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Synthesis of biodiesel from sunflower oil at room temperature in the presence of various cosolvents

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ABSTRACT

Synthesis of biodiesel fuel (BDF) from sunflower oil by using a KOH catalyst at 25 °C in the presence of various cosolvents, i.e., dimethyl ether (DME), diethyl ether (DEE), tert-butyl methyl ether (TBME) and tetrahydrofuran (THF), was investigated in a closed batch reactor. The minimum cosolvent/methanol molar ratio required for the complete dissolution of methanol and sunflower oil was determined. Addition of a cosolvent enhanced the transesterification rate at the methanol/oil molar ratio of 6 at 25 °C, and sunflower oil was almost completely converted into BDF after 20 min reaction while only approximately 78% conversion was reached in the absence of a cosolvent. The oil conversion was influenced by the cosolvent/methanol molar ratio, methanol/oil molar ratio, and catalyst concentration. The maximum oil conversion for each cosolvent was obtained at the minimum cosolvent/methanol molar ratio. DME could be considered as an effective cosolvent in BDF production and was more easily recovered from the products after depressurization of the reaction system. The synthesis of BDF in a microtube reactor in the presence of a cosolvent was examined by using a microscope camera, to observe the flow behaviors as the reaction progressed. A homogeneous flow was obtained at the entrance region of the microtube. However, the homogeneous flow was broken with the formation of immiscible glycerol, and transformed to a dispersed flow of fine glycerol droplets.

1. Introduction

Global emissions of CO_2 and other harmful gases such as CO, SO_x, NO_x and particulates generated by fossil fuel combustion have led to a serious greenhouse effect, acid rain, and the deterioration of human health and the environment. The price of crude petroleum has risen to its highest level. Therefore, the identification of environmentally friendly and renewable sources of alternative energy is becoming an urgent mission for researchers internationally. Biodiesel fuel (BDF) is defined as the mono-alkyl esters of long-chain fatty acids synthesized by transesterification of triglyceride in vegetable oils or animal fats with alcohol, and is therefore a renewable energy resource [1,2].

BDF and petroleum diesel have similar properties and performance parameters. Compared with petroleum-based diesel, BDF has a relatively high flash point (150 °C) and good lubricating properties. BDF has physical properties and energy content close to those of petroleum diesel, so it can be used directly in conventional diesel engines with no modification. Furthermore, BDF is biodegradable and non-toxic, with low emissions of CO, particulates and unburned hydrocarbons. In addition, the promotion of plantation without the destruction of nature in order to get enough feedstock for biodiesel would recycle more CO_2 by photosynthesis and, as a result, minimize the effects of greenhouse gases on the earth's environment [2]. The possible methods for BDF production by transesterification of vegetable oils or animal fats with alcohol can be mainly classified into the following four processes: (1) base-catalysis process [3–7]; (2) acid-catalysis process [8]; (3) non-catalysis process [9,10]; and (4) lipase catalysis process [11–13]. The use of lipase for production of biodiesel has shown promising results in recent years, but the research on this topic is still in progress due to the enzyme flexibility and the high cost in commercializing enzymes as catalysts. The non-catalysis process required high temperature and high pressure. To date, commercial biodiesel is generally produced by using an acid or base catalyst.

Since the oil and alcohol phases in a transesterification system are immiscible, the mass transfer between the two phases becomes a significant factor that affects the reaction rate. Although the miscibility of the two phases can be enhanced by increasing the temperature, this is an energy-consumptive process. Boocock et al. [14] suggested that addition of a cosolvent such as tetrahydrofuran (THF) could enhance the miscibility of the phases and speed up the reaction rate, because of the disappearance of interphase mass transfer resistance in the heterogeneous two-phase reaction

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system. THF is a widely used solvent in the transesterification reaction system, but it tends to form peroxide on storage. Guan et al. [15] used DME as a cosolvent to transform the oil–methanol two-phase system to a homogeneous one-phase system. Vegetable oil, such as corn, sunflower, rapeseed, soybean, and palm oil, can be completely transesterified into biodiesel fuel in 20 s under vigorous shaking using a KOH catalyst [15]. Maeda et al. also reported that the transesterification with DME was 100 times faster than that without DME [16]. Furthermore, DME can be easily recovered from the obtained BDF through a depressurization procedure. DME has little toxicological effect on health and the environment, and it can be produced from various resources such as coal, natural gas and biomass. DME could, therefore, be a promising alternative cosolvent for BDF production.

