination at 800 °C for 2 h.

Transesterification of waste palm oil

12:1 molar ratio of methanol to oil and 2 wt.% catalysts were used to carry out the transesterification reaction through reflux method. 19.8 mL methanol was mixed with 0.8 g CaO/h-ZSM-5 in a round-bottom flask. 40 g preheated oil at 65 °C was added into the flask and the flask was connected with a condenser. The flask was placed in a water bath with a temperature of 65 °C and stirred for 2 h. The catalyst was removed from the product using centrifuge at 6000 rpm for 30 min. In order to separate biodiesel and glycerol completely, the reaction product was moved to the separating funnel and kept overnight. The biodiesel (top layer) was washed using warm distilled water to eliminate remaining glycerol. Finally, remaining water and methanol was eliminated by evaporating for 2 h at 105 °C to obtain high purity of biodiesel. The reaction was optimized with reaction time, catalyst amount, methanol to oil molar ratio and reaction temperature.

Analysis of waste palm oil conversion

Analysis of waste palm oil conversion, the amount of the oil converted into biodiesel was determined using titration method following Kumar et al. [12] method. 2 mL sample was mixed with 40 mL 0.1 N sodium hydroxide solution and the mixture was stirred for 6 h. 2 drops of phenolphthalein were added to the mixture as an indicator. 0.1 N sulfuric acid was used to titrate the mixture until it became colorless. The NaOH solution was also titrated to determine the blank. The experiment was carried out 3 times for each sample. The methyl ester content has been verified using GC-MS.

The following formula was used to calculate the conversion value:

$$\text{Conversion (\%)} = \frac{(V_B - X_f) \times N_a \times MW}{1000} \times 100\%$$

where,

V_B is volume of H_2SO_4 required for titration of blank (mL)

X_f is NaOH solution needed to neutralize (mL)

N_a is normality of H_2SO_4

MW is molecular weight of biodiesel (284.91 g/mol, obtained by calculating the average of the compounds molecular weight in the biodiesel)

Analysis of biodiesel properties

The properties of obtained biodiesel were analyzed including density 15 °C, kinematic viscosity at 40 °C, acid value and FAME content. In order to determine the FAME content, 325 mg of biodiesel sample was weighed in a vial. Then, 5 mL of 10 mg/ml methyl heptadecanoate solution was added as an internal standard and mixed evenly for being analyzed using GS-MS. The initial temperature was 50 °C for 5 min and the final temperature was 250 °C for 20 min with heating rate of 10 °C/min. 250 °C was set as the injector temperature.

The measurement was run in 45 min where helium was used as a carrier gas. To calculate the FAME content (%), the formula as reported by Duvekot [13] was used.

RESULT AND DISCUSSION

Properties of Waste Palm Oil

The properties of fresh and waste palm oil are shown in Table 1. Acid value was found to increase with an increase in frying cycles. The increase in acid value after frying was due to the hydrolysis and oxidation of triglycerides during frying. The hydrolysis of oil can be accelerated with the presence of moisture coming from the potato since the water can initiate the hydrolysis of triglycerides leading the formation of monoglyceride, diglycerides, glycerol and free fatty acids. Carbonyl compounds such as free fatty acids also can be formed from the oxidation of oil [14].

Kinematic viscosity of fresh palm oil also increased after frying. Lalas et al. [15] reported that the formation of higher molecular weight compounds and the increase in saturation of triglycerides during frying resulted in the increasing of kinematic viscosity. Kochhar and Gertz [16] also explained that the increase in kinematic viscosity was influenced by polymer compounds. The polymerization of oil was enhanced caused by the water content leaching from fried product during frying process. Furthermore, the presence of oxygen with high temperature during frying led to the reaction resulting in formation of polymeric compounds. As repeated frying process, the density of the oil was observed to increase. The increase in density also was expected due to the formation of higher

