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Transesterification of Vegetable Oils in Pulsed-Corona Plasma Discharge Process

Young-Jin Hyun† · Young-Sun Mok · Doo-Il Jang

†*Department of Chemical Engineering and Life Science, College of Engineering, Cheju National University, Jeju-Shi, 690-756, Korea*
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Abstract : The biodiesel production characteristics in a pulsed-corona plasma reactor has been investigated through parametric tests. Transesterification of rapeseed oil together with camelina oil was done with the change of such variables as voltage of power, molar ratio, KOH catalyst and temperature. The energetic electrons emitted from pulsed-corona plasma has contributed to the enhancement of yield on rapeseed oil in short time (15 min). The higher yield on camelina oil was observed in 5 min. The optimal parameters were shown as the voltage of 23 kV, the molar ratio of 5/1, the content of KOH catalyst of 0.6 wt% and the temperature of 28 ℃ under the rotating rate of spark gap of 900 rpm.

Keywords : *pulsed-corona plasma reactor, transesterification, higher biodiesel yield, energetic electrons, optimal parameters.*

1. Introduction

The consumption of petroleum has been continuously increased, and the resource of fossile fuels lasts to be depleted until now. In addition, an uncontrolled usage of petroleum has affected environmental quality. That is why it is necessary to find an alternative fuel, especially the fuel for diesel engines. A renewable fuel is, that is to say, biodiesel[1~3]. There exit such many feed-stocks as vegetable oils and animal fats for biodiesel. In the initial stage, they have been used directly as a mixture of oil and diesel fuel in a appropriate ratio. Their direct usage has shown to be unavailable due to their high viscosity, carbon deposit and gum formation of free fatty acid[4,5]. Above this direct usage, other usage methods contain pyrolysis, microemulsion and transesterification. Biodiesel consists of long chain fatty acid methyl ester (FAME) produced by transesterification reaction of oils or fats with methanol or ethanol using an alkali, acid or enzyme catalyst. Transesterification depends upon molar ratio of methanol to oil, catalyst type and content, reaction time and temperature. Even the commercial process using alkali catalyst shows some drawbacks, one of which is a viscosity rising due to soap formation during winter[6,7]. To soothe this problem, a washing step is required to remove alkali catalyst dissolved in biodiesel. In the course of this treatment, more wastewater discharges. Also, the cost for the

†Corresponding author
(E-mail : yjhyun@jejunu.ac.kr)

separation of biodiesel goes up. Hence, heterogeneous catalysts or enzymes have been replaced by homogeneous catalysts. But heterogenous catalytic and enzymatic processes at high molar ratio of methanol to oil takes long time to produce biodiesel. As a result, more energy is needed in this cases[8]. Consequently, an alternative process using microwave radiation or plasma discharge appeared to lessen those troubles. Hernando et al., conducted transesterification of soybean oil with 3 wt% NaOH-dissolved methanol using 100 kW microwave radiation at the molar ratio of methanol to oil of 12/1 for short time, and 97% conversion efficiency was obtained. It was thought that the methanol was excited by the local temperature rise due to microwave radiation and that higher conversion efficiency was obtained. The microwave radiation process shows some disadvantages : i.e., high molar ratio and higher power[9]. Recently, to overcome these problems, the corona plasma technology especially called the pulsed-corona plasma was adopted. The pulsed-corona plasma delivers energy directly at the strong and weak paces to the reactants during discharge, and the reactants as well as catalyst are efficiently activated during short reaction time[10]. The effective transesterification using the pulsed-corona plasma is ascribed to the direct attack of pulsed-corona plasma on reactants and catalyst. This technology is expected to reduce the reaction time as well as the reaction temperature considerably because of the role of strong electrons. Istadi et al., produced biodiesel from palm oil in plasma reactor at a higher voltage of about 948 V, the temperature of 65℃ and the molar ratio of methanol to oil of 10/1 without alkali catalyst. In the course of the pulsed-corona discharge, the soap was not formed, but no addition of alkali catalyst brought about much less conversion efficiency[11,12]. My experiment of transesterification using alkali catalyst in a pulses-corona plasma reactor was the first attempt to save operating temperature and time. The biodiesel yield was estimated with the change of power, molar ratio, content of KOH catalyst, temperature and vegetable kinds. This paper was aimed at presenting the optimal process parameters in biodiesel production in the pulsed-corona plasma reactor.

2. Materials and Method

2.1. Materials

Rapeseed oil (Jeju Euchae, Co.) and camelina oil (Bio Chemical International, FL.) were purchased in Korea and from US respectively. Potassium hydroxide, n-hexane, methanol (99%) and chloroform (Oriental Chemical Industries, Incheon) were purchased in Korea.

