BIODIESEL PRODUCTION BY ESTERIFICATION OF OLEIC ACID WITH ETHANOL UNDER ULTRASONIC IRRADIATION

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Abstract

Production of fatty acid ethyl ester (FAEE) from oleic acid (FFA) with ethanol under ultrasonic irradiation was investigated in this work. Batch esterification of oleic acid was carried out to study the influence of: including reaction temperatures of 10–60 °C, molar ratios of ethanol to oleic acid of 1:1–10:1, quantity of catalysts of 0.5 – 10% (wt of sulfuric acid/wt of oleic acid) and irradiation times of 10 hour. The optimum condition for the esterification process was molar ratio of ethanol to oleic acid at 3:1 with 5 wt% of H_2SO_4 at 60 °C with an irradiation time of 2 hour. The amount of oleic acid was reduced from 100 wt% to less than 10 wt% at the end of the esterification process.

Keywords: Oleic acid; Ultrasound; Biodiesel; Esterification

1. Introduction

We have investigated the transesterification of triolein with regard to many parameters such as catalyst concentration, various catalysts, various alcohols, molar ratio, and test temperature under the stirring and ultrasonic irradiation conditions [1-4]. On the basis of the results obtained, the optimal condition for the transesterification of triolein was determined for many parameters. It is presumed that the optimal condition would be applied to the vegetable oils, exhausted oils and so on with the similar structure and composition as those of triolein. However, there are some oils including a significant high amount of free fatty acids (FFA) such as non-edible oils, animal fats and oils, recycled or waste oil and byproducts of the refining vegetable oils; for examples, crude mahua oil contains about 20 % FFAs [5], Jatropha oil contains about 14% free fatty acid (FFA) [6], Tobaco seed oils contains about 17 % FFA [7] and the waste oil (canola oil, derived from rapeseed oil (Brassica napus ssp. oleifera), free of erucic acid) contained 6% by weight of free fatty acid (FFA) [8]. If an oil contains higher amounts of FFA (> 1%w/w), FFAs form soap with the base catalysts. Consequently, it is considered that the ester conversion is decreased by the formation of soap that can prevent separation of the biodiesel fuel from the glycerin. At present, there was little data about the esterification of free fatty acids with alcohol under ultrasonic irradiation condition as well as the effects of molar ratio (ethanol to free fatty acid), acid catalyst concentration (H_2SO_4, CH_3COOH), and temperature.

Therefore, in this paper, we tried to elucidate the esterification of FFAs with ethanol for the parameters under the ultrasonic irradiation and stirring conditions by using acid catalyst, but not base catalyst.

2. Experimental

2.1. Reagents and materials

Free fatty acids (Oleic acid, palmitic acid, stearic acid) and catalysts (H_2SO_4, CH_3COOH) were purchased from Wako Chemicals; the alcohol (ethanol) purchased from Wako Chemicals had more than 99.5% purity. Analytical standards of ethyl ester were purchased from Wako Chemicals.

2.2. Procedures

A biodiesel fuel from free fatty acids with ethanol was investigated in the presence of various types of homogeneous acid catalyst. The temperatures were 10, 20, 30, 40, 50 and 60 °C. The reaction mixtures consisted of oleic acid with ethanol and acid catalyst (H_2SO_4, CH_3COOH). The molar ratio of ethanol to oleic acid was 1:1, 2:1, 3:1, 4:1, 6:1, and 10:1 and the quantity of the homogeneous catalysts were 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, and 10%wt to the weight of oleic acid. All the experiments were conducted for 10 hour under the ultrasonic irradiation condition and stirring conditions.

The stirring experiments were performed using a Matsushita Electric Ind., (SCV 35W stirrer at 1800 rot/min). The ultrasonic experiments were carried out using a Honda Electronics Ultrasonic Cleaner (WS 1200-40, 40 kHz with a maximum power of 1200W). The working power was set at 60% of the maximum power, which corresponds to 700W for 10L solution by calorimetry. After sonication, 3 ml of reaction mixture was taken and neutralized immediately by a sodium hydroxide solution to stop the further reaction.

