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# Novel biodiesel production technology from soybean soapstock

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**Abstract**−This paper describes an attractive method to make biodiesel from soybean soapstock (SS). A novel recovery technology of acid oil (AO) from SS has been developed with only sulfuric acid solution under the ambient temperature (25±2 °C). After drying, AO contained 50.0% FFA, 15.5% TAG, 6.9% DAG, 3.1% MAG, 0.8% water and other inert materials. The recovery yield of AO was about 97% (w/w) based on the total fatty acids of the SS. The acid oil could be directly converted into biodiesel at 95 °C in a pressurized reactor within 5 hours. Optimal esterification conditions were determined to be a weight ratio of 1 : 1.5 : 0.1 of AO/methanol/sulfuric acid. Higher reaction temperature helps to shorten the reaction time and requires less catalyst and methanol. Ester content of the biodiesel derived from AO through one-step acid catalyzed reaction is around 92%. After distillation, the purity of the biodiesel produced from AO is 97.6% which meets the Biodiesel Specification of Korea. The yield of purified biodiesel was 94% (w/w) based on the total fatty acids of the soapstock.

Key words: Biodiesel, Soybean Soapstock (SS), Acid Oil (AO), One Step Esterification

## INTRODUCTION

Although biodiesel is becoming more and more important as an environmentally friendly and renewable fuel, the high cost of feedstock for biodiesel production is still the biggest problem to be resolved for more proliferated use of it. Hence much effort has been devoted to develop new biodiesel production processes by using cheaper feedstocks [1-4].

Soybean soapstock (SS), as a lipid-rich byproduct produced during vegetable oil refining process, is one of the most promising candidates for biodiesel production because of its easy collection. SS is generated at a rate of 6% of the volume of the crude oil produced. At the same time, the price of SS is only one-tenth of refined oil [5].

Conventional way to utilize SS involves the acidulation of SS which needs high temperature steam (80-95 °C) and excess acid [6]. The product is acid oil (AO) containing free fatty acid (FFA) and glyceride, which is typically sold as a feed of livestock. Acid oil is also used as a feedstock for soaps and fatty acid industrial production. But acidulation of soapstock is one of the least desirable processes in an integrated facility because the process is rather difficult to perform effectively and its cost cannot have significant return [7]. Another approach to recover acid oil from SS is to use isopropanol as a solvent. Reaney mixed the SS with alcohol (isopropanol) and sulfuric acid and heated to 60 °C and then the mixture was allowed to settle at room temperature for 8 hours. The upper liquid phase was heated to remove volatile materials and the yield of AO was increased to 95% [8].

Extensive works to obtain biodiesel from AO have been carried out by Haas et al. [4-6,9,10]. He developed a two stage process to make biodiesel from AO. In this process, SS was fully saponified by using an excess alkaline catalyst in the first stage. In the second stage, conventional acidulation has been applied to separate high acid oil (HAAO) having over 96% free fatty acid from water and other substances.

The process developed by Haas has three major disadvantages. First, the process takes the conventional acidulation method to recover AO from SS, which requires high temperature steam. Secondly, the technology should require an additional process, saponification of the glycerides, to convert them to free fatty acid salts. Finally, the esterification reaction time is too long, 14 hours, which leads to low productivity.

Feedstock with high acid value like AO can also be used to make biodiesel with excess methanol, catalyzed by sulfuric acid at elevated temperature and pressure. It is still a reasonable option compared with the alkaline catalyzed biodiesel production process [3,11]. Both esterification and transesterification are catalyzed by acid catalyst, which will eliminate the washing step and waste streams compared with the two-step process of acid catalysis followed by base catalysis [12].

We describe here a new technology which may produce biodiesel from SS more efficiently than the processes reported in the literature. Detailed work will be described as follows.

