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Biodiesel Fuel from Vegetable Oil by Various Supercritical Alcohols

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Abstract

Biodiesel was prepared in various supercritical alcohol treatments with methanol, ethanol, 1-propanol, 1-butanol, or 1-octanol to study transesterification of rapeseed oil and alkyl esterification of fatty acid at temperatures of 300 and 350°C. The results showed that in transesterification, the reactivity was greatly correlated to the alcohol: the longer the alkyl chain of alcohol, the longer the reaction treatment. In alkyl esterification of fatty acids, the conversion did not depend on the alcohol type because they had a similar reactivity. Therefore, the selection of alcohol in biodiesel production should be based on consideration of its performance of properties and economics.

Index Entries: Supercritical alcohol; biodiesel; fatty acids alkyl ester; transesterification; alkyl esterification.

Introduction

Biodiesel is believed to be a promising alternative fuel to substitute petroleum-derived diesel fuel in diesel engines, and essentially no engine modifications are required to substitute biodiesel for diesel fuel. In addition, biodiesel is better than diesel fuel in terms of sulfur content, flash point, aromatic content, and biodegradability *(1)*. Research on the commercial application of biodiesel has therefore been started in European countries, the United States, and Japan *(2,3)*.

However, one of the limitations of using biodiesel fuel for diesel engines is higher cold flow properties compared with petroleum diesel fuel *(4)*. Cold properties consist of cloud point, pour point, and cold filter plugging point. The cloud point is a temperature at which the fuel starts to thicken and cloud, the pour point is a temperature at which the fuel thickens and no longer pours, and the cold filter plugging point is the lowest temperature at which fuel still flows through a specific filter. These

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cold flow properties of biodiesel restrict its utilization in very cold weather.

Cold properties of biodiesel are highly correlated to the fatty acid composition. Biodiesel with a high content of saturated fatty acids, such as that from palm oil and coconut oil, possesses poor cold flow properties. On the other hand, biodiesel with a high content of unsaturated fatty acids possesses better flow properties at lower temperatures. However, biodiesel from highly unsaturated fatty acids with more than two double bonds has combustion problems. Therefore, in some countries, the content of highly unsaturated fatty acid methyl esters in biodiesel is kept low *(5)*.

To improve the cold properties of biodiesel, the use of alcohol with longer alkyl chain has been studied in the alkaline-catalyzed method. The cloud point for ethyl esters is approx 2°C lower than that of the corresponding methyl esters, while butyl esters are 10°C lower than methyl esters *(6)*. Furthermore, cetane number is appropriate for alkyl esters from the alcohol with the longer alkyl chain *(7)*.

In the alkaline-catalyzed method, however, the reaction condition should be adjusted as various alcohols are used, and sometimes, a complete conversion is difficult to achieve. Gauglitz and Lehman *(8)* studied the rate of transesterification using alkaline catalyst at 60°C, and found that an addition of one alkyl carbon to the alcohol doubled the reaction time. Additionally, Nimcevic et al. *(9)* found that transesterification of rapeseed oil by *n*-propanol or alcohol with longer alkyl chain always failed even after several hours of treatment at the boiling point of alcohol.

We have developed a catalyst-free method of biodiesel fuel production by supercritical methanol *(10–12)*, and we found that the process becomes much simpler and that the yield of biodiesel is higher compared with the alkaline-catalyzed method. The aim of the present work was, therefore, to investigate the possibilities of biodiesel fuel production from rapeseed oil with various alcohols by supercritical treatment. In addition, the supercritically prepared biodiesel fuel was studied for its cold properties.

Materials and Methods

Rapeseed oil and its fatty acids (stearic, palmitic, oleic, linoleic, and linolenic acids) were chosen as the samples of vegetable oil. The experiments were performed in the batch- and flow-type supercritical biomass conversion systems developed in our laboratory. For the batch-type system, a reaction vessel was made of Inconel-625 with a volume of 5 mL; for the flow-type system, the supercritical treatment tube was constructed from Hastelloy stainless steel (HC 276) with length of 84 m and an id of 1.2 mm, with the total volume being about 95 mL. Detailed information about the equipment can be found elsewhere *(13)*.

