

BIODIESEL PRODUCTION FROM WASTE OILY SLUDGE BY ACID-CATALYZED ESTERIFICATION

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Abstract

Waste oily sludge (WOS) with high free fatty acids (FFA) content was used as a feedstock for biodiesel production. Oil content was firstly extracted from WOS containing water using hexane, and approximately 71 wt% of the extracted oil was FFA. The extracted oil was esterified with methanol to produce biodiesel using sulfuric acid or solid ferric sulfate catalyst. The fatty acid methyl ester yield reached above 86% for both catalysts. In addition, ferric sulfate can be easily recovered from the reaction system and reused two times without rapid decrease in the catalyst activity.

Keywords: Biodiesel; esterification; free fatty acid; ferric sulfate.

1. Introduction

Biodiesel fuel (BDF) has been considered to have great potential as an alternative diesel fuel. To date, edible oil such as soybean oil in USA, rapeseed oil in Europe, and palm oil in southeastern Asia has been used to produce biodiesel [1,2]. However, the increase in cost and human demand of edible oils will prevent it from being used for the BDF production. In many countries, the government does not encourage the research on biodiesel production using edible oils. Therefore, non-edible oils, waste vegetable oil [3-8] and animal fats such as greases [9,10], poultry fat [11], beef tallow [10], and salmon oil [12] could become alternative feedstocks for the BDF production. The founding of other low cost feedstock is also of interest. For example, Jin et al. [13] used the mixture of oil sediments and soapstock for BDF production, and a process consisting of three steps was employed in order to get a high conversion. However, these low quality oils often contain large amounts of FFA, which makes soap during the transesterification of triglyceride by an alkali catalyst.

Solid acid catalysts such as sulfated zirconia [14], and organosulfonic acid mesoporous silica [15] have been developed for the esterification of long chain fatty acids. However, the activities and stability of these solid acid catalysts are very low in comparison with sulfuric acid. Recently, Hara et al. [16] and Zong et al. [17] prepared a sugar catalyst by incomplete carbonization of D-glucose followed by sulfonation, and found that this sugar catalyst was a highly effective, minimally polluting and re-usable catalyst that is highly suitable for the BDF production from waste oils with a high acid value. Ni et al. [18] reported that a silica-supported Nafion® resin (SAC-13) can be used for the esterification of palmitic acid dissolved in commercial sunflower oil. The SAC-13 catalyst exhibited a good reusability without activation treatment. Chai et al. [19] indicated that

heteropolyacid $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ had a higher catalytic activity than sulfuric acid at low temperature in the transesterification of *Eruca sativa* Gars (ESG) oil. Also FFA and moisture contents in the oil did not affect the activity of this heteropolyacid catalyst, which could be reused several times. The immobilized diphenylammonium triflate catalysts exhibited similar activity to the homogeneous diphenylammonium salts in the reduction of FFA content in greases and could be reused for BDF production from FFA-rich oils [9]. In many BDF productions from FFA-rich oils, the esterification of FFA using acid catalysts was carried out after a pretreatment of feedstock [20-24]. Wang et al. [20] used ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$) as a solid acid catalyst for esterification of FFA in waste cooking oil. The conversion of FFA was 97.22 % after 4 h reaction at 95 °C when the methanol/oil ratio was 10:1 with a catalyst content of 3 wt%. The catalyst can be reused at least 10 times with 10 wt% of fresh addition.

In machine industries, vegetable oils are commonly used as cutting fluids, particularly, metal cutting and metal forming. Thus waste cutting oils containing a large amount of water and solid sludge could be a potential feedstock for BDF production. In this study, BDF synthesis from waste oily sludge (WOS) was investigated. The feed stock oil was extracted from WOS by hexane, and the extracted oil was reacted with methanol to produce BDF by using a sulfuric acid or ferric sulfate catalyst.

2. Experimental

2.1. Materials

Dehydrated methanol, hexane, acetone, sulfuric acid (96 %), iron (III)

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sulfate n-hydrate, iron (II) sulfate heptahydrate, iron (III) chloride, oleic acid, and palmitic acid were obtained from Wako Pure Chemistry Industry, Japan. Iron (III) sulfate n-hydrate and iron (II) sulfate heptahydrate were calcinated in N₂ flow at 200 °C for 5 h before use.

