PREPARATION OF BIODIESEL USING SUPERCRITICAL METHANOL

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Abstract. Transesterification of soybean oil in supercritical methanol has been carried out in the absence of catalyst. A co-solvent was added to the reaction mixture in order to decrease the operating temperature, pressure and molar ratio of alcohol to vegetable oil. With CO_2 as co-solvent in the reaction system, there was a significant decrease in the severity of the conditions required for supercritical reaction.

Keywords: Biodiesel; Supercritical; Co-solvent; Methyl ester; CO_2; Transesterification

1. INTRODUCTION

As energy demands increase and fossil fuels are limited, research is directed towards alternative renewable fuels. Biodiesel, consisting of methyl esters of fatty acids transesterified by vegetable oils with methanol, has become more attractive recently because of its environmental benefits and the fact that it comes from renewable resources [1]. Indeed, biodiesel is superior to diesel oil in terms of sulphur content and aromatic content as well as safety and biodegradability.

A number of studies of the preparation of biodiesel by the transesterification of vegetable oils have been reported using a variety of oil or alcohol precursors and different reaction conditions [2], [3], [4] and [5]. The reaction may be carried out using either basic or acidic catalysts, but these processes require relatively time consuming and complicated separation of the product and the catalyst, which results in high production costs and energy consumption. In order to overcome these problems, Saka and Dadan [6] and Demirbas [7] have proposed that biodiesel fuels may be prepared from vegetable oil via non-catalytic transesterification with supercritical methanol. Supercritical methanol is believed to solve the problems associated with the two-phase nature of normal methanol/oil mixtures by forming a single phase as a result of the lower value of the dielectric constant of methanol in the supercritical state [8]. As a result, the reaction was found to be complete in a very short time. Compared with the catalytic processes, purification of products is much simpler and more environmentally friendly. However, the reaction requires temperatures of 350–400 °C and pressures of 45–65 MPa, which are not viable in practice in industry. Furthermore, such high temperatures and pressures lead to high production costs and energy consumption.

It has been reported that the solubility parameter of methanol as determined by theoretical calculation is about 26 (MPa)1/2 and that under supercritical conditions its value may decrease and become closer to that of vegetable oil if an appropriate temperature and pressure are employed [8]. It was also reported by Ma [9] that the solubility of vegetable oils in methanol increases at a rate of 2 ± 3% (w/w) per 10 °C as the reaction temperature is increased. It is, thus, of great interest from a practical point of view to investigate the use of a co-solvent, which can increase the mutual solubility of methanol and vegetable oil at low reaction temperatures. Furthermore, since

there is more than one possible critical point for a binary system, it is believed that addition of an appropriate co-solvent can decrease the critical point of methanol, and allow the supercritical reaction to be carried out under milder conditions [10].

Propane is an excellent solvent for vegetable oil. We have succeeded using propane as a co-solvent in our preceding study. This showed that the use of co-solvent is feasible. Supercritical CO_2 is a good solvent for small and moderate organic molecule and it is a low-cost and facile material. We, therefore, use CO_2 as the co-solvent in this study. We have made a fundamental study of the transesterification of soybean oil in methanol under supercritical conditions in the presence of CO_2 to investigate the possibility of converting soybean oil to methyl esters as biodiesel fuels.

2. EXPERIMENTAL

2.1. Materials

Soybean oil from SC SEMITECH SRL Bacău was used as the vegetable oil. Methanol was purchased from SC DOLJCHIM SA and purified prior to use. The methyl esters of fatty acids (palmitic, stearic, oleic, linoleic and linolenic acids) used as standards were supplied by SC SEMITECH SRL Bacău.

