Two-step Biodiesel Production from Crude *Jatropha curcas* L. Oil Using Ultrasonic Irradiation Assisted

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Abstract: In this paper, the feasibility of crude *Jatropha curcas* L. oil (CJCO) as raw material to produce biodiesel under low-frequency ultrasonic irradiation (40 kHz) assisted is examined. A two-step transesterification process (acid catalyzed esterification followed by alkaline catalyzed transesterification) is employed to produce biodiesel. In the first step, the high level of free fatty acid (FFA), 12.5%, of CJCO is successfully reduced to less than 3% by acid catalyzed esterification with 15% w/w methanol to oil ratio, catalyst concentration 3.0% w/w, ultrasonic irradiation time 20 min at under reaction temperature 30°C, which are selected as optimum conditions for the acid catalyzed esterification. Then, the second step, alkaline catalyzed transesterification is carried out as methanol to oil ratio 15% w/w, catalyst concentration 1% w/w, reaction temperature 30°C and ultrasonic irradiation time 30 min. This results to high percentage of conversion to biodiesel about 98%. Comparing the results obtained under the ultrasonic irradiation in this study with those under conventional stirring conditions, ultrasonic irradiation technique significantly illustrated the higher efficiency than the conventional method, especially for the high FFA oil.

Key words: biodiesel, two-step transesterification, crude *Jatropha curcas* L. oil, ultrasonic irradiation

1 INTRODUCTION

Nowadays, diesel fuel has been widely use in industry and in automobiles. However, the petroleum price continues to rise, while the diesel supply becomes scarce and the concern for environment grows lately, scientists have carried out considerable effort in searching for renewable substitutes of diesel fuel. Biodiesel from vegetable oils or animal fats appears to be the most promising alternative. It has many advantages over diesel fuels; produce less smoke and particle, have higher cetane number, produce low carbon monoxide (CO) and hydrocarbon (HC) emission, renewable, biodegradable, and non-toxic

Despite many advantages, the biodiesel has to compete economically with the diesel fuel in order to survive in the market. The higher cost of biodiesel is the major obstacle to its commercialization. Biodiesel production obtained from neat vegetable oil is expensive compared to the diesel fuels. Many researchers have reported approximately 60-95% of total cost of biodiesel production arises from the cost of raw materials. There has been a renewed focus on the way to reduce the cost of biodiesel production. The problem can be approached in two different ways: by finding cheap source of raw materials or by intensifying the synthesis process by using novel reactor. Reducing the cost of the feedstock is necessary for biodiesel’s long-term commercial viability. One way of reducing the biodiesel production cost is to use the less expensive feedstock containing fatty acid such as non edible oils, animal fats and waste cooking oil. There are several non edible oil seed species which could be utilized as a source for oil production. The *Jatropha curcas* L. oil (CJCO) is considered as the high potential and cheap feedstock for biodiesel production compared with refine and edible oils. Basically, the oil content of *Jatropha curcas* L. seed ranges from 25 to 40% and the kernel from 45 to 60% by weight. Typically, the crude *Jatropha curcas* L. oil (CJCO) revealed a high free fatty acid (FFA) content about 7-18%. At present, *Jatropha curcas* is widely cultivated in most part of Thailand such as Ubonratchathani and Nakhonratchasima province. It can supply part of raw material for biodiesel production in Thailand.

Biodiesel can be synthesized by transesterification reaction using alkaline or acid catalyst. An alkaline catalyzed transesterification is the most commonly method used for biodiesel production, because the process can be accomplished in a short reaction time under mild reaction conditions. For an alkaline catalyzed transesterification, feedstocks should contain low FFA and moisture content. Also,
the alcohol must be substantially anhydrous, because moisture and water makes the reaction partially change to saponification. The saponification formation is reducing the yield of biodiesel production. Thus, this process is not suitable for feedstocks with high FFA content. Rather, acid catalyzed transesterification is advantageous for oil having high FFA content, as acid catalyzes the FFA esterification to produce biodiesel, increasing the biodiesel yield, however, the reaction time and alcohol requirement is very high\textsuperscript{[13]}. To solve these problems, a two-step transesterification process (acid catalyzed esterification followed by alkaline catalyzed transesterification) was developed to remove the high FFA content in order to improve the biodiesel yield\textsuperscript{[14,15]}.

