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Biodiesel production from canola oil using ultrasonic reactor in small scale circulation process

Le Tu Thanh[1]*, Kenji Okitsu[2], Yasuhiro Sadanaga[1], Norimichi Takenaka[1], Hiroshi Bandow[1]

[1]Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University,
1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, JAPAN
[2]Department of Materials Science, Graduate School of Engineering, Osaka Prefecture University,
1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, JAPAN
*e-mail: lethanh@chemosakafu-u.ac.jp

Abstract

Currently, most of the biodiesel is produced from vegetable oils and methanol in the presence of base catalysts using mechanical stirring method at temperature 50-65°C. This method consumes much energy because oils and methanol must be heated up to desired temperature, and also requires rather long reaction time. Ultrasound-assisted reaction can reduce the reaction time much shorter than mechanical stirring and the reaction can be carried out at room temperature, so energy can be saved. In the pilot scale the trans-esterification was performed by circulation process under low frequency ultrasound (20 kHz) with the input capacity of 1 kW. Effect of various process parameters such as the amount of KOH, molar ratio of oil to methanol and also reaction time were investigated. The optimal conditions for the process were: oil/methanol molar ratio 1:5, the amount of KOH to oil 0.7 % w/w. Under these conditions, conversion of triglycerides to fatty acid methyl esters (FAMEs) was 96.3% within the reaction time 60 minutes . Glycerin, catalyst and excess methanol were separated easily from FAMEs phase. Crude biodiesel was purified by washing with tap water and drying at 65°C under reduced pressure at 520torr.

Keywords: canola oil; ultrasonic irradiation; trans-esterification; KOH catalyst; circulation process.

Introduction

The price of fossil diesel is rapidly increasing in recent years, and it will be exhausted some day. Thus, looking for alternative way to develop a substitute for fossil diesel is necessary. Biodiesel, defined as 'a substitute for, or an additive to diesel fuel that derived from the oils and fats of plants and animals' is becoming popular in the markets of developing countries as well as developed ones (Yong Wang *et al.,* 2007). Furthermore, biodiesel fuels have many advantages over petrolium fuel: Produce less smoke and particales, lower carbonmonoxide and hydrocarbon emissions, have high cetane number, and are renewable, easily biodegradable and non-toxic (H. Nuoreddini *et al*., 1998).

Trans-esterification reactions have been studied for many vegatable oils such as soybean, rapeseed, sunflower, safflower, and so on (Feedman. B *et al*., 1984). Common catalysts for trans-esterification are NaOH, KOH, and CH_3ONa. Most of biodiesel is produced by transesterification reaction using mechanical stirring. This method consumes much energy because oils and methanol must be heated up to desired temperature, and also requires rather long reaction time. Because reaction is carried out at high temperature and long reaction time, the soap formation is usually much, resulting in difficult purifying of final product.

It is known that power ultrasonic is a useful tool for strengthening mass transfer of liquid-liquid heterogeneous system (Jianbing Ji *et al*., 2006). In this process, cavities would be created by the irradiation of power ultrasonic with sufficient energy in the immiscible liquids. As a result, micro bubbles are formed. The collapse of the cavitation bubbles disrupts the phase boundary and impinging of the liquids creates micro jets, leading to intensive emulsification of the system (Carmen Stavache *et al*., 2007). By this way, oil and methanol are easily mixed together, and the trans-esterification occurs fast.

In this study, the trans-esterification between oil and methanol in the presence of KOH catalyst was perfomed by ultrasoud irradiation. Some significant conditions such as: molar ratio of oil to methanol, amount of catalyst and reaction time were investigated. It is hoped to establish the optimum reaction conditions for good yields in the minimum reaction time as well as meterial and energy consumption.

Materials and Methods

Materials and apparatus

Canola oils were of commercial edible grade with acid value 0.8 (free fatty acid 0.4%), KOH (95.5%) and methanol (99%) were purchased from Wako Pure Chemical Industries.

Dr. Hielscher ultrasonic transducer model UIP 2000 having a frequency of 20kHz and total power of 1kW was used as an ultrasound source, and connected to a reactor with the working volume of 3L. System to separate glycerin and crude biodiesel, and to purify biodiesel was designed by Kimura Chemical Plants Co., Ltd with the capacity of 100lit/one batch process.

Procedures

The experimental setup for the trans-estrification process is schematically depicted in Fig.1. In each experiment, 54L oil and methanol in a given molar ratio containing KOH were fed to the reactor and a circulation tank by a liquid pump. The feeding ratio of the reactants was controlled by a valve system. After 10 minutes, all reactants were transferred to the circulation tank. Feeding valves for oil and methanol were closed, and the circulation tank valve was opened. Then the circulation of the reactants was carried out for 60 minutes. The reaction mixture was settled for a given time e.g. 4-10 hours to separate glycerin, excess methanol, and crude biodiesel. The crude biodiesel was purified by washing 3 times with tap water (water to biodiesel: 20% v/v), and dried by heating up to 65^{o}C with a mild flushing of a dry air under reduced pressure at 520torr.

