초임계 메탄올을 이용한 팜오일의 에스테르 교환 반응

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Transesterification of palm oil using supercritical methanol

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1. Introduction

Biodiesel (fatty acid methyl esters; FAME) has attracted much attention as an alternative for petroleum fuel because of the great molecular similarities of biodiesel to parafinic diesel fuel compounds and the fact that it comes from renewable resources [1]. Recently biomass has been considered as one of the renewable energy resources due to its high potential, economical feasibility and environmental benefits. Several sources for producing biodiesel have been studied such as rape seed, coal seed, palm oil, sunflower oil, waste cooking oil, soybean oil, etc.

Existing conventional methods for biodiesel production use a basic or acidic catalyst. However, the catalytic methods 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, the processes using supercritical alcohol without catalyst have been extensively studied [2 - 4]. Saka et al [5, 6] have proposed that biodiesel fuels can be produced using supercritical methanol process without using any catalyst. They reported that new supercritical methanol process requires the shorter time and simpler purification procedure because of the unused catalyst. Though preparation of biodiesel with supercritical way has many advantages compared to the catalytic methods, it also has some disadvantages.

2. Experimental

2.1. Materials

Palm olein oil was supplied by Sinar Konex Co. Ltd. Methanol (Extra pure grade 99.5 %) was purchased from Daesung Chemical Co. Ltd. Methyl heptadecanoate [$CH_3(CH_2)_{15}COOCH_3$] used as an internal standard and n-heptane (≥99 %, analytical grade) for GC analysis were supplied by Aldrich and Kanto Chemical, respectively.

2.2. Transesterification

The reaction of transesterification was carried out in a flow type tubular reactor (4.35 mm i.d., 6 m) equipped with a condenser, product collector and preheaters. Two plunger type high-pressure pumps were used for feeding methanol, and palm olein oil, respectively. First, Palm olein oil needs to be heated to 60℃ to supply as liquid state. Then the preheaters (50 - 350℃) and reactor (200 - 400℃) were preheated at a designated temperature, respectively. Calculated amounts of methanol were fed into the reactor by the high pressure pumps. After the reactor was filled by methanol and palm olein oil was supplied to the reactor. The residence time of reactants in the reactor was 40min. The temperature and pressure inside the reactor were controlled by an electric thermostat and back pressure regulator, respectively. After reaching the steady state, the product cooled to the normal temperature through the condenser was sampled. The product was evaporated at 70℃ for 20 min using rotary evaporator to remove the residue methanol. Finally, the product was separated to the crude methyl esters and grycerol.

2.3. Analysis

The methyl ester content was quantified using a gas chromatography (HP-6890) equipped with a HP-INNOWax capillary column (30 m × 0.32 mm × 0.25 μm) and a frame ionization detector. European Standard (EN ISO 5508) method was used to calculate the methyl ester content. 10.00 mg methyl heptadecanoate (internal standard) was dissolved in 1 ml heptane to prepare the standard solution. 50 mg crude methyl ester was dissolved in 1 ml standard solution for GC analysis. Samples (1 μl) were injected into the GC by a sampler at an oven temperature of 210℃. GC oven was heated at 2℃/min to 250℃ and at 4℃/min to 260℃, and held for 7.5 min. The content of fatty acid methyl esters was calculated by the following formula.

$$C = \frac{(\sum A) - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{W} \times 100(\%)$$

$\sum A$ = The total peak area of` methyl ester

$\sum A_{EI}$ = The peak area of` methyl heptadecanoate

$\sum C_{EI}$ = The concentration (mg/ml) of` standard solution (methyl heptadecanoate)

$\sum V_{EI}$ = The volume (ml) of` standard solution (methyl heptadecanoate)

W = The weight (mg) of` Sample

3. Results and Discussion

Temperature is important factor for the supercritical fluid. Figure 2 shows the influence of temperature on the FAME yield. As the temperature increased, the FAME yield increased. The FAME yield reached the maximum (86.3%) at 350℃ and then decreased with increasing the temperature. It was found that the optimal temperature is 350℃.

