

CONTINUOUS PRODUCTION OF BIODIESEL FROM WASTE COOKING OIL BY A TWO-STEP PROCESS WITH MICROTUBE REACTORS

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Abstract

In order to produce biodiesel continuously from waste cooking oil (WCO), a two-step process with microtube reactors (MRs) was developed. Esterification of fatty acid using acid catalyst proceeded in the first MR and then, the acid methanol phase as well as produced water was continuously separated from the oil phase in a simple separation cell, and finally, the oil phase flowed into the second MR for the transesterification of the remained triglyceride using KOH catalyst. It is found that the acidic methanol phase can be separated from the oil phase using a simple separation cell located downstream of the first MR in a short period. FAME yield reached 99.3 % at a total residence time of 46.2 min with a reaction temperature of 333 K, when WCO containing 14 mol% of free fatty acid was converted in the two-step reaction system composed of a first MR with 5000 mm length and a second MR with 1000 mm length.

Keywords: Transesterification, Esterification, Waste Cooking Oil, Triolein, Palmitic Acid

1. Introduction

Biodiesel (fatty acid methyl ester; FAME) is a renewable and environmentally friendly alternative fuel. The most common technique to produce biodiesel fuel (BDF) is transesterification of triglycerides which are reacted with methanol in the presence of a catalyst, usually potassium or sodium hydroxide (KOH or NaOH). Most commercial BDF are produced from edible vegetable oils such as soybean, rapeseed, sunflower seed and palm oils. However, the price of vegetable oils has increased along with the increases in BDF production. The raw materials of BDF production has shifted to low quality oils with high free fatty acid (FFA), which cause soap formation in the presence of alkali catalyst. The soap formation can be avoided by pre-treating the oil with an acid catalyst to convert the FFA to FAME before the alkali catalyst is used. However, the acid-catalyzed reaction is much slower than the alkali-catalyzed reaction [1,2].

Transesterification of sunflower oil and waste cooking oil (WCO) with methanol in the presence of a KOH catalyst was carried out in a microtube reactor (MR) [3-6]. Compared with the lab-scale batch reactor, the MR showed better mass and heat transfer properties and resulted in high conversion of sunflower oil [3]. Flow patterns along the microtube were simultaneously observed and characterized using optical measurements as the reaction progressed. Oil conversion in the MR increased with the methanol/oil molar ratio as well as with the reaction temperature, which significantly affected the flow pattern [4]. In the case of

transesterification of WCO in the MR, the soap produced from FFA could change the interface properties to a great extent. The FAME yield for the transesterification of WCO reached higher than 89 % in MRs of inner diameter of 0.46-0.96 mm with a residence time of 252 s at 333K [6]. Accordingly, the esterification rate of FFA in the presence of an acid catalyst would be improved by using an MR due to the enhancement of mass transfer.

A two-step process for the biodiesel production from rubber seed oil [1], tobacco seed oil [7], rice bran oil [8,9], salmon oil [10] and WCO [11] have been investigated. The method included an acid-catalyzed esterification followed by an alkali-catalyzed transesterification in batch reactors. To avoid the consumption of the alkali catalyst by the neutralization of residual acid and the hindrance to subsequent transesterification, the separation of oil phase from the first step products is necessary to remove an acid catalyst and water, but time consuming.

The objective of this study was to develop a novel two-step process using MRs for continuous production of BDF from corn oil with oleic acid, triolein with palmitic acid or WCO. In this process, esterification in the presence of H₂SO₄ in a MR, continuous separation of oil phase by gravitation force in a separator and transesterification in the presence of KOH in the other MR were subsequently carried out. The effects of FFA content, catalyst amount, and residence time on the yield of BDF production were investigated. In addition, phase

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diagram of oil, fatty acid and methanol with or without H_2SO_4 was also determined in order to clarify the effect of the interface between the phases.

2. Experimental

2.1 Chemicals

WCO was provided from a biodiesel production factory. Corn oil, triolein, oleic acid (60 %), palmitic acid (>99 %), dehydrated methanol, potassium hydroxide, acetic acid, Phloxine B and Brilliant Blue FCF were obtained from Wako Pure Chemical Ind. Ltd., Japan. The acid and saponification values of the oil were determined using standard titration methods [12]. The molecular weight of the oil was determined from the saponification and acid values. Water content in the oil was determined using a Karl-Fischer moisture titrator (MKC-610, Kyoto Electronic Manufacturing Co. Ltd.). The viscosity was determined with a torsion-balanced, oscillation-type viscometer (VM-1G, CBC Materials Co., Ltd.). The density was determined using a pycnometer. The physical properties of the oils are summarized in Table 1. When FFA is assumed to be composed of oleic acid, an acid value of $3.7 \text{ mgKOH}\cdot\text{g}^{-1}$ for WCO corresponds to 1.9 wt% (5.2 mol%) of oleic acid.

