A Novel Non-Catalytic Biodiesel Production Process by Supercritical Methanol as NEDO "High Efficiency Bioenergy Conversion Project"

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Biodiesel fuel (BDF) is one of the most promising bioenergies, which can be produced from oils/fats through transesterification. A current commercial process for BDF production involves the use of alkali catalyst, followed by the removal of the catalyst and saponified products from free fatty acids (FFA). In addition, water-containing waste oils/fats depress the catalyst activity. These cannot allow the low-quality feedstocks such as waste cooking oil and waste industrial oil.

For solving these problems, our research group has been working to develop non-catalytic biodiesel production by supercritical methanol treatment (>239℃, >8.09MPa) since 1998. Variables affecting the reaction were investigated followed by proposing the optimum conditions to be 350℃, 20MPa and 9 min. Compared with the alkali-catalyzed method, the supercritical methanol method has superiorities in terms of reaction time and purification step. In addition, the yield of BDF is higher than that of alkali-catalyzed method due to a simultaneous conversion of FFA to its methyl esters through esterification. These findings indicate that the supercritical methanol treatment has a great availability to perform transesterification of triglycerides (TG) and esterification of FFA, and it would provide a clue as to establishment of the efficient biodiesel production process.

Although the catalyst-free supercritical methanol method (Saka process) has been proven to produce BDF in high yield, it requires a restrictive reaction condition compared to the conventional alkali- and acid-catalyzed methods. Therefore, further effort was made to develop an alternative method through the two-step preparation; hydrolysis of TG in subcritical water and subsequent methyl esterification of the fatty acids in supercritical methanol. In this two-step method (Saka-Dadan process), therefore, esterification is the main reaction for BDF production, while in the conventional supercritical method, transesterification is the most major one. The proposed reaction conditions were 270℃, 7MPa and 20 min for hydrolysis and methyl esterification, respectively. For such conditions, the common stainless steel can be applicable and resist enough for reaction vessel. Furthermore, the BDF product was found to be low in total glycerol content which satisfies the biodiesel specification standards in EU, US and Kyoto City.

Fortunately, this research project has been selected as one of the NEDO "High Efficiency Bioenergy Conversion Projects" in FY2003 for coming 3 years with a budget of about ¥840 million to produce high quality BDF (total glycerol content < 0.24wt% through a high energy efficiency > 80%) in commercial scale. In this paper, current progress of this project is introduced on process design for the two-step method and BDF product evaluation.