In recent years, continuous synthesis of BDF using a microreactor system has been considered a promising process [17–19]. Guan et al. [20] reported that BDF yields in a microchannel reactor reached greater than 90% with a residence time of 2 min even in the absence of cosolvent, and the required residence time was remarkably reduced when a microtube reactor was used instead of a lab-scale batch reactor. However, no data was reported when cosolvents were simultaneously introduced into the microreactor for BDF production. In the present study, BDF production from sunflower oil by using a KOH catalyst at 25 °C in the presence of various readily available ether-related cosolvents, i.e., dimethyl ether (DME), diethyl ether (DEE), tert-butyl methyl ether (TBME) and THF, was investigated in detail. The flow pattern along the microtube in the presence of the cosolvent was observed and characterized using optical measurement, and the relationship between flow pattern and oil conversion was examined.

2. Experimental

Dehydrated THF without stabilizer, DEE, TBME, dehydrated methanol, and KOH were obtained from Wako Pure Chemical Ind. Ltd., Japan. DME in a pressurized can was purchased from Tamiya Inc., Japan. The physical properties of the cosolvents used are shown in Table 1. Sunflower cooking oil was purchased. The acid value (0.41 mg KOH/g) and the saponification value (192.4 mg KOH/g) of the sunflower oil were determined using standard titration methods [20–21]. The molecular weight of sunflower oil, determined from the saponification value and the acid value, was 876.6.

A pressure-proof glass cylinder (volume = 10 mL, HPG-96-1, Taiatsu Techno®, Japan) was used as a reactor. The minimum amount of DME required for the complete dissolution of methanol and oil was determined using the following method: sunflower oil and methanol with a pre-determined molar ratio were added to the reactor and the reactor was then connected to the DME pressurized can via a tube. The reactor was shaken by hand during the introduction of DME into the cylinder. The point when the two-phase system became a one-phase clear solution was considered the phase boundary, and the weight of DME dissolved in the oil–methanol system was determined from the change in weight of the DME can before and after the input. The minimum amount of the other liquid cosolvents required for the complete dissolution of methanol and oil with stirring in a flask was determined by turbidimetric analysis using a titration method [17,22]. The liquid cosolvent was added into the oil–methanol mixture. The amount of cosolvent added was recorded at the point the mixture changed from turbid to transparent.

Transesterification of sunflower oil with methanol in the presence of DME was performed as follows: sunflower oil, KOH and methanol were added to the reactor and the reactor was then connected to the DME pressurized can via a tube. DME with a pressure of approximately 500 kPa was introduced into the reactor at 25 °C. The reactor was then immersed in a water bath with a shaker. We confirmed that the inhomogeneous solution became transparent and homogeneous after shaking for a short period. The molar ratio of methanol to oil varied from 4.0 to 8.0, and the weight concentration of KOH based on the oil ranged between 0.1 and 1.0 wt%. Reactions were carried out at 25 °C and at a shaking speed of 2.6 Hz. After the prescribed reaction period, the reactor was opened to release pressure. DME in the reactor escaped from the liquid phase, and the homogeneous reaction solution separated into an upper ester phase and a lower glycerol phase. This two-phase solution was centrifuged at 6000 rpm for 20 min. The upper ester layer was rinsed with deionized water and the mixture was centrifuged again. These procedures were repeated several times until the pH value of the aqueous phase reached 7.0. For analysis, 0.2 ml of the rinsed sample was diluted by 2.0 ml of hexane. For comparison, transesterification reactions in the presence of other liquid cosolvents were performed in the same reactor.

