Research Report

還流条件下 CaO 触媒によるﾋﾏﾜﾘ油からのﾊﾞｲｵﾃﾞｨｰｾﾞﾙ製造

Biodiesel production from sunflower using CaO catalyst under reflux conditions

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Transesterification of sunflower oil (SFO) 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 CaO catalyst showed good catalytic activity 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).

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[1-3]. 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 is produced using a homogeneous catalyst such as KOH, NaOH, HCl and H_2SO_4 under the mild conditions[4-7]. 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[4]. However, heterogeneous solid catalysts can solve these problems due to the easy separation of the catalyst from the FAME and to the reusable properties of the catalyst[4, 8, 9, 10].

In this study, transesterification of SFO 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.

BDF Production Process

Transesterification of oil with methanol was performed in a 100 mL flask equipped with a magnetic stirrer, a thermometer and a reflux condenser. 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 flask was immersed in an oil bath. The reaction temperature was varied from 60-120 °C. 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 chromatograph (HPLC, Tosoh Corp., Japan) equipped with a silica-gel column (Shimpack CLC-SIL, Shimadzu Corp., Japan) and a refractive index detector. 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.

BDF production from SFO

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[8]. 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 11). In the case of CaO catalyst, Kouze *et al.*[12] 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.*[13] reported that the optimum molar ratio for the transesterification of soybean oil at 65 °C was 12:1. As

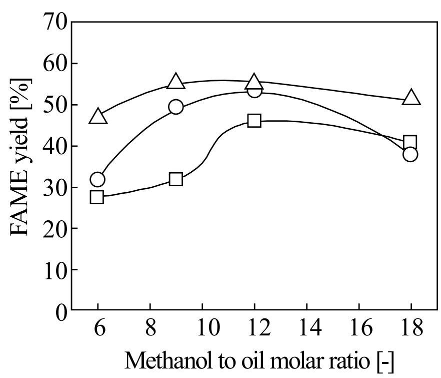

Fig. 1. Effect of the molar ratio of methanol to oil on the FAME yield for transesterification of SFO: Reaction temperature, □, 80 °C; ○, 100 °C; △, 120 °C; 5 wt% CaO catalyst; Reaction time = 30 min.

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.

The effects of reaction time and temperature on the FAME yield for transesterification of SFO are shown in Fig. 2. As the reaction time progressed, the FAME yield showed S-shape curves, which, according to Kouzu *et al.*[12] 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 mixture. Guan *et al.*[7] 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.

Fig. 3 shows the effect of reaction temperature on FAME yield for the transesterification of SFO.

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.*[8] 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.

Fig. 4 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[13, 14]. The FAME yield was also affected by mass transfer between the reactant and catalyst[8, 13, 14]. 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[15, 16].

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 2hr 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 1 summarizes the fuel properties of the produced BDF.

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[17, 18]. 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/100g) 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.

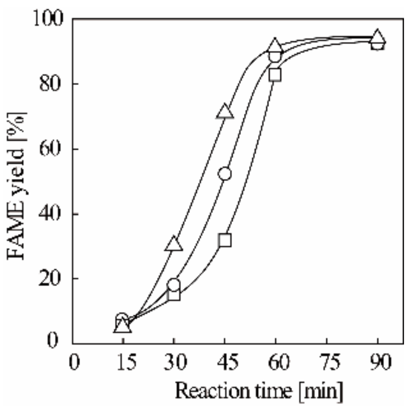

Fig. 2. Effects of reaction time on FAME yield for transesterification of SFO: □, 80 °C; ○, 100 °C; △, 120 °C; 3 wt% CaO; Molar ratio of methanol to oil = 6:1.

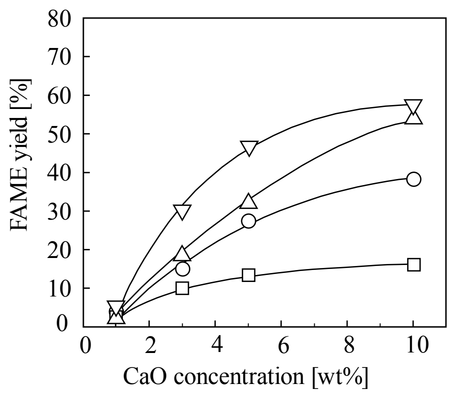

Fig. 3. Effects of reaction temperature on FAME yield: □, 3 wt% CaO; ○, 5 wt% CaO; ▽, 10 wt% CaO; Molar ratio of methanol to oil = 6:1; Reaction time = 30 min.

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).

