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PAPER TITLE:

Effect of CO₂/N₂ addition to supercritical methanol on reactivities
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ABSTRACT:

Addition of the third component to supercritical methanol has been studied in the literature for biodiesel production in order to reduce reaction temperature without deteriorating the reaction rate. However, effect of pressure had often been neglected in the discussion. In this paper, therefore, effect of pressure was examined with hexane, carbon dioxide (CO₂) and nitrogen (N₂) as one of the third components, using batch-type and flow-type reactors. As a result, it was found that an addition of the third component did not contribute to better product yield at constant reaction pressure. Furthermore, the reaction rate was found to be determined by pressure and concentration of the reactants involved in transesterification, not by the function of so-called co-solvent. Additionally, N₂ addition was found to contribute to improvement in oxidation stability and reduction of the total glycerol content, thus offering high-quality biodiesel production.

Keywords: biodiesel, supercritical methanol, third component, oxidation stability,

total glycerol content

1. INTRODUCTION

The production of biodiesel as defined by fatty acid methyl ester is one of the major trends in the world to mitigate environmental loading by global warming. With increasing demand, on the other hand, feedstock is getting serious in its availability. Technological advancement is thus required for biodiesel production to utilize various oil/fat feedstocks, including waste oils with high contents of water and free fatty acids. Consequently, non-catalytic supercritical methanol method was found to be suitable for such low-grade wastes with high free fatty acids and water in oils and fats [1].

However, this method requires high temperature and high pressure in its condition, e.g., 350°C/43MPa for one-step method (Saka Process), compared with conventional alkali-catalyzed method at 60°C under atmospheric pressure. Previous study revealed that at this severe reaction condition, fatty acid methyl esters are denaturated, e.g., *cis-trans* form isomerized or decomposed, thereby decreasing in yield [2]. In order to make a reaction condition milder without

reducing the reaction rate compared to previous studies, an addition of the third components has recently been investigated with carbon dioxide (CO₂) and propane [3,4]. In these works, it was reported that the higher yield of fatty acid methyl esters could be obtained by adding the third component. The authors, thus, concluded that CO₂ and propane act as co-solvents, which increases mutual solubility between triglyceride and methanol, thereby facilitating transesterification reaction.

It should be, however, noted that a set of experiments was conducted in a constant volume reactor with each experimental run loaded with a constant amount of triglyceride and methanol. Therefore, an addition of CO₂ or propane to this system might increase in reaction pressure, thus in reaction rate. However, the pressure is assumed to be constant. Furthermore, it seems doubtful that mutual solubility is a dominant effect on the reaction rate of transesterification, although the third component can reduce the critical point of the mixture [5]. In this study, therefore, an effect of the third component such as carbon dioxide (CO₂), nitrogen

(N₂) and hexane to supercritical methanol was investigated on transesterification of rapeseed oil in order to clarify the effect of reaction pressure.

2. MATERIALS AND METHODS

Rapeseed oil in reagent grade and methanol (water content < 100ppm) purchased from Nacalai Tesque, Inc., Kyoto were both placed in a 5.3mL reactor made of Inconel-625 equipped with gas valve, in which air was substituted by nitrogen in advance. To this reactor, CO₂ (>99.99%) or N₂ (>99.999%) was compressed inside at various concentrations, determined by measuring the temperature and pressure with help of thermodynamic properties data [6-8]. Rapeseed oil is treated in supercritical methanol or its mixture with CO₂ or N₂ at 270 and 300°C for 1~90min.

To study an effect of hexane to the reaction system, the flow-type reactor made of Hastelloy C-276 was used under the temperature between 270~350°C with a constant pressure of 20MPa.

The reaction time t (s) was determined by dividing the tubular volume V (mL)

in the reactors by volumetric flow-rate of reactants at designated reaction conditions as in the following equation:

$$t = \frac{V}{\sum F \frac{\rho}{\rho'}} \quad (1)$$

where F , ρ and ρ' are setting as flow rate (mL/s), specific densities (g/mL) at normal condition and reaction condition. It should be noted that a density of each component used in the calculation is that of pure component, instead of bulk density. As the value of ρ' for methanol, a reference data of the literature [9] was used, while that for hexane was calculated by Soave-Redlich-Kwong equation of state [10], and for rapeseed oil, it was assumed to be equal to ρ at any reaction conditions. Experimental set-ups for batch-type reactor and flow-type reactor are described elsewhere [1,11]. Uncertainties for measured temperature, pressure are $\pm 1.5^\circ\text{C}$ and $\pm 1.5\%$ over full-scale, respectively.

