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Biodiesel Synthesis and Properties from Sunflower and Waste Cooking Oils using CaO Catalyst under Reflux Conditions

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Abstract: Transesterification of sunflower oil (SFO) and waste cooking oil (WCO) with methanol was performed using CaO catalyst at 80-120°C under reflux conditions. The effects of the reaction temperature, the catalyst concentration and the molar ratio of methanol to oil on Fatty Acid Methyl Ester (FAME) yields were investigated. The FAME yield for transesterification of SFO indicated the maximum value at a molar ratio of 9:1 at 120°C. The water containing in WCO activated the CaO catalyst for transesterification. Therefore, the FAME yield for transesterification of WCO decreased as the molar ratio increased, due to the dilution of water by methanol. The FAME yields of SFO were higher than that of WCO under the same conditions, due to the presence of free fatty acids in WCO. At a reaction temperature of 80°C for 120 min with 3 wt.% CaO catalyst, the FAME yields of SFO and WCO reached more than 92 and 84%, respectively. The fuel properties of the biodiesel fuel (BDF) produced from SFO at 120°C with 5 wt.% CaO catalyst satisfied the values required in the EU standard for BDF (EN-14214).

Key words: Biodiesel, calcium oxide, high temperature

INTRODUCTION

BDF is catalytically synthesized through the transesterification of triglyceride in vegetable oils and animal fats with excessive methanol and is used as an alternative petroleum diesel fuel because of its similar combustion properties (Graboski and McCormick, 1998; Fangrui and Milford, 1999; Schuchardt et al., 1998). BDF is environmentally attractive because a reduction in emissions of greenhouse gases, SOx and aromatics can be achieved when it is used in place of petroleum diesel fuel.

BDF production using a homogeneous base catalyst such as potassium hydroxide (KOH) or sodium hydroxide (NaOH) obtained high FAME yields with high reaction rates, even under mild conditions such as atmospheric pressure, mild temperature and short reaction time (Guan et al., 2009a, b; Meher et al., 2006; Vicente et al., 2004). The transesterification reaction rate in the presence of acid catalysts (H_2SO_4 and HCl) was very slow compared to the base catalyst (Fukuda et al., 2001; Guan et al., 2009c). Homogeneous catalysts caused problems such as equipment corrosion and the need for wastewater treatment after removing the dissolved catalyst from BDF with a large amount of water

(Vicente et al., 2004). Furthermore, alkali-hydroxides led to soap formation in the presence of free fatty acids in oil, reducing the FAME yield. These problems can result in increased production costs for BDF (Dorado et al., 2004; Ebiura et al., 2005; Kim et al., 2004; Liu et al., 2008a).

Heterogeneous solid catalysts can solve these problems due to the easy separation of the catalyst from the FAME products and to the reusable properties of the catalyst (Kim et al., 2004; Liu et al., 2008a; Di Serio et al., 2008; Vicente et al., 2004). Various solid catalysts have been examined for use in the transesterification reaction supported alkali (Arzamendi et al., 2008; Benjapornkulaphong et al., 2009; Noiroj et al., 2009; Ma et al., 2008), alkali earth oxides and supported alkali earth oxides (Antunes et al., 2008; Kawashima et al., 2009; Kouzu et al., 2008a, b; Liu et al., 2008a-c; Verziu et al., 2008; Yan et al., 2008), metal oxides and metal complexes (Babu et al., 2008; Ngamcharussrivichai et al., 2008; Sree et al., 2009; Xie and Yang, 2007), hydrotalcite (Barakos et al., 2008; Macala et al., 2008; Wang et al., 2008; Zeng et al., 2008), solid acid catalysts (Garcia et al., 2008; Kansedo et al., 2008) and other catalysts (Guan et al., 2009d; Kim et al., 2008). However, the activities of supported alkali and resin catalysts were

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dramatically decreased when reused several times, due to the dissolution of active components in methanol (Ebiura *et al.*, 2005; Liu *et al.*, 2008a, c). Solid acid catalysts revealed a relatively slower reaction rate compared with solid base and strong homogeneous acid catalysts (Kawashima *et al.*, 2009). CaO catalyst has low solubility in organic solvents and exhibits reasonable activity under mild conditions (Kouzu *et al.*, 2008a, b; Liu *et al.*, 2008b, c; Yan *et al.*, 2008).

