

Production of biodiesel from soapstock using an ion-exchange resin catalyst

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Abstract—The feasibility of biodiesel production from soapstock containing high water content and fatty matters by a solid acid catalyst was investigated. Soapstock was converted to high-acid acid oil (HAAO) by the hydrolysis by KOH and the acidulation by sulfuric acid. The acid value of soapstock-HAAO increased to 199.1 mg KOH/g but a large amount of potassium sulfate was produced. To resolve the formation of potassium sulfate, acid oil was extracted from soapstock and was converted to HAAO by using sodium dodecyl benzene sulfonate (SDBS). The maximum acid value of acid oil-HAAO was 194.2 mg KOH/g when the mass ratio of acid oil, sulfuric acid, and water was 10 : 4 : 10 at 2% of SDBS. In the esterification of HAAO using Amberlyst-15, fatty acid methyl ester (FAME) concentration was 91.7 and 81.3% for soapstock and acid oil, respectively. After the distillation, FAME concentration became 98.1% and 96.7% for soapstock and acid oil. The distillation process decreased the total glycerin and the acid value of FAME produced a little.

Key words: Biodiesel, Soapstock, Acid Oil, Anionic Surfactant, High-acid Acid Oil, Solid Acid Catalyst

INTRODUCTION

Due to the increase in the price of the petroleum and the environmental concerns about air pollution from vehicles, the use of renewable resources as alternative feedstock for petroleum is gaining growing interest [1,2]. Biodiesel, defined as an alternative diesel fuel derived from the oils and fats of plants and animals, has become a fast growing market product during the last few years [3-6]. Biodiesel has been mainly produced from edible vegetable oils including soybean, palm, and rapeseed oil. Since the prices of edible vegetable oils are quite high, many efforts have been devoted to find cheaper feedstock such as non-edible vegetable oils or waste oils for the biodiesel production [7].

Soapstock, a by-product of the refining of vegetable oils, is a potential biodiesel feedstock. It is a heavy alkaline aqueous emulsion of lipids containing about 50% water, with free fatty acids, phosphatides, triglycerides, pigments and other minor non-polar compounds. Soapstock is generated at a rate of about 6% of the volume of crude oil refined. Its market value is about one-tenth the price of crude vegetable oil [8]. Acid oil is also a possible feedstock for biodiesel. Acid oil is prepared from typical industrial processing of soapstock by acidulation, wherein sulfuric acid and steam are employed to achieve partial acid hydrolysis or removal of the triglyceride and phosphatide ester bonds of soapstock. The heavy emulsion of soapstock is destroyed, resulting in spontaneous separation of two phases, an aqueous and an oil layer. The oil layer is termed acid oil. It is used as an animal feed ingredient and as a source of industrial fatty acid [9].

Extensive works to produce biodiesel from soapstock and acid oil have been carried out by Hass et al. [2,8-11]. They prepared high-acid acid oil (HAAO) containing 96.2% of free fatty acid (FFA)

by the saponification and the acidulation. And then the esterification reaction of HAAO was catalyzed by sulfuric acid. By applying this process, Hass et al. significantly reduced the amount of methanol but the sodium sulfate waste produced during the preparation of HAAO remained as a problem [9].

The esterification of oil using a homogeneous acid catalyst like sulfuric acid has some disadvantages: the catalyst cannot be recovered, the biodiesel must be neutralized at the end of reaction, and there is a limited use for continuous process. To overcome these, the use of solid acid catalyst, which can be easily recovered and reused, was proposed [12-14]. Lopez et al. evaluated the performance of several kinds of solid acid and base catalysts [14]. Amberlyst-15 among acid catalysts and ETS-10 (Na) among base catalysts showed the best activity for biodiesel production.

In this study, the biodiesel production from soapstock by a solid acid catalyst, Amberlyst-15, was investigated. Soapstock-HAAO was prepared by the procedures described by Hass and the esterification efficiency of Amberlyst-15 was examined [9]. To resolve the formation of potassium sulfate waste, a new process to convert soapstock to HAAO by using an anionic surfactant, sodium dodecyl benzene sulfonate (SDBS), was suggested.

