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Production of biodiesel from Vietnamese *Jatropha curcas* oil by a co-solvent method

Phuong Duc Luu [a,b,*], Hoa Thi Truong [c], Boi Van Luu [b], Lan Ngoc Pham [b], Kyoshi Imamura [d], Norimichi Takenaka [a], Yasuaki Maeda [d]

[a] *Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan*
[b] *Faculty of Chemistry, Hanoi University of Science, VNU, 19 Le Thanh Tong St., Hoan Kiem District, Hanoi, Viet Nam*
[c] *Danang Environmental Technology Center, Institute of Environmental Technology, Vietnam Academy of Science and Technology, Tran Dai Nghia Road, Ngu Hanh Son District, Danang, Viet Nam*
[d] *Research Organization for University-Community Collaborations, Osaka Prefecture University, 1-2 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan*

HIGHLIGHTS

- Biodiesel was produced from low-quality oil with a high FFA content of 15.93%.
- Acetonitrile was used as a co-solvent for the esterification reaction.
- Biodiesel was produced from *Jatropha curcas* oil with 99% efficiency.

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ABSTRACT

Biodiesel fuels (BDFs) was successfully produced from Vietnamese *Jatropha curcas* oil with high content of free fatty acids (FFAs) in two stages. In the first stage, the esterification process was carried out with the optimal conditions as follows; a methanol-to-FFAs molar ratio of 6:1, 1 wt% H_2SO_4, at a temperature of 65 °C, and using 30% (wt/wt) acetonitrile as co-solvent. This step reduced the concentration of FFAs in the reaction mixture from 15.93 to 2 wt% in 60 min. In the second stage, the transesterification process generated fatty acid methyl esters (FAMEs) with 99% efficiency was performed in 30 min with the optimal conditions as follows; a methanol-to-oil molar ratio of 6:1, 1 wt% KOH, at a temperature of 40 °C, and 20% (wt/wt) acetone as co-solvent. The produced biodiesel quality meets the standards JIS K2390 and EN 14214 regarding FAME yield, FFAs and water contents.

1. Introduction

There is a demand to find an alternative energy source to meet the increasing energy needs of the world. Because of the inevitable future decline of fossil fuel resources and the current increasing prices of such fuels. Biodiesel fuels (BDFs) are considered a potential replacement for diesel, and have a number of advantages, such as higher cetane index and lower emissions of carbon dioxide. They are also renewable, biodegradable, non-toxic, environmentally friendly, and carbon neutral (Noureddini et al., 1998; Canakci and Gerpen, 2001).

Vietnam is a developing country and, as such, its energy requirements increase each year. It is estimated that, by 2025, Vietnam will consume approximately 43 million tons of fossil fuels annually, which is problematic because the country can only produce approximately 15 million tons of fuel per year, or 35% of the required amount. The development of BDF production in Vietnam offers a means of avoiding heavy dependence on imported fuels while simultaneously generating an environmentally friendly fuel to meet domestic energy needs, and thus is one of the best solutions to this Nation's energy problems.

BDFs are composed of simple alkyl esters of fatty acids, most typically methyl esters (Haas et al., 2006) and are able to be produced from various raw materials, including waste cooking oils

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* Corresponding author at: Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan. Tel.: +81 804 396 8558; fax: +81 72 254 9863.

E-mail addresses: luuphuongtheday@gmail.com (P.D. Luu), hoa.danetc@gmail.com (H.T. Truong), luu.vanboi@vnu.edu.vn (B.V. Luu), phamngoclan49@gmail.com (L.N. Pham), k_imamura@riast.osakafu-u.ac.jp (K. Imamura), takenaka@chem.osakafu-u.ac.jp (N. Takenaka), y-maeda@chem.osakafu-u.ac.jp (Y. Maeda).

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(Thanh et al., 2010), vegetable oils (Ghadge and Raheman, 2006; Thanh et al., 2010), algae oils (Chen et al., 2012) and inedible oils (Ramadhas et al., 2005). The most commonly used alkali catalysts in the transesterification process are NaOH, CH_3ONa, and KOH (Demirbaş, 2003). The amount of alkali catalysts depends on other parameters of the transesterification reaction including the content of free fatty acids in the oils or fats. Typically, the alkali amount of KOH or NaOH catalysts varied 0.8–1.5 wt% relative to oils or fats used (Rashid et al., 2008; Dias et al., 2008). The reaction mechanism for alkali-catalyzed transesterification has been identified as consisting of three steps (Demirbas, 2009) and the alkali-catalyzed transesterification of vegetable oils is known to proceed more quickly than the acid-catalyzed reaction. Acid-catalyzed reaction also results in lower yields of BDF, requires a greater quantity of methanol, and higher reaction temperatures compared to those of the alkaline reaction (Miao et al., 2009; Campos et al., 2014).

