# Modeling of continuous operation esterification of fatty acid catalyzed by Amberlyst15 in the presence of molecular sieve

Kiattisak Pinmai[1,2], Navadol Laosiripojana[1,2,*]

[1]*The Joint Graduate School of Energy and Environment, King Mongkut's University of Technology Thonburi, Bangkok, Thailand*
[2]*Center of Energy Technology and Environment, Ministry of Education, Thailand*

**Abstract:**
*The esterification is reaction that can convert fatty acid from vegetable oil to biodiesel. This is alternative biodiesel production in case of feedstock contains high free fatty acid (FFA) content. In this study, the model of continuous esterification in the presence of solid acid catalyst was developed and simulated at different methanol/FFA molar ratios and reactant flow rates. Importantly, the effect of molecular sieve adding on FFA conversion and product yield were determined. The results demonstrate that conversion of FFA can reach to 99% when molecular sieve along with catalyst were added due to the water adsorbed by molecular sieve, resulting the equilibrium of the esterification reaction more shifted to biodiesel.*

**Keywords:** *Biodiesel; Free fatty acid; Esterification; Molecular sieve*

*\*Corresponding author. Tel.: +662-872-9014; Fax: +662-872-6736*
*E-mail address: navadol@jgsee.kmutt.ac.th*

## 1. Introduction
Currently, the problem related to energy crisis are rising due to the energy resources are limited. Hence, several researchers have been attempting to survey the new energy resources, which are sustainable and low cost. Among the renewable fuels, biodiesel is known to be the promising alternative to petroleum diesel that most used in transportation section. Generally, it is well known that the transesterification method by using alkali as catalyst is the most wildly used technique for producing biodiesel. Nevertheless, this method is not suitable for raw material that contains high FFA content, because FFA can react with the alkali catalyst to release soap and water during the process which also consumes the catalyst and lowers the yield of biodiesel. A possible solution to this drawback could be the development of new technologies enabling to employ waste raw materials such as the esterification reaction, this reaction can be used both as biodiesel direct production and as pre-treatment step in the conventional transesterification and can also use both homogeneous acid catalyst and solid acid as heterogeneous catalysts. The purpose of this work is to predict the esterification performance by simulation approach. The catalytic packed bed reactor model was used, from which FFA (oleic acid) and methanol were chosen as esterification agent and selected acid solid catalyst was Amberlyst 15. Importantly, molecular sieve was chosen as desiccant to absorb water in the product.

## 2. Materials and Methods
The internal diameter of reactor was 2.5 cm, catalytic bed length was 70 cm, catalyst loading was 196 g. The developed model was based on the assumptions as follows; (1) this reactor operated as isothermal along reactor length, (2) no pressure drop along reactor length, and (3) ideal gas behaviour was applied to all gas components. The esterification reaction of oleic acid and methanol over acid catalyst was applied. The reaction was based on the Elay-Rideal mechanism with the kinetic parameters as reported by Tesser et al. (Tesser et al., 2009). Performance of the molecular sieve used to absorb the water was presented in term of water sorption isotherm as reported by Al-Asheh et al. (2004).

## 3. Results and Discussion
### 3.1 Effect of reaction temperature
Reaction temperature is one factor that influences the esterification rate. The esterification reaction is favored by high temperature and hence oleic acid conversion should increase. Figs. 1a and 1b show the effects of temperature from 60°C to 120°C on oleic acid conversion with, without

*5th International Conference on Sustainable Energy and Environment (SEE2014):*
*Science, Technology and Innovation for ASEAN Green Growth*
*19-21 November 2014, Bangkok, Thailand*

