

Non-catalytic biodiesel fuel production with supercritical methanol technologies

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Study presents that supercritical methanol has the ability to convert oils/fats consisting of triglycerides and free fatty acids (FFAs) into fatty acid methyl esters through transesterification and methyl esterification, respectively, without any catalyst. This one-step method (Saka process) is simpler process realizing shorter reaction time and higher yield of methyl esters than those of the conventional alkali-catalyzed method. To improve the biodiesel quality that satisfies the standard specification, another reaction route was also developed by the two-step method (Saka-Dadan process), which consists of hydrolysis step for oils/fats in subcritical water and subsequent methyl esterification of the hydrolyzed products of fatty acids from oils/fats in supercritical methanol. These new methods are highly tolerant against the presence of FFAs and water in oils/fats. Therefore, compared to the alkali-catalyzed method, proposed methods can be applied for various types of oils/fats and their wastes as raw materials to produce biodiesel fuel.

Keywords: Biodiesel, Fatty acid, Hydrolysis, Methyl esterification, Oils/fats, Supercritical methanol, Transesterification, Triglyceride

Introduction

Biomass is considered as one of the key renewable energy resources owing to its large potential, economic feasibility and various social and environmental benefits. In addition, the depletion in world petroleum reserves has stimulated the search for alternative sources for petroleum-based fuel, including diesel fuels. Converting waste oils/fats to biodiesel (fatty acid methyl esters) for diesel engines is considered as an important step in terms of recycling and reusing material, and reducing CO₂ emission.

Biodiesel is produced by transesterification of triglyceride, which is a major component of oils/fats, with methanol¹. Majority of the methods for biodiesel production involve the use of alkali catalyst. In this method, however, free fatty acids (FFAs) in oils/fats react with alkali-catalyst producing saponified products². Therefore, complicated purification steps are necessary to remove saponified products as well as the catalyst, which further cause adverse environmental effects. Besides, in case of hydrous oils/fats, water depresses the catalyst activity². The acid-catalyzed method has, on the other hand, a tolerance for the presence of FFAs because of their

simultaneous methyl esterification to methyl esters. However, the use of acid-catalyst results in long reaction time and this process is still sensitive to water³. Although a combination of acid- and alkali-catalyzed processes has been developed to overcome such disadvantages caused by the presence of FFAs and water^{4,5}, they will be essentially solved if a non-catalytic biodiesel production is realized. In such a situation, supercritical fluid has recently received attention as a new reaction field due to its unique properties.

When temperature and pressure go over critical point, the substance becomes to be supercritical fluid. In supercritical state, molecules in the substance have high kinetic energy like a gas and high density like a liquid. It is, therefore, expected that the chemical reactivity in supercritical fluid can be enhanced. In addition, dielectric constant of supercritical fluid is lower than that of liquid; dielectric constant of supercritical methanol becomes about 7 at critical point, while that of liquid methanol is about 32 at ambient temperature^{6,7}. The former value is equivalent to that of non-polar organic solvent, and it can dissolve well many kinds of non-polar organic substances such as oils/fats. In supercritical methanol, therefore, a homogeneous (one-phase) reaction between oils/fats and methanol is realized.

Furthermore, in supercritical state of protic solvent such as water and methanol, the ionic product is