The production of BDF from the high FFAs content oils requires the two-stage reaction, in which the esterification process as the first stage will be normally proceeded with acid catalysts. In this case, both homogeneous and heterogeneous catalysts have been used for esterification of free fatty acids (Berrios et al., 2007; Tesser et al., 2005). Homogeneous catalysts such as sulfuric acid, hydrochloric acid, nitric acid and other can be used to catalyze esterification, but sulfuric acid has been used the most (Berrios et al., 2007; Sendzikiene et al., 2004). Concerning sulfuric acid, it was used by different researchers with different amount relatively to oil or fat, depending on the reaction conditions. Generally, the sulfuric acid amount is in the range of 1.0–2.0 wt% to oil or fat (Boucher et al., 2008; Jayasinghe et al., 2014). Larger amount of sulfuric acid catalyst, 5 wt%, was also used for esterification of FFAs in animal fats (Canakci and Gerpen, 2001). In fact, for the esterification reaction, enzymes or solid catalysts also can be used, however the enzymatic reaction rate is very slow and the fuel products may exhibit poor purity (Liu et al., 2012; Maceiras et al., 2009). Solid catalysts are being used more frequently because such catalysts may be re-used many times, however, high amounts of methanol with molar ratios to oil from 15:1 to 20:1 will be required (Lou et al., 2008; Wang et al., 2013), and lower yield of FAMEs can be obtained even with prolonged reaction times (Sheikh et al., 2013; Li et al., 2011)

Jatropha curcas oil (JCO) is one of the best raw materials for producing BDFs due to its inedible property and thus its production does not compete with food crops. It is relatively inexpensive compared with the low acid edible oils, although JCO has a quite high acid index (Thanh et al., 2012). It was reported that biodiesel was produced from *J. curcas seeds* and JCO by using solid catalyst, however the low of FAME yield was obtained, 80.2% and 92.5% respectively (Lian et al., 2012; Guo et al., 2013).

In this study, we used a co-solvent method with acid-catalyzed esterification and base-catalyzed transesterification processes to produce BDF from Vietnamese *J. curcas* oil (JCO) which has high FFAs content of 15.93 wt%, based on the use of acetonitrile and acetone as co-solvents, respectively. Acetonitrile and acetone act as co-solvent to dissolve reagents and the catalyst to form a homogeneous reaction system. Therefore the reaction occurs more easily, higher FAME yield and lower cost than traditional methods (Maeda et al., 2011; Thanh et al., 2013).

The effects of solvents, temperature, molar ratio of methanol to FFAs or oil, catalyst concentration, and reaction time were investigated in both stages. The purpose of this work is to produce the high quality biodiesel far meeting the standards JIS K2390 K2390 (Japanese Industrial Standard for biodiesel and testing method) and EN 14214 (European Standard for testing method) biodiesel fuels, and to develop a new co-solvent method for the first stage of production.

2. Methods

2.1. Materials

The JCO used in this work was obtained from Vietnam. KOH (95.5% pure), methanol (99%), acetone (99.7%), acetonitrile (99.7%), isopropanol (99%), and sulfuric acid (96–98%) were purchased from Wako Pure Chemical Industries, Osaka, Japan, and used without further purification. Chemical standards such as methyl oleate, methyl linoleate, diolein, and triolein were purchased from Sigma–Aldrich, Tokyo, Japan.

2.2. Apparatus

FFAs contents were analyzed using a Shimadzu LC-6A high-performance liquid chromatograph (HPLC), equipped with a Cadenza CD-C18 column (250 × 3 mm × 3 μm) and a refractive index (RI) detector (Shimadzu RID-10A). The analytical conditions were performed with a column temperature of 35 °C, a mobile phase consisting of a 70:30 (v/v) mixture of acetone and acetonitrile at a flow rate of 0.5 mL min^{-1}, and a sample injection volume of 20 μL.

The triglycerides (TG), diglycerides (DG), monoglycerides (MG), and FAME contents of samples were determined by a Shimadzu LC-10AD HPLC. Gel permeation column (GPC) using with an Asahipak GF 310 HQ column (300 × 7.5 mm × 5 μm) and a Shimadzu RID-10A RI detector. The analytical conditions were performed using a column temperature of 30 °C, acetone as the mobile phase at a flow rate 0.5 mL min^{-1}, and a sample injection volume of 20 μL.

Water contents in samples were determined using an MKC-501 Karl Fisher titration instrument.

2.3. Procedures

In the first stage as the esterification process, a 50 g of JCO was mixed with an amount of solvent at ambient temperature. A mixture of sulfuric acid and methanol was subsequently added to the above JCO solution. In this experiment, most of free fatty acids in the JCO are esterified by methanol under acidic catalysis in order to reduce the FFAs content to 3 wt%, which is necessary for transesterification stage. For each certain time interval of reaction, about 5 ml sample was taken out and titrated to determine the remaining FFA content in the mixture. After this reaction was complete, the reaction mixture was transferred into a separatory funnel, in which two liquid layers were separated. The bottom layer, consisting of residual methanol, solvent, and sulfuric acid, was removed and the upper product layer was set aside for use in the second stage.

The general process by which esterification was accomplished both without a co-solvent and with acetonitrile as a co-solvent is summarized in Fig. 1.

