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Two-Step Preparation for Catalyst-Free Biodiesel Fuel Production

Hydrolysis and Methyl Esterification

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Abstract

Biodiesel fuel was prepared by a two-step reaction: hydrolysis and methyl esterification. Hydrolysis was carried out at a subcritical state of water to obtain fatty acids from triglycerides of rapeseed oil, while the methyl esterification of the hydrolyzed products of triglycerides was treated near the supercritical methanol condition to achieve fatty acid methyl esters. Consequently, the two-step preparation was found to convert rapeseed oil to fatty acid methyl esters in considerably shorter reaction time and milder reaction condition than the direct supercritical methanol treatment. The optimum reaction condition in this two-step preparation was 270°C and 20 min for hydrolysis and methyl esterification, respectively. Variables affecting the yields in hydrolysis and methyl esterification are discussed.

Index Entries: Supercritical methanol; biodiesel; methyl esters; transesterification; methyl esterification.

Introduction

Biodiesel fuel has long been considered an alternative or emergency fuel for diesel engines because its properties are close to those of petroleum diesel fuel. Generally, biodiesel fuel is produced through transesterification of vegetable oils/fats with alcohol (mostly methanol) in the presence of a catalyst *(1)*. This method, however, is only applicable for refined vegetable oils/fats or those with a low content of free fatty acids and water. In the case of high content of fatty acids and/or water, as found in crude oils/fats, waste-frying oil, and soap stocks, the yield of methyl esters is low since fatty acids and water inhibit the reaction. Therefore, a combination of acidic-

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and alkaline-catalyzed processes has been developed to overcome this problem owing to the presence of fatty acids and water *(2–4)*.

Besides transesterification, there is another route for converting vegetable oil to methyl esters through hydrolysis and subsequent methyl esterification. Hydrolysis of vegetable oils is an old technology that can be traced back to the mid nineteenth century *(5)*. Several methods have been developed in vegetable oil hydrolysis including acidic/alkaline-catalyzed, lipase-catalyzed, and catalyst-free methods *(6–8)*. Both acidic- and alkaline-catalyzed methods are mostly practiced in commercial applications. In the acidic-catalyzed method, the reaction is performed in the presence of sulfonic acid at a boiling temperature of water and requires 20–48 h for a complete conversion. In the alkaline-catalyzed method, the reaction conditions are 185°C and 1 MPa for 6–10 h. In both methods, removal of the catalyst after the reaction is necessary. In the catalyst-free process, on the other hand, steam-based hydrolysis and subcritical water treatment of vegetable oils have been reported *(9)*.

Methyl esterification of fatty acids with methanol is generally conducted in the presence of acid catalyst at an elevated temperature close to the boiling point of methanol. Recently, we found that fatty acids could be successfully methyl esterified in supercritical methanol without the use of a catalyst *(10)*. In addition, from a comparative study between transesterification of vegetable oil and alkyl esterification of fatty acids with supercritical alcohols at 300°C in a batch-type reaction system, the reaction rates of alkyl esterification were found to be faster than those of transesterification *(11)*. An additional finding was that alkyl esterification of fatty acids could be performed at a lower reaction temperature than transesterification.

A catalyst-free supercritical methanol method for biodiesel fuel production was proposed with the optimum conditions of 350°C, 20 MPa, a molar ratio of 42 in methanol, and a 4-min treatment period *(12–13)*. This method has been proved to produce a high yield, because of simultaneous reactions of transesterification of triglycerides and methyl esterification of free fatty acids *(10)*. The only shortcoming of this one-step method is that it requires a severe reaction condition compared with the conventional commercial method with acid or alkaline catalyst. Consequently, our method would require a special alloy to cover the high temperature and high pressure of the reaction system.

