



Continuous production of biodiesel from high acid value oils in microstructured reactor by acid-catalyzed reactions

Peiyong Sun, Juan Sun, Jianfeng Yao, Lixiong Zhang*, Nanping Xu

State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing University of Technology, 5 Xin Mofan Road, Nanjing, Jiangsu 210009, PR China

ARTICLE INFO

Article history:

Received 25 November 2009

Received in revised form 9 January 2010

Accepted 7 April 2010

Keywords:

Biodiesel

Acid oil

High acid value oil

Microstructured reactor

ABSTRACT

Acid-catalyzed esterification and transesterification reactions, suitable for biodiesel production from high acid value oils, face a problem of long reaction time. In this study, we developed a two-step process for fast acid-catalyzed biodiesel production from high acid value oil in a microstructured reactor, which was assembled with an SIMM-V2 micromixer connected with a 0.6 mm i.d. stainless steel capillary. Esterification of oleic acid and transesterification of cottonseed oil with methanol were separately carried out to find suitable reaction conditions. The influences of the residence time, the methanol to acid/oil molar ratio, the catalyst concentration, the water/acid concentration and the reaction temperature were examined. The highest oleic acid conversion was obtained when esterification of oleic acid with methanol was carried out at 100 °C with the residence time of 5 min, while the highest yield of fatty acid methyl ester (FAME) was achieved when transesterification of cottonseed oil with methanol was conducted at 120 °C with the residence time of 20 min. Thereafter, a two-step process was developed based on the above reaction conditions with the first and second steps separately conducted under the esterification and transesterification reaction conditions. The results indicated that the acid value of the acid oil was reduced from 160 to 1.1 mg KOH/g with a methanol to acid molar ratio of 30, the H₂SO₄ concentration of 3 wt%, a residence time of 7 min at 100 °C in the first step. The final FAME yield reached 99.5% with a methanol to triglyceride molar ratio of 20, the H₂SO₄ concentration of 3 wt%, a residence time of 5 min at 120 °C in the second step. Therefore, biodiesel production from high acid value oil can be continuously achieved at high yields by acid-catalyzed transesterification in microstructured reactors with total reaction times of less than 15 min.

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1. Introduction

With the depletion of the fossil fuel, renewable energy sources have been developed rapidly worldwide in the last decade. Biodiesel, also named as fatty acid methyl ester (FAME), is an alternative fuel obtained from renewable biological sources by the transesterification of triglycerides (TGs) or the esterification of free fatty acids (FFAs) with methanol [1,2]. Compared to petroleum diesel, biodiesel has unique advantages, such as renewable, biodegradable, and non-toxic [3].

Biodiesel production can be carried out by alkali, acid, or enzyme-catalyzed processes or in catalyst-free supercritical methanol. Homogeneous alkali catalysts (CH₃ONa, NaOH or KOH) [4,5] are commonly used in conventional biodiesel production by using refined vegetable oils because of mild reaction conditions in the alkali-catalyzed process. As the price of virgin vegetable oils is

normally high, cheap biodiesel feedstocks, such as waste cooking oil [6–8] and acid oil [9,10], are used to produce cost-competitive biodiesel because the feedstock cost accounts for about 75% of the total estimated production cost of biodiesel [3,11]. However, the high amounts of FFA in these cheap biodiesel feedstocks make them unsuitable for base-catalyzed transesterification because of the formation of soap between FFA and base catalysts, such as NaOH and KOH. Soap renders biodiesel purification and catalyst removal even more challenge due to the formation of a stable emulsion [12]. Although enzyme-catalyzed process is suitable for using high acid value feedstock and exhibits some advantages, such as mild reaction condition and easy recovery of the final product, high production cost and short life time of enzyme restrict its wide application in biodiesel production [13]. Similarly, the strict demand of equipment and high cost of production process limit wide application of biodiesel production in the catalyst-free supercritical methanol [14]. Therefore, acid-catalyzed process might be a good choice for biodiesel production from high acid value oils because it is insensitive to FFAs in the feedstock [15] and can simultaneously transform FFAs and TGs to FAME by esterification (Eq. (1))

* Corresponding author.

E-mail address: lixiongzhang@yahoo.com (L. Zhang).

