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Fast Biodiesel Production with One-Phase Reaction

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Abstract The feasibility of fatty acid methyl ester (FAME) as a co-solvent used to increase the mass transfer between oil and methanol was investigated. FAME, as the co-solvent, does not require additional separation after the reaction because it is the end product of the reaction. To examine intermediate phenomena during the transesterification of soybean oil, the agitation speed was controlled at a slow rate. When the molar ratio of oil to methanol was 1:6 at 0.8wt.% of KOH to oil, oil was at the bottom layer, and methanol and the catalyst were at the top layer. Under the slow agitation process, the contact surface became initially darkened with the production of FAME and glycerol. After a few minutes, the entire top layer became dark. The top layer, containing methanol, KOH, FAME, and glycerol, fell to the bottom layer and then formed the one-phase system. When 0, 5, and 10 wt.% of FAME to oil was initially introduced to the reaction mixture, the FAME content rapidly increased with the FAME concentration level. After forming the one-phase system, the rate of increase of the FAME content was very slow. The time required for the formation of the one-phase system decreased with the amount of FAME and KOH and with temperature.

Keywords Biodiesel · Transesterification · Co-solvent · Fatty acid methyl ester · One-phase reaction

Introduction

An interest in biodiesel produced from oils and fats as an alternative fuel for diesel engines has been increasing due to the increase in the price of petroleum and environmental concerns about air pollution caused by vehicles [1–3]. Countries produce biodiesel from

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various vegetable oils, depending upon their agricultural policies, local crop availability, and/or feedstock prices [4–6]. The transesterification rate for biodiesel production is limited by agitation efficiency, temperature, alcohol amount, and/or the catalyst. Although a wide range of alcohols can be used for the transesterification of oils and fats, only methanol and ethanol are practically useful on an industrial scale due to their low costs [7]. Agitation is one of the important factors determining the reaction rate because oils and fats are not completely miscible with alcohols such as methanol and ethanol. Because the reaction of oils and fats with alcohols occurs only on the contact surface of the two-phase system, agitation is required to increase the mass transfer.

To agitate the reaction mixture efficiently, the tubular reactor for which the Reynolds number of the flow was greater than 2,300 was used as the reactor for biodiesel production [8]. However, turbulent flow is usually generated by increasing the length of the reactor or the flow rate. Excess turbulence may create the problem of glycerol suspension into biodiesel, which may make biodiesel purification difficult. Another approach was the one-phase reaction that made oils and fats completely miscible with alcohols with the addition of a co-solvent to the reaction mixture [7, 9, 10]. Boocock [7] suggested cyclic ethers as the most effective co-solvents because they form hydrogen bonds with polar compounds such as water and alcohols, contain sufficient non-polar hydrocarbon groups to dissolve the high molecular weight of oils and fats, and are chemically inert. Cyclic ethers increased the reaction rate by 15 times. However, co-solvents need to be separated from the end product after the reaction is complete.

In this study, fatty acid methyl ester (FAME) was used as the co-solvent to increase the mass transfer between oil and methanol. FAME does not need to separate because it is the end product of the transesterification. The influence of the initial addition of FAME on the FAME production rate was investigated.

Experimental Methods

Materials

Soybean oil was purchased from Sajo Haepyo (Seoul, Korea). Methanol (Duksan Pure Chemical Co., Ansan, Kyungki, Korea; >99.5%) and potassium hydroxide (Junsei Chemical Co., Chuo, Tokyo, Japan; >95%) were used for the transesterification. Soybean biodiesel was prepared for the initial addition of FAME. The reaction conditions were as follows: 1:6 of the molar ratio of oil to methanol, 0.8 wt.% of KOH to oil, and 300 rpm of agitation speed for 20 min at 60 °C. For FAME analyses, *n*-heptane (J.T. Baker, Phillipsburg, NJ, USA; >99.0%) and methyl heptadecanoate (Fluka, Buchs SG, Switzerland; >99.5%) were used.

Transesterification of Soybean Oil

For the transesterification, the mixture of oil, methanol, and KOH was agitated by an impeller at 100 rpm and 60 or 70 °C in temperature. The molar ratio of oil to methanol was 1:6 and the KOH was 0.8 wt.% to oil. The amount of FAME introduced initially was 0, 5, and 10 wt.% to oil. The agitation speed was determined at a slow rate to examine the intermediate phenomena of the transesterification. The amount of methanol and the catalyst, as well as the temperature, was determined on the basis of previous studies of the transesterification of oils [11, 12].

