1. Introduction

Biodiesel (fatty acid methyl esters) obtained from the transesterification of plant oil (triacylglycerol) is used as an alternative to fossil diesel. Biodiesel is usually produced using an alkali catalyst. However, when the raw material contains free fatty acids, undesired saponification reactions occur. Furthermore, a purification step is required to remove the catalyst after the reaction. As an approach to solving these problems, a noncatalytic method using supercritical methanol has been reported. Other alcohols, such as ethanol and propanol, methyl acetate and dimethyl carbonate are also available for the production of biodiesel in their supercritical states. In these methods, free fatty acids are converted into fatty acid methyl esters by esterification. However, high temperatures (>350 °C) are required for the transesterification of triacylglycerol, leading to thermal deterioration of the biodiesel. Furthermore, reducing the amount of monoacylglycerol in biodiesel is difficult due to the reverse reaction between glycerol and fatty acid methyl ester, which regenerates monoacylglycerol. The monoacylglycerol content is limited to less than 0.7 wt% by the European biodiesel standard. The addition of co-solvent, such as acetone, tetrahydrofuran, hexane, and carbon dioxide, has been studied to ease the severe reaction conditions of the supercritical methanol method, and succeeded in reducing the reaction temperature and pressure. However, in these direct transesterification from triacylglycerol to biodiesel, the problem of reverse reaction remained because glycerols exist in the reaction system.

Therefore, our research group has proposed a two-step reaction that combines hydrolysis in hot-compressed water and esterification in supercritical methanol to mitigate the drawbacks of the supercritical methanol method. First, triacylglycerol is hydrolyzed into fatty acids and glycerol in hot-compressed water. After removing glycerol and water by phase separation, the resulting fatty acids are treated in supercritical methanol to obtain fatty acid methyl esters by esterification. As glycerol is removed before the esterification reaction, the reverse reaction of glycerol with the methyl esters is suppressed. Therefore, our research group has proposed a two-step reaction that combines hydrolysis in hot-compressed water and esterification in supercritical methanol to mitigate the drawbacks of the supercritical methanol method. First, triacylglycerol is hydrolyzed into fatty acids and glycerol in hot-compressed water. After removing glycerol and water by phase separation, the resulting fatty acids are treated in supercritical methanol to obtain fatty acid methyl esters by esterification. As glycerol is removed before the esterification reaction, the reverse reaction of glycerol with the methyl esters is suppressed. Tri-, di-, and monoacylglycerols remaining in the hydrolysate can also be converted into fatty acid methyl esters by transesterification in supercritical methanol. In this method, fatty acids are present in both the hydrolysis and esterification reactions, acting as an acid catalyst to allow the reaction temperature to be reduced to below 300 °C.

However, this two-step method also has drawbacks.

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**Keywords**

Biodiesel, Oleic acid, Supercritical methanol, Esterification, Methyl formate
As a result of the esterification reaction of fatty acids, one mole of water is produced along with one mole of fatty acid methyl ester, as shown in Eq. (1):

\[
\text{RCOOH} + \text{CH}_3\text{OH} \leftrightarrow \text{RCOOCH}_3 + \text{H}_2\text{O} \quad (1)
\]

The presence of water in the reaction system causes a reverse reaction in which the fatty acid methyl ester is hydrolyzed, regenerating the fatty acid. Therefore, the acid value of biodiesel is difficult to reduce and that is a problem inherent in the two-step method. According to the European standard\(^{11}\), the acid value should be limited to less than 0.5 mg-KOH/g, which corresponds to a fatty acid content of approximately 0.25 wt%. Increasing the amount of methanol or repeating the esterification reaction after removing the water is considered a simple approach to improve the ester yield, but it will lead to an increased process burden. No other methods have not been reported to improve the ester yield.

In this study, we aimed to improve the ester yield and reduce the acid value by adding methyl formate during the esterification reaction in supercritical methanol. When methyl formate is present in the esterification reaction of Eq. (1), methyl formate (HCOOCH\(_3\)) is expected to undergo hydrolysis instead of the fatty acid methyl esters, consuming water in the process, as shown in Eq. (2):

\[
\text{HCOOCH}_3 + \text{H}_2\text{O} \leftrightarrow \text{HCOOH} + \text{CH}_3\text{OH} \quad (2)
\]

The hydrolysis of methyl formate also produces methanol, which can contribute to the esterification of fatty acids in Eq. (1).