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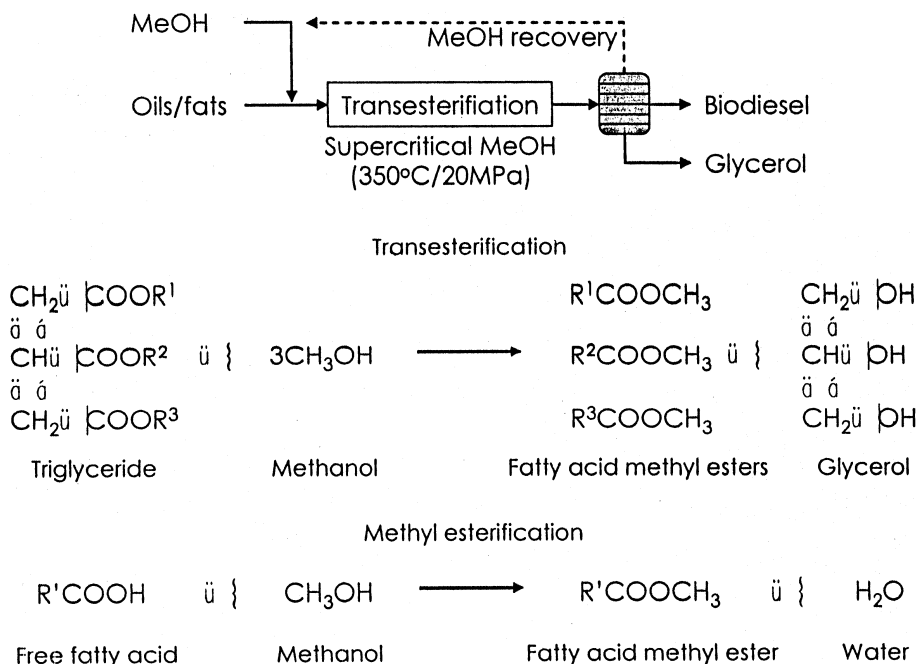


Fig. 1—Scheme of the one-step supercritical methanol method (Saka process) and reactions of oils/fats for biodiesel production^{9,10} (R^1 , R^2 , R^3 , R' : Hydrocarbon groups)

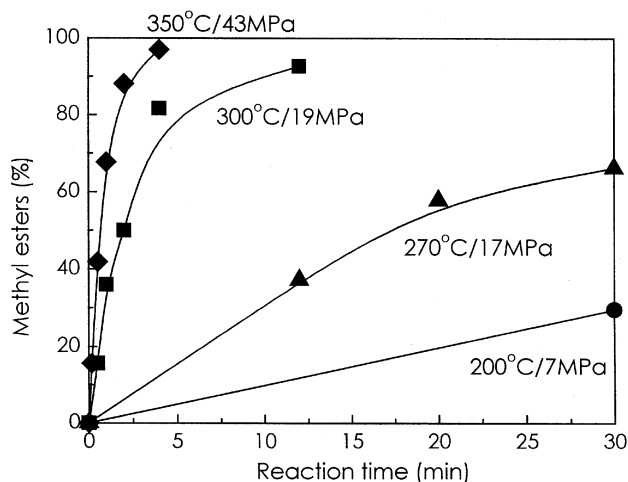


Fig. 2—Transesterification of rapeseed oil to fatty acid methyl esters in supercritical methanol at various temperatures¹⁰ (42 in molar ratio of methanol to triglyceride)

increased by increasing pressure⁸. Therefore, solvolysis reaction field can be expected, for example, hydrolysis in water and methanolysis in methanol.

On these properties, authors have been working in developing non-catalytic biodiesel production methods by supercritical methanol treatments during the last decade^{9,10}. In this laboratory, a batch-type and flow-type supercritical fluid biomass conversion systems have been developed and used to study chemical conversion of oils/fats to biodiesel fuel¹¹.

This paper reviews a recent progress in developing supercritical methanol methods as non-catalytic biodiesel production process from oils/fats.

One-Step Supercritical Methanol Method (Saka Process)

In this method, triglycerides in oils/fats are converted to fatty acid methyl esters without any catalyst (Fig. 1) due to its methanolysis ability^{9,10}. Yield of methyl esters (Fig. 2) from oil treated in subcritical and supercritical methanol¹⁰ varies with temperature. Since the experiment was carried out in a batch-type reactor, the reaction pressure was varied for each temperature. At 200 and 270°C, the relatively low conversion of refined rapeseed oil to methyl esters was observed. Beyond 300°C, however, the conversion rate remarkably increased; 97 percent of ester yield was achieved after the treatment for 4 min at 350°C. In this reaction, the reactants initially form a two-phase liquid system at ambient temperature and pressure because solvent properties of methanol are significantly different from those of rapeseed oil, such as dielectric constant. As the reaction temperature rises, however, the dielectric constant of methanol decreases to be closer to that of rapeseed oil, allowing the reactants to form one-phase between methanol and oil so that the reaction takes place homogeneously¹². In addition, since supercritical methanol is more likely to be gaseous in properties in terms of