After the reaction, methanol and the remaining third components were completely evaporated from the obtained samples by rotary evaporator at 70°C for

15min. Remaining portion was then diluted in acetone in HPLC grade, purchased from Nacalai Tesque, Inc., Kyoto and analyzed by high-performance liquid chromatography with a Shimadzu LC-10A system under the following conditions: column, Asahipak GF310-HQ; flow-rate, 1.0mL/min; eluent, acetone; detector, refractive index detector (RID); temperature, 40°C. Yield of fatty acid methyl ester was calculated with calibration curve using area peak, repeatability of which is more than 99.7%. Oxidation stability was also evaluated with Rancimat equipment (Metrohm Co., Ltd) in accordance with EN14112 [12].

3. RESULTS AND DISCUSSION

3.1 Effect of hexane addition in supercritical methanol

Critical point is the point at which fluid starts to become supercritical state and no longer condensable by raising the pressure alone. In this state, the molecules have high kinetic energy like gas and high density like a liquid; chemical reactivity is expected to be enhanced. Following are the critical parameters for the solvent used in this study: methanol, $T_c=239.4^{\circ}\text{C}(512.6\text{K})$, $P_c=8.09\text{MPa}$; CO_2 ,

$T_c=30.9^{\circ}\text{C}(304.1\text{K})$, $P_c=7.37\text{MPa}$; N_2 , $T_c=-146.9^{\circ}\text{C}(126.2\text{K})$, $P_c=3.39\text{MPa}$;

n-hexane, $T_c=234.4^{\circ}\text{C}(507.6\text{K})$, $P_c=3.02\text{MPa}$ [13]. As can be seen, all experiments

in this study were performed under supercritical condition for any substances.

To clarify the effect of hexane addition in supercritical methanol, the flow-type reactor was used to keep the reaction pressure constant at 20MPa during the reaction. Fig.1 shows the obtained yield of fatty acid methyl esters in rapeseed oil as treated in supercritical methanol at various temperatures with hexane at various concentrations. The $[\text{Hexane}]_0/[\text{MeOH}]_0$ indicates an initial molar ratio of hexane to methanol. For every case in Fig.1, the yield clearly decreases with increasing the hexane concentration, although a slight increase was observed between $[\text{Hexane}]_0/[\text{MeOH}]_0=0$ and 0.05 at 270°C . Maximum yield was obtained to be 84.8wt%, 42.9wt% and 13.7wt% for 270°C , 310°C and 350°C , respectively, as seen in Fig.1.

Since triglyceride is miscible with hexane, an addition of hexane must contribute to its solubility in liquid phase. However, no significant improvement

in yield can be observed. This behavior observed can be explained by the fact that hexane can contribute to the reactants diluted in their concentration, thus decreasing the reaction rate. Since kinetic constants are getting higher with increasing temperature, an effect of reactants diluted must be apparent at higher temperature, 310°C and 350°C, compared at 270°C, which is reflected on the larger decrease in the yield. Since the reaction is primarily controlled by reaction temperature, as mentioned by Sawangkeaw et al (2007), hexane addition in supercritical methanol can be concluded to have only a negative effect on the transesterification when the reaction pressure is constant. This conclusion must be very reasonable, because, in a molecular level, hexane molecules must be located between reactants and methanol to improve the mutual solubility. Such a concept is very much appreciated by a compatibilizer in polymer science. However, in a transesterification reaction, hexane molecules located between the reactants and methanol are rather obstacles to successful reaction.

3.2 Effect of CO₂ addition in supercritical methanol

Fig.2 shows the yield of fatty acid methyl esters in rapeseed oil as treated in supercritical methanol at 270°C under different pressures for 15min as a function of CO₂ concentration. The [CO₂]₀/[MeOH]₀ indicates an initial molar ratio of CO₂ to methanol. This experiment has been done without controlling the inner pressure of the batch-type reactor which was calculated by Soave-Redlich-Kwong equation of state with Modified Huron-Vidal 1st order (MHV1) model as a mixing rule.

