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Effects of ultrasonification and mechanical stirring methods for the production of biodiesel from rapeseed oil

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Abstract−This study was conducted to compare the effects of ultrasonic energy and mechanical stirring methods in bio-diesel production from rapeseed oil under base catalysis conditions. With the transesterification of rapeseed oil, the molar ratio of methanol to vegetable oil was 6 : 1, and the amount of catalysts added to the vegetable oil was 0.3, 0.5 and 1.0% (wt/wt). The main components of methyl esters from the transesterification of rapeseed oil were oleic acid (48.5%, C18:1) and linoleic acid (18.1%, C18:2). In addition, the optimum conditions to produce fatty acid methyl esters (96.6%) were 0.5% KOH after 25 min of ultrasonification at 40 °C as compared to mechanical stirring at 60 °C. The maximum conversion ratio was 75.6% with 1.0% NaOH after 40 min of ultrasonification at 40 °C. These results indicate that ultrasonic energy could be a valuable tool for transesterification of fatty acids from rapeseed oil in terms of the reaction time and temperature.

Key words: Bio-diesel Production, Fatty Acid Methyl Esters, Rapeseed Oil, Transesterification, Ultrasonification

INTRODUCTION

The social needs for alternative fuels of traditional diesel fuel are becoming increasingly important due to the exhaustion of fossil resources and reserves and the environmental consequences caused by gases from petroleum-fired industry. Many researchers have concentrated on the development of environmentally friendly chemical processes to use vegetable oils or other natural sources for bio-diesel production. Both vegetable oils and animal fats contain mixtures composed of triglycerides, which can be used as a fuel, such as esters having a tri-alcohol (glycerol) with three different fatty acids. In particular, vegetable oils are able to commonly be extracted from seeds, but their viscosity is 10-20 times higher than that of petroleum fuel. The high viscosity using directly vegetable oils as a fuel is one drawback because it can cause problems in engine operation such as injector fouling and particle agglomeration [1].

Bio-diesel consists of fatty acid methyl esters with short chain alcohols, and mainly methanol affords the corresponding alkyl esters (Fig. 1). It has gained an important position as an environmentally friendly chemical process to substitute for diesel fuel. Fatty acid methyl esters have a significant potential as alternative to diesel fuel because their characteristics are almost the same. Biodiesel is chemically simple, since it is made of no more than six or seven fatty acid methyl esters. Different esters have very different fuel properties, including cetane number, density, viscosity, melting point, calorific values, and the degree of un-saturation [1]. Among of the many advantages of biodiesel over petroleum-derived diesel fuel, the most prominent is the reduction of greenhouse gas emissions. The amount of CO_2 production from pure bio-diesel fuel is 78.45% lower than that of petroleum diesel. If petroleum is blended with 20% biodiesel, net CO_2 emissions can be reduced by 15.66% [2].

Transesterification of vegetable oil to biodiesel (fatty acid methyl esters, FAMEs) can be catalyzed by bases, acids, and enzymes [3,4]. In fact, there are many parameters affecting the transesterification reaction. Well known influencing factors are temperature, methanol to oil molar ratio, mixing rate, and catalytic types and amount [5,6]. Considering a homogeneous alkali catalytic system, the optimal temperature tends to be the close to the boiling point of the alcohol used. Excess alcohol is necessary to promote a good conversion, and the best methanol to oil molar ratio (6 : 1) was reported [7]. Mixing rate should be high enough to promote the mixture of the reactants, which is particularly important because the system behaves as a two phase system (oil and alcohol with dissolved catalyst). In this case, the catalysts normally used are sodium and potassium hydroxides, sodium and potassium methoxides as well as sodium and potassium carbonates (metal alkoxides generally show better performance than hydroxides), and amount of catalyst used might vary from 0.2 to 2 (wt%), the typical value being 1 (wt%).

Base catalysts include homogeneous and heterogeneous base catalysts [5]. The commonly used homogenous catalysts are KOH, NaOH, and their alkoxides. Homogenous alkali-catalyzed transesterification is much faster than acid-catalyzed one [8]. However, a large amount of water is required to remove the residual catalyst from bulk bio-diesel after reaction. Base-catalyzed process is strongly affected by the degree of mixing reactants and/or by heat. Mixing can produce tiny droplets, thus increase the reaction area [9]. Ultrasonic irradiation of low frequency is widely used in industry for emulsification of immiscible liquids [10]. Carmen [11] reported that the conversion of FAMEs at the end of 60 min sonication (40 kHz)