Concentrations of unreacted oil remaining in the synthesized BDF were analyzed by high performance liquid chromatography (HPLC, TOSOH, Japan) equipped with a silica-gel column (Shimpack CLC-SIL, Shimadzu, Japan) and a refractive index detector using a mobile phase of *n*-hexane/2-propanol = 99.5/0.5 (v/v). Column temperature was kept at 40 °C. The sum of fatty acid methyl esters and the unreacted glycerides (sum of mono-, di- and tri-glycerides) were represented by two peaks separated in the chromatograph [23]. The conversion of oil to BDF was calculated as follows:

$$\text{oil conversion} = \frac{C_0 - C}{C_0} \times 100\% \qquad (1)$$

where C_0 and C are the concentrations of glycerides before and after the reaction in the reaction system, respectively.

The remaining DME in the produced BDF was determined using a gas chromatograph (Shimadzu GC-8A, Japan) equipped with a Gaskuropack 54 60/80 column. The viscosity was determined with a torsion-balanced, oscillation type viscometer (VM-1G, CBC Materials Co. Ltd., Japan).

For the BDF production in a microtube reactor, DEE was first mixed with methanol containing 1 wt% of KOH catalyst base on the oil. The DEE/methanol molar ratio was fixed at 0.73. The mixed solution was dyed with inert red phloxine B to obtain clear images of the flow patterns in the microtube. Syringe pumps were used to feed the oil and methanol, which were mixed at a T-shape joint and then flowed into a transparent FEP (fluoroethylene polymer) microtube reactor (inner diameter = 0.96 mm, length = 80 cm). The molar ratio of methanol to sunflower oil was fixed at 8 by adjust-

Table 1
Physical properties of cosolvents.

Cosolvent	Molecular formula	Molecular weight (g/mol)	Density (g/cm^3)	Boiling point (°C)	Viscosity (mPa s)
TBME	$CH_3OC(CH_3)_3$	88.15	0.74	55.2	0.27 (20 °C)
DEE	$C_2H_5OC_2H_5$	74.12	0.71	34.6	0.224 (25 °C)
DME	CH_3OCH_3	46.07	0.67[a]	−23.6	0.122 (25 °C)
THF	C_4H_8O	72.11	0.885	66	0.48 (20 °C)

[a] Liquid state.

ing the flow rates. The total flow rate was 10 cm^3/h, corresponding to the residence time of 208.3 s at the microtube length of 80 cm. For comparison, the same experiment was also carried out in the absence of DEE. The reaction was performed at 25 °C. The images of the entire microtube were taken with a digital single-lens reflex camera (Nikon D40). Details of the flow patterns in the microtube were observed and recorded using an optical microscope equipped with a digital camera (Nikon DS Fi-1). The shutter speed was 1/40 s. The samples at 12 cm, 36 cm, 68 cm and 80 cm away from the inlet, which correspond to the residence time of 31.2 s, 93.6 s, 176.8 s and 208.3 s respectively, were taken and analyzed in order to determine the oil conversions along the microtube.

3. Results and discussion

3.1. Batch reactor

Fig. 1 shows that the minimum cosolvent/methanol molar ratio required for the complete dissolution of methanol and oil increased as the methanol/oil molar ratio increased. This figure indicates that the methanol–oil system kept a heterogeneous phase below the line for each cosolvent. In the present study, the minimum DME/oil molar ratio was the highest among those for the tested ethers, indicating that more DME molecules are required in order to get a homogeneous reaction mixture.

Transesterification of sunflower oil was carried out for 20 s with vigorous shaking. As shown in Fig. 2, the oil conversion reached its maximum near the point of the minimum cosolvent/oil molar ratio required for the complete dissolution of methanol and oil. This indicates that excessive addition of cosolvent into the reaction system decreased the transesterification rate, due to a dilution effect on the reagents. When the cosolvent/methanol molar ratio was lower than the minimum ratio, the oil conversion decreased because of the immiscibility of the oil and methanol. However, even when the cosolvent–methanol–oil system did not become homogeneous, the transesterification rate was improved when compared to the system without cosolvents.