Table 1 Physical properties of WCO, corn oil and triolein

	Triolein	Corn oil	WCO
Water content, wt%	0.105	0.024	0.107
Acid value, $\text{mgKOH}\cdot\text{g}^{-1}$	-	-	3.70
Saponification value, $\text{mgKOH}\cdot\text{g}^{-1}$	-	193	215
Molecular weight, $\text{g}\cdot\text{mol}^{-1}$	885	870	793
Viscosity, $\text{mPa}\cdot\text{s}^{-1}$ (298K)	60.01	50.01	60.07
Density, $\text{kg}\cdot\text{m}^{-3}$ (298K)	0.86	0.91	0.94
Fatty acid contents			
Oleic acid, mol%	89.5	89.1	89.8
Palmitic acid, mol%	7.8	10.8	10.0

2.2 Phase diagram of oil, fatty acid and methanol

The phase diagram was determined by turbidmetric analysis using the titration method under isothermal conditions. The measurement in the triolein-palmitic acid-methanol system was carried out in a constant temperature reservoir at 323 K to avoid the white turbidity of the solution. The other measurements were carried out at 298K. Methanol was fed to the mixture of oil and fatty acid while stirring with a magnetic stirrer through a microtube with a syringe pump. The point when the mixture transferred from transparent (homogeneous) to turbid (heterogeneous) was considered to be the saturation point of the methanol. The amount of added methanol (with or without H_2SO_4) was determined with an analytical balance.

2.3 Observation of flow patterns

Transparent Teflon (FEP) tubes with an inner diameter of 1.0 mm

were used for the biodiesel production and for the observation of flow patterns. A schematic illustration of the two-step experimental process is shown in Fig. 1. To obtain clear images of the flow patterns in the microtube, methanol solutions in the first and second MR were colored with an inert blue dye (Brilliant Blue FCF) and an inert red dye (Phloxine B), respectively. Both dyes are soluble in methanol, but insoluble in oil. Transparent FEP tube with length of 1000, 3000 and 5000 mm were wound on glass cylinders for the first MR and immersed in a constant temperature bath. A subsequent 1000 mm-FEP tube fixed onto a silicon rubber plate was placed on a hot plate for the second MR. A transparent glass plate closely covered the microtube for prevention of heat loss. Syringe pumps were used to feed the oil and methanol. They were mixed at a T-shaped joint before entering the MRs. The total flow rates of oil, a methanol solution of H_2SO_4 and a methanol solution of KOH were fixed at $1.4 \times 10^{-9} \text{ m}^3\cdot\text{s}^{-1}$, corresponding to a residence time of 4.7 min per 1000 mm tube. The reaction temperatures were fixed at 333 K. Pictures of the microtube were taken with a digital single-lens reflex camera. Details of the flow behavior in the microtube were observed and recorded using an optical microscope equipped with a digital camera.

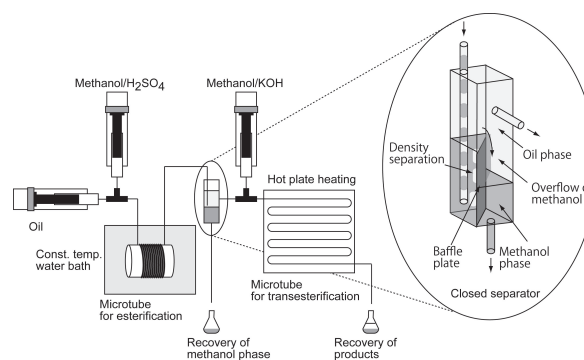


Fig.1 Microtube reactors for two-step BDF production

2.4 Determination of FAME yield

To investigate the effect of fatty acid on FAME yield for esterification and transesterification, oleic acid and palmitic acid were added to corn oil and triolein, respectively. Esterification of oleic acid in corn oil and palmitic acid in triolein were carried out with H_2SO_4 catalyst. Transesterification of corn oil with oleic acid or triolein with palmitic acid was carried out with KOH catalyst. The weight concentrations of H_2SO_4 based on the oil was varied to 1, 3 and 5 wt%. The weight concentration of KOH was fixed to 5 wt%. The two-step BDF production from the triolein with palmitic acid, corn oil with oleic acid, WCO, and WCO with oleic acid was carried out as follows. After the esterification of fatty acid with H_2SO_4 catalyst in the first MR (length = 1000, 3000 and 5000 mm), oil and methanol phase were continuously separated in a rectangular separating cell (10 mm x 10 mm x 30 mm, volume = $3 \times 10^{-6} \text{ m}^3$) by density difference. A

