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## An approach to Produce Biodiesel From Non-edible *Jatropha curcus* Oil through Dual Step Process: Preesterification and Transesterification

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### Abstract

Studies were carried out to produce potential biodiesel from non-edible oil of *Jatropha curcus*. Due to its high free fatty acid (12% FFA), the crude *Jatropha* oil was processed in two steps: the acid-catalyzed esterification and followed by the base-catalyzed transesterification. The first step reduced the FFA level to less than 1% in 1h at 50°C for the 0.40 w/w methanol-to-oil ratio with 1% w/w of H<sub>2</sub>SO<sub>4</sub>. After the reaction, the mixture was stagnated for an hour and the methanol-water upper layer was discarded. The second step converted the product of the first step into biodiesel and glycerol through transesterification using 0.20 w/w methanol-to-oil and 0.5% w/w NaOH to oil as alkaline catalyst at 65°C. The maximum yield of biodiesel (organic phase of upper layer) and fatty acid methyl esters (FAME) yield were achieved at about 95% and 84% within 1 hour respectively. The glycerol concentration in the byproduct (glycerol layer) obtained after dual step transesterification was found 32%.

**Key words :** *Jatropha curcus*, Biodiesel, Esterification, Glycerol and Fatty acid

### Introduction

In recent years researchers have been directed to explore plant-base fuels because it is renewable, non-toxic, biodegradable and environment friendly. One hundred years ago, Rudolf Diesel tested vegetable oil as fuel for his engine. With the advent of cheap petroleum, appropriate crude oil fractions were refined to serve as diesel fuels and diesel engines evolved together (Ma *et al.* 1999). Compared with petroleum diesel in diesel engines, biodiesel greatly decreases the emission of CO, sulfur, hydrocarbons, particle matter and smoke during the combustion process. Furthermore, burning biodiesel has no net addition to atmospheric CO<sub>2</sub> levels, because it is made from agriculture materials produced via photosynthesis carbon fixation (Shu *et al.* 2007).

Vegetable oil is mainly composed of triglyceride. Besides this it contains FFA, phospholipids, sterols, water, odorants and other impurities. The FFA and water content have high significant effects on the transesterification of oils and fats. Biodiesel is produced by the transesterification of C<sub>14</sub>-C<sub>20</sub> fatty acid triglycerides with short-chain alcohol such as methanol or ethanol in the presence of a catalyst such as NaOH, KOH etc. (Shu *et al.* 2007). Bio-diesel can be defined

as "Biodiesel is the mono alkyl esters of long chain fatty acids derived from renewable feed stocks, such as vegetable oil or animal fats, for use in compression ignition engine". In most developed countries, biodiesel is produced from soybean, rapeseed, sunflower, groundnut, sesame, palm oil which are essentially edible oils and thus face high demand and more expensive than diesel fuel. In this case non-edible oil sources such as *Jatropha curcas*, *Pongamia pinnata* would be potential biodiesel source for most of the developing countries (Karmee and Chandha, 2005; Meher *et al.* 2005; Tiwari *et al.* 2007; Naik *et al.*, 2008 and Berchmans and Hirata, 2008). *Jatropha curcas* in comparison with sources has rapid growth, higher seed productivity and is climatically suitable for both tropical and subtropical countries of the world (Ramesh *et al.*, 2002).

Literature search shows few references about base catalyzed single step transesterification reaction and acid catalyzed dual step transesterification reactions and information about how to synthesize biodiesel by using different techniques from fats and oils (Berchmans and Hirata, 2008; Tiwari *et al.* 2007).

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**Table 1. Fatty acid composition of *Jatropha* oil<sup>a</sup>**

Fatty acid	Systemic name	Formula	Structure <sup>b</sup>	wt%
Palmitic	Hexadecanoic	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	16:0	11.3
Stearic	Octadecanoic	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	18:0	17.0
Arachidic	Eicosanoic	C <sub>20</sub> H <sub>40</sub> O <sub>2</sub>	20:0	4.7
Oleic	cis-9-Octadecenoic	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	18:1	12.8
Linoleic	cis-9,cis-12-Octadecadienoic	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	18:2	47.3

a Adapted from Tiwari *et al.*, 2007.

b xx:y indicates xx carbons in the fatty acid chain with y double bonds.