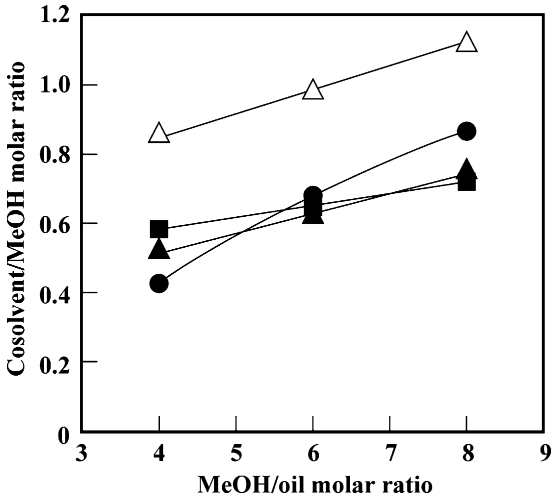

Fig. 1. Minimum colsovent/methanol molar ratio required for complete dissolution of methanol and oil. Cosolvents: △, DME; ▲, THF; ●, TBME; ■, DEE.

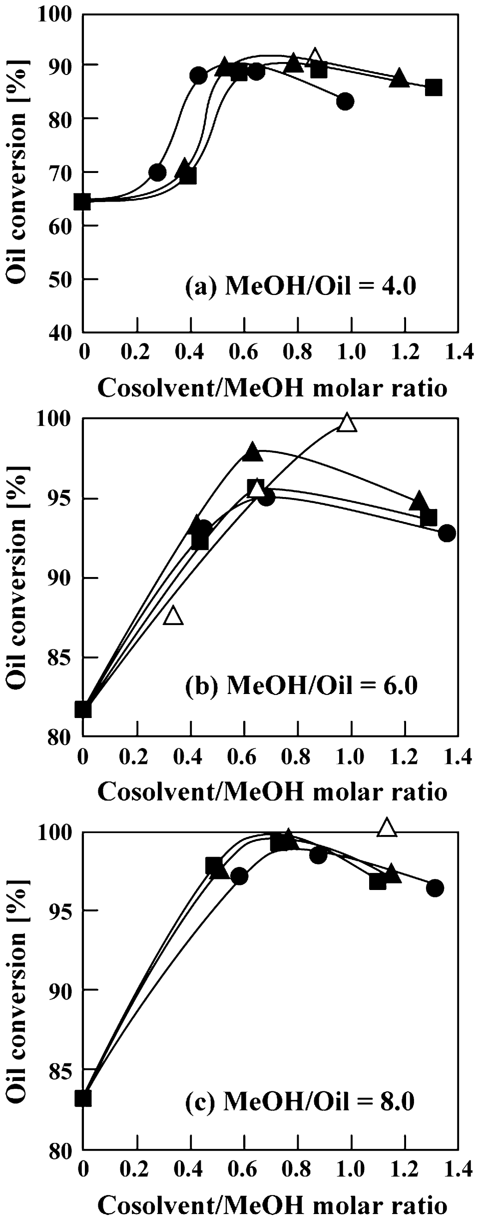

Fig. 2. Oil conversion as a function of cosolvent/methanol molar ratio at different methanol/oil molar ratios. Reaction conditions: vigorous shaking for 20 s at 25 °C; 1 wt% KOH based on oil weight. Cosolvents: △, DME; ▲, THF; ●, TBME; ■, DEE.

Fig. 3 shows changes in oil conversion with reaction time in the presence of various cosolvents when the transesterification reactions were carried out under the conditions of slow shaking at 25 °C with a 0.5 wt% KOH catalyst. The minimum cosolvent/oil molar ratios required for miscibility were adopted in each case. Transesterification of triglycerides with methanol is a reverse equilibrium reaction [9]. Thus, a relative high methanol/oil is required to force the reaction to proceed in the direction of methyl ester formation. At a relatively high methanol/oil molar ratio of 6.0 or 8.0, oil conversion increased as reaction time increased. At the beginning of the reaction time (especially before 20 min), oil conversion in the presence of a cosolvent was much higher than that in the absence of a cosolvent. At the methanol/oil molar ratio of 4 in the presence of DME, it was found that the reaction reached an equilibrium point and the oil conversion stayed at a constant level.

Fig. 4 shows the effect of KOH concentration on oil conversion in the presence or absence of a cosolvent. The minimum cosolvent/oil molar ratios were adopted. Catalyst concentration in the reaction system had a strong influence on the transesterification reaction rate, and oil conversion increased with the increase in KOH concentration in any case.