Kouzu *et al.* (2008a) examined many different types of Ca compounds as transesterification catalysts of soybean oil and waste cooking oil with refluxed methanol. CaO catalyst exhibited the highest transesterification activity among those examined. FAME yields were as high as 93 and 99% for the transesterification of soybean oil for 1 h and of waste cooking oil for 2 h, respectively. However, the reaction temperature was not clearly indicated. Liu *et al.* (2008a) studied transesterification of soybean oil with CaO catalyst.

An optimum FAME yield of 95% was obtained under the following conditions: 12:1 molar ratio of methanol to oil, 8 wt.% CaO, reaction temperature of 65°C and 2.03% water content in methanol. Although, CaO catalyst showed very promising results for BDF production, further research would be required to reduce the cost. Transesterification of waste cooking oil using CaO catalyst is an appropriate way to reduce the cost of BDF production. When a reactor with a condenser is used, BDF can be produced in the liquid phase at a temperature higher than the boiling point of methanol and as a result, the reaction rate is increased.

In this study, transesterification of SFO and WCO with methanol using CaO catalyst in a reactor with a condenser was investigated at a temperature higher than the boiling point of methanol. The fuel properties and quality of the produced BDF were examined.

MATERIALS AND METHODS

Materials: Dehydrated methanol and CaO were obtained from Wako Pure Chemical Ind. Ltd. Japan. The volume average diameter of CaO catalyst was 27.1 μm. The CaO catalyst was activated by calcinations at 900°C for 2 h under N_2 atmosphere before use since CaO catalyst is poisoned very fast by atmospheric water and CO_2. SFO was purchased and WCO was provided from a BDF production factory. The acid and saponification values of the oil were determined using standard titration methods (Gryglewicz, 1999). The molecular weight of the oil was determined from the saponification and acid values (Cheng *et al.*, 2008). Water content in the oil was determined using a Karl-Fisher moisture titrator (MKC-610, Kyoto Electronic Manufacturing Co. Ltd). The properties of SFO and WCO are summarized in Table 1.

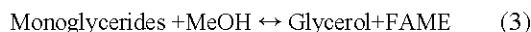Table 1: Properties of waste cooking oil and sunflower oil

Oil	Water content (wt.%)	Acid value	Saponification value	Molecular weight (g mol^{-1})
		----------(mgKOH g^{-1})----------		
SFO	<0.10	0.41	192.4	876.6
WCO	0.65	7.70	223.6	779.5

Table 2: Reaction conditions

	SFO	WCO
Amount of oil (mL)	16.22	14.14
Amount of MeOH (mL)	4.04 ~ 12.12	4.04 ~ 12.12
Catalyst amount (g)	0.146 ~ 1.461	0.13 ~ 1.301
Reaction temperature (°C)	60 ~ 120	60 ~ 120
Magnetic stirrer speed (rpm)	600	600

Tansesterifiacation procedure and analysis method: Transesterification of oil with methanol was performed in a 100 mL flask equipped with a magnetic stirrer, a thermometer and a reflux condenser. A mixture of methanol and oil was prepared using a magnetic stirrer and the solid catalyst was then added to the flask. And then the flask was placed in the constant temperature oil bath. The amount of SFO and WCO were 16.22 and 14.14 mL, respectively. The methanol/oil molar ratio was changed within the range of 6:1 to 18:1. The weight concentration of CaO catalyst based on the oil was varied from 1-10 wt.%. The reaction temperature was varied from 60-120°C. The reaction conditions of SFO and WCO are given in Table 2. The reaction product was centrifuged at 6000 rpm for 20 min. The upper ester layer was rinsed with deionized water and the mixture was centrifuged again. These procedures were repeated several times until the pH value in the aqueous phase reached 7.0. Then 0.1 mL of the rinsed sample was diluted by 3 mL of hexane for analysis. The concentration of unreacted oil that remained in the BDF was analyzed using a high performance liquid chromatography (HPLC, Tosoh Corp., Japan) equipped with a silica-gel column (Shimpack CLC-SIL, Shimadzu Corp., Japan) and a refractive index detector. The mobile phase was n-hexane/2-propanol = 99.5/0.5 (v/v) and the column temperature was kept constant at 40°C. Two peaks that were attributed to the sum of FAMEs and the unreacted glycerides (sum of mono-, di- and tri-glycerides) appeared in the liquid chromatogram. The reaction of trasesterification with methanol is a reversible reaction. The reaction mechanism was three steps as follows:

$$\text{Triglycerides} + \text{MeOH} \leftrightarrow \text{Diglycerides} + \text{FAME} \qquad (1)$$

$$\text{Diglycerides} + \text{MeOH} \leftrightarrow \text{Monoglycerides} + \text{FAME} \qquad (2)$$

$$\text{Monoglycerides} + \text{MeOH} \leftrightarrow \text{Glycerol} + \text{FAME} \qquad (3)$$