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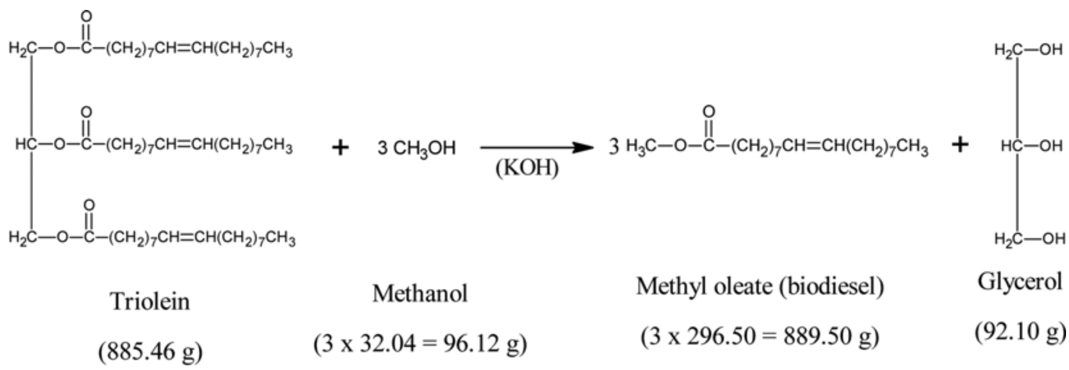

Fig. 1. Overall scheme of the triglyceride transesterifications. The given amounts are consistent with of 3 : 1 of a molar ratio of methanol : vegetable oil.

was almost the same regardless of the types of vegetable oils, meaning that the reaction mixture was in a steady state (i.e., equilibrium concentration was reached) at reaction temperature of 36±2 °C. Based on these results, it was concluded that 40 kHz ultrasound is much more effective in the reduction of reaction time (10-20 min), although 28 kHz gives slightly better yield (98-99%) with consuming the high energy. The optimization of the bio-diesel process should take into an account such parameters as well as the type of feedstock used. It is also necessary to know that even when the same vegetable oil is used, different behaviors of the produced oil might be found according to the refinement processes adopted during the production [12].

The aim of this study was to compare the effect of mixing methods of ultrasonic energy and mechanical stirring on bio-diesel production from rapeseed oil with a base catalyst added.

EXPERIMENTAL

1. Reagents and Materials

Both NaOH (>98.0%) and KOH (>85.0%) were purchased from DAEJUNG Chemicals (Seoul, Korea). The rapeseed oil was of commercial edible grade.

2. General Procedure

A 1 L glass reactor was prepared and equipped with a glass anchor shaped stirrer and a thermocouple. Two sets of experiments were performed. In the first set, the reaction was carried out with mechanical mixing. Mixing of 200 rpm was provided to the reactor with a mechanical mixer. During the reaction, the temperature was maintained at 60 °C with a heating mantle controllable with a proportional integral derivative (PID) temperature controller. The molar ratio of methanol to vegetable oil was 6 : 1, and catalysts of 0.3, 0.5, and 1.0% (wt/wt) were added to the vegetable oil. The hydroxides were dissolved into the methanol prior to the addition of vegetable oil. To estimate the bio-diesel yield from the studied oil, the mixture samples were collected intermittently for 60 min during the transesterification reaction. Then the samples were allowed to separate over night. Methyl ester and glycerol were formed in the upper and lower layers of the mixtures, respectively. After the phase separation, the traces of catalysts and methanol were washed three times with distilled water, filtered and stored at 4 °C until the samples were analyzed for fatty acid methyl esters. All the experiments were done in triplicate, and the average data are presented.

In the second set of experiments, ultrasound of low frequency (40 kHz) was supplied to the reactor during the reaction, the temperature of which is maintained at 40 °C. The other experimental procedure is the same with the first set.

3. Analysis and Calculations

For analyzing fatty acid methyl esters, a sample of 0.25 g was taken from bio-diesel mixtures and mixed with 5 g internal standard solution which had been prepared by dissolving 0.5 g methyl heptadecanoate into 50 g n-heptane. The composition of methyl esters was analyzed using an Agilent GC-FID with DB wax column (Agilent, Korea). The analytical condition was as follows: the carrier gas was helium, the temperatures of injector and detector were 250 and 280 °C, respectively, and the oven temperature was started at 50 °C and increased to 200 °C at the rate of 25 °C/min. Methyl ester contents (%) were calculated from the following equation.

$$E=(A_T-A_{C17}/A_{C17})\times(5\ C/M_S)\times 100 \tag{1}$$

where E=the methyl ester content (%), A_T=an area of all peaks (C_{14}-C_{24}), A_{C17}=an area of C_{17} peak, C=a concentration of C_{17} standard solution (mg/ml), and M_S=a mass of sample (mg).

