

# Enhancement of Pretreatment Process for Biodiesel Production from Jatropha Oil Having High Content of Free Fatty Acids

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**Abstract-** Biodiesel fuel (BDF) is derived from renewable resources and it is possible to avoid the dependence on petroleum fuel. The main challenge is to reduce the high BDF production cost resulting from the consumption of raw material and energy. In this study, two different mixing methods, namely the mechanical mixing method and the emulsification mixing method, were used for the esterification reaction to reduce the free fatty acid (FFA) contents in the Jatropha curcas oil. The conversion of FFA in Jatropha curcas oil to methyl esters was carried out using 98% Sulfuric ( $H_2SO_4$ ) acid as a catalyst. The main objective of this study is to establish a proper mixing method that reduces the consumption of methanol intake and energy. The results showed that by using the emulsification mixing method, the acid value of Jatropha oil could be reduced from 9.3 mgKOH/1g oil to less than 2 mgKOH/1g oil using 1% w/w of  $H_2SO_4$  acid with the molar ratio of methanol to oil of 0.8:1 at the temperature of 60°C, whereas the mechanical mixing method required 1.25% w/w of  $H_2SO_4$  acid with the methanol to oil molar ratio of 0.9:1 and stirring speed of 600 rpm at the temperature of 60°C. The test results revealed that the emulsification mixing method is a promising alternative mixing method to the mechanical mixing method for the esterification reaction.

**Keywords-** Biodiesel; Jatropha; Esterification; Free Fatty Acids; Emulsification mixing

## I. INTRODUCTION

Biodiesel oil is comprised of mono- alkyl esters of long chain fatty acids derived from the reaction of vegetable oils or animal fats and alcohol with or without the presence of a catalyst [1]. It is renewable, non-toxic, biodegradable, non-inflammable and has relatively less emission of carbon monoxide, sulfur dioxide and unburned hydrocarbons than petroleum based diesel oils [2]. In addition, biodiesel is comparable to petroleum fuel in terms of sulfur content, flash point, aromatic content and cetane number [3]. Due to the limitation of fossil fuels, fluctuation in the petroleum price and increasing environmental concerns, there is a great demand for alternative sources of petroleum-based fuel. Biodiesel, which is a clean renewable fuel, has recently been considered as the best alternative to diesel fuel because it can be used in any compression ignition engine without the need for modification [4,5].

However, a major obstacle in the commercialization of biodiesel fuel is its high production cost, which is due to the higher cost of edible oil. The use of cheaper and non-edible vegetable oil, waste cooking oil, and animal fats as raw feedstock, is an effective way of reducing the cost of biodiesel. Many authors have proposed alternatives to edible oil such as Jatropha Curcas [6,7], sludge palm oil [2], Zanthoxylum bungeanum seed oil [8], mahua (Madhuca indica) [9], rubber seed oil [10], Karanja (Pongamia pinnata) [11] and waste cooking oil [3]. Among the crop options, Jatropha Curcas, a shrub that can sustain itself under difficult climatic and soil conditions, which is much less expensive than edible vegetable oil is being considered as a promising alternative to edible vegetable oil [2,7]. However, these kinds of oil have high content of free fatty acids (FFA). High FFA content (>1% wt) causes soap formation during the process of transesterification using alkaline catalyst, resulting in the reduction of the yield of biodiesel [2,9]. Thus, the one step process involving an alkali-catalyzed transesterification is not sufficient for high FFA feedstock. Acid-catalyzed transesterification, despite its insensitivity to FFA in the feedstock, has been largely ignored mainly because of its relatively slow reaction rate [1]. Therefore, for feedstock with high FFA content, investigations have been made by many authors by a process combining the acid-catalyzed esterification followed by the alkaline-catalyzed transesterification [1,2,6,8,9].