Typically *Jatropha curcus* oil, collected for the present investigation, was observed to contain about 12% of FFA. This paper discloses the outcomes of experiments carried out to optimize the first step i.e. acid catalyzed esterification for reducing the FFA of crude *Jatropha* oil below 1% and the second step i.e. base catalyzed transesterification for obtaining maximum yield of biodiesel as well as FAME yield. Besides this, the concentration of glycerol in the byproduct (glycerol layer) was also determined.

## 2. Materials and Method

### 2.1 Materials

Crude *Jatropha* oil was obtained by the courtesy of Energy Technology Center, Agency for Assessment and Application of Technology, Kawasan Puspiptek, Serpong, Tangerang 15314, Indonesia and Rapeseed oil and Net coconut oil were collected from Japan and Bangladesh respectively. Chemicals used in the present work were of reagent grade. The reactions were carried out in a 15 cm<sup>3</sup> special kind glass tube of which thickness was 2mm and was sealed tightly with a silicon rubber cap which prevented any leakage. AS ONE temperature controller (TC-1000) and magnetic stirrer (HS-4SP) made by Japan, were used for transesterification process. In this study, experiments were conducted in a laboratory-scale setup developed by Berchmans and Hirata, 2008.

### 2.2 Experimental procedure

#### 2.2.1 Single step transesterification

In this research, transesterification reactions of rapeseed oil, net coconut oil and crude *Jatropha* oil were carried out with the fix reaction conditions (temperature 65.0 ± 0.5 °C, agitation rate 400rpm and reaction time 2h) that were selected

after the extensive preliminary experiments. Firstly, in the transesterification process, different catalyst NaOH-to-oil ratios (1.0% to 4.0% w/w) and different methanol-to-oil ratios (20% to 120% w/w) were used to investigate their influence on the biodiesel and FAME yields of the oils. All the reactions were carried out in the reaction glass tubes, which were immersed in a glass water bath placed on the plate of magnetic stirrer with the fix reaction conditions that are mentioned above. After the reaction, the mixture was allowed to settle for overnight and then glycerol layer and the biodiesel (organic phase of upper layer) including methyl ester fraction were separated, weight and analyzed by GC. In case of crude *Jatropha* oil, no layer was found. Purification stage after separation was skipped as small amount of oil was used for each experiment.

#### 2.2.2 Dual steps process

##### 2.2.2.1 Acid catalyzed esterification- first step in biodiesel production

Crude *Jatropha* oil contains about 12% FFA. First a series of tests were conducted for reducing the FFA in *Jatropha* oil by converting it to ester. In this process, oil was treated with acid catalyst (1.0% H<sub>2</sub>SO<sub>4</sub> based on the oil weight) and different methanol-to-oil ratio (10% to 60 % w/w) to investigate their influence on the acid value as well as FFA of crude *Jatropha* oil. Reaction conditions set for this experiment were temperature 50°C, agitation rate 400rpm and time 1h. After one hour of reaction, the mixture was allowed to settle for 1 h and the methanol-water fraction at the top layer was removed. The optimum condition having the lowest acid value was used for the main transesterification reaction.

### 2.2.2.2 Base catalyzed transesterification- second step in biodiesel production

The acid pretreated oil was used in the second step for investigated the optimum condition of methanol-to-oil ratio, NaOH-to-oil ratio and temperature. Firstly, the oil product has been heated at about 50°C and mixed with methanolic NaOH solution. The transesterification process was carried out with different catalyst NaOH-to-oil ratios (0.5% to 1.5% w/w), different methanol-to-oil ratios (10% to 50% w/w) and different temperatures (½ h to 2 h) for used to investigate their influence on the biodiesel, FAME yields in biodiesel and FAME recovery of the oils. The reaction mixture was heated and stirred again at  $65.0 \pm 0.5$  °C and 400 rpm. The mixture was allowed to settle overnight before separation the glycerol layer to get the FAME on the top. Then the produced methyl esters were determined by GC.

## 2.3 Analytical method

### 2.3.1 Acid value

Acid value is defined as "The number of milligram of potassium hydroxide required to neutralize the 1gm of oil or fat". In the first stage, the acid value of the reaction mixture was determined by a standard acid base titration method (ASTM, 2003) where a standard solution of one mol KOH solution was used.