Table 1. Properties of fresh and waste palm oil

Frying cycle	Acid value (mg KOH/g)	Kinematic viscosity (cSt)	Density (g/mL)
0	0.29±0.013	31.78±0.128	0.9051±0.00039
1	0.35±0.019	31.93±0.064	0.9061±0.00030
2	0.38±0.017	32.10±0.127	0.9075±0.00072
3	0.43±0.019	32.38±0.064	0.9089±0.00034

Table 2. Fatty acid composition of waste palm oil

Fatty acid	Amount (wt.%)
Lauric acid	0.14
Myristic acid	0.73
Pentadecanoic acid	0.14
Palmitic acid	35.22
Palmitoleic acid	0.31
Heptadecanoic acid	0.10
Stearic acid	5.11
Oleic acid	41.92
Linoleic acid	13.58
Linolenic acid	0.23
Arachidic acid	0.33
11-Eicosenoic acid	0.16

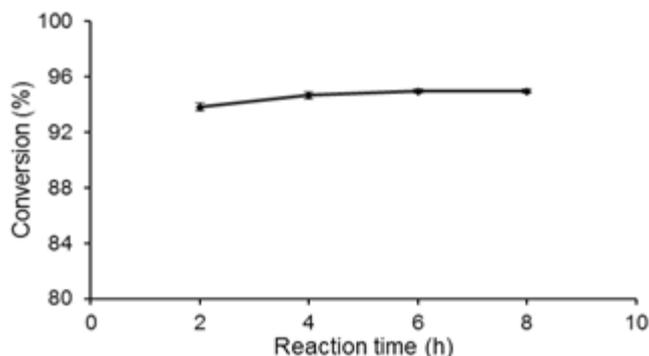


Fig 1. Effect of reaction time on the conversion of waste palm oil. Reaction conditions: catalyst amount of 2 wt.%, methanol to oil molar ratio of 12:1, reaction temperature of 65 °C

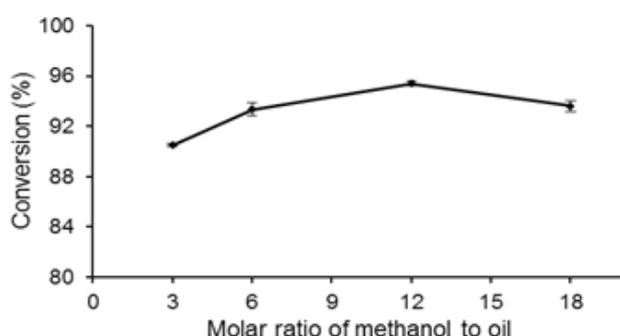


Fig 3. Effect of methanol to oil molar ratio on the conversion of waste palm oil. Reaction conditions: reaction time of 6 h, catalyst amount of 3 wt.%, reaction temperature of 65 °C

molecular weight products in polymerization and oxidation reactions during frying [17].

Fatty acid composition of waste palm oil (3 times cooked oil) as shown in Table 2 was analyzed using GC-MS. Based on the Table 2 waste palm oil was mainly composed of palmitic acid, oleic acid and linoleic acid. This composition was in a good agreement with the fatty composition of fresh palm oil as reported by Leung et al. [1] where it was mainly composed of palmitic acid (42.8%), oleic acid (40.5%) and linoleic acid (10.1%)

Transesterification of Waste Palm Oil

Effect of reaction time

The effect of reaction time on the transesterification of waste palm oil is shown in Fig. 1. A high conversion of 93.78% was obtained for 2 h showing the high activity of the catalyst. The conversion was found to increase with an increase in reaction time from 2h to 6 h. At long reaction time, the reactants were reacted completely resulting in high conversion. The increase of reaction time up to 8 h had no effect on the conversion.