## EXPERIMENTAL

### 1. Materials

SS with 47% water content was provided by CJ Company in Korea. Total fatty acid content of SS is 35%. Anhydrous methanol and sulfuric acid (96-99%) were purchased from DUKSAN Pure Chemical Co. Ltd (Korea) and DC Chemical Co. Ltd (Korea) re-

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spectively. 1,2,4-Butanetriol and 1,2,3-tricaproylglycerol standards for the analysis of mono-, di- and triglycerides were purchased from SUPEL-Co (USA). N-methyl-N-trimethylsilyltrifluoroacetamide (MSTFA) and methyl heptadecanoate were obtained from SIGMA-ALDRICH Co (Switzerland). HPLC grade methanol, n-hexane and 2-propanol were obtained from J.T. BAKER Co (USA).

### 2. Separation of AO from SS

Three 100 g SS were mixed with 40 g, 60 g and 100 g de-ionized water by magnetic stirrer separately at 25 °C in beakers. pH values were measured after every gram of 20% $H_2SO_4$ aqueous solution until the mixture was separated in 2 layers. The top layer is lipid-rich phase. The bottom layer is water phase including soluble substance and small amount of lipid.

The waste water layer was discharged and the lipid rich layer was poured in 250 ml plastic bottles followed by centrifugation. The centrifugation was performed for 7 min, at 3,000 rpm and 25 °C. It was separated into three layers after centrifuging. The top layer is the AO, the middle layer is an emulsified material containing lipids, salts and water and the bottom layer primarily contains salt water.

To prepare sufficient amount of AO for biodiesel production, a 2 liter glass reactor was used to make AO from SS and the agitation speed was fixed at 450 rpm. Finally, the whole process to recover AO from SS at ambient temperature was optimized.

### 3. Biodiesel Production from AO

The experiment was carried out in a 500 ml stainless steel reactor, equipped with two tanks. One of the tanks is for adding feedstock (feed tank). The other is a buffer tank, through which the pressure of the reactor can be maintained with inert gas (nitrogen). The pre-specified amounts of AO and methanol were introduced into the reactor, when the temperature of the reactor reached the set points. The pre-specified amount of sulfuric acid was fed to the reactor by the pressure of nitrogen. The reaction temperature was maintained at 80 °C for the first 1 hour and 95 °C for the following 4 hours under the pressurized condition (4 kgf/cm$^2$). The agitation speed was maintained at 250 rpm.

Samples (1.5 ml) were withdrawn at 1 hour interval. After centrifuging, the methanol layer was drained off and the biodiesel layer was left. Then the biodiesel layer was washed by de-ionized water three times. The water content of the samples was decreased to 0.05% by vacuum evaporation. Determination of ester contents was done by HP 6890 gas chromatograph system. Determination of free and total glycerols and mono-, di-, triglyceride contents was done by another 6890N gas chromatograph system.

The experiments were done under the same reaction condition without withdrawing samples during reaction to get the true yield of biodiesel based on AO and SS. Calcium oxide was added to neutralize sulfuric acid in the reactants and methanol was recovered at 50 °C and 10 mmHg vacuum. Calcium sulfate was drained off by filtering and glycerol was decanted; crude biodiesel was left. A simple distillation system was used to purify the biodiesel. The vacuum was adjusted to be at 5±1 mmHg. The temperature was first raised to 160 °C for about 1 h; the distillate collected was referred to as the first fraction. The temperature was then raised to 200 °C in 30 min; the distillate collected was referred to as the second fraction. Finally, the temperature was raised to 220 °C in 20 min and the distillate was collected. The distillation was terminated when no more distillate appeared.

### 4. Analysis Methods

The pH values were measured by pH meter (ORION 720A, USA).

Water content was measured by Karl Fisher Titrator (METTLER TOLEDO DL31, USA).

The composition of the methyl esters was analyzed by HP 6890 gas chromatograph system equipped with 7683 auto-injector, a split/splitless injection system. The INNOWAX GC column (60 mm× 0.32 mm×0.5 μm, Agilent Inc, USA) was used for the analysis of FAME. The oven temperature was started at 150 °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 and then held at the temperature for 2 min. Methyl heptadecanoate was used as the internal standard.