Table 1—Comparison of ester yield from various oils/fats feedstocks by alkali-catalyzed, acid-catalyzed and one-step supercritical methanol (SCM) methods

Feedstocks	FFA wt%	Water wt%	Ester yield, wt%		
			Alkali	Acid	SCM
Rapeseed oil ^a	2.0	0.02	97.0	98.4	98.5
Palm oil	5.3	2.1	94.4	97.8	98.9
Waste cooking oil ^b	5.6	0.2	94.1	97.8	96.9
Waste soybean oil	35.5	1.7	N.A.	68.8	98.9
Waste industrial oil	37.7	3.3	N.A.	71.2	97.9
Dark oil	40.5	1.6	N.A.	66.0	96.3
Waste palm oil ^c	>20.0	61.7	N.A.	N.A.	95.8

^a2.0 wt% of oleic acid was added to refined rapeseed oil, ^bfrom household sector in Kyoto City, ^cemulsified form

diffusivity and viscosity, there are no limitations of mass-transfer on the reaction, allowing the reaction to proceed in a very short time. Compared to the alkali-catalyzed method, in which the mixing effect is significant in a heterogeneous two-phase system, the mixing is not necessary in supercritical methanol because the reactants are already in a homogeneous form.

Another important achievement in this method is that FFAs can be converted (Fig. 1) to their methyl esters by methyl esterification¹³, while in alkali-catalyzed method they are saponified. Therefore, the one-step method can produce higher yield of methyl esters than alkali-catalyzed method especially for low-quality oils/fats containing FFAs¹³. Besides FFA, existence of water in oils/fats is serious for the acid- and alkali-catalyzed transesterification^{2,3,14}. Since used cooking oil and waste palm oil have a high content of FFAs, the alkali-catalyzed method resulted in a lower yield, while acid-catalyzed method gave a high yield (Table 1). However, waste palm oil, which contains a high amount of water, failed in reaction for both acid- and alkali-catalyzed methods. On the contrary, all the results obtained by the one-step method were high in yield for all samples studied. Thus, crude oils/fats as well as their wastes could be readily used for biodiesel production by the one-step method.

Based on these observations, superiority of the one-step method (Saka process) can be summarized, compared to the alkali-catalyzed method, as follows: i) Production process becomes much simpler; ii) Reaction is fast; iii) FFAs in oils/fats can be converted to their methyl esters through methyl esterification; and iv) Yield of methyl esters is higher. Although this process has many advantages to produce a high yield of biodiesel fuel, it requires restrictive reaction

conditions of, for example, 350°C, 20MPa, 9 min and 42 in molar ratio of methanol to triglyceride¹². In such conditions, special alloys (Inconel and Hastelloy) are required for the reaction tube to avoid corrosion. In addition, methyl esters particularly from polyunsaturated fatty acids, such as methyl linolenate, are partly denatured under this severe condition¹².

Two-Step Supercritical Methanol Method (Saka-Dadan Process)

To realize more moderate reaction conditions, further effort was made through the two-step preparation; hydrolysis of oils/fats in subcritical water and subsequent methyl esterification of fatty acids in supercritical methanol¹⁵⁻¹⁷ (Fig. 3). In this method, oils/fats are, first, treated in subcritical water for hydrolysis reaction to produce fatty acids. After hydrolysis, the reaction mixture is separated into oil phase and water phase by decantation. The oil phase (upper portion) is fatty acids, while the water phase (lower portion) contains glycerol. The separated oil phase is then mixed with methanol and treated at supercritical condition to produce methyl esters thorough methyl esterification. After removing unreacted methanol and water produced in reaction, fatty acid methyl esters can be obtained as biodiesel. Therefore, in this process, methyl esterification is the main reaction for methyl esters formation, while in the one-step method (Saka process), transesterification is the most major one.

