

Effects of water on the esterification of free fatty acids by acid catalysts

Ji-Yeon Park^a, Zhong-Ming Wang^b, Deog-Keun Kim^a, Jin-Suk Lee^{a,*}

^a Korea Institute of Energy Research, 71-2, Jang-dong, Yuseong-gu, Daejeon 305-343, Republic of Korea

^b Guangzhou Institute of Energy Conversion, No. 2 Nengyuan Rd, Wushan, Tianhe, Guangzhou 510-640, China

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ABSTRACT

To maximize the production of biodiesel from soybean soapstock, the effects of water on the esterification of high-FFA (free fatty acid) oils were investigated. Oleic acid and high acid acid oil (HAAO) were esterified by reaction with methanol in the presence of Amberlyst-15 as a heterogeneous catalyst or sulfuric acid as a homogeneous catalyst. The yield of fatty acid methyl ester (FAME) was studied at oil to methanol molar ratios of 1:3 and 1:6 and reaction temperatures of 60 and 80 °C. The rate of esterification of oleic acid significantly decreased as the initial water content increased to 20% of the oil. The activity of Amberlyst-15 decreased more rapidly than that of sulfuric acid, due to the direct poisoning of acid sites by water. Esterification using sulfuric acid was not affected by water until there was a 5% water addition at a 1:6 molar ratio of oil to methanol. FAME content of HAAO prepared from soapstock rapidly increased for the first 30 min of esterification. Following the 30-min mark, the rate of FAME production decreased significantly due to the accumulation of water. When methanol and Amberlyst-15 were removed from the HAAO after 30 min of esterification and fresh methanol and a catalyst were added, the time required to reach 85% FAME content was reduced from 6 h to 1.8 h.

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1. Introduction

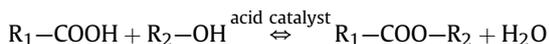
Biodiesel is an alternative diesel fuel derived from the oils and fats of plants and animals. Due to the high price of petroleum and the increased regulation of carbon emissions resulting from the Kyoto protocol, biodiesel is currently becoming a fast-growing market product [1–5]. As the demand for biodiesel has increased, the price of edible vegetable oils, including soybean oil and rapeseed oil, has risen abruptly. Waste oils, such as used frying oil, trapped grease, soapstock (SS), and acid oil should be considered as a promising alternative feedstock for the production of biodiesel [6,7].

SS, a by-product generated during the refining of vegetable oils, is one such potential biodiesel feedstock. It is a heavy alkaline aqueous emulsion of lipids that contains about 50% water, and includes free fatty acid salts, phosphatides, triglycerides, pigments and other minor non-polar compounds. Its free fatty acid salts and triglycerides can be converted to biodiesel. SS is generated at a rate of about 6% of the volume of crude vegetable oil that is refined [8]. Its market value on a dry weight basis is about one-fifth of the price of crude vegetable oil [8]. Extensive research into the production of

biodiesel from SS has been performed by Hass et al. [8–11]. They prepared high acid acid oil (HAAO) containing 96.2% free fatty acids (FFAs) through the saponification and the acidulation of SS. Next, the esterification of HAAO was catalyzed by sulfuric acid. Hass et al. [11] concluded that esterifying after the conversion of SS to HAAO was more efficient than the direct esterification of SS.

The use of a homogeneous acid catalyst such as sulfuric acid for esterification presents difficulties in recovery after the reaction, and produces toxic wastewater. Esterification by solid acid catalysts, which have the advantages of being easily recovered and reused as well as being compatible with environmental considerations, has also been studied [12–14].