methanol solution of KOH was merged with the separated oil through a T-shaped joint for transesterification of triglyceride and fed into the second MR at 333 K.

Samples after esterification and transesterification were collected and a dilute KOH and an acetic acid solution were added respectively for the termination of the reaction. The sample was then centrifuged at 4000 rpm for 900 s. The upper FAME layer was washed several times with deionized water to remove residual inorganic components. Then, $1 \times 10^{-4} \text{ mm}^3$ of the washed sample was diluted in $3 \times 10^{-3} \text{ mm}^3$ of hexane for analysis.

The concentration of unreacted triglyceride that remained in the sample was analyzed using a high-performance liquid chromatograph (HPLC, Tosoh Corp.) equipped with a silica-gel column (Shimpack CLC-SIL, Shimadzu Corp.) and a refractive index detector. The mobile phase was n-hexane/2-propanol=99.5/0.5 (v/v) and the column temperature was kept constant at 313K. Two peaks that were attributed to the sum of FAMEs and the unreacted glycerides (sum of mono-, di- and tri-glycerides) appeared in the liquid chromatogram. The concentrations of oleic acid methyl ester and palmitic acid methyl ester were determined with a gas chromatograph (Shimadzu GC-8A) equipped with a glass column (Shimpack CLC-SIL, Shimadzu Corp.) and a flame ionized detector.

The FAME yield in the product after the two-step BDF production was calculated as follows:

$$\text{FAME Yield} = \frac{C_{\text{FAME}}}{3C_{\text{oil}} + C_{\text{FA}}} \times 100 \quad (1)$$

where C_{oil} and C_{FA} are the concentrations of triglycerides and fatty acids in the feed, respectively. C_{FAME} is the FAME concentration in the product.

For the acid-catalyzed reaction of the triolein and palmitic acid mixture in the first MR, the FAME yields of oleic acid methyl ester (OAME) from triolein by transesterification and palmitic acid methyl ester (PAME) from palmitic acid by esterification were calculated independently by

$$\text{FAME Yield} = \frac{C_{\text{OAME}}}{3C_{\text{o, triolein}}} \times 100 \quad (2)$$

$$\text{FAME Yield} = \frac{C_{\text{PAME}}}{C_{\text{o, palmitic acid}}} \times 100 \quad (3)$$

where $C_{\text{o, triolein}}$ and $C_{\text{o, palmitic acid}}$ are the initial concentrations of triolein and palmitic acid in the feed, respectively.

3.1 Phase diagram

Fig. 2 shows phase equilibriums of corn oil-oleic acid-methanol at 298 K, triolein-oleic acid-methanol at 298 K and triolein-palmitic acid-methanol at 323 K. The phase boundaries of oil-oleic acid-methanol, triolein-oleic acid-methanol and triolein-palmitic acid-methanol were close to each other regardless of the difference in temperature and constituent fatty acid. When H_2SO_4 was mixed with methanol as a catalyst, most of the phase diagram indicated two phases. Expansion of the two phase region was due to the loss of interfacial activity by the conversion from dissociative to undissociative oleic acid. Thus, a two phase separation after consumption of fatty acids by an esterification was confirmed.