2.2. Apparatus and Method

The schematic representation HV pulse apparatus set-up is shown in Fig. 1. The main components consisted of the pulsed-corona plasma reactor (80 mL) fabricated by acryl resin, a DC high voltage source, a digital oscilloscope (TDS 3032, Taker onix), a rotary spark gap switch and a current transformer. Positive powers was applied to the electrode. The rotating rate of spark gap to produce pulsed-corona plasma was set to be 60 Hz (900 rpm). The mixture of rapeseed oil and KOH-dissoved methanol was fed into the the pulsed-corona plasma reactor. While mixing it with magnetic bar, transesterification was started under the rotating rate of spark gap of 900 rpm at 28 and 35 ℃, respectively. Batch transesterification was performed at 65 ℃. We ajusted the operating parameters as the molar ratio of methanol to oil (3:1, 5:1 and 8:1), the content of catalyst KOH (0.4, 0.6 and 0.8 wt% based on the oil) and the applied voltage (18, 23 and 28 KV). After the

reaction was completed, the product was taken to the cone settler.

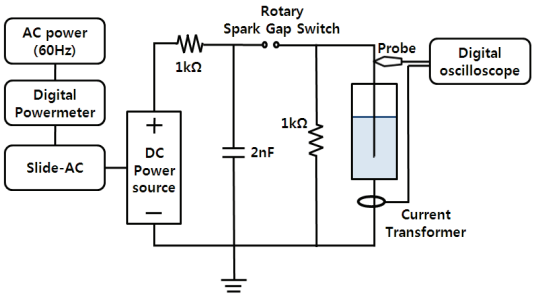

Fig. 1. Schematic representation of HV pulse apparatus setup.

2.3. Analysis

After evaporating the methanol in the product, the glycerol of product was extracted using the mixed solvent which is composed of n-hexane and chloroform (Oriental Chemical Industries, Korea) at the volume ratio of n-hexane (2 mL) to chloroform (1 mL) two times. Biodiesel yield (%) was calculated by the following expression.

$$\text{Yield (\%)} \fallingdotseq (m_{glycerol,actual} / m_{glycerol,theoretical}) \times 100 \quad (1)$$

Where $m_{glycerol,actual}$ (g) is the actual amount of glycerol and $m_{glycerol,theoretical}$ (g) is the thoretical amount of glycerol.

3. Results and Discussion

3.1. Effect of voltage of electrode on biodiesel yield

The increase of applied voltage brings more energetic electrons discharge from the electrode. The energetic electrons then excite and activate the OH group of methanol[10]. While energetic electrons attack methanol and catalyst, the formed methoxide ion is an initiator for transesteification[11]. To compare the effect of power voltage on biodiesel yield, transesterification of rapeseed oil using 0.6 wt% KOH catalyst was conducted in the pulsed-corona plasma reactor at a molar ratio of 5:1, rotating rate of spark gap of 900 rpm and 28 ℃. Fig. 2 shows the dependence of power voltage on biodiesel yield. When the power increased up to more than 23 kV, the biodiesel yield increased to 98% in 15 min as seen in Fig. 2, At the higher voltage than 23 kV, the biodiesel yield was nearly not changed due to no effect of the higher voltage on amount and intensity of methoxide ion formed by strong electron discharge. Accordingly, there existed an optimal voltage of 23 kV.

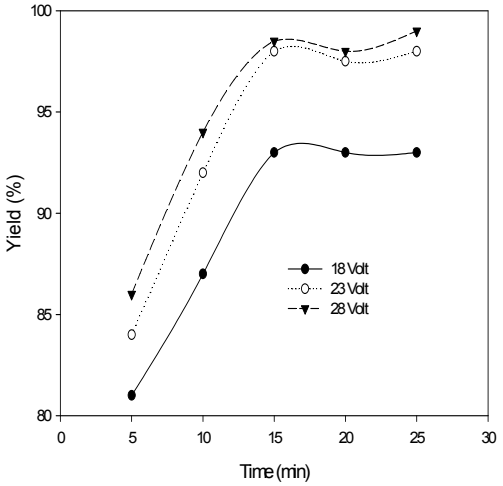

Fig. 2. Effect of voltage on biodiesel yield.

3.2. Effect of molar ratio of methanol to oil on biodiesel yield

The molar ratio of methanol to oil is able to determine the direction of transesterification. As the molar ratio goes up, more methoxide ions are formed by the attack of energetic electrons on methanol. The ions lead to the further cleavage of glyceride bond of oil. So, the transesterification proceeds forward.