Recently, many researchers have reported the biodiesel production by two-step transesterification process of biodiesel produces from CJCO by the conventional technique. In the first step, the acid catalyzed esterification process used longer reaction time about 2-5 h to reduce FFA content\textsuperscript{[13]}. Second step, the alkaline catalyzed transesterification process required 1-3 h for making ester and the conversions of triglyceride were observed to be in the range of 50-95\%\textsuperscript{[16,17]}. Because of the lower rates of synthesis have been conventional stirring method attributed to mass transfer limitation due to heterogeneous conditions existing during the reaction\textsuperscript{[18]}.

An alternative method, low frequency ultrasonic irradiation is known to be a useful tool for the emulsification of alcohol and oil. Ultrasonic irradiation causes cavitation bubbles to form near the phase boundary between the alcohol and oil phases. The collapse of the cavitation bubbles disrupts the phase boundary and causes emulsification by ultrasonic jets that impinge from one liquid upon the other. The cavitation may also lead to a localized increase in local temperature and pressure at the phase boundary enhancing the transesterification reaction\textsuperscript{[19,20]}.

As reported in the literature, many researchers have successfully applied ultrasonic irradiation in the transesterification process. In addition, research has been reported on the advantages of the ultrasonic irradiation assisted transesterification process that indicates advantages such as excellent biodiesel yield, a much shorter reaction time, a low amount of catalyst required than with the conventional mechanical stirring method\textsuperscript{[5,19-24]}.

The aim of the study is to investigate the biodiesel transesterification process using an ultrasonic irradiation mixing technique to obtain the optimal procedure for achieving the higher conversion rate of biodiesel. The main goal is to develop a two-step catalyzed transesterification process for the production of biodiesel from the high FFA of CJCO. Initially, the attention was paid to optimize the first step of the process for reducing the FFA content of CJCO to below 3\%. Then the main focus was to optimize the alkaline catalyzed transesterification reaction conditions for the optimum catalyst concentration, methanol to oil ratio, reaction temperature, and ultrasonic irradiation time.

### 2 MATERIALS AND METHODS

#### 2.1 Materials and Equipment

Crude *Jatropha curcas* L. oil (CJCO), in this study, was obtained from the kernel of *Jatropha curcas* L. tree belongs to the Euphorbiaceae family, which is a medium to large tree found in most part of Thailand. The *Jatropha curcas* L. fruits were collected from field crops in Warin Chamran District, Ubon Ratchathani province, Northeastern of Thailand. The *Jatropha curcas* L. fruit and seeds were separated from the peels by a 2 hp cracking machine (100-120 kg seeds per hour). The *Jatropha curcas* L. seed is small, black in color, and ellipsoid, with an average size of about 1.7-1.9 cm long and 0.8-0.9 cm thick. The weight of 100 seeds is about 69.8 g. The *Jatropha curcas* L. seeds were dried in the oven at 100°C for 2-3 h. The CJCO was obtained by grinding the seeds and extracting the oil by the 5 hp hydraulic press machine at the room temperature. The CJCO was first filtered to remove solid impurities. CJCO was then heat to evaporate the possible water present in it at 105°C for 1-1.5 h. The fatty acid composition of the CJCO is given in Table 1\textsuperscript{[25]}. An initial acid value of CJCO was measured to be 25 mg KOH/g oil, which corresponds to 12.5\% of free fatty acids (FFA). The chemicals used in the experiment, which are sulfuric acid (H\textsubscript{2}SO\textsubscript{4}), potassium hydroxide (KOH), and methanol, were purchased from the Merck Chemical Company (Germany), their purities being greater than 98\%, 95\%, and 99.8\%, respectively.