Therefore, the purpose of the present work was to study an alternative method for biodiesel fuel production that has a lower reaction condition than the one-step supercritical methanol method, through the two-step preparation consisting of hydrolysis of triglycerides in subcritical water and subsequent methyl esterification of the fatty acids by supercritical methanol treatment. In this article, we present various parameters affecting the yield of fatty acids in hydrolysis from triglycerides followed by methyl esterification of the fatty acids. We also compare the one- and two-step preparation methods and propose a production scheme of the latter.

Materials and Methods

The vegetable oil used was rapeseed oil (Nacalai Tesque; Kyoto, Japan) without further treatment. The fatty acid content of the rapeseed oil mainly consisted of unsaturated fatty acids (93 wt%), with the saturated fatty acids of palmitic and stearic acids accounting for only a small amount (7 wt%). Various fatty acids of oleic ($C_{18\text{-}1}$), linoleic ($C_{18\text{-}2}$), linolenic ($C_{18\text{-}3}$), and palmitic ($C_{16\text{-}0}$) acids as well as their methyl esters were purchased from Nacalai Tesque. Anhydrous methanol and distilled water were also supplied by the same company.

Experiments were carried out in batch-type and flow-type supercritical biomass conversion systems. The batch-type reaction system was the same as reported previously *(14)*. In brief, it consisted of a tube reaction vessel (Inconel-625; 5 mL in volume) equipped with a thermocouple and a pressure gage. For hydrolysis reaction, 1 mL of rapeseed oil mixed with 4 mL of water was fully charged into the reaction vessel. The reaction vessel was then heated with molten tin preheated at desired temperatures. It took about 12 s to reach the reaction temperature. Subsequently, the vessel was moved into a water bath to quench the reaction. Reaction time was counted from the time a mixture reached the reaction temperature to when it was quenched. The obtained product was then kept for about 30 min until the two phases separated; the upper portion is the hydrolyzed product, while the lower is a mixture of water and glycerol. The upper portion was then evaporated in a vacuum evaporator to remove any water.

The same procedure and equipment for hydrolysis were used in the second step: methyl esterification of fatty acids by supercritical methanol treatment. Authentic fatty acids as well as fatty acids prepared by hydrolysis (the products of subcritical water treatment) and methanol were charged into the reaction vessel at a molar ratio of 42 in methanol for all runs.

The products obtained from hydrolysis and methyl esterification were analyzed for then composition by using high-performance liquid chromatography (HPLC) (LC -10AT; Shimadzu) consisting of a column (STR ODS-II, 25-cm length × 4.6-mm id; Shinwa) and refractive index detector (RID-10A; Shimadzu) operated at 40°C with a 1.0 mL/min flow rate of methanol as a carrier solvent. The methyl esters were also analyzed using a gas chromatography (GC-14B; Shimadzu) equipped with a flame ionization detector and thermogravimetric analysis (TGA-50; Shimadzu) with a 50 mL/min nitrogen purge flow.

To perform experiments at a constant pressure, a flow-type supercritical biomass conversion system was used. Major sections of the flow-type system consisted of pump stations, preheaters, supercritical treatment tube, cooling system, and separatory tank. The reaction time was calculated by dividing the volume of the treatment tube by the volumetric flow rate at the given conditions. Knowledge of the thermodynamic properties of the solvent, particularly correlation among temperature, pressure, and specific gravity, is important in order to accurately calculate the reaction treatment. Detailed information of the treatment with this equipment can

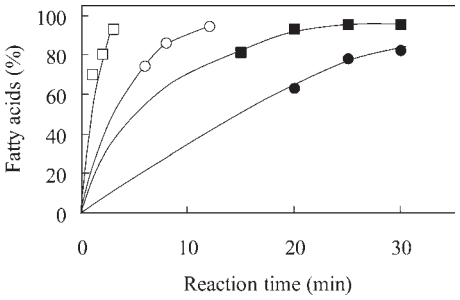

Fig. 1. Effect of reaction temperature on yield of fatty acids. The volumetric ratio of rapeseed oil to water was 1/4 (molar ratio: 1/217). □, 350°C; ○, 300°C; ■, 270°C; ●, 255°C.

be found elsewhere *(14)*. The experiment was performed at a temperature between 255 and 350°C and a pressure range from 5 to 20 MPa.