2. Experimental Methods

2.1. Chemicals

As a fatty acid sample, oleic acid (extra pure reagent) was purchased from Nacalai Tesque Inc., Kyoto, Japan. As solvents, methanol (guaranteed reagent, \(>99.8\)% anhydrous, \(<50\) ppm) and methyl acetate (guaranteed reagent, \(>99.0\)% anhydrous, \(<50\) ppm) were purchased from Nacalai Tesque, while methyl formate (\(>98.5\)% anhydrous, \(<50\) ppm) was obtained from Sigma-Aldrich, MO, USA. These chemicals were used as received without purification.

2.2. Supercritical Methanol Treatment

Supercritical methanol treatment of oleic acid was performed using a flow-type reactor shown in Fig. 1. The solvent (pure methanol or methanol/water, methanol/methyl formate, or methanol/methyl acetate mixtures) and oleic acid were supplied to a coiled tubular reactor through preheaters using high-pressure pumps at designated flow rates. The internal pressure was maintained at 20 MPa using a back-pressure regulator. The tubular reactor, made from Hastelloy HC-276 steel (outer diameter, 3.2 mm; inner diameter, 1.2 mm; length, 160,000 mm; inner volume, approximately 180 mL), was placed in a molten salt bath and maintained at the designated temperature. After passing through the reactor, the reaction mixture was cooled using a cooling jacket and collected in glass bottles.

The average residence time, \(t\), was estimated by dividing the inner volume of the reactor, \(V\) (180 mL), by the volumetric flow rate of the reaction mixture, as shown in Eq. (3), and it was defined as the reaction time:

\[
t = \frac{V}{F_0 \rho_0 + F_s \rho_S} \quad (3)
\]

where \(F_0\) is the designated flow rate, and \(\rho_0\) and \(\rho_S\) are the densities of oleic acid under ordinary and reaction conditions, respectively. Terms with subscript ‘s’ are the same values for the solvent. The density of oleic acid was assumed to be unchanged (\(\rho_0 = \rho_S\)) because oleic acid was in the liquid phase under the given reaction conditions. Density changes for the solvent were estimated with the Non-Random Two-Liquid model that runs on a steady-state process simulator, Pro/II ver 10.1 (Schneider Electric, Rueil-Malmaison, France), and the thermodynamic data and interaction parameters of methanol, water, methyl formate, methyl acetate, and other chemicals were from SimSci bank in Pro/II. Pro/II was also used for the process simulation shown in section 3.3. The influence of water generated by the esterification reaction was ignored in the calculation of the reaction time. Therefore, the evaluated reaction time only served as a guide. In order to ensure that the reaction reached a steady-state, the reaction mixture was collected after at least twice the estimated residence time has passed.

In order to confirm the temperature dependence of the reaction equilibrium of esterification, a 5-mL batch-type reaction vessel made of Inconel 625 was used\(^{15}\). For the esterification reaction, designated amounts of methanol and oleic acid were placed in the vessel, sealed, and then immersed into a salt bath preheated at 270-310 °C for the predetermined reaction time.

The acid value of the resulting product was determined after removing the solvents (methanol, methyl formate or formic acid, methyl acetate or acetic acid) using a rotary evaporator. Just in case, the sample was then washed with distilled water before analysis to re-
move any formic acid and acetic acid that might remain in the product.

2.3. Analytical Methods

According to standard JIS K 007018), the acid value was measured by dissolving the sample in ethanol and titrating with a standard 0.1 mol/L KOH ethanol solution. The acid value is defined as the amount of KOH (mg) required to neutralize 1 g of sample. Using the molar masses of oleic acid (282.47) and KOH (56.11), the oleic acid content, \(Y_o\), was estimated from the acid value, \(A_V\) (mg-KOH/g), using Eq. (4):

\[
Y_o = \frac{A_V}{1000} \times \frac{282.47}{56.11} \times 100 = 0.50 \times A_V \text{ wt%} \quad (4)
\]

From this result, the ester yield, \(Y_e\), was evaluated using the equation \(Y_e = 100 - Y_o\).

The ester yield was also determined by high-performance liquid chromatography (HPLC) under the following conditions: Column, STR ODS-II (4 mm × 250 mm, Shinwa Chemical Industries, Ltd., Kyoto, Japan); mobile phase, methanol; flow rate, 1.0 mL/min; and column temperature, 40 °C. Detection was conducted using a refractive index detector (RID).