For evaluation of bio-diesel yield under different conditions, the conversion ratio of bio-diesel from vegetable oil was estimated from the following equation.

$$\text{Conversion (\%)}=[\text{weight of bio-diesel} \times \text{methyl ester content (\%)}]/(\text{weight of oil}) \tag{2}$$

RESULTS AND DISCUSSION

Currently available primary methods for the production of biodiesel fuel using vegetable oils are direct use and blending of raw oils, micro-emulsions, thermal cracking, and transesterification. The most commonly used production method for converting vegetable oils or animal fats to biodiesel is transesterification, which was also used in this study. Composition of fatty acid methyl esters from transesterification of rapeseed oil with different mixing methods is described in Fig. 2. There were no significant differences in methyl ester concentrations in the products from the reaction with two different mixing methods. The products, i.e., methyl esters, consisted of 48.5% oleic acid (C18:1) and 18.1% linoleic acid (C18:2). These results with rapeseed oil showed 12.4% lower oleic acid than that from

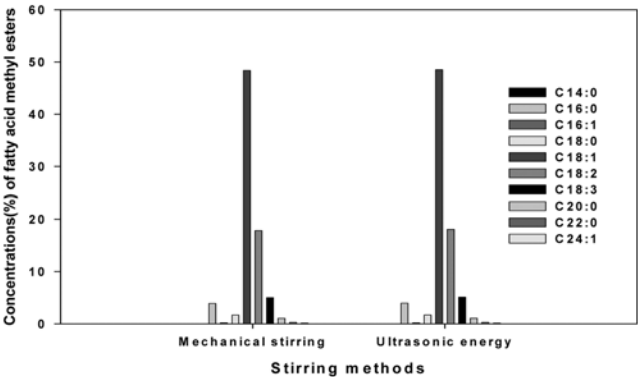

Fig. 2. Composition of fatty acid methyl esters after transesterification of rapeseed oil with different mixing methods.

the research by Imahara [13]. High un-saturation of fatty acid methyl esters causes polymerization and oxidation of fuel [13]. Compared with the results from a study with corn, bio-diesel from rapeseed oil had high contents of oleic acid for oxidation stability without any adverse effect on fuel cold properties; the methyl ester contents of the bio-diesel made from corn consisted of 25.5% oleic acid and 42.3% linoleic acid (data not shown). Generally, soybean oil and grape seed oil among commercialized vegetable oils mainly contain linoleic acid (54.9-68.9%), while canola oil and corn oil contain oleic acid of more than 60% [14].

Concentration of fatty acid methyl esters from the reaction was calculated using Eq. (1). In the reaction with the mixing supplied with ultrasound, content of fatty acid methyl esters was 96.6% with 0.5% KOH and 25 min reaction, and 98.1% with 1.0% NaOH and 40 min reaction at 40 °C. Regarding energy efficiency, it is strongly recommended that the proper reaction time is 25 min of sonification with 0.5% KOH addition for biodiesel production. In the one mixed with a mechanical stirrer, methyl esters of 96.5% could be obtained with 0.5% NaOH and 50 min reaction time at 60 °C (Fig. 3). High yield of fatty acid methyl esters by using these alkali catalysts

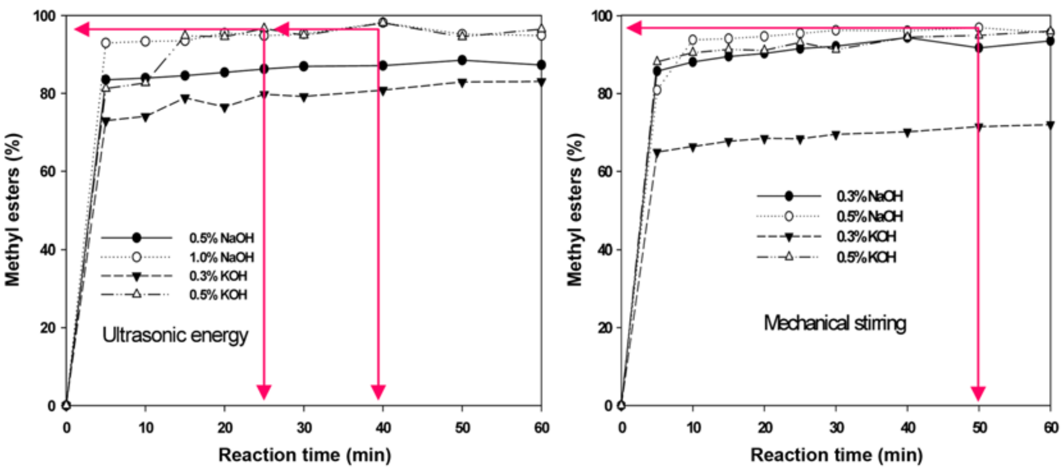

Fig. 3. Comparison of fatty acid methyl ester contents between mechanical stirring method and ultrasonic energy with different reaction conditions.

