

# Biodiesel Production by Countercurrent Flow Reactor in Supercritical Methanol

Ming-Tsai Liang<sup>1</sup>, Huang-Jhe Huang<sup>1</sup>, Xi-Ri, Lu<sup>1</sup>, Zu-Chien Liang<sup>2</sup>

<sup>1</sup> Dept. of Chem. Eng., I-Shou University, Kaohsiung, Taiwan 840, R.O.C.

<sup>2</sup> Asia Giant Eng. CO. LTD. Ta-Fa Industrial Park, Kaohsiung, Taiwan 830, R.O.C.

## Abstract

A continuous countercurrent flow reactor was set up to conduct transesterification of soybean oil in supercritical methanol. Methanol was firstly pumped into the flow reactor from the bottom to pressurize and to heat up the reactor followed by pumping soybean oil into the reactor from the top. Inside the reactor, the oil flowed down and reacted with the upflowed methanol to produce biodiesel. The transesterified oil was then discharged from the bottom of the reactor, and part of the unreacted oil and FAME was dissolved into the upflowed methanol and discharged from the top of the reactor. Both liquid effluents discharged from top and bottom of the reactor were vacuum dried to remove methanol, and prepared for GC analysis to find their content of FAME. It was found that the conversion of transesterification in oil phase was higher than that in fluid phase, and the conversion increased with temperature from 260 C to 320 C. Increasing the ratio of methanol to oil increases the recovery of FAME in fluid phase and decreases that in oil phase. As hexane was pre-mixed with methanol to act as cosolvent, the reaction conversion was decreased in both liquid and gas phases. This work demonstrated the feasibility of employing countercurrent flow reactor in transesterification of soybean oil and the reaction kinetics was also examined. This study shows that the countercurrent flow reactor is an alternative to the technology of biodiesel production.

## 1. INTRODUCTION

Recently, the production of biodiesel by transesterification of vegetable oils and animal fats in supercritical alcohols was widely studied [1-15]. It is recognized that conducting transesterification in supercritical state can prompt the reaction rate without adding catalysts and simplify the separation in downstream processes. In supercritical state, triglycerides reacted with methanol in one phase and it was found that the existence of water in the oils would not inhibit the transesterification [7]. In spite of the advantages of using supercritical alcohols, the experimental results from several studies showed that the reaction conditions were still far above the critical temperature and pressure of the pure methanol and ethanol. Decomposition and pyrolysis of the fatty acids may happen at such crucial condition. Researchers then

found that cosolvents, such as propane and carbon dioxide, could reduce the temperature and pressure and it can also decrease the capital cost and energy consumption [12, 13].

The production of fatty acids by the hydrolysis of triglycerides has been widely applied since 1940's. Among various processes, Colgate-Emery process was the continuous countercurrent hydrolysis process under high pressure. No catalysis was needed for the Colgate-Emery process. Oil and grease was preheated and pumped into the hydrolysis tower reactor from the bottom of the tower. Inside the reactor, the upflowed oil and grease will react with the downflowed water. The downflowed water will continuously remove the byproduct of glycol from the oil and grease and discharged from the top of the tower. The continuous removing glycol drove the transesterification toward the products. It was reported that the conversion rate can reach above 99.5% under the condition of 260 C and 50 bar.

In this study, we set up a countercurrent flow reactor to investigate the feasibility of applying Colgate-Emery process to the transesterification of soybean oil by methanol. Effects of temperature and feed ratio of methanol to oil on the conversion were also investigated. Effects of cosolvent on the transesterification was also examined by mixing hexane in methanol.