EXPERIMENTAL METHODS

1. Materials

Soybean soapstock was kindly supplied by CJ Corp. in Korea. The compositions of soapstock are shown in Table 1. The water content of soapstock was 44.2%. Because soapstock is the alkaline

Table 1. The composition of soapstock

Water content (%)	Fatty matters (%)	Not measured (%)
44.2	46.1	9.7

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Table 2. The composition of acid oil

Free fatty acids (%)	Water content (%)	Fatty matters (%)	Not measured (%)
54.9	1.4	42.6	1.1

aqueous emulsion of lipids, there was little FFA. However, it contained fatty matters such as soap, tri-, di-, monoglycerides, and phosphatides which could be converted to fatty acid methyl ester (FAME). KOH (Junsei, >85%) and sulfuric acid (DC Chemical, >95%) were used for preparation of HAAO from soapstock.

Acid oil was extracted from soapstock by the process developed by the co-workers of Guangzhou Institute of Energy Conversion in China [15]. The compositions of acid oil extracted are shown in Table 2. The water content of acid oil was 1.4%. Acid oil contained FFAs and fatty matters like tri-, di-, and monoglycerides. SDBS (Sigma, >80%), an anionic surfactant, was used for the preparation of HAAO from acid oil.

For the esterification reaction, methanol (Duksan Chemical, >99.5%) and Amberlyst-15 (Aldrich) were used. For GC analyses, n-heptane (J.T. Baker, >99.0%), methyl heptadecanoate (Fluka, >99.5%), 1,2,4-butanetriol (Supelco, >98.5%), 1,2,3-tricaproylglycerol (Supelco, >99.9%), and N-methyl-N-trimethylsilyl-trifluoroacetamide (Sigma-Aldrich) were used.

2. Preparation of HAAO

HAAO was prepared from soapstock and acid oil. Soapstock-HAAO was prepared by the procedures of Hass including the hydrolysis by KOH and the acidulation by sulfuric acid at room temperature [9]. The acid oil extracted from soapstock was mixed with sulfuric acid, SDBS, and water to prepare the acid oil-HAAO at 80 °C.

3. Esterification of HAAO by Amberlyst-15

HAAO was reacted with methanol in the presence of 30% Amberlyst-15 as a catalyst. The molar ratio of HAAO to methanol was 1 : 3, 1 : 6, and 1 : 9. A round flask was connected with a condenser to minimize the loss of methanol. The reaction temperature, 80 °C, was maintained in the oil bath. FAME concentrations were measured intermittently.

4. Analyses

The acid values of acid oil and HAAO were measured by the titration method using KOH. Water content was measured by Karl Fisher Titrator (Mettler Toledo DL31, USA).

FAME content was analyzed by gas chromatography equipped with auto-injector (Agilent 6890A, USA). The INNOWAX column (30 mm×0.32 mm×0.5 μm) was used for the analysis of FAME. The oven temperature was started at 50 °C for 1 min, increased to 200 °C at a rate of 15 °C/min, held at the temperature for 9 min and again increased to 250 °C at a rate of 2 °C/min and then held at the temperature for 2 min. Methyl heptadecanoate was used as the internal standard.

Free glycerin, tri-, di-, and monoglycerides were determined by gas chromatography equipped with on-column injector (Agilent 6,890N, USA). A DB-5HT column (15 m×0.32 mm×0.1 μm) was used for the analytical work. The oven temperature was held at 50 °C for 1 min, increased to 180 °C at a rate of 15 °C/min and increased to 230 °C at a rate of 7 °C/min and again increased to 370 °C at a rate of 10 °C/min, and then held at the temperature for 10 min. 1,2,4-

butanetriol and 1,2,3-tricaproylglycerol were used as the internal standards.

RESULTS AND DISCUSSION

1. Esterification of Soapstock-HAAO by Amberlyst-15

When the FFA content of feedstock is within 1 to 5%, it is desirable to esterify the FFA by using acid catalyst before transesterification by alkali catalyst. However, because soapstock contained nearly 50% of fatty acid soap, the preparation of HAAO was introduced. Soapstock-HAAO was prepared by the procedures of Hass and the acid value was 199.1 mg KOH/g. The acid value can be converted to the FFA content theoretically. Assuming 1 : 1 stoichiometry in the neutralization of FFA by KOH, 1 mg KOH/g corresponds to the FFA content of 0.5 wt% [9]. Therefore, soapstock-HAAO containing 99.6 wt% of FFA. 39.7 g of soapstock-HAAO was obtained from 100 g of soapstock.

