Production of *Jatropha curcas* Biodiesel Using Oscillatory Flow Reactor

Supriyono, Hary Sulistyo, Suryo Purwono, Bardi Murrachman, and Joana M. Dias

Abstract*—Jatropha curcas* is very promising biodiesel feedstock. Oscillatory Flow Reactor (OFR) Oscillatory Flow Reactor (OFR) has a compact size and might be useful when reaction needs to be performed for a long time in a turbulence flow. A two step reaction was performed for biodiesel production from High Free Fatty Acid (FFA) oil; the first step aimed to reduce the FFA content by esterification process catalyzed by H_2SO_4 and the second step consisted on a transesterification process catalyzed by KOH. Initial FFA on Jatropha curcas oil was 16.45 %wt. The first step was performed in a Stirred Tank Reactor for 90 minute, 60 ^{O}C, using etanol 50% V/V and H_2SO_4 1.5% V/V and a 500 rpm stirring. After acid esterification, 94.5% of the FFA was converted. The second step was performed in an Oscillatory Flow Reactor for 60 minute at 60 ^{O}C, using ethanol 25% V/V, Sodium Metoxide 0.5 M (1% V/V) and a 91% final conversion was observed after this step. It was concluded that OFR is a good alternative for biodiesel production using High FFA *Jatropha curcas* oil as feedstock.

***Keywords*—**Jatropha curcas Oil, Oscillatory Flow Reactor, esterification, transesterification

I. Introduction

JATROPHA curcas is one of the most feasible sources for biodiesel production [1], [2]. Some advantages of *Jatropha curcas* oil are being non edible, growing in arid soil, and presenting high oil yield from seed [3]. However due to the oil composition of *Jatropha curcas* oil dominated by unsaturated fatty acid oil, this oil tends to be more easily oxidized to form Free Fatty Acid (FFA) which is great disadvantage [4]. Transesterification is one of the most popular processes for biodiesel production [5], [6] Transesterification by alkaline catalyzed process generally requires less than 1% FFA content in the feedstock oil [7], for this reason *Jatropha curcas* oil should be pretreated to adjust its FFA content before performing the transesterification process. In the pretreatment step Free Fatty Acids will react with an alcohol generally using Sulfuric acid as catalyst to produce Fatty Acid Alkyl Esters (FAAE) and Water as follows[8]:

$$R_1\text{—}COOH + R_2\text{—}CH_3 \rightleftharpoons R_1\text{—}COO\text{—}R_2 + H_2O \quad (1)$$

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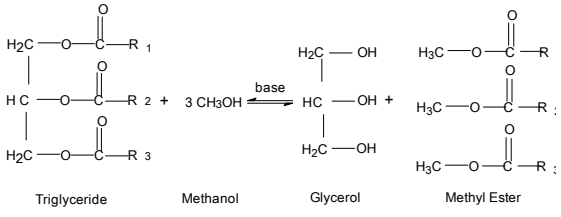
In the density separation process, there are two layers formed in this step, the upper phase is a mixture between Alcohol, Sulfuric Acid and Water and the lower phase is the remaining organic phase, consisting on a mixture between oil, FAAE, and also alcohol. After removing the alcohol from the oil phase, oil and FAAE proceed to the second step called transesterification process in which the rest of the oil will react with alcohol in the presence of a Sodium Methoxide catalyst to produce FAAE and glycerol as shown in equation 2 [9], [10]



(2)

Oscillatory Flow Reactor (OFR) was developed from plug flow reactor (PFR) [11], the idea was to increase turbulence of the fluid flow by mounted a ring shape on the tubular reactor as a baffles, later this kind of ring was replaced by an orifice shape. Oscillatory Flow Reactor is useful when reaction should performed for a long time in a turbulence flow, the other advantage of the OFR is in the fact that has a compact size because substantially smaller length to diameter ratios than conventional tubular reactors are used [12].

