Development of biodiesel fuel production by supercritical methanol

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

A set of experiments was carried out to study the optimum condition for transesterification of vegetable oils in supercritical methanol to biodiesel fuel. The effect of temperature and pressure was then quantified in terms of reaction rate constant. It is apparent that the course of reaction is both temperature and pressure dependence. Another result demonstrated that free fatty acids are effectively converted to their fatty acid methyl esters through methyl esterification reaction in supercritical methanol.

Introduction

Since Rudolf Diesel's invention on the compression (diesel) engine over 100 years ago, it has been known that the engine can operate on vegetable oils. Biodiesel, transesterified product of vegetable oil, is considered as the most promising one for diesel fuel substitute. And now biodiesel development can be found in 28 countries in which Germany and France are so far the world's largest producer of biodiesel fuel. Recently, Japan has started a project in Kyoto to put biodiesel in the commercial level municipal city owned trucks running by 100% biodiesel fuel and this trial has been extended into 81 municipal busses with a blend of 20% biodiesel and 80% petroleum diesel fuel.

Most of methods for biodiesel production use an alkaline catalyst in a batch-type processing, followed by additional effort to remove the catalyst and saponified products from free fatty acids. Recently, there has been a strong interest in developing a flow-type transesterification of vegetable oil as an effort intended to put more applicable process in commercial scale. In this work, we have developed a continuous-simpler process in the absence of alkali catalyst for biodiesel fuel production.

Materials and Methods

Several common vegetable oils such as rapeseed, soybean, cottonseed and corn oils and their fatty acids were chosen as the sample of vegetable oil. Experiments 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) equipped with STR ODS II column and RID detector with methanol as a carrier solvent. To study unmethyl esterified compounds liquid chromatography-mass spectrometry (LC-MS) was used in the positive ion atmospheric pressure chemical ionization (APCI) mode. The obtained methyl esters were also analyzed by gas chromatography (GC) equipped with FID detector and bonded phase fused silica column.

Results and Discussion

The basic idea of supercritical treatment is a relationship between pressure and temperature upon thermophysical properties of the solvent (methanol) such as dielectric constant, viscosity, specific weight, and polarity. Therefore, a set of experiments was carried out to study the effect of reaction temperature, pressure and molar ratio on the methyl esters formation. It is revealed that the supercritical treatment at 350^{o}C, 30 MPa and 240 sec in 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.

The experimental data were then evaluated further in terms of reaction rate constant to quantify the effect of reaction pressure and temperature observed as presented in Figure 1. It is evident that at subcritical state of methanol (<239°C, <8.1MPa), reaction rate is so low and gradually increased as either pressure or temperature rises. Furthermore, at the transition state between subcritical and supercritical, a relatively low rate constant is apparent. The reaction rate is increased by a factor of 85 at 350°C and 30 MPa. In addition, a considerable change in the rate constant can be seen for the pressure above 20 MPa. From this result, it is further concluded that the rate constant of the reaction is corresponding linearly to both temperature and pressure.

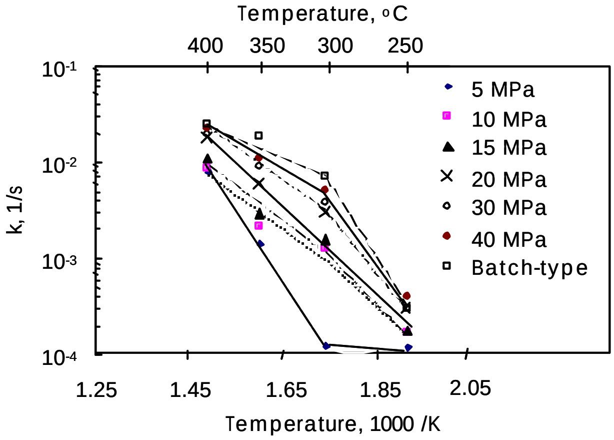

Figure 1. Arrhenius plot on rapeseed oil transesterification in supercritical methanol

In the common catalyzed method, a direct use of crude vegetable oil as a raw material for transesterification results in incomplete reaction because the presence of free fatty acids leads to catalyst destruction. Therefore, it is suggested that vegetable oil is refined to have free fatty acids content as low as possible, below 0.5%. In our method, it is, however, free fatty acids could be converted to their fatty acid methyl esters through methyl esterification reaction. Unsaturated fatty acids (oleic, linoleic and linolenic acids) are converted effectively at the lower temperature, while for saturated fatty acids (palmitic and stearic acids), a relatively higher reaction temperature is necessary to allow methyl esterification reaction to take place as shown in Figure 2. At average above 75% of free fatty acids were converted to their fatty acid methyl esters. Fortunately, the optimum condition of free fatty acids conversion is similar to that of transesterification lying in the temperature of 350°C. These facts suggest that free fatty acids which become wastes as saponified products in the common catalyzed method can be available as biodiesel fuel in our proposed method.

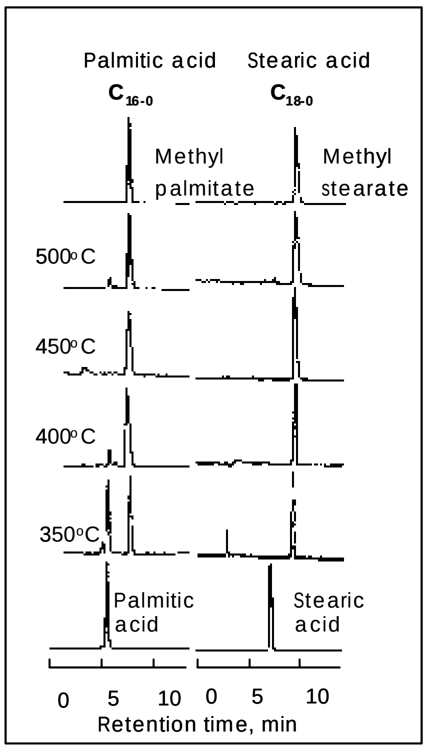

Figure 2. HPLC chromatograms of saturated fatty acids treated at various temperatures of supercritical methanol.

The experiment was expanded to other vegetable oils. The result showed that the optimum condition of the reaction is different among different vegetable oils. For high-saturated vegetable oils such as coconut and cottonseed oils, a relative longer treatment is needed to achieve a high conversion. While for soybean and corn oils, the optimum condition is similar to that of rapeseed oil, because of their similarity in fatty acid composition. A highly complete conversion of methyl esters was obtained for all those samples.

Conclusion

These observations suggest that supercritical methanol has a high potential for both transesterification of triglycerides and methyl esterification of free fatty acids to methyl esters for diesel fuel substitute.

References

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