In summary, 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. The FAME yield of SFO reached more than 92 % 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 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). The results obtained in this study are suitable for commercialization.

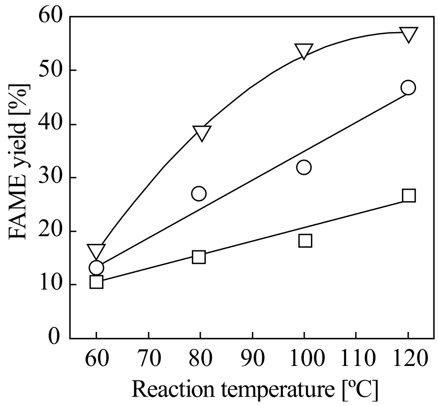

Fig. 4. Effects of catalyst concentration on FAME yield: Reaction temperature □, 60 °C; ○, 80 °C; △, 100 °C; ▽, 120 °C; Molar ratio of methanol to oil = 6:1; Reaction time = 30 min.

Table 1. Fuel specifications of BDF from sunflower oil

BDF sample	Catalyst	3wt% KOH	5wt% CaO	5wt% CaO	EU guide line
	Reaction temp.	60°C	60°C	120°C	
Pour point (°C)		-7.5	-7.5	-2.5	-
Flash point (°C)		188.5	178.5	182.5	≥120
Alkali metal Na (ppm)		<2	-	-	≤5
Alkali metal K (ppm)		<2	-	-	≤5
Alkali earth metal Ca (ppm)		-	<14 (4600)[a]	<2 (13000)[a]	≤5
Alkali earth metal Mg (ppm)		-	<2 (<2)[a]	<2 (<2)[a]	≤5
Iodine value (gI/100g)		119	123	123	≤120
Monoglyceride (wt%)		0.53	0.12	0.26	≤0.80
Diglyceride (wt%)		0.07	0.04	0.04	≤0.20
Triglyceride (wt%)		<0.05	<0.05	<0.05	≤0.20
Free glycerin (wt%)		<0.005	<0.005	<0.005	≤0.20
Total glycerin (wt%)		0.15	0.04	0.07	≤0.25

a : unwashed BDF

Reference

1) M.S. Graboske, R.I. Mcdormick, *Prog. Energy Combust. Sci.* **24**, 125 (1998).
2) U. Schuchardt, R. Sercheli, R.M. Vargas, J. Braz. *Chem. Soc.* **9**, 199 (1998).
3) F. Ma, M.A. Hanna, *Bioresour. Technol.*, **70**, 1(1999).
4) G. Vicente, M. Martinez, J. Aracil, *Bioresour. Technol.*, **92**, 297 (2004).
5) L.C. Meher, D.V. Sagar, S.N. Naik, *Renew. Sustain. Energy Rev.*, **10**, 248 (2006).
6) G. Guan, N. Sakurai, K. Kusakabe, *Chem. Eng. J.*, **146**, 302 (2009).
7) G. Guan, K. Kusakabe, K. Moriyama, N. Sakurai, *Ind. Eng. Chem. Res.*, **48**, 357 (2009).
8) X. Liu, H. He, Y. Wang, S. Zhu, X. Piao, *Fuel*, **87**, 216 (2008).
9) H.K. Kim, B.S. Kang, M.J. Kim, Y.M. Park, D.K. Kim, *Catal. Today*, **93**, 315 (2004).
10) M.P. Dorado, E. Ballesteros, F.J. Lopez, M. Mittelbach, *Energy Fuels*, **18**, 77 (2004).
11) H. Fukuda, A. Kondo, H. Noda, *J. Biosci. Bioeng.*, **92**, 405 (2001) .
12) M. Kouzu, T. Kasuno, M. Tajika, Y. Sugimoto, S. Yamanaka, J. Hidaka, *Fuel*, **87**, 2789 (2008).
13) X. Liu, X. Piao, Y. Wang, S. Zhu, H. He, *Fuel*, **87**, 1076 (2008).
14) X. Liu, X. Piao, Y. Wang, S. Zhu, *Energy Fuels*, **22**, 1313 (2008).
15) S. Yan, H. Lu, B. Liang, *Energy Fuels*, **22**, 646 (2008).
16) W. Xie Z. Yang, *Catal. Lett.*, **117**, 159 (2007).
17) J. van Gerpen, B. Shanks, R. Pruszko, D. Clements, G. Knothe (Eds). *National Renewable Energy Laboratory, Colorado*, 37 (2004).
18) J.M. Encinar, J.F. Gonzalez, A. Rodriguez-Reinares, *Fuel Process. Techonol.*, **88**, 513 (2007).