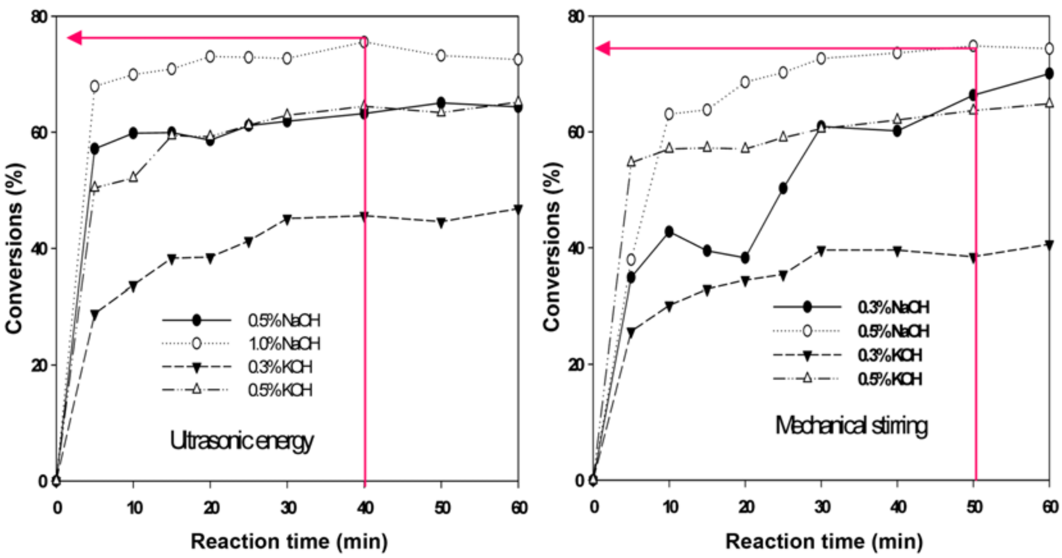

Fig. 4. Comparison of conversion ratio between mechanical stirring method and ultrasonic energy with different reaction conditions.

shows that they are the most economic catalysts able to be used under low temperature and pressure conditions. The yield of fatty acid methyl esters from both reaction methods guaranteed high enough to exceed the qualifying content (96.5%) of the esters in biodiesel set by the Korean Ministry of Industry and European Committee for Standardization, EN14214:2003 [15]. Carmen et al. [16] reported that concentrations of fatty acid methyl esters from corn, grape seed, canola and palm were 93.7, 93.6, 95.2 and 92.9%, respectively, with the addition of 0.5% KOH, 50 min reaction time, and 36±2 °C reaction temperature under ultrasonic irradiation. They observed slightly lower contents of fatty acid methyl esters than our study (about 1.4%), probably due to their low reaction temperature. Recently, Chung and Park [14] reported that the yield of fatty acid methyl esters reached at 68 to 86% in soybean, grape seed, corn and canola oils using 1.0% KOH catalyst addition to soybean oil under ultrasonic irradiation.

Conversion ratio of biodiesel from rapeseed oil was estimated from Eq. (2). The conversion ratios under ultrasonic irradiation by 40 min reaction with 1.0% NaOH addition at 40 °C and mechanical stirring by 50 min reaction with 0.5% NaOH at 60 °C were 75.6% and 74.8% (Fig. 4). Conversion yield of biodiesel from vegetable oil is theoretically equivalent to the amount of oil used for transesterification (Fig. 1). Some factors, including more ease of solubility of KOH catalyst in methanol than NaOH and the more quick reaction of methanol with triglycerides [5], can affect the yield of biodiesel. Over 1.5% NaOH would make glycerin byproduct that would turn to a gel or even solid. Conversion ratio did not reach at 100% because biodiesel was turning into the soap during the process of removing the residual catalyst with distilled water.

In short, the conversion ratio of the reaction with ultrasonic irradiation was not significantly different from the one with mechanical stirring. However, there is the advantage of supplying mixing to the reaction to produce biodiesel from vegetable oil with ultrasonic irradiation in that reaction temperature and time by using the method can be lowered and reduced, respectively, indicating the saving of production cost.

CONCLUSIONS

The effects of different mixing methods on the composition of fatty acid methyl esters from transesterification of rapeseed oil were compared. In one reaction, mixing was supplied with ultrasonic energy, and in the other reaction, mechanical stirring was applied. In short, no significant difference was observed between the reactions with two different mixing methods. The main compositions of methyl esters were 48.5% oleic acid (C18:1) and 18.1% linoleic acid (C18:2). However, when ultrasound energy is applied to mix reactants, fatty acid methyl esters can be obtained under even much lower temperature environment with supply of sufficient catalyst. This suggests that ultrasonic energy can be used as a valuable tool for transesterification of fatty acids from vegetable oil.

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