



much slower than the alkaline-catalyzed one [2]. Enzymatic catalyst, such as lipase, easily converts FFA into FAME and gives high conversions to FAME in alcoholysis of waste edible oils [3]. Enzymatic alcoholysis requires lower energy, but the cost of lipase is still too high compared to alkaline catalyst. Therefore, alkaline catalysts are the commonly used catalyst in commercial BDF production. This method, however, requires refining process to remove alkaline catalysts and saponified products, which results in complex process, lower yield and higher production cost. Therefore, noncatalytic alcoholysis method to produce BDF is considered to be more advantageous.

There are numbers of studies on BDF production by an alkaline catalyzed alcoholysis of natural oils and fats [4 – 13]. However, quite a few studies have been done on non-catalytic alcoholysis for BDF production. Kinetics of non-catalytic alcoholysis of soybean oil was investigated by Diasakou *et al.* [14], and the experiments were carried out at 220 and 235°C with various methanol/oil ratios. Saka and Kusdiana [15] showed that noncatalytic alcoholysis with supercritical methanol treatment has a high reaction rate. This method can convert 2 g of rapeseed oil into FAME in 240 s with 95% conversion. However, this method requires high reaction temperature and pressure, 350–450°C and 45–65 MPa, respectively, to keep methanol in supercritical state. To overcome this disadvantage, Kusdiana and Saka [16] proposed a two-step preparation for biodiesel production by hydrolysis and methyl esterification to reduce reaction temperature and pressure to 270°C and 7 MPa respectively. Dasari *et al.* [17] investigated more moderate reaction conditions than the previous studies. Experiments were done at 120 to 180°C, the maximum conversion was about 17% at 32 h. All of the analysis in these studies was done mainly for FAME, and the reaction efficiency was evaluated by conversions to FAME. However, analysis on intermediates are few, and kinetic studies are not sufficient. Moreover, reactor costs will be expensive for their pressurized reactions, since reaction pressure increases with reaction temperature in batch reactors.

In this study, a new reactor was developed to produce FAME under around atmospheric pressure without using any catalysts. The effects of five reaction variables on reaction rate were investigated.

## 2. Materials and Methods

### 2.1 Materials

High-oleic sunflower oil was obtained from Nippon Lever K. K. (Tokyo, Japan). The fatty acid composition was oleic acid 82.3%, linoleic acid 10.1%, palmitic acid 4.3%, and stearic acid 3.3%. Methanol (99%) and molecular sieves (4A 1/16) were purchased from Wako Pure Chemical Industries (Osaka, Japan). Molecular sieves were used for dehydrating high-oleic sunflower oil and methanol.

Squalane, benzene, and hexane for Thin Layer Chromatography/Flame Ionization Detector (TLC/FID) analysis were purchased from Wako Pure Chemicals (Osaka, Japan). Squalane was used as internal standard, benzene as developing solution, and hexane as solvent. Triolein, diolein, monolein, oleic acid, and methyl oleate were obtained from Sigma Chemicals (St. Louis, USA) and used as standards. Acetonitrile and glycerol were purchased from Wako Pure Chemicals (Osaka, Japan), and used as carrier solvent and standard, respectively.

### 2.2 Apparatus

The reactor consisted of an oil reservoir, a methanol reservoir, a pump, a dehydrating column for methanol, a reactor vessel, and a cooling unit (Fig. 2). The volume of the reactor vessel was about 500 mL, its inner diameter was 55.5 mm, its height was 227.5 mm (Fig.3). The reactor vessel was equipped with a stirrer for mixing the liquid phase and a heater to control the reaction temperature.

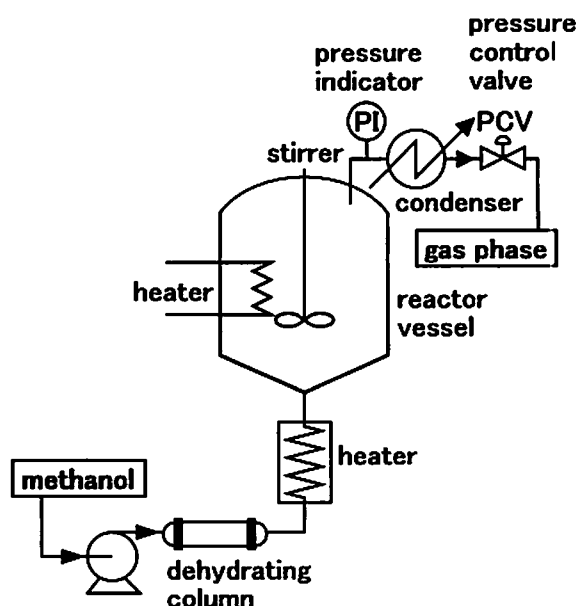


Fig. 2 A schematic flow diagram of the reactor.

