CHEMICAL ENGINEERING TRANSACTIONS, Volume 14, 2008
Edited by G. Marino, E. Bardone, A. Viglia
 ISBN 978-88-95608-02-0

Continuous production of biodiesel using a microtube reactor

Guoqing Guan, Katsuki Kusakabe*, Kimiko Moriyama, Nozomi Sakurai
Department of Living Environmental Science, Fukuoka Women's University,
1-1-1 Kasumigaoka, Higashi-ku, Fukuoka 813-8529, Japan
kusakabe@fwu.ac.jp

Transesterification of sunflower oil to biodiesel was carried out in a microtube reactor with either a T-type mixer or a micromixer. The effects of molar ratio of methanol to sunflower oil, flow rate, reaction temperature, and microtube size on the oil conversion were investigated. The oil conversions obtained in the microtube reactors were higher than those obtained in the lab-scale batch reactor. The oil conversions were obviously improved when a T-type mixer was replaced by a micromixer. Sunflower oil was completely converted to biodiesel even if the residence time was as short as 112 s at a reaction temperature of 60ºC for a microtube reactor (1 mm i.d. and 160 mm in length) with a micromixer.

1. Introduction

Biodiesel fuel (BDF) is a promising environmental-friendly fuel compared to petroleum diesel fuel (Al-Zuhair, 2007, Huber et al., 2006, Lotero et al., 2005), and generally produced by transesterification of vegetable oils or animal fats with methanol in the presence of an alkaline catalyst. However, the reaction rate is mainly controlled by diffusion between oil and methanol phases due to the low solubility of oil in the methanol phase. Therefore, a stirred batch reactor is commercially used to produce small amounts of BDF. In recent years, microreactor systems designed for small-scale continuous production have been widely studied (Hessel et al. 2005). In the microreactor system, mass and heat transfer could be greatly intensified due to its small

space with a large surface area-to-volume ratio. As a result, molecular diffusion through the interface could become less significant resistance to the two-phase reaction. In the present study, microreaction systems composed of microtube reactors and microfluidic mixers were used for the continuous production of BDF. Transesterification of sunflower oil to BDF with methanol and KOH catalyst was carried out in the microtube reactor. The effects of molar ratio of methanol to sunflower oil, flow rate, reaction temperature, microtube size on the oil conversion were investigated. The oil conversions in the microtube reactor with a micromixer were compared to those with a conventional T-type mixer.

2. Experimental

Sunflower oil for cooking use was purchased from a market, and dehydrate methanol, potassium hydroxide and acetic acid were obtained from Wako Pure Chemical Ind. Ltd., Japan. All chemicals were not purified before use. Stainless-steel microtube reactors (inner diameter = 0.4, 0.6 and 0.8 mm) were used to facilitate contact between oil and methanol phases. Transparent teflon FEP tubes (inner diameter = 0.8 and 1 mm) were also used for the production of BDF and the observation of fluid motion. A stainless-steel micromixer, provided by Okayama Prefecture Industrial Promotion Foundation, was a split and recombine type mixer.

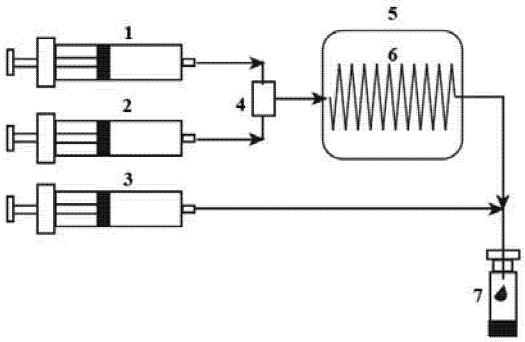

Fig.1 *Microreaction system for biodiesel production*
1. Vegetable oil; 2. Methanol/KOH; 3. Acetic acid;
4. T-type mixer or micromixer; 5. Thermostat oil bath;
6. Microtube; 7. Collection bottle.

A scheme for the experimental setup is shown in **Fig.1**. KOH was dissolved in methanol to adjust its concentration based on the oil weight to 1 wt%. Syringe pumps were used

for the feed of the liquids. The molar ratios of methanol to sunflower oil were adjusted by changing the liquid flow rates, and were 4.6, 11.3, and 23.9. Sunflower oil and methanol containing KOH were mixed at the T-type mixer or the micromixer. The mixture was then flowed into the heated microtube. The product was collected at the outlet of the microtube after the termination of reaction by addition of acetic acid. For comparison, a lab-scale batch experiment was performed using a 50 mL flask at 60ºC. Sunflower oil and methanol containing KOH were introduced into the flask simultaneously, and stirred at 600 rpm. The samples were recovered from the reaction mixture after the prescribed reaction time and immediately quenched by addition of acetic acid. The reaction was performed at 20, 40 and 60ºC.