The esterification of carboxylic acid with alcohol produces ester and water. This reaction is described in the following equation:



However, the rate of acid-catalyzed esterification is slow, and the water that is produced hinders the reaction. For this reason, a full understanding of esterification kinetics is required to increase the efficiency of the reaction. In previous studies on esterification kinetics, the effects of water on the esterification of long-chain FFAs such as oleic acid have rarely been considered [15–17]. Liu et al. [15] studied the effects of water on esterification by catalyst type and water concentration level, but they examined only the short-chain

* Corresponding author. Tel.: +82 42 860 3553; fax: +82 42 860 3495.
E-mail address: bmjslee@kier.re.kr (J.-S. Lee).

carboxylic acids, such as acetic, propionic, butyric, hexanoic, and caprylic acid.

In this study, oleic acid and HAAO were esterified by two acid catalysts, sulfuric acid and Amberlyst-15. The effects of water on esterification by catalyst type were compared, and operating conditions for the esterification of high FFA oils were suggested.

2. Experimental methods

2.1. Materials

Oleic acid was purchased from Reidel-de Haen (Germany, 65–88%). For esterification, methanol (Duksan Pure Chemical, Korea, >99.5%) and sulfuric acid (Junsei Chemical, Japan, >95%) or Amberlyst-15 (Rohm & Haas, USA) were used. Soybean SS was kindly supplied by CJ Corp. (Korea). The composition of SS is shown in Table 1. The water content of SS was 44.2%. KOH (Junsei Chemical, Japan, >85%) and sulfuric acid were used for the preparation of HAAO from SS. For GC analyses, *n*-heptane (J.T. Baker, USA, >99.0%) and methyl heptadecanoate (Fluka, Switzerland, >99.5%) were used.

2.2. Esterification of oleic acid

To simulate the effects of water on esterification, the initial water content was varied with 0, 1, 2, 5, 10 and 20% of oil. Two temperature conditions, 60 and 80 °C, were selected. The molar ratio of oil to methanol was 1:3 and 1:6. As acid catalysts, Amberlyst-15 and sulfuric acid were used. The one-step esterification was performed for 6 h under each reaction condition. In the two-step esterification, the original methanol and catalyst were replaced with fresh methanol and catalyst after 30 min of esterification. The round flask was connected to a condenser to minimize the loss of methanol. The reaction temperature was maintained in the oil bath. FAME content was measured intermittently.

2.3. Esterification of HAAO

HAAO was prepared from SS using the procedures of Haas et al. [11] including hydrolysis by KOH and acidulation by sulfuric acid at room temperature. The composition of HAAO is shown in Table 2. The FFA content of HAAO was 96.9%. The esterification of HAAO was performed at a 1:3 molar ratio of oil to methanol at 80 °C. The operation time of one-step esterification was 6 h. For the two-step esterification, the original methanol and catalyst were replaced with fresh methanol and catalyst after 30 min of esterification.

2.4. Analyses

The acid value was measured through the titration method (AOCS official method Cd 3d-63) using a KOH–ethanol solution. Water content was measured using the Karl Fisher Titrator (Mettler Toledo DL31, USA). The FAME content was analyzed using a Gas Chromatograph system equipped with an auto-injector (Agilent 6890A, USA). The INNOWAX column (Agilent, USA, 30 mm × 0.32 mm × 0.5 μm) was used for the analysis of FAME. The initial oven temperature was 50 °C for 1 min, and was increased to 200 °C at a rate of 15 °C/min, then maintained for 9 min and

Table 1
Composition of soapstock (SS).

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

Table 2
Composition of high acid acid oil (HAAO).

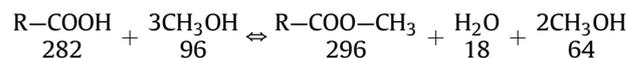
Water content (%)	Free fatty acids (%)	Not measured (%)
0.1	96.9	3.0

subsequently increased again to 250 °C at a rate of 2 °C/min, and then maintained for 2 min. Methyl heptadecanoate was used as the internal standard.