Results and Discussion

Hydrolysis of Rapeseed Oil with Subcritical Water

The hydrolysis reaction was carried out at various temperatures ranging from 255 to 350°C. Figure 1 demonstrates the effect of reaction temperature on the yield of fatty acids from triglycerides throughout the hydrolysis reaction. From Fig. 1, it is apparent that the course of the reaction for fatty acids formation was correlated with reaction temperature. At 350°C, a complete conversion could be achieved by 3 min of treatment. However, to get the same yield, it took 12 and 20 min at 300 and 270°C, respectively, while at 255°C only about 80% of the yield was achieved, and the yield was not increased for prolonged reaction treatment. Therefore, the reaction conditions of 270°C and 20 min were considered the mildest.

From Fig. 1 it can also be seen that the reaction rate was high at the beginning and tended to be lower in the prolonged treatment. We previously observed a similar trend in the transesterification reaction of rapeseed oil by supercritical methanol treatment *(13)*. This phenomenon is believed to be correlated with the reaction mechanism of vegetable oil/triglyceride in subcritical water which is known to consist of three stepwise reactions—triglyceride to diglyceride, diglyceride to monoglyceride and finally monoglyceride to glycerol—in which fatty acid is deliberated at each step. It was speculated that monoglyceride is the most difficult to be hydrolyzed, because monoglyceride is more stable than triglyceride and diglyceride.

The hydrolysis reaction is a reversible reaction, so it will be completed only if a large excess of water is used or if one of the products is removed from the reaction mixture. Therefore, we extended the experiment to study the effect of the amount of water on the hydrolysis reaction.

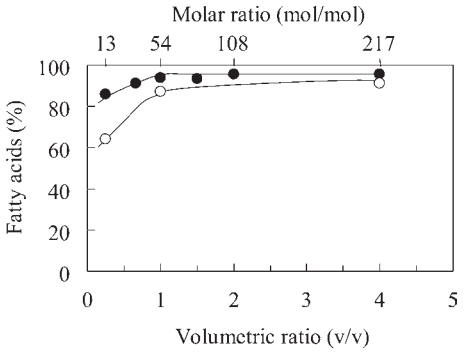

Fig. 2. Effect of volumetric ratio of water to rapeseed oil on yield of fatty acids treated at 270°C for 20 min. ●, Flow-type system; ○, batch-type system.

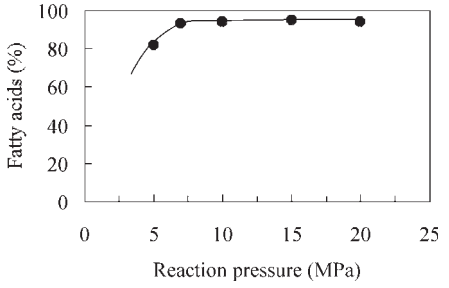

Fig. 3. Effect of reaction pressure on yield of fatty acids from rapeseed oil. Reaction conditions were 270°C and 20 min.

Figure 2 presents the effect of the various volumetric ratios of water to rapeseed oil on the yield of fatty acids as prepared with both flow- and batch-type reaction systems at 270°C for 20 min. The volumetric ratios of 1/4 and 4 correspond to the molar ratios of 13 and 217, respectively. For the batch-type system, the hydrolysis rate of triglycerides seemed to be affected more by the amount of water, and a slightly better conversion was seen with the flow-type reaction system. Even though the volumetric ratio of 1/4 is equivalent to the molar ratio of 13 in water, which is theoretically higher than its stoichiometry of 3, the formation of fatty acids in both reaction systems was obviously low. In addition, it was found that at a volumetric ratio less than 2/3, it was difficult to separate hydrolysis products from the water portion that contained glycerol. On the other hand, the presence of water in fatty acids would have a negative effect on the methyl esterification reaction *(15)*.