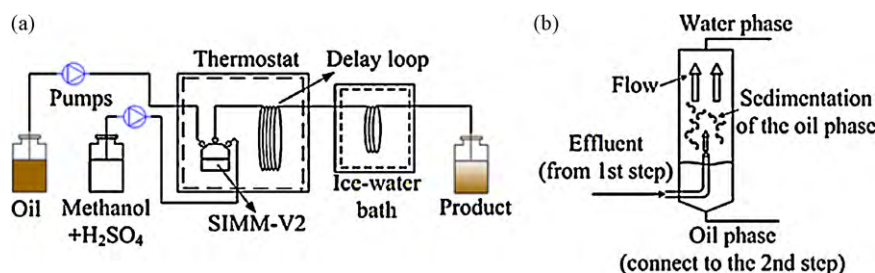
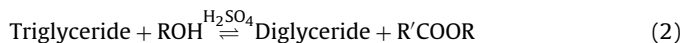
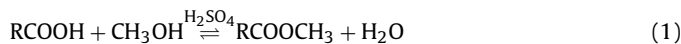


Fig. 1. (a) Scheme of the microstructured reactor system for esterification and transesterification and (b) scheme of the laminar flow separator.

and transesterification (Eqs. (2)–(4)), respectively [9,16,17]:



Acid-catalyzed process can be carried out with both homogeneous and heterogeneous acids as the catalysts. Many heterogeneous catalysts, such as acid zeolites, heteropolyacids, sulfated zirconia and mixed metal oxides, ion-exchange resins and immobilized sulfonic acids, double-metal cyanide complexes [18], have been investigated because they are environmentally-friendly and easy to be recycled. However, they exhibited some disadvantages, such as harsh reaction conditions and limited life [19]. For this reasons, homogeneous catalysts, such as sulfuric acid [20], have been employed in biodiesel production from high acid value oils in both research and industry [20–24]. Haas et al. [9] prepared FAME using acid oil with 59.3 wt% FFA by acid-catalyzed transesterification at 65 °C for 26 h with H₂SO₄ (the H₂SO₄ to oil molar ratio of 1.5:1) and methanol (the methanol to oil molar ratio of 15:1). The resulting products were consisted of FFA (3.2 wt%), triacylglycerol (1.3 wt%) and diacylglycerol (0.2 wt%). Zullaikah et al. [22] employed a two-step acid-catalyzed process for the efficient conversion of rice bran oil (FFA: 6–25 wt%) into fatty acid methyl ester. After reaction at 60 °C in the first step and 100 °C at the second step with a total reaction time of 8 h, about 98% of FAME in the product can be obtained. Although a two-step acid-base catalyzed process was developed to shorten the total reaction time [25,26], the product in the first acid-catalyzed step has to be washed to remove the acid catalyst before it can be used as the feedstock for the second base-catalyzed step. Thereby, long reaction time and high catalyst concentration should be applied in the acid-catalyzed process for biodiesel production since the acid-catalyzed transesterification process is approximately 4000 times slower than the homogeneous alkali-catalyzed reaction [16]. Thus it has been largely ignored [19].

Recently, there are some reports on alkali-catalyzed transesterification for biodiesel production [27–30] and esterification of acids with alcohols [31,32] in microstructured reactors. The results indicated that the reaction time could be significantly reduced. It is quite possible to prepare biodiesel in a short time by using microstructured reactors via esterification of FFA and transesterification of TG with methanol. In this study, we examined two-step sulfuric acid-catalyzed process using acid oil, a by-product of vegetable oil refinery, as the raw material in a microstructured reactor for biodiesel production. The esterification of oleic acid and the transesterification of cottonseed oil with methanol were investigated as the model reactions. The influences of methanol to FFA or oil molar ratios, residence times, catalyst concentrations, reaction temperatures, and water contents on biodiesel production were examined. Based on these reaction results, an acid-catalyzed two-step process was then developed with acid oil as the feedstock.

2. Experimental

2.1. Materials

Acid oil in reddish brown color was collected from the local market. Its average molecular weight is 420 g/mol, and the acid value is 160 mg KOH/g. Cottonseed oil with an acid value of 1.65 mg KOH/g was purchased from the local market. Methanol and ethanol (purity: ≥99.5%), potassium hydroxide, ethylether, sulfuric acid (AR grade) and oleic acid (CP grade) were supplied by Shanghai Chemical Reagent Co. Ltd. n-Hexane (HPLC grade) was purchased from Shandong Yuwang Co. Ltd. The acid value of oleic acid is 201.2 mg KOH/g.