2.2. Supercritical methanol and CO_2 transesterification method

The supercritical methanol/co-solvent reaction system employed in this work is shown in Fig. 1. A 250 ml cylindrical autoclave made of stainless steel, equipped with a magnetic stirrer and internal cooling was used. The pressure and temperature were monitored in real time up to maximum values of 100 MPa and 450 °C, respectively. The reaction vessel was charged with a given amount of soybean oil (50–70 g) and liquid methanol (60–80 g) with different molar ratios, and a known amount of CO_2 was then added to the autoclave as co-solvent. The reaction vessel was then heated with an external heater, and the power adjusted to give a heating rate of 20 °C/min, the desired temperature can be reached in 13–15 min. The temperature of the reaction vessel was measured with an iron–constantan thermocouple and controlled at ±5 °C for a set time. The system was then transferred to an ice–water bath to quench the reaction.

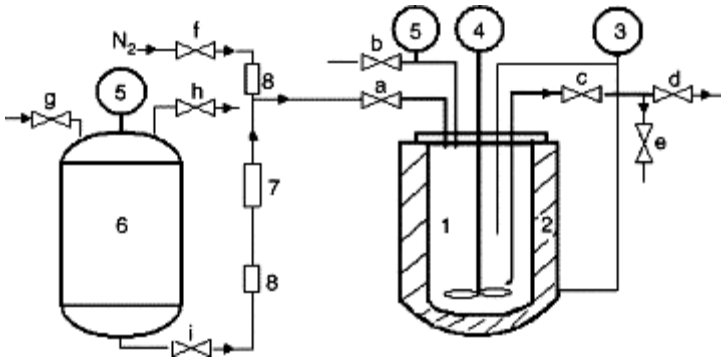

Fig. 1. Supercritical methanol and co-solvent transesterification system: 1, autoclave; 2, electric furnace; 3, temperature control monitor; 4, magnetic stirrer; 5, pressure control monitor; 6, co-solvent tank; 7, co-solvent flowmeter; 8, filter and a–i, needle valve

After each run, the gas was vented and the contents of the autoclave were poured into a collecting vessel. The remainder of the contents of the autoclave was removed by washing with methanol. The treated soybean oil was then allowed to settle for about 60 min in order to allow two phases to separate. The upper and lower phases were evaporated at 70 °C for 30 min in order to remove the methanol.

2.3. Analysis of vegetable oil and methyl esters of fatty acids

After measuring their residual weight, the composition of the upper and lower portions were analyzed by gas chromatography (GC) (Shimadzu, GC-2010, FID), using a column of dimensions 15 m × 0.25 mm × 0.5 μm with DH-1ht as stationary phase. Eicosane was used as an internal standard. A stock solution of hexane with a known amount of eicosane was prepared. Samples were prepared by adding approximately 0.05 g of the oil phase to 5 ml of n-hexane. About 1 ml of this mixture was put into GC auto sampler vials. Two microliters of the sample were injected into the column. The parameters for the oven temperature program consisted of: start at 150 °C (2 min), ramp at 5 °C/min to 250 °C/min).

3. RESULTS AND DISCUSSION

Vegetable oils are triglycerides containing three fatty acids linked by ester linkages to a glycerin moiety. The fatty acids vary in their carbon chain length and in numbers of double bonds. The fatty acid compositions of the oil samples used are shown as follows (wt%): Palmitic, 11.2; Stearic, 3.7; Oleic, 22.1; Linoleic, 55.0; Linolenic, 6.8 and other acids, 1.2. There was little difference between the gross heat content of any of the vegetable oils [11]. Heat contents were ≈88% of that of No. 2 diesel.

It can be assumed that the transesterification of soybean oil in supercritical methanol proceeds by the same reaction mechanism as that for transesterification with liquid methanol. It is believed that CO_2 has no effect on the reaction mechanism. The reaction proceeds without any catalyst as follows: triglycerides + methanol = glycerin + methyl esters.

Transesterification is an equilibrium reaction. In the reaction system, an excess of methanol was used in order to shift the equilibrium to the right and produce more methyl esters as product.

