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Investigation of Factors Affect Biodiesel Production in Microreactor with T-Mixer

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Abstract. Biodiesel is a promising alternative fuel due to the shortness of fossil fuels. Microreactor was utilized to overcome numerous issues of the traditional methods for biodiesel production. The transesterification of sunflower oil using sodium hydroxide, as a catalyst, in a microreactor as a continuous reactor was investigated. Investigation of some factors which influence biodiesel production in microreactor was done. A comparison between different mixer's diameters was studied over varied conditions. The effect of some reaction factors (including; molar ratios of methanol to oil, temperature and the residence time) on Fatty Acid Methyl Ester (FAME) transesterification reaction were studied using deferent T-shaped mixers. The maximum percentage of methyl esters for sunflower oil using 3% NaOH was obtained at 60℃. The T-shaped joint with 0.05in internal diameter recorded the highest conversion ratio of 97% within 80 s using 9:1 molar ratio of methanol to oil at the optimum conditions.

Keywords: Biodiesel production, transestrification, microreactor, biofuels.

1. Introduction

There is a growing enthusiasm in using renewable energies to reduce greenhouse effect as well as to reduce the dependence on fossil fuels [1]. These days, when fossil fuel recourses are diminishing quickly, biodiesel fuels are turning out to be more intriguing. Being environmentally beneficial, biodegradable, non-toxic and with low pollution emission makes biodiesel interesting for consumption [2]-[4]. Different techniques have been accounted for biodiesel production such as micro-emulsification, pyrolysis and transesterification [5]. Main problems of this traditional approach in biodiesel production are long residence time, high operation costs and energy consumption and low efficiency. To defeat these issues new technologies for process intensification are being developed. Main features of these processes are enhanced reaction rate, reduced molar ratio of alcohol to oil, and low energy input realized by intensification of mass and heat transfer [6].

With a specific end goal to expand the conversion efficiency of biodiesel under continuous operation, microreactor can be utilized. Microreactor as a continuous reactor has numerous advantages, for example, high volume/surface ratio, higher transport (e.g., heat and mass transfer) rates, short diffusion distance, simplify process control and so on used in the industrial process [7], [8]. Many methods were engaged to design the experiments and inquiry about optimum condition in this process [9]-[12].Sun et al. [13] used a microstructure reactor with a 0.6 mm stainless steel capillary diameter for transesterification of cotton seed oil with methanol. They studied many parameters on transesterification and obtained the maximum yield of methyl ester at 120℃ with a residence time of 20 min. In another work by Sun et al. [14], it was shown that the obtained yield of methyl ester in micro-structured reactors could be get to 94% at the residence time of less than 1 min. The experiments took place with two different kinds of stainless steel capillary tube and a PTFE tube that connected to a micro-mixer.

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In another study, transesterification reaction of sunflower oil with ethanol in microreactors was investigated by Richard et al. [15]. They anticipated a kinetics model under various ethanol to oil molar ratios and validated it with their measured values. In the present study, a microreactor with T-shaped junction was used, as continuous flow reactor, for transesterification of sunflower oil with methanol in presence of NaOH. The influences the some process factors such as; molar ratio of methanol to oil, residence time, T-mixer diameter and reaction temperature on transesterification of triglycerides was investigated.

2. Experimental

Methanol (99.9%), sodium hydroxide, and acetic acid were obtained from Alpha Chemical Company. Sunflower oil was purchased from a local market and employed as feed for transesterification reactions. The molecular weight of the sunflower oil, as determined from the saponification and acid values, was 876.6. All chemicals were used as purchased. Stainless steel microtube with inner diameter of 1.0 mm and 1 m length was used as microreactor.

A schematic illustration of the experimental setup is shown in Fig. 1. A 3 wt % amount of NaOH was dissolved in methanol. Syringe pumps were used to feed the liquids. The molar ratios of methanol to sunflower oil were adjusted from 6 to 22 by changing the volumetric flow rates. Methanol/oil molar ratios correspond to methanol/oil volume ratios from 0.273 to 1.0, respectively. The total liquid flow rates of the methanol solution and oil ranged from 0.6 to 2 ml/min. Sunflower oil and the methanol containing NaOH came into a two separated preheaters which made from the same stainless steel microtubes with inner diameter of 1.0 mm but 0.17 cm length then the two fluids came into contact at the T-shaped joint and then flowed into the microtube, which was immersed in an water bath maintained at a prescribed temperature. The product was collected at the outlet of the microtube. The reaction termination was done by addition of acetic acid solution (20%).