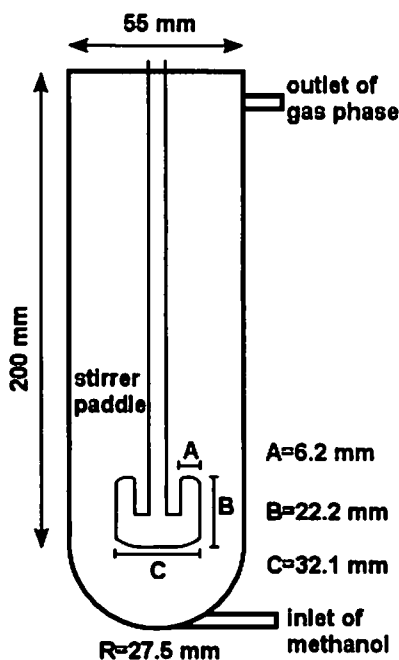


Fig. 3 Detailed configuration of the reactor vessel.

Both the stirrer and the heater were controlled with a controller. The upper part of the reactor vessel was equipped with an oil inlet and a gas phase outlet, while the bottom part of the reactor vessel was equipped with methanol gas inlet and liquid phase outlet. A pressure control valve (PCV) was installed for regulating the operating pressure during the reaction.

**2.3 Procedures**

Oil and methanol were dehydrated with molecular sieves before introduced into the reactor. Oil was fed into the reaction vessel with fixed initial oil volume, then the

reaction started by blowing superheated methanol bubbles continuously into the reactor vessel at fixed flow rate. The reaction temperature and stirring rate were kept constant with controller; the operating pressure was kept constant with a PCV. The methanol gas reacted with oil and flowed out from the reactor vessel as gas phase. The gas phase was liquefied by a condenser, and periodically collected with a fraction collector. The reactants (liquid phase) were collected at a scheduled time.

**2.4 Reaction conditions**

Experiments were designed to evaluate the effect of reaction temperature, methanol feed flow rate, operating pressure, stirring rate, and initial oil volume on the reaction process. One reaction variable was changed while the rest were kept constant during one cycle of the process. The range of each variable is shown in Table 1.

**2.5 Analysis**

Before analysis, methanol was removed from the gas phase samples using a rotary evaporator. The compositions of the gas phase and the liquid phase samples were analyzed by using TLC/FID and High Performance Liquid Chromatography (HPLC). Contents of TG, DG, MG, FFA, and FAME in the product were analyzed with an Iatroscan MK-5 TLC/FID Analyzer (Iatron, Tokyo, Japan). The flame ionization detector was operated with hydrogen and air flow rates of 160 and 2000 mL/min, respectively. Solutions to be analyzed were diluted in solvent (hexane containing 0.9 wt% squalane), and then spotted on type S-III Chromarods in 1 μL per rod. Five replicates were used for each solution. The rods were developed in glass tank containing benzene for about 30 min, oven-dried at

Table 1 Reaction conditions for alcoholysis reaction.

No.	Reaction temperature (°C)	Methanol feed flow rate (mL/min)	Operating pressure (MPa)	Stirring rate (rpm)	Initial oil volume (mL)
1	250	0.9	0.1	700	200
2	270	0.9	0.1	700	200
3	290	0.9	0.1	700	200
4	310	0.9	0.1	700	200
5	330	0.9	0.1	700	200
6	290	5	0.5	700	200
7	290	5	1	700	200
8	290	5	3	700	200
9	290	5	5	700	200
10	290	0.6	0.1	700	200
11	290	5	0.1	700	200
12	290	10	0.1	700	200
13	290	0.9	0.1	400	200
14	290	0.9	0.1	1000	200
15	290	0.9	0.1	700	150
16	290	0.9	0.1	700	250

60°C for 5 min, and then analyzed.