2.3 Analysis

The samples were analyzed for ethyl ester, and glycerol by using a High Performance Liquid Chromatography (HPLC) (Shimadzu, SCL-10Asp), which consisted of an ODS column (STR ODS-II, 25cm in length x 4.6mm in inner diameter, Shinwa Ch. Ind. Co.) and refractive index detector (Shimadzu, RID-10A) the temperature of column oven was kept at 40°C and flow rate of carrier solvent of acetone/acetonitrile (70/30) was 0.4 ml/min. The sample injection volume was 50μl and the peak identification was made by comparing the retention time between the sample and standard compound.

2.4 Statistical analysis

All the experiments were carried out four times in order to determine the variability of the results and to assess the experimental errors. In this way, the arithmetical averages and the standard deviations were calculated for all the results.

3. Results and discussions

3.1 Effect of molar ratio (ethanol to oleic acid) on the ethyl ester conversion

Fig. 1 shows the relationships between the ethyl ester conversion and reaction time at 20°C, molar ratio 3/1and 5 %wt H_2SO_4 concentration under the ultrasonic irradiation condition and stirring conditions. As seen in Fig 1, the ethyl ester conversion increases rapidly at 1 hour and then increases gradually with reaction time under both conditions. In addition, the ethyl ester conversion appeared not to reach a steady state under both conditions. It was also found that the ethyl ester conversion under the ultrasonic irradiation condition was higher than under the stirring condition. In addition, we have found that there was no ethyl ester conversion at various molar ratios of ethanol to oleic acid with 5 %wt acetic acid concentration (CH_3COOH) under the ultrasonic irradiation and stirring conditions.

As seen in Fig. 2, although the behavior of the ethyl ester conversion is the similar to that in Fig. 1 at each molar ratio, the degree of the ethyl ester conversion depends largely upon molar ratio. From Fig. 2, the relationship between the ethyl ester conversion at an irradiation time of 10 hours and molar ratio is drawn as shown in Fig. 3. As seen in Fig. 3, the ethyl ester conversion increases rapidly with increasing molar ratio, reaches maximum at a molar ratio of 3/1 and then decreases gradually.

From these results, we can conclude that for the esterification of oleic acid, (1) the time to reach the maximum ethyl ester conversion is much longer and (2) the maximum ethyl ester conversion is smaller in comparison to those for the transesterification of triolein [1-4].

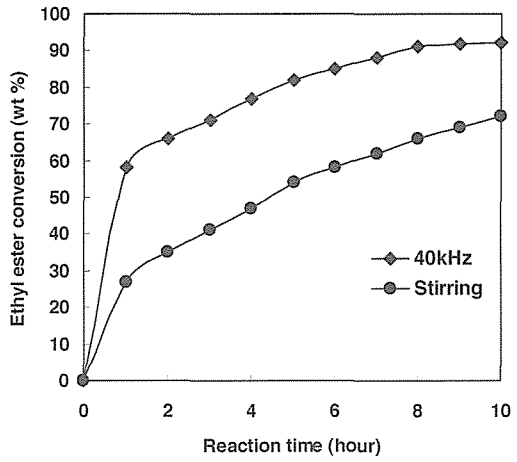

Fig.1. Relationships between the ethyl ester conversion and reaction time at 20°C, molar ratio 3/1and 5 %wt H_2SO_4 concentration under the ultrasonic irradiation condition and stirring conditions.