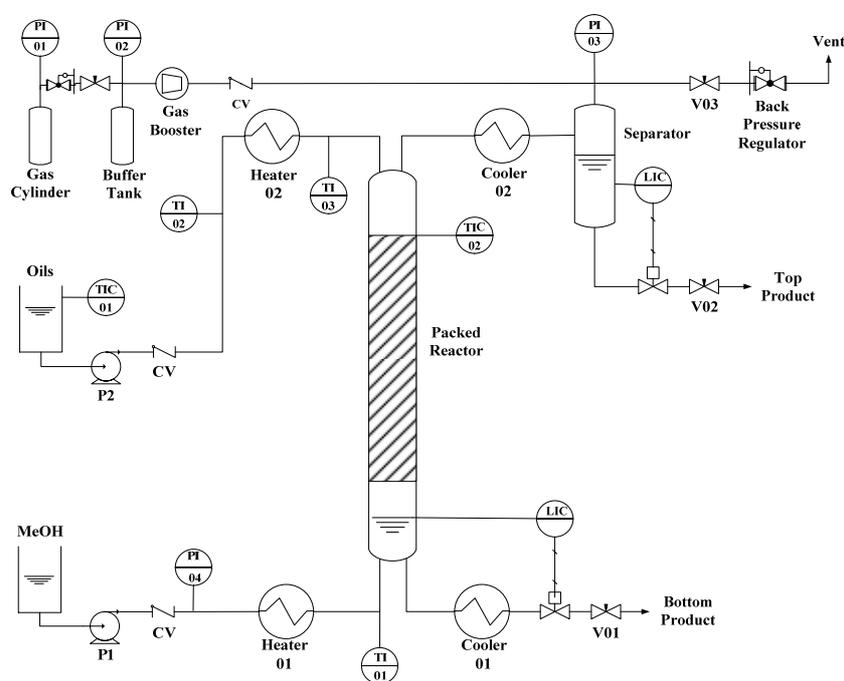


Fig. 1. The illustration of the countercurrent transesterification reactor

## 2. EXPERIMENTS AND MATERIALS

Refinery soybean oil was purchased from local supermarket. Methanol is

industrial grade with purity higher than 99.5 %. Fig. 1 illustrates the flow system for the transesterification. The flow reactor was made of 3/8" stainless tube with 38 cm in length. About 53 grams of stainless beads with 0.1 mm in diameter was packed inside the flow reactor. The void volume of the packed reactor was calculated as 4.198 ml. The flow reactor was installed in an electric furnace. Inside the furnace, two coiled tubes with 12 meters long of 1/8" tubes were also installed to pre-heat methanol and oil.

The flow system was firstly started by pumping methanol into the reactor. After methanol flowed into the separator, high pressure nitrogen was applied to pressurize the system followed by heating up the flow system. After temperature and pressure reached steady state, the oil pump was started and the liquid effluents discharged from the top and the bottom of the reactor were collected for analysis.

The collected liquid effluents from the top and the bottom were vacuum dried to remove methanol, and then submitted to GC analysis to find out their content of FAMES. GC (Hitachi E-500) equipped with a FID detector and a capillary column (Restek Co. RTX-65TG) was used to analyze the samples. In soybean oil there are four major free fatty acids i.e. C16:0, C18:0, C18:1, and C18:2, therefore the total weight of these four FAMES were assumed as equal to the total FAME. On GC analysis, methyl ester of C17:0 was added as the internal standard to calculate the weight of each FAME. Part of the vacuum dried liquid effluents were also further transesterified by mixing them with methanol in which tetramethyl ammonium hydroxide was pre-dissolved as catalyst. The untransesterified glycerides left in the mixture were then totally transesterified within half hour with supersonic stirring. Methanol and catalyst was removed by decant and washed by water followed by vacuum dried to remove water, and then submitted to GC analysis again. The total FAME in the effluents was then found, and the conversion was calculated according to the following equation.

$$x = \frac{\sum_{FAME} w_i}{\sum_{FAME} w_i^t} \quad (1)$$

where  $w_i$  are the weight fraction of the four major four FAMES in effluents, and  $w_i^t$  are those after total transesterification.

In order to find the residence time for the reaction, the oil density at high temperature and pressure was assumed as equal to that of oil in ambient condition, and the fluid phase density was assumed as pure methanol in its supercritical state and found from thermodynamic tables [16].

