

# Synthesis of biodiesel using supercritical methanol

Hong-shik Lee<sup>1</sup>, Sung Jin Yoo<sup>1</sup>, Jaehoon Kim<sup>2</sup>, Jae-Duck Kim<sup>2</sup>, Youn-Woo Lee<sup>1\*</sup>

<sup>1</sup>School of Chemical and Biological Engineering & Institute of Chemical Processes, Seoul National University, 599 Gwanak-ro, Gwanak-gu, Seoul 151-744 Korea

<sup>2</sup>Supercritical Fluid Research Laboratory, Energy and Environment Research Division, Korea Institute of Science and Technology, 5 Wolsong-gil, Seongbuk-gu, Seoul 136-791 Korea

E-mail : [ywlee@snu.ac.kr](mailto:ywlee@snu.ac.kr), Fax : +82-2-883-9124

## INTRODUCTION

Recently, the biodiesel fuel has been given attention as a promising alternative fuel because it can be applied easily to present automotive engines and infrastructure without modification. Because biodiesel is synthesized from vegetable oil, it takes much shorter time than fossil fuel to fix the carbon dioxide emitted by the combustion of biodiesel. Conventionally, homogeneous basic catalyst such NaOH, KOH and NaOCH<sub>3</sub> was used in the synthesis of biodiesel. However, this process requires complex pretreatment and separation process because the catalysts can cause several side reactions with impurities in oil [1-3]. Although various types of catalyst have been proposed to replace these catalysts, they also have some problems such as high cost or low reaction rate [1]. The catalyst-free supercritical methanol process was proposed as a solution, which requires simple process and has very high reaction rate [4-7]. In this study, the effect of process parameters on the synthesis of biodiesel in supercritical methanol was investigated and the kinetic study and economic analysis was performed.

## MATERIALS AND METHODS

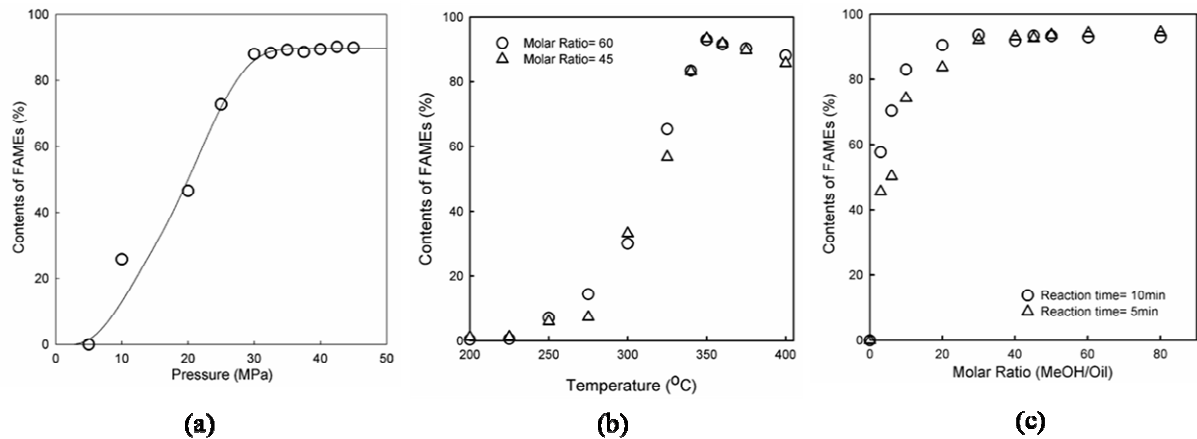
Methanol (99.5%, Samchun Pure Chemicals Co. Ltd., Korea), palm oil (Dong Nam Oil & Fats Co. Ltd., Korea), rapeseed oil (KCI Ltd., Korea), soybean oil (Sajo Haepyo Co., Ltd., Korea), safflower oil (Guworl Co., Korea), and flaxseed oil (Jarrow Formulas Inc., USA) was used as reactants. For analysis by gas chromatography, n-heptane (99.0%, Samchun Pure Chemicals Co. Ltd., Korea) and methyl heptadecanoate (99.5%, Sigma-Aldrich Ltd., USA) was used as solvent and internal standard, respectively.

Most experiments were carried out using batch reactors, and some experiments were carried out to obtain mass flow data. In batch experiments, salt bath was used to heat the reactors. And reaction pressure and molar ratio were controlled by the content of reactants. In continuous experiments, reaction temperature was controlled by electric furnaces and reaction pressure was controlled by back-pressure regulator. Molar ratio and retention time were determined by pumps. The content of fatty acid methyl esters (FAMEs), triglycerides (TGs), diglycerides (DGs), and monoglycerides (MGs) in products was measured by gas chromatography (Agilent 6890).