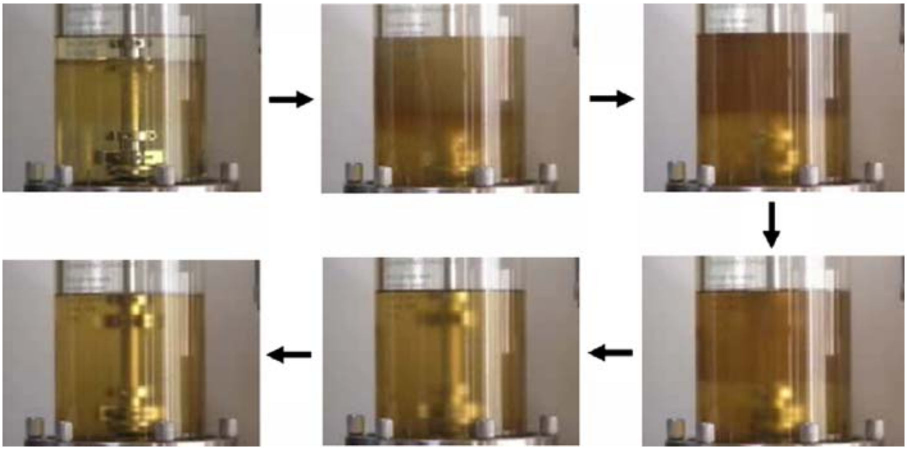


Fig. 1 Procedure of FAME production (1:6 molar ratio of oil to methanol; 0.8 wt.% of KOH to oil; 60 °C; 100 rpm; no initial addition of FAME)

Analyses

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

Results and Discussion

FAME Production from Soybean Oil

The procedure of FAME production under the slow agitation of the reaction mixture is shown in Fig. 1. At the beginning of the reaction, soybean oil was found at the bottom layer, and methanol and the catalyst were found at the top layer. The contact surface

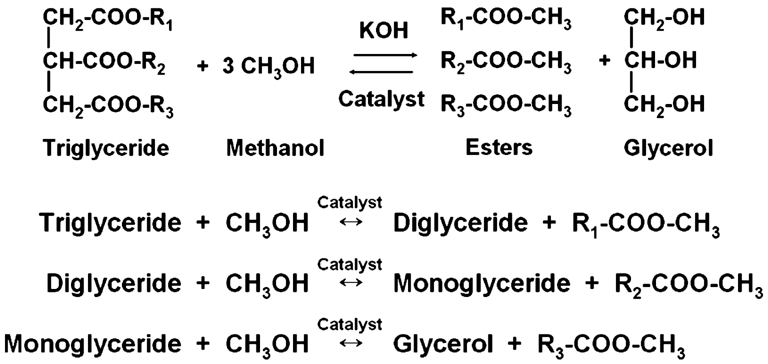


Fig. 2 Transesterification of oils and fats

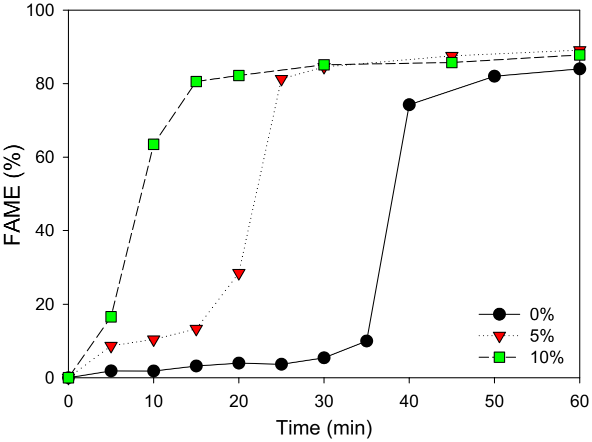


Fig. 3 Profile of FAME content (1:6 molar ratio of oil to methanol; 0.8 wt.% of KOH to oil; 60 °C; 100 rpm; initial addition of 0, 5, and 10 wt.% of FAME to oil)