The collected product was then centrifuged at 6000 rpm for 20 min. The upper BDF layer was rinsed with deionized water for several times to remove the residual inorganic components. 0.2 ml of the rinsed sample was diluted in 2 ml of hexane for analysis. Concentrations of the unreacted oil remaining in the products were analyzed by a 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 ºC.

3. Results and discussion

3.1 Comparison of the microtube reactor with the batch reactor

Segmented flow was observed in the transparent teflon FEP tube at the outlet of T-type mixer. **Fig.2** shows the comparison of the oil conversion between the batch reactor and the microtube reactor (0.8 mm i.d.) with T-type mixer. In the case of microtube reactor, the

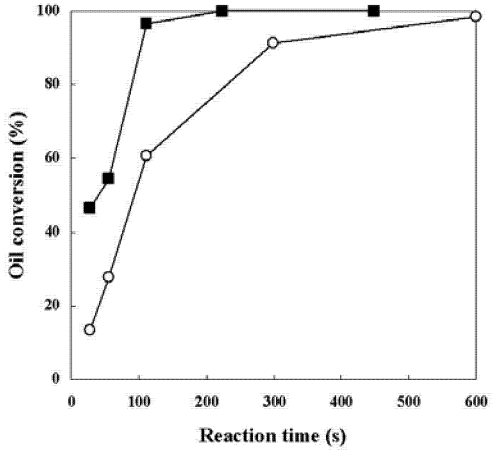

Fig.2 *Comparison of oil conversions when using microtube reactor and batch reactor. Molar ratio of methanol to oil = 4.6, reaction temperature = 60^{O}C*

reaction time was controlled by the length of microtube and the flow rate. The oil conversion was found to reach 100% after a reaction time of approximately 600 s for the batch reactor. For comparison, a reaction was carried out under the same conditions except for the reactor type. The 100% conversion was achieved for the reaction time of 240 s for the microtube reactor. The enhancement of the apparent reaction rate in the microtube reactor was caused by the mass transfer and temperature effects. Microtube provides high contact surface area between the immiscible two phases due to the formation of fine segments in the tube. Therefore the mass transfer rate can be enhanced through segmentation by providing a large specific interfacial area and phase internal flow (Malsch et al., 2008). In addition to the mass transfer effect, temperature in the reaction liquids rose quickly in the microtube compared to the batch reactor because of the small reaction volume.

3.2. Effects of microtube size and methanol/oil molar ratio

Transesterifications of sunflower oil were carried out at 60°C in the microtube reactors with different tube sizes and lengths. To fix the total flow rate and the value of the residence time to 28 s, microtube lengths were varied to 1000 mm for 0.4 mm i.d. tube, 640 mm for 0.6 mm i.d. tube, 360 mm for 0.8 mm i.d. tube and 160 mm for 1.0 mm i.d. tube. When the size of microtube was decreased, the flow rate in the microtube became high and therefore the oil conversion was increased due to small molecular diffusion distance as shown in **Fig.3**. Simultaneously, the behaviors of segmented flow were thought to be changed by the size of microtube and might be affected to the mass transfer. Detail observation of flow behaviors in microtube was need in the future work. Also we have to consider the pressure drop in the small microtube reactor.

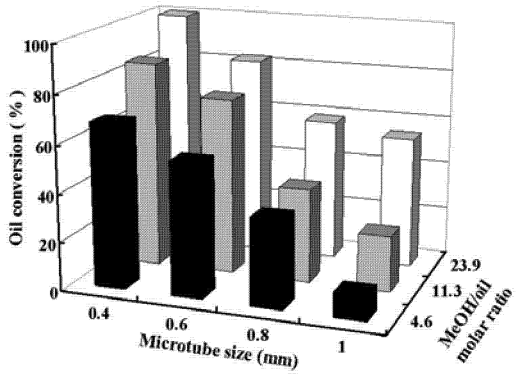

Fig.3 *Effects of microtube sizes and methanol/ oil molar ratios on oil conversions. Reaction temperature=60ºC; residence time=28s.*

The oil conversion increased with increase in the molar ratio of methanol to the oil as shown in Fig.3. This result is consistent with the results obtained in stirred batch reactors (Lotero et al., 2005). It is well recognized that transesterification of triglyceride with methanol is a reversible reaction. The excess mount of methanol shifted the equilibrium to the product side and thus increased the oil conversion. In the microtube reactor, segmented flow pattern was usually formed, and the molar ratio of methanol to the oil was adjusted by changing the flow rates of methanol and oil individually. From the observation of flow state, the length of segments, especially oil segments, was reduced by increasing the methanol flow rate. The change in flow behavior also affected the mass transfer rate.