In the second stage as transesterification process, a 30 g portion of the above product from first stage was mixed with acetone in a round bottom flask, controlling the temperature of the mixture in a water bath. A solution of KOH in methanol was then quickly added to the flask with stirring. After allowing for various reaction times, the reaction was stopped and the mixture was transferred into a separatory funnel and allowed to stand for approximately 30 min, then the lower glycerol layer was removed and the upper layer, containing a mixture of FAME, TG, DG, MG) acetone, catalyst, and un-reacted methanol was left. Acetone and methanol were then removed from this mixture by distillation and the remaining solution was subsequently washed three times with water until a pH value of approximately 7 was obtained, whereupon water was removed by a second distillation at 70–80 °C under reduced pressure. The composition and degree of conversion of the final product were analyzed on the reserved phase-HPLC. The two-stage

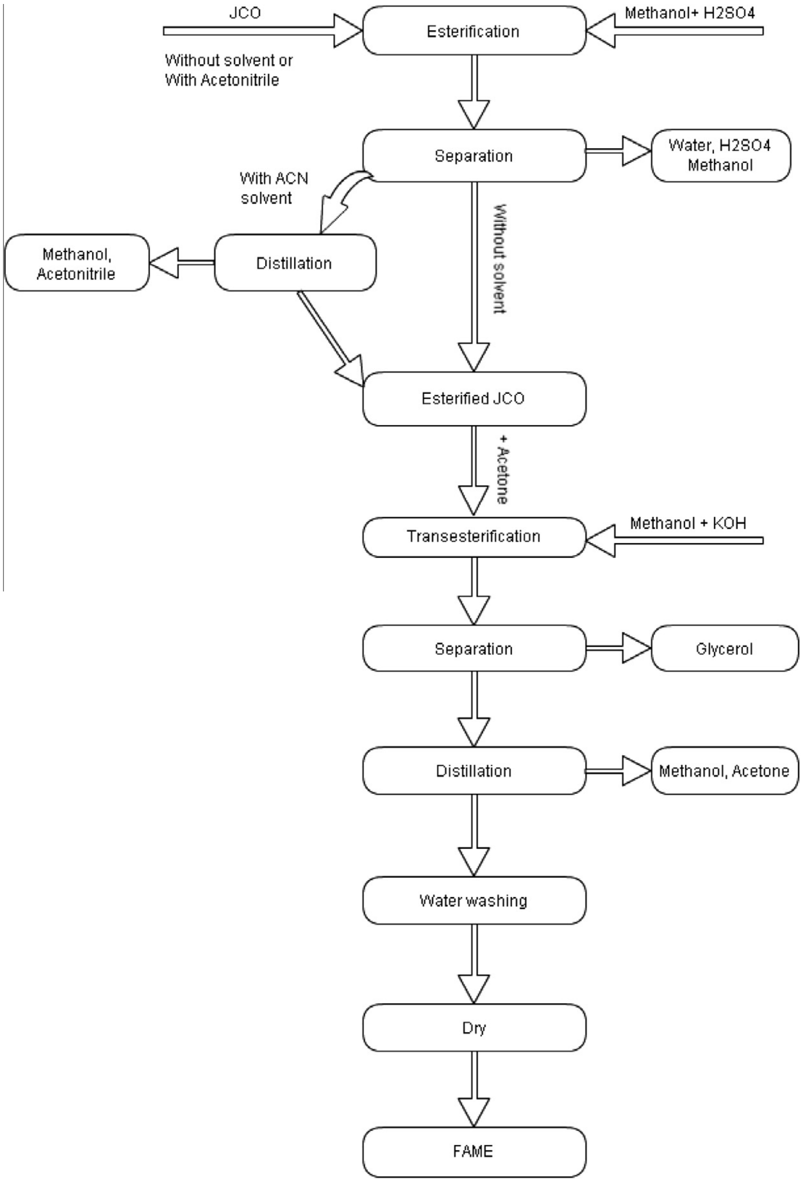

Fig. 1. Summary of the two-step process for producing biodiesel from *Jatropha curcas* oil.

technology applied to BDF production in this work is summarized in Fig. 1.

2.4. Analysis of raw material and product quality

2.4.1. Chemical and physical properties of raw material

To determine the FFAs contents of samples from first stage of the process, 5-mL reaction mixture aliquots were obtained at regular time intervals and placed into separate test tubes. After the solution in each tube separated into phases, 1 mL of the product from the upper layer was dissolved in 10 mL of isopropanol and the FFA content was determined by acid–base titration with phenolphthalein as the indicator. FFA levels were then calculated according to the formula below:

$$\mathrm{FFA}\ (\%) = \frac{C_{\mathrm{KOH}} \times V_{\mathrm{KOH}} \times M_{\mathrm{Free\ fatty\ acid}}}{1000} \times 100 \tag{1}$$

here C_{KOH} is the concentration of the KOH solution (M), V_{KOH} is the volume of KOH required for the titration (mL), and M (g/mol) is the average molecular weight of the FFAs. The acid value (AV) of the sample was then calculated according to the following equation.

$$\mathrm{AV} = C_{\mathrm{KOH}} \times V_{\mathrm{KOH}} \times M_{\mathrm{KOH}}\ (\mathrm{mg/g}) \tag{2}$$

The FFAs content of the JCO used in this studied were 15.93 ± 0.07 wt%. Some specified FFAs consents including oleic acid, linoleic acid, linolenic acid, palmitic acid, stearic acid were determined by the Shimazu LC-6A HPLC by using external standard calibration curves and the concentrations were 41.43 ± 0.60; 37.06 ± 0.50; 1.35 ± 0.20; 12.28 ± 0.30; and 5.80 ± 0.30 wt%, respectively. The density and the water content were 0.91 g cm^{-3} and 0.1455 wt%, respectively. The mean molecular weight of FFAs in used JCO was 278.79 ± 13.8 g mol^{-1}.