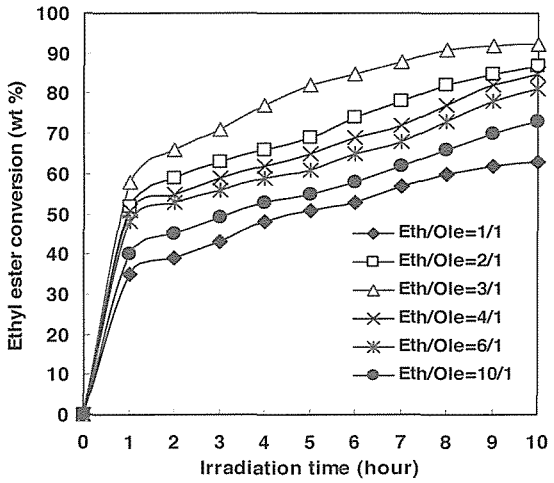

Fig. 2. Relationships between the ethyl ester conversion and irradiation time with various molar ratios, 5%wt H_2SO_4 concentration and 20 °C under the ultrasonic irradiation condition.

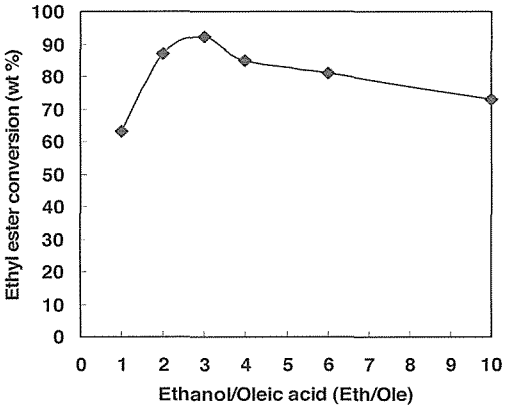

Fig. 3. Relationship between the ethyl ester conversion and molar ratio at 5%wt H_2SO_4 concentration and 20 °C under the ultrasonic irradiation condition.

Fig. 2 shows the relationships between the ethyl ester conversion and irradiation time at various molar ratios (ethanol/oleic acid), 5%wt H_2SO_4 concentration and 20 °C under the ultrasonic irradiation condition.

3.2 Effect of acid catalyst concentration on the ethyl ester conversion

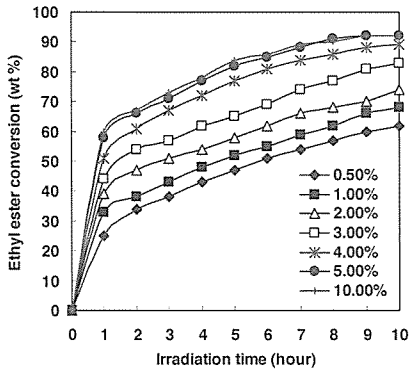

Fig. 4. Relationships between the ethyl ester conversion and irradiation time at various catalyst (H_2SO_4) concentrations with molar ratio 3:1 and 20 °C under the ultrasonic irradiation condition.

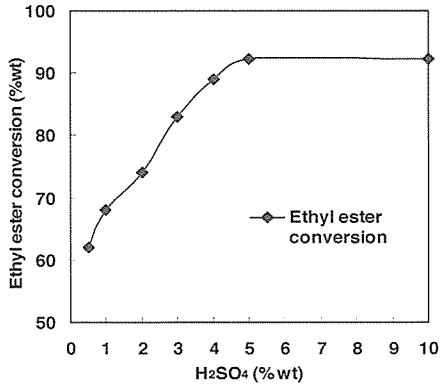

Fig. 5. Relationship between the ethyl ester conversion and H_2SO_4 concentration at molar ratio 3/1 and 20 °C under the ultrasonic irradiation condition.

Fig. 4 shows the relationships between the ethyl ester conversion and irradiation time at various catalyst (H_2SO_4) concentrations, molar ratio 3:1 and 20 °C under ultrasonic irradiation condition. As seen in Fig. 4, in this case the ethyl ester conversion increased with increasing the catalyst concentration, although it can not reach the steady state even at an irradiation time of 10 hours.