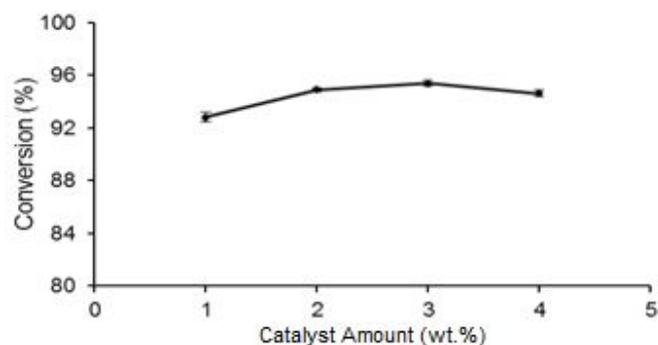


Fig 2. Effect of catalyst amount on the conversion of waste palm oil. Reaction conditions: reaction time of 6 h, methanol to oil molar ratio of 12:1, reaction temperature of 65 °C

Therefore, 6 h was considered as the optimum reaction time resulting a conversion of 94.92%.

Effect of catalyst amount

Fig. 2 shows that as the catalyst amount increased from 1 wt.% to 3 wt.%, the conversion also increased. This result showed that the increasing of active basic sites number resulted in the increasing of conversion. A high conversion of 92.83% obtained at 1 wt.% also showed the high activity of the catalyst. The addition of excessive catalyst at 4 wt.% resulted in a lower conversion. The decrease in conversion was due to the low mass transfer at high amount of catalyst resulting in low conversion. In this case, enhancing mass transfer was more important than increasing the catalyst amount [10]. Hence, the amount of catalyst was fixed at 3 wt.% for subsequent investigations. A similar result was conducted by Wu et al. [10] in the transesterification of soybean oil using CaO/NaY as a heterogeneous base catalyst resulting in 94.6% biodiesel yield.

Effect of methanol to oil molar ratio

Theoretically, the molar ratio of methanol to oil in the transesterification reaction is 3:1. An excess amount of methanol was used to force the reaction towards the formation of biodiesel since transesterification reaction is a reversible reaction. Based on Fig. 3, the conversion increased with an increase in methanol to oil molar ratio from 3:1 to 12:1. However, a further increasing of methanol to oil molar ratio to 18:1 resulted in the decreasing of conversion. The increasing of methanol amount led to the decrease in catalyst content reducing the conversion. Furthermore, at higher methanol to oil molar ratio, stable emulsions generated leading to the difficult purification of biodiesel [10]. In addition, using the methanol amount more than the optimum ratio will not

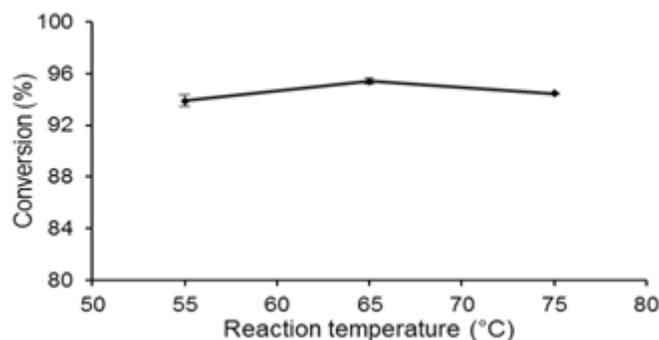


Fig 4. Effect of reaction temperature on the conversion of waste palm oil. Reaction conditions: reaction time of 6 h, catalyst amount of 3 wt.%, methanol to oil molar ratio of 12:1

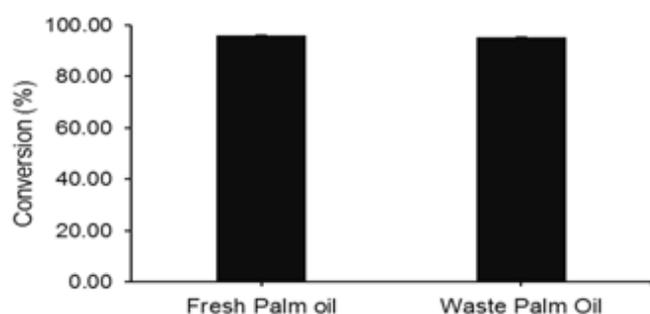


Fig 6. The comparison of fresh and waste palm oil potential as feedstock in biodiesel production. Reaction conditions: reaction time of 6 h, catalyst amount of 3 wt.%, methanol to oil molar ratio of 12:1, reaction temperature of 65 °C

increase the conversion but will increase the cost for alcohol recovery [18]. Therefore, 12:1 can be recommended as the optimum molar ratio of methanol to oil in the study.