2.4.2. Determination of BDF conversion

The FAME yields of the transesterification reactions were calculated using the following formula (Thanh et al., 2010).

$$\mathrm{FAME\ yield}\ (\%) = \frac{W_{\mathrm{FAME}}/M_{\mathrm{FAME}}}{3W_{\mathrm{JCO}}/M_{\mathrm{JCO}}} \times 100 \tag{3}$$

here W_{FAME} and W_{JCO} represent the weights of FAME in the FAME phase and the weight of JCO originally used, while M_{FAME} and M_{JCO} are the molecular weights of the FAME and the JCO.

3. Results and discussion

3.1. The first stage: esterification

3.1.1. Effects of solvents on the esterification reaction

We initially conducted a survey of solvents for the reaction between oleic acid and methanol with sulfuric acid as the catalyst, investigating the effects of using diethyl ketone, methyl ethyl ketone, acetonitrile, ethyl acetate, and no solvent. These solvents have high ability to dissolve FFAs in the mixture with methanol and sulfuric acid to form a homogeneous solution. Furthermore they can promote the dissociation of sulfuric acid into proton catalyzed esterification reaction. The addition of high boiling point solvents increases the boiling point of whole solution over boiling point of methanol that gives advantage to carry out the reaction at higher temperature. In our investigation all reactions were carried out under the following conditions: 50 g oleic acid, MeOH/oleic acid molar ratio of 6:1, 30% solvent (wt/wt based on oleic acid), and 1% sulfuric acid (wt/wt). The data from these trials are presented in Fig. 2, from which it is evident that acetonitrile produced the best transformation results. This is due to the fact that acetonitrile better dissolves *J. curcas* oil and its FFAs, making the reaction mixture more homogeneous, the esterification process proceed more rapidly. So acetonitrile was selected as the most suitable solvent for the reaction in the first stage. In a similar survey of (Jiang et al., 2010), by using a solid catalyst for the esterified oleic acid with methanol was 96% conversion of methyl oleate. However, catalyst concentration and molar ratio of methanol to oleic acid is used more with 10 wt% and 9/1 (mol/mol) respectively.

3.1.2. Effects of reaction temperature

The reaction was also performed at a variety of temperatures (30, 40, 50 and 65 °C), using acetonitrile with a MeOH/JCO molar ratio of 6:1, and 1 wt% H_2SO_4. The results are presented in Fig. 3a and b. Here, it can be seen that the rate of esterification as well as the rate of FFA reduction are directly proportional to the temperature. Our study data also showed (not included here) that when much higher temperatures were used the reaction rate was faster, but because methanol boils at 64.7 °C so the higher temperature makes methanol lost considerably due to evaporation. Thus, 65 °C is the suitable temperature to be chosen for this reaction stage.

3.1.3. Effects of MeOH/FFA molar ratio

The reaction was carried out at various MeOH/FFA molar ratios (from 3:1 to 12:1), using acetonitrile and 1 wt% H_2SO_4 at 65 °C, and the resulting data are summarized in Fig. 4a and b. Based on the reaction stoichiometry, one mole of FFA should require one mole of MeOH, however, because the esterification is an equilibrium process, higher methanol concentrations will increase the rate of reaction. From Fig. 4, it is evident that increasing the MeOH/oil ratio from 4.5:1 through 6:1 and 9:1–12:1 shortens the time required to reduce the FFA content to 2% to, 90, 60, 30 and 25 min. respectively From an economic point of view and due to the fact of gaining suitably pure BDF, the molar ratio 6:1 for methanol to oil was chosen. It is also seen from this figure that the addition of acetonitrile as the co-solvent accelerates the rate of the esterification reaction. With no solvents used, Veljkovic et al. (2006) have shown that in order to reduce the concentration of FFAs in the Tobacco oil below 2 wt%., it needed much higher molar ratio of methanol to oil (18:1).