3. Results and discussion

3.1. Effects of initial water content on esterification

Fig. 1 shows the profile of FAME content of oleic acid biodiesel when the initial water content was varied with 0, 1, 2, 5, 10 and 20% of oil. Sulfuric acid as a homogeneous catalyst was compared to Amberlyst-15 as a heterogeneous catalyst. If the esterification of oleic acid was completed at a molar ratio of 1:3 of oil to methanol, the water content of the mixture of oleic acid biodiesel and excess methanol can increase up to 4.8% through the reaction described as follows:



As the initial water content increased, FAME content gradually decreased. Even when the initial water content was 1% of oil, water hindered the esterification, accelerating the inverse reaction. The activity of Amberlyst-15 decreased more rapidly than that of sulfuric acid due to the poisoning of acid sites by water, as well as the poor accessibility of reactants to acid sites due to the presence of water [18]. FAME content was higher at 80 °C than at 60 °C for each catalyst. When there was no addition of water, FAME content increased from 87% to 91% in accordance with temperature in both catalysts.

3.2. Effects of methanol amount on esterification

Fig. 2 shows the profile of the FAME content of oleic acid biodiesel when the initial water content was varied with 0, 1, 2 and 5% of oil. To determine the effects of the amount of methanol on esterification, the molar ratio of oil to methanol was set to 1:3 and

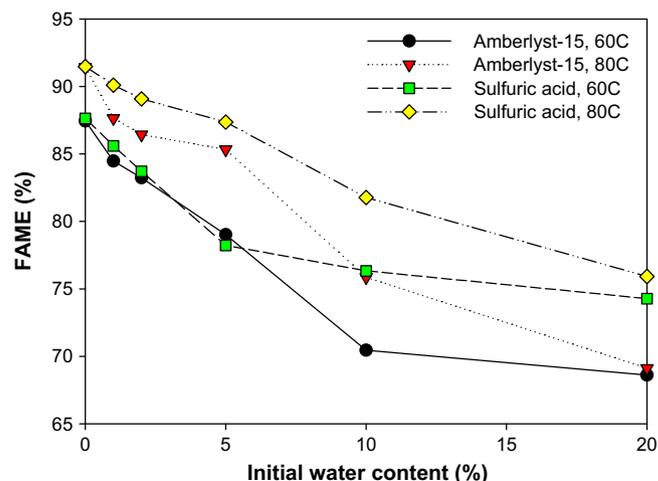


Fig. 1. Profile of FAME content of oleic acid biodiesel at molar ratio of 1:3 of oil to methanol and 6 h of reaction time.

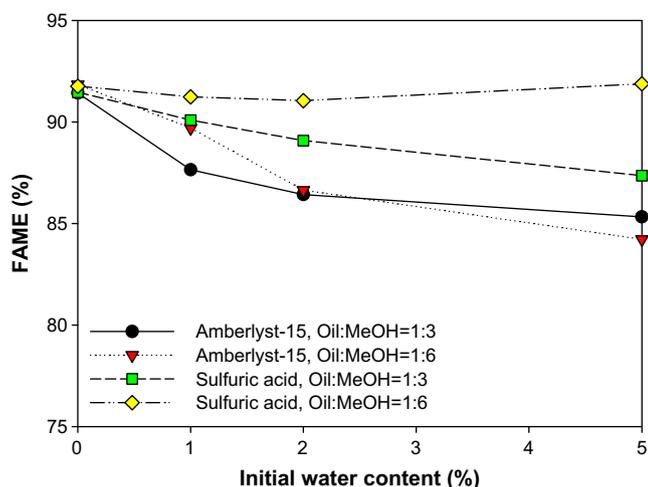


Fig. 2. Profile of FAME content of oleic acid biodiesel at 80 °C of temperature and 6 h of reaction time.