Figure 3 shows the effect of reaction pressure on the yield of fatty acids from rapeseed oil treated at 270°C for 20 min. It clearly demonstrates that a complete conversion of triglycerides to fatty acids was achieved when the

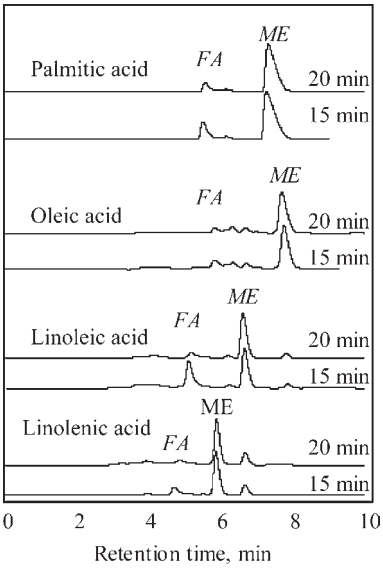

Fig. 4. HPLC chromatograms of various fatty acids treated in supercritical methanol at 270°C. FA corresponding fatty acids; ME, cooresponding methyl esters.

reaction pressure was above 7 MPa. Note that in the transesterification, the higher pressure was necessary to allow a complete conversion of triglycerides to methyl esters, as we observed previously *(13)*. However, as pressure was lowered to 5 MPa, a reduction in yield of fatty acids was apparent.

Hydrolysis is a homogeneous reaction that takes place in the water-oil phase as a result of rapeseed oil/triglycerides dissolving in the water. The capability of water to dissolve nonpolar triglycerides depends on the temperature and specific weight, which is further quantified as the dielectric constant. Under ordinary conditions, the dielectric constant of water and rapeseed oil is 80 and 3.1, respectively. To allow the reactants to form a soluble mixture, their dielectric constants should be close to each other. At 270°C, the dielectric constant of water tends to decrease to about 25, while that of rapeseed oil is 3.1 *(16,17)*. Judging from the results, it is then assumed that their dielectric constants at 270°C are close enough to form a homogeneous mixture.

Methyl Esterification of Fatty Acids with Supercritical Methanol

The second part of the present work deal with methyl esterification of fatty acids, the hydrolyzed products of triglycerides, in supercritical methanol treatment. We investigated the methyl esterification of several fatty acids present in rapeseed oil such as palmitic, oleic, linoleic and linolenic acids by supercritical methanol at 270°C and 17 MPa. Figure 4 shows

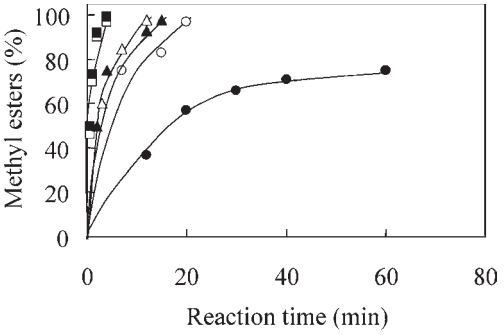

Fig. 5. Comparison in yield of methyl esters between transesterification of triglycerides and methyl esterification of fatty acids by supercritical methanol treatment at various temperatures. ●, Transesterification at 270°C; ▲, transesterification at 300°C; ■, transesterification at 350°C; ○, methyl transesterification at 270°C; △, methyl transesterification at 300°C; □, methyl transesterification at 350°C.

the obtained HPLC chromatograms. At a reaction time of 15 min, peaks of fatty acids marked by FA were present but disappeared mostly at 20 min of treatment. By contrast, the peaks of methyl esters dominate in the chromatograms.