An ultrasonic generator (KCME-KORN, Model AK-Nano/ Bio-system 400 UL, Thailand) was used as the source of the ultrasonic irradiation for assisting the production of biodiesel. The processor operated at 40 kHz with the power of

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Fatty acid composition of crude <em>Jatropha curcas</em> L. oil.</th>
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<tbody>
<tr>
<td>Fatty acid</td>
<td>wt%</td>
</tr>
<tr>
<td>Palmitic acid (C16:0)</td>
<td>15.2</td>
</tr>
<tr>
<td>Palmitoleic acid (C16:1)</td>
<td>0.7</td>
</tr>
<tr>
<td>Heptadecanoic acid (C17:0)</td>
<td>0.1</td>
</tr>
<tr>
<td>Stearic acid (C18:0)</td>
<td>6.8</td>
</tr>
<tr>
<td>Oleic acid (C18:1)</td>
<td>44.6</td>
</tr>
<tr>
<td>Linoleic acid (C18:2)</td>
<td>32.2</td>
</tr>
<tr>
<td>α-Linolenic acid (C18:3)</td>
<td>0.2</td>
</tr>
<tr>
<td>Arachidic acid (C20:0)</td>
<td>0.2</td>
</tr>
<tr>
<td>Total saturated fatty acids</td>
<td>23.77</td>
</tr>
<tr>
<td>Total unsaturated fatty acids</td>
<td>77.7</td>
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400 W. The ultrasonic irradiation times for the reactions were adjustable from 1 to 90 min. All the experimental reactions were carried out in an ultrasonic bath reactor (1000 mL) made of stainless steel and equipped with a thermostate probe and a sampling port, as shown in Fig. 1. An ultrasonic batch reactor was immersed in a water bath placed on the hot plate. The tip of a horn (titanium horn) with a diameter of 10 mm and a length of 120 mm was used to transmit the ultrasound into the solution and was submerged up to 55 mm deep into the solution contained in the ultrasonic batch reactor (in the methanol phase). The temperature of the reaction mixture was controlled by a water bath.

2.2 Two-step catalyzed transesterification process

The key factors to obtain success transesterification reaction are the percentages of the presence of FFA and moisture. These two faster favor the side reactions like saponification and lower the yield of biodiesel. Thus, before proceeding transesterification reaction, the characterization of raw material must be performed judge the transesterification reaction, either one or two steps. If FFA presence goes beyond the limit, two-step catalyzed transesterification process, first neutralization of FFA with acid catalyst (esterification) and then transesterification with alkaline catalyst should be applied to guarantee the higher yield of biodiesel. Meher et al. recommended a single step transesterification reaction with alkaline catalyst when FFA content is less than 3%°. It was examined that the percentage of FFA in the CJCO was 12.5%. Therefore, the two-step catalyzed transesterification process, acid catalyzed esterification process following by the alkaline catalyzed transesterification process, was selected for converting CJCO to biodiesel in this study.

2.2.1 Acid catalyzed esterification

The objective of the first step is to reduce the FFA of the CJCO to less than 3%. The operating parameters used in this step, to optimize conditions of acid catalyzed esterification reaction, included methanol to oil ratio, catalyst concentration (sulfuric acid), and ultrasonic irradiation time. The CJCO (150 g) was poured into the reactor. The mixtures consist of CJCO, methanol and sulfuric acid (H2SO4). The sulfuric acid catalyst concentration of 1, 2, 3, 3.5, 4 and 5% w/w (based on the weight of raw oil) were prepared and then added to the reactor. Ratios of methanol to oil were 10, 15, 20, 25, 30 and 40% w/w (based on the weight of raw oil). The reaction was activated by with an ultrasonic irradiation time for 10, 20, 30, 40, 50 and 60 min at room temperature (30°C). After the reaction complete, mixture was allowed to settle for 8 h or overnight. Then, gum, methanol, and water fraction at the bottom layer were removed. The acid value and FFA of the product were determined by titration technique (ASTM D664) and the product was then used for the alkaline catalyzed transesterification reaction in this second step.