### 2.3.2 GC method

Biodiesel compositions obtained from rapeseed oil and net coconut oil were analyzed using a Gas Chromatography of Hewlett Packard Plus 6890 series that equipped with a flame ionization detector and a capillary column of acidified polyethylene glycol (HP-624, 30 m × 25µm × 0.25 µm). The GC oven was kept at 80 °C for 5 min, heated at 10 °C/min up to 310 °C, where it was kept for 1 min, and a total analytical time was 29 min. The carrier gas was helium (0.7 ml/min). The analysis of a sample by GC was carried out by injecting 1 µl of the sample solution into the GC. The formed methyl ester was identified by comparing its retention time to the retention time of standard methyl ester of fatty acids. The composition of biodiesel products obtained from crude Jatropha oil were analyzed by Gas Chromatography GC-14B, Shimadzu Corporation, made in Japan. The GC-14B was equipped with high resolution GC column (J and W

Scientific, DB-FFAP, 30 m × 0.25 mm × 0.25µm). Injector and Detector temperature was 270°C and Oven/column was operated between 45-200°C. The GC oven was kept at 45 °C for 5 min, heated at 15°C/min up to 220°C, where it was kept for 14 mins, and a total analytical time was 30 min. Helium was used as a carrier gas and each time 1µl sample was injected. Quantitative analysis of the weight percentage of the produced biodiesel and methyl esters were determined by internal standard method where decane was used as internal standard (Berchmans and Hirata, 2008).

### 2.3.3 LC method

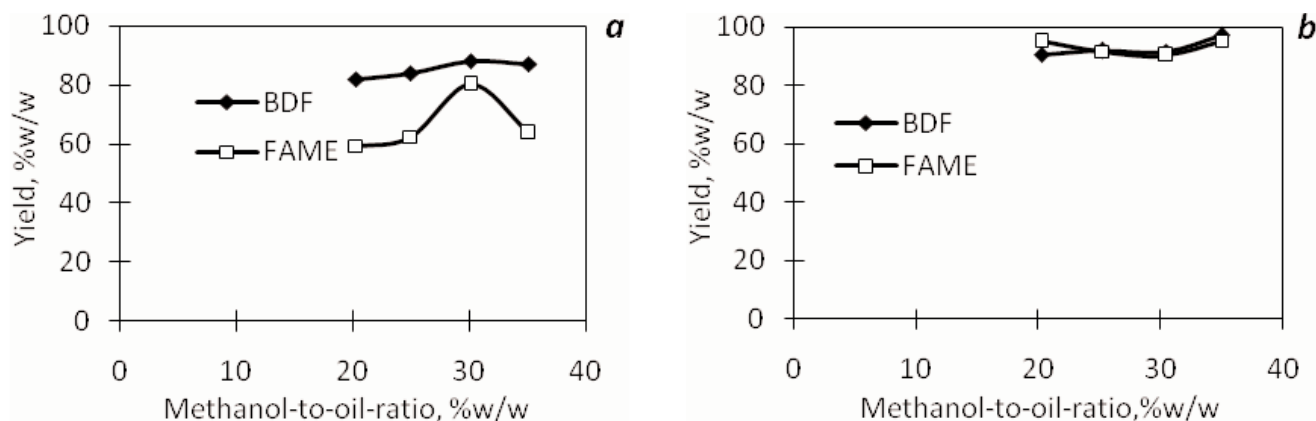
High performance liquid chromatography, HPLC (LC-10A System, Shimadzu) was used to determine the concentration of glycerol. HPLC equipped with a shim-pack SPR-H column (250mm in length × 7.8mm in inner diameter, Shimadzu) and a refractive index detector (RID-10A, Shimadzu) operated at 40°C with a flow rate of 0.6 ml/min where 4mM HClO<sub>4</sub> was used as mobile phase. For analysis, each time 10µl sample was injected and peak was identified by comparing with the retention time of the sample and the standard.