Many previous studies have proved that the esterification reaction strongly depends on the intensity of mixing, the methanol to oil molar ratio, the catalyst amount, the temperature and time [1,2]. Longer reaction time, increasing the amount of raw materials and increasing the temperature and speed, improves the performance of the reaction but on the other hand, negatively affects the price of the end product. The main challenge is to improve the product quality while reducing the cost of production. One main obstacle is that the mass transfer is limited because the oil and the alcohol are immiscible due to the low solubility of short chain alcohol [12]. The intensity of mixing has a strong influence on the reaction rate, which has been investigated by many authors [13,14]. In this study, the emulsification mixing method was used to enhance the reaction rate. The main advantage of the emulsification mixing is that the motionless mixers typically have lower energy consumption and reduced maintenance requirements because they have no moving parts. An emulsification mixer consists of a series of fixed

geometric mixing elements enclosed within a tubular pipe. The energy of the flow stream itself is used in the mixing process. The emulsification mixer performs a series of mechanisms to mix reactants [15].

In this study, a comparative study on acid-catalyzed esterification from *Jatropha curcas* oil was performed by employing two mixing methods, namely the mechanical mixing method and the emulsification mixing method (static mixer). Many researches also have shown that the static mixer has effective results when applied to the transesterification process for biodiesel reaction [16,17]. The main goal of this research is to establish an appropriate mixing method that will be possible to reduce the amount of methanol intake for the esterification reaction (pretreatment process) and thereby to reduce the production cost.

## II. MATERIALS AND METHODS

### A. Raw Materials and Chemicals

*Jatropha* oil was obtained from the Kasetsart University, Thailand. For the pretreatment, 99.8% solution of methanol, and 98% solution of  $\text{H}_2\text{SO}_4$  acid were purchased from the Wako Pure Chemicals Industries Ltd, Japan. For the titration, 0.1 mol/L potassium hydroxide ethanolic solution, diethyl ether super dehydrated solution and 99.5% solution of ethanol were purchased from the Wako Pure Chemicals Industries Ltd, Japan and 10 g/L phenolphthalein solution was purchased from Kanto Chemical Co. Inc, Japan.

### B. Acid Catalysed Pretreatment

For a successful reaction, the raw oil must be free of water and other impurities. Initially, *Jatropha* oil was heated to 105°C for 1h to remove water by evaporation. Then, the acid catalyzed pretreatment was conducted with two different methods, namely the mechanical mixing method and the emulsification mixing method.

The experiments were performed at different operating conditions including five methanol to oil molar ratios (1:1, 0.9:1, 0.8:1, 0.7:1 and 0.6:1), five different catalyst amounts of 0.5, 0.75, 1, 1.25, 1.5(wt%) and at room temperature, 40°C and 60°C, respectively.

#### 1) Mechanical Mixing Method:

The laboratory scale apparatus consisted of a 200 ml round bottom reaction flask, an oil bath with an electric heater and a magnetic stirrer (Fig. 1). A known amount of *Jatropha* oil feedstock was poured into the reaction flask and heated to the desired temperature. Required amounts of methanol and  $\text{H}_2\text{SO}_4$  acid were mixed separately and then added to the preheated oil. The measurement of time was started at this point. Heating and stirring were continued for 30 minutes, 1 hour and 2 hours respectively. The stirring speed was kept constant for all the tests at 600 rpm.

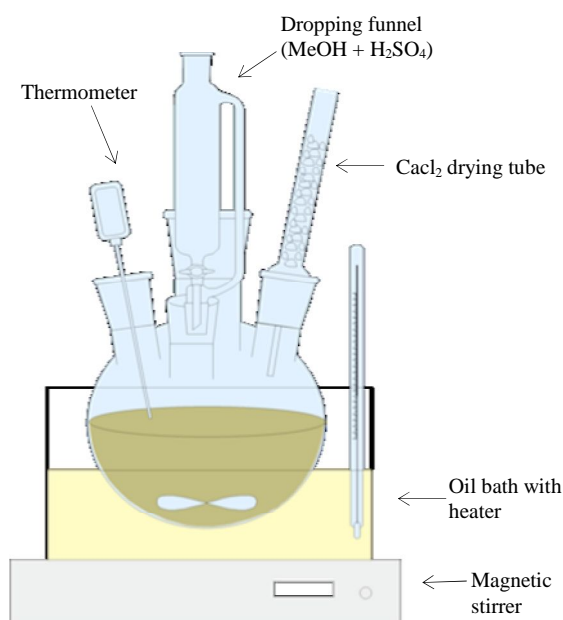


Fig. 1 Schematic diagram of the mechanical mixing experimental setup

After the reaction, the reaction mixture was poured into a separation funnel and was allowed to settle overnight. The excess methanol with water and the catalyst moved to top layer and was removed. The oil with lower content of FFA settled at the bottom layer. The bottom layer was collected and was titrated to check the acid value of the treated oil.