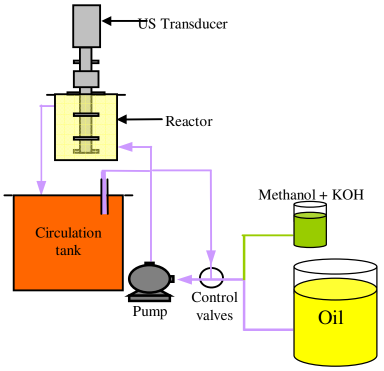

Figure 1 Schematic diagram of the setup of ultrasonic circulation process for BDF production

Analysis

Reactant and products were determined by HPLC (Shimadzu LC-6A HPLC pump with RID 10A detector). The column used was Cadenza CD-C18, 25cmx3.0mm with 4µm particle. Mobile phase was an acetone/acetonitrile: 70/30 v/v, with a flow rate of 0.4ml/min. Using the standard chemicals, triolein, diolein, monoolein and methyl oleate (from Sigma Aldrich Corporation), calibration was made for the quantification of triglycerides (TGs), diglycerides (DGs), monoglycerides (MGs), and fatty acid methyl esters (FAMEs or biodiesel). 5mL samples were taken from the circulation tank, and neutralized by 1ml of H_3PO_4 5% aqueous solution to stop reaction. About 70mg sample was diluted in 10ml of the mobile phase and injected to HPLC.

Results and Discussion

Changing in the concentration of reactants versus time

Figure 2 shows the progress of trans-esterification reaction for canola oil. The concentration of KOH was 0.7%, and the oil/methanol molar ratio was 1:5. In the initial stage of the reaction, conversion of TGs and also the yield of FAMEs were rapid. The rate then decreased and approached to equilibrium in about 50 min; after 70min, TGs and FAMEs concentration were 2.5% and 95%, respectively. The highest concentrations of MGs and DGs were observed in the first 10 min.

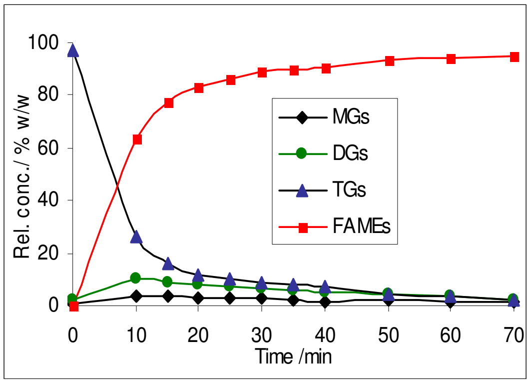

Figure 2 Time profile of reactant and products for transesterification reaction of canola oil to FAMEs with molar ratio of oil to methanol 1:5, KOH 0.7%

Effect of catalyst amount

The base-catalyzed trans-esterification of vegetable oils proceeds faster than the acid-catalyzed reaction. Due to this reason, together with the fact that the alkaline catalyst are less corrosives than acidic compounds, industrial processes usually favor base catalysts, such as alkaline metal alkoxides and hydroxides as well as sodium or potassium carbonates (Ulf Schuchardt *et al.*, 1998).

In this study, KOH was used as the catalyst and its concentration was in the range of 0.5-1.0 %w/w

(KOH to oil). The effect of catalyst amount on the conversion efficiency is shown in Fig.3. Increase in the amount of catalyst substantially increased the conversion of FAMEs. However, the increase of the catalyst led to the formation of soap, and thus washing and purifying BDF became difficult. The optimal amount of KOH was 0.7%, and with this condition the maximum conversion of FAMEs achieved was 95%.

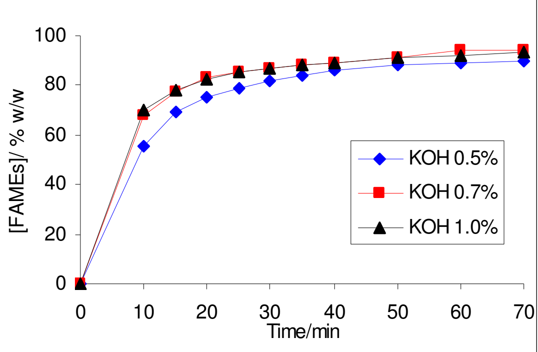

Figure 3 Effect of KOH catalyst amount on the conversion of FAMEs. Molar ratio of oil to methanol was 1:5

Effect of molar ratio between methanol and oil

An excess amount of alcohol is necessary for the trans-esterification of TGs. Because the trans-esterification is an equilibrium reaction, the lager amount of alcohol can enhance the alcoholysis result in the equilibrium favorable to fatty acid alkyl ester (FAMEs in the case of methanol). The optimal conversion of FAMEs achieved was 95% at the molar ratio of oil to methanol being 1:5 as shown in Fig.4. It is noteworthy the results show the lower the molar ratio the faster the conversion in the initial stage of the reaction (10min). This fact suggested oil and methanol easily mix together under the condition of the small amount of methanol, so the rate of methanolysis is increased. This fact may imply that under ultrasound irradiation small size droplets of methanol are formed rapidly and easily dissolved in oil phase leading to emulsion at the initial stage for small amount of methanol, so that the reaction can take place rapidly. In contrast, the droplet size of emulsion is bigger for the case with large amount of methanol than for the case with small amount of methanol, resulting in the slower reaction at the initial stage. Figure 4 reveals that the maximum conversion obtains with molar ratio of oil to methanol is more than 1:6.