The gas analysis described in section 3.2. was conducted by micro-gas chromatography (micro-GC, CP-4900, Varian Inc., CA, USA) under the following conditions: channel 1; column, MS5A 10 m; carrier gas, Ar; column temperature, 100 °C; detector, thermal conductivity detector (TCD); channel 2; column, PorapLOT Q 10 m; carrier gas, He; column temperature, 80 °C; detector, TCD.

3. Results and Discussion

3.1. Effect of Water

To elucidate the reaction equilibrium of the esterification reaction, oleic acid was treated with supercritical methanol at 290 °C and 20 MPa, adding water to methanol at various ratios (methanol/water = 100/0, 80/20 and 60/40, v/v), with the result shown in Table 1 and Fig. 2. As shown in Table 1, the ester yields evaluated from acid value (AV) and HPLC analysis were in good agreement in the range of 0.3 to −2.6 wt%, but the deviation tended to be slightly larger when the ester yield approached 100 wt%. In the HPLC analysis, when oleic acid decreased by esterification, its peak was too small and broad to determine an appropriate baseline. Such a problem could reduce the accuracy of HPLC analysis. Therefore, in this study, the ester yield calculated from the acid value by titration was used. Titration is generally reliable even if the concentration is low, because sufficient titration volume can be obtained by increasing the sample volume. Since formic acid and acetic acid were not detected by HPLC after evaporation and washing with water, the acid value was considered an accurate method for evaluating ester yield.

As shown in Fig. 2, when treated with methanol only, the esterification reaction was almost in equilibrium at approximately 96 wt%. As the water ratio was increased, the ester yield decreased due to occurrence of the reverse reaction of methyl oleate and water to regenerate oleic acid. The ester yields were about 86 wt% and 69 wt% when the methanol/water ratios were 80/20 (v/v) and 60/40 (v/v), respectively.
Compared with the experimental results, the average Fig. 2 um were calculated, as shown by dashed lines in
4.24. Using this average, the ester yields at equilibri-
the average value was estimated to be 3.71, while the reactions with methanol/water ratios of 80/20 (v/v) and 60/40 (v/v) had K values of 4.74 and 4.26, respectively. The small K for methanol only is probably because the reaction has not yet reached full equilibrium. In Fig. 2, the ester yield slightly increased when the reaction time was prolonged from about 50 to 100 min. It seems that K = 3.71 was a little underestimated. It is unclear why the K values were slightly different between 20 % and 40 % of water, but the values possibly include experimental error. Note that Table 2 intended only to estimate the effect of water roughly, not to show the true equilibrium constant. Although there was some variation in the estimated equilibrium constants, the average value was 4.24. Using this average, the ester yields at equilibri-
was proposed that oleic acid acts as an acid catalyst during esterification in a decreased reaction rate. Our previous paper proposed that oleic acid acts as an acid catalyst during esterification in supercritical methanol(17), and the kinetic equation is described as follows:

\[
\frac{dC_{\text{FAME}}}{dt} = (k_f C_{\text{FA}} C_{\text{Me}} - k_r C_{\text{FAME}} C_W) \times C_{\text{FA}}
\]  

(6)

where C_{\text{FAME}}, C_{\text{FA}}, C_{\text{Me}}, and C_W are the concentrations of fatty acid methyl ester, fatty acid, methanol, and water (mol m^{-3}), respectively, while k_f and k_r (m^6 mol^{-2} s^{-1}) are rate constants of the forward and reverse reactions, respectively. The formula in parentheses expresses a second-order reaction, and the subsequent multiplication by C_{\text{FA}} represents autocatalysis by fatty acids. Based on Eq. (6), the reaction rate (\text{i.e.,} rate of ester formation) r_0 (s^{-1}) at the beginning of the reaction (t = 0) is expressed as follows:

\[
r_0 = \left. \frac{1}{C_{\text{FA}}} \frac{dC_{\text{FAME}}}{dt} \right|_{t=0} = k_f C_{\text{FA}} C_{\text{Me}}
\]  

(7)

Due to this autocatalytic effect, when the methanol ratio is high, the oleic acid concentration becomes low, and thus the reaction rate is slowed. However, if the methanol ratio is high, the ester yield becomes high due to the reaction equilibrium. Figure 3 shows the ester yield when oleic acid was treated in supercritical methanol at 290 °C and 20 MPa with various molar ratios, in which the solid lines are the results of least-squares
slower due to the low oleic acid concentration. There was further increased, but the reaction rate became very slow. The treatment temperature was slightly increased to 290 °C and 20 MPa for comparison. Unfilled circles show the results when treated with methanol only at 290 °C and 20 MPa for comparison.