Fig. 5 shows relationship between the ethyl ester conversion and irradiation time at various catalyst concentrations (H_2SO_4) at molar ratio 3/1 and 20 °C under the ultrasonic irradiation condition. As seen in Fig. 5, the ethyl ester conversion increased with increasing catalyst concentration and became constant at a catalyst concentration of more than 5%wt.

Effect of temperature on the esterification of oleic acid

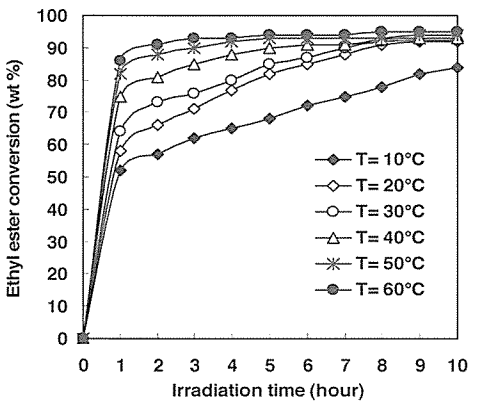

Fig. 6. Relationships between the ethyl ester conversion and irradiation time at various temperatures with molar ratio 3/1 and 5 %wt H_2SO_4 concentration under the ultrasonic irradiation condition.

Fig. 6 shows the relationships between the ethyl ester conversion and irradiation time at various temperatures with molar ratio 3/1 and 5 %wt H_2SO_4 concentration under the ultrasonic irradiation condition. The ethyl ester conversion increased with increasing temperature as well as that of catalyst concentration. In addition, the time for the ethyl ester conversion to reach the steady state tended to becomes short with the increase in temperature; for example, the maximum ethyl ester conversion was obtained at 2 about hours at 60 °C, but not at 10 °C.

5.3.4 Esterification of other fatty acids (palmitic acid and stearic acids)

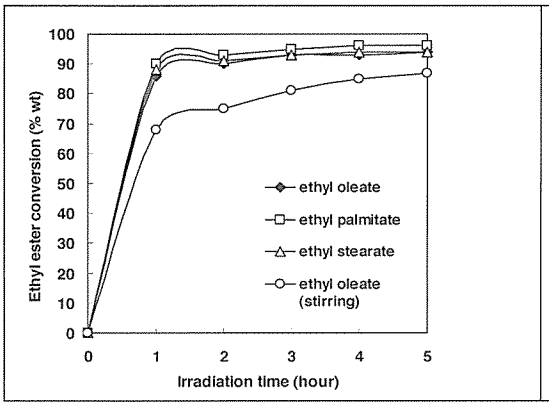

Fig. 7. Relationships between the ethyl esters conversion and irradiation time for various fatty acids at 60°C, molar ratio 3/1 and 5 %wt H_2SO_4 concentration under the ultrasonic irradiation and stirring conditions.

Fig. 7 shows the relationships between conversion of fatty acids (oleic, palmitic and stearic acids) and irradiation time at 60°C, molar ratio 3/1and 5 %wt H_2SO_4 under ultrasonic irradiation condition, where the result obtained under the stirring condition was drawn in this figure for comparison. As seen in Fig. 7, the irradiation time dependence of the ester conversion was almost the same irrespective of a kind of free fatty acid.

4. Conclusions

Ultrasonic irradiation condition is efficient, time saving and economically functional for esterification of free fatty acid with ethanol to produce biodiesel fuel. The optimum condition for the production of ethyl ester under the ultrasonic irradiation condition was as follows: molar ratio of ethanol to oleic acid 3:1 with H_2SO_4 concentration of 5%wt and irradiation time 2 hour at 60°C. The increasing in the irradiation time, as well as molar ratio contributes to high conversion and quality of esters. The esterification of fatty acid with ethanol under ultrasonic irradiation provides a possibility for producing cheap alternative fuels, which could reduce pollution and protect the environment.

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