Rapeseed oil or fatty acid was mixed with alcohol in a molar ratio of 42:1 in alcohol to oil/fatty acids, and the mixture was treated at 300 and 350°C. In the batch-type system, the pressure was the maximum one reached during the treatment in which the pressure depends on the kind of alcohol. On the other hand, the flow-type system allowed treatments in a constant reaction pressure. Reaction times ranged from 1 to 14 min at reaction pressures of 10–40 MPa. In transesterification, the treated oil was allowed to settle for about 30 min into three separate phases. The top phase, consisting of alcohol, was then pipetted away, and the remaining two phases were heated for 20 min to remove the alcohol further. The upper phase consisted of methyl esters, intermediates of methyl esters (diglycerides and monoglycerides), and unreacted rapeseed oil (triglycerides), while glycerol was present in the lower phase. In the case of esterification, the treated fatty acids were heated to remove the alcohol.

The products obtained were analyzed for composition using high-performance liquid chromatography (HPLC) (LC -10AT; Shimadzu, Kyoto, Japan), which consisted of a column (STR ODS-II, 25 cm in length × 4.6 mm in id; Shinwa Chemical, Osaka, Japan) operated at 40°C at a flow rate of 1.0 mL/min with methanol as a carrier solvent. The column was packed with silica particles (5-μm particle diameter and 12-nm pore diameter). The cloud and pour points of the obtained biodiesel were then determined by a mini–cloud/pour point tester (Model MPC-102; Tanaka Scientific, Tokyo, Japan) based on ASTM D2500 for cloud point and ASTM D6749 for pour point *(14)*.

Results and Discussion

To evaluate the reaction of rapeseed oil and fatty acids in supercritical treatment, five kinds of alcohols were selected: methanol, ethanol, 1-propanol, 1-butanol, and 1-octanol. Figure 1 shows the obtained HPLC chromatograms for rapeseed oil (triglycerides) treated in the batch-type reaction system with various alcohols under supercritical conditions at 350°C. The rapeseed oil consisted of 98.5% triglycerides. Therefore, it was considered a triglyceride. The peaks of the corresponding alkyl esters were slightly shifted as alkyl chains of alcohols became longer. Each alkyl ester emerged as a single peak. In addition, a distinct separation could be achieved for all kinds of alkyl esters, unreacted and intermediate compounds, in 30 min of retention time. By comparing them with the standard compounds, peaks of mono-, di-, and triglycerides were observed, respectively, at about 5 min, between 15 and 22 min, and after 22 min of retention time. From the HPLC chromatograms shown in Fig. 1, peaks of mono-, di-, and triglycerides were detected from treatments of 3 and 6 min. On the other hand, for the prolonged reaction times (10 and 14 min), peaks of alkyl esters were increased. Instead, peaks of unreacted and intermediate compounds decreased and further disappeared, demonstrating a formation of the alkyl esters.

Figure 2 shows changes in the yields of fatty acid alkyl esters treated in the batch-type reaction system with various supercritical alcohols at 350°C. In the case of methanol, >90% yield of methyl esters was achieved

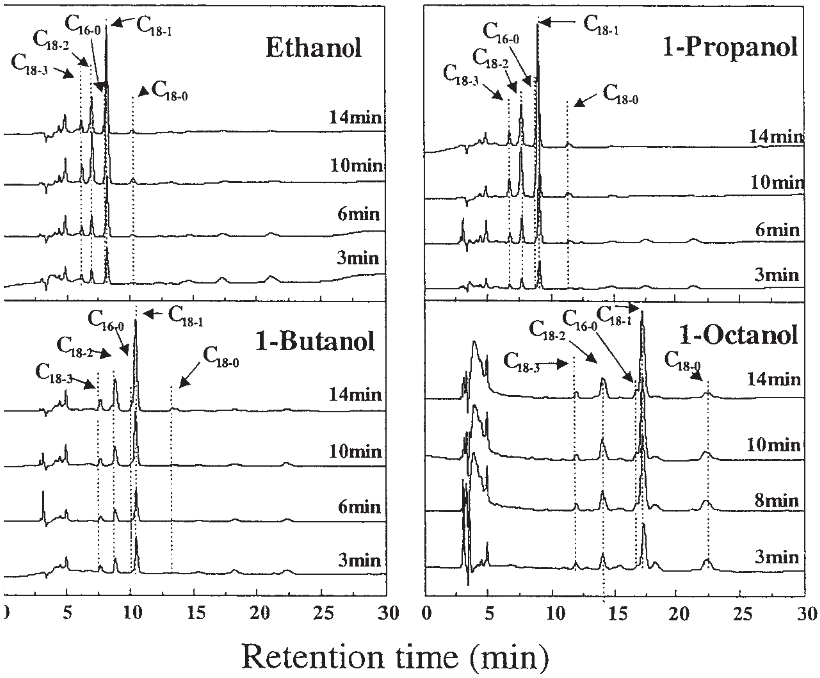

Fig. 1. HPLC chromatograms for rapeseed oil treated with various supercritical alcohols at 350°C in batch-type reaction system.