## 2) Emulsification Mixing Method:

The experiment was conducted by using a laboratory scale static mixer as shown in Fig. 2. The length of the mixer, the external diameter and the internal diameter are 26 cm, 0.8 cm and 0.6 cm, respectively.

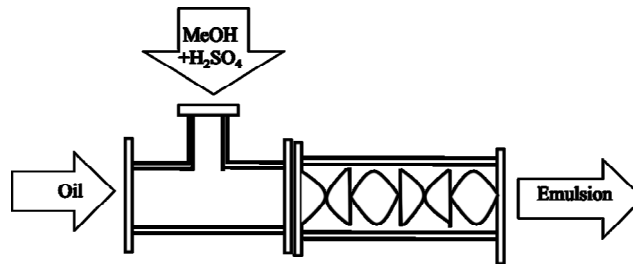


Fig. 2 Schematic diagram of the emulsification mixing experimental setup

Required amounts of oil, methanol and H<sub>2</sub>SO<sub>4</sub> acid were allowed to mix inside the inline cutter to form an emulsion solution, where small droplets of methanol-H<sub>2</sub>SO<sub>4</sub> were uniformly dispersed in the oil. In this method, the emulsification mixing was carried out at room temperature and the reaction mixture was kept at 600C, 400C and room temperature for 1 hour to complete the reaction. The mixing speed was not an experimental parameter because there were no moving parts in the facility.

After formation of the emulsion, it was allowed to settle in the separation funnel and the bottom layer was titrated to check the acid value.

## C. Analytical Method

### 1) Acid Value:

The acid value of the reaction mixture after the acid catalyzed pretreatment was determined by the acid base titration technique (EN14104).

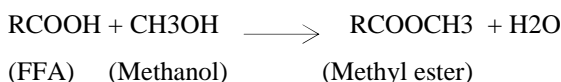
## III. RESULTS AND DISCUSSION

### A. Characterization of Jatropha oil

The acid value of the Jatropha oil was found to be 9.3 mg KOH/1g oil, which corresponded to the FFA value of 4.7% ( as of oleic acid) and it was clear and brown in color.

### B. Acid catalyzed esterification as a pretreatment process for biodiesel production

It has been reported that for a successful transesterification using the alkaline catalyst, the acid value of the oil should be less than 2 mg KOH/1g oil (FFA<1%). To reduce the acid value of Jatropha oil from 9.3 mg KOH/1g oil to less than 2 mg KOH/1g oil, Jatropha oil was esterified with methanol by using 98% H<sub>2</sub>SO<sub>4</sub> acid as the catalyst. The esterification reaction can be represented as follows.



The main parameters that affect the esterification reaction are the methanol to oil molar ratio, the mixing method, the catalyst amount, the reaction temperature and time. In this study, different methanol to oil molar ratios (1:1, 0.9:1, 0.8:1, 0.7:1 and 0.6:1), catalyst amounts (0.5, 0.75, 1, 1.25, 1.5 % w/w), temperatures (600C, 400C, room temperature) and mixing methods (the mechanical mixing and the emulsification mixing) were used to investigate their effects on the reduction of the acid value of the Jatropha oil.

### 1) Effect of the Methanol to Oil Molar Ratio and the Mixing Method on the Reduction of the Acid Value:

The quantity of methanol used is an important factor that affects the reduction of the acid value of the product and the production cost. The influence of five different molar ratios was studied. Figure 3 shows the effects of the methanol to oil molar ratio and the mixing method on the reduction of the acid value, where the catalyst concentration was 1% w/w, the reaction temperature was 600C and the reaction time was 1 hour.

It was found that the reaction rate of the acid-catalyzed esterification increased with the increase of the methanol amount. This agrees with the results obtained by several researches [1,2]. Further increase of the methanol to oil molar ratio should be avoided because the target acid value reduction is achieved with the present amount of methanol and the reduction of the acid value is insignificant while the cost was higher. Therefore, the methanol to oil molar ratio of 0.8:1 was the lowest ratio that

provided the acid value of the oil less than 2 mgKOH/1g oil by the emulsification mixing method, so it was selected as the optimum methanol to oil molar ratio.