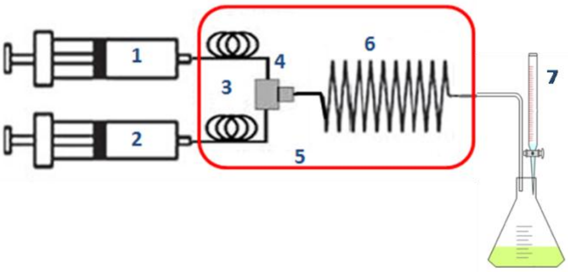
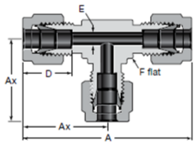
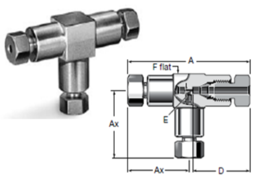


Fig. 1: Experimental setups of microtube reactor for transesterification:
(1) Syringe pump for methanol; (2) Syringe pump for sunflower oil; (3) Preheaters;
(4) T-shaped joint;(5) Water bath;(6) Microtube reactor;
(7) An acetic acid

Table 1: Specifications of the micromixers used in this work.

No.	Scheme	Tube OD	Dimensions				
			A	Ax	D	E	F
Dimensions, in.							
T1		1/16	1.40	0.70	0.34	0.05	3/8
T2		1/8	1.76	0.88	0.50	0.09	3/8
T3		1/16	1.32	0.66	0.61	0.013	3/8

The collected product was then centrifuged at 5000 rpm for 10 min. The upper fatty acid methyl ester (FAME) layer was rinsed several times with distilled water to remove residual inorganic components. Then, 1 ml of the rinsed sample was diluted in 9 ml of methanol then it filtered by a syringe filter (0.45 μm) for analysis. The concentration of un-reacted oil that remained in the product was analyzed using a gas chromatograph GC 2010 plus (AOC-20i)

The continuous methanolysis of sunflower oil was carried out in microreactor which was assembled by combining three mixers with three different diameters. The specifications of the three continuous mixers used in this work are shown in Table 1. The T-mixers made from stainless steel from Swagelok Company.

3. Result and Discussion

3.1. Effect of Molar Ratio

The theoretical methanol to oil ratio is 3:1. However, higher molar ratio should be utilized to coercion the reaction to be completed because transesterification reaction cannot be achieved in that stoichiometric ratio. In this study, the molar ratio of methanol to oil was differed from 6 to 22. Fig. 2 demonstrates the impact of molar ratio of methanol to oil on percentage of methyl esters conversion. In this figure, every point is identified with mean percentage of methyl esters for all runs at the same molar ratio. The figure elucidates that the percentage of methyl esters increased almost linearly as the molar ratio of methanol increased from 6:1 to 9:1. However, extra enlarge in the molar ratio of methanol from 9:1 to 11:1 caused a slender decrease in the percentage of methyl esters. This behaviour might be a sign of that due to separation of glycerine and methyl ester, an extra molar ratio of methanol can decrease the percentage of produced methyl esters.

3.2. Effect of Reaction Temperature

Fig. 3 shows the influence of the temperature on percentage of methyl esters conversion. The experiment was conducted at variety of temperatures at two values for the residence time about 24s and 31.5s. In this figure, each point confirms the mean percentage of methyl esters for all runs at the same temperature. It should be denoted that at low temperature, the reaction rate was slow and with increasing temperature, the percentage of methyl esters extremely increased. It was found that the maximum percentage of methyl esters for sunflower oil using NaOH was achieved at 60℃. However, as far as the temperature of reaction is higher than the boiling point of methanol in normal pressure condition, further increase in temperature to 65℃ caused in the decrease in percentage of methyl esters. Besides, due to high content of FFA in oil, increase in reaction temperature accelerates the glycerides saponification by the alkaline catalyst.

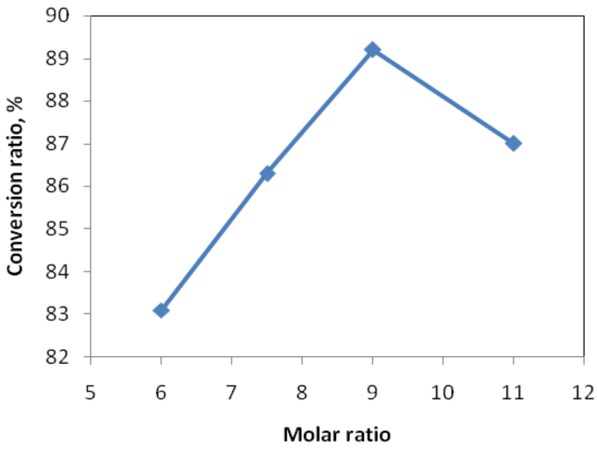


Fig. 2: Effect of molar ratio on conversion ratio.

