Kinetics in Hydrolysis of Oils/Fats and Subsequent Methyl Esterification in Two-Step Supercritical Methanol Method for Biodiesel Production

Eiji Minami and Shiro Saka
Graduate School of Energy Science, Kyoto University
Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan
Tel/Fax: +81-75-753-4738, E-mail: saka@energy.kyoto-u.ac.jp

A potential fossil diesel fuel substitute is biodiesel (fatty acid methyl esters) produced by transesterification of triglycerides with methanol. At present, most of the methods in transesterification are employing alkaline catalysts, even though this process needs complicated purification steps for removal of the catalyst and saponified products. Our research group has, therefore, developed catalyst-free processes by employing supercritical methanol; one-step method (Saka process) and two-step method (Saka-Dadan process).

In the one-step supercritical methanol method, fatty acid methyl esters can be produced by transesterification reaction of triglycerides without any catalyst due to high ionic product of methanol in supercritical state. However, a severe reaction conditions (>350℃/20~50MPa) are required in this case. The two-step method involves, on the other hand, oils/fats hydrolysis to fatty acids in subcritical water and subsequent methyl esterification to fatty acid methyl ester in supercritical methanol. This process has been selected as one of the NEDO "High Efficiency Bioenergy Conversion Projects" for its commercialization since it can allow more moderate conditions (270℃/7~20MPa) than those of one-step method. In this paper, a kinetic study was carried out on each reaction to optimize reaction conditions and propose more efficient process design for the two-step method.

For the hydrolysis reaction, the rate of fatty acid formation was increased with the concentration of fatty acid in the reaction system, though it was very slow in the early stage of the reaction. This phenomenon can be explained by assuming that fatty acid acts as acid catalyst. For the esterification reaction, similarly, the reaction was found to proceed by the autocatalytic mechanism due to dissociation of fatty acid itself in supercritical methanol.

In this way, it was found that the produced fatty acid plays an important role in the non-catalytic two-step supercritical methanol method. In case of transesterification of triglycerides (one-step method), however, the reaction proceeded according to a typical pseudo-first order reaction, since there are no fatty acids in the reaction system. That is a main reason why the two-step method can realize more moderate temperature and pressure than those of the one-step method. These findings will contribute to development of more efficient reaction conditions for the two-step method.