2.2.2 Alkaline catalyzed transesterification

In the second step, optimum conditions for catalyst concentration (KOH), methanol to oil ratio, reaction temperature, and ultrasonic irradiation time were investigated. Firstly, the oil product pre-treated from the first step was poured into the reactor. KOH pellets were dissolved in methanol before being poured in the reactor containing the pre-treated oil. The reaction was then carried out with ultrasonic irradiation time varied from 0 to 60 min. Ratios of methanol to oil varied from 10 to 20% w/w, while the amount of KOH catalyst was ranged from 0.5 to 2% w/w. Samples (10 mL) were taken from the reacted mixture at a predetermined time intervals (0, 3, 5, 10, 15, 20, 30, 40, and 60 min). The sample was then placed in a bath of iced water to stop the reaction and it was allowed to settle for 8 h or overnight. The mixing of KOH and glycerol settles at the bottom of the funnel, whereas little amount of catalyst and methanol are still in the upper biodiesel layer. The upper layer is collected for further purification by washed and analyzed by Nuclear Magnetic Resonance (NMR).

2.3 Analytical method

The biodiesel products were analyzed by using Nuclear Magnetic Resonance (NMR) method. NMR analyses were performed on a Bruker DMX 300 MHz spectrometer using chloroform-d (CDCl3) as the solvent. For each analysis, 0.2 mL of each biodiesel sample was dissolved in 0.4 mL deuterated chloroform and transferred to an NMR probe (5 mm internal diameter). Spectra were recorded at room temperature with tetramethylsilane (TMS) as internal standard. The relaxation times were measured for all samples using an inversion recovery pulse sequence. The conversion to biodiesel was determined by the ratio of the signals at 3.68 ppm (hydrogen of the methoxy groups in the methyl esters) and 2.30 ppm (hydrogen of the methylene groups of all fatty acid derivatives). The conversion to biodiesel can be calculated by the following Eq (1):
Conversion to biodiesel(%) = \([\frac{(A/3)}{(B/2)}] \times 100\)  \((1)\)

where A is the peak area of hydrogen of the methoxy groups in the methyl esters and B is the peak area of hydrogen of the CH₂ groups of all fatty acid derivatives.

3 RESULTS AND DISCUSSION

3.1 Acid catalyzed esterification

3.1.1 Effect of catalyst concentration

The effect of catalyst concentration was the first parameter examined. The sulfuric acid \(H_2SO_4\) concentration on the acid catalyzed esterification of CJCO was varied from 1 to 5% w/w. Figure 2 shows the effect of catalyst concentration on amount of FFA at methanol to oil ratio of 20% w/w, ultrasonic irradiation of 20 min and a reaction temperature of 30°C. From the figure, the FFA was decreased from 12.5% to the minimum value of 2.2% in 20 min. The FFA reduced sharply to 3% at 3% w/w of \(H_2SO_4\) concentration and then decreased gradually to 2.2% at 4% w/w of \(H_2SO_4\) concentration. Increasing the \(H_2SO_4\) concentration was significantly affected to the reduction of FFA. 3% w/w of \(H_2SO_4\) was found to be optimum to reduce the FFA value to 3% effectively. Lower \(H_2SO_4\) concentration did not reduce the FFA value of the reactants to the desired limit. Therefore, it can be concluded that the catalyst concentration at 3% w/w was the optimum value, because the recommended transesterification reaction with alkaline catalyst are less than 3% FFA raw material\(^{26}\).

3.1.2 Effect of methanol to oil ratio

The effect of methanol to oil ratio on the amount of FFA was investigated. The methanol to oil ratios was set at 10, 15, 20, 25, 30, and 40% w/w respectively. The effect of methanol to oil ratio on amount of FFA at \(H_2SO_4\) concentration of 1% w/w, ultrasonic irradiation of 20 min and a reaction temperature of 30°C is drawn in Fig. 3. The figure indicates that the FFA concentration was influenced by the quantity of methanol to oil ratio. The FFA was decreased from 12.5 to 1.5% as methanol to oil ratio increased from 10 to 30% w/w. The FFA reduced sharply to 3% at 15% w/w of methanol to oil ratio and then decreased gradually to 1.5% at 30% w/w of methanol to oil ratio. Moreover, it was observed that the higher methanol to oil ratio, beyond 30% w/w, had no significant effect on the FFA reduction. The optimum amount of methanol to oil ratio was suggested to be 15% w/w.