In a commercial application, the methanol in the methano/water fraction, which is separated from the top layer after the esterification step, can be removed by the fractional distillation and returned to the process. Meanwhile, it is possible to further reduce the methanol consumption by continuous removal of water from the mixture during the reaction. Thus, the methanol consumption is reduced, resulting in the reduction of the production cost [9].

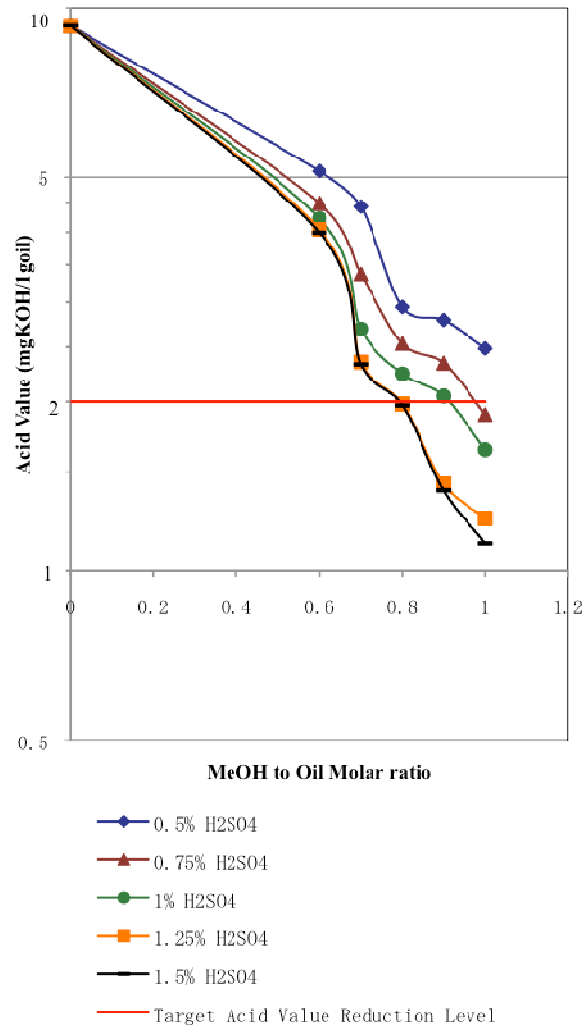


Fig. 3 The effects of the methanol to oil molar ratio and the mixing method on reduction of the acid value. (catalyst amount = 1% w/w, reaction temperature = 60°C and reaction time = 1 hour)

In this study two different mixing methods, namely the mechanical mixing method and the emulsification mixing method, were used to identify the effect of the mixing method on the acid value reduction. Fig. 3 also proves that the intensity of the mixing has a strong influence on the esterification reaction. Oil is immiscible with methanol-H<sub>2</sub>SO<sub>4</sub> solution. Therefore, the mixer with more uniform methanol-H<sub>2</sub>SO<sub>4</sub> droplet size distribution can promote the reaction. Berrios et al. proved that methanol is only sparsely soluble in oil [19], so that it requires agitation in order to avoid mass transfer taking control over the process.

Figure 3 shows that for the emulsification mixing method, the methanol to oil molar ratio of 0.8:1 and the catalyst amount of 1% w/w were sufficient to reduce the acid value to less than 2 mgKOH/1g oil. For the mechanical mixing method, at least 1:1 of the methanol to oil molar ratio and the catalyst amount of 1% w/w were required to reduce the acid value to less than 2 mgKOH/1g oil. The good result of the emulsification mixing was due to the distributive mixing creating stretching, dividing and reorienting of the flow of the reactants to eliminate the variations in the material distribution to realize a more homogeneous mixture [15]. The static mixer generates smaller sized droplets of methanol-H<sub>2</sub>SO<sub>4</sub> than the mechanical mixer and the mechanical stirring creates less uniform, various sized droplets compared with the emulsification mixing. Apart from

the excellent mixing performance, other advantage of the emulsification mixing is its reduced energy consumption due to the machine without any moving parts.