Reactions of supercritical methanol with soybean oil were carried out in a batch-type reaction vessel. In all of the experiments, the amount of the soybean oil loaded was kept constant. Therefore, the temperature and the pressure inside the reaction vessel vary with reaction conditions. The critical point of methanol occurs at 239 °C (Tc) and 8.09 MPa (Pc), while for CO_2 it is 31.0 °C (Tc) and 7.28 MPa (Pc).

Critical points for the binary system are determined by the content of CO_2 in the binary system. It was found that the critical points of the binary system were achieved at temperatures, which decreased with increasing molar ratio of CO_2 to methanol.

Though increasing the molar ratio of CO_2 to methanol decreases the critical point of the system, the optimal temperature for the supercritical reaction does not decrease continuously. Fig. 2 shows the changes in weight percentage of methyl esters formed with different molar ratios of CO_2 and methanol under supercritical conditions as a function of reaction temperature.

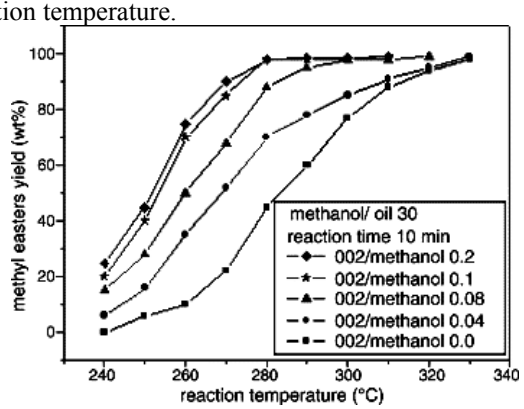

Fig. 2. Changes in weight percentage of methyl esters formed with different molar ratios of CO_2 and methanol under supercritical conditions as a function of reaction temperature.

Fig. 2 gives the relationship between the molar ratio of CO_2 to methanol and the reaction temperature. It is clear that when the molar ratio is very low, the optimal reaction temperature drops sharply with increasing amounts of CO_2. However, when the ratio reaches a certain point, the optimal temperature remains constant. This indicates that the transesterification reaction has a high-energy barrier, and that either a high reaction temperature or the presence of a catalyst is required if the reaction to proceed. It was found that the optimal temperature is 280 °C when the molar ratio of CO_2 to methanol is 0.1 or higher.

The molar ratio of methanol to vegetable oil is one of the most important variables affecting the yield of methyl esters. In this reaction, an excess of methanol was used in order to shift the equilibrium in the direction of the products. Kusdiana and Saka have suggested that higher molar ratios of methanol to oil also result in a more efficient transesterification reaction, due perhaps to the increased contact area between methanol and triglycerides [12]. However, higher molar ratios of methanol to oil result in increased reaction pressures, which impose stringent requirements on the reaction vessel. In this work, CO_2 as co-solvent is added to the reaction system in order to increase the mutual solubility between methanol and vegetable oil under supercritical conditions. Since supercritical CO_2 is a good solvent for vegetable oil, it allows the reaction mixture to form a single phase at a much lower temperature. Therefore, a much lower molar ratio of methanol to oil is needed, and accordingly the reaction pressure is reduced significantly.

In order to determine the effect of varying the molar ratio of methanol to oil on the formation of methyl esters, transesterification reactions of soybean oil were carried out at a fixed temperature of 280 °C and a fixed CO_2/methanol ratio of 0.1. As shown in Fig. 3, for molar ratios ranging from 6 to 42, the optimal ratio is 24. For molar ratios less than 24, the reaction is incomplete, whereas at higher ratios, the supercritical pressure rises significantly. With a reaction temperature of 280 °C, a CO_2/methanol ratio of 0.1 and a methanol/oil ratio of 24, a high conversion of soybean oil to methyl esters is observed with a yield of 98.5% in 10 min at a reaction pressure of only 14.3 MPa.