## RESULTS

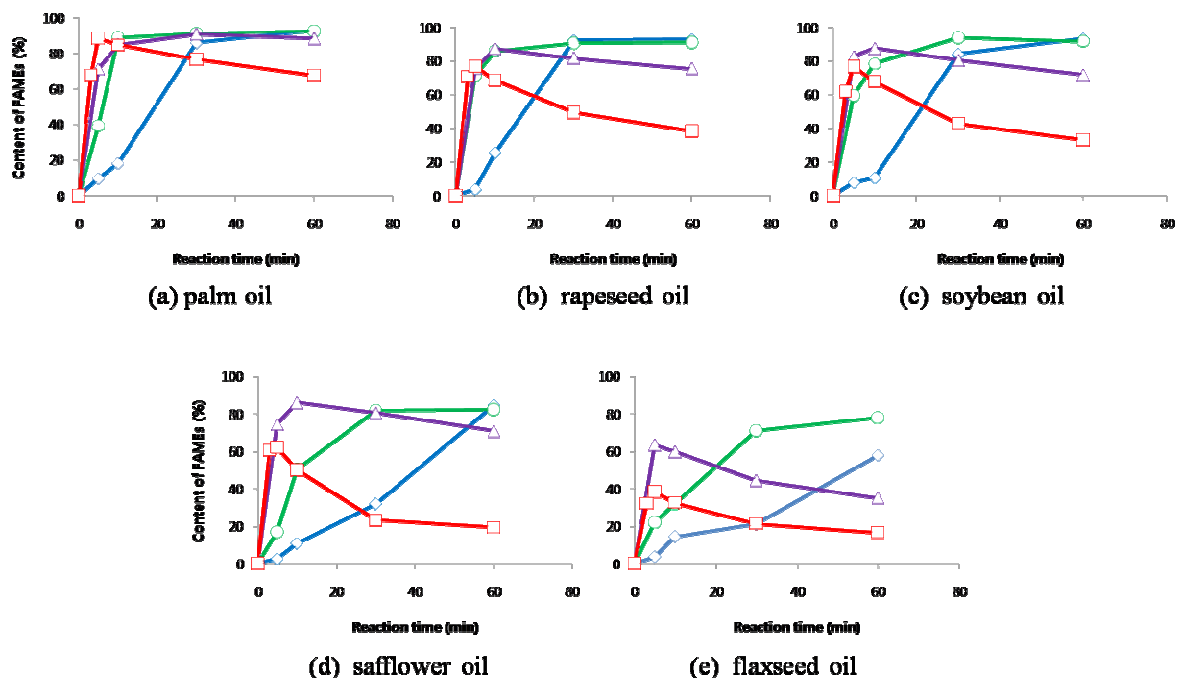
Figure 1 shows the effect of several parameters on the content of FAMEs synthesized from

palm oil [4]. The content of FAMES increased as reaction temperature, reaction pressure and molar ratio of methanol to oil increased. However, when the reaction pressure exceeded 30MPa and molar ratio exceeded 40, the content of FAMES didn't increase further. When the reaction temperature exceeded 350°C, the content of FAMES decreased due to thermal decomposition.



**Figure 1** : Effect of parameters on the transesterification of palm oil in supercritical methanol  
 (a) pressure, (b) temperature, (c) molar ratio of methanol to oil

Figure 2 shows the change of content of FAMES synthesized from 5 kinds of vegetable oil along with reaction temperature and reaction time. As reaction temperature and reaction time increased, the decrease of FAMES content became significant. In addition, the decrease of FAMES was more prominent when the degree of unsaturation of vegetable oil was higher.



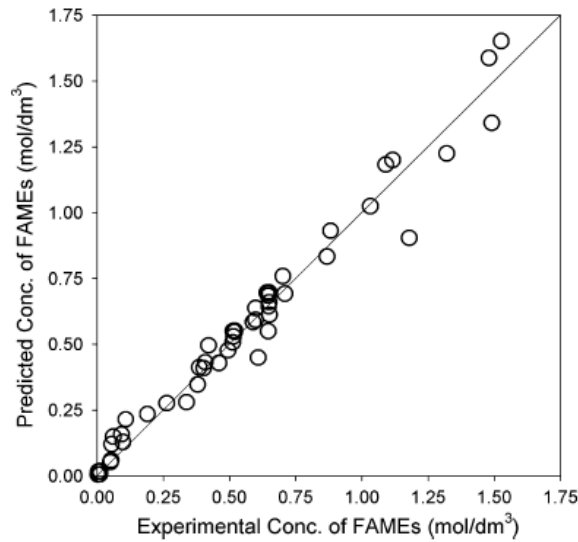
**Figure 2** : Effect of vegetable oil on the transesterification in supercritical methanol  
 (◇ : 250°C, ○ : 300°C, △ : 350°C, □ : 400°C)