molecular sieve, respectively. It demonstrates that reaction rate (conversion) rapidly sped up by the increased temperature. The conversion increased up to 95.91% and 99% with esterified without and with molecular sieve at 120°C, respectively. However, reaction pressure was limiting factor for increasing temperature because the normal boiling point of methanol is 65°C. When temperature was higher than 65°C, pressure also increased to ensure that methanol maintained in the liquid state.
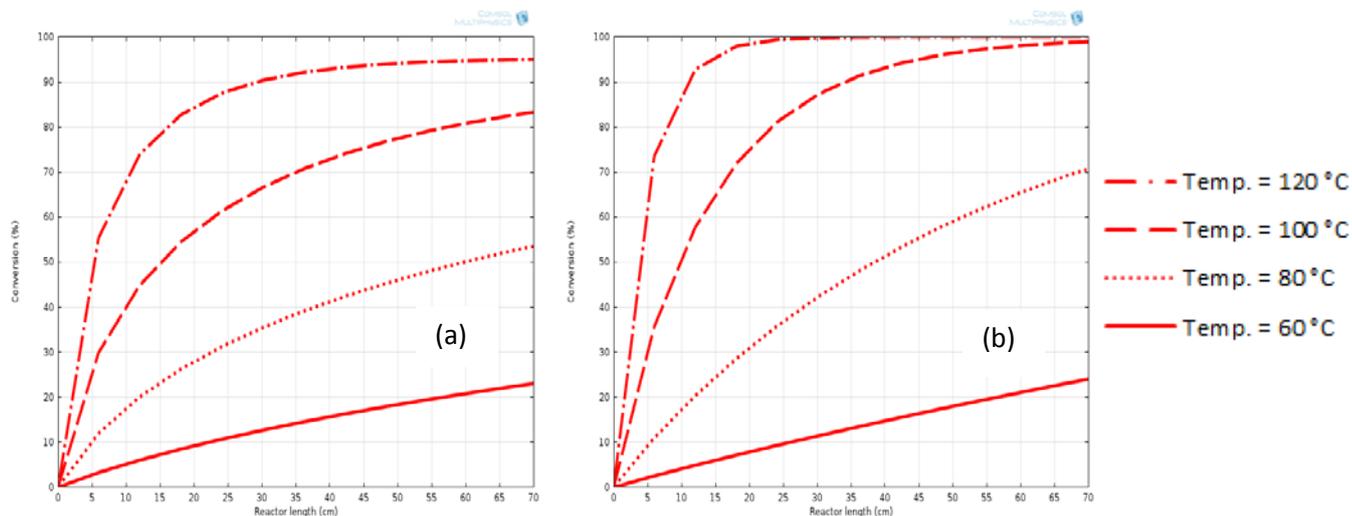


**Fig. 1** Concentration profiles of oleic acid at different temperature with (b) and without (a) molecular sieve adding (simulated at 100°C, alcohol/acid molar ratios = 7/1).

### 3.2 Effect of Methanol/Oleic acid molar ratio
Figs. 2a and 2b show the effect of methanol/oleic acid molar ratio on concentration of oleic acid. The conversion increased with increasing mole ratio. When methanol concentration increased, the equilibrium of the esterification reaction shifted toward the side of the products i.e. FAME and water, resulting in higher conversion of oleic acid to FAME. Furthermore, increasing the methanol to molar ratio, an excess of methanol could speed up the reaction and thus the viscosity of the reacting mixture decreased. This in turn promoted better mixing between reactants and catalyst as well as enhanced the mass transfer rate leading to a higher conversion.

### 3.3 Effect of flow rate
Figs. 3a and 3b demonstrate that feed flow rate affect directly to the conversion of oleic acid. When decreasing of feed flow rate, the conversion of oleic acid increased that similar with theory. Especially, at the lowest flow rate of 1 dm$^3$/h, the conversion of oleic acid rapidly increased because at lower flow rate, the reactants stayed inside the reactor longer. This implied that the oleic acid could react with methanol longer or oleic acid could be higher adsorbed on the specified catalyst surface due to the longer residence time in the reactor, resulting in higher FAME yield. However, when simulated with molecular sieve, the conversion of oleic acid reached to 99% constantly after flow through 50 cm of reactor length. The other case, 2,3 and 4 dm$^3$/h show the same relationship between feed flow rate and the conversion of oleic acid, It could be concluded that higher conversion of oleic acid could be obtained from the case of longer residence time in reactor or the lower feed flow rate.
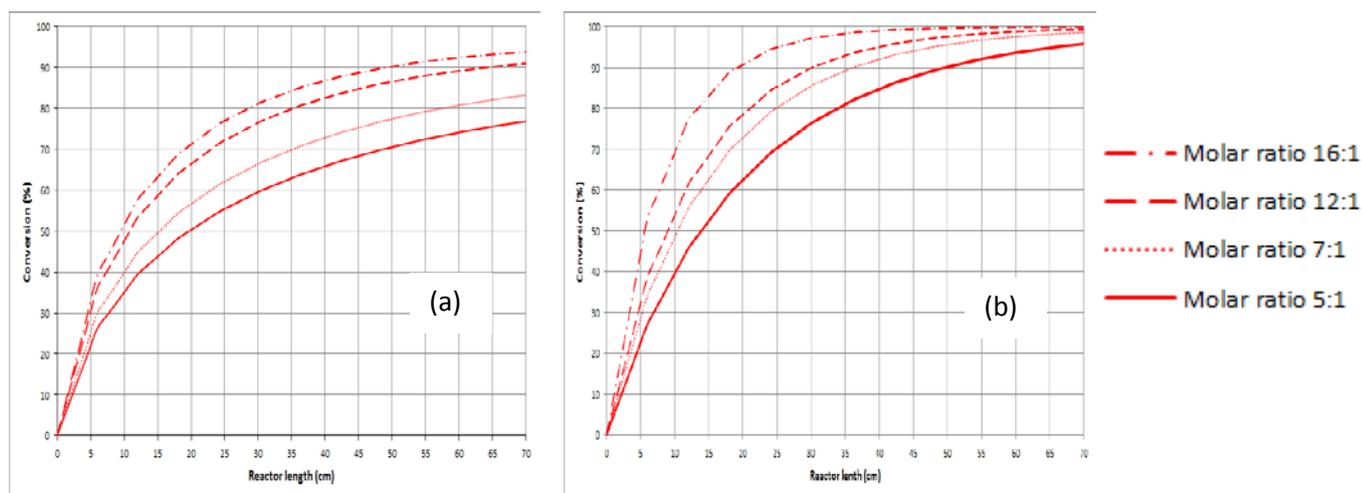
*5th International Conference on Sustainable Energy and Environment (SEE2014):*
*Science, Technology and Innovation for ASEAN Green Growth*
*19-21 November 2014, Bangkok, Thailand*