Analysis of glycerol composition was performed with HPLC (880-PU, DG-2080-53, CO-2060 Plus, 855-AS, JASCO, Tokyo, Japan) which consisted of a column (CAPCELL PAK NH<sub>2</sub> UG80, 25 cm in length×4.6 mm in inner diameter, Shiseido, Tokyo, Japan) and a refractive index detector (GL Science, RI Model 408, Tokyo, Japan) operated at 40°C with 1.0 mL/min flow rate of carrier solvent (acetonitrile/water = 85/15). The sample injection volume was 10 μL. Solutions to be analyzed were diluted in water, filtered with 0.20 μm hydrophilic filter, and then analyzed.

### 3. Results and Discussion

The first experiment was performed to explore 100% conversion of TG to FAME. The reaction was done at reaction temperature of 290°C, operating pressure of 0.1 MPa, methanol feed flow rate of 10 mL/min, stirring rate of 700 rpm, and initial oil volume of 200 mL, and showed that the liquid phase disappeared in 90 min. If conversion is defined as decrease ratio of TG, then 100% conversion could be regarded to be achieved under this reaction condition, since the boiling point of TG is much higher than 290°C. Therefore, the production rate of FAME was chosen as an evaluation standard, instead of conversion ratio. In this reactor, production rate of FAME can be defined in two ways. The first one is an outflow rate of FAME produced by the reactor as gas phase, and the other one is the total production rate of FAME in the whole system including gas phase and liquid phase.

A typical change in composition of the gas and liquid phases is shown in Fig. 4, where reaction temperature, methanol feed flow rate, operating pressure, stirring rate and initial oil volume were kept at 290°C, 0.9 mL/min, 0.1 MPa, 700 rpm, and 200 mL, respectively. Major component of the gas phase appeared to be FAME, while that of the liquid phase appeared to be TG and DG. Since no complex refining process is required to use the gas phase as BDF, then the FAME contained in the gas phase can be regarded as objective component of the reaction. As the composition and amount of gas phase was constant during the whole reaction excluding its early phase (Fig.4), outflow rate of FAME defined by Eq.(1), which is the average production rate of FAME in gas phase during the whole reaction time, will be used as a standard to evaluate the reaction.

Outflow rate of FAME [g/min]

$$= \frac{\text{Total mass of FAME produced in gas phase in whole reaction [g]}}{\text{whole reaction time [min]}} \quad (1)$$

Total production rate of FAME defined by Eq.(2) will also be used as another standard to evaluate the FAME production in both the gas and liquid phases. By comparing the total production rate to the outflow rate, it is possible to evaluate the distribution of FAME between the gas phase and the liquid phase. The effects of five variables studied in this experiment were evaluated with these two standards.

Total production rate of FAME [g/min]

$$= \frac{\text{Total mass of FAME produced in gas and liquid phases in whole reaction [g]}}{\text{whole reaction time [min]}} \quad (2)$$

#### 3.1 Effect of reaction temperature

Reaction rate is known to be increased with reaction temperature [4, 5, 10-12, 18, 17]. Therefore, total produc-

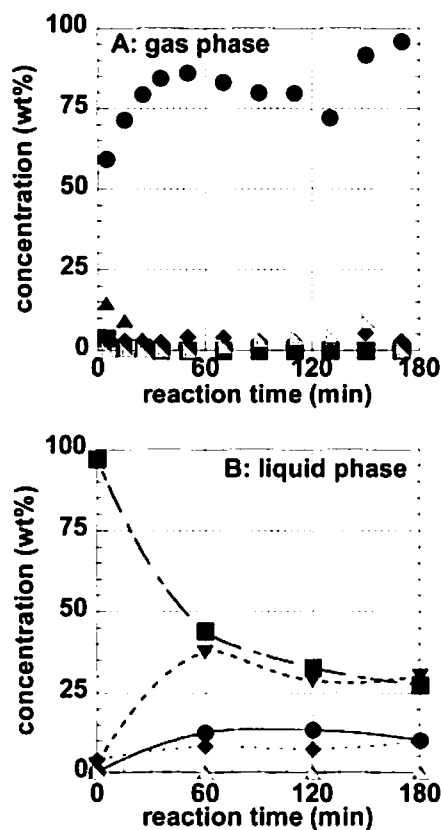


Fig. 4 Changes in composition of gas and liquid phases with reaction time. A : gas phase, B : liquid phase (reaction conditions; reaction temperature : 290°C, operating pressure : 0.1 MPa, methanol feed flow rate : 0.9 mL/min, stirring rate : 700 rpm, initial oil volume : 200 mL). ● : FAME, ■ : TG, ▲ : FFA, ▼ : DG, ◆ : MG, ◊ : GL