2.2. Esterification of oleic acid and transesterification of cottonseed oil

Both the esterification and transesterification reactions were carried out in a microstructured reactor assembled with a micromixer (SIMM-V2, IMM, Germany) and connected with 0.6 mm i.d. stainless steel capillary as the delay loop. The reactor was immersed in a thermostat. Since the reaction was carried out at temperatures higher than the boiling point of methanol (64.5 °C), a 1.2 mm i.d. tube with a length of 1 m was connected to the outlet of the delay loop and was immersed in an ice-water bath to condense the methanol vapor and terminate the reaction (Fig. 1(a)). During the reaction, the methanol with a specified amount of sulfuric acid previously dissolved in and oleic acid (or cottonseed oil) were separately fed by two HPLC pumps (Knauer K501, Germany) into the micromixer. The methanol to oleic acid (or cottonseed oil) molar ratio was changed by adjusting the flow rates of the two feedings. The total flow rate of methanol–sulfuric acid phase and oil phase was 0.2 ml/min, and the residence times were adjusted by changing the length of the delay loop. Effluent was collected at the outlet of the cooling tube. At reaction temperatures of 65–120 °C and a total flow rate of 0.2 mL/min, the maximum pressure value shown on the HPLC pump was 1.8 MPa. Under such circumstances, the boiling point of methanol inside the 0.6 mm i.d. capillary was 160 °C, as calculated by Antoine equation. Thus, methanol in the delay loop was incompletely vaporized, resulting in three-phase (methanol vapor, oil and liquid methanol) flow therein [33]. Consequently, the effluent came out of the cooling tube with pulse at an interval of ca. 10 s. For esterification reactions, the effluent was automatically separated to water phase at the top and oil phase at the bottom. After separated from the water phase, the oil phase was treated by evaporating to remove the methanol and washing with water. Afterwards, it was ready for analysis by titration. For transesterification reactions, the effluent was automatically separated to oil phase at the top and glycerol phase at the bottom. After separated from the glycerol phase, the oil phase was treated by evaporating to remove the methanol and washing with water. Afterwards, it was ready for analysis by gas chromatograph.

2.3. Biodiesel production from acid oil by a two-step process

Biodiesel production from acid oil was also conducted in the reaction system shown in Fig. 1 by a two-step process. In the first step, the methanol with a specified amount of sulfuric acid previously dissolved in and the acid oil were separately fed by the two pumps into the micromixer. The effluent after the reaction was collected in a laminar flow separator shown in Fig. 1(b) [34], in which the effluent was automatically and quickly separated to the water phase at the top and the oil phase at the bottom. The oil phase in the separator was directly used as the feedstock in the second step and was fed into the reactor for transesterification through a tube at the bottom of the separator by a pump. Since the oil phase contained small amount of sulfuric acid and methanol, their contents were also analyzed and the results were used to calculate the amount of methanol and sulfuric acid which would be fed into the reactor for transesterification by another pump. No obvious phase separation could be observed in the reaction product. Thus, it was just treated by evaporating to remove the methanol and washing with water for purification and analysis.

2.4. Analyses

The oleic acid conversion in the esterification and the FFA conversion in the two-step process were analyzed by titration with a 0.05 mol/L KOH solution and phenolphthalein as an indicator. A weighted amount of the sample was dissolved in ethanol and ethylether to make titration analyses (The mixed solvent of ethanol and ethyl ester was used for better dissolving of acid oil with free fatty acid and triglyceride or fatty acid methyl ester). The acid value was calculated using the following Eq. (5) with the amount of KOH consumed:

$$AV = \frac{V \times c \times 56.1}{m} \quad (5)$$

where AV is the acid value of the sample, V is the volume of the KOH solution of the titration (mL), c is the concentration of the KOH solution (mol/L), m is the weight of the sample (g), and 56.1 is the molecular weight of KOH.