**Fig. 2** Concentration profiles of oleic acid at different alcohol/acid molar ratios with (b) and without (a) molecular sieve adding (simulated at 100°C, flow rate = 1 dm$^3$/h).
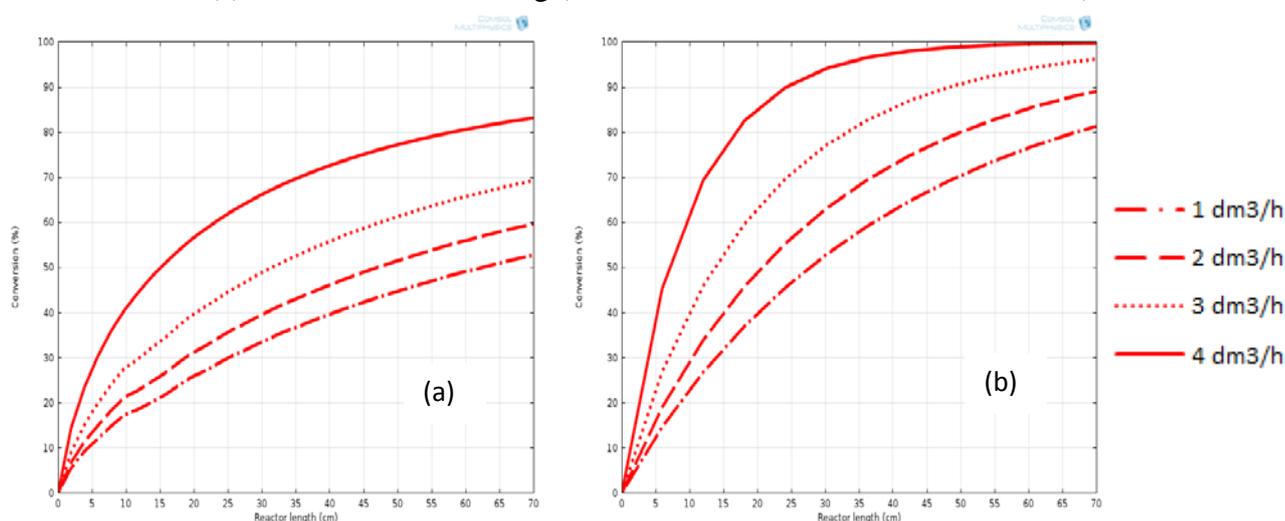


**Fig. 3** Concentration profiles of oleic acid at different feed flow rate with (b) and without (a) molecular sieve adding (simulated at 100°C, alcohol/acid molar ratios = 7/1).

## 4. Conclusion

The model of continuous biodiesel production was simulated with the different conditions, the highest yield of FAME was obtained from case of without molecular sieve are 120°C, 1 dm$^3$/h and molar ration 16:1. The optimal condition was temperature 100°C, flow rate 1 dm$^3$/h and molar ratio 7:1 because when simulated in this condition with molecular sieve, the conversion of oleic acid was reached to 99%.

## 5. References

Al-Asheh, S., Banat, F., and Al-Lahtah, N. 2004. Separation of Ethanol-Water Mixtures Using Molecular Sieve and Biobased Adsorbents. Chemical Engineering Research and Design 82: 855-864.

Tesser, R., Casale, L., Verde, D., Serio, M.D., and Santacesaria, E. 2009. Kinetics of free fatty acids esterification: Batch and loop reactor modeling. Chemical Engineering Journal 154: 25-33.