## 2) The Effect of the Amount of the Catalyst and the Mixing Method on the Reduction of the Acid Value:

Another important parameter that affects the acid catalyzed esterification is the catalyst concentration. Berrios et al. verified that the esterification reaction does not take place without catalyst [19]. Sulfuric acid ( $\text{H}_2\text{SO}_4$ ), the most common acid catalyst, is used in the esterification because of its low cost and readily availability [2]. 98%  $\text{H}_2\text{SO}_4$  acid showed a good catalyst activity for the oil with high FFA content.

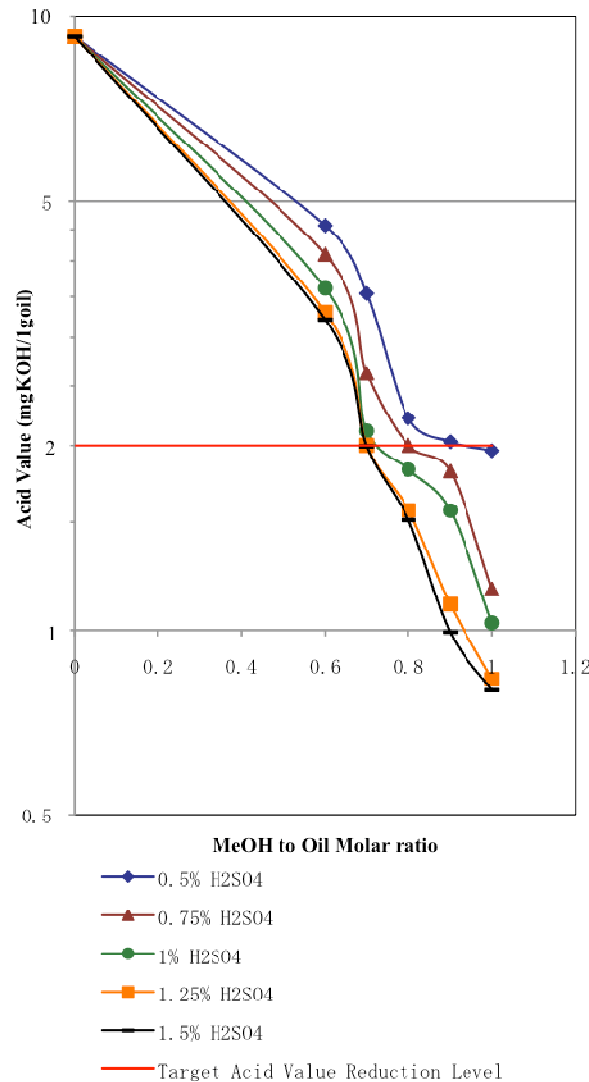


Fig. 4 The effect of the amount of the catalyst on reduction of the acid value by the mechanical mixing method (reaction temperature =  $60^\circ\text{C}$ , reaction time = 1hour and stirring speed = 600rpm).

The reaction was carried out at different dosages of  $\text{H}_2\text{SO}_4$  acid (ranged from 0.5 to 1.5% w/w) and the methanol to oil molar ratios (ranged from 0.6:1 to 1:1) for resting their effects on the reduction of the acid value of the oil. The results of the mechanical mixing and the emulsification mixing are shown in Figs. 4 and 5, respectively. From these figures, it can be observed that increase of the catalyst amount could reduce the acid value because the ester formation rate increased with the increase of the catalyst concentration. However, at lower catalyst concentration of 0.5%w/w, the acid value could not be reduced to below 2 mgKOH/1g oil even when the methanol to oil molar ratio was 1:1 for both mixing methods. When the catalyst amount was 1.25%w/w and 1.5%w/w, the results were almost the same, showing that there is an upper limit of the amount of catalyst, above which there is no significant differences in reduction of the acid value.