It is apparent from Fig.2 that the inner pressure is increasing as [CO₂]₀/[MeOH]₀ is increasing. Under a constant molar ratio of [Triglyceride]₀/[MeOH]₀=42, the highest yield, thus the highest reaction rate can be achieved at [CO₂]₀/[MeOH]₀=0.11 (fatty acid methyl ester, 51.9wt% in yield). This optimum value is similar to that in the literature, using CO₂ as the third component [4]; further addition of CO₂, however, had a negative effect on reaction rate to decrease the yield even if the reaction pressure was increased.

In order to rectify the difference in pressure, quasi-constant pressure of 10.8MPa was set as in Table 1, for several experimental runs by adjusting the amount of rapeseed oil and methanol with the third components loaded. The

experimental results obtained under these reaction conditions are shown in Fig.2.

Consequently, the yield is highest when no CO₂ was added (fatty acid methyl ester, 59.1wt% in yield), with decreasing monotonously with increasing [CO₂]₀/[MeOH]₀. This behavior is, in fact, similar to that found in Fig.1 with hexane.

From these lines of findings, transesterification of triglyceride in supercritical methanol with third component can be determined by reaction pressure and concentrations of the reactants involved such as triglyceride, diglyceride and monoglyceride. When the third component increases in amount, the reaction pressure apparently becomes higher. Furthermore, in a previous report on transesterification with methanol [14,15], reaction rate was found to be proportional to the reaction pressure, because the higher pressure provides higher chance of reaction due to the higher density of methanol. Therefore, addition of CO₂ in the initial stage up to [CO₂]₀/[MeOH]₀=0.11 must contribute to a reaction rate increased. However, since increased pressure is not by methanol involved in transesterification, an excessive addition of CO₂ eventually results in only

dilution of the reactants in their concentrations. As a result, reaction rate becomes slower.

3.3 Effect of N₂ addition in supercritical methanol

To support the effect of reaction pressure on transesterification by addition of the third component, N₂ instead of CO₂ was also compressed to the batch-type reactor with supercritical methanol, and studied on the yield of fatty acid methyl esters. Fig.3 shows the obtained result as a function of [N₂]₀/[MeOH]₀ prepared at 270°C for 15min. As in a similar manner to CO₂ addition, the obtained yield has a maximum value at [N₂]₀/[MeOH]₀=0.24 under the constant amount of rapeseed oil and methanol (fatty acid methyl ester, 59.9wt% in yield). However, in quasi-constant pressure condition, where reaction pressure was rectified to be 10.8MPa, no positive correlation can be found between the yield and N₂ concentrations added.

Interestingly, a noticeable difference was not existed at the maximum yield between CO₂ in Fig.2 and N₂ in Fig.3. As is well known, CO₂ has much higher

solubility in methanol, compared with N_2 [16], that is, CO_2 has higher affinity to methanol compared with N_2 . It is, therefore, expected that effect of methanol dilution with the third component is much higher in the case of CO_2 . However, the yield of fatty acid methyl esters was basically the same between the two systems. This comparison clearly supports a conclusion that the reaction rate is determined by both pressure and concentration of the reactants, but not by the third component as so-called co-solvent in the literature [3,4].

3.4 Effect of the third component on oxidation stability

Since biodiesel is oxidized with the oxygen, lower concentration of oxygen is preferable for better stability of the fuel. Our previous research revealed that oxidation stability of biodiesel is shortened as treated in supercritical methanol [17]. Therefore, in this study, the effect of the third component was investigated on its oxidation stability.

Fig.4 shows the results obtained for the time course of conductivity during Rancimat test of three kinds of biodiesels as prepared by supercritical methanol at

300°C/14MPa for 40min. One without the third component indicates standard biodiesel prepared by supercritical methanol, whereas the one with CO₂ or N₂ is biodiesel prepared with the third component. It is apparent from the figure that an induction period is greatly prolonged by N₂ addition. This could be attributed to the lower concentration of oxygen by compressed N₂. However, in the case of CO₂, an induction period became extremely shorter. It was suggested that CO₂ could release O₂, and consume a part of natural antioxidant during transesterification. Additionally, CO₂ can react with water present in the reaction system to become carbonic acid which causes oxidation. From these results, it was found that CO₂ as the third component has a negative effect, but N₂ can have positive effect on oxidation stability of biodiesel.