Fig. 4 Methyl Oleate Yield when Oleic Acid was Treated with Supercritical Methanol at 310 °C and 20 MPa with the Addition of Methyl Formate at Various Molar Ratios

fitting using Eq. (6). When the molar ratio of methanol/oleic acid was small (= 2/1), the esterification reaction was fast ($r_0$ was estimated to be 0.024 s$^{-1}$) due to the high concentration of oleic acid and reached equilibrium around 20 min, but the ester yield was low at approximately 90 wt%. When the ratio of methanol/oleic acid was increased (= 8/1), the reaction rate became slow ($r_0 = 0.014$ s$^{-1}$) due to the low concentration of oleic acid and equilibrated around 50 min, but the ester yield was improved to be approximately 96 wt%. Larger methanol/oleic acid ratios (28/1 and 42/1) led to slower reaction rates ($r_0 = 0.006$ s$^{-1}$ and 0.004 s$^{-1}$, respectively) and the reaction did not reach equilibrium. Note that we could not prolong the reaction time until equilibrium due to the limitation of pump flow-rate in these cases. However, prolonging the reaction time until equilibrium will result in higher ester yields. In fact, the curve of 28/1 (methanol/oleic acid) eventually exceeded the ester yield of 2/1 and continued to increase.

This trade-off between the ester yield and reaction rate is a problem of the esterification reaction in supercritical methanol. To improve the ester yield, we performed a second treatment after removing methanol and water by distillation, as shown by the cross marks in Fig. 3. After removing water once, the ester yield was further increased, but the reaction rate became very slow due to the low oleic acid concentration. Therefore, complete esterification was difficult to achieve in supercritical methanol, even when the treatment was repeated.

3.2 Effect of Methyl Formate

To improve the ester yield, the addition of methyl formate was studied, with the results shown in Fig. 4. The treatment temperature was slightly increased to 310 °C because the reaction rate tended to be slow when methyl formate was added. The reaction with methanol only (methanol/oleic acid = 4/2, mol/mol, at 290 °C) is also shown for comparison (unfilled circles in Fig. 4), with an ester yield at equilibrium of around 90 wt%. Since the reaction equilibrium constant is generally temperature dependant, the ester yield was checked at 270 to 310 °C when the methanol/oleic acid mixture (4.5 mL, molar ratio = 2/1) was treated in the 5-mL batch reactor until the reaction reached equilibrium, with the results shown in Table 3. The experiments were carried out twice and the average values are shown. Although the ester yield tended to decrease slightly as the temperature increased, there was little difference between 290 °C and 310 °C. Therefore, we believe that using the data at 290 °C for comparison is not a real problem.

As shown in Fig. 4, when methyl formate was added to methanol (methanol/methyl formate/oleic acid = 3/1/2), the ester yield was improved, reaching approximately 92 wt%, despite the molar ratio of methoxyl groups to oleic acid being the same (3 + 1 = 4). When methyl formate was further increased (methanol/methyl formate/oleic acid = 2/2/2), the ester yield was further improved, reaching 95.1 wt% after treatment for 87 min. Note that the molar ratio of methoxyl group/oleic acid was 4/2 in these experiments. Since methyl formate can provide methanol when hydrolyzed, the ratio of methoxyl groups must be the same in order to compare the ester yields. Furthermore, when the methoxyl ratio was doubled (methanol/methyl formate/oleic acid = 4/4/2), the ester yield was 98.7 wt% after 80 min. For methanol only, as shown in Fig. 3, even at a methanol/oleic acid ratio of 8/1 (= 16/2), the ester yield was only 96.5 wt%. Therefore, adding methyl formate apparently improved the ester yield.

Under the condition of methanol/methyl formate/oleic acid = 4/4/2, there was a slight decrease (= 0.2 wt%) in the ester yield at 120 min, but this is considered within the range of experimental error and not due to ester degradation. Similarly, under the condition of methanol/water = 60/40 in Fig. 2, the reaction reached equilibrium at 25 min and the ester yield remained almost constant until 100 min; however, as shown in Table 1, the numerical data were 69.8 wt% at 25 min, 69.5 wt% at 50 min, and 69.8 wt% at 100 min, with an experimental uncertainty level of 0.3 wt%. Even if the methyl ester is stable in this way, a preferred process...
design is to quench the reaction immediately after reaching equilibrium.