1:6, respectively. Under sulfuric acid, the esterification rate decreased with the initial water content at a molar ratio of 1:3. Water accelerated the inverse reaction towards the reactant direction. However, the esterification rate did not decrease up to 5% of water at a molar ratio of 1:6 using sulfuric acid. The reaction towards the product direction due to the increase of the amount of methanol counterbalanced with the inverse reaction by water. Under sulfuric acid, therefore, the use of a large amount of methanol could decrease the inhibition of water on esterification by accelerating the reaction. Under Amberlyst-15, the final FAME content similarly decreased, with initial water content at a molar ratio of 1:3 and 1:6. The addition of a large amount of methanol did not have the effect of increasing the esterification rate. The use of a large amount of methanol could not control the inverse reaction by water because the active sites of Amberlyst-15 were directly poisoned by water. Under Amberlyst-15, therefore, the poisoning of catalyst was a crucial factor on esterification.

Fig. 3 shows the distribution of methanol and the catalyst after esterification. Because Amberlyst-15 adsorbed some water and methanol, there was no separated methanol layer at a molar ratio of 1:3 (Fig. 3(a)). At a molar ratio of 1:6 using Amberlyst-15, the methanol layer existed at the top because the methanol amount exceeded the adsorption ability of Amberlyst-15 (Fig. 3(b)). As the density of the mixture of sulfuric acid, methanol and water at a molar ratio of 1:3 using sulfuric acid was higher than that of FAME, the methanol layer existed at the bottom (Fig. 3(c)). However, the methanol layer at a molar ratio of 1:6 using sulfuric acid existed at the top because the excess methanol lowered the density of the mixture (Fig. 3(d)).

Table 3 shows the distribution of water at each layer after 12 h storage. Under Amberlyst-15, the water in the catalyst was

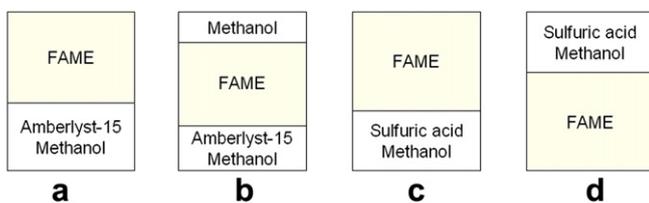


Fig. 3. Distribution of methanol and catalyst after esterification of oleic acid; (a) molar ratio of 1:3 of oil to methanol using Amberlyst-15, (b) molar ratio of 1:6 of oil to methanol using Amberlyst-15, (c) molar ratio of 1:3 of oil to methanol using sulfuric acid, (d) molar ratio of 1:6 of oil to methanol using sulfuric acid.

Table 3
Water distribution after the esterification of oleic acid by Amberlyst-15(a) and by sulfuric acid(b).

(a)			
Molar ratio of oil to methanol	FAME (%)	Amberlyst-15 (%)	Methanol (%)
1:3	11.80	88.20	–
1:6	11.58	60.58	27.84
(b)			
Molar ratio of oil to methanol	FAME (%)	Sulfuric acid & methanol (%)	Error (%)
1:3	9.33	90.39	0.28
1:6	9.26	90.24	0.50

numerically calculated by subtracting the water of FAME and methanol layers. At a molar ratio of 1:3, 11.80% of water produced was distributed in the FAME layer. At a molar ratio of 1:6, 27.84% of water produced was distributed in the top methanol layer. Under sulfuric acid, about 90% of the water produced was distributed in the sulfuric acid & methanol layer at both molar ratios. As nearly 90% of the water produced was distributed in the catalyst and methanol layer after esterification, the two-step esterification process, in which the original methanol and catalyst were replaced with fresh methanol and catalyst to remove water after the first esterification, was investigated as a way of enhancing the efficiency of esterification.