Fig. 1 shows the profile of FAME concentration with time when the molar ratio of HAAO to methanol was 1 : 9. After 9 hrs, FAME content became 91.7%. Within 10 min, about 60% of methyl ester

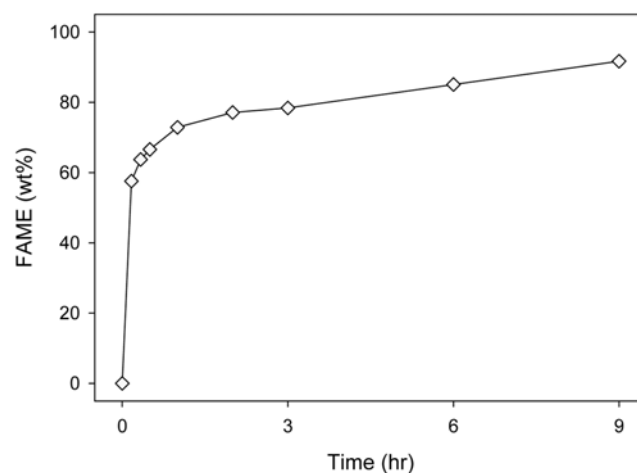


Fig. 1. Profile of FAME content at 1 : 9 of the molar ratio of soapstock-HAAO to methanol.

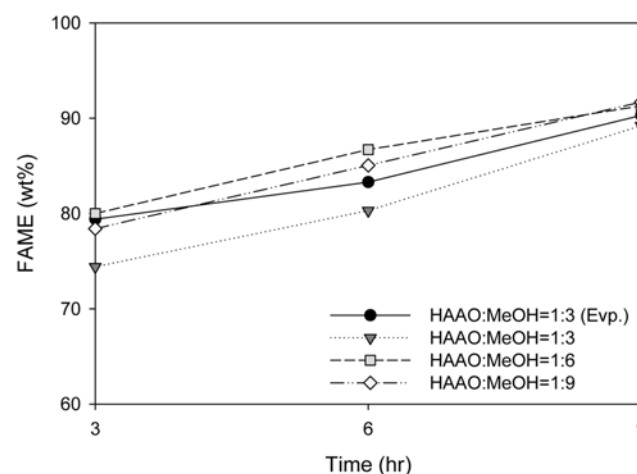


Fig. 2. Profile of FAME content with the molar ratio of soapstock-HAAO to methanol.

was produced and the esterification rate gradually decreased. Fig. 2 shows the profile of FAME concentration when the molar ratio of oil to methanol was changed to 1 : 3, 1 : 6, and 1 : 9. The esterification by a solid acid catalyst is generally slower than by sulfuric acid, but 9 hrs was agreeable compared with the result of Hass et al. [9,14]. The result at 1 : 6 of the molar ratio was similar to that of 1 : 9. At 1 : 3 of the molar ratio, the FAME content was a little low. When the molar ratio was 1 : 3, the evaporation process was conducted after 3 and 6 hrs to remove water produced from esterification reaction. In this case, the FAME concentration was higher than at 1 : 3 of the molar ratio without the evaporation and similar to the cases of 1 : 6 and 1 : 9. The final FAME content was 90.3, 89.2, 91.3, and 91.7%, respectively. 91.7% was the maximum purity of biodiesel produced from soapstock, and Hass et al. also obtained a similar result using sulfuric acid [9]. Because the maximum purity was about 90% after 9 hrs, in some cases, the distillation of 80% biodiesel produced after 3 hrs could be the best way for process economics.

2. Preparation of Acid Oil-HAAO Using SDBS

The acid value of acid oil extracted from soapstock was 109.8 mg KOH/g, and 46.8 g of acid oil was obtained from 100 g of soapstock.

Acid oil was mixed with sulfuric acid, water, and SDBS to prepare HAAO. SDBS is an anionic surfactant containing sulfonate group. There is no reference for use of SDBS to make HAAO, but the capability of sulfonate groups of SDBS was tested. When SDBD was added to the mixture, the acid value increased more than the case without surfactant (Fig. 3). The concentration of surfactant was based on the weight of acid oil. The optimum point was located at 2% of SDBS. Generally, when the concentration of surfactant is low, the surfactant solution forms the mono-, di-, triphase according to their ratio. As the concentration of surfactant increases, the surfactant solution forms viscous solution, gel, or lamellar liquid crystalline. Therefore, SDBS concentration having a maximum acid value was determined by the complex nature of the surfactant solution containing acid oil and sulfuric acid [16-18]. When there was no surfactant, the acid value increased a little more than the initial value, 109.8 mg KOH/g. This meant that high temperature, water,