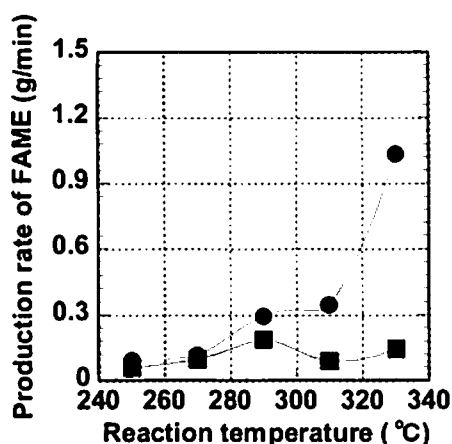


Fig. 5 Effect of reaction temperature on total production rate and outflow rate of FAME (reaction conditions; operating pressure : 0.1 MPa, methanol feed flow rate : 0.9 mL/min, stirring rate : 700 rpm, initial oil volume : 200 mL). ● : total production rate of FAME, ■ : outflow rate of FAME

tion rate of FAME will also be increased with reaction temperature as it is shown by this experiment (Fig. 5). Maximum outflow rate of FAME was occurred at reaction temperature of 290°C. At the reaction temperature higher than 290°C, evaporation of FAME might be interrupted by unknown reason, which will be investigated in our future work.

At the reaction time of 180 min, the total amount of identified components in the liquid phase was only 80% (Fig. 4). The content of unknown product increased with reaction time and reaction temperature, suggesting the polymerization or pyrolysis of oil. To avoid the production of unexpected product, it is necessary to modify the reactor in order to achieve a lower reaction temperature and shorter reaction time.

### 3.2 Effect of methanol feed flow rate

Figure 6 shows that both total production rate and outflow rate of FAME increased with methanol feed flow rate. Increase in gas-liquid interface area due to increase in methanol feed flow rate enhanced the reaction rate, leading to the increase in total production rate of FAME. Increase in methanol feed flow rate also removed FAME efficiently from the reactor, resulting in increase in outflow rate of FAME. Decrease in product inhibition due to the increase in outflow rate of FAME led to additional increase in total production rate.

### 3.3 Effect of operating pressure

In the literature [4, 5, 9 -12, 14, 15, 17, 18], reactions were carried out with batch reactors, therefore it was diffi-

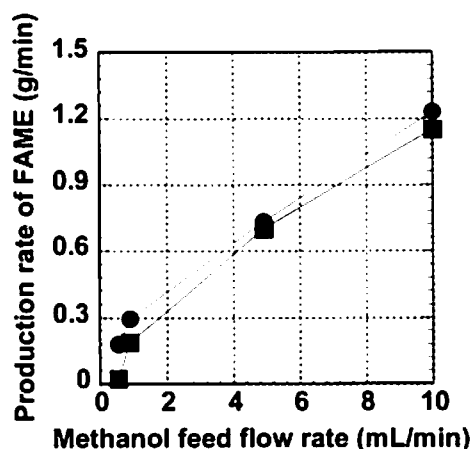


Fig. 6 Effect of methanol feed flow rate on total production rate and outflow rate of FAME (reaction conditions; reaction temperature : 290°C, operating pressure : 0.1 MPa, stirring rate : 700 rpm, initial oil volume : 200 mL). ● : total production rate of FAME, ■ : outflow rate of FAME

cult to control the reaction pressure independently. This work was accomplished in semi-batch reaction mode, so that, it was possible to control the reaction pressure independently. Effect of operating pressure on the reaction is shown in Fig. 7. Outflow rate of FAME showed maximum value at 0.1 MPa. FAME vapor pressure was assumed to be constant in all operating pressure because of the constant reaction temperature, while total pressure increased. The decrease in outflow rate of FAME with operating pressure was supposed to be caused by the decrease in FAME partial pressure inside the reactor vessel. The total production rate of FAME increased with the operating pres-