If the oil contains free fatty acids (FFAs), such as WCO, the esterification reaction was Eq. 4.

$$FFAs+MeOH \leftrightarrow H_2O + FAME \qquad (4)$$
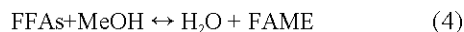
The FAME yield in the product was calculated as follows:

$$FAME\ yield = \frac{C_{FAME}}{3C_{oil}} \times 100 \qquad (5)$$

where, C_{oil} and C_{FAME} are the concentrations of triglycerides in the inlet and FAME in the product, respectively.

The standard tests (JIS K 2390) of fuel properties of the BDF including flash point, pour point, metal content, iodine value and impurity concentrations, were carried out by Shimadzu Techno-Research Inc.

RESULTS AND DISCUSSION

BDF production from SFO and WCO: The effect of molar ratio of methanol to oil on FAME yield for transesterification of SFO is shown in Fig. 1. The molar ratio in the mixture of oil and methanol loaded in the flask before heating was adopted in Fig. 1. FAME yield increased as the molar ratio of methanol to oil increased and reached a maximum value. A decrease in FAME yields at higher levels of methanol content was caused by the dilution effect of catalyst and reactants (Liu *et al.*, 2008a). A molar ratio of methanol to oil higher than the stoichiometric ratio has generally been adopted for BDF production, to obtain a high FAME yield. The optimum molar ratio of methanol to oil for the transesterification of SFO with KOH catalyst at 25°C was in the range of 6:1 to 8:1 (Fukuda *et al.*, 2001). In the case of CaO catalyst, Kouzu *et al.* (2008a) adopted a 12:1 molar ratio of methanol to oil for the transesterification of soybean oil and waste cooking oil with refluxed methanol. Liu *et al.* (2008b) reported that the optimum molar ratio for the transesterification of soybean oil at 65°C was 12:1. As shown in Fig. 1, the optimum molar ratio at the reaction temperatures of 80 and 100°C was 12:1 and shifted to 9:1 at 120°C.

BDF production in this experiment was carried out at a reaction temperature higher than the boiling point of methanol and therefore, a considerable amount of methanol was vaporized from the mixture of methanol and oil in the flask. The actual molar ratio of methanol to oil under the reflux conditions was determined from the methanol concentration in the mixture in the absence of CaO catalyst. Figure 2 shows the relationship between the molar ratio of methanol to oil before and after heating. There was little difference among the actual molar ratios determined at 80, 100 and 120°C. This means the total
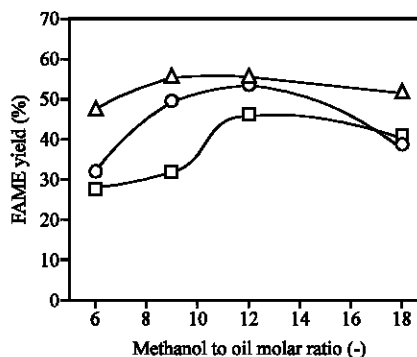

Fig. 1: Effect of the molar ratio of methanol to oil on the FAME yield for transesterification of SFO: Reaction temperature, □, 80°C; O, 100°C; Δ, 120°C; 5 wt.% CaO catalyst; Reaction time = 30 min
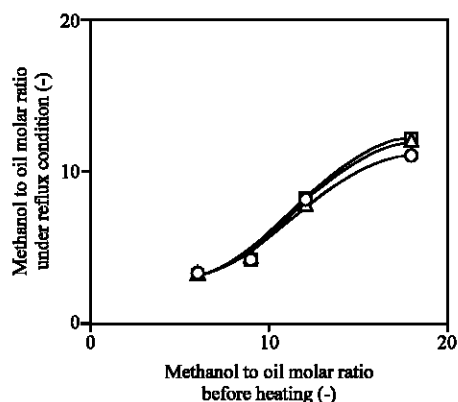

Fig. 2: Actual molar ratio of methanol to oil in the reactor under reflux conditions: Reaction temperature, □, 80°C; O, 100°C; Δ, 120°C

methanol content in the vapor phase could be made similar by keeping the temperature level of the condenser low. As a result of Fig. 1 and 2, the actual molar ratios to obtain the highest FAME yield were roughly estimated to be 8:1 at 80-100°C and 4:1 at 120°C.