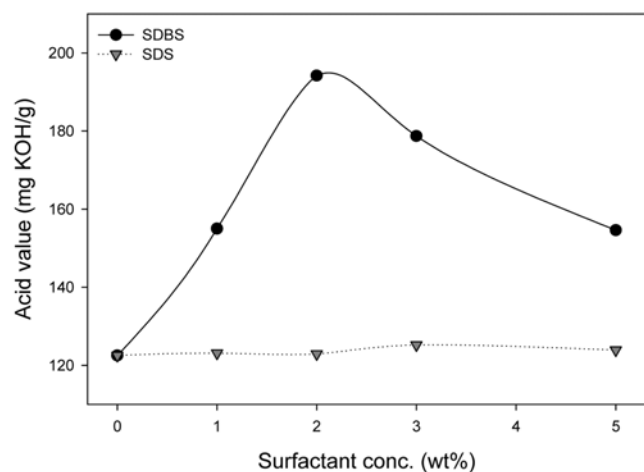


Fig. 3. Profile of acid value of acid oil with surfactant (acid oil : sulfuric acid : water = 10 g : 4 g : 10 g).

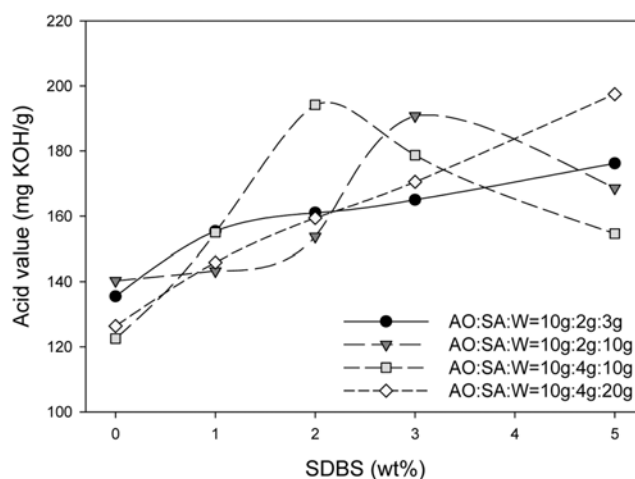


Fig. 4. Profile of acid value of acid oil.

and sulfuric acid slightly affected the production of FFA. Another anionic surfactant, sodium dodecyl sulfate (SDS, Sigma, >95%) containing sulfate group, was not effective in converting acid oil to HAAO. Fig. 4 shows the profile of acid value under different ratios of acid oil, sulfuric acid, and water. The ratios were selected to examine the effects of the amount and concentration of sulfuric acid solution on the acid value. When the ratios were 10 : 2 : 10 and 10 : 4 : 10, there were maximum points within 5% of SDBS. In the cases of 10 : 2 : 3 and 10 : 4 : 20, the acid value increased up to 5% of SDBS, and there was a maximum point at more than 5%. When the ratio was 10 : 2 : 10 and SDBS concentration was 3%, the acid value was 190.8 mg KOH/g. At the ratio of 10 : 4 : 10 and 2% of SDBS, the acid value was 194.2 mg KOH/g. When the amount of water increased 3 g to 10 g, it caused a decrease of the maximum point of SDBS. When the amount of sulfuric acid increased 2 g to 4 g, it also made the maximum point of SDBS go down. However, too great an amount of water caused the dilution of solution and so more surfactant was needed.

3. Effect of SDBS on the Esterification of Acid Oil-HAAO

HAAO prepared from acid oil using SDBS and sulfuric acid had

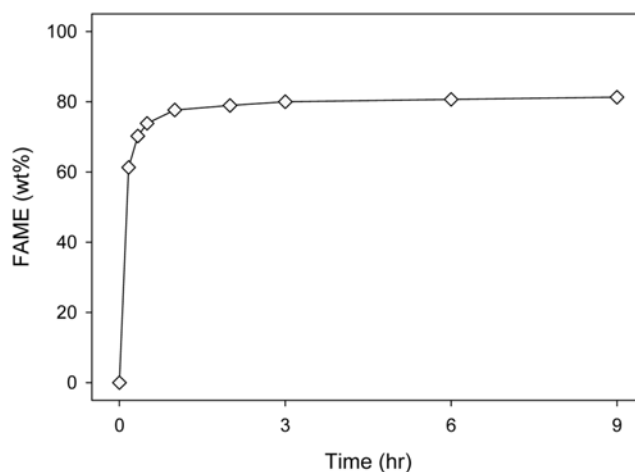


Fig. 5. Profile of FAME content at 1 : 9 of the molar ratio of acid oil-HAAO to methanol.