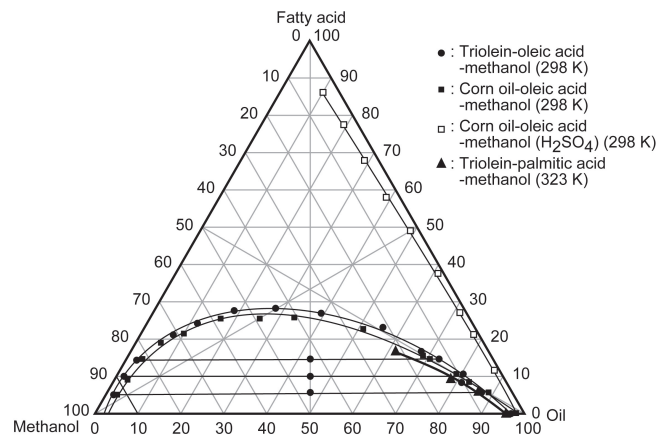


Fig.2 Phase diagram of oil-fatty acid-methanol

3.2 Esterification of fatty acid

Esterification of palmitic acid and transesterification of triolein were performed simultaneously in the presence of H_2SO_4 catalyst at 333 K. In this case, the length of MR was fixed to 1000 mm, corresponding to the residence time of 4.7 min. Fig. 3 shows the effect of H_2SO_4 concentration on the FAME yields. FAME yields for the transesterification of triolein were low after the esterification completed. Similar results were obtained in the BDF production from tobacco seed oil with a high fatty acid in the presence of H_2SO_4 catalyst for 1 h [7]. Meanwhile, the FAME yield reached more than 50% in BDF production from corn oil with the H_2SO_4 catalyst for 8 h [2]. Fatty acid reacted with methanol to form methyl ester and water. When produced water concentrated in a methanol phase, the acid hydrogen ion was able to bind the water, resulting in the inhibition of the acid catalysis function of transesterification [2]. In addition, the transesterification did not significantly proceed in the methanol solution containing an H_2SO_4 catalyst during the progress of esterification [13]. Son et al. [14] carried out simultaneous esterification and transesterification in a fixed-bed reactor packed with a cation exchange resin catalyst at 373 K. In the fixed-bed

reactor, the removal of water by vaporized methanol flow inhibited the reverse esterification and caused high FAME yields in oleic acid containing water.

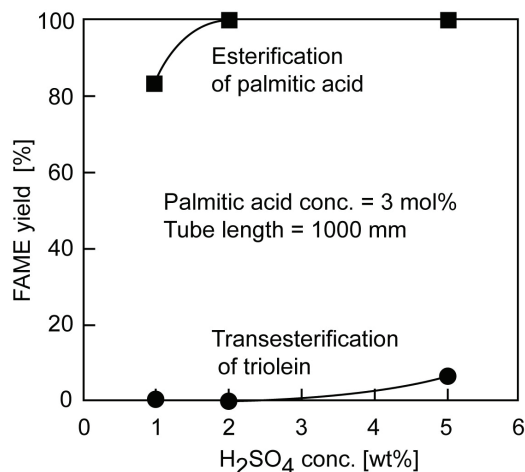


Fig. 3 Effect of H₂SO₄ concentration on FAME yield

Fig. 4 shows the effect of palmitic acid concentration in triolein on the FAME yield for the esterification. The FAME yield at the palmitic acid concentration of 3 mol% was 100 % in the MR with 1000 mm length. For the high concentration region (10-20 mol%), palmitic acid concentration in triolein had little influence on the FAME yield in the MR with 1000 mm length. As shown in Fig. 5, the FAME yield for esterification increased with the increase in the length of microtube. The FAME yield for the esterification in triolein with 10 mol% palmitic acid reached 80 % at the residence time of 23.5 min in a microtube with 5000 mm length. Meanwhile, the FAME yield for the transesterification of triolein was less than 5 %.

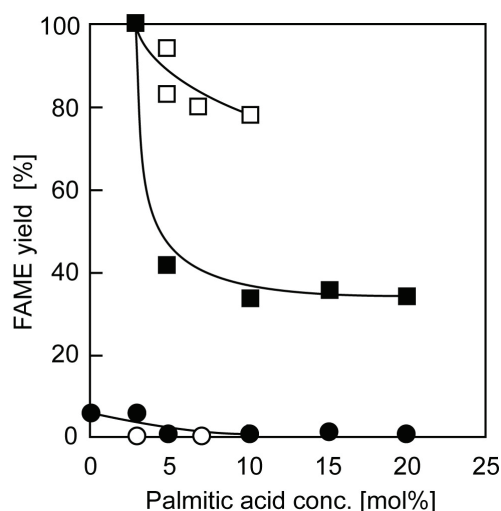


Fig. 4 Effect of palmitic acid concentration on FAME yields, $\square$ $\blacksquare$: Esterification of palmitic acid; $\circ$ $\bullet$: transesterification of

triolein; $\square$ $\circ$: tube length = 5000 mm; $\blacksquare$ $\bullet$: tube length = 1000 mm; H₂SO₄ conc. = 5 wt%; temperature = 333 K