### 3. RESULTS AND DISCUSSION

### 3.1 Effects of Temperature

Both samples collected from the top and the bottom were analyzed by GC to find their content of FAME, and the conversion of the transesterification was obtained according to equation (1). In order to study the effect of residence time, flow rates of methanol and oil were simultaneously changed with constant ratio. As shown in Figs. 2 and 3, it was observed that the conversion increased with residence time for both top and bottom products. The slope of the conversion to residence time represented the reaction rate constant, if pseudo-first order reaction was assumed. Increasing temperature from 260 to 320 C will also increase the reaction rate constant. The solid lines in Figs. 2 and 3 are the regression fitting, and Fig. 4 illustrates the Arrhenius plot for both downflowed oil phase and up-flowed fluid phase. The linear correlations were found as

$$\begin{cases} \ln k^l = -\frac{8151}{T} + 10.561 \\ \ln k^f = -\frac{6003}{T} + 5.806 \end{cases} \quad (2)$$

Obviously, the reaction rate in oil phase is higher than that in fluid phase. Also, the reaction in oil phase has higher activation energy. Because the intercept of the Arrhenius equation represented the extent of association of the complex, it is presumed that the association of the transition complex in oil phase is larger in extent than that in fluid phase.

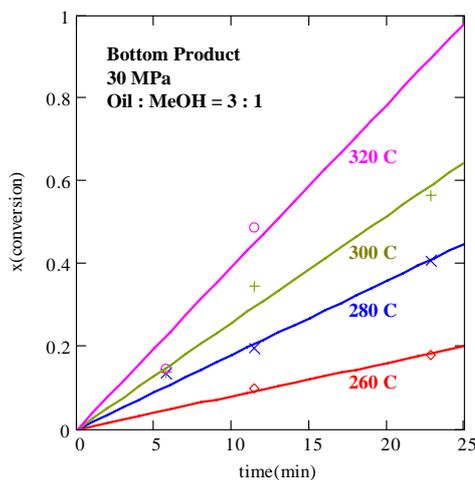


Fig. 2. The conversion of soybean oil in oil phase

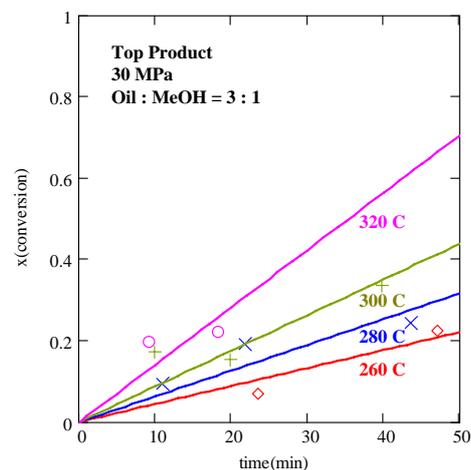


Fig. 3. The conversion of soybean oil in fluid phase

### 3.2 Effects of Feeding Ratio of Methanol to Oil and of Cosolvent

Increasing the feeding ratio of methanol to oil from 1/3 to 1/1 decreased the

conversion rate in oil phase as shown in Figure 5, but increased in fluid phase as shown in Figure 6. The total conversion is found about 30% less for higher ratio of methanol to oil. This was presumed that the residence time significantly decreased while increasing the methanol flow rate. Increasing the ratio of methanol to oil may also change the partition of FAMES between the fluid phase and the oil phase. This needs more researches on the phase diagrams. The phase behavior would certainly play an important rule in this countercurrent flow reactor. It is worth to start the researches on the phase diagram at high temperature and high pressure.