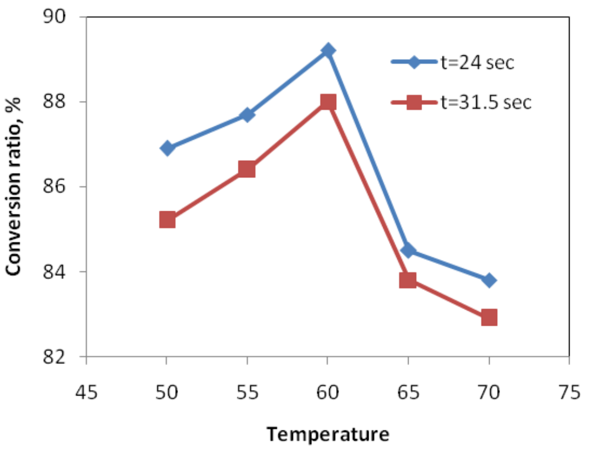


Fig. 3: Effect of temperature on conversion ratio.

3.3. Effect of the Flow Rate and the Residence Time

Because of the short diffusion distance and high transport rate, the reaction time in microreactor is very short. Fig. 4 shows the effect of various reactant residence times, which means different flow rates (the sum of flows oil and methanol), on the percentage of methyl esters conversion. The experiment was conducted at temperature of 60℃, NaOH concentration of 3 wt.% and the molar ratio (methanol/oil) of 9. The results designate that percentage of methyl esters conversion increased from 81.6% to 97 % when the residence time was increased from 24 to 80 s. The percentage of methyl esters conversion first increased extremely with increase in residence time from 24 to 47 s and after that increased slightly. The maximum value of the methyl ester attained almost 80 s and transesterification of oil is almost complete. It can be observed that, at residence time longer than 47 s, the percentage of methyl esters conversion did not change notably. Therefore, at the optimum condition with minimum residence time a high percentage of methyl esters were attained with the lowest biodiesel production cost.

At low flow rate, although the residence time of reactants in the reactor is adequate but a straight borderline between the two immiscible fluids is quite obvious [8]. This indicates a non-efficient mixing in this flow rate. It was found that despite of low residence time, because of efficient mixing in microreactor, the conversion percentage of methyl ester was almost high.

3.4. Effect of Mixer Diameter

To analyze the effect of the inner diameter and geometry of the mixer on the yield of FAEE the influences of flow rate and reaction time had to be eliminated. Therefore the results of the experiments T1, T2 and T3 at a residence time of 24 sec were done. These experimental points are characterized by the same reactor volume, flow rate and residence time. Differences in the FAEE yield should be caused by differences of the used mixer. The observed yields for experiment at a temperature of 60℃ are shown in Fig. 5. The increase of the yield is higher if the mixer shows lower micromixing efficiency. An increase of the yield of esters at the base catalyzed methanolysis of sunflower oil by using tube reactors with small diameters was reported by Sun et al. [16]. They observed the formation of a slug-flow during the reaction. A decrease of the tube diameter led to smaller slugs and therefore a higher interfacial area. A similar effect could influence the yield of the base catalyzed methanolysis. The T1 (T-shaped joint with 0.05in internal diameter) recorded the highest conversion ratio of 97% within 80 s using 9:1 molar ratio of methanol to oil at the optimum conditions.

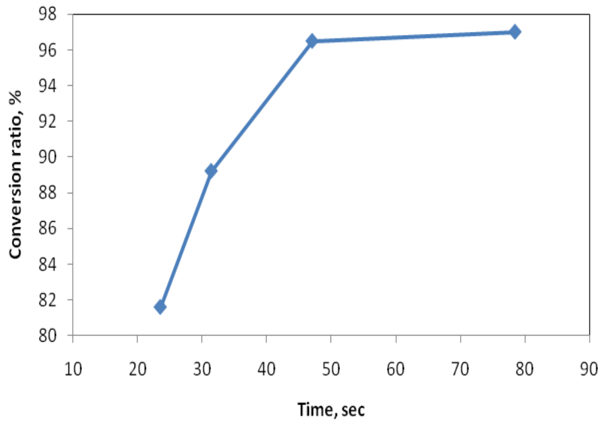


Fig. 4: Effect of residence time on conversion ratio.