The acid value of the oil separated from the WOS was determined using standard titration methods [21]. The compositions of FFA in the separated oil was determined by a FID-GC (Shimadzu GC-8A, Japan) with a Silar 10C 10 % Uniport HP glass column after methylation. Column temperature was kept at 190 °C and helium was used as the carrier gas. The average molecular weight of the FFA was calculated from the obtained compositions. Water content in the oil was determined with a Karl-Fisher titrator (MKC-610, Kyoto Electronic Manufacturing Co. Ltd). The concentration of triglycerides in the oil was analyzed using high performance liquid chromatography (HPLC, TOSOH, Japan) equipped with a silica-gel column (Shimpack CLC-SIL, Shimadzu, Japan) and a refractive index detector using a mobile phase of n-hexane/2-propanol = 99.5/0.5 (v/v). The column temperature was kept constant at 40 °C.

2.2. Method

Extraction tests of WOS were performed by using methanol, acetone and hexane. WOS was mixed with organic solvent and vigorously stirred for 1h for extraction. The obtained mixture was centrifuged at 6000 rpm for 20 min for removal of solid particles or water-rich phase. The obtained liquid phase was evaporated at 85 °C to remove organic solvent. Thus, the obtained oil phase changed from a liquid to a solid at room temperature.

Esterification of the oil extracted from the WOS with methanol in the presence of a catalyst was performed in a 200 mL flask equipped with a magnetic stirrer, a thermometer and a reflux condenser. The methanol/oil molar ratio was in a range of 5-30. Sulfuric acid with four different concentration (1, 2, 3 and 5 wt% based on the oil), and ferric sulfate with three different concentrations (4, 8 and 10 wt% based on the oil) were used as catalyst. The reaction temperatures were 30, 60 and 100 °C. For comparison, oleic acid and palmitic acid were also used for the production of the fatty acid methyl ester (FAME) by esterification. The used ferric sulfate catalyst were recovered by filtration from the slurry after the reaction, washed by hexane several times, and reused for FAME production.

The reaction product (10 mL) was washed with distilled water and centrifuged at 6000 rpm for 20 min. The upper ester layer, resulting from centrifugation, was rinsed with distilled water and the mixture was centrifuged again. These procedures were repeated several times until the pH value in the aqueous phase reached 7.0. For analysis, 0.1 ml of the rinsed sample was diluted with 3 ml of hexane. Concentrations of triglycerides and FAME were analyzed using high performance liquid chromatography.

The FAME yield in the product was calculated as follows:

$$FAME\ yields = C_{FAME} / (C_{FFA} + 3C_{TG}) \times 100 \quad (1)$$

where C_{FAME}, C_{FFA} and C_{TG} are the concentrations of FAME in the feedstock, FFA and triglyceride in the product, respectively.

3. Results and discussion

When 10.623 g of WOS was extracted by 30 ml of hexane, 3.3 g of the oil containing 0.12 wt% H₂O was obtained. When the remaining solid phase was extracted by hexane again, only 0.29 g of the oil was obtained, suggesting that almost all oil components in the WOS were recovered through a single hexane extraction procedure. The recovery ratios of the oil component from the WOS were 31, 27 and 15 % for hexane, acetone and methanol extraction, respectively. Thus hexane was used as extraction solvent in this study. The acid value of the extracted oil was 148.5 mg-KOH/g. The compositions of FFA in the oil determined with GC after methylation are shown in Table 1. The average molecular weight calculated from this composition was approximately 269 g/mol. The weight fraction of FFA in the oil, which can be determined from the acid value and the average molecular weight, was as high as 71 wt%. The weight fraction of triglyceride in the oil evaluated from the analysis of HPLC was approximately 3.3 wt%. The weight fraction of the remaining impurities such as diglyceride and monoglyceride was approximately 26 wt%. Therefore, acid catalysts were chosen for esterification of the extracted oil.

Table 1 : FAME compositions in the extracted oil (wt%)

Palmitic (16)	Oleic (18:1)	Linoleic (18:2)	Linoleic (18:3)	Arachidic (20)
55.1	37.9	6.4	0.2	0.4

Fig. 1 shows the effect of H₂SO₄ concentration on FAME yield at a reaction temperature of 60 °C. The methanol/oil molar ratio was fixed at 10. When 1.0 wt% of H₂SO₄ based on oil weight was used, FAME yields after a reaction time of 30 min reached 87.6 and 88.6% for the esterification of oleic acid and palmitic acid, respectively. However, the FAME yield of the oil extracted from WOS was significantly lower under the same conditions because the catalyst was deactivated by various impurities contained in the oil and therefore increased with an increase in H₂SO₄ concentration. The FAME yield attained to above 80 % after a reaction time of two hours at the H₂SO₄ concentration of 2wt%. Generally, water formed in FFA esterification could shift esterification equilibrium toward reactant and deactivate the catalyst [22]. Thus, the reaction reached

equilibrium after two hours in this study. Lucena et al. [25] introduced a water adsorption unit in the esterification process to remove water produced by the reaction, and found that the yield reached 99.7 % from 88.2 % for the esterification of oleic acid.