The oleic acid conversion and the FFA conversion were calculated by using the following Eq. (6):

$$X(\%) = \left(1 - \frac{AV_2}{AV_1}\right) \times 100 \quad (6)$$

where X is the FFA conversion, AV₁ is the initial acid value of the mixture and AV₂ is the acid value of mixture after reaction.

The composition of the methyl esters was analyzed by a gas chromatograph (Agilent 6890N) equipped with a flame ionization detector (FID), a 7683B auto-injector, a cool on-column injector system and an Ultra-Alloy-HT1 column (Frontier, 10 m × 0.53 mm × 0.15 μm). The oven temperature was started at 70 °C for 1 min, then increased to 160 °C at a rate of 15 °C/min, to 260 °C at a rate of 7 °C/min, to 380 °C at a rate of 5 °C/min, and held at this temperature for 5 min. The FID temperature was set at 380 °C and the injector temperature was tracked to the column temperature. About 1 μl of the sample diluted with hexane was injected into the column.

3. Results and discussion

3.1. Esterification process with oleic acid

The esterification reactions of oleic acid and methanol were first conducted in the microstructured reactor with the H₂SO₄ concentrations of 1–5%, the methanol to oleic acid molar ratios of 10–50 and the residence time of 5 min at 100 °C. Fig. 2 shows the reac-

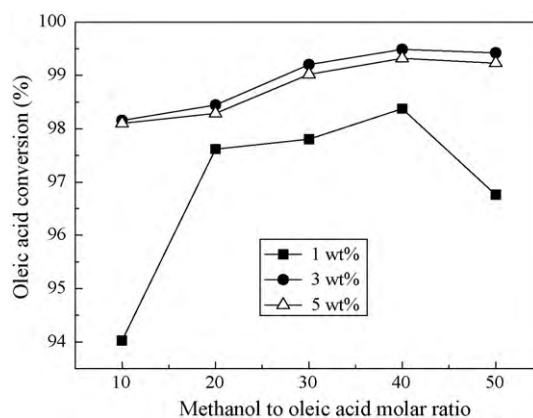


Fig. 2. Oleic acid conversions at different methanol to oleic acid molar ratios with the catalyst concentrations of 1, 3 and 5 wt% at 100 °C in 5 min.

tion results. The oleic acid conversion exhibited a 1.5% increment with the methanol to oleic acid molar ratio increased from 10 to 50 at the H₂SO₄ concentrations of 3 and 5 wt%. Meanwhile, the oleic acid conversion was slightly higher at the H₂SO₄ concentration of 3 wt%. Zheng et al. [20] also reported similar results, in which 2.5 mol% concentration of H₂SO₄ resulted in higher waste cooking oil conversion than that of 3.5 mol%. At the catalyst concentration of 1 wt%, the oleic acid conversion increased firstly with increase in the methanol to oleic acid molar ratio from 10 to 40, and then decreased with further increase in the methanol to oleic acid molar ratio to 50. This might be ascribed to the reduction of the catalyst concentration at low sulfuric acid concentration [35] and too high methanol content. The highest oleic acid conversion of 99.5% was obtained at the catalyst concentration of 3 wt% and the methanol to oleic acid molar ratio of 40.

Effects of reaction temperatures on oleic acid conversion was then examined with the catalyst concentration of 3 wt% and the methanol to oleic acid molar ratio of 30 at 60–110 °C (Fig. 3). The oleic acid conversion increased when the reaction temperature increased from 60 to 100 °C. With the reaction temperature further increased to 110 °C, the oleic acid conversion had no obvious change. This might be ascribed to the endothermic feature of the esterification reaction.

The effect of the residence time was also examined with the catalyst concentration of 3 wt% and the methanol to oleic acid molar ratio of 30 at 100 °C. The residence time was increased from 5 to 10 and 13 min, the oleic acid conversion was almost kept at 99%, indicating no obvious effect of the residence time on the reaction. This might result from the good miscibility between oleic acid and methanol.