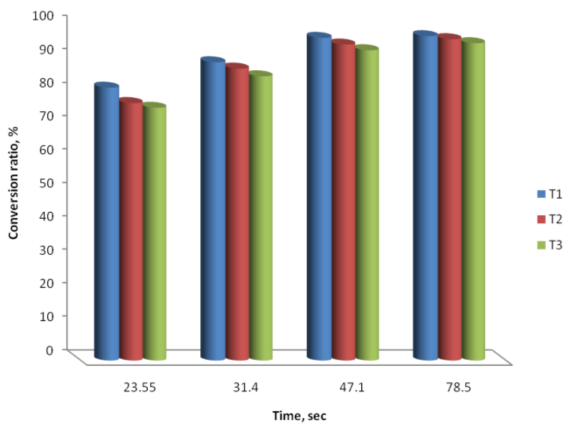


Fig. 5: Effect of the T-mixer on conversion ratio.

4. Conclusion

The continuous base catalyzed methanolysis of sunflower oil was done by T-mixers with three different diameters. The T1 (T-shaped joint with 0.05in internal diameter) recorded the highest conversion ratio of 97% within 80 s using 9:1 molar ratio of methanol to oil at the optimum conditions. It was shown that the yield of fatty acid ethyl esters depends strongly on mass transfer limitations. The mass transfer expanded with developing efficiency of micromixing. It was found that the maximum percentage of methyl esters for sunflower oil using NaOH was accomplished at 60℃.

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6. References

[1] Demirbas MF, Balat M. Recent advances on the production and utilization trends of bio-fuels: a global perspective. *Energy Energy Convers Manage* 2006;47(15):2371 – 81.

[2] Meher, L., Vidyasagar, D., Naik, S., Technical aspects of biodiesel production by transesterification: a review. *Renewable and Sustainable Energy Reviews* 2006;10, 248–268.

[3] Demirbas A. Comparison of transesterification methods for production of biodiesel from vegetable oils and fats. *Energy Convers Manage* 2008; 49:125 – 30.

[4] Stamenković, O.S., Veličković, A.V., Veljković, V.B., 2011. The production of biodiesel from vegetable oils by ethanolysis: current state and perspectives. *Fuel* 90, 3141–3155.

[5] Ma F, Hanna MA. Biodiesel production: a review. Bioresour Technol 1999;70:1 – 15.

[6] Stefan Schwarz, Ekaterina S. Borovinskaya, Wladimir Reschetilowski, Base catalyzed ethanolysis of soybean oil in microreactors:Experiments and kinetic modeling. *Chemical Engineering Science* 104 (2013) 610–618.

[7] Kumar V, Paraschivoiu M, Nigam KDP. Single-phase fluid flow and mixing in microchannels. *Chem Eng Sci* 2011; 66(7):1329 – 73.

[8] Masoud Rahimi, Babak Aghel, Mohammad Alitabar, Arash Sepahvand, Hamid Reza Ghasempour, Optimization of biodiesel production from soybean oil in a microreactor. *Energy Conversion and Management* 79 (2014) 599 – 605.

[9] Al-Dawody MF, Bhatti SK. Optimization strategies to reduce the biodiesel NOx effect in diesel engine with experimental verification. *Energy Convers Manage* 2013;68:96 – 104.

[10] Tashtoush GM, Al-Widyan MI, Al-Jarrah MM. Experimental study on evaluation and optimization of conversion of waste animal fat into biodiesel. *Energy Convers Manage* 2004;45(17):2697 – 711.

[11] Somnuk K, Smithmaitrie P, Prateepchaikul G. Optimization of continuous acidcatalyzed esterification for free fatty acids reduction in mixed crude palm oil using static mixer coupled with high-intensity ultrasonic irradiation. *Energy Convers Manage* 2013;68:193 – 9.

[12] Jaliliannosrati H, Amin NAS, Talebian-Kiakalaieh A, Noshadi I. Microwave assisted biodiesel production from Jatropha curcas L. seed by two-step in situ process: Optimization using response surface methodology. *Bioresour Technol* 2013;136:565 – 73.

[13] Sun P, Sun J, Yao J, Zhang L, Xu N. Continuous production of biodiesel from high acid value oils in microstructured reactor by acid-catalyzed reactions. *Chem Eng J* 2010; 162(1):364 – 70.

[14] Sun P, Wang B, Yao J, Zhang L, Xu N. Fast synthesis of biodiesel at high throughput in microstructured reactors. *Ind Eng Chem Res* 2009; 49:1259 – 64.

[15] Romain R, Sophie TR, Laurent P. Modelling the kinetics of transesterification reaction of sunflower oil with ethanol in microreactors. *Chem Eng Sci* 2013;87:258 – 69.

[16] Sun, J., Ju, J., Ji, L., Zhang, L., Xu, N.,. Synthesis of biodiesel in capillary microreactors. *Industrial and Engineering Chemistry Research* 2008; 47, 1398–1403.