Hydrolysis reaction was carried out using a batch-type reaction vessel at various temperatures. Fatty acids formation from refined rapeseed oil¹⁵ was found correlated with reaction temperature (Fig. 4). At 350°C, almost complete conversion could be achieved after the treatment for 3 min. However, to get the same yield, it took 12 and 20 min at 300°C and 270°C, respectively, while at 255°C only about 80 wt% of the yield was achieved after 30 min, and the yield was not increased for more prolonged treatment. Therefore, reaction conditions of 270°C for 20 min were considered to be the most moderate. In this way, hydrolysis reaction successfully proceeded even at lower temperatures compared to the one-step transesterification. On the other hand, second part of this process is dealing with methyl esterification of fatty acids, the hydrolyzed products of triglycerides, by supercritical methanol treatment. Similar to hydrolysis reaction, esterification of fatty acids from rapeseed oil¹⁵ could be almost completely performed at 270°C for 20 min of the treatment and optimum reaction conditions for esterification were comparable

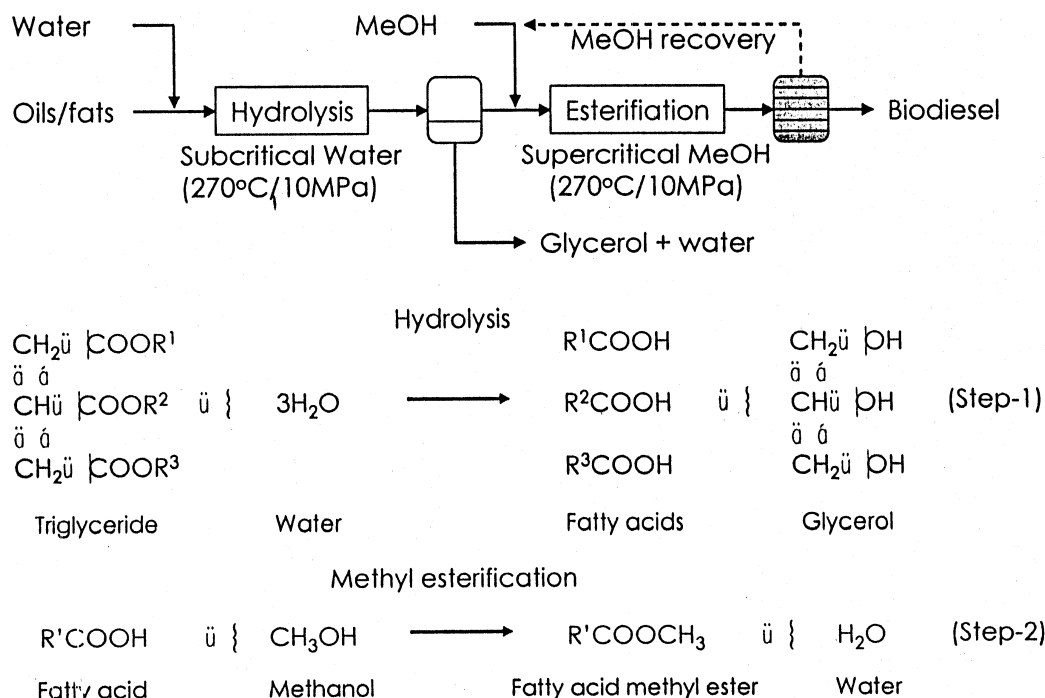


Fig. 3—Scheme of the two-step supercritical methanol method (Saka-Dadan process) and reactions of oils/fats for biodiesel production^{15, 16} ($\text{R}^1, \text{R}^2, \text{R}^3, \text{R}'$: Hydrocarbon groups)

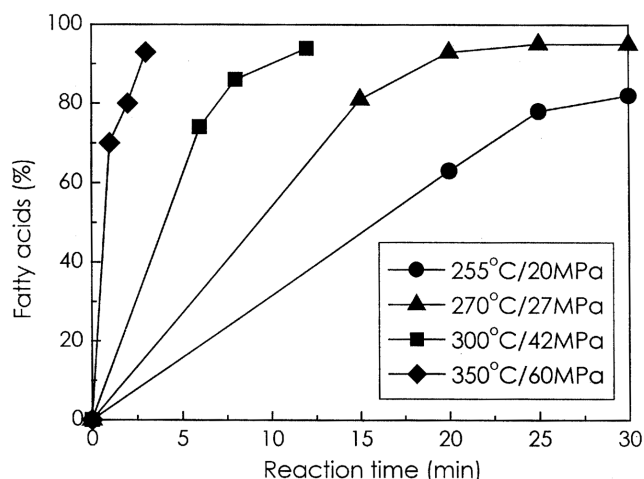


Fig. 4—Hydrolysis of rapeseed oil to fatty acids in subcritical water at various temperatures¹⁵ (54 in molar ratio of water to triglyceride)

to hydrolysis reaction (Fig. 5). This is because methyl esterification occurs in homogeneous one-phase system since fatty acids can dissolve easily in methanol.