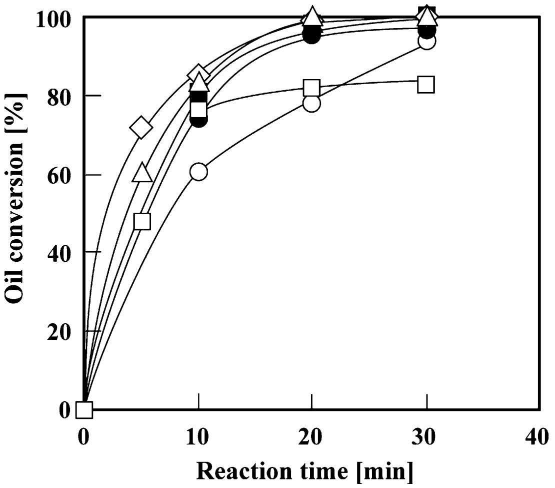

Fig. 3. Oil conversion as a function of reaction time in the presence of various cosolvents. Reaction conditions: shaking frequency = 2.6 Hz; reaction temperature = 25 °C. Methanol/oil molar ratio (cosolvent): □, 4 (DME); △, 6 (DME); ◊, 8 (DME); ■, 6 (DEE); ▲, 6 (THF); ●, 6 (TBME); ○, 6 (no cosolvent). 0.5 wt% KOH based on oil weight.

Fig. 5 summarizes the oil conversion at the minimum cosolvent/methanol molar ratio required for miscibility. When the methanol/oil molar ratio was 8, the oil was almost completely converted to BDF in 10 min with any cosolvent. Oil conversion decreased with decreasing methanol/oil molar ratios, since transesterification of triglyceride with methanol is a reversible reaction.

In this experiment, approximately 0.82 wt% of DME remained in the produced BDF, and the viscosity of the BDF was 4.87 mPa s. In order to investigate the influence of remaining cosolvents on the BDF viscosity, THF, DEE and TBME were added to the BDF produced in the absence of cosolvents and their viscosities at 25 °C were measured. As shown in Fig. 6, the viscosity of mixtures of BDF and cosolvents decreased as the concentration of cosolvent in the BDF increased, and the decreased extent at the same weight concentration was in the order of DME > DEE > TBME > THF, which is in accordance with the viscosity order of these cosolvents (as shown in Table 1). The decrease in the viscosity was suitable for injection of BDF into diesel engine systems.

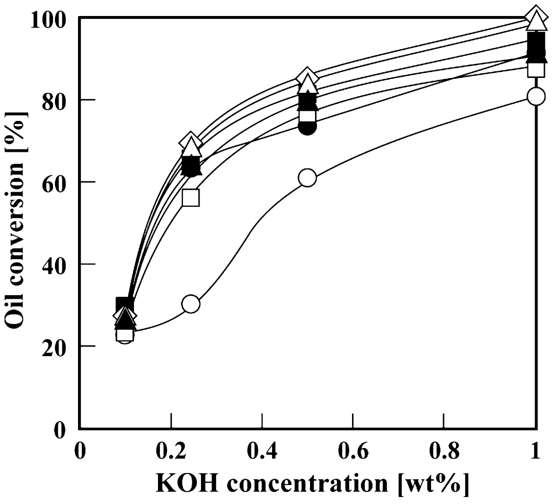

Fig. 4. Oil conversion as a function of catalyst concentrations. Reaction conditions: shaking frequency = 2.6 Hz; reaction temperature = 25 °C; reaction time = 10 min. Methanol/oil molar ratio (cosolvent): □, 4 (DME); △, 6 (DME); ◊, 8 (DME); ■, 6 (DEE); ▲, 6 (THF); ●, 6 (TBME); ○, 6 (no cosolvent).