3.1.3 Effect of ultrasonic irradiation time

In order to optimize the ultrasonic irradiation time, the difference ultrasonic irradiation times were selected as 10, 20, 30, 40, 50 and 60 min. Figure 4 represents the effect of ultrasonic irradiation time on amount of FFA at a \(H_2SO_4\) concentration of 1% w/w, ultrasonic irradiation of 20 min and a reaction temperature of 30°C. In this figure, the FFA reduced sharply to 3.3% at 10 min of ultrasonic irradiation time and then decreased gradually to 1.2% at 50 min of ultrasonic irradiation time. Further increasing an ultrasonic irradiation time did not significantly affect to FFA concentration reduction. Therefore, the optimal reaction time condition was 20 min where the FFA concentration was less than 3%.

3.2 Alkaline catalyzed transesterification

3.2.1 Effect of catalyst concentration

The effect of catalyst concentration (KOH) to biodiesel conversion was investigated with the variation from 0.5 to 2% w/w. The relationships between the conversion to biodiesel and ultrasonic irradiation time at various KOH
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concentrations with methanol to oil ratio of 15% w/w and a reaction temperature of 30°C is shown in Fig. 5. The experimental result indicated that the conversion to biodiesel increase with an increasing catalyst loading. However, the rate of the increase in conversion to biodiesel dropped when catalyst concentration was increased beyond 1% w/w. It was observed the maximum conversion to biodiesel at 1% w/w of KOH was higher than other KOH concentrations. The maximum conversion to biodiesel of 96% was obtained using 1% w/w KOH concentration in 30 min irradiation time. The results clearly indicated that the optimum concentration of catalyst (KOH) for effective catalyzed transesterification was 1% w/w. With the higher concentration of the catalyst, the formation of soap would occur. This increased the viscosity of the reactants and lowered the product yield with the prop KOH concentration. Hydroxide ions from KOH react with the methanol molecule and produce methoxide ions, this increased the rate of reaction.

3.2.2 Effect of methanol to oil ratio

The methanol to oil ratio is one of the most important parameter affecting the conversion to biodiesel. The experiment was performed by varying methanol to oil molar ratio in the range of 10 to 20% w/w. Figure 6 depicts the relationship between the conversion to biodiesel and ultrasonic irradiation time at various methanol to oil ratios at the catalyst concentration of 1% w/w and a reaction temperature of 30°C. This demonstrates that the percent of conversion to biodiesel increases with an increasing methanol to oil ratio. It shows that with methanol to oil ratio of 10% w/w, the conversion to biodiesel is 90% after 40 min of reaction. The best results (96%) can be obtained from the methanol to oil ratio of 15% w/w. Nevertheless, a further increase of methanol to oil ratio to 20% w/w does not give the higher biodiesel conversion. The lower value is obtained (94%), because at higher methanol to oil ratio, the separation of ester from glycerol layer becomes more difficult. Hence the methanol to oil ratio of 15% w/w can be considered as an optimum operating ratio in this study. Adding more than 15% w/w methanol to oil ratio had no significant effect on the conversion to process, biodiesel, because alkaline catalyzed transesterification is already in equilibrium. But the lower methanol to oil ratio may result in an incomplete transesterification. Increasing the methanol to oil ratio will shift the reaction to the ester formation direction. However, when the methanol to oil molar ratio is set too high, the excessive alcohol may favor conversion of diglycerides to monoglycerides and a slight recombination of esters and glycerol to monoglycerides, because their concentrations keep increasing during the course of the reaction.
3.2.3 Effect of reaction temperature