Fig. 1 Arrangement of the experiment equipment

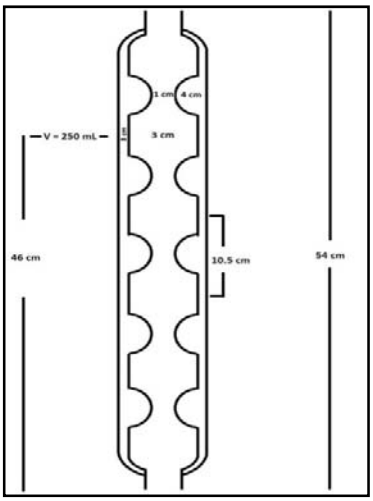


Fig. 2 Oscillatory Flow Reactor

The Reynolds number of OFR as turbulence parameter are defined as follows [13]

$$\mathrm{Re} = \frac{2\,\pi f X\,\rho D}{\mu} \quad (3)$$

where X is the center to peak amplitude of oscillation; f is oscillatory frequency (Hz); D is the tube diameter (m); ρ is fluid density (kg m-3) and μ is fluid viscosity (Pa s).

II. Materials and Method

A. Materials

Crude *Jatropha curcas* oil was bought from ATMI Solo Indonesia with an initial Free Fatty Acid content of 16.45% wt, all chemical used for the experiments (Ethanol, Sulfuric Acid 98%, and Sodium Methoxide 0.5 M) were analytical reagent grade supplied by Sigma Aldrich.

B. Experimental Method

One liter of crude *Jatropha curcas* oil was reacted in a glass vessel equipped with mechanical stirring device in a water bath heater, experiment was conducted at 60 ^{O}C, 90 min, 500 rpm speed, 50% volume of ethanol to oil and using 1,5% wt of Sulfuric acid to oil. Reaction product was poured into a separatory funnel and 2 phases were observed, the upper phase side is Sulfuric acid, water and ethanol [14], the bottom phase layer is Fatty Acid Ethyl ester (FAAE), oil, ethanol and small amount of water and Sulfuric acid. After recovery of the ethanol, purification of the oil is using 50 ^{O}C water to remove the rest of Sulfuric acid, the rest of the water was removed using vacuum distillation. The second step of biodiesel production is transesterification process, in which 200 gram esterified *Jatropha curcas* oil from from the first step was reacted with 50 mL of ethanol and catalyzed by 2 mL Sodium Methoxide. Transesterification process was conduct in Oscillatory Flow Reactor equipped with water jacket, which was operated at the condition 60 ^{O}C, 60 min, oscillation speed of 180 rpm. Two milliliter of sample was taken in 5, 10, 15, 30 and 60 minute for the purpose of analysis. Each sample was quenched into ice to prevent further reaction [15], wash 3 times using 10 mL of warm water. Water separation was performed using a centrifuge at a speed 5000 rpm, the rest of the water and ethanol was removed using vacuum distillation.

C. Analytical Method

Free Fatty Acid content was determined by a titrimetric method which allowed the measurement of the Acid Value [16]. Raw material composition of *Jatropha curcas* oil was analyzed by Shimadzu Gas Chromatography in Gadjah Mada University Indonesia. Biodiesel production was done in LIP, University of Minho Portugal, Biodiesel composition was analyzed by DANI, GC 1000 DPC in FEUP, Porto University. The gas chromatography was equipped with a 30 m capillary column, the oven temperature program started at 120 ^{O}C, Carrier gas, N_2, was kept at a constant rate of 2 mL/min. Injector and detector (flame ionization) temperature were kept at 250 ^{O}C and 255 ^{O}C . The individual fatty acid compositions were identified by comparison of their retention time with those of the authentic standards (Sigma), and were quantified by comparing their peak area with that of the standard, using a methodology adapted from the standard EN 14103, used for FAME [15].

III. Results and Discussion

A. Jatropha curcas Oil Composition

The composition of *Jatropha curcas* oil before