Free and total glycerol and mono-, di-, triglycerides were determined by 6890N gas chromatograph equipped with on-column injector and FID. The DB-5HT column (15 m×0.32 mm×0.1 μm, Agilent Inc, USA) was used for the analytical work. The column temperature was held at 50 °C for 1 min, increased to 150 °C at a rate of 15 °C and increased to 230 °C at a rate of 7 °C and again increased to 370 °C at a rate of 10 °C and then held at the temperature for 5 min. 1,2,4-butanetriol and 1,2,3-tricaproylglycerol are used as the internal standards.

## RESULTS AND DISCUSSION

### 1. Separation of extracted AO from SS

60% de-ionized water (w/w) based on SS was found to be the least amount needed to disperse the fresh SS completely. Less than 60% de-ionized water (w/w) could not disperse the SS very well and it affected the following acidulation process.

At the same time, the rate of adding sulfuric acid had to be controlled very carefully. Otherwise, the water would not separate from the lipid-rich layer. The whole mixture has to be centrifuged to obtain AO; a large emulsion layer will form after centrifugation. The emulsion layer may entrain some lipid, which should decrease the yield of AO from SS. Table 1 shows some examples of different results.

In Table 1, data of experiment 1 and experiment 2 were the results of inappropriate operation due to adding sulfuric acid too fast. The mixture could have been emulsified again before the free fatty acid had been released completely. Once this emulsion occurred, it

**Table 1. Major experimental results of the soybean soapstock (SS) splitting work**

| Experiments | 1 | 2 | 3 |
|---|---|---|---|
| SS (g) | 100 | 100 | 100 |
| De-ionized water (g) | 60 | 60 | 60 |
| 20% $H_2SO_4$ aqueous solution (g) | 25 | 25 | 25 |
| Water separated before centrifugation (g) | 0 | 0 | 122.5 |
| Emulsion layer (g) | 16.0 | 157 | 7.0 |
| AO (g) | 40 | 26 | 46.8 |
| Water separated after centrifugation (g) | 127 | 0 | 6.2 |
| Acid value of AO gKOH/kg | 100.2 | 101 | 99.8 |
| Water content of EAO % | 2.75 | 2.25 | 3.15 |
| Weight loss of whole process g | 2 | 2 | 2.5 |

was very difficult to break the emulsion.

It was found that adding of 20% $H_2SO_4$ aqueous solution had to be stopped when pH value of the mixture reached to 7. After 10-15 min, the color of the mixture became yellow; then 20% $H_2SO_4$ aqueous solution could be added again until most of the water separated from the mixture.

Experiment 3 (Table 1) was operated as described above; finally, most of the water in the SS precipitated together with the water added afterwards in the bottom (122.5 g). The water phase was drained out, and then the remaining lipid-rich phase (60 g) was centrifuged to separate the AO from it. 46.8 g AO with 3.15% water content from 100 g SS can be obtained by centrifugation. At the same time, additional 6.2 g water was separated by centrifugation. The emulsion layer was only 7 g; the main components of the emulsion layer were phospholipids and water.

To confirm the results, five experiments were repeated under the same conditions. The yield of AO varied from 46% to 47% with water content between 2.75%-3.50%. After the water content of AO was decreased to 0.8%, an average yield of 45% of AO based on SS could be obtained.

In Table 1, it was also noticed that water content increased from 2.25% to 3.15% while the yield of AO increased from 26% to 46.8% and the acid values of resulting AO were almost at the same level. Emulsion layer may act as a filtering film to entrain some water from AO phase and baffle the water in the water phase.

Fig. 1 shows the change of pH value of experiment 3, accompanied with the adding of sulfuric acid. Initially, a flat line with a pH value of 7 was expected since the alkaline remaining in the SS is to be neutralized and the addition of sulfuric acid is going to release the free fatty acid in the soapstock. However Fig. 1 indicates a hydrolysis reaction happened before the pH value reached 7. It indicates that the sulfuric acid reacted with alkaline and free fatty acid salt at the same time. When the pH value reached 5.3, the pH decreased more quickly with the addition of sulfuric acid while the lipid-rich layer was separated from water. This indicates that most of the free fatty acid had been released at this pH value and excess sulfuric acid may have sped up the separation.