When methyl formate was added, gas bubbles were found in the reaction mixture at the outlet of the reaction equipment. Methyl formate was considered to react with water to form methanol and formic acid. The produced methanol can contribute to the esterification reaction of oleic acid, while formic acid will undergo thermal decomposition into gases even around 300 °C without catalyst, as reported by some literature\(^1\),\(^2\), through the routes shown in Eqs. (8) and (9):

\[
\text{HCOOH} \rightarrow \text{CO} + \text{H}_2\text{O} \quad (8)
\]

\[
\text{HCOOH} \rightarrow \text{CO}_2 + \text{H}_2 \quad (9)
\]

From the reaction in Eq. (8), water remains in the reaction system, contributing to the reverse reaction of methyl ester. However, the reaction in Eq. (9) indirectly removes water from the reaction system, suppressing the reverse reaction of the methyl ester. The observed gas bubbles were attributed to the generation of these gases produced.

To confirm the product gas, a mixture of methyl formate, water, and methanol (0.5 mL each), which is a model of the reactants, was treated in the 5-mL batch reactor at 310 °C for 30 min. The product gas was then collected in a gasbag along with air and analyzed by micro-GC. It was difficult to collect the product gas quantitatively in our system, so the following discussion is qualitative. As shown in Fig. 5, the formation of H\(_2\) and CO\(_2\) was found, but CO (around 80 s in Ch1) was not observed. This indicates that formic acid decomposed into H\(_2\) and CO\(_2\) under the reaction conditions of this study. The H\(_2\)/CO\(_2\) ratio was evaluated to be 1/0.92 (mol/mol), which also strongly indicates the decomposition of formic acid; the slightly lower ratio of CO\(_2\) than 1 was probably due to its dissolution in water. Yu and Savage\(^2\) also showed that the reaction in Eq. (9) was dominant in the thermal decomposition of formic acid. Therefore, the improvement in ester yield might be due to water removal by the reaction in Eq. (9).

For comparison, methyl acetate was added instead of methyl formate during the reaction, with the results shown in Fig. 6, where the molar ratio of methoxyl group/oleic acid was set to 4/1. The dashed line in Fig. 6 represents the predicted equilibrium ester yield when treated with methanol only (methanol/oleic acid = 4/1, mol/mol). When adding methyl acetate (methanol/methyl acetate/oleic acid = 2/2/1, mol/mol), the ester yield was about 91 wt% at equilibrium, which was lower than that with methanol only. Compared with the case using methyl formate (methyl formate/methanol/oleic acid = 2/2/1, mol/mol), the difference in ester yield was apparent, despite the ratio of methoxyl groups being the same. Methyl acetate can be hydrolyzed into acetic acid and methanol, but acetic acid is stable.

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Fig. 5 Micro-GC Chromatogram of the Gaseous Product (including air) when Methyl Formate was Treated with Methanol/Water in a 5-mL Batch Reactor at 310 °C for 30 min, Compared with That of Air

Fig. 6 Methyl Oleate Yield when Oleic Acid was Treated with Supercritical Methanol at 310 °C and 20 MPa with the Addition of Methyl Formate or Methyl Acetate
at 310 °C. Therefore, no gas bubbles were found in the reaction mixture and a reaction equilibrium occurred between acetic acid, methyl acetate, water, methanol, oleic acid, and methyl oleate. This equilibrium did not favor an improved ester yield.

*Figure 7* summarizes the esterification of oleic acid in this study. In the case of methanol only, oleic acid remained to some extent because its esterification competed with the hydrolysis of methyl oleate. When methyl formate was added to the reaction system, methyl formate was hydrolyzed to formic acid and methanol, consuming water. Methanol produced from methyl formate can be reused for the esterification of oleic acid. Formic acid was thermally decomposed into CO$_2$ and H$_2$, and water was thus indirectly removed from the reaction system. Therefore, the reverse reaction of methyl oleate by hydrolysis was suppressed, and the reaction equilibrium shifted in the direction of an improved methyl oleate yield. When using methyl acetate, acetic acid and methanol were produced by hydrolysis, but acetic acid did not decompose into gases in supercritical methanol. Therefore, water was not removed from the reaction system and the ester yield was not improved.

Note that this study used supercritical methanol, but this expression may not be strictly correct. It is a difficult question whether or not a mixture of oleic acid, methanol, and methyl formate is a supercritical fluid. For example, Redlich and Kister presented a theory to predict the critical point of the mixture$^{31}$, but such a discussion is beyond the scope of this study. We used the term supercritical methanol to mean that the reaction was performed under conditions above the critical point of methanol.