3.3. Two-step esterification of oleic acid

Fig. 4 shows the profile of the FAME content of oleic acid biodiesel without the addition of water. After the FAME content rapidly increased for the first 30 min, the esterification rate gradually decreased. FAME content was lower under Amberlyst-15 than under sulfuric acid until 2 h of esterification. After 6 h, FAME content was 91.43% under Amberlyst-15, and 91.47% under sulfuric acid (Table 4). To overcome the decrease in the esterification rate, the methanol and catalyst containing water were replaced with fresh methanol and catalyst after 30 min of esterification. This two-step esterification process reduced the time required to reach FAME of over 90%; from 5 h to 1.7 h under Amberlyst-15 and from 4 h to 1.3 h under sulfuric acid. After the washing of biodiesel by 1 N NaOH, the acid value was reduced to less than 0.5 mg KOH/g. Through the two-step reaction, the esterification process of oleic acid was enhanced due to the removal of water.

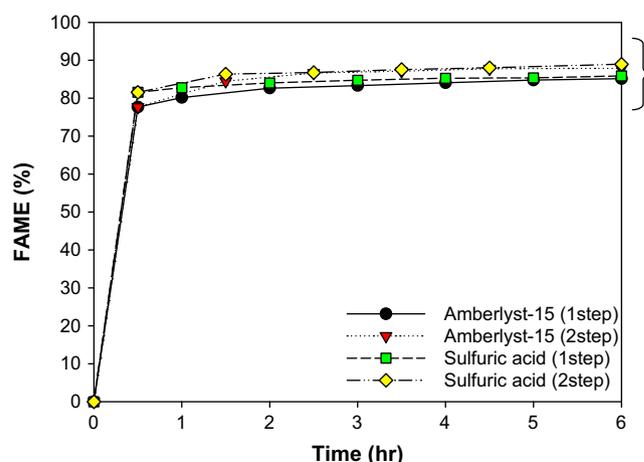


Fig. 4. Profile of FAME content in one-step and two-step esterification of oleic acid at a molar ratio of 1:3 of oil to methanol, and temperature of 80 °C.

Table 4
FAME content in one-step and two-step esterification of oleic acid after 6 h.

Condition		FAME (%)	Acid value (1 N NaOH washing)
Amberlyst-15	1 step	91.43	6.7 → 0.42
	2 step	92.94	2.4 → 0.48
Sulfuric acid	1 step	91.47	8.9 → 0.43
	2 step	92.98	2.1 → 0.37

Lee et al. [19] performed an extended durability test of Amberlyst-15 in the continuous plug flow reactor for the pretreatment of used frying oil. Through esterification, the FFA content of used frying oil was reduced from 1.1% to less than 0.5%. It was possible to use Amberlyst-15 continuously for 180 h at 80 °C, and 390 h at 120 °C. However, the activity of Amberlyst-15 in the esterification of oleic acid with a high FFA content rapidly decreased, because the water produced deactivated the acid sites of the catalyst and blocked the access of the reactants to the acid sites.

It was already found that the esterification of acetic acid with methanol by sulfuric acid was strongly inhibited by water [20]. As acetic acid was short-chain carboxylic acid, the effect of water was more severe than that of oleic acid. The esterification rate of oleic acid with a high FFA content by sulfuric acid rapidly decreased with time, because water as by-product accelerated the inverse reaction. Although the rate of FAME production using Amberlyst-15 was initially slower than that using sulfuric acid, both catalysts showed similar performance after 3 h. As the rate of esterification rapidly decreased with time, the difference between two catalysts became small.

3.4. Two-step esterification of HAAO

Fig. 5 shows the profile of the FAME content of SS biodiesel without the addition of water. The FAME content of SS biodiesel rapidly increased within 30 min. The activity of Amberlyst-15 decreased more rapidly than that of sulfuric acid due to the poisoning of acid sites by water, as well as the impurity of HAAO. FAME contents after 6 h under Amberlyst-15 and sulfuric acid were 85.16% and 85.58%, respectively (Table 5). To increase the esterification rate, the methanol layer and catalyst were replaced with a fresh methanol layer and catalyst after 30 min. The two-step esterification process reduced the time required to reach FAME of over 85%; from 6 h to 1.8 h under Amberlyst-15 and from 4 h to