between the two layers began to darken with the production of FAME and glycerol. After the top layer became cloudy and wider, the entire top layer became darker. The top layer, containing methanol, KOH, FAME, and glycerol, fell toward the bottom layer, which contained oil, forming the one-phase system. Finally, the bottom layer, containing glycerol, methanol, and KOH, was gravitationally separated from the top layer, containing FAME. With the transesterification, the triglycerides of oils are converted to diglycerides, and diglycerides are converted to monoglycerides. Finally, monoglycerides are converted to glycerol (Fig. 2). Because the intermediate diglycerides and monoglycerides contain one and two hydroxyl groups, respectively, they have a greater preference for the methanol phase than for the oil phase. Once they are formed in methanol, these intermediates have the opportunity to react further there rather than transfer back to the soybean oil phase [7]. Therefore, the reaction mixture has been changed to a one-phase from a two-phase state, making oil miscible with the methanol phase. Because the mass transfer in the one-phase reaction is superior to that in the two-phase reaction, due to an increase in the contact surface, the production rate of FAME by the one-phase reaction increases. Therefore, the initial addition of a co-solvent enhances the miscibility of oil to methanol and reduces the time required to form the one-phase system.

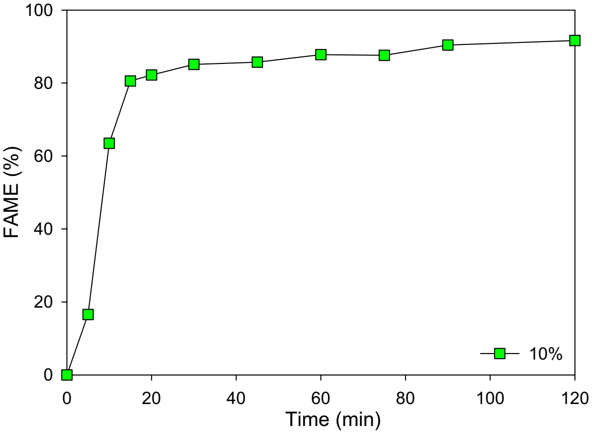
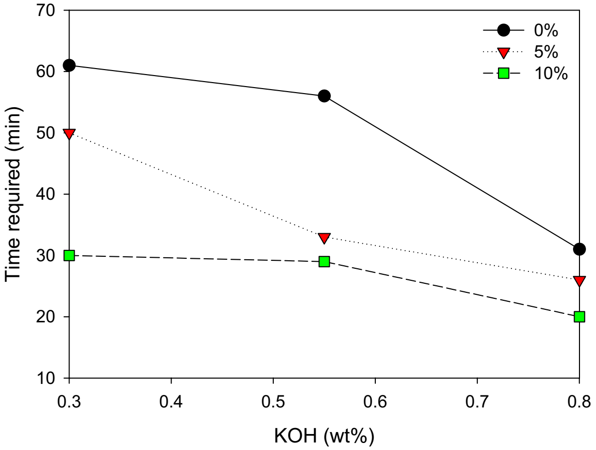


Fig. 4 Profile of FAME content (1:6 molar ratio of oil to methanol; 0.8 wt.% of KOH to oil; 60 °C; 100 rpm; initial addition of 10 wt.% of FAME to oil)

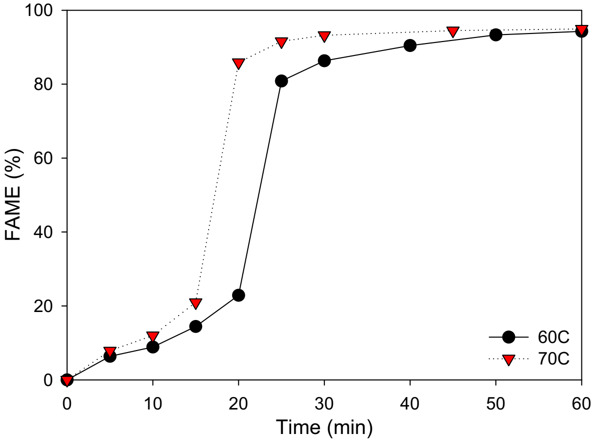
Fig. 5 Profile of the time required for the formation of the one-phase state (1:6 molar ratio of oil to methanol; 0.3, 0.55, and 0.8 wt.% of KOH to oil; 60 °C; 100 rpm; initial addition of 0, 5, and 10 wt.% of FAME to oil)



Effects of the Initial Addition of FAME

Boocock [7, 10] recommended tetrahydrofuran as a co-solvent, but the introduction of other material to the reaction may cause side effects. FAME produced from soybean oil was tested as the co-solvent to use to increase the miscibility of oil to methanol. When 5 and 10 wt.% of FAME was initially added to the reaction mixture, the production rate of FAME increased (Fig. 3). FAME content abruptly increased with the formation of the one-phase system. As the amount of FAME added was increased, the time required for the formation of the one-phase system decreased due to the increase in the miscibility of oil to methanol. After forming the one-phase system, the production rate of FAME was very slow (Fig. 4). The reduction of the time required for the formation of the one-phase system can decrease processing costs. Figure 5 shows the time required for a change from the two-phase to the one-phase state by the amount of the catalyst and FAME. With the addition of 10 wt.% of FAME to oil, the time required to form the one-phase system was remarkably reduced, due to the increase in the miscibility of the oil to methanol phase. When the amount of KOH increased, the time required to form the one-phase system decreased due to the increase of the driving force for the reaction. With the addition of 10 wt.% of FAME, however, the