Effect of reaction temperature

Fig. 4 reveals the effect of reaction temperature on the transesterification of waste palm oil in which increasing reaction temperature affected the conversion positively. Carried out with all optimum condition obtained before, a maximum conversion of 95.40% was achieved at a temperature of 65 °C. The viscosity of oil decreased at high reaction temperature leading to the high reaction rate resulting in a higher conversion [19]. However, the conversion decreased when the temperature was further increased to 75 °C. There was an optimum temperature used for the reaction in the study related to the boiling point of methanol. The maximum conversion was obtained at 65 °C since this temperature is the boiling point of methanol. Methanol could diffuse completely to react with triglyceride molecules at this temperature. When the temperature

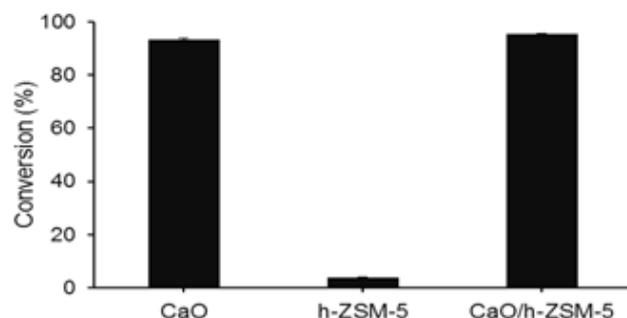


Fig 5. The comparison of three catalysts activities in the transesterification of waste palm oil. Reaction conditions: reaction time of 6 h, catalyst amount of 3 wt.%, methanol to oil molar ratio of 12:1, reaction temperature of 65 °C

increased above the boiling point of methanol, the bubbles were formed on the surface inhibiting the mass transfer phase [20].

From the investigation on the effects of reaction conditions, it could be concluded that the optimum conditions for the transesterification of waste palm oil with methanol catalyzed by CaO/h-ZSM-5 were the reaction time of 6 h, the catalyst amount of 3 wt.%, the methanol to oil molar ratio of 12:1 and the reaction temperature of 65 °C. A similar study was conducted by Wu et al. [10] in the transesterification of soybean oil using CaO/NaY where the optimum conditions were obtained at the reaction time of 3 h, the catalyst amount of 3 wt.%, the methanol to oil molar ratio of 9:1 and the reaction temperature of 65 °C.

Effect of catalyst

The comparison of three catalysts activities is presented in Fig. 5 where CaO/h-ZSM-5 exhibited the highest activity. As a pure catalyst, the activity of h-ZSM-5 was very low resulting in a conversion of 3.89%. When h-ZSM-5 was used as a support for CaO since it had a high surface area, it could enhance the activity of the main catalyst resulting in the increasing of conversion from 93.17% to 95.40%. In this case, h-ZSM-5 allowed a good dispersion of CaO on it leading to the increasing of CaO active basic sites resulting in a higher conversion. The different was not too high since CaO was very active when it was used as a pure catalyst.

Effect of oil

Fig. 6 gives the comparison of fresh and waste palm oil potential as feedstock in biodiesel production. The conversion of fresh and waste palm oil was 95.92% and 95.40%, respectively. There was no significant different in the conversion of fresh and waste palm oil showing a high potential of waste palm

Table 3. Properties of biodiesel from the transesterification of waste palm oil

Properties	Value	Limit	Method
Methyl ester content (%)	97.18	96.5 (min)	EN 14103
Acid value (mg KOH/g)	0.24±0.032	0.50 (max)	D 664
Kinematic viscosity at 40 °C (cSt)	4.64±0.04	1.9–6.0	D 445
Density at 15 °C (kg/m ³)	869.9±0.46	860–900	EN 3675

