Biodiesel fuel for diesel fuel substitute prepared by a catalyst-free supercritical methanol

D. Kusdiana, S. Saka*
Grad. School of Energy Science, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan
Fax : +81-75-753-4738; Shiro Saka, E-mail : saka@energy.kyoto-u.ac.jp

A novel process of biodiesel fuel production has been developed by a catalyst-free supercritical methanol method. The purification becomes much simpler, and it produces higher yield. From our calculation, the energy use and production cost are competitive with those of the common catalyzed method.

Introduction

The depletion of world petroleum reserves and the increased environmental concerns have stimulated the search for alternative sources for petroleum-based fuel, including diesel fuels. Because of the closer properties, biodiesel fuel (fatty acid methyl ester) from vegetable oil is considered as the best candidate for diesel fuel substitute in diesel engines.

Different technologies are currently available and used in the industrial production of biodiesel fuel. Alkaline catalyzed method is mostly developed among biodiesel production processes. This method has, however, some drawbacks such as difficulties in the recovery of glycerin, a need for removal of the catalyst and the energy intensive nature of the process. Furthermore, oil containing free fatty acids and/or water are incompletely transesterified and those free fatty acids react with alkaline catalyst to form saponified products which have to be removed after the reaction.

The disadvantages resulted from the use of a catalyst and its removal from the products can be eliminated if a non-catalytic transesterification reaction of vegetable oils with alcohol is realized. We have carried out a fundamental work of a catalyst-free biodiesel production process by supercritical methanol [1]. This paper reports and discusses a recent progress of biodiesel fuel development for diesel fuel substitute by supercritical methanol.

Materials and Methods

Rapeseed oil and their fatty acids were chosen as the sample of vegetable oil. Reaction were carried out in both batch-type and flow-type supercritical biomass conversion systems developed in our laboratory. Major sections of the flow-type system consist of the pump station, preheaters, supercritical treatment tube, cooling system and separatory tank. The supercritical treatment tube was made of Hastelloy 276, while in the batch-type, the reactor was constructed from Inconel 625.

Product analysis was made by the high performance liquid chromatography (HPLC), liquid chromatography-mass spectrometry (LC-MS) and gas chromatography (GC). The obtained product was compared with those prepared by alkaline catalyzed method and commercial biodiesel fuels. A brief energy use and economical analysis of biodiesel production by supercritical methanol was proposed through comparisons with the common conventional method.

Results and Discussion

A set of experiments was carried out to study the effect of reaction temperature, reaction pressure and molar ratio of methanol to triglycerides in the methyl esters formation. The results revealed that the supercritical treatment of 350^{o}C, 30 MPa and 240 sec with molar ratio of 42 in methanol is the best condition for transesterification of rapeseed oil to biodiesel fuel. In addition, the methyl esters produced are similar to those by the common catalyzed process as it shown in Figure 1. Since typical properties of biodiesel fuel are mainly governed by methyl esters composition, it further means that biodiesel fuel prepared by our new method has similar properties to those commercial biodiesel fuels.

Most important result of this experiment is that free fatty acids which become wastes as saponified

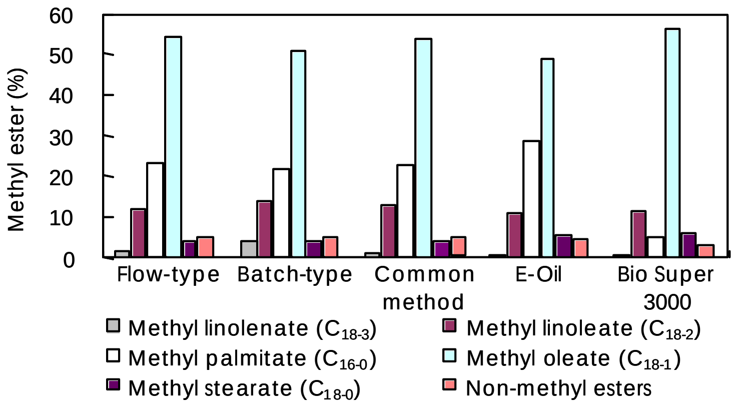

Figure 1. Methyl esters composition of biodiesel fuels prepared by supercritical methanol and those of commercial biodiesel fuels

products in the common catalyzed method can be available as biodiesel fuel in our proposed method. As a result, a direct use of crude vegetable oil can be realized as a raw material for transesterification, which, in the common catalyzed method results in incomplete reaction because the presence of free fatty acids leads to catalyst destruction. Therefore, in addition to a simpler purification process, a higher yield of methyl esters can be obtained as free fatty acids conversion through methyl esterification reaction proceeds simultaneously with transesterification of vegetable oil in supercritical methanol.

The total energy use for biodiesel production in the common method is 17.9 MJ/l biodiesel. Transesterification process alone consumes 4.3 MJ/l, while from our calculation, the supercritical methanol method requires as much as 3.3MJ/l, or energy reduction of 1.0 MJ for each liter of biodiesel fuel. In the common catalyzed method, mixing is significant during the reaction. In our method, since the reactants are already in a single phase, mixing is not necessary. Since our process is much simpler, particularly in purification step which only needs a removal of unreacted methanol, it is further expected that about 20% of cost reduction can be realized from transesterification process. Therefore, the production cost for biodiesel fuel from rapeseed oil falls to be US$0.59/l, compare to US$0.63/l for the common catalyzed method.

Table 1. Comparisons between the common method and supercritical methanol method for biodiesel fuel production from rapeseed oil

	Common method	SC MeOH method
Reaction time	1 - 6 h	240 sec
Reaction condition	0.1 MPa, 30 - 65^{o}C	35 MPa, 350^{o}C
Catalyst	acid or alkali	none
Free fatty acids	saponified products	methyl esters
Yield	97 % (normal)	98.5 % (higher)
Removal for purification	methanol, catalyst and saponified products	methanol
Process	complicated	Simple

Table 1 summarizes the superiority of supercritical methanol process over the common catalyzed method. The merit is that this process is free of catalyst, simpler purification and higher yield of methyl ester. In addition, the energy use for the process is lower. When these advantages are considered, the supercritical methanol method would be more effective and efficient than the common commercial process. The supercritical process, therefore, offers a potentially low cost with simpler technology for producing an alternative fuel for diesel engines. The considerable yield of methyl esters by the environmentally friendly method renders this technique ideally suitable for industrial application.

Reference

[1] Saka S, Kusdiana D. Biodiesel fuel from rapeseed oil as prepared in supercritical methanol, Fuel, 80, 2001 p. 225.