The effect of reaction temperature on the conversion to biodiesel was also studied by carrying out the reaction at three different temperatures over the range of 30 to 65°C. Figure 7 represents the relationships between the conversion to biodiesel and ultrasonic irradiation time at various reaction temperatures at the methanol to oil ratio of 15% w/w and a catalyst concentration of 1.0% w/w. It reveals that, the final percentage conversion to biodiesel was almost reached in 40 min. After 40 min the conversion to biodiesel present in the 30, 50 and 65°C runs were 97, 96.5 and 85%, respectively. The conversion to biodiesel obtained in the 30 and 50°C run were quite similar, while the one in the 65°C run was clearly less. This experimental result indicates that at lower temperature the extent of conversion to biodiesel is higher, but when the temperature is increased, the conversion to biodiesel decreased. This showed that the increase of temperature had a negative influence on methanolysis of CJCO. The extent of cavitation effect is dampened at higher operating temperature due to the cavitation may also lead to the localized increase in temperature at the phase boundary of mixing reaction. At higher reaction temperature, there is a chance of loss of methanol due to the evaporation. Then, the reaction temperature above the boiling point of alcohol should be avoided; also the high temperature reaction tends to accelerate the saponification of glycerides by the alkaline catalyst.

3.3 Comparison of ultrasonic irradiation method with conventional stirring method

A comparison of the effect of ultrasound irradiation in the alkaline catalyzed transesterification reaction was carried out at the optimal operating conditions (methanol to oil ratio of 15% w/w, catalyst concentration of 1% w/w and reaction temperature of 30°C). Experiment was also performed using conventional stirring method under optimized set of operating parameters to compare the efficacy of two modes of mixing. The mechanical stirrer reactor consists of a two blade turbine with a diameter of 4 cm and operates at 600 rpm.

Figure 8 show the percentage of conversion to biodiesel obtained from the ultrasonic irradiation method and the conventional mechanical stirring method. In both methods, the conversion to biodiesel increased with increasing reaction time. The initial rate of reaction under ultrasonic irradiation was considerably faster than that under stirring method. It can be seen from Fig. 8 that ultrasonic irradiation method results in 98% conversion whereas the conventional stirring method results in lower extent of conversion 79% over the similar operation time of 25 min. This can be attributed to the fact that the reaction is mass transfer controlled, the micro level turbulence generated due to cavitation bubbles results into the higher availability of the interfacial area, also increase in the local temperature and pressures, hence the higher conversion. Moreover, Fig. 8 indicated that use of ultrasonic irradiation accelerates the limiting equilibrium conversion to biodiesel from about 98% in 60 min to about 98% in 25 min of reaction time. In addition, the emulsion droplets would be smaller under ultrasonic irradiation. Smaller emulsion droplets will result increased contract surface area between the immiscible phases. Thus, the use of ultrasonic irradiation in both phases simultaneously enhances the rate of reaction as well as shifting the equilibrium and resulting in higher conversion to biodiesel. The results indicated that ultrasonic irradiation can be successfully
applied to transesterification reactions with more than 96% yield of conversion to biodiesel in as low as 20 min of the reaction time. The technique hence appears to be effective compared to the conventional approach. The present study thus reveals that the use of ultrasonic irradiation mixing method gave shorter reaction time and higher biodiesel yield (percent conversion to biodiesel) than the conventional mechanical stirring method. This brings about considerable time as well as cost.

4 CONCLUSIONS

In summary, the two-step process coupled with ultrasonic irradiation condition is an efficient method and time saving for biodiesel production from crude jatropha curcas L.(CJCO) having high FFA. A two-step catalyzed transesterification process was selected to improve the conversion to biodiesel. The first step was acid catalyzed esterification process, which could reduce the FFA level of CJCO to less than 3%. The second step, alkaline catalyzed transesterification process gave more than 98% of conversion to biodiesel. The optimum conditions for production of methyl ester (biodiesel) under the ultrasonic irradiation condition were as follows: the first step process was obtained at methanol to oil ratio of 15% w/w, catalyzed concentration of 3% w/w, ultrasonic irradiation-time of 20 min and temperature of 30°C (room temperature). While, the second step process was obtained at methanol to oil ratio of 15% w/w, catalyzed concentration of 1% w/w, ultrasonic irradiation time of 30 min and temperature of 30°C. The conversion to biodiesel achieved was 98%. Finally, the comparison with the conventional mechanical stirring method has clearly illustrated the role of ultrasonic irradiation in inducing an effective emulsification and mass transfer so that the rate of ester formation is significantly enhanced.

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