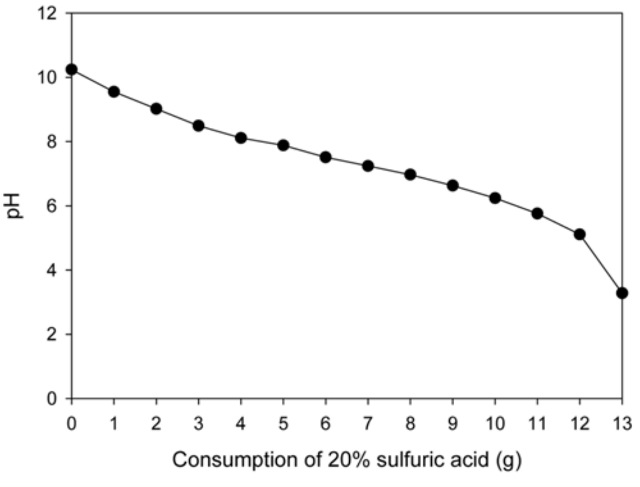

**Fig. 1. Profile of pH values during acidulation of soybean soapstock (SS).**

**Table 2. Composition of the dry acid oil (AO)**

| | FFA | MG | DG | TG | Water | Other inert materials |
|---|---|---|---|---|---|---|
| % (w/w) | 50.0 | 3.1 | 6.9 | 15.5 | 0.8 | 23.7 |

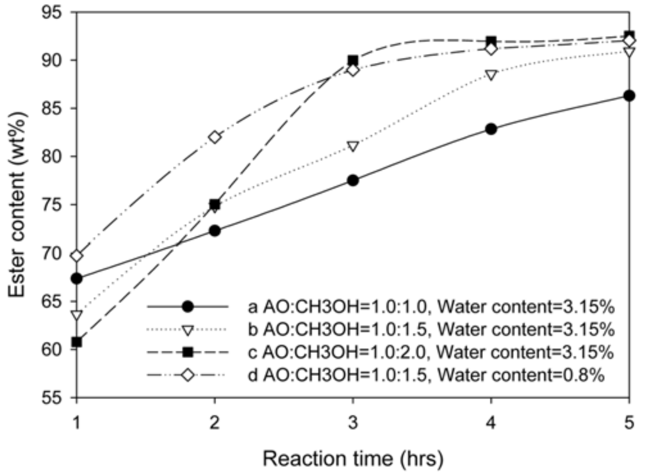

**Fig. 2. Conversion of acid oil to biodiesel as a function of methanol : acid oil weight ratios. The water content of acid oils was 3.15% and 0.8%. Reaction temperature was 80 °C for first hour and then increased to 90 °C for next four hours.**

After water removal, the major composition of AO was analyzed by GC. Table 2 represents the results. A trace of fatty acid salts existed in the AO, which could be converted into FAME in the following process. Compared to the reported results [8], the yield of AO by this process is considered to be competitive.

## 2. Biodiesel Production from AO

AO from SS contained a certain amount of water, from 2.75% to 3.50%. Here we used the AO with an average water content of 3.15% to react with excess methanol catalyzed by sulfuric acid. The reaction of the first 1 hour was operated at 80 °C and the reaction of the following 4 hours was done at 95 °C. Fig. 2 shows the effect of AO/methanol weight ratio and water content of AO to the ester production reaction, while 10% (w/w) sulfuric acid based on AO was added.

After 1 hour, the reaction with higher excess methanol ratio showed less conversion of AO. The excess methanol might dilute the sulfuric acid, and hence lowered the conversion at the first stage. When the weight ratio of AO to methanol was 1.0 : 2.0, the ester content of the biodiesel reached 90% in 3 hours and was increased to 92.51% after 5 hours reaction. If the weight ratios of AO to methanol were 1.0 : 1.5 and 1.0 : 1.0, the ester contents of biodiesel were 91% and 86%, respectively. It indicates that excess methanol is needed to convert AO having high water content into esters.