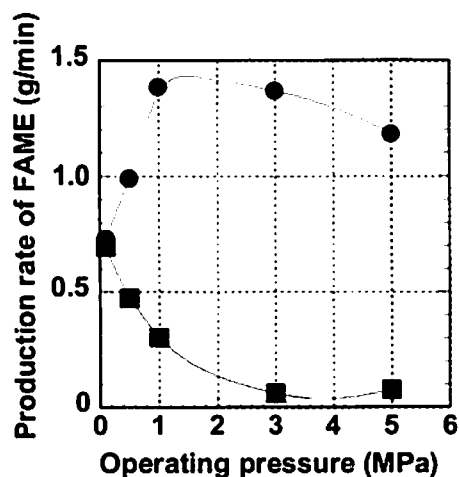


Fig. 7 Effect of operating pressure on total production rate and outflow rate of FAME (reaction conditions; reaction temperature : 290°C, methanol feed flow rate : 5 mL/min, stirring rate : 700 rpm, initial oil volume : 200 mL). ● : total production rate of FAME, ■ : outflow rate of FAME

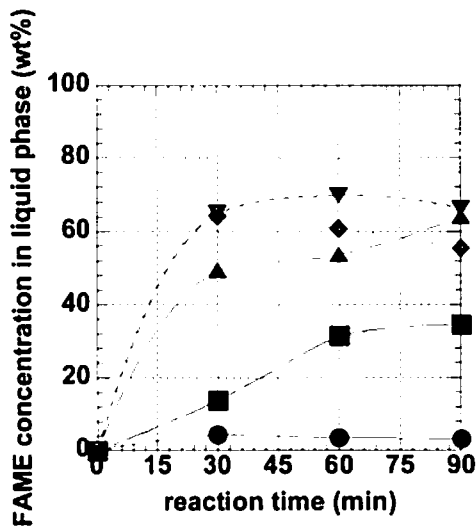


Fig. 8 Effect of operating pressure on FAME concentration in liquid phase (reaction conditions; reaction temperature : 290°C, methanol feed flow rate : 5 mL/min, stirring rate : 700 rpm, initial oil volume : 200 mL). ● : 0.1 MPa, ■ : 0.5 MPa, ▲ : 1.0 MPa, ▼ : 3.0 MPa, ◆ : 5.0 MPa

sure until 1.0 MPa, but was saturated under operating pressure above 1.0 MPa. At higher operating pressure, outflow rate of FAME was decreasing, but FAME concentration in the liquid phase was increasing (Fig. 8). The increasing FAME concentration in the liquid phase might inhibit the reaction and lower the total production rate of FAME at higher operating pressure.

### 3.4 Effect of stirring rate

Noureddini and Zhu [15] investigated the effect of mixing at 50°C, which turned out to have significant effect during the slow rate region of the reaction. In the present work, effect of stirring rate was investigated by comparing stirring rates of 400, 700 and 1000 rpm at reaction temperature of 290°C. The experiments show that both total production rate and outflow rate of FAME decreased with the increase in stirring rate (Fig. 9). The stirring process made a vortex in the liquid phase and lowered its surface in the central part, especially at faster stirring rate. Duly, the residence time of methanol bubble in the liquid phase was shorter.

In the work of Noureddini and Zhu, the conversion was increasing with the stirring rate for it is in liquid-liquid reaction. It was revealed that the residence time of methanol bubble in the liquid phase was an important factor in this reaction. This information will be useful for redesigning the reactor.

Moreover, change in stirring rate might have affected the diameter of the methanol bubble. More detailed anal-

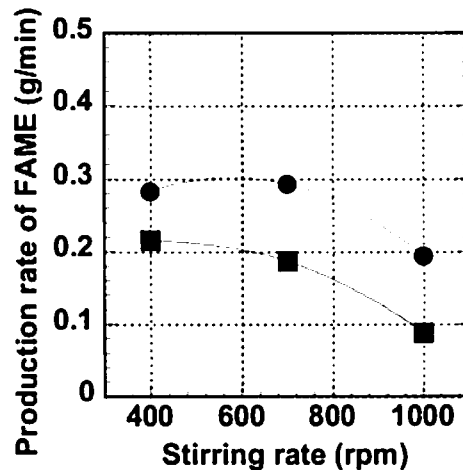


Fig. 9 Effect of stirring rate on total production rate and outflow rate of FAME (reaction conditions; reaction temperature : 290°C, operating pressure : 0.1 MPa, methanol feed flow rate : 0.9 mL/min, initial oil volume : 200 mL). ● : total production rate of FAME, ■ : outflow rate of FAME

ysis based on kinetics of the bubbles will be performed in our future work.