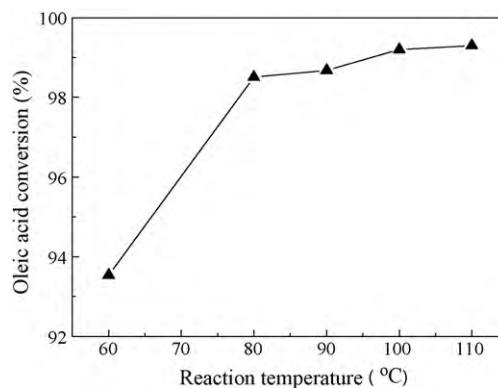


Fig. 3. Oleic acid conversions at different reaction temperatures with a methanol to oleic acid molar ratio of 30 and a catalyst concentration of 3 wt% in 5 min.

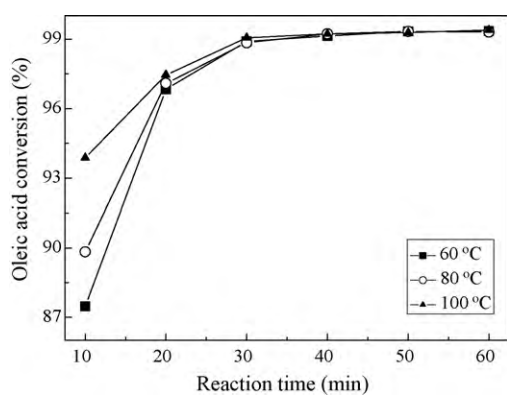


Fig. 4. Oleic acid conversions at different residence times with a methanol to oleic acid molar ratio of 30 and sulfuric acid concentration of 3 wt% at 60, 80, and 100 °C in a batch reactor.

For comparison, the esterification reactions were carried out in a three-neck flask with a methanol to oleic acid molar ratio of 30 and a sulfuric acid concentration of 3 wt% at 60, 80 and 100 °C for 60 min. The results are presented in Fig. 4. The oleic acid conversions were 80.5, 89.8 and 93.9% after 10 min at 60, 80 and 100 °C, respectively. They increased rapidly to about 97% with the extension of the reaction time to 30 min. Further increase in reaction time did not result in obvious change of the oleic acid conversion. The same trend was also observed by Marchetti et al. in their study of acid-catalyzed esterification of FFAs with the presence of TGs [36]. Thus, shorter reaction time was needed in microstructured reactors than in batch reactors to obtain the same acid conversion.

In order to clarify the influence of water content in oleic acid on the oleic acid conversion, 0.01, 0.5, 1, 2, and 5 wt% of distilled waters were added to the oleic acid. The esterifications were conducted at 100 °C, a methanol to acid molar ratio of 30 and a catalyst concentration of 3 wt% in 5 min. The results were shown in Table 1. The oleic acid conversion was reduced significantly from 99.1 to 10.4% with the water content increased from 0.01 to 5 wt%, similar to the results in sulfuric acid catalyzed esterification of acetic acid with methanol [37]. It can be ascribed to the equilibrium behavior of the esterification reaction and reduction of the catalyst concentration at high water content, since more water can lead to movement of the reaction equilibrium to the reverse direction and loss in acid strength of catalytic protons [16,37].

3.2. Transesterification with cottonseed oil

The transesterification reactions of cottonseed oil with methanol were first conducted in the microreactor with the H₂SO₄ concentrations of 1–6 wt%, the methanol to oleic acid molar ratio of 50, and the residence time of 20 min at different temperatures. Fig. 5 shows the reaction results. Apparently, the FAME yield increased significantly with elevation of the reaction temperature from 65 to 120 °C, suggesting higher reaction temperature favors the acid-catalyzed transesterification reaction. On the other hand,

Table 1
Effect of water content on oleic acid conversion.

Water content (%)	Oleic acid conversion (%)
0.01	99.1
0.5	90.3
1	75.4
2	55.8
5	10.4

Reactions were carried out with a methanol to oleic acid molar ratio of 30, a catalyst concentration of 3 wt% at 100 °C in 5 min.