In designing a manufacturing plant for supercritical fluid process, lower temperature and lower pressure are more desirable. In case of the two-step process, the optimum reaction condition was found to be

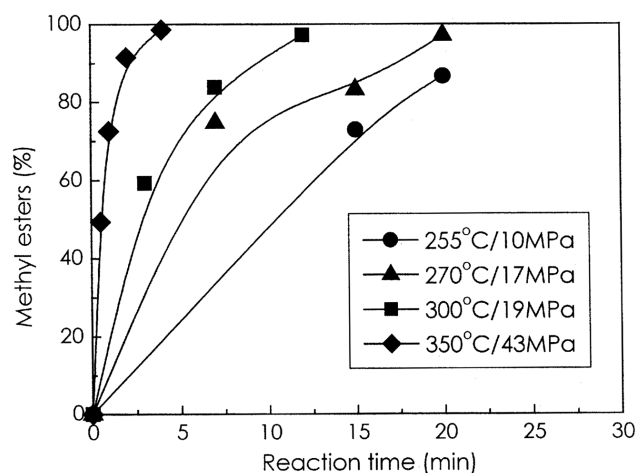


Fig. 5—Methyl esterification of fatty acids to their methyl esters in supercritical methanol at various temperatures¹⁵ (42 in molar ratio of methanol to fatty acid)

270°C at 7-15MPa pressure for both of hydrolysis and esterification, through additional studies using a flow-type reactor¹⁵. It allows the use of common stainless steel instead of special alloy for reactors such as Inconel or Hastelloy. In this condition, furthermore, any denaturation was not found for polyunsaturated fatty acid methyl esters.

Two-step method can produce high-quality biodiesel fuel, compared with the one-step method¹⁵⁻¹⁷

(Fig. 6). It is obvious that peaks of the two-step method only consist of methyl esters, while for the one-step method, some peaks of intermediate compounds such as monoglycerides and diglycerides are present. In case of the one-step method, glycerol always exists in the reaction system. Therefore, as a backward reaction, glycerol reacts with methyl ester to reproduce monoglyceride. Similarly, monoglyceride and diglyceride are also reversely reproduced to triglyceride and diglyceride, respectively, consuming one molecule of methyl ester. In the two-step method, on the other hand, glycerol is removed after the hydrolysis reaction so that such a backward reaction can be depressed in the methyl esterification step.

Biodiesel Fuel Properties

Among the specification standards of biodiesel fuel, total glycerol content is one of the most important character since glycerides significantly

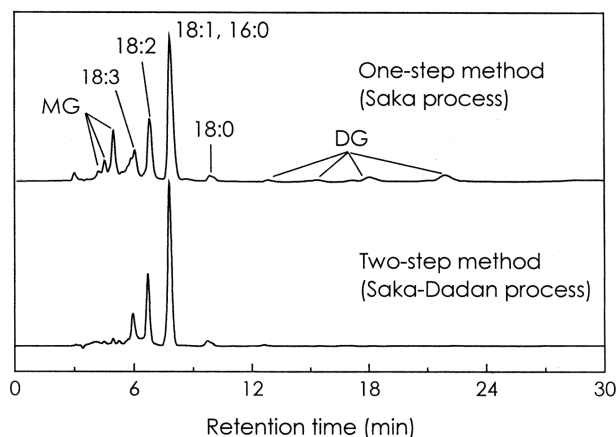


Fig. 6—HPLC chromatograms of biodiesel fuel from rapeseed oil prepared by one-step and two-step supercritical methanol methods¹⁵ (one-step method: 350°C/43MPa/4min, two-step method: 270°C/27MPa/20min for hydrolysis and 270°C/17MPa/20min for methyl esterification)

affect other fuel properties such as viscosity, pour point, amount of carbon residue and so on, causing problems on filterability and deposition on the injector and combustion chamber. The total glycerol content G_s (wt% on mass of biodiesel fuel) is defined as follows¹⁸:

$$G_s = 0.1044W_{TG} + 0.1488W_{DG} + 0.2591W_{MG} + W_G$$

where W_{TG} , W_{DG} , W_{MG} and W_G are amounts of triglycerides, diglycerides, monoglycerides and free glycerol (wt% on mass of biodiesel fuel), respectively. As is well known in EU and US biodiesel specification standards, the G_s value must be less than 0.24 and 0.25 wt%, respectively^{19, 20}.