For the design of commercial process, the kinetic model was studied [4]. The obtained rate

equation was as followed.

$$\frac{dC_{TG}}{dt} = -(4.3376 \times 10^5) \times \exp\left(-\frac{1.0527 \times 10^5}{RT}\right) \cdot C_{TG}^{0.9565} \cdot C_{MeOH}^{1.0493} \quad (1)$$

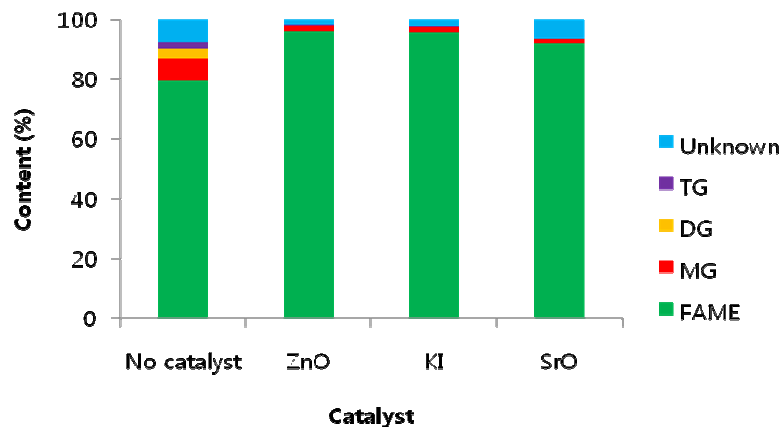
The estimated values from equation (1) agreed well with the experimental results as shown in Figure 3.



**Figure 3** : Comparison of experimental and predicted concentration of FAMES

In addition to the kinetic model, the mass flow data were collected from a continuous reactor for the analysis economic potential of supercritical methanol process. As a result, because the supercritical methanol process doesn't require complex separation process, it is more economical than conventional process in spite of severe reaction conditions such as high temperature and pressure.

Figure 4 shows the change of FAMES, TG, DG and MGs when heterogeneous catalysts were applied to the supercritical methanol method. With heterogeneous catalysts, the content of FAMES increased considerably at lower temperature compared with the result obtained without catalyst.



**Figure 4** : Effect of catalysts on the transesterification of rapeseed oil in supercritical methanol

## **CONCLUSION**

In this study, the synthesis of biodiesel fuel in supercritical methanol was investigated. As reaction temperature, reaction pressure and molar ratio of methanol to oil increased, the content of FAMES increased. When the reaction temperature exceeded 350oC, the content of FAMES decreased due to thermal decomposition. The decrease of FAMES was more severe when the degree of unsaturation of vegetable oil was higher. From kinetic study and economic potential analysis, it was concluded that supercritical methanol process is more economical than conventional process because of simple separation process. Moreover, using heterogeneous catalysts could achieve milder reaction conditions without losing advantages of supercritical methanol process.

## **REFERENCES :**

- [1] MEHER, L. C., VIDYA SAGAR, D., NAIK, S. N., *Renew. Sust. Energ. Rev.*, Vol. 10, **2006**, p. 248
- [2] VAN GERPEN, J., *Fuel Process. Technol.*, Vol. 86, **2005**, p. 1097
- [3] DEMIRBAS, A., *Energ. Convers. Manage.*, Vol. 44, **2003**, p. 2093
- [4] SONG, E.-S., LIM, J.-w., LEE, H.-S., LEE, Y.-W., *J. Supercrit. Fluids*, Vol. 44, **2008**, p. 356
- [5] BUNYAKIAT, K., MAKMEE, S., SAWANGKEAW, R., NGAMPRASERTSITH, S., *Energ. Fuel.*, Vol. 20, **2006**, p. 812
- [6] MADRAS, G., KOLLURU, C., KUMAR, R., *Fuel*, Vol. 83, **2004**, p. 2029
- [7] SAKA, S., KUSDIANA, D., *Fuel*, Vol. 80, **2001**, p. 225