The effects of reaction time and temperature on the FAME yield for transesterification of SFO are shown in Fig. 3. The FAME yields under reflux conditions (80-120°C) were higher than those determined at 60°C. As the reaction time progressed, the FAME yield showed S-shape curves, which, according to Kouzu *et al.* (2008a) could be explained that by a variation of the reaction order as transesterification progressed. Transesterification obviously occurred at the boundary between oil and methanol in the early stage, where the reaction rate might be zeroth-order kinetics with respect to oil concentration. The reaction rate was then changed from the zeroth to first order kinetics, due to good miscibility in the reaction
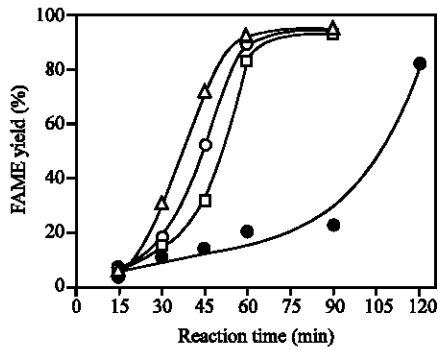
Fig. 3: Effects of reaction time on FAME yield for transesterification of SFO: ●, 60°C □, 80°C; ○, 100°C; Δ, 120°C; 3 wt.% CaO; Molar ratio of methanol to oil = 6:1
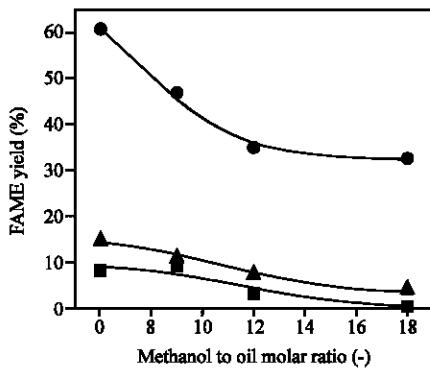

Fig. 4: Effects of molar ratio of methanol to oil on FAME yield for transesterification of WCO: ●, 3 wt.% CaO (60 min); ■, 3 wt.% CaO (30 min); ▲, 5 wt.% CaO (30 min); Reaction temperature = 80°C

mixture. Guan *et al.* (2009b) observed the flow behavior in a microtube reactor during the transesterification of SFO and reported that a quasi-homogeneous flow of dispersed fine droplets of glycerol and methanol in the continuous FAME/oil phase was formed above the oil conversion of 70%. As shown in Fig. 3, FAME yields reached more than 92% after 90 min of reaction time.

The effect of the molar ratio of methanol to oil on the FAME yields for transesterification of WCO is shown in Fig. 4. The FAME yield decreased as molar ratio of methanol to oil increased. Liu *et al.* (2008a) investigated the transesterification of soybean oil with CaO catalyst and reported that the highest FAME yield was obtained with a water content in methanol of 2.03-2.80 wt.% by weight of soybean oil (29-35 wt.% by weight of CaO catalyst). Water molecules were adsorbed on the CaO surface to form an OH group that accelerated the reaction rate (Kouzu *et al.*, 2008b; Liu *et al.*, 2008a). In addition,
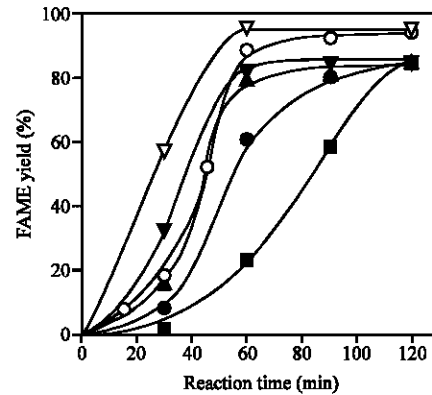

Fig. 5: Comparison of FAME yields for the transesterification of SFO and WCO: ○ Δ, SFO; ■ ● ▲ ▼, WCO; ■, 1 wt.% CaO (80°C); ○ ●, 3 wt.% CaO (80°C); ▲, 5 wt.% CaO (80°C); ▼ 10 wt.% CaO (80°C); Δ, 10 wt.% CaO (120°C), Molar ratio of methanol to oil = 6:1

CaO was reacted with methanol to form calcium methoxide during the early stage of the reaction (Liu *et al.*, 2008a-c) and then to form calcium diglyceroxide (Kouzu *et al.*, 2008a) with the glycerol formed. These compounds also exhibited catalytic activity for the transesterification of triglyceride.