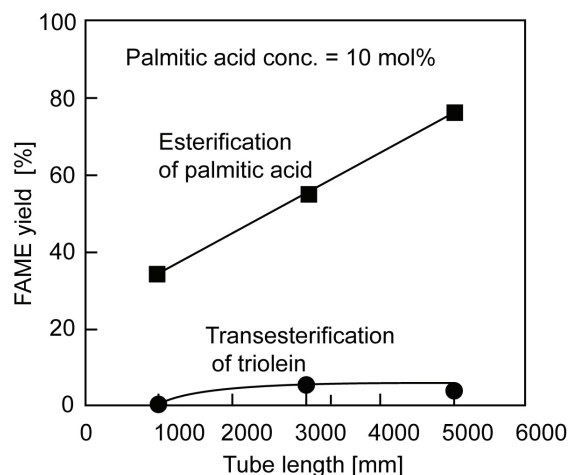


Fig. 5 Effect of length of microtube on FAME yields, $\blacksquare$: Esterification of palmitic acid; $\bullet$: transesterification of triolein; palmitic acid concentration = 10 mol%; temperature = 333 K

3.3 Gravitational separation

The two-step process for BDF production was usually carried out in batch reactors. Therefore, at the end of esterification in the first batch reactor, liquid in the reactor was transferred to a separating vessel to remove the methanol phase. El-Mashad et al. [10] used a glass elementary flask as an experimental batch reactor and a separating funnel as a separator for the two-step BDF production. The settling time in a separating funnel was reported to be as high as 3 hours to separate methanol and oil phase clearly due to the formation of fine droplets during agitation in the reactor. In the present study, a rectangular cell with a separating baffle connected to the end of the first MR was used as the separator for the continuous separation of methanol and oil phase as shown in Fig.1.

The two-step BDF production of WCO with water was carried out after the addition of 0.1, 0.3 and 0.5 wt% H₂O. As indicated in Table 1, WCO essentially contains approximately 0.1 wt% H₂O and, therefore, the measured water content in the raw oils for BDF production were 0.2, 0.4 and 0.6 wt% as shown in Fig. 6. During the reaction in the first MR, the water content was further increased by the esterification. After the separator located downstream of the first MR, the water content in the separated oil phase was less than 0.07 wt%. Also no incorporation of the green colored segments of the methanol phase into the oil phase in the second MR could be observed as shown in Fig. 7. It is possible that the good separation at a relatively short time (18 min) was caused by the segmented flow in the first MR.

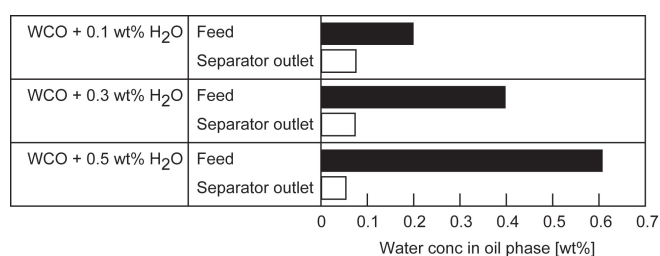


Fig. 6 Water contents in oil phase at separator outlet

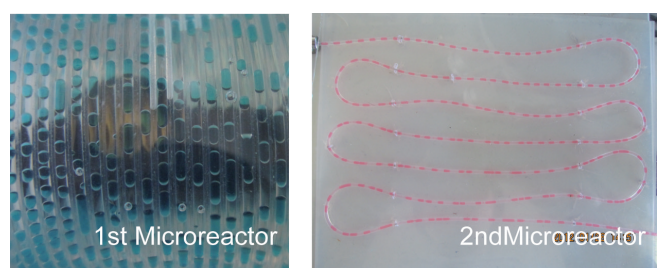


Fig. 7 Flow behaviors in first and second microtube reactor under continuous operation

3.4 Transesterification of triolein

Transesterification of corn oil with oleic acid and triolein with palmitic acid were performed in the presence of 1, 3 and 5 wt% KOH at 333 K. The length of MR was fixed to 1000 mm, corresponding to the residence time of 4.7 min. As indicated in Table 2, the FAME yield decreased gradually with increase in fatty acids concentration and reached 92.7 and 97.8 % for the transesterification of corn oil and triolein, respectively. Accordingly, an allowable fatty acid concentration in oil at the outlet of the first MR should be less than 5 mol%.