3.1.4. Effects of H_2SO_4 concentration

The reaction was carried out with H_2SO_4 catalyst amounts of 0.5%, 1%, 1.5%, 2% and 3% (wt/wt relative to the amount of FFA), using acetonitrile at 65 °C and a MeOH/FFA ratio of 6:1. The obtained results are presented in Fig. 5a and b. As can be seen, when the catalyst concentration increased from 0.5 to 1.0 wt%, the FFA content decreased, while further increase in the catalyst concentration in the range of 1–2 wt% led to a decline in the rate of FFA decrease and a catalyst level of 3 wt% caused the esterification reaction rate to increase again. Fig. 5a and b also show that the reaction rate was improved when using acetonitrile as the co-solvent. The conditions necessary to reduce the FFA content to below 2% consisted of a catalyst concentration of 1 wt% and a reaction time of 60 min when using 20 wt% acetonitrile, while the non-solvent method required 1.5 wt% catalyst and 90–120 min. It is worthy to note that by using co-solvent method, the amount of sulfuric

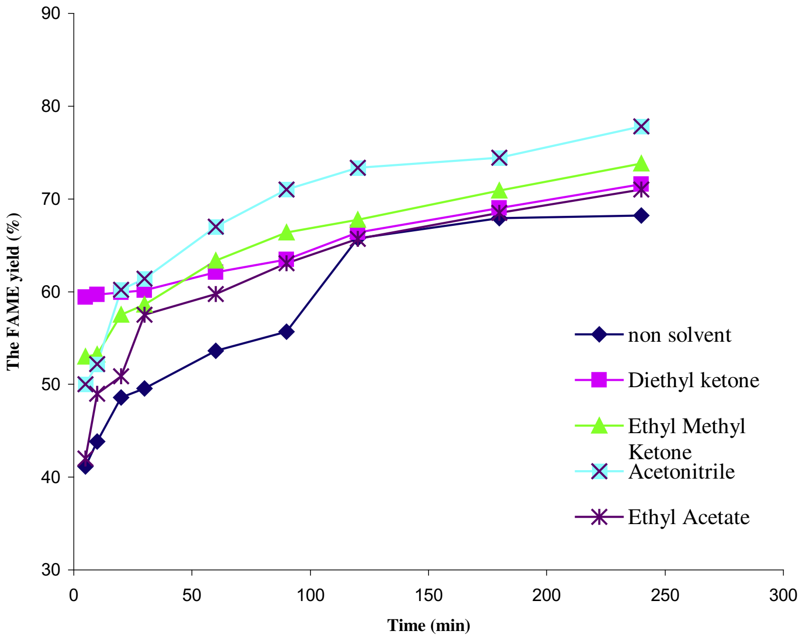

Fig. 2. Results of an initial survey identifying a suitable esterification solvent.

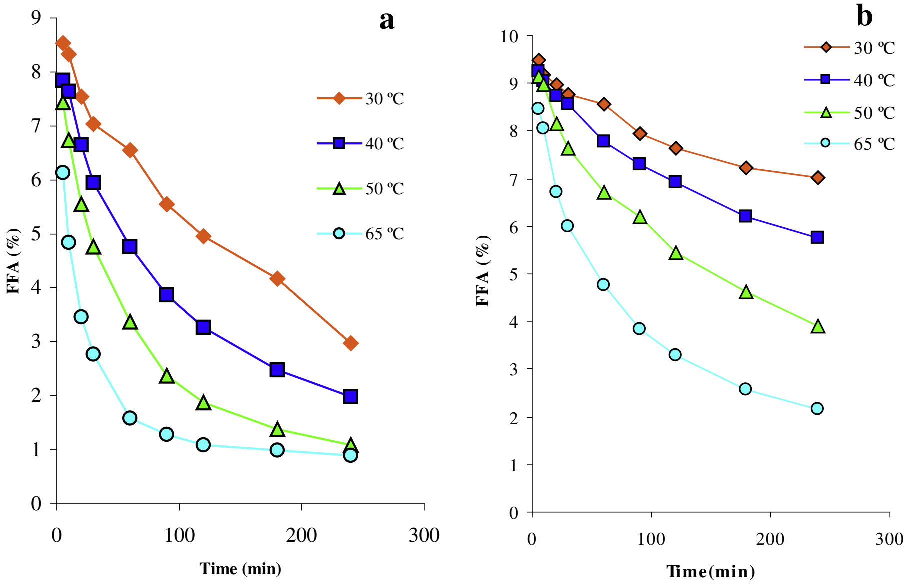

Fig. 3. Effects of reaction temperature on reaction progress (a) with and (b) without acetonitrile as a co-solvent.