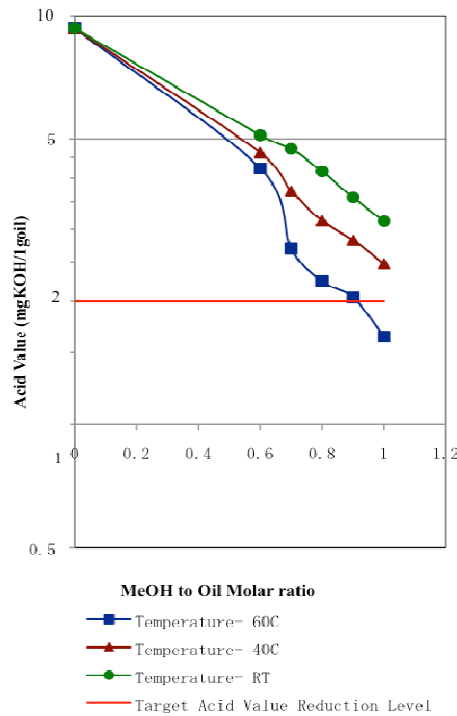


Fig. 5 The effect of the amount of the catalyst on reduction of the acid value by the emulsification mixing method. (reaction temperature = 60°C and reaction time = 1 hour)

From these results, 1.25% was selected as the optimum catalyst concentration for the mechanical mixing method and 1% chosen as the optimum catalyst concentration for the emulsification mixing method because it was the lowest catalyst concentration which provided the acid value less than 2 mgKOH/1g oil with the minimum value of the methanol to oil molar ratio. The above results also prove that the emulsification mixing performs better than the mechanical mixing with the same experimental parameters.

### 3) Effects of the Reaction Temperature and the Mixing Method on Reduction of the Acid Value:

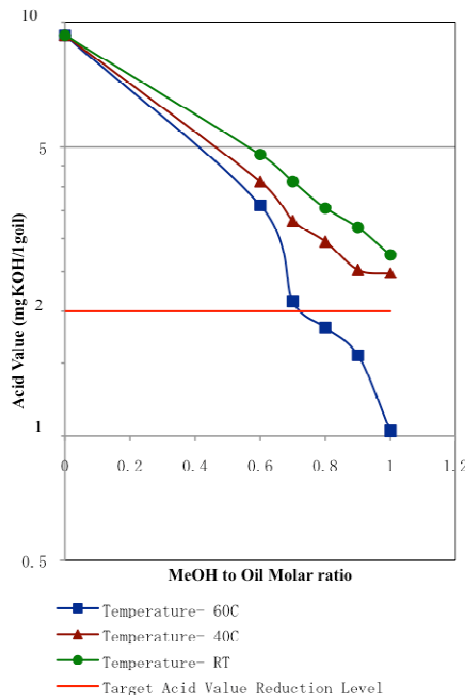


Fig. 6 The effect of the reaction temperature on reduction of the acid value by the mechanical mixing method. (catalyst amount = 1% w/w, reaction time = 1 hour and stirring speed = 600 rpm ).

The reaction temperature maintained by most researches varied from 40 to 60°C [1,2]. From the results obtained by Hayyan et al., it was observed that the conversion of FFA to methyl esters decreased with the increase of the reaction temperature higher than 60°C [2]. In order to study the influence of the reaction temperature on the acid catalyzed esterification, reactions were conducted at room temperature, 40°C and 60°C. The results of the mechanical mixing and the emulsification mixing are shown in Figs. 6 and 7, respectively. The results showed that the reaction temperature played an important role in the acid-catalyzed esterification. As can be seen in these figures, the rate of the reaction increased with increasing reaction temperature. It was observed that the acid catalyzed esterification could occur at room temperature and at the temperature of 40°C but the acid value of the oil could not be reduced to less than 2 mgKOH/1g oil by either mixing methods. The highest reaction rate was observed at 60°C and the acid value reduced from 9.3 mgKOH/1g oil to less than 2 mgKOH/1g oil by both mixing methods. Hence, the reaction temperature of 60°C can be considered the optimum temperature for this reaction.

