

Mechanisms of methyl esterification of free fatty acid using cation-exchange resin catalyst

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Abstract

Biodiesel fuel (BDF) is an alternative fuel to petroleum, and attracting the attention from carbon-neutral renewable energy and high safety¹. BDF is fatty acid methyl ester (FAME), and generally produced by transesterification of triglyceride (TG) with methanol using alkaline catalysts. In Japan, mainly waste cooking oils are used for BDF raw material oils. The waste cooking oils are oxidized and contain a large amounts of free fatty acids (FFA). FFAs are produced by hydrolysis of TG, and react with alkaline catalyst to produce soap. When used oxidized oils are used without any pretreatment, the yield drops by the production of soap, additionally it makes difficult to separate the by-product glycerol in the separation process after the reaction process. FFA and methanol react to yield FAME². Cation-exchange resins have been studied as the catalyst. However, there are many unclear points about the mechanism of esterification of FFA using cation-exchange resins. The objective of this study is to clarify the reaction mechanism and the reaction rate of methyl esterification of free fatty acid over cation-exchange resins.

The reaction was carried out in the batch reactor using an eggplant flask. As raw material oil, high acid value oils were prepared by adding oleic acid as FFA to rapeseed oil. The acid value of the oil phase was measured by titration using potassium hydroxide solution. Methanol and cation-exchange resin (Amberlyst 15 DRY, Organo), used as catalyst, were added to this feedstock oil, and the reaction was carried out while stirring in a hot water bath. The conversion was calculated from the measured acid values. Amount of MeOH and the ratio of MeOH/FFA were changed for each run.

In the previous study³, the relationship between the molar ratio of MeOH/TG and the FFA conversion showed a characteristic trend. The relationship between the molar ratio of MeOH/TG and the FFA conversion showed maximum and minimum points as shown in Fig. 1. This behavior is considered to be based on the fact that the oil phase and the MeOH phase exist in the resins separately. The esterification proceeds at different reaction rates in each phase. Since the ratio of oil and MeOH phases in the resins changed with the ratio of oil and MeOH in the bulk phase, the overall reaction rate would be affected by the ratio in the resins. Fig. 1 shows the relationship between the molar ratio of MeOH/TG and the conversion after 3 h at temperatures of 313K, 323K and 333K. As the temperature decreased, not only conversion decreased, the MeOH/TG molar ratio where the maximum and the minimum peaks of the conversions appeared moved to the smaller values. It would be considered that the change in the amount of ratio of the oil phase to the MeOH phase in the resins is also influenced by the temperature.

Fig. 2 shows the results when FFA amounts were changed. The temperature was 333 K. The maximum and minimum peaks of conversion were observed at the almost same molar ratio even when the amount of FFA was changed. The conversion was higher for lower concentration of FFA in the oil phase when the ratio was increased. From this result, it would be considered that the reaction in the oil phase was not so affect the overall reaction rate.

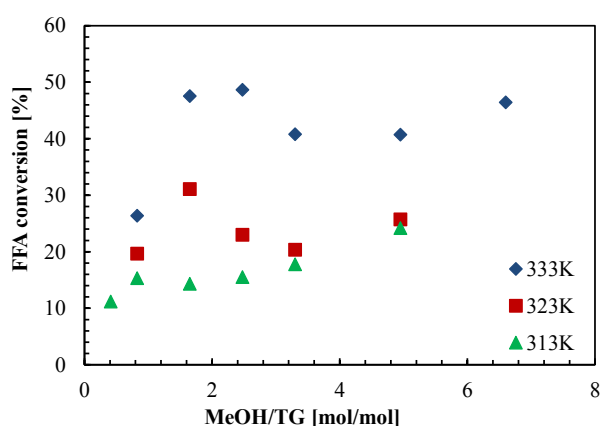


Fig. 4. Effect of temperature on conversion.

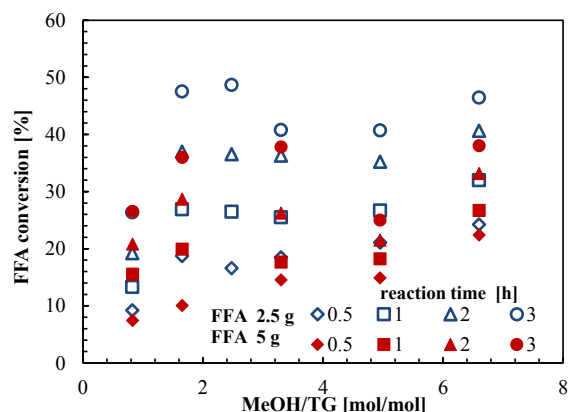


Fig. 5. Effect of amount of FFA on conversion.

References

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- 3) Kai, T. et al., Abst. 45th SCEJ Autumn Meeting, Okayama, H126 (2013)