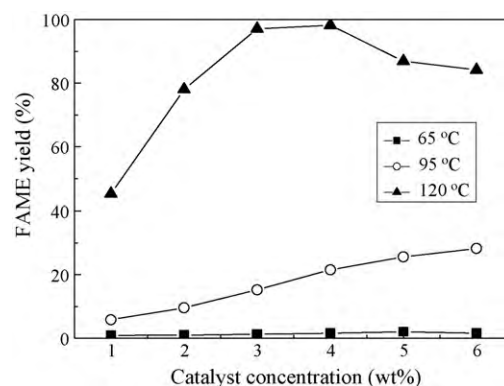


Fig. 5. FAME yields at different catalyst concentrations with a methanol to oil molar ratio of 50 at 65, 95, and 120 °C in 20 min.

the FAME yield increased with increase in the catalyst concentration in the range of 1–6 wt% at 65 and 95 °C. But it increased first with increasing catalyst concentration from 1 to 3 wt% to a maximum at catalyst concentrations of 3–4 wt%, and then slightly decreased at 120 °C. This was quite possibly resulted from carbonization or polymerization at 120 °C with high sulfuric acid content. Increase in darkness color in the collections under this reaction condition can be observed. Similar phenomenon was also reported by several groups [24,38,39] in their work on biodiesel preparation using H₂SO₄ as the catalyst and refined soybean oil, high acid value palm fatty acid distillate and waste cooking oil as the raw materials at reaction temperatures of 70–200 °C. The above result suggested that 3–4 wt% was the suitable H₂SO₄ concentration at this reaction temperature.

Fig. 6 illustrates the effect of the methanol to oil molar ratio on the FAME yield. The reactions were carried out at 120 °C with the residence time of 20 min and the catalyst concentrations of 3 wt%. Obviously, the FAME yield increased with the increase in methanol to oil molar ratio from 10 to 50 to a stable value of 97.1%, indicating that a large amount of methanol favors the forward transesterification reaction. These results were close to those reported by Crabbe et al. [40]. They obtained a FAME yield of about 97% in biodiesel production from palm oil (AV: 6.9 mg KOH/g) with a H₂SO₄ concentration of 5 wt% and a methanol to oil molar ratio of 40 at 95 °C in 9 h. But Zheng et al. [20] achieved a 99% FAME yield in acid-catalyzed biodiesel production from waste cooking oil with a FFA content of 6 wt% at 70 °C for 4 h with a methanol to oil molar ratio of as high as 250.

Fig. 7 shows the effect of the residence time on the FAME yield. The reactions were carried out at 120 °C with the catalyst concen-

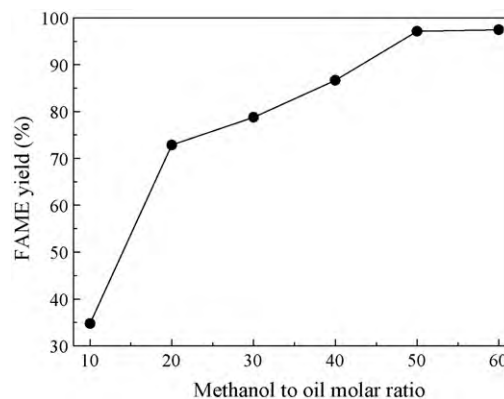


Fig. 6. FAME yields at different methanol to oil molar ratios with a catalyst concentration of 3 wt% at 120 °C in 20 min.

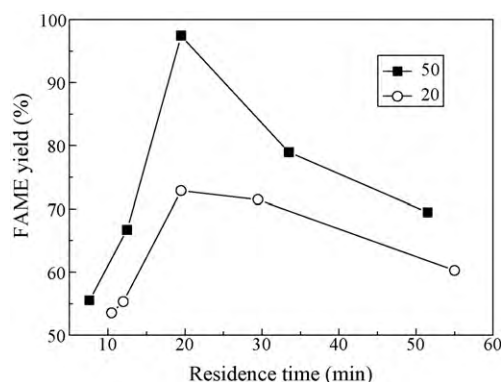


Fig. 7. FAME yields at different residence times with methanol to oil molar ratios of 20 and 50 and a catalyst concentration of 3 wt% at 120 °C.

tration of 3 wt% and the methanol to oil molar ratios of 20 and 50. We can see that the FAME yield reached a maximum when the residence time was prolonged from 7.6 to 20 min, and then decreased with further prolongation of the residence time. Highest FAME yields of 72.9 and 97.5% were, respectively, obtained at the residence time of 20 min when the methanol to oil molar ratios were 20 and 50. This was resulted from reversible reaction of transesterification at long residence times, leading to increase in the amount of diglyceride and monoglyceride in the reaction products, which were detected by GC. Furthermore, some FAME could be carbonized or polymerized with the presence of sulfuric acid when they were exposed at 120 °C for too long time [24,38,39], thus resulting in decrease in the FAME yield. In fact, we observed increase in darkness color in the collections at longer residence times. The time is much shorter than that the reported 19 h to achieve a 99% FAME yield during H_2SO_4 -catalyzed transesterification of soybean oil with a methanol to oil molar ratio of 9 and a H_2SO_4 concentration of 1 wt% at 120 °C [41]. These results indicated that the transesterification time can be significantly shortened in microstructured reactors.