Two-step method can depress the backward reaction of glycerol, a higher yield of methyl esters and lower total glycerol content can be expected compared with the one-step method. Actually, total glycerol contents of biodiesel prepared by the one-step and two-step supercritical methods were 0.39 and 0.15 wt%, respectively (Table 2). Therefore, the latter method can fulfill requirements in EU and US biodiesel specification standards. Concomitantly, other fuel properties such as viscosity, pour point, cold filter plugging point (CFPP) and so on also satisfy the standard specification¹⁷ (Table 3). In this way, the two-step supercritical methanol method can

Table 2—Comparisons in ester yield and total glycerol content of biodiesel prepared by three different methods

Method ^a	Ester yield wt%	Total glycerol wt%
Alkali-catalyzed	94.6	0.17
One-step ^b (Saka process)	98.5	0.39
Two-step ^b (Saka-Dadan process)	99.1	0.15

^ain each case, rapeseed oil including 2.0wt% of oleic acid was treated. ^bprepared in a batch-type reactor

Table 3—Various fuel properties of biodiesel from rapeseed oil prepared by the two-step supercritical methanol method.¹⁷

Property	Unit	EU ¹⁹	Specification US ²⁰	Kyoto ¹⁷	Biodiesel ^a
Viscosity (40°C)	mm ² /s	3.5~5.0	1.9~6.0	3.5~5.0	4.820
Pour point	°C	-	-	<-7.5	-10
Cloud point	°C	-	-	-	-1
CFPP	°C	-	-	<-5	-10
Flash point	°C	>120	>130	>100	172.5
Carbon residue ^b	wt%	<(0.3)	<0.05	<(0.3)	0.02
Ester content	wt%	>96.5	-	-	98.2
Total glycerol	wt%	<0.25	<0.24	<0.25	0.24
Iodine value	g-I ₂ /100g	<120	-	<120	110

^aprepared in a flow-type reactor, ^bnumbers in parentheses are on 10% residual oil basis

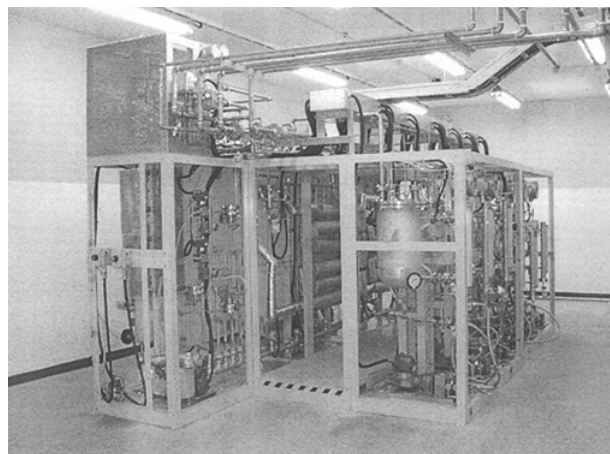


Fig. 7—Bench-scale plant for the two-step supercritical methanol method

produce high-quality biodiesel fuel through relatively milder reaction conditions.

NEDO National Project for the Two-Step Method

For commercialization of the two-step method, an industry-university joint research project (Fig. 7) has started as one of the “High-efficiency Bioenergy Conversion Projects” by the New Energy and Industrial Technology Development Organization (NEDO) in FY2003 under the collaboration with Asahi KASEI Corp. Group and Toyota Tsusho Corp. to produce high-quality biodiesel (total glycerol < 0.24 wt% through a high energy efficiency, > 80%). As a result, in FY2003, a flow-type bench-scale plant has been designed and developed for biodiesel production. Through this research project, high-quality biodiesel fuel produced by the two-step supercritical methanol method will be commercialized in the near future.

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