### 3.5 Effect of initial oil volume

The effect of initial oil volume on the reaction was investigated at 150, 200 and 250 mL. Both total production rate and outflow rate of FAME increased with initial oil volume (Fig. 10), because an increase in the height of liquid phase brought an increase in residence time of methanol bubble in the liquid phase. This result also reconfirm the significant effect of residence time of methanol bubble on the

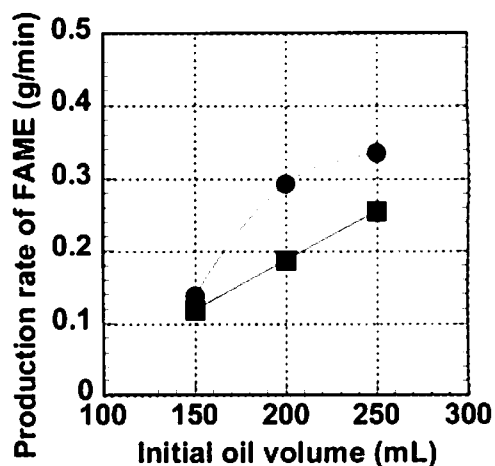


Fig. 10 Effect of initial oil volume on total production rate and outflow rate of FAME (reaction conditions; reaction temperature: 290°C, operating pressure: 0.1 MPa, methanol feed flow rate: 0.9 mL/min, stirring rate: 700 rpm). ● : total production rate of FAME, ■ : outflow rate of FAME

reaction. It indicates that the effect of the interface between methanol bubbles and its surrounding liquid phase is more significant than the interface between top surface of liquid phase and the gas phase above. It is predicted that increasing this interface area and prolonging the residence time of methanol bubble in the liquid phase could lead to an improvement in reaction rate. Future work will be focused on the discussion on bubble interface and kinetic analysis of this reaction.

### 3.6 Advantages over conventional method

The method proposed in this work does not require refining process to remove catalyst as in the conventional alkaline catalyzed method. Therefore, applying this method might reduce production cost of biodiesel fuel. Economical efficiency of this noncatalytic alcoholysis method was evaluated by Ishikawa et al. [19] based on the data obtained in this study. They designed a practical scale reactor that could produce 1000 kg of FAME in an hour and the production cost was estimated. The calculation indicated that the production cost of FAME would become half of the conventional alkaline catalyzed method. This result indicates the possibility of this method in reducing BDF production cost compared with conventional method. Energy balance and economical efficiency of the method proposed here will be further estimated by using a pilot scale reactor in the future.

### 4. Conclusions

A new reactor was developed to produce BDF (FAME) without using any catalysts. Effects of variables such as reaction temperature, methanol feed flow rate, operating pressure, stirring rate and initial oil volume were investigated based on outflow rate and total production rate of FAME. The maximum outflow rate of FAME, was achieved at reaction temperature of 290°C and pressure of 0.1 MPa. Increase in methanol feed flow rate and initial oil volume, and decrease in stirring rate, was found to increase the outflow rate of FAME. Increase in outflow rate of FAME with methanol feed flow rate indicates the large effect of product inhibition in this reaction. Decrease in outflow rate and total production rate of FAME with increase in stirring rate shows the significant effect of methanol bubble residence time in the liquid phase. Effect of initial oil volume on the reaction also indicates the same effect.

From these results, the interface between methanol bubbles and the surrounding liquid phase seemed to

affect the reaction more than the interface between top surface of liquid phase and bottom of gas phase. It is predicted that the increase in the interface area and prolonging the residence time of methanol bubble in the liquid phase could lead to the improvement in reaction rate. These results would be useful for redesigning the reactor to be more efficient. Future work will be focused on the discussion on bubble interface and kinetic analysis of this reaction.

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