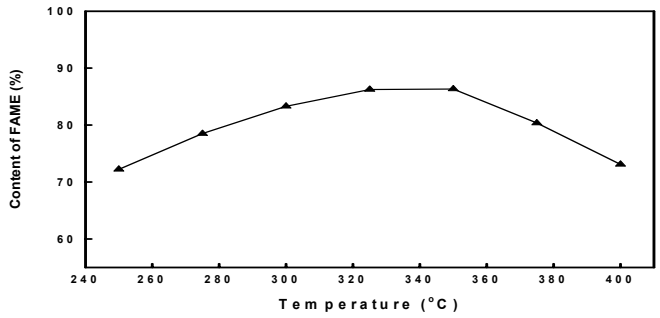

Figure 2. Influence of temperature on the FAME yield. (Molar ratio of methanol/palm oil: 60, 40 MPa)

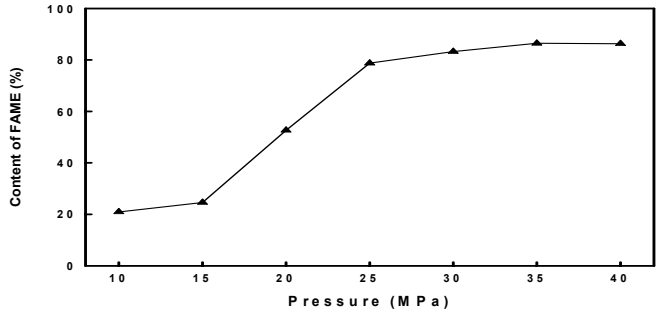

Figure 3. Influence of pressure on the FAME yield. (Molar ratio of methanol/palm oil: 60, 350℃)

Pressure has also a great impact on the properties of supercritical fluid, such as density, hydrogen bond intensity and so on. Figure 3 shows the influence of pressure on the FAME yield. The FAME yield increased with the increase of the pressure. After the pressure increased to 35 MPa, the increase of pressure did not improve the FAME yield. Therefore, the optimal pressure was fixed on 35 MPa in our experiment.

The molar ratio of methanol to palm oil is one of the most important variables affecting the FAME yield. The reaction of transesterification proceeds without any catalyst as follows:

Triglycerides + Methanol ↔ Glycerin + Methyl esters

In this reaction, an excess of methanol should be used in order to shift the equilibrium in the direction of the products. Namely,in order to reach a high FAME yield, it requires a high molar ratio of alcohol to oil. As the consumption of methanol increases, production cost and energy to evaporate and recover the methanol increase. Therefore, it is important to reduce the amount of methanol used in the supercritical methanol process. The effect of molar ratio of methanol to palm oil on the FAME yield is shown in Figure 4. When the molar ratio of methanol to palm oil was lower than 10, the FAME yield increased rapidly with the increase of molar ratio. Whereas at higher ratios, the FAME yield increased slightly with the increase of molar ratio.

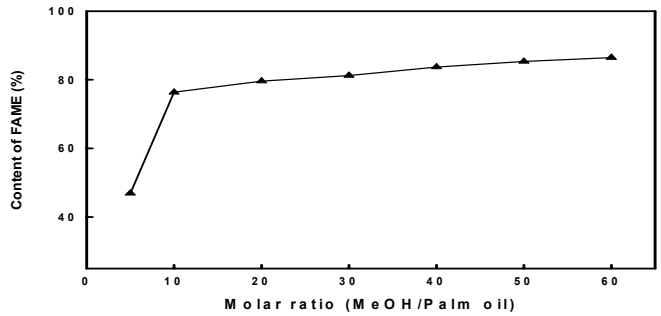

Figure 4. Influence of the molar ration of methanol to palm oil on the FAME yield. (350℃, 35 MPa)

4. Conclusions

Transesterification of thepalm oil in supercritical methanol was investigated without using any catalyst. The supercritical method requires a high molar ratio of alcohol to oil in order to reach a high FAME yield. HCFC-141b was used as a co-solvent in order to reduce the amount of methanol.

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