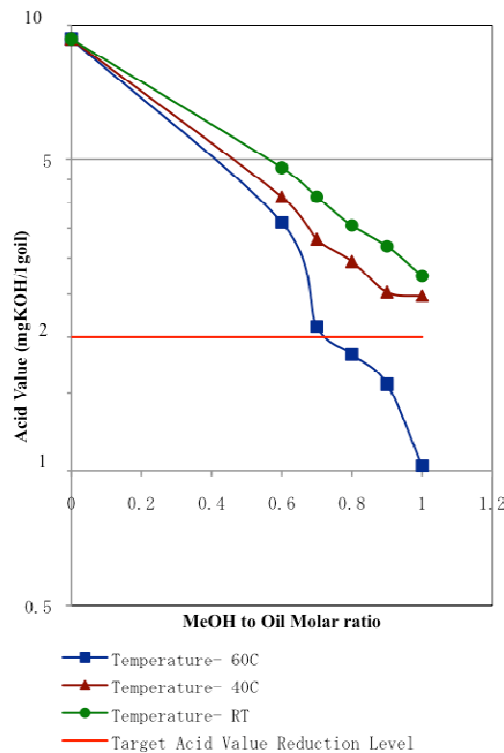


Fig. 7 The effect of the reaction temperature on reduction of the acid value by the emulsification mixing method. (catalyst amount = 1% w/w and reaction time = 1 hour)

When the reaction temperature was room temperature and 60°C, the reaction time was 1 hour and the methanol to oil molar ratio was 1:1, the acid value reduction for the mechanical mixing was from 9.3 mgKOH/1g oil to 3.14 mgKOH/1g oil and 1.64 mgKOH/1g oil, respectively, while that for the emulsification mixing was from 9.3 mgKOH/1g oil to 2.74 mgKOH/1g oil and 1.02 mgKOH/1g oil, respectively. The above results also prove that the emulsification mixing method has a high potential to enhance the esterification reaction compared with the mechanical mixing method.

#### 4) The Effect of the Reaction Time on Reduction of the Acid Value:

The acid value also appeared to be decreasing with the increase of the reaction time in the case of the mechanical mixing method. For achieving perfect mixing of the oil and the reagents during the esterification reaction, it is necessary to stir well at constant agitation speed and constant reaction temperature for a specified reaction time [3]. To investigate the effect of the reaction time, experiments were conducted for 30 minutes, 1 hour and 2 hours with the mechanical mixing method. Fig. 8 shows that the longer the reaction time was, the better the result was, yet there was almost no difference between the results obtained after 1 hour and 2 hours. Thus, 1 hour of the reaction time can be selected as the optimum reaction time of the mechanical mixing method since longer reaction time increases the production cost.

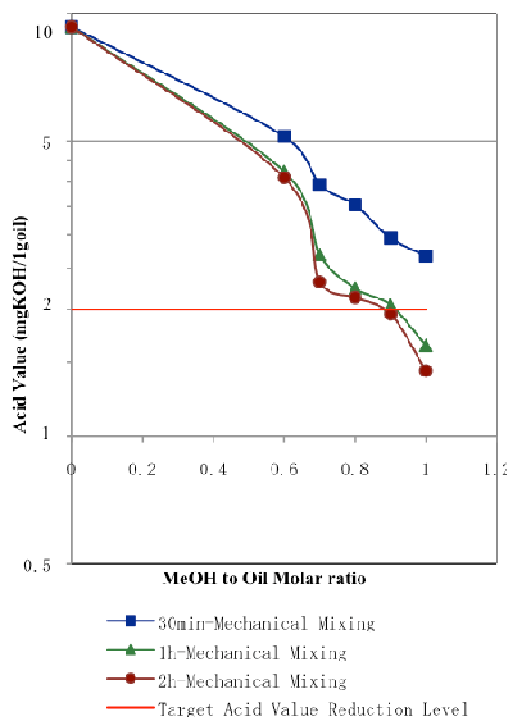


Fig. 8 The effect of the reaction time on reduction of the acid value by the mechanical mixing method.  
(catalyst amount = 1% w/w and reaction temperature = 60°C)

#### IV. CONCLUSIONS

As a result, in this study it can be concluded that the emulsification mixing method has a high potential for accelerating the esterification reaction compared with the mechanical mixing method.

The methanol to oil molar ratio of 0.8:1, the catalyst amount of 1% w/w, the reaction temperature of 60°C and the reaction time of 1 h were sufficient to reduce the acid value of *Jatropha* oil from 9.3 to less than 2 mg KOH/1g oil through the emulsification mixing method.

The methanol to oil molar ratio of 0.9:1, the catalyst amount of 1.25% w/w, the reaction temperature of 60°C, the reaction time of 1 h and the stirring speed of 600 rpm were sufficient to reduce the acid value of *Jatropha* oil from 9.3 to less than 2 mg KOH/1g oil with the mechanical mixing method.

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