Figure 5 shows a comparison of the yields of methyl esters between transesterification of triglycerides (rapeseed oil) and methyl esterification of fatty acids by supercritical methanol at various temperatures. At 350°C, both reactions could produce very similar results. At 300°C, transesterification produced about 90% methyl esters at 12 min of treatment, whereas methyl esterification resulted in a complete conversion. When triglycerides were transesterified at 270°C, a plateau was reached at about 40 min of treatment with a yield of about 76%. However, much higher yield could be achieved by methyl esterification at 20 min of treatment. These results, therefore, indicate that the reaction rate in methyl esterification is higher than that in transesterification.

The molar ratio of methanol to fatty acids is also an important parameter that controls the reaction. Figure 6 shows the obtained yields of methyl esters from oleic acid, a model of fatty acids, treated at various molar ratios of methanol to fatty acid. Interestingly, compared with the transesterification reaction shown by the dashed line *(13)*, methyl esterification proceeded more at the lower molar ratio, and it is apparent that at a molar ratio of 3, oleic acid was mostly converted to its methyl ester. This result is important in designing the production process, since a reaction with a low molar ratio requires less energy for the process.

Figure 7 shows a direct comparison of the yield of methyl esters between the one- and two-step supercritical methanol treatments at 270°C.

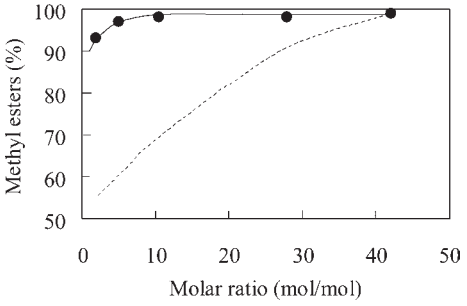

Fig. 6. Effect of molar ratio of methanol to oleic acid on yield of oleic acid methyl esters at 270°C for 20 min. The dashed line (- - -) represents data in transesterification from ref.*13*.

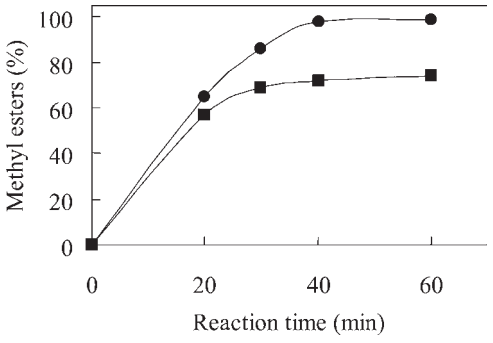

Fig. 7. Comparison of yields of methyl esters between one- and two-step supercritical methanol treatments at 270°C. ■, One-step supercritical methanol; ●, two-step supercritical methanol. The reaction time in the two-step method is a sum of those of hydrolysis and methyl esterification.

One-step treatment refers to a direct supercritical methanol method of rapeseed oil that involves mainly transesterification, while two-step treatment involves hydrolysis and subsequent methyl esterification. Figure 7 clearly demonstrates that at the same reaction time of 40 min, a significantly higher yield of methyl esters could be produced when the rapeseed oil was first treated with water, followed by methyl esterification of the hydrolyzed products.

Figure 8 shows a comparison of the HPLC chromatograms of rapeseed oil between one- and two-step preparation methods. As a comparison, the HPLC chromatogram of rapeseed oil treated with supercritical methanol in the presence of water is also shown. It is obvious that peaks of the two-step method only consist of methyl esters, whereas for other supercritical methanol methods, some peaks of intermediate compounds such as monoglycerides and diglycerides as well as unreacted triglycer-