As the case studied for the molar ratio, Darnoko et al., did the continuous

transesterification of palm oil using 1 wt% KOH at the 6:1 molar ratio and 65 ℃ in 60 min and presented the conversion of 97.3%[13]. Anggoro et al., showed the molar ratio of methanol to palm oil during trasesterification was 10:1 at higher voltage of about 948 V and temperature of 65℃ without alkali catalyst. It took about 11 min to obtain the biodiesel conversion of 37.8%[14]. To find the dependence of molar ratio on biodiesel yield, transesterification of rapeseed oil using 0.6 wt% KOH was carried out in a pulsed-corona plasma reactor at 23 kV and 28℃under the rotating rate of spark gap of 900 rpm. Fig. 3 represents the dependence of molar ratio on biodiesel yield. As plotted in Fig. 3, biodiesel yield increased with molar ratio and appeared to be 98% at molar ratio of 5/1, 28℃ and 0.6 wt% KOH in 15 min. Despite the conventional molar ratio of 6/1-8/1, the molar ratio of 5/1 was obtained due to an easy activation of methanol by strong electrode emitted from the pulsed-corona plasma. Therefore, an optimal molar ratio appeared to be 5/1.

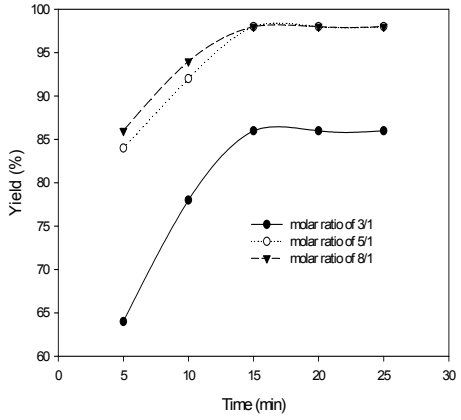

Fig. 3. Effect of molar ratio of methanol to oil on biodiesel yield.

3.3. Effect of catalyst content on biodiesel yield

The catalyst is an important variable to enhance or retard the reaction rate due to lowering or raising of the activation barrier of methanol. The catalysts suitable for transesterification have such various types as acid (H_2SO_4, para Toluene sulfamic acid), alkali (KOH, NaOH) and enzymatic (Novozym) catalysts[15]. KOH as a conventional alkali catalyst was used for transesterification of rapeseed oil at molar ratio of 5/1, temperature of 28℃, voltage of 23 kV and rotating rate of spark gap of 900 rpm in the pulsed-corona plasma reactor and a batch reactor, respectively. Fig. 4. indicates the effect of catalyst content on biodiesel yield. When the content of KOH increased to 0.6 wt% KOH, the biodiesel yield of rapeseed oil rose up to 98% in 15 min. Therefore, the higher surface activation of KOH led to lowering the activation barrier during the pulsed-corona discharge. However, the biodiesel yield at 0.6 wt% KOH, molar ratio of 5/1 and temperature of 28℃ in a batch reactor was significantly lower in 15 min due to no discharge of pulsed-corona plasma. It is thought that 0.6 wt% KOH in a pulsed-corona plasma reactor was an appropriate content in short time.

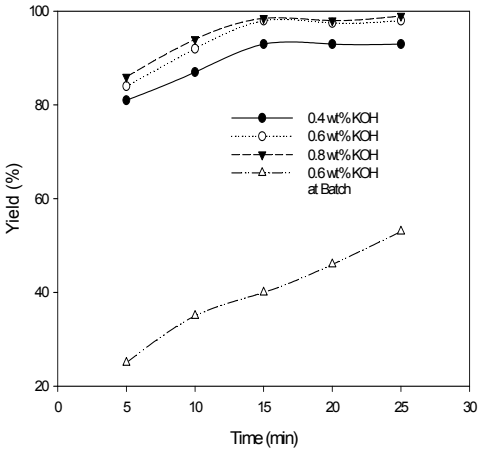

Fig. 4. Effect of catalyst content on biodiesel yield.

3.4. Effects of reaction temperature on biodiesel yield

The reaction temperature is an operating variable to decide the energy cost in the course of transesterification reaction[15]. As the electrons emitting from pulsed-corona plasma attack the catalyst and the reactants easily, there is no need to elevate temperature to obtain high yield of oil in the plasma reactor. In this research the transesteification of rapeseed oil in a pulsed-corona plasma reactor at power of 23 kV, a molar ratio of 5/1, 0.6 wt% KO,H, rotating rate of spark gap of 900 rpm with the change of temperature and in a batch reactor at 65 ℃ was done respectively. The dependence of reaction temperature on biodiesel yield is presented in Fig. 5.