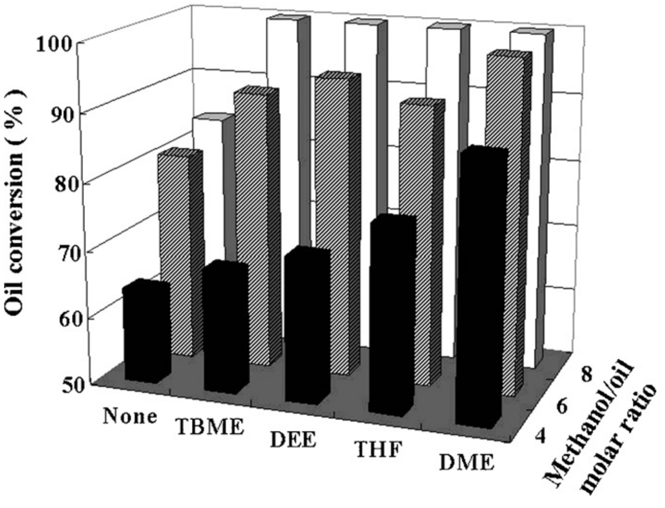

Fig. 5. Comparison of oil conversions in the presence of different cosolvents. Reaction conditions: shaking frequency = 2.6 Hz; reaction temperature = 25 °C; reaction time = 10 min; cosolvent/methanol molar ratio = minimum colsovent/methanol molar ratio required for miscibility, 1 wt% KOH based on oil weight.

3.2. Microtube reactor

When a cosolvent was introduced into a microtube reactor, the relationship between the flow patterns and the transesterification rate were investigated. Fig. 7 shows the flow patterns in the microtube reactor in both the absence (Fig. 7(a)) and presence (Fig. 7(b)) of DEE at 25 °C. Numerical values in Fig. 7 indicate the oil conversions at the tips of the arrows. The flow pattern gradually changed along the length of the microtube. In the absence of the cosolvent, clear stable segments (Fig. 7(a), i) were observed approximately 60 cm from the reaction inlet, and then red methanol segments began to aggregate, forming larger segments (Fig. 7(a), ii) at the exit region. In this case, the reaction rate was very low due to the hindrance of mass transfer between the two immiscible phases. Therefore, oil conversion at the exit was only 35.6%.

In the presence of the cosolvent, the flow pattern at the entrance region of the microtube was homogeneous (Fig. 7(b), i, ii). As stated above, the reaction of oil with methanol was enhanced due to the disappearance of mass transfer resistance that existed in the heterogeneous phase. However, as the reaction proceeded, glycerol was formed and separated from the homogeneous phase, and fine

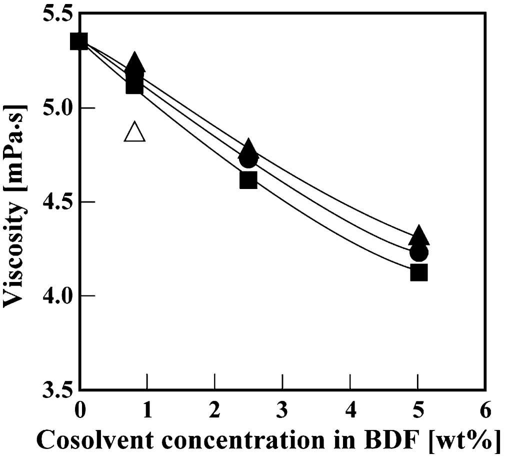

Fig. 6. Viscosities of cosolvent–BDF mixtures at 25 °C. Cosolvent: △, DME; ▲, THF; ●, TBME; ■, DEE.