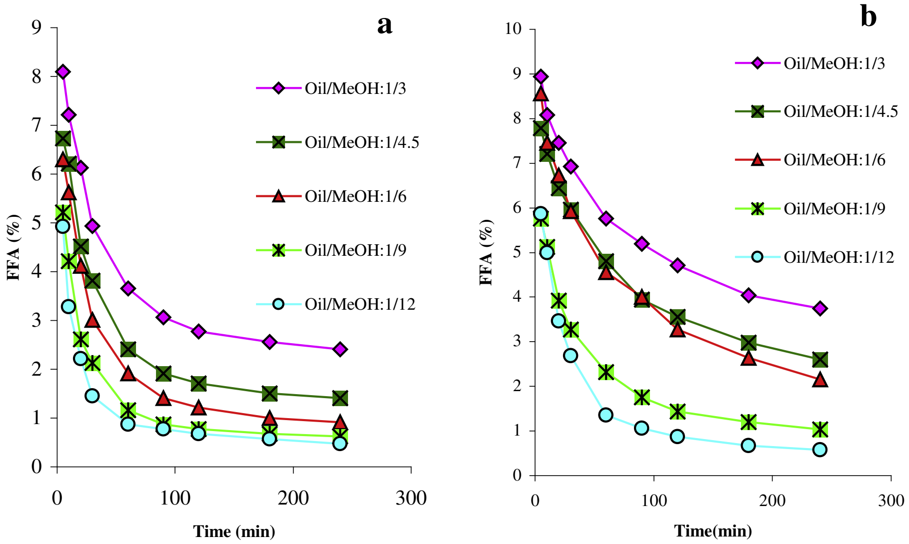

Fig. 4. Effects of the MeOH/FFA molar ratio on reaction progress (a) with and (b) without acetonitrile as a co-solvent.

acid used as a catalyst, 1 wt%, is relatively low compared to non-solvent method. As mentioned in introduction part, generally, many authors had to use larger amount of sulfuric acid to catalyze the esterification of fatty acid in the oils and fats.

3.1.5. Effects of solvent amount

The reaction was additionally carried out using 10%, 20%, 30%, 40% and 60% (wt/wt) acetonitrile, at 65 °C with a MeOH/FFA molar ratio of 6:1 and a catalyst amount of 1 wt%, producing the data shown in Fig. 5c. These results show that increasing the concentration of the co-solvent from 10 to 30 wt% resulted in a rapid decrease in the amount of FFA but that co-solvent concentrations above 40 wt% led to a reduced rate of decrease in the FFA level and then an increase. This can be explained by noting that increasing co-solvent contents higher than 40 wt% dilute the concentrations of the catalyst and reactants and thus reduce the reaction rate. Without using co-solvent for the first stage, the reaction time for reducing FFAs content to below 2 wt% was about 120 min (Fig. 3b), while using 30 wt% of acetonitrile as co-solvent, the required time for this first stage was only 60 min (Fig. 5c). It means that the co-solvent method applied for the first stage was very beneficial for reducing the reaction times, thus leading to a decrease of production cost which is very necessary for the BDF manufacturing.

3.2. The second stage: transesterification

Following the survey to find optimal conditions for the transesterification reaction, we attempted to identify the optimal conditions for conducting the transesterification, assuming that acetone was the preferred co-solvent (Maeda et al., 2011).

3.2.1. Effects of reaction temperature

The transesterification was performed at several different temperatures (30, 40, 50 and 60 °C), using 30 g JCO (first stage