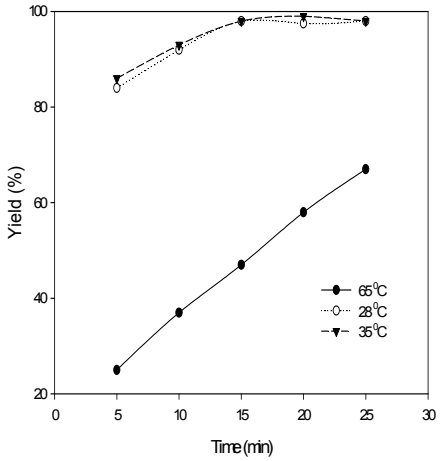

Fig. 5. Effect of reaction temperature on biodiesel yield.

The temperature, which was varied from 28 to 35 ℃ did not affect biodiesel yield in a pulsed-corona plasma reactor. It is founded that the biodiesel yield in a pulsed-corona plasma reactor was independent of the temperature range from 28 to 35℃. On the other hand, the biodiesel yield using 0.6 wt% KOH in a batch reactor despite high temperature (65 ℃) was much less than that in a pulsed-corona plasma reactor at 28 ℃ in 15 min. This was ascribed to the absence of a pulsed-corona plasma discharge during alkali-catalyzed batch transesterifictation.

3.5. Effect of vegetable kinds on biodiesel yield

There are many feed-stocks of such vegetable oils as rapeseed, camelina, soybean, palm and jatropha oils for biodiesel production. The rapeseed, which has been cultivated and utilized for various usages in Jeju Province since a 1960s, is an useful crop[16]. Above those, the rapeseed oil contains higher amount of unsaturated fatty acid among various vegetable oils. In recent years, the camelina has been cultivated mainly in foreign countries, and its oil shows the amount of unsaturated fatty acid of 96.5 wt%[17]. Accordingly, two oils have been adopted as feed-stock for biodiesel. Transesterification of rapeseed oil together with camelina oils was done, respectively, in the pulsed-corona plasma reactor at molar ratio of 5/1, power of 23 kV, temperature of 28℃ and 0.6 wt% KOH, rotating rate of spark gap of 900 rpm. Fig. 6 represents the effect of kinds of vegetable oil on biodiesel yield. Since camelina oil is composed of almost unsaturated fatty acids except for saturated fatty acid of 3.1 wt% and free fatty acid of 0.34 wt%, its biodiesel yield increased to 95% abruptly in 5 min. It is observed that sudden enhancement of yield in 5 min depended upon the easy cleavage of glyceride bond by methoxide ions.

It should be noted that camelina oil shows shorter reaction time than rapeseed oil and might be better feed-stock. Rapeseed oil has been produced in Jeju province until now, but camelina oil should be imported. Considering another respects of supplying costs of feed-stock, it is suitable to use the mixed feed-stock, which camelina oil is combined with rapeseed oil.

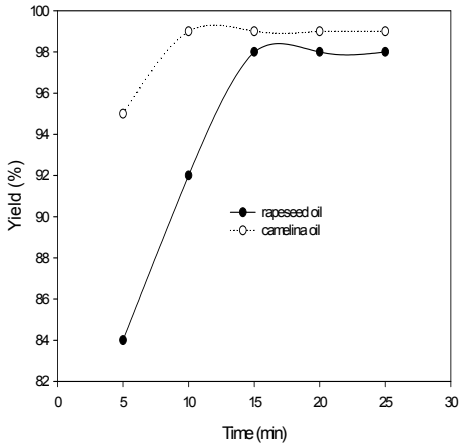

Fig. 6. Effect of kinds of vegetable oil on biodiesel yield.

4. Conclusions

The transesterification of rapeseed oil along with camelina oil in the pulsed-corona plasma reactor has been performed through a series of parametric tests. The following conclusions have been drawn. The high biodiesel yield from rapeseed oil was obtained with power of 23 kV for short time. The higher improvement of yield in short time was due to the pulsed-corona electrons to overcome the activation energy of methanol. their yield appeared to be 98% at the power of 23 kV, the molar ratio of 5/1, 0.6 wt% KOH and 28 ℃ under the rotary rate of spark gap of 900 rpm in 15 min. The easier cleavage of glyceride bond in camelina oil than rapeseed oil by methoxide ion ended up sudden enhancement of yield in 5 min.

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