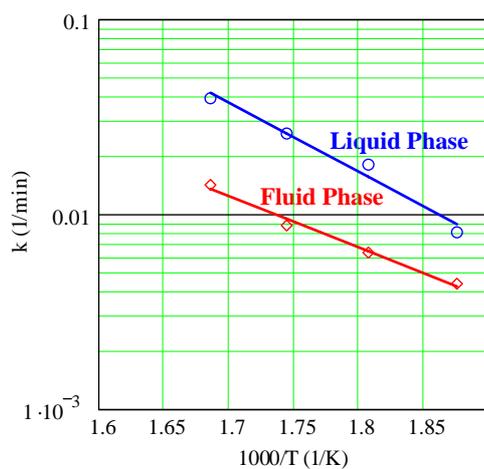


Fig. 4. Arrhenius plot for both oil and fluid phases

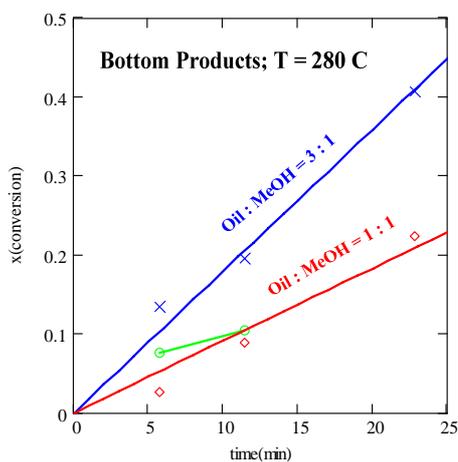


Fig. 5. Effects of molar ratio and cosolvent on conversion in oil phase

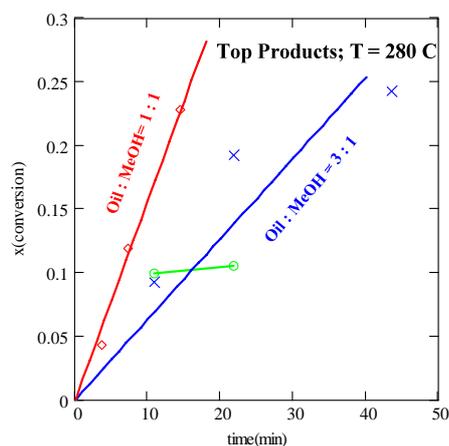


Fig. 6. Effects of molar ratio and cosolvent on conversion in fluid phase

If hexane was pre-mixed with methanol, the conversion decreased in oil phase but no significant change in fluid phase. The circles in Figs. 5 and 6 represented the conversion with hexane as cosolvent. This was presumed that hexane will decrease

the solubility of methanol in the oil phase such that the reaction rate was depressed. Also, the study of the phase behavior will help to reveal the cosolvent effect on this flow reactor.

#### 4. CONCLUSION

This work demonstrated the feasibility to use countercurrent flow reactor to conduct the transesterification of soybean oil. Also, conversion of the transesterification was calculated at various conditions to study the reaction kinetics at high temperature and high pressure. Effects of molar ratio of methanol to oil and cosolvent were also investigated.

#### ACKNOWLEDGEMENTS

Financial support from NSC-96-2221-E-214-034 is gratefully acknowledged.

#### REFERENCES

1. S. Saka, D. Kusdiana, *Fuel*, 80 (2001) 225-231
2. D. Kusdiana, S. Saka, *Fuel*, 80 (2001) 693-698
3. Demirbas, *Energy Conversion and Management*, 43 (2002) 2349-2356
4. X. Guo, H.Y. He, T. Wang, S.L. Zhu, *Modern Chem. Ind.*, 23 (2003) 15-18
5. Demirbas, *Energy Conversion and Management*, 43 (2003) 2093-2109
6. Y.Y. Gao, W.W. Chen, R.S. Ruan, X.Y. Lin, C.S. Chen, *Renewable Energy*, 115 (2003) 6-10 (in Chinese)
7. D. Kusdiana, S. Saka, *Fuel*, 91 (2004) 289-295
8. G. Mardras, C. Kolluru, R. Kumar, *Fuel*, 83 (2004) 2029-2033
9. H.W. Han, W.L. Cao, J.C. Zhang, *Fuel*, 84 (2005) 3148-3151
10. W.L. Cao, H.W. Han, J.C. Zhang, *Fuel*, 84 (2005) 347-351
11. B. Liang, *Chemical Industry and Engineering Progress*, 24 (2005) 577-585
12. X.L. Bo, D.K. Xia, T. Qiu, *Chemical Industry Times*, 19 (2005) 32-37
13. J.W. Lin, J.H. Choi, H.S. Lee, and Y.W. Lee, *The 4th International Symposium on Supercritical Fluid Technology for Energy, Environment and Electronics Applications*, Nov. 20-23, 2005, Taipei, Taiwan
14. R.W. Johnson, and E. Fritz, Marcel Dekker Inc., New York (1989)
15. B. Kunchana, M. Sukunya, S. Ruengwit, N. Somkiat, *Energy and Fuel*, 20 (2006) 812-817
16. K.M. de Reuck and R.J.B. Craven, *Methanol International Thermodynamic Tables of the Fluid State—12.*, IUPAC Blackwell Scientific Publication (1993).