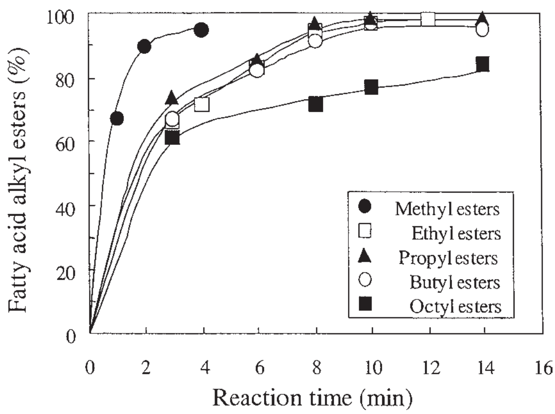

Fig. 2. Changes in yields of fatty acid alkyl esters of rapeseed oil treated with various supercritical alcohols at 350°C in batch-type reaction system.

after 2 min of treatment. On the other hand, it took 8 min for ethanol, 1-propanol, and 1-butanol to obtain the same yield of the corresponding alkyl esters, and even longer for 1-octanol. In the case of ethanol, 1-propanol, and 1-butanol, about 8–14 min of supercritical treatment was necessary to achieve almost complete conversions of triglycerides to fatty acid alkyl esters, while for 1-octanol, 20 min was required to obtain the same yield.

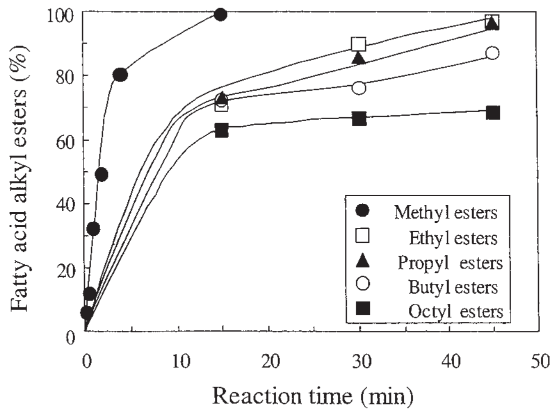

Fig. 3. Changes in yields of fatty acid alkyl esters of rapeseed oil treated with various supercritical alcohols at 300°C in batch-type reaction system.

These results demonstrate that the yields of fatty acid alkyl esters were not significantly different when rapeseed oil was treated in the batch-type system with ethanol, 1-propanol, and 1-butanol at 350°C.

Figure 3 presents changes in the yields of fatty acid alkyl esters as rapeseed oil treated at 300°C in the batch-type reaction system. As expected, the reaction rates were less than those in the 350°C treatment and there was an obvious difference in the reactivity for each alcohol. In all cases, the yield of alkyl esters increased as the reaction time was prolonged, while for identical reaction times, alcohols with the shorter alkyl chains gave better conversions. The highest yield of alkyl esters was obtained with 15 min of treatment with methanol, while ethanol and 1-propanol required 45 min to obtain the same yield. Under the same temperature condition, supercritical treatment with 1-butanol and 1-octanol produced only about 85 and 62% of the corresponding fatty acid alkyl esters, respectively. Therefore, it can be concluded that under the same temperature condition in the batch-type reaction system, the reaction time is correlated with the length of alkyl chain: the longer the alkyl chain of alcohol, the longer the supercritical treatment required to obtain comparable conversion of triglycerides to the alkyl esters.

In the batch-type reaction system, however, the pressure cannot be controlled during the treatment. Table 1 shows a maximum pressure for various supercritical alcohols at 300 and 350°C. It can be observed that at the same temperature, they gave different maximum pressure and that the pressure tended to be lower as the alkyl chain of the alcohol became longer. Previously, it was found that the reaction pressure is an important reaction parameter in enhancing the reaction rate *(11)*. Therefore, the flow-type reaction system, which can control the reaction pressure up to 50 MPa, was used to study the effect of the reaction pressure on the formation of alkyl esters. Reaction temperature and reaction time were set at 300°C and 20

Table 1
Critical State of Various Alcohols Studied and Their Maxiumum Temperature in Batch-Type Reaction System