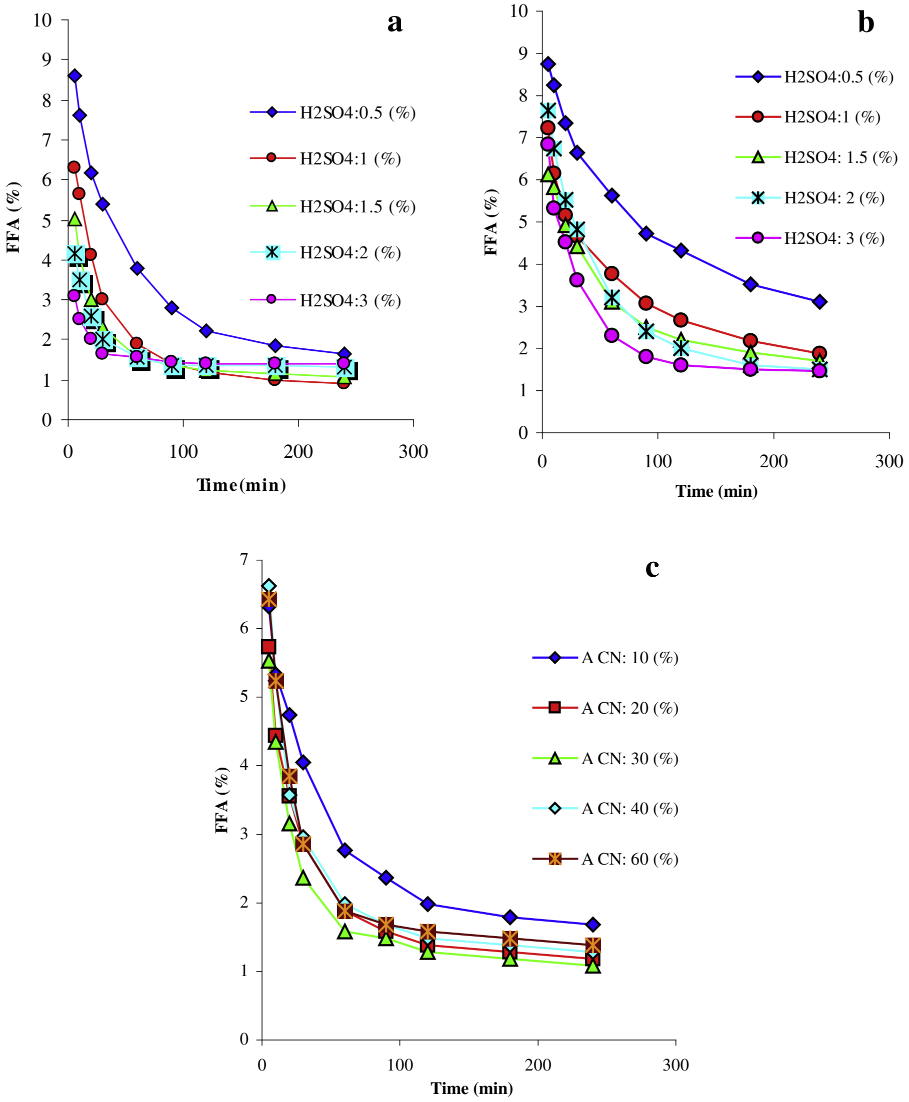

Fig. 5. Effects of the catalyst amount on reaction progress (a) with and (b) without acetonitrile as a co-solvent, and (c) effects of the amount of acetonitrile.

product), a 6:1 M ratio of MeOH/JCO, 20% acetone (wt/wt based on the mass of JCO), 0.3 g KOH, and a 60-min reaction time. The obtained results are presented in Fig. 6a, from which it can be seen that increasing the temperature from 30 to 40 °C increased the conversion yield as high as 99%. Above 40 °C, however, the conversion remained stable. Therefore, 40 °C was selected as the optimal temperature for further study. Furthermore we think that in this reaction stage solvent used was acetone had a low boiling point (56–570 °C) so we do not pick 640 °C under optimum condition. On the other hand, with the optimum temperature of 400 °C and ensure the quality of BDF and economic efficiency. In fact, with no solvent used biodiesel was usually produced at higher temperature of 600 °C (Suganya et al., 2013) or 650 °C (Berchmans and Hirata, 2008)

3.2.2. Effects of the MeOH/JCO molar ratio

The transesterification was also assessed using MeOH/JCO (first-stage product) molar ratios of 3:1, 4.5:1, 6:1, 9:1 and 12:1, along with 30 g JCO (first-stage product), 20% acetone, 0.3 g KOH, a reaction span of 60 min, and a temperature of 40 °C, generating the data in Fig. 6b. Stoichiometrically, the required methanol/triglycerides molar ratio is 3:1, but in practice this is not sufficient to complete the reaction, and higher molar ratios are required to drive the reaction forward. In the graph in Fig. 6b, the transesterification yield is seen to increase as the methanol/JCO molar ratio is increased up to a value of 9:1, beyond which the yield decreases at a ratio of 12:1. The conclusion from these data was that the highest conversion was reached at a methanol/oil molar ratio of 6:1. With non-solvent method the transesterification reaction of oil usually needed to be conducted under harder conditions, like longer reaction time, higher methanol to oil molar ratio or higher catalyst concentration, eventhough, the BDF yield was not sufficiently high, only around 90–92% (Berchmans and Hirata (2008) and Suganya et al. (2013))

3.2.3. Effects of catalyst amount

The transesterification was carried out using catalyst concentrations of 0.5, 1, 1.5, 2 and 3 wt% together with 30 g JCO (first stage product), a MeOH/JCO molar ratio of 6:1, 20 wt% acetone, a reaction time of 60 min, and a temperature of 40 °C, with the results shown in Fig. 6c. The transesterification yield increased dramatically as the percentage of the KOH catalyst was increased from