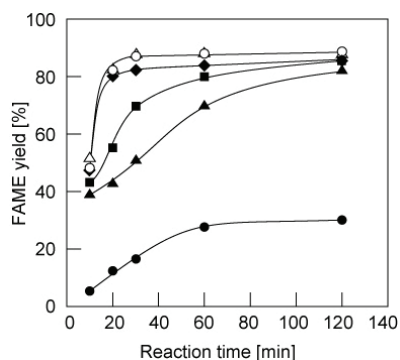


Figure 1 : Effect of H_2SO_4 concentration on FAME yield. Oil extracted from WSO (●▲■◆), oleic acid (○) and palmitic acid(△). Methanol/oil molar ratio: 10; reaction temperature: 60 °C. H_2SO_4 concentration based on oil weight: ●○△, 1 wt%; ▲, 2 wt%; ■, 3 wt%; ◆, 5 wt%.

Fig. 2 shows the effect of reaction temperature on FAME yield when the H_2SO_4 concentration was 3 wt% and methanol/oil molar ratio was 10. The reaction rate was greatly enhanced by the increase in the reaction temperature. FAME yield reached equilibrium value for 30 min at 100 °C. Hayyan et al. [24] showed that the optimum temperature of FFA conversion for the esterification of sludge palm oil was 60 °C and that FFA conversion decreased at 80 °C. Son et al. [26] investigated the esterification of oleic acid with vaporized methanol in a fixed-bed reactor packed with cation exchange resin catalyst at a reaction temperature of 100°C. The formed water was easily evaporated at a higher temperature and thus the FAME yield increased with the reaction temperature.

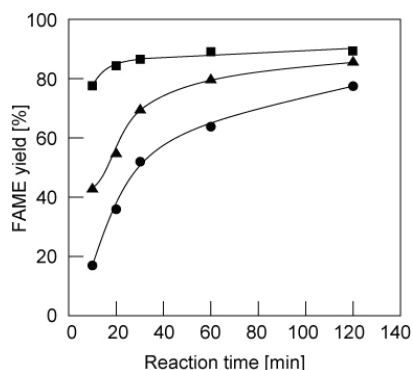


Figure 2 : Effect of reaction temperature on FAME yield. Methanol/oil molar ratio: 10; H_2SO_4 concentration based on oil weight: 3 wt%; Reaction temperatures: ●, 30 °C; ▲, 60 °C; ■, 100 °C.

Fig. 3 shows the effect of the methanol/oil molar ratio on FAME yield at a reaction temperature of 60 °C for 1 h. The FAME yield was not greatly influenced by the methanol/oil molar ratio when the ratio was above 10. Also transesterification of triglyceride in the oil did not completely proceed in the presence of an H_2SO_4 catalyst.

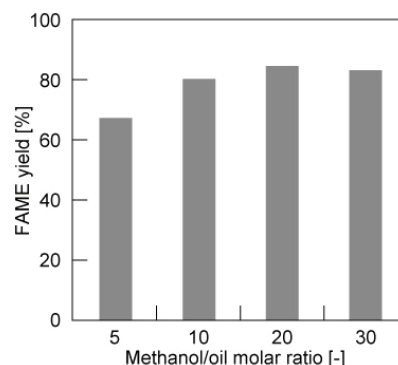


Figure 3 : Effect of methanol/oil molar ratio on FAME yield. H_2SO_4 concentration based on oil weight: 3 wt%; Reaction temperature: 60 °C; Reaction time: 1 h

In the present study, WOS was provided from the machine industry and the main content of the sludge was composed of fine steel particles. Therefore, fine steel powder was added to the oil extracted from the WOS and the esterification of the resulting slurry was carried out. As a result, fine steel powder had no effect on the FAME yield. The presence of residual iron salts in the oil might be unavoidable. Considering the beneficial usage of residual iron salts as a catalyst for BDF production, some iron salts catalysts were screened for the esterification of the extracted oil. As indicated in **Table 2**, $FeCl_3$ has a similar activity to $Fe_2(SO_4)_3$ but is soluble in methanol. $FeSO_4$ is insoluble in methanol but shows low catalyst activity for the esterification. Therefore, $Fe_2(SO_4)_3$ was chosen as a solid catalyst for the esterification hereafter.