As indicated in Table 1, the water content in WCO was 0.65 wt.% which corresponded to 22 wt.% by weight of CaO catalyst in the case of 3 wt.% CaO catalyst. Accordingly, the catalytic activity decreased as the molar ratio of methanol to oil increased, due to the dilution effect of water.

As shown in Fig. 5, the FAME yields in SFO at 80°C and the catalyst concentration of 3 wt.% were higher than those in WCO. As indicated in Table 1, WCO contains a high level of free fatty acids which reduced the number of catalytic active sites due to calcium soap formation. As a result, the equilibrium yield of FAME in SFO reached 97% and that in WCO was approximately 84%.

Figure 6 shows the effect of reaction temperature on FAME yield for the transesterification of SFO and WCO. Transesterification of oil with methanol in the presence of heterogeneous catalysts is a three-phase reaction system. Accordingly, the reaction rate might be reduced due to mass transfer resistance on the boundary between the oil and methanol phases. FAME yield increased as reaction temperature increased, due to the enhancement of miscibility at high temperatures. Liu *et al.* (2008a) indicated that methanol was vaporized at high temperature and formed a large number of bubbles which inhibited the reaction on the three phase interface. However, the evolution of bubbles enhanced the turbulence in the reactor and reduced mass transfer resistance in this study.

Table 3: Fuel specifications of BDF from sunflower oil

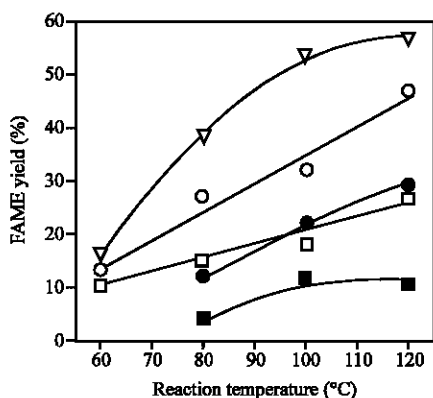| | Catalyst | | | | | |
| | 3 wt.% KOH | 5 wt.% CaO | 5 wt.% CaO | 1wt.% KOCH₃ (Palm)[b] | 1wt.% KOCH₃ (Sunflower)[b] | |
| | Reaction temp.(°C) | | | | | |
BDF sample	60	60	120	60	60	EN-14214
Pour point (°C)	-7.5	-7.5	-2.5	-	-	-
Flash point (°C)	188.5	178.5	182.5	176	177	≥120
Alkali metal Na+K (ppm)	<2	-	-	-	-	≤5
Alkali earth metal Ca+Mg (ppm)	-	<14 (4600)[a]	<2 (13000)[a]	-	-	≤5
Iodine value (gI/100g)	119	123	123	57	132	≤120
Monoglyceride (wt.%)	0.53	0.12	0.26	0.17	0.37	≤0.80
Diglyceride (wt.%)	0.07	0.04	0.04	0.06	0.07	≤0.20
Triglyceride (wt.%)	<0.05	<0.05	<0.05	0.04	0.04	≤0.20
Free glycerin (wt.%)	<0.005	<0.005	<0.005	0.01	0.00	≤0.02
Total glycerin (wt.%)	0.15	0.04	0.07	0.06	0.09	≤0.25

[a]Unwashed BDF, [b]Ramos *et al.* (2009)

Fig. 6: Effects of reaction temperature on FAME yield: □ O △, SFO; ■ ●, WCO; □ ■, 3 wt.% CaO; O ●, 5 wt.% CaO; △, 10 wt.% CaO; Molar ratio of methanol to oil = 6:1; Reaction time = 30 min
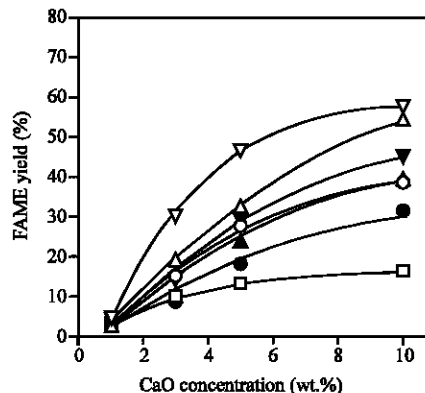