The effect of the water content on the FAME yield was also examined by purposely adding 1–5 wt% distilled water in cottonseed oil. Fig. 8 shows the reaction results carried out at 120 °C with the methanol to oil molar ratio of 40, the catalyst concentration of 3% and the residence time of 20 min. The FAME yield decreased sharply as the water content was increased from 1 to 3%. Addition of 5 wt% water resulted in decrease in the FAME yield to less than 20%. Similar results had been reported by Canakci and Gerpen [26] and Kusdiana and Saka [42] by sulfuric acid-catalyzed transesterification of grease and rapeseed oil with methanol in batch reactors.

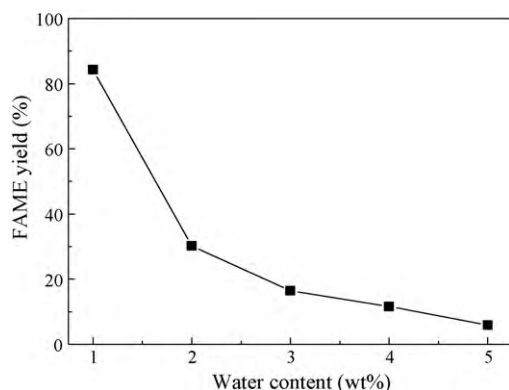


Fig. 8. FAME yields at different water contents with a methanol to oil molar ratio of 40 and a catalyst concentration of 3 wt% at 120 °C in 20 min.

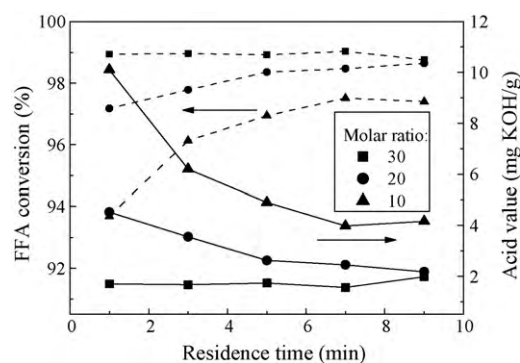


Fig. 9. FFA conversions and acid values at different residence times with methanol to FFA molar ratios of 10, 20 and 30 and H_2SO_4 concentration of 3 wt% at 100 °C (solid lines: acid value; dashed lines: FFA conversion).

3.3. Biodiesel production from acid oil by a two-step process

Based on the above results, we know that esterification of oleic acid with methanol was suitably carried out at 100 °C with the residence time of 5 min, while transesterification of cottonseed oil with methanol was best conducted at 120 °C with the residence time of 20 min. Apparently, the rate of transesterification is slower than that of esterification in microstructured reactors. Warabi et al. observed similar results in batch reactors [43]. Thereby, the two reactions could not be carried out under the same reaction condition. Thus, we developed a two-step process for biodiesel production from acid oil. The first step was conducted at the optimum esterification reaction condition while the second step at the optimum transesterification reaction condition. Since the reactions were carried out in a continuous mode, the two-step process could be operated also in a continuous mode.

Reactions were first conducted in the microstructured reactor using the acid oil at 100 °C with the H_2SO_4 concentration of 3 wt%. Fig. 9 shows the reaction results with the methanol to FFA molar ratios of 10, 20 and 30 and the residence times in the range of 1–9 min. At a fixed methanol to FFA molar ratio, the FFA conversion increased with the extension of the residence time to a maximum at 7 min. At the same residence time, the FFA conversion increased with increase in the methanol to FFA molar ratio. The highest FFA conversion of 99.0% and the lowest acid value of acid oil of 1.6 mg KOH/g were obtained at the residence time of 7 min with a methanol to FFA molar ratio of 30.