Table 4. Composition of biodiesel from the transesterification of waste palm oil

Compound	Amount (wt.%)
Methyl laurate	0.33
Methyl myristate	0.96
Methyl palmitate	30.56
Methyl palmitoleate	0.28
Methyl heptadecanoate	13.35
Methyl stearate	4.34
Methyl oleate	35.42
Methyl linoleate	11.79
Methyl nonadecanoate	0.10
Methyl linolenate	0.24
Methyl arachidate	0.34
11-Eicosenoic acid methyl ester	0.17
Methyl behenate	0.06
Palmitic acid	1.04
Margaric acid	0.16
Methyl lignocerate	0.06
Oleic acid	0.58

oil in biodiesel production. This difference conversion could be related with the acid value of two oils. The acid value of waste palm oil was higher than that of fresh palm oil resulting a lower conversion. It was known that high acid value showing the high amount of free fatty acid in the oil affected the transesterification reaction since it could produce soap via saponification reaction lowering the conversion. Wu et al. [10] also observed the effect of acid value where the conversion of soybean oil was found to decrease from 95% to 72% with an increase in acid value from 1 to 8 mg KOH/g.

Properties of Biodiesel

The physical and chemical properties of biodiesel obtained from the transesterification of waste palm oil were tested and compared to the limitations as shown in Table 3. Biodiesel is mainly composed of methyl ester in which the minimum content of methyl ester should be 96.5%. The methyl ester content of biodiesel in the study was over the minimum requirement by a value of 97.18%.

The acid number shows the amount of free fatty acids in the biodiesel. The acid number of the biodiesel in the study was 0.22 mg KOH/g where the limitation was 0.50 mg KOH/g in maximum value. Biodiesel with a high acid value had effects in increasing of fueling system deposits and corrosion possibility. The density of fuel is a key property affecting engine performance. The

fuel density affects the energy content and air-fuel ratio within the combustion chamber [21]. The density of biodiesel from the transesterification of waste palm oil was 869.9 kg/m³ and in the range of EN 3675 specification. That result indicated that the density of waste palm oil (908.8 kg/m³) was reduced by the transesterification reaction.

Viscosity becomes an important property since it has effects in the fuel injection behavior. High viscosity leads to the great cylinder penetration of the fuel spray, narrow injection spray angle, poor fuel atomization and large droplet size resulting in high emission, oil dilution and combustion [21]. Therefore, transesterification of vegetable oil is carried out to reduce its high viscosity. In the study, the kinematic viscosity of waste palm oil was reduced from 32.41 cSt to 4.64 cSt through transesterification process. The kinematic viscosity of the biodiesel met the D 445 specification (1.9–6.0 cSt). In conclusion, the properties of biodiesel from the transesterification of waste palm oil required the limits of biodiesel specification according to ASTM D6751-08 and EN 14214.

Table 4 shows the composition of biodiesel from the transesterification of waste palm oil analyzed using GC-MS. The obtained biodiesel was mainly composed of methyl palmitate, methyl oleate and methyl linoleate. This result showed that the methyl esters of the biodiesel were in accordance with the free fatty acids of the oil used. A high content of methyl heptadecanoate in the chromatogram came from the internal standard used in GC-MS analysis. The presence of fatty acids in the chromatogram showed that the oil was not completely converted into biodiesel.

CONCLUSION

Acid value, kinematic viscosity and density of the palm oil increased with an increase in frying cycles. The optimum condition in the transesterification of waste palm oil was achieved at a reaction time of 6 h, a catalyst amount of 3 wt.%, a methanol to oil molar ratio of 12:1 and a reaction temperature of 65 °C resulting a maximum conversion of 95.40%. As a support, hierarchical ZSM-5 could enhance the activity of calcium oxide resulting an increase in conversion from 93.17% to 95.40%. Furthermore, waste palm oil could be addressed as a potential feedstock in biodiesel production since there was no significant different in the conversion of fresh palm oil (95.92%) and waste

palm oil (95.40%). The produced biodiesel fulfilled the requirements of biodiesel standard according to ASTM D6751-08 and EN 14214 in which it was mainly composed of methyl palmitate, methyl oleate and methyl linoleate.

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