Alcohol		Critical temperature (°C)	Critical pressure (MPa)	Pressure (MPa) 300°C	Pressure (MPa) 350°C
Methanol	(CH_3OH)	239	8.1	20	43
Ethanol	(CH_3CH_2OH)	243	6.4	15	25
1-Propanol	($CH_3[CH_2]_2OH$)	264	5.1	10	23
1-Butanol	($CH_3[CH_2]_3OH$)	287	4.9	9	23
1-Octanol	($CH_3[CH_2]_7OH$)	385	2.9	6	19

min, respectively. Figure 4 shows the relationship between the yield of fatty acid alkyl esters and reaction pressure. It is obvious that the higher reaction pressure slightly improved the yield through reaction rate enhancement, and that the pressure effect was lower for alcohols with a longer alkyl chain. However, compared with the results obtained with the batch-type system shown in Fig. 3, the yields were slightly lower. Therefore, it can be speculated that at pressures higher than the maximum one reached in the batch-type reaction system as shown in Table 1, the effect of the reaction pressure would not result in a significant increase in reaction rate. Thus, it further means that optimum reaction pressures are lower for a longer alkyl chain of alcohol. On the other hand, longer reaction times are required for alcohol with a longer alkyl chain.

The basic idea of supercritical fluid treatment is to take advantage of the relationship between pressure and temperature on thermophysical properties of the solvent (alcohol) such as dielectric constant, viscosity, specific gravity, and polarity. For example, the ionic product, which is an important parameter for chemical reaction, can be improved by increasing the pressure. Therefore, in the supercritical alcohol treatment of rapeseed oil, alcohol is expected to act, in addition to being a reactant, as an acid catalyst. Since the acidity of alcohol tends to decrease in the longer alkyl chain of alcohols, the reactivity would be correspondingly lower. This is one possible reason why the reaction rate is decreased in the longer alkyl chain of alcohol. Another factor might be that the smaller size of the alcohols could facilitate the simultaneous attack of alcohol on all three chains of triglycerides, resulting in the higher reaction rate of fatty acid alkyl ester formation as observed by others *(15)*.

Using similar reaction conditions with rapeseed oil, fatty acids were treated with various supercritical alcohols. From the HPLC analysis, it was shown that selective reactions could be obtained. Figure 5 presents the yields of alkyl esters of five fatty acids treated in various supercritical alcohols at 300°C. In the case of methanol, the reaction time for the complete conversion

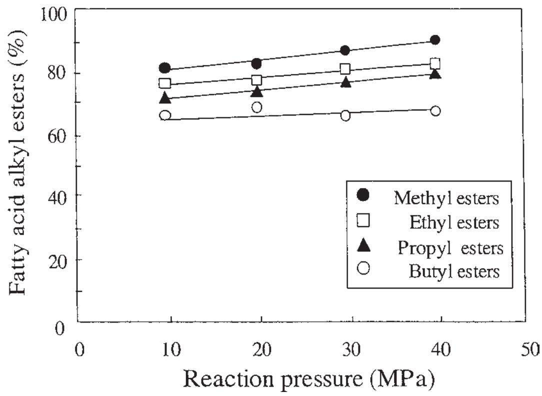

Fig. 4. Effect of reaction pressure on yield of fatty acid alkyl esters of rapeseed oil treated with various supercritical alcohols at 300°C for 20 min in flow-type reaction system.

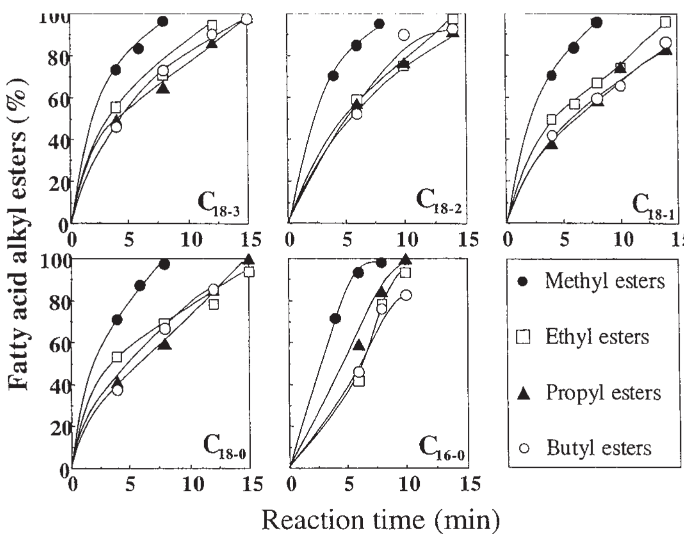

Fig. 5. Changes in yields of fatty acid alkyl esters from various fatty acids treated with supercritical alcohols at 300°C in batch-type reaction system.