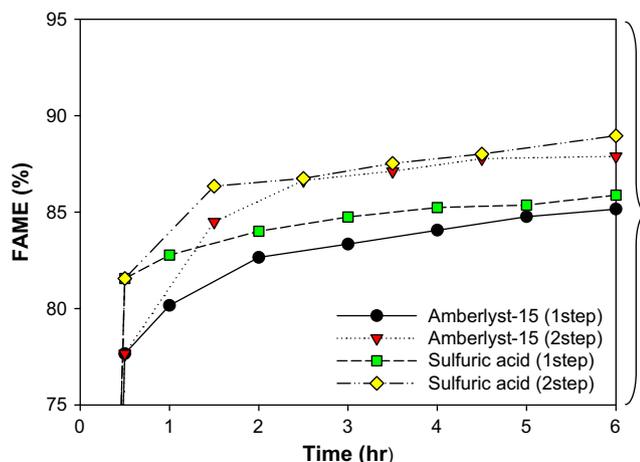


Fig. 5. Profile of FAME content in one-step and two-step esterification of HAAO at molar ratio of 1:3 of oil to methanol and temperature of 80 °C.

Table 5
FAME content in one-step and two-step esterification of HAAO after 6 h.

Condition		FAME (%)	Acid value (1 N NaOH washing)
Amberlyst-15	1 step	85.16	10.1 → 1.52
	2 step	87.89	7.59 → 1.58
Sulfuric acid	1 step	85.58	9.83 → 1.58
	2 step	88.96	5.61 → 1.72

Table 6
Fatty acid distribution of SS biodiesel.

Fatty acid	%
Myristic acid (C14:0)	0.11
Palmitic acid (C16:0)	14.64
Stearic acid (C18:0)	4.10
Oleic acid (C18:1)	21.84
Linoleic acid (C18:2)	52.38
Linolenic acid (C18:3)	6.20
Behenic acid (C22:0)	0.45
Not identified	0.28

1.2 h under sulfuric acid. Although SS biodiesel was washed by 1 N NaOH, the acid value was still more than 1.5 mg KOH/g. To reduce the acid value of SS biodiesel to less than 0.5 mg KOH/g, another washing procedure is required. The esterification rate of HAAO increased in the two-step reaction.

The activity of Amberlyst-15 in the esterification of HAAO with a high FFA content rapidly decreased, because the water produced deactivated the acid sites of the catalyst and blocked the access of the reactants to the acid sites. The esterification of HAAO with a high FFA content by sulfuric acid rapidly decreased, because water as by-product accelerated the inverse reaction. The activity of the Amberlyst-15 catalyst initially decreased more rapidly than that for the sulfuric acid catalyst. However, the difference of activities between two catalysts gradually reduced, as the rate of esterification rapidly decreased with time.

The composition of HAAO is shown in Table 6. SS biodiesel contains 52.4% linoleic acid, 21.8% oleic acid, and 14.6% palmitic acids.

4. Conclusions

It was found that the water resulting from the esterification of oleic acid severely inhibits the esterification reaction. The inhibiting effect of water was more dominant under Amberlyst-15 than under sulfuric acid due to the poisoning of acid sites on Amberlyst-15 by water. When sulfuric acid was used as a catalyst, a molar ratio of 1:6 of oil to methanol eliminated the hindrance of water until a 5% addition of water, accelerating the reaction due to the increase of the amount of reactants. The two-step esterification of oleic acid, which included replacing the methanol and catalyst with fresh methanol and catalyst after 30 min, reduced the reaction time required to reach FAME of over 90%. The two-step esterification of SS-HAAO also reduced the reaction time required to reach FAME of over 85%. As water inhibition is severe in the production of biodiesel from low-quality oils, the minimization of the effect of water on esterification is very important. The two-step reaction is a good method of removing water during esterification. Combination with pervaporation for water removal or the development of efficient water-resistant catalysts could be suggested as other solutions.

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