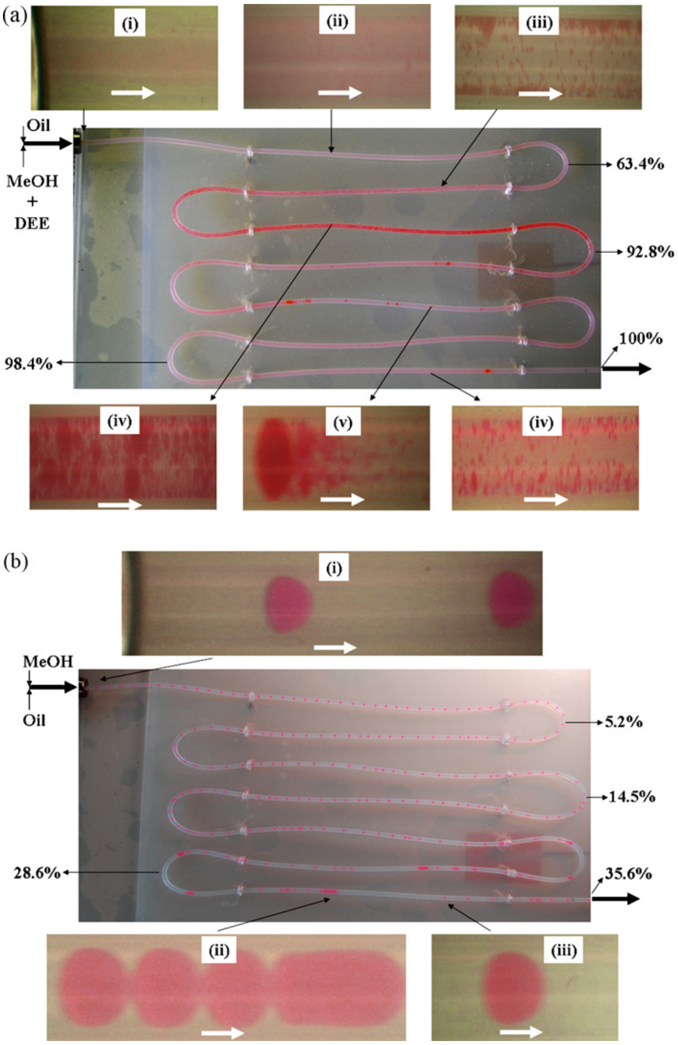

Fig. 7. Microscopic images of flow behavior in a transparent FEP microtube reactor in the absence (a) and presence (b) of DEE. DEE/methanol molar ratio = 0.73; methanol/oil = 8; total flow rate = 10 cm^3/h; reaction temperature = 25 °C. Numerical value indicates oil conversion.

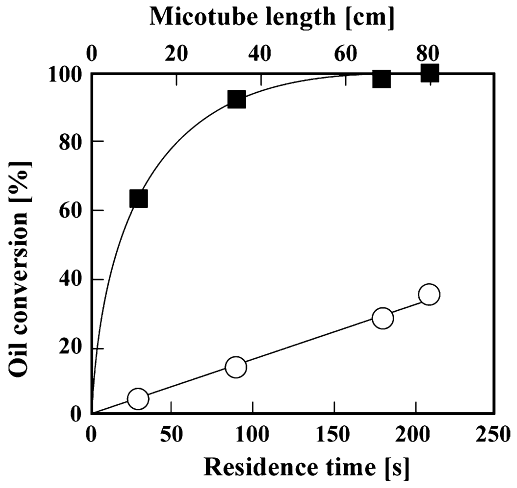

Fig. 8. Oil conversion in the microtube reactor. Methanol/oil = 8; total flow rate = 10 cm^3/h; reaction temperature = 25 °C.

red drops of glycerol (Fig. 7(b), iii) were observed in the microtube. A portion of the glycerol fine drops gradually aggregated to form larger drops (Fig. 7(b), iv), and finally, red segments were formed in the microtube (Fig. 7(b), v). A large amount of fine red drops that did not aggregate existed along the microtube (Fig. 7(b), vi). This phenomenon could not be easily observed when using a batch reactor with stirring or shaking.

Fig. 8 shows the oil conversion along the microtube reactor. In the presence of the cosolvent, oil conversion reached 63.4% at a microtube length of 12 cm and 92.8% at the point where most of the glycerol drops formed (microtube length = 36 cm, residence time = 93 s). When a batch reactor was used in the presence of DEE, as shown in Fig. 3, the oil conversion only reached 80.3% after the transesterification proceeded for 600 s, suggesting that the mass transfers can be enhanced when using a microreactor system for the transesterification of vegetable oil to BDF.

4. Conclusions

The minimum cosolvent/methanol molar ratios required for complete dissolution in the presence of various ether-type cosolvents were determined. It was found that the optimum amount of cosolvent in the transesterification system corresponded to the minimum cosolvent/methanol molar ratio. Excessive addition of cosolvent into the reaction system could reduce the transesterification rate and increase the operating cost. The flow pattern of transesterification of sunflower oil with methanol in the presence of diethyl ether with a microtube reactor indicated that the homogeneous flow was transformed to a dispersed flow consisting of fine droplets of glycerol.

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