of fatty acids to methyl esters was observed after 8 min of treatment. Interestingly, for other alcohols, 14 min of treatment was required to achieve complete conversions. The results with ethanol, 1-propanol, and 1-butanol show that saturated fatty acids of palmitic (C_{16-0}) and stearic (C_{18-0}) acids have slightly lower reactivity than those of unsaturated fatty acids such as oleic (C_{18-1}), linoleic (C_{18-2}), and linolenic (C_{18-3}) acids. This result is in good agreement with those found previously *(12)*.

Table 2
Cloud and Pour Point of Biodiesel Prepared by Supercritical Alcohol Treatment at 350°C and Alkaline-Catalyzed Method

Fatty acid alkyl esters	Cloud point (°C)	Pour point (°C)
Methyl esters	–4	–11
Ethyl esters	–7	–7
Propyl esters	–8	–10
Butyl esters	–10	–14
E-Oil[a]	–4	–12
Bio Super 3000[b]	–5	–12

[a] Biodiesel from waste rapeseed oil, used in Kyoto city from 1997 to 2002.
[b] Biodiesel from virgin rapeseed oil (from Austria).

Table 2 presents cloud and pour points of biodiesel prepared by our supercritical alcohol method at 350°C. For comparison, the results of the commercial biodiesel fuels are also shown. These results demonstrate that the cloud point of ethyl esters was 3°C lower than that of methyl esters, while that of butyl esters was even lower. The cloud point of methyl ester was similar to that of commercial biodiesel fuels.

Regardless of the kind of alcohols, our results revealed that supercritical treatment could convert both triglycerides and fatty acids to fatty acid alkyl esters. On the other hand, complete conversions are barely achieved by the alkaline-catalyzed method even at prolonged treatment. Considering the reactivity of triglycerides and fatty acids in various supercritical alcohols, it was noted that fatty acids are more reactive than triglycerides. With the exception of methanol, the alcohols studied had a similar reactivity in esterification of fatty acids under the same condition. Conversely, in transesterification, the formation of fatty acid alkyl esters greatly depended on the length of alcohol. The selection of alcohol in biodiesel production should therefore be based on its performance properties and economics.

Acknowledgments

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References

1. Fukuda, H., Kondo, A., and Noda, H. (2001), *J. Biosci. Bioeng*. **92,** 405–416.
2. Ma, F. and Hanna, A. M. (1999), *Bioresour. Technol.* **70,** 1–15.

3. The Institute of Energy Economics, Japan. (1994), report on *Research on Feasibility of Utilization of Spent Vegetable Oils as Substitutes for Petroleum-Derived Oils*, (in Japanese), pp. 114–118.
4. Gomez, M. E. G., Hildige, R. H., Leahy, J. J., and Rice, B. (2002), *Fuel* **81,** 33–39.
5. Mittelbach, M. (1996), *Bioresour. Technol.* **56,** 7–11.
6. Lang, X., Dalai, K. A., Bakhshi, N. N., Reaney, J. M., and Hertz, B. P. (2001), *Bioresour. Technol.* **80,** 53–62.
7. Knothe, G., Matheaus, C. A., and Ryan, W. T. (2003), *Fuel* **82,** 971–975.
8. Gauglitz, E. J. and Lehman, L. W. (1963), *JAOCS* **40,** 197,198.
9. Nimcevic, D., Puntigam, R., Wörgetter, M., and Gapes, R. J. (2000), *JAOCS* **77,** 275–279.
10. Saka, S. and Kusdiana, D. (2001), *Fuel* **80,** 225–231.
11. Kusdiana, D. and Saka, S. (2001), *Fuel* **80,** 693–698.
12. Kusdiana, D. and Saka, S. (2001), *Chem. Eng. Japan* **34,** 383–387.
13. Kusdiana, D., Minami, E., Ehara, K., and Saka, S. (2002), in *Proceeding of 12th European Biomass Conference*, James & James (Science Publishers), London, UK, pp. 789–792.
14. Tanaka Scientific (2003), Mini-Pour/Cloud Point Tester, Instruction Manual, Ver. 1.01, Tokyo, Japan.
15. Freedman, B., Butterfield, R. O., and Pryde, E. H. (1986), *JAOCS* **63,** 1375–1380.