3.5 Effect of the third component on total glycerol content

In the supercritical methanol method with transesterification, it is generally difficult to produce biodiesel with low total glycerol content (G_T), as described in

the equation (2), since glycerol is kept remaining in the same reaction system with fatty acid methyl esters.

$$G_T = W_G + 0.255W_{MG} + 0.146W_{DG} + 0.103W_{TG} \quad (2)$$

where W_G , W_{MG} , W_{DG} and W_{TG} are a weight percentage of glycerol, monoglyceride, diglyceride and triglyceride in a biodiesel sample.

However, when N_2 was added into the rapeseed oil in supercritical methanol as shown in Fig.5, total glycerol content at equilibrium was found to be reduced to a value within specification standard (0.24wt%) in EN14214. By comparing with the case without N_2 , its significance is evident. Blanchard and Brennecke (2001) investigated the addition of CO_2 to ethyl esterification of acetic acid at $60^\circ C(333K)/58.6bar$ and found that the addition affects the fugacity coefficients of the reactants and shifts the reaction toward completion [18]. This could be an explanation of the phenomenon shown in Fig.5. Moreover, inert-gas nature of N_2 helps inhibiting a contact between glycerol and fatty acid methyl esters. As a

result, reversed reaction could be prevented and thus lower total glycerol content was obtained.

4. CONCLUSION

The effects of CO₂/N₂ addition and hexane addition to supercritical methanol on biodiesel production were studied in batch-type and flow-type reactors, respectively, in terms of reaction rate and equilibrium composition. As a result, it was found that hexane addition hardly contributed to improvement in reaction rate when reaction pressure was set to be constant. Similar results were also found for CO₂ and N₂ at quasi-constant pressure. Therefore, it was concluded that reported improvement in reaction rate as a result of the third component addition is not attributed to the function of so-called co-solvent, but to the effect of reaction pressure and concentration of the reactants in transesterification.

Furthermore, N₂ addition was found to contribute to improvement in oxidation stability and reduction of the total glycerol content at equilibrium of transesterification. From these lines of evidence, it was clarified that N₂ addition

to supercritical methanol process can be a promising treatment for high-quality biodiesel production.

5. ACKNOWLEDGEMENTS

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Table 1 Experimental conditions using batch-type reactor for transesterification of rapeseed oil in supercritical methanol at 270 °C/quasi-constant pressure of 10.8 MPa with various third components (CO₂ and N₂).

Composition (wt.%)			Density (g/cm ³)
Rapeseed oil	Methanol	Third component	
39.7	60.3	—	0.42
<i>CO₂</i>			
35.7	54.3	10.0	0.38
32.2	48.6	19.2	0.37
24.9	37.5	37.6	0.34
<i>N₂</i>			
36.5	55.7	7.8	0.36
35.2	53.6	11.2	0.33
34.0	51.6	14.4	0.32

Figure 1 Yield of fatty acid methyl esters as prepared by supercritical methanol under the constant pressure of 20MPa for 15min as a function of hexane concentration; $[\text{Hexane}]_0/[\text{MeOH}]_0$ indicates an initial molar ratio of hexane to methanol

Figure 2 Yield of fatty acid methyl esters as prepared by supercritical methanol at 270°C under different pressures for 15min as a function of CO₂ concentration; [CO₂]₀/[MeOH]₀ indicates an initial molar ratio of CO₂ to methanol

Figure 3 Yield of fatty acid methyl esters as prepared by supercritical methanol at 270°C under different pressures for 15min as a function of N_2 concentration; $[N_2]_0/[MeOH]_0$ indicates an initial molar ratio of N_2 to methanol

Figure 4 Time course of conductivity during Rancimat oxidation stability test of biodiesel as prepared by supercritical methanol treatment at 300°C/14MPa for 40min; without third component; $[\text{CO}_2]_0/[\text{MeOH}]_0=0$, with N_2 ; $[\text{N}_2]_0/[\text{MeOH}]_0 = 0.24$, with CO_2 ; $[\text{CO}_2]_0/[\text{MeOH}]_0=0.24$; $[\text{MeOH}]_0/[\text{Triglyceride}]_0=42$

Figure 5 Total glycerol content of biodiesel as prepared by supercritical methanol treatment at 300°C/14MPa; $[MeOH]_0/[Triglyceride]_0=42$; shadowed area is a satisfactory range in EU standard