3.3. Biodiesel production in microtube reactor with micromixer

A conventional T-type mixer is utilized to form a stable segmented flow in a microtube. Meanwhile, a dispersed flow of fine methanol droplets was observed at the outlet of the micromixer used in this experiment. The flow was then transferred from a dispersed flow to a segmented flow along the microtube. Large surface area obtained in the dispersed flow could enhance the reaction rate at the initial stage of transesterification.

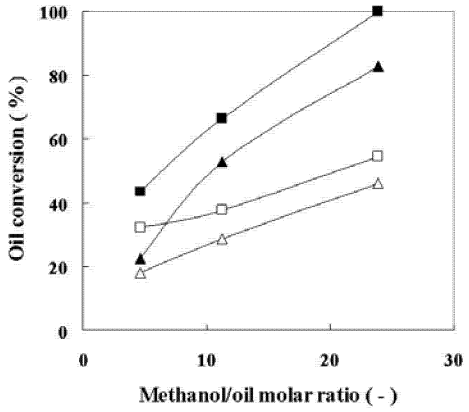

Fig.4 *Reaction enhancement by mixing effect. Residence time in microtube reactor (1 mm i.d. and 160 mm in length): ▲△; 56s; ■□;112s. Closed symbols: micromixer, Open symbols: T-type mixer. Reaction temperature=60 ºC.*

Fig.4 shows the comparison of the oil conversion between microtube reactors (inner diameter = 1 mm, 160 mm in length) with the T-type mixer and the micromixer. The oil conversions were high when the micromixer instead of the T-type mixer was used. The oil conversion was greatly improved at high molar ratio of methanol to oil in the

microtube reactor with the micromixer. Sunflower oil was completely converted to biodiesel when the residence time was as short as 112 s at a reaction temperature of 60℃ for a microtube reactor with a micromixer. Stamenkovic et al. (2007) investigated the transesterification of sunflower oil with methanol and KOH in a stirred batch reactor. Droplet size was approximately constant at the initial stage of the reaction and then rapidly reduced. The surface active compounds such as monoglycerides and diglycerides could inhibit the drop coalescence and favor formation of stable emulsion of small drops. Therefore the reaction system established in the microtube reactor with the micromixer would maintain the dispersed flow state for a while. In the previous paper (Guan et al., 2007), homogeneous production of BDF from corn oil was carried out by the addition of dimethyl ether as a cosolvent. The corn oil conversion of 100% was attained at room temperature by

