The 29th International Symposium on Chemical Engineering, December 2-3, 2016,
Sheraton Grande Ocean Resort, Miyazaki, Japan

Kinetic study of methylesterification of free fatty acids using ion-exchange resin catalysts

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Abstract

Used cooking oils are the main raw materials for production of biodiesel fuel in Japan because of the high cost of fresh vegetable oils and effective use of resource. However, used cooking oils have large amounts of free fatty acids (FFAs). FFAs produce soap in reaction with alkali metal hydroxide. To prevent the soap formation, FFAs should be esterified using acid catalysts before the transesterification. Many reaction rate equations were proposed for the reactor design[1, 2) using ion exchange resins as catalysts. The relationship between the molar ratio of methanol/oleic acid and the conversion showed a characteristic trend[3)]. It is required to elucidate this characteristic trend in order to derive the reaction rate equation. In addition, the reaction rate should be represented by the concentration of each component in the resin by considering the chemical equilibrium. The objective of this study is to establish the reaction rate over the ion exchange resins by these approaches.

In this study, molar ratios of methanol to oleic acid were changed. **Fig. 1** shows the effect of the ratio on the FFA conversion. The conversion increased with the ratio when it was below 10. It decreased and showed the lowest conversion at the molar ratio of 20. The conversion increased again when the ratio was above 20. The results indicate that the reaction rate was not simply affected by the concentrations of bulk liquid. The composition of the mixtures inside and outside of the resin must be different. Moreover, the relationship between them is probably complicated. **Fig. 2** shows the relationship between MeOH/FFA molar ratio and the reaction rate of FFA. It is clear that this relationship was not affected by the concentration of FFA in the oil phase. The change in the reaction rate can be divided into two curves. In the first curve, the conversion increased with the molar ratio and decreased after reaching the maximum point. In the other curve, the conversion increased with the molar ratio, and it approached asymptotically to a constant value. The volumetric fraction of methanol in the resin increased sharply with that in the bulk liquid phase. However, the volume ratio of methanol in the resin was almost constant and about 80% when the molar ratio MeOH/FFA was above 10. From the results described above, the following mechanism was considered. The reactions in the methanol phase and oil phase of the resins proceed with the different concentration dependency. Consequently, the characteristic trends shown in Figs. 1 and 2 were observed. Detailed analysis of the reaction rate will be conducted based on this mechanism.

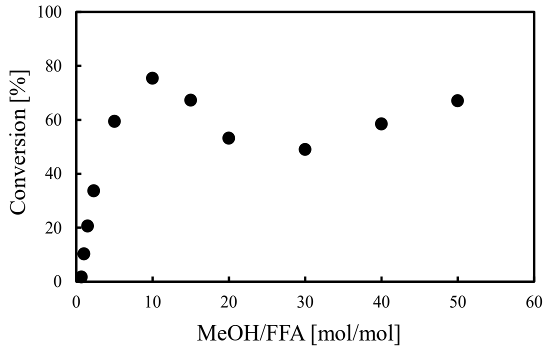

Fig. 1. Effect of molar ratio of methanol/oleic acid on the FFA conversion

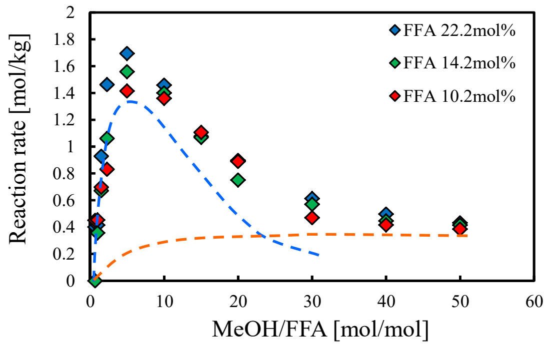

Fig. 2. Effect of FFA molar ratio on the reaction rate

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