The effects of the reaction temperature and the H_2SO_4 concentration were also examined with the methanol to FFA molar ratio of 30 and the residence time of 7 min, as shown in Fig. 10. We can see that the FFA conversion increased with increase in the reac-

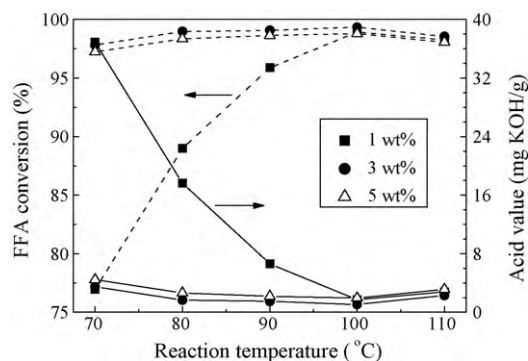


Fig. 10. FFA conversions and acid values at different reaction temperatures with a methanol to FFA molar ratio of 30 in 7 min (solid lines: acid value; dashed lines: FFA conversion).

Table 2

Effect of different methanol to oil molar ratios on FAME yields.

Molar ratio	FAME yield (%)
6	96.1
10	99.3
20	99.9
30	99.7
40	95.4

Reactions were carried out with the H₂SO₄ concentration of 3 wt% and the residence time at 120 °C of 5 min.

tion temperature and to a maximum at 100 °C. On the other hand, higher FFA conversion was obtained at the catalyst concentration of 3 wt% than at 1 and 5 wt%. These results are the same as those reported in Section 3.1. Thus, the optimum reaction condition for the first step was the methanol to oil molar ratio of 30, the sulfuric acid concentration of 3 wt% at 100 °C with the residence time of 7 min. Under such circumstance, the acid value of the acid oil could be reduced to 1.1 mg KOH/g.

Reactions were then conducted in the microstructured reactor using the product of the first step (AV: 1.1 mg KOH/g) at 120 °C with the H₂SO₄ concentration of 3 wt% and the residence time of 5 min. Shorter residence time was chosen here than in transesterification of cottonseed oil because the feedstock from the first step contained about 75 wt% FAME, which enhanced the solubility between TG and methanol. Table 2 lists the reaction results with the methanol to TG molar ratios of 6–40. We can see that the FAME yield increased from 96.1 to 99.9% with increase in the methanol to TG molar ratio from 6 to 20. Further increase in the methanol to TG molar ratio to 30 and 40 resulted in decrease in the FAME yield. These results indicated that less methanol to TG molar ratio and shorter residence time were used in the second step than the transesterification of cottonseed oil with methanol. This might be ascribed to the existing large amount of FAME formed by esterification of FFA with methanol, which increases the solubility of TG in methanol.

4. Conclusion

Acid oil with an acid value of as high as 160 mg KOH/g was used to produce biodiesel in a microstructured reactor assembled with a micromixer and a capillary delay loop by a two-step acid-catalyzed process. Esterification of oleic acid and transesterification of cottonseed oil with methanol were examined as the model reactions to explore the optimum condition for the two-step process. For the esterification of oleic acid with methanol, the oleic acid conversion increased with increase in the reaction temperature and the methanol to oleic acid molar ratio. The residence time had no obvious effect on the conversion since good miscibility between oleic acid and methanol. The water content should be less than 0.5 wt% to get a conversion of more than 90%. For the transesterification reaction, the FAME yield increased with increase in the reaction temperature and the methanol to oil molar ratio and exhibited a maximum at a residence time of 20 min. Based on the reaction conditions of esterification and transesterification reactions, the two-step process was developed to produce biodiesel from acid oil. The acid value of the acid oil was decreased to 1.1 mg KOH/g with a methanol to FFA molar ratio of 30 and a sulfuric acid concentration of 3 wt% at 100 °C for 7 min in the first step, and the final FAME yield reached 99.5% after the second step with a methanol to TG molar ratio of 20 and a sulfuric acid concentration of 3 wt% at 120 °C for 5 min. Thus, biodiesel production from acid oil could be completed in tens of minute by using the microstructured reactors.

Acknowledgement

This work is supported by the National Natural Science Foundation of China (No. 20733009).

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