Fig. 7: Effects of catalyst concentration on FAME yield: □ O △ ▽, SFO; ● ▲ ▼, WCO; Reaction temperature □, 60°C; O ●, 80°C; △ ▲, 100°C; △ ▼, 120°C; Molar ratio of methanol to oil = 6:1; Reaction time = 30 min

Figure 7 reveals that the FAME yield increased as the concentration of CaO catalyst increased, due to the increase in the total number of available catalytic active sites for the reaction (Liu *et al.*, 2008b, c). The FAME yield was also affected by mass transfer between the reactant and catalyst (Liu *et al.*, 2008a-c). Accordingly, high catalyst concentration caused the reactant mixture to be more viscous, which caused a decrease in the reaction rate due to mass transfer resistance (Xie and Yang, 2007; Yan *et al.*, 2008).

Fuel properties of the produced BDF: BDF samples for the analysis of fuel properties were produced from the transesterification of SFO with 5 wt.% CaO at 60 and 120°C for 2 h and washed with water several times. The BDF properties obtained using CaO catalyst were compared with that obtained those using 3 wt.% KOH catalyst. Table 3 summarizes the fuel properties of the produced BDF with the results of Ramos *et al.* (2009).

The pour point is the lowest temperature at which frozen oil can flow and is often used to specify the cold temperature usability of fuel oil (Van Gerpen *et al.*, 2004; Encinar *et al.*, 2007). The pour points evaluated by JIS K2269 were -7.5 and -2.5°C for BDF samples produced with CaO catalyst at 60 and 120°C, respectively. The flash point is the lowest temperature at which liquid oil can form an ignitable mixture in air. All the flash points evaluated by JIS K2265 were higher than the values described as the minimum requirements for BDF in the European standard (EN-14214). The amounts of alkali metal and alkali earth metal were evaluated using the EN14108 and EN14538 standards, respectively. The amount of alkali earth metal in unwashed BDF was as much as 1.3 wt.%, perhaps Ca compounds such as calcium methoxide and calcium diglyceroxide were partially dissolved in the FAME at high temperatures. After washing the FAME phase with water, the amount of alkali earth metal in the FAME

produced with CaO catalyst at 120°C was lower than the minimum value (5 ppm) stipulated by the EN-14214 standard.

The results of iodine values evaluated by JIS K0070 were close to the maximum value (120 gI/100 g) stipulated by the EN-14214 standard. The iodine value is related to the number of double bonds of fatty acids and mainly depends on the origin of the vegetable oil. Monoglyceride, diglyceride and glycerol were formed during the transesterification of triglyceride and these compounds should be removed from BDF. The total glycerin results, which include the amounts of mono-, di- and triglyceride and glycerol, were lower than the minimum requirements for BDF in the European standard (EN-14214). In particular, the amounts of intermediates (mono- and triglyceride) of BDF obtained using CaO catalyst were lower than those obtained using KOH catalyst. Thus, the quality of BDF produced using CaO catalyst at 120°C was acceptable, judging from the quality required in the European standard (EN-14214).

CONCLUSIONS

High temperature BDF production using CaO catalyst under reflux conditions was proposed. The FAME yield for transesterification of SFO indicated a maximum value in the molar ratio range from 6:1 to 18:1. Meanwhile, the water containing in WCO activated the CaO catalyst for the transesterification. Also, the FAME yield decreased as the molar ratio increased, due to dilution of water by methanol. The FAME yield of SFO was higher than that of WCO under the same conditions, due to the presence of free fatty acids in WCO. The FAME yield of SFO and WCO reached more than 92 and 84%, respectively, at a molar ratio of 6:1 and a reaction temperature of 80°C for 120 min with 3 wt.% CaO catalyst. Thus, CaO catalyst showed good catalytic activity at 120°C under reflux conditions. In addition, the fuel properties of the BDF produced at 120°C with 5 wt.% CaO catalyst satisfied the values required in the EU standard for biodiesel fuel (EN-14214).

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