Fig. 6 Profile of FAME content (1:6 molar ratio of oil to methanol; 0.8 wt.% of KOH to oil; 60 and 70 °C; 100 rpm; initial addition of 5 wt.% of FAME to oil)



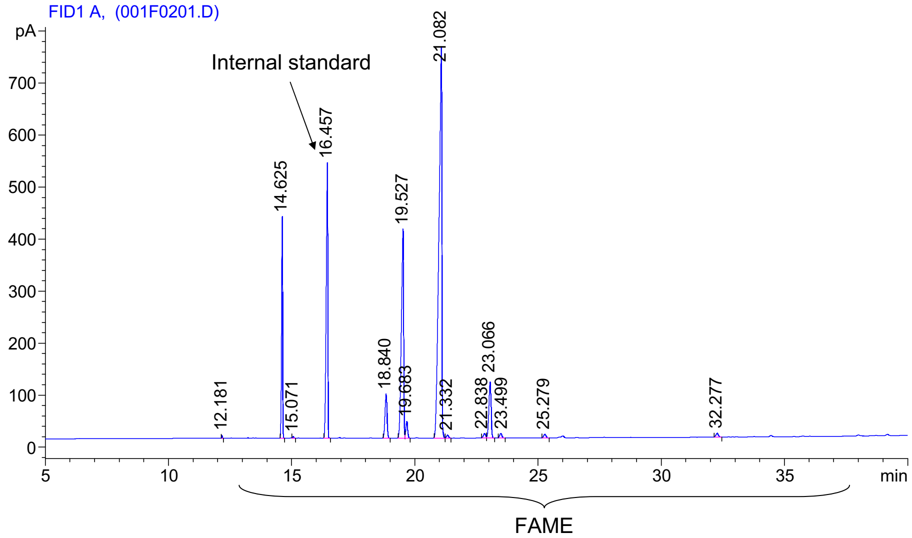


Fig. 7 Gas chromatogram of soybean biodiesel

difference in the time required for the formation of the one-phase system was not large according to the amount of catalyst used. In this case, the dominant factor affecting the reaction rate was the initial amount of FAME. When the reaction temperature increased from 60 to 70 °C, the production rate of FAME increased (Fig. 6). It is a common phenomena that a reaction rate is proportional to temperature. The time required for the formation of the one-phase system decreased at higher temperature levels due to an increase in the mass transfer between oil and methanol.

Characteristics of FAME

Figure 7 shows the peaks of the components in the gas chromatogram. The highest peak represents linoleic acid. Table 1 shows the fatty acid composition of FAME. The major components of soybean biodiesel were oleic acid and linoleic acid. The oxidation stability of soybean biodiesel was 4.18 h, measured using the Rancimat method. The cold filter plugging point of soybean biodiesel was −3 °C. These characteristics of soybean biodiesel were the same as found in the previous study [13].

Table 1 Fatty acid distribution of soybean biodiesel.

Fatty acid	Weight percent
Myristic acid (C14:0)	0.08
Palmitic acid (C16:0)	11.00
Stearic acid (C18:0)	4.19
Oleic acid (C18:1)	23.57
Linoleic acid (C18:2)	53.62
Linolenic acid (C18:3)	6.62
Arachidic acid (C20:0)	0.39
Not identified	0.53

Conclusions

To investigate the feasibility of FAME as a co-solvent used to increase mass transfer between oil and methanol, the transesterification of soybean oil under slow agitation was performed. The transesterification was initially conducted at the contact surface between the top and bottom layers, and FAME and glycerol were produced. After a few minutes, the entire top layer became darkened and fell toward the bottom layer. With FAME added, the reaction mixture was made miscible within a short period of time. As the amount of FAME and catalyst, as well as the temperature, increased, the production rate of FAME increased. Because the introduction of FAME as the co-solvent used to increase the reaction rate was very successful, the recycling of a portion of FAME produced to the reaction mixture can be recommended to improve the production rate of biodiesel.

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