### 3.3. Merits and Demerits of Adding Methyl Formate

By adding methyl formate, the ester yield was improved without using a large amount of methanol. For example, as shown in *Figure 4*, when the molar ratio of methanol/methyl formate/oleic acid was 4/4/2, the ester yield reached 98.7 wt%. The volume ratio corresponds to 0.26 methanol and 0.39 methyl formate per 1 oleic acid (*Table 4*). To achieve the same ester yield without methyl formate, about 18 mol methanol is necessary for 1 mol oleic acid, as calculated from the average equilibrium constant ($K = 4.24$). It corresponds to about 2.3 methanol per 1 oleic acid in volume ratio; the amount of solvent is 3.5 times that of adding methyl formate (0.26 methanol and 0.39 methyl formate = 0.65). Reducing the amount of solvent will lead to a reduction in heating energy for the reaction, and thus a reduction in operating costs.

*Table 4* shows a comparison of raw material ratios, reaction conditions, and energy consumption to obtain 98.7 wt% ester yield. The process shown in *Figure 8*, which includes a reactor for esterification and a distiller for solvent removal, was simulated using Pro/II with the following conditions: Minimum temperature difference for heat exchange (counter-current), 10 K; the number of theoretical plates in the distillation column, 5; reflux ratio, the value that minimizes heating energy. Due to the difference in the solvent amount, the difference in energy consumption of the distiller, which accounts for the largest proportion, is large. As a result, the total energy consumption per 1 mol of oleic acid was estimated to be 1115 kJ with methanol only, which was 2.3 times when methyl formate was added (483 kJ).
Concerns about using methyl formate are the corrosion of the reactor due to formic acid and the cost of methyl formate compared to methanol. It may be necessary to use corrosion-resistant materials in the reactor. Crude methanol synthesized from natural gas or biomass contains methyl formate to some extent as an impurity. For example, it has been reported that crude methanol produced from syngas obtained by wood gasification contains 6 wt% methyl formate. Therefore, if such crude methanol is used for the method of this research, the cost may be suppressed. It might also be possible to partially synthesize methyl formate from methanol to prepare the methanol/methyl formate mixture.

4. Conclusions

This study has demonstrated that the fatty acid methyl ester yield was improved by adding methyl formate during the esterification reaction of fatty acids in supercritical methanol. This was attributed to methyl formate being hydrolyzed, which consumed water in the reaction system, and then decomposing into gases such as CO₂ and H₂. Therefore, the water produced by the esterification of fatty acids was removed and the reaction equilibrium was shifted to a higher ester yield. As treated with methanol only (methanol/oleic acid = 2/1, mol/mol), the yield of methyl oleate was approximately 90 wt%. In contrast, when methyl formate was added (methanol/methyl formate/oleic acid = 1/1/1, mol/mol), the ester yield was improved to be approximately 95 wt%. Furthermore, when the ratio of the solvent was increased twice (methanol/methyl formate/oleic acid = 2/2/1, mol/mol), the ester yield reached 98.7 wt%, the highest value in this study.

More generally, in reactions with supercritical fluids, similar processes might be possible in which a byproduct is decomposed, gasified, and removed from the reaction system, causing the reaction equilibrium to favor production of the target compound.

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要 旨

ギ酸メチルを添加した超臨界メタノール中でのオレイン酸のエステル化反応

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バイオディーゼルとして使用されている脂肪酸メチルエステルは、超臨界メタノール中で脂肪酸をエステル化することによっても製造できる。しかし、エステル化反応で生成する水により、脂肪酸メチルエステルが加水分解され脂肪酸へと戻る逆反応が存在する。そのため、脂肪酸が残り、高いエステル収率を得ることが困難である。そこで本研究では、流通式反応器による超臨界メタノール中（310℃/20 MPa）でのオレイン酸のエステル化において、ギ酸メチルの添加を検討した。その結果、メタノールのみを使用した場合と比較し、エステル収率が約90 wt%から95 wt%に向上した。超臨界メタノール中では、ギ酸メチルは脂肪酸エステルと同様に加水分解されギ酸とメタノールを生成するが、ギ酸はさらに熱分解によりH₂やCO₂などのガスへと分解する。この反応により水が間接的に反応系から除去されるため、逆反応が抑制され、反応平衡がエステル収率を改善する方向にシフトしたと考えられた。