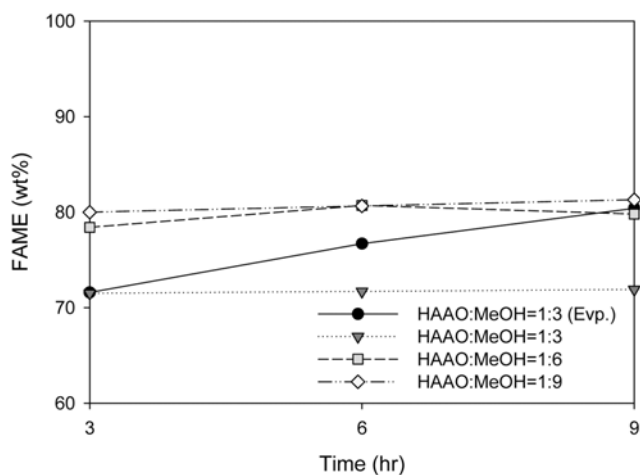


Fig. 6. Profile of FAME content with the molar ratio of acid oil-HAAO to methanol.

194.2 mg KOH/g of acid value. Fig. 5 shows the profile of FAME concentration with time when the molar ratio of HAAO to methanol was 1 : 9. Within 1 hr, about 80% of methyl ester was produced and the concentration did not increase. Fig. 6 shows the profile of FAME concentration when the molar ratio of oil to methanol was changed to 1 : 3, 1 : 6, and 1 : 9. The result at 1 : 6 of the molar ratio was similar to that of 1 : 9. At 1 : 3 of the molar ratio, the FAME content was quite low. When the molar ratio was 1 : 3, the evaporation process was conducted after 3 and 6 hrs to remove water produced from the esterification reaction. In this case, the FAME concentration increased with time. The final FAME content was 80.4, 71.9, 79.8, and 81.3%, respectively. When HAAO was prepared by using surfactant to remove the production of potassium sulfate waste, the maximum purify of biodiesel was about 80%. It is assumed that surfactant remaining in HAAO hindered the reaction of esterification. Because maximum purity was low, it needed distillation.

4. Distillation of FAME Produced from HAAO

When the molar ratio of HAAO to methanol was 1 : 9, FAME content was 91.7 and 81.3% for soapstock and acid oil (Table 3). The acid values were 4.07 and 4.87 mg KOH/g, respectively. Total glycerin was 0.063 and 0.090%, and the standard of total glycerin is 0.26%. Because total glycerin amount was very low, it could be thought that most of the soapstock and acid oil was converted to HAAO well. The purity of soapstock biodiesel was 10% higher than biodiesel produced from acid oil. It was assumed that SDBS inhibited the making of biodiesel from acid oil.

FAME obtained from HAAO of soapstock and acid oil was distilled to satisfy the FAME standard of biodiesel, 96.5%. After distil-

lation, the purity was 98.1% for soapstock biodiesel and 96.7% for acid oil biodiesel. Final acid value was 3.17 and 3.75 and decreased a little. Because the standard specification of acid value is 0.5 mg KOH/g, the acid value has to be reduced by neutralization with alkali solution. Total glycerin decreased to 0.005 and 0.003%.

CONCLUSIONS

It was possible to make biodiesel from soapstock containing high concentration of fatty materials. Soapstock was converted to HAAO and then esterified by a solid acid catalyst, Amberlyst-15. This method can be a good alternative for biodiesel production from oils with high FFA. The solid acid catalyst had several advantages for the process such as easy recovery of the catalyst and repeated use. HAAO preparation using the anionic surfactant was a nice suggestion because it did not produce the potassium sulfate waste. The evaporation process was applied to remove water during esterification reaction of FFA. Technology to remove water produced during esterification should be developed to reduce the amount of methanol, increase biodiesel purity, and reduce the operation time. In this study, the reuse of solid acid catalyst was not investigated. For further work, a reuse test of a solid catalyst will be performed.

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Table 3. Characteristics of biodiesels produced from soapstock and acid oil

	Soapstock		Acid oil	
	Before distillation	After distillation	Before distillation	After distillation
FAME (wt%)	91.7	98.1	81.3	96.7
Acid value (mg KOH/g)	4.07	3.17	4.87	3.75
Total glycerin (wt%)	0.063	0.005	0.090	0.003

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