Table 2 : Catalytic activity of different Fe-based solid catalysts

Catalyst	FAME yield [%]	Solubility in methanol
$Fe_2(SO_4)_3$	85.7	Small
$FeCl_3$	84.8	Large
$FeSO_4$	5.2	Small

Methanol/oil molar ratio: 10; Reaction temperature: 60 °C
Catalyst concentration: 3 wt%; Reaction time: 2 h

Fig. 4 shows the catalyst activity of $\text{Fe}_2(\text{SO}_4)_3$ for esterification of palmitic acid as well as the oil extracted from WSO at 60 °C with a methanol/oil molar ratio of 10. $\text{Fe}_2(\text{SO}_4)_3$ is insoluble in methanol, FFA, triglyceride or FAME, but is soluble in water. Esterification was catalyzed by iron salts as a heterogeneous catalyst. Water produced in esterification could have a negative effect on the catalyst activity. However, $\text{Fe}_2(\text{SO}_4)_3$ in the presence of water becomes basic compounds like $\text{Fe}_2[(\text{SO}_4)_x(\text{OH})_{6-2x}]$ and hydroxonium ions $[\text{H}^+]$ which are effective to the acid-catalyzed esterification in the homogeneous phase.

As a result, the induction period of the esterification was observed for a $\text{Fe}_2(\text{SO}_4)_3$ catalyst as shown in **Fig. 4**. Various impurities in the oil could also have the undesirable effect of deactivating the catalysts. Comparing with the esterification of palmitic acid, larger amounts of $\text{Fe}_2(\text{SO}_4)_3$ catalyst were necessary for esterification of the oil extracted from WSO to get a high FAME yield. Comparing with the results of an H_2SO_4 catalyst shown in **Fig.1**, catalyst activities of both catalysts were almost same despite the fact that a larger amount of solid $\text{Fe}_2(\text{SO}_4)_3$ catalyst was needed. In addition, the solid $\text{Fe}_2(\text{SO}_4)_3$ catalyst was easily separated from the reaction system by filtration.

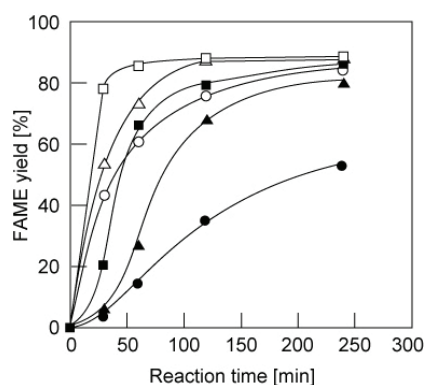


Figure 4 : Effect of $\text{Fe}_2(\text{SO}_4)_3$ concentration on FAME. Oil extracted from WSO (●▲■), palmitic acid (○△□). Methanol/oil molar ratio: 10; reaction temperature: 60 °C. $\text{Fe}_2(\text{SO}_4)_3$ concentration based on oil weight: ○, 1 wt%; △, 2 wt%; □, 3 wt%; ●, 4 wt%; ▲, 8 wt%; ■, 10 wt%.

As shown in **Fig. 5**, the catalyst activity of $\text{Fe}_2(\text{SO}_4)_3$ decreased with the number of repetitions for esterification of palmitic acid as well as the oil extracted from WSO. However, the FAME yields still reached 84.3 % and 73.2 % for palmitic acid and WSO, respectively, after the 2 repetitions, suggesting that $\text{Fe}_2(\text{SO}_4)_3$ is appropriate as a solid catalyst for repeated use.

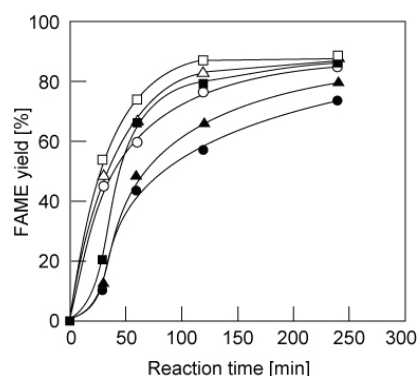


Figure 5 : Reusability of $\text{Fe}_2(\text{SO}_4)_3$ catalysts. Oil extracted from WSO (●▲■, $\text{Fe}_2(\text{SO}_4)_3$ concentration: 10 wt%), palmitic acid (○△□, $\text{Fe}_2(\text{SO}_4)_3$ concentration: 2 wt%). Methanol/oil molar ratio: 10; reaction temperature: 60 °C; Fresh catalysts: ■□, used catalysts (repetition time = 1); ▲△, used catalysts (repetition time = 2); ●○.

4. Conclusions

FFA-rich oil extracted from WSO was used as a feedstock of BDF production. H_2SO_4 and $\text{Fe}_2(\text{SO}_4)_3$ were successfully used as catalysts for the esterification of FFA. The FAME yields reached approximately 86 % for both catalysts under suitable condition. $\text{Fe}_2(\text{SO}_4)_3$ was appropriate as a solid catalyst for repeated use.

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