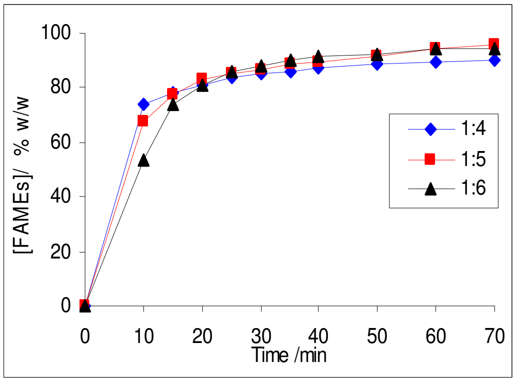

Figure 4 Effect of the molar ratio of oil to methanol on the conversion of FAMEs. Concentration of KOH was 0.7%

Glycerin separation

Separation of the reaction mixture, which contains excess methanol as well as the products, *i.e.* FAMEs and glycerin, needs rather long time such as a several hours, in general. Interestingly, the separation occurred faster for the case of less-excess methanol than for the case of larger-excess methanol in the reaction mixture. This fact would be explained by the difference in the density of glycerin phase between the less- and larger-excess methanol conditions. Glycerin has much higher density (d_{20}=1.25 g cm^{-3}) than that of methanol (d_{20}=0.79 g cm^{-3}), and both liquids dissolve each other at any mixing ratios yielding a uniform phase. Therefore, the glycerin layer from the less-excess methanol condition could have higher density than that from larger-excess methanol condition. This results in the faster phase separation between the FAMEs layer (typical density is *ca*. 0.88 g cm^{-3}) and the glycerin layer for the less-excess methanol condition due to the larger difference in the density between both layers. There was a visible difference between the upper and the lower layers. The upper layer, *i.e.* FAMEs layer, was of lighter color than the lower layer, *i.e.* glycerin layer with excess methanol. The volume of the glycerin layer was 9-12 % compared to that of FAMEs layer. Table 1 shows the change in the volume of glycerin layers collected under various reaction conditions. Excess methanol could be recovered from the glycerin layer by heating the glycerin phase up to the boiling point of methanol 65°C at the reduced pressure around 520torr, and this methanol was used for the next experiment.

Purification of biodiesel

Washing process: The purpose of washing the FAMEs with water is to remove: soap, methanol, catalyst, and glycerin which may be left in the FAMEs layer even after the phase separation. Washing process was carried out 3 times with tap water about 20% v/v compared to the FAMEs. The mixture was slightly stirred within 10 minutes, and then settled at 20 minutes to separate water. pH values of the FAMEs and water layers were in the range of 6-7 after washing.

Drying process: After washing the FAMEs contains about 0.5% w/w water. Water could be removed by heating the FAMEs up to 65°C at pressure around 520torr within 2 hours. After drying water contained less than 500 ppm (ASTM standard) in the final biodiesel product. The chemical compositions in biodiesel products obtained in this study are summarized in Table 2.

Table 1 The volume of glycerin after separation

V_{MeOH} (lit)	KOH %	Oil:MeOH	V_{FAMEs} (lit)	$V_{Glycerin}$ (lit)
9.1	0.7	1:4	52	5.5
11.4	0.7	1:5	54	6.0
11.4	0.5	1:5	53	6.1
13.6	0.7	1:6	53	7.2
13.6	0.5	1:6	54	7.1

Oil:MeOH: molar ratio of oil to methanol

The volume of oil: 54 lit for each experiment

Table 2 Main components in the final biodiesel products

Oil:MeOH	KOH%	MGs	DGs	TGs	FAMEs
1:4	0.7	1.1	3.1	2.6	93.2
1:5	0.7	0.5	1.9	1.3	96.3
1:5	0.5	1.2	2.4	2.3	94.1
1:6	0.7	1.5	2.8	1.3	94.4
1:6	0.5	1.7	2.9	1.5	94.1

MGs, DGs, TGs and FAMEs in %w/w

Conclusions

The results mentioned above show that trans-esterification reaction of canola oil with methanol in the presence of catalyst KOH assisted by ultrasound is very efficient. This process saves energy consumption, reduces reaction time as well as soap formation. Electricity consumption to produce 50 lit biodiesel was 5kW. The optimal conditions were found as molar ratio of oil to methanol 1:5; amount of KOH 0.7%. Under those conditions, the yield of FAMEs archives 96.3%. However, the product still contained impurity components (MGs, DGs, and TGs). In order to establish an efficient production of biodiesel with high purity, our group is now modifying the reaction and purification system.

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