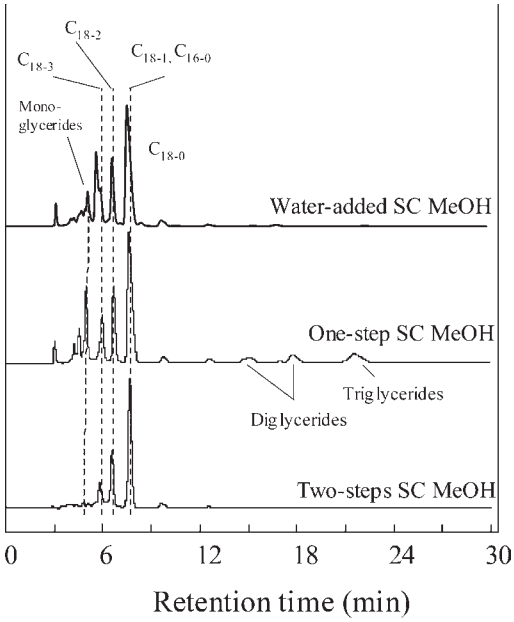

Fig. 8. Comparison in HPLC chromatograms of rapeseed oil treated using various supercritical methanol methods at 270°C for 40 min. SC MeOH, supercritical methanol.

ides are present. Compared with the one-step supercritical methanol method, a slightly higher conversion was achieved from the one-step supercritical methanol treatment in the presence of water *(15)*.

Figure 9 shows a schematic process of biodiesel production by the two-step supercritical methanol method. Several advantages have been attributed to the two-step reaction method. At temperature of 270°C, a common type of 316 stainless steel can fulfill the requirements of good corrosion resistance and cover the reaction condition *(5)*. Energy requirements may be less because mild reaction conditions for hydrolysis and methyl esterification are employed, whereas high-temperature treatment causes operational and equipment problems with, in some cases, the formation of undesirable degradation products. In addition, a reaction temperature of 270°C is commonly used in industries, so such a reaction condition is applicable for commercial applications.

Acknowledgments

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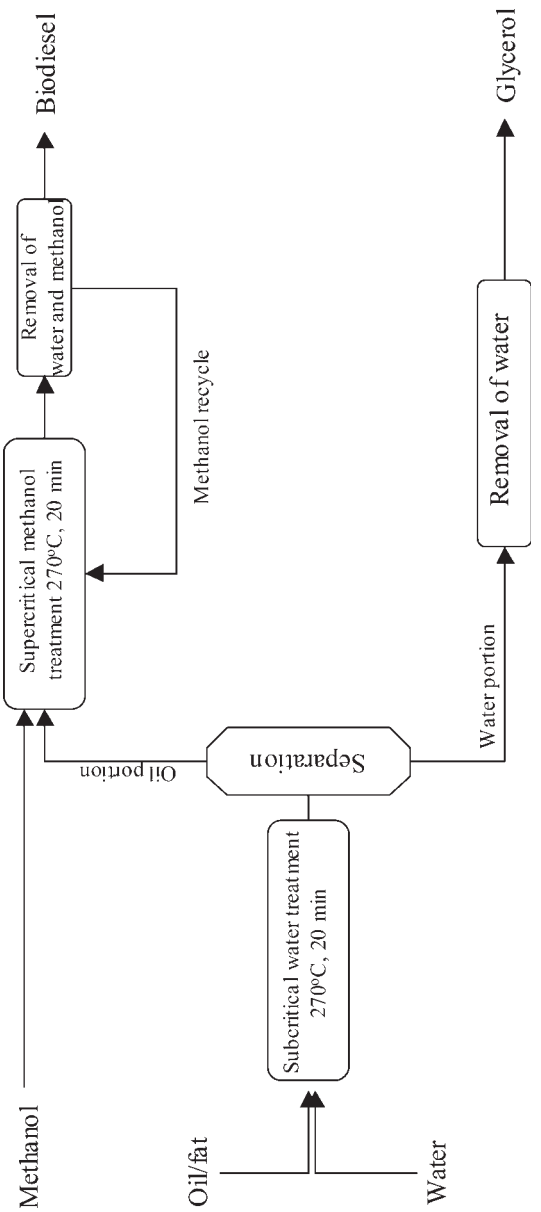

Fig. 9. Schematic process of biodiesel production by two-step preparation.

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