## 3. Results and Discussion

### 3.1 Single step transesterification

Reinvestigation of alkali base catalyzed transesterification results of rapeseed oil and net coconut oil were done by fixing NaOH-to-oil ratio (1.0% based on the oil weight) changing with methanol-to-oil ratios (20% to 35% w/w) as shown in fig.1. The high conversion of FAME yield for rapeseed oil (80.01%) and net coconut oil (95.0%) were obtained with 1.0% of catalyst NaOH-to-oil ratio and 30.01% and 35% of methanol-to-oil ratio respectively. For crude Jatropha oil, alkali base catalyzed transesterification results were investigated with different NaOH-to-oil ratios (1.5% to 4.0% w/w) and different methanol-to-oil ratios (30% to 120% w/w).

Optimum conditions for crude Jatropha oil were found 2.2% NaOH-to-oil ratio and 90.0% methanol-to-oil ratio and the FAME yield was 63.92%. Important observation of single stage transesterification was the FAME yield of crude Jatropha oil was low (63.92%) in compared with rapeseed oil (80.01%) and net coconut oil (95.0%) and no layer separation was observed for Jatropha oil biodiesel like rapeseed and coconut oil.



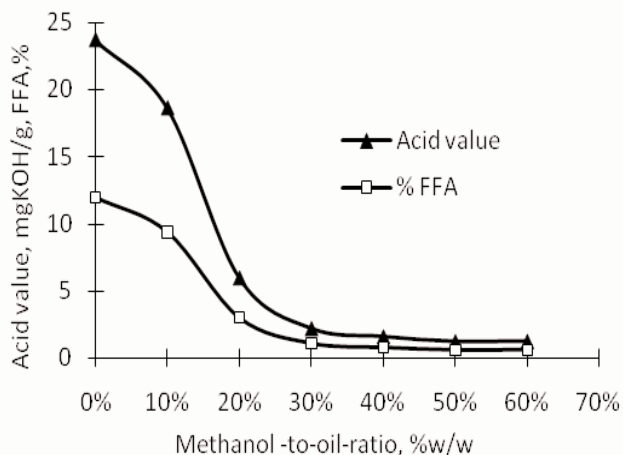
**Fig. 1. BDF and FAME yield by base catalyzed transesterification. a. Rapeseed oil and b. Net coconut oil.**

### 3.2 Dual steps process

As the crude Jatropha oil contain high FFA (about 12%), so it creates problem to separate methyl esters layer from the glycerin fraction by formation of fatty acid salts i.e. soap. An alternative route is to use i.e. acid catalysis, which is able to esterify FFA. Therefore, the dual steps process, acid-catalyzed esterification process and followed by base-catalyzed transesterification process, were selected for converting crude Jatropha oil to methyl esters of fatty acids (Berchmans and Hirata, 2007).

#### 3.2.1 Acid catalyzed esterification

Acid-catalyzed pretreatment process of crude Jatropha oil depends on different variables such as methanol-to-oil ratio, acid-to-oil ratio, reaction temperature and time. According to