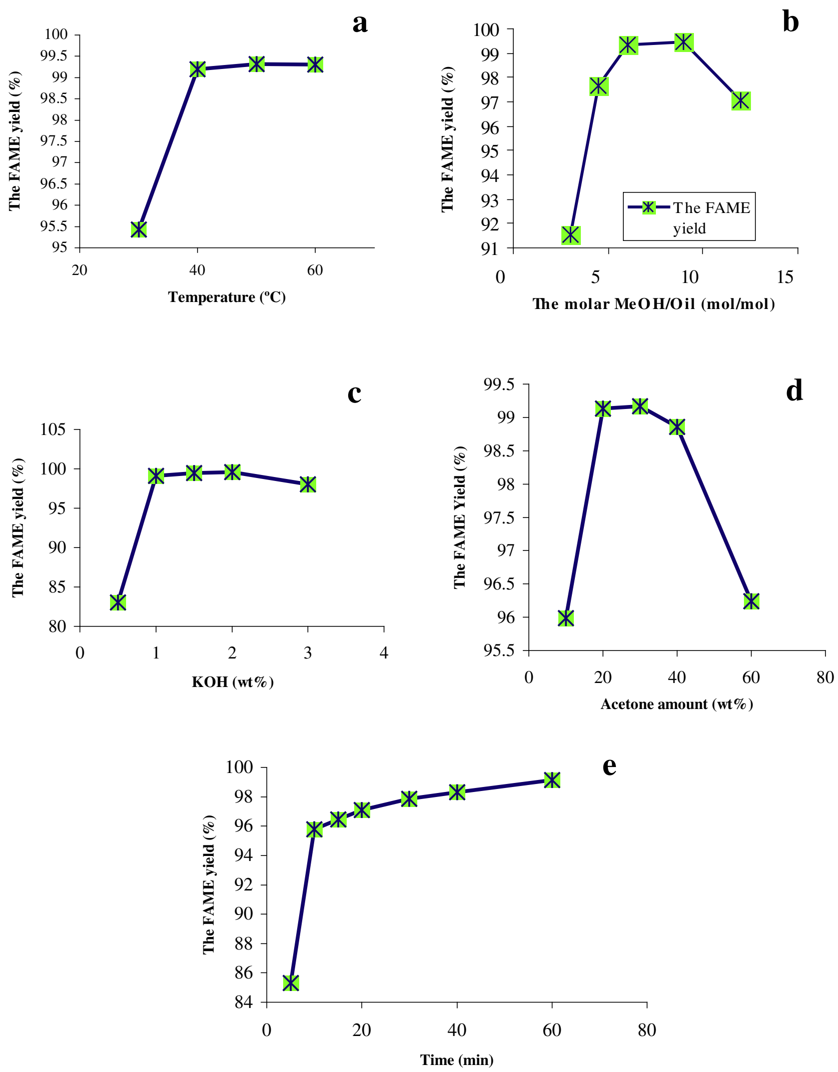

Fig. 6. Effects of (a) reaction temperature, (b) methanol-to-JCO molar ratio, (c) KOH amount, (d) acetone amount, and (e) reaction time during stage 2 transesterification.

0.5 to 1 wt% and the conversion reached a maximum of 99% at 1 wt% KOH. Hence, the optimal KOH concentration for the transesterification process is 1 wt%. The addition of excess amounts of KOH catalyst gave rise to the formation of an emulsion that increased the solution viscosity and in turn generated a gel. On the other hand the use of 1w% KOH ensures the BDF performance to meet the demand for fuel for diesel engines. And after reaction without using H_3PO_4 acid to neutralize KOH when used too much.

3.2.4. Effects of solvent amount

The transesterification was also performed using 10%, 20%, 30%, 40% and 60% (wt/wt) acetone together with 30 g JCO (first-stage product), a MeOH/JCO molar ratio of 6:1, a 60 min reaction time, a temperature of 40 °C, and 1% catalyst. The results are presented in Fig. 6d, from which we can see that the conversion yield increased as more acetone was added, changing from over 96% to nearly 99% as the amount of acetone co-solvent was varied from 10 to 20 wt%. When the co-solvent was further increased from 30 to 60 wt%, the yields of FAME were reduced from 99% to 96%. This occurs probably because too much more co-solvent will dilute the starting reactants and thus decrease the reaction rate. Based on these data, a co-solvent level of 20 wt% was selected for further investigation.

3.2.5. Effects of reaction time

The transesterification was allowed to proceed for 5, 10, 15, 20, 30, 40 and 60 min, using 30 g JCO (first stage product), a MeOH/JCO molar ratio of 6:1, a temperature of 40 °C, a catalyst level of 1 and 20 wt% acetone. The resulting data are summarized in Fig. 6e. It is evident that the reaction yield increased with increasing duration and reached a maximum after 30 min, beyond which the FAME yield plateaued. Thus, a reaction span of 30 min was selected as optimal for the transesterification process.

The application of co-solvent technology for transesterification in our research has shown many advantages in comparison to conventional method which has used non solvent. Results are shown in Table 1. In the case of using conventional method, transesterification takes place between two phases of methanol and oil. However, co-solvent is good solvent for methanol, TG and FAME but poor for glycerin. So glycerin is automatically separated out of reaction solution. Then the transesterification is promoted to form more products with higher conversion and yield. The produced BDF based on our method has high quality as follows: a FAME yield of 99%, a FFA content of 0.23%, and a water content of 187 mg/kg

Table 1
Comparison of conventional and co-solvent biodiesel processing technologies.

Production conditions	Production process	
	Conventional	Co-solvent
Catalyst KOH/oil, (Fat), wt%	1.2–2.0	0.1–1
Methanol/oil, (Fat)/mol/mol	6.0/1	6.0/1
The amount of water allowed in oil, Fat, wt%	Not excess 0.5	Max 2
Reaction time, min	>60	10–30
Reaction temperature, °C	50–60	30–40(room temperature)
Product separation time, min	300–1200	10–30
The FAME yield, %	80–96	99
Waste, kg/100kg Oil(Fat)	26	3.8
The cost of biodiesel fuels, USD	1.3–1.5	0.9–1.0
FFA in final BDF, wt%	–	0.23
Water content mg kg^{-1}	–	187

which all meet the requirement of standards JIS K2390 and EN 14214 for BDF's quality.

4. Conclusion

The two-stage co-solvent method was used to successfully produce a high quality of BDF from Vietnamese *J. curcas* oil which has high FFA content of 15.93%. The using of 30 wt% of acetonitrile as co-solvent in the first stage accelerated the reaction 2 times and a smaller amount of acid catalyst were used compared to that of without using co-solvent. This new approach for the esterification process corresponding with the co-solvent method using acetone for the second stage has demonstrated a high transformation efficiency, shorter reaction times and lower production costs in the production of BDF.

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