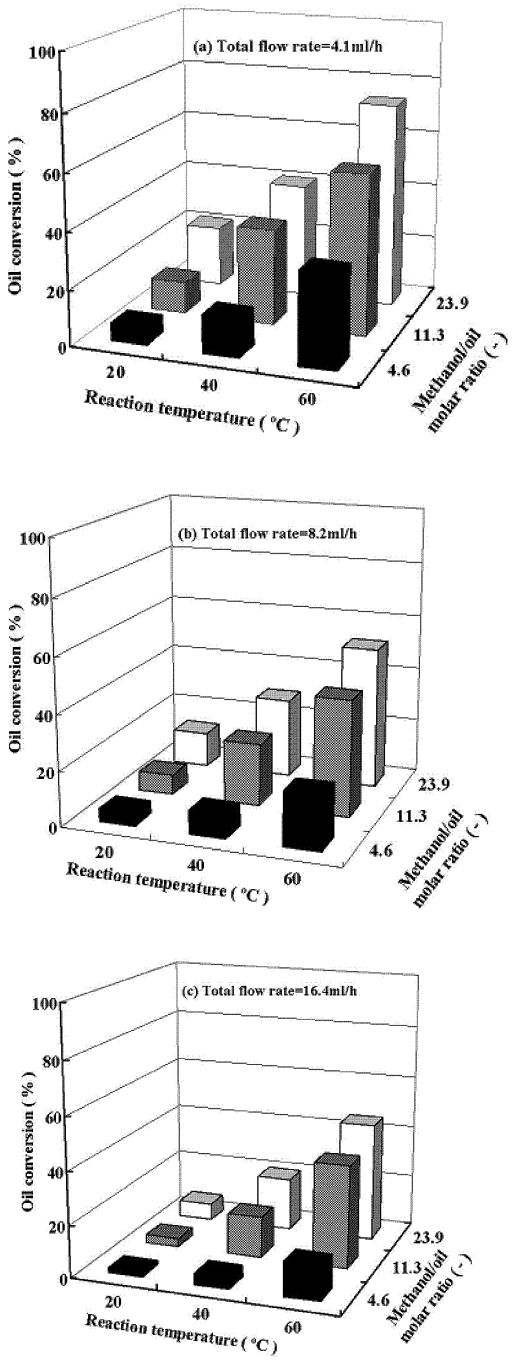

Fig.5 *Direct production of BDF in the micromixer. Total flow rate: (a); 4.1 mL/h, (b); 8.2 mL/h, (c); 16.4 mL/h.*

vigorously shaking within 20 s.

3.4. Biodiesel production in micromixer

Direct production of BDF in the micromixer was carried out at 20, 40 and 60°C. The product was collected at the outlet of the micromixer. As shown in **Fig.5**, the oil conversion at the reaction temperature of 20°C was less than 20%. Data of the oil conversion in the microtube with the micromixer in Fig.4 was obtained from the combination of the micromixer at room temperature and the microtube at 60°C. As a result, main reaction was performed in the microtube at 60°C in the case of Fig.4. .

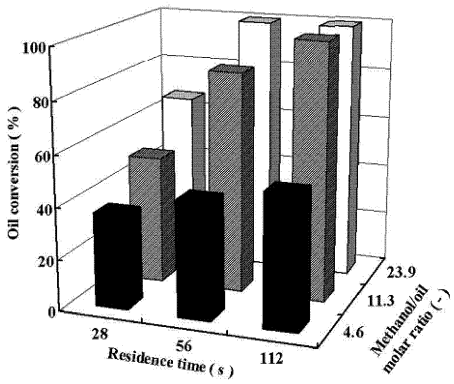

Fig.6 *Theoil conversion obtained when micromixer and microtube were heated at 60°C*

The oil conversion was rapidly increased with increase in the reaction temperature. The oil conversion at 60°C could attain 73.5% when the total flow rate was 4.2ml/h with a methanol/oil molar ratio of 23.9. If the problems with the pressure drop and the clogging in the complicated microchannel structure in the micromixer were discharged, the complete oil conversion would be realized only in a modified micromixer.

As shown in Fig.4, sunflower oil was completely converted to BDF for 112 s in the methanol molar ratio of 23.9 by using the microtube heated at 60°C and the micromixer at room temperature. When the micromixer and the micotube were heated at 60°C, the residence time and the methanol molar ratio to reach the 100% conversion became half as shown in **Fig.6**.

4. Conclusion

Continuous production of BDF by transesterification of sunflower oil was carried out in a microreaction system composed of a microtube with a T-type mixer or a micromixer. Comparing with the lab-scale batch reactor, microtube reactor showed better mass and heat transfer properties and obtained high conversion of sunflower oil. The oil conversion was obviously improved when a T-type mixer at the inlet of the microtube was replaced by a micromixer. It was found that 100% sunflower oil was converted to BDF even if the residence time was as short as 112 s at a reaction temperature of 60℃ for a microtube (1 mm i.d. and 160 mm in length) reactor with a micromixer. The oil conversion was increased with the decrease in microtube size.

5. References

Al-Zuhair S., 2007, Biofuels Bioproducts Biorefining, **1**, 57.

Guan, G., K. Kusakabe, N. Sakurai, K. Moriyama, 2007, Chem. Lett., 36, 1408.

Hessel V., H. Löwe, A. Müller, G. Kolb, 2005, Chemical Micro Process Engineering – Processing, Applications, and Plants, Wiley-VCH, Weinheim, Germany

Huber G., W., S. Iborra, A. Corma, 2006, Chem. Rev., **106**, 4044.

Lotero E, Y. Liu, D. E. Lopez, K. Suwannakarn, D. A. Bruce, J. G. Goodwin Jr., 2005, Ind. Eng. Chem. Res., **44**, 5353.

Malsch, D., M. Kielpinski, R. Merthan, J. Albert, G. Mayer, J.M. Köhler, H. Süβe, M. Stahl, T. Henkel, 2008, Chem. Eng. J., **135S**, S166.

Stamenkovic O.S., M.L. Lazic, Z.B. Todorovic, V.B. Veljkovic, D.U. Skala, 2007, Bioresouce Technol. ,98, 2688.