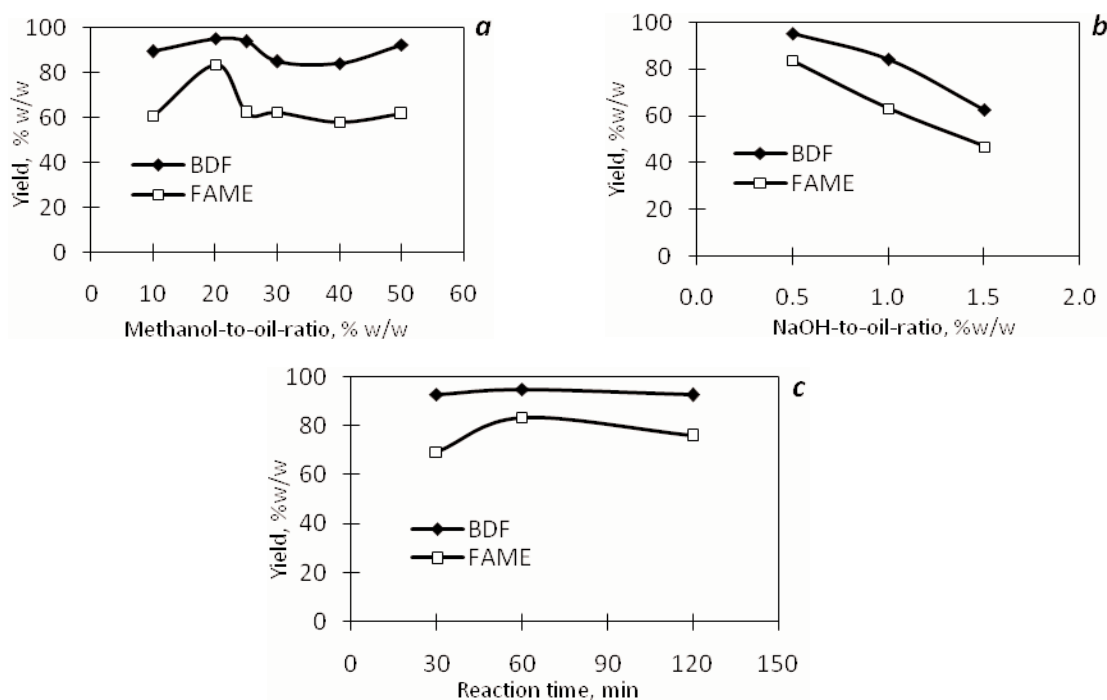


**Fig. 2. Acid value and FFA level of crude Jatropha oil changes with the amount of methanol in the acid catalyzed pretreatment (esterification) step.**

literature review, the optimum conditions for acid-catalyzed transesterification were selected as reaction temperature 50°C, reaction time 1h and 1% acid ( $H_2SO_4$ )-to-oil ratio (Berchmans and Hirata, 2007). Only different methanol-to-oil ratios (10% to 60% w/w) were used to investigate the effect on acid values and FFA. The results of the acid-catalyzed pretreatment of high FFA (12%) crude Jatropha oil are shown in Fig. 2. The optimum methanol-to-oil ratio was selected 40% w/w at which acid value and FFA were 1.58 mg KOH/g-oil and 0.79% respectively.

#### 3.2.2 Base catalyzed transesterification

Besides the presence of FFA and moisture, base catalyzed transesterification process of crude Jatropha oil is also affected by the catalyst-to-oil ratios, the methanol-to-oil ratios and the reaction temperature. The transesterification process was carried out with different catalyst NaOH-to-oil ratios (0.5% to 1.5% w/w), different methanol-to-oil ratios (10% to 50% w/w) and different reaction temperatures (½h to 2h) to investigate their influence on the biodiesel and FAME yield of the oils. The reaction mixture was heated and stirred again at  $65.0 \pm 0.5$  °C and 400 rpm. Fig. 3 shows that the optimum catalyst-to-oil ratio was 0.5% w/w, optimum methanol-to-oil ratio was 20% w/w and reaction time was 1h. At this optimum condition, biodiesel 95.1% and FAME yield 83.53% were obtained, which was higher than the FAME yield of single or direct transesterification.



**Fig. 3.** BDF and FAME yield by base catalyzed transesterification process with a. different methanol to oil ratio b. different catalyst (NaOH) to oil ratio and c. different reaction time.

Qualitative and quantitative analysis results of methyl esters components in Crude Jatropha oil transesterification products were methyl myristate (0.05%), methyl palmitate (11.68%), methyl palmitoleate (0.66%), methyl stearate (5.00%), methyl oleate (51.06%) and methyl linoleate (31.54%).

### 3.2.3 Glycerol concentration

Glycerol is the main byproduct of biodiesel. Glycerol concentration in lower layer was determined by HPLC method and it was found around 32%.

## 4. Conclusion

In this study, the production of Biodiesel from crude Jatropha oil having high FFA content was investigated. Due to high concentration of FFA (12%), the conventional base catalyzed route of biodiesel production does not work out effectively. However, the dual-steps process of transesterification using acid-catalyzed and followed by base-catalyzed reaction proves effective in producing the biodiesel. The experimental study revealed that the optimum reaction conditions for transesterification of crude Jatropha oil were catalyst-to-oil ratio 0.5% w/w, methanol-to-oil ratio 20% w/w,

reaction time 1h, reaction temperature 65°C and agitation rate 400 rpm. The first step i.e. acid pretreatment process reduced the FFA level less than 1% and the second step i.e. base catalyzed transesterification process gave biodiesel and FAME yield 95.1% and 83.53% respectively. The glycerol concentration in the byproduct (glycerol layer) obtained after dual step transesterification was found 32%.

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