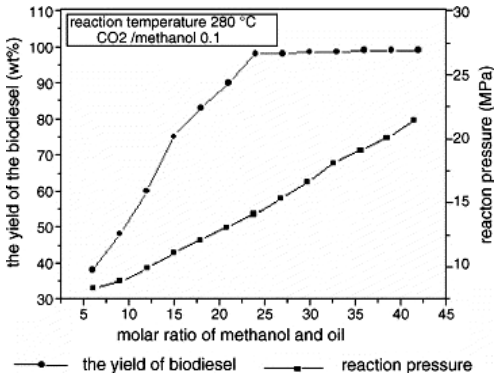

Fig. 3. Effects of varying the molar ratio of methanol to oil on the formation of methyl esters and on the pressure of the reaction system.

The effects of varying temperature in the range of 200–310 °C on the formation of methyl esters were investigated. The reactions of soybean oil were carried out with a fixed methanol/oil ratio of 24 and a CO_2/m ethanol ratio of 0.1. The resulting experimental data are shown in Fig. 4.

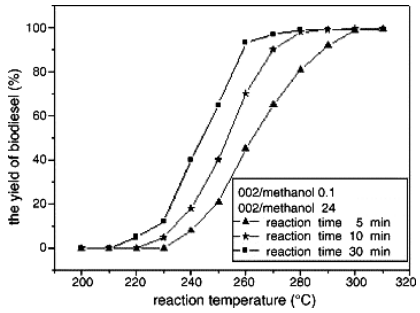

Fig. 4. Effect of temperature on the yield of the transesterification reaction of soybean oil.

As shown in Fig. 4, at temperatures of 200 and 230 °C, the yields of methyl esters are relatively low. This is perhaps due to the subcritical state of methanol or the instability of the supercritical state of methanol. Under these conditions, the yield of methyl esters is very low even after reaction for 30 min. The similar result has been reported by Diasakou et al. [13]. At a temperature of 260 °C, the conversion increases significantly. After 10 min, about 70% conversion to methyl esters is observed. At 280 °C, conversion to methyl esters exceeds 98% after 10 min and when the temperature is increased to 300 °C, the transesterification reaction is essentially complete within 5 min.

These results indicate that addition of a co-solvent allows the reaction to be carried out under significantly milder conditions compared with previous reports. In addition, a kinetic study clearly indicates that the reaction rate constant for transesterification increases markedly when the co-solvent is added to the supercritical system.
A mixture of methyl esters of vegetable oil, or biodiesel, is very similar to conventional diesel fuel. Its viscosity is only twice that of diesel and its molecular weight is roughly one-third that of vegetable oil. The viscosities of the methyl esters obtained from soybean oil were slightly higher than that of No. 2 diesel. The measured values of the viscosities of the methyl esters were in the range 3.5–4.0 mm^2/s at 20 °C.

The transesterification reaction of soybean oil to methyl esters proceeds efficiently at a temperature of 280 °C with supercritical methanol and CO_2 as a co-solvent in the absence of any catalyst. The optimal molar ratios of methanol/oil and of CO_2/methanol are 24 and 0.1, respectively. The composition of the resulting biodiesel is analyzed by the GC trace, which indicated that over 98% triglycerides were transformed to methyl esters within 10 min.

4. CONCLUSION

Supercritical methanol with a co-solvent process is superior to the conventional supercritical methanol method. As a co-solvent, CO_2 is both easy to add to the system beforehand and to remove from the system when the reaction is complete. The merit of this method is that much lower reaction temperatures and pressures are required. In addition, because of the absence of catalyst, the purification of products after transesterification is much simpler and more environmentally friendly.

Compared with the conventional supercritical methanol method, less energy is required for the process. Furthermore, the reaction pressure required is significantly reduced, which makes the process safer and lowers production costs. The relatively mild reaction conditions and high yield of methyl esters using this environmentally friendly method make it viable for practical use in industry.

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