Water content of AO can be easily decreased to 0.8%. AO with lower water content behaved much better than AO with high water content. Hence, with AO of 0.8% water content, more than 92% ester content of biodiesel can be obtained within 5 hours reaction, while the weight ratio of AO to methanol was 1 : 1.5 as shown in Fig. 2. As a result, the reaction d with 0.8% water content and the weight ratio 1.0 : 1.5 shows similar performance to reaction c, where the water content is 3.15% and the weight ratio 1.0 : 2.0. As a conclusion with these findings, we decided to use AO of 0.8% water

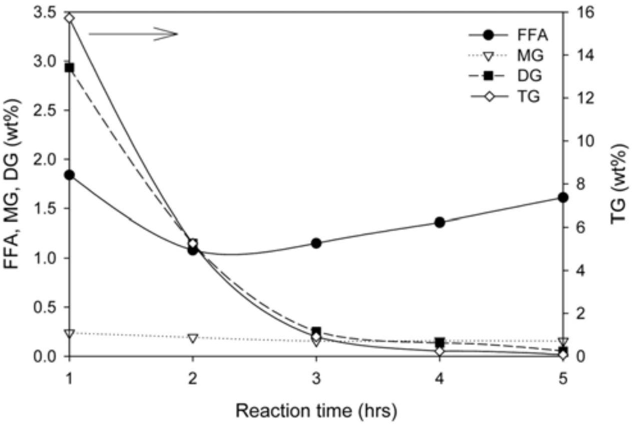

**Fig. 3. Profiles of MG, DG, TG and FFA during the incubation of 80 g dry acid oil with 120 g methanol and 8 g sulfuric acid. Reaction temperature was 80 °C for first hour and then maintained at 90 °C for following 4 hours. Agitation speed, 250 rpm.**

for the following experiments.

Fig. 3 shows the change of MG, DG, TG and FFA during reaction d. The initial AO contained 50.0% FFA, 3.1% MG, 6.9% DG and 15.5% TG. The TG concentration in the biodiesel phase continued to decrease with the increase of reaction time. Five hours later, TG concentration of the biodiesel was negligible (0.07%). During the reaction process, DG decreased continuously and MG concentration remained almost constant. The final concentrations of MG, DG are about to be only 0.27%. The contents of MG, DG and TG were negligible compared with the FFA in the biodiesel, which is determined to be about 1.61%. FFA decreased very fast to the minimum, and then rebounded. A similar phenomenon has been found by other researchers [13]. The reason for this rebound can be assumed that the consumption of methanol and the increment of ester had activated the hydrolysis of ester a little to produce free fatty acids. After 5 hours reaction, the reaction reached equilibrium and the maximum purity of biodiesel was around 92%. Considering the amount of glyceride and free fatty acid existing in the biodiesel, even though all of them were converted into esters, the purity of biodiesel obtained could not meet the Korean biodiesel specification (96.5%).

Distillation is necessary to purify the biodiesel from AO. At the same time, the yield of purified biodiesel based on SS was investigated. Reaction d (Fig. 2) was analyzed as an example. The biodiesel content of AO was determined to be 92%. After distillation, the purified biodiesel contained 97.6% fatty acid esters and no detectable TG, DG, MG. The average yield of the purified biodiesel was 94% based on total fatty acids in SS.

## SUMMARY

An efficient method to recover acid oil (AO) from soybean soapstock (SS) has been developed. This soap splitting process can be successfully operated at ambient temperature only with water and sulfuric acid. Maximum yield (97%) of AO was achieved based on the total fatty acids of SS. And the yield of AO was comparable to the values reported in the literature.

Biodiesel production from AO was also simplified through single stage reaction catalyzed by sulfuric acid. The reaction time was shortened to 5 hours from 14 hours and the yield of purified biodiesel was 94% based on the total fatty acids of the SS. The advantages of this process revealed a prospect option to utilize SS for biodiesel production.

## ACKNOWLEDGMENT

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