Table 2 FAME yields for transesterification

	Fatty acid conc. [mol%]	FAME yield [%]
Corn oil + oleic acid	1	92.7
	3	92.5
	5	92.1
Triolein + palmitic acid	1	97.8
	3	92.2
	5	91.8

3.5 Continuous two-step process

Two-step BDF production from triolein with palmitic acid was performed in the first MR with 5000 mm length and the second MR with 1000 mm length at 333 K. The KOH concentration in the second

reactor was fixed to 5 wt%. Although 2 wt% H₂SO₄ might be enough to maintain a high FAME yield for the esterification as shown in Fig. 2, 5 wt% H₂SO₄ was adopted to clear the effects of H₂SO₄ entering into the second reactor because of insufficient separation.

Fig. 8 shows the effect of palmitic acid concentration on the FAME yield in the two-step BDF production. For BDF production from triolein with 7 mol% palmitic acid, the concentration of palmitic acid was reduced to 1.4 mol% at the outlet of the first MR and therefore, the FAME yield was approximately 90% at the outlet of the second MR.

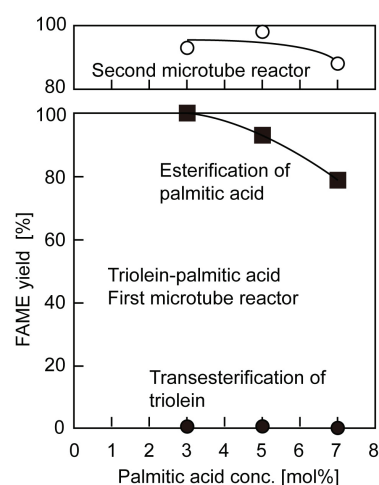


Fig. 8 FAME yields at the outlets of first and second microtube reactor in BDF production from triolein + palmitic acid

The FAME yield of triglyceride in WCO was determined through the two-step BDF production for the purpose of examining the impurity effect. As indicated in Table 3, the FAME yield of WCO was higher than those of corn oil with 3 mol% oleic acid and triolein with 3 mol% palmitic acid. In addition, no triglyceride in the produced BDFs from triolein, corn oil and WCO could be detected with HPLC.

Table 3 FAME yields in two-step BDF process^{a)}

	FAME yield of two-step BDF production [%]
Triolein + 3 mol% palmitic acid	92.2
Corn oil + 3 mol% oleic acid	92.5
WCO ^{b)}	100
WCO + 0.1 wt% H ₂ O	99.0
WCO + 0.3 wt% H ₂ O	100
WCO + 0.5 wt% H ₂ O	100
WCO + 5 wt% oleic acid	99.3
WCO + 10 wt% oleic acid	96.6

a) Tube length of first microtube reactor = 5000 mm , Tube length of second microtube reactor = 1000 mm

b) FFA content 5.2 mol%, water content 0.107 wt%

As indicated in Table 1, the WCO used in this study contains relatively low water and FFA contents. When more than 0.5 wt% water was added to WCO, WCO containing water indicated turbidity during stirring and the solution became incompletely-separated after the stirring was stopped. Accordingly, two-step BDF productions were performed after the addition of 5 and 10 mol% oleic acid or 0.3-0.5 wt% water to WCO. As a result, high FAME yields were probably achieved in any of the above cases due to the separation of water and hydrophilic impurities in the separator.

4. Conclusions

A two-step continuous process using MRs with a separator was found to be effective for BDF production from the oils with high fatty acid. For the H₂SO₄ catalyzed reaction of triolein with 10 mol% palmitic acid, esterification of palmitic acid proceeded effectively in the first MR with 5000 mm length, resulting in a FAME yield of 80% at the residence time of 23.5 min. Meanwhile, the FAME yields for transesterification of triolein were less than 5 %.

Complete removal of acidic methanol from the products in a simple separator located downstream of the first MR was continuously performed. As a result, the water content in the oil phase was reduced to less than 0.1 wt% at the residence time of 18 min due to the transfer of water in oil phase to the methanol phase in segmented flows.

A successful KOH-catalyzed transesterification was achieved by using the second MR with 1000 mm length. As a result of the two-step continuous BDF production, FAME yields in the case of WCO with 10 mol% oleic acid reached 99.3 % at the residence time of 23.5 min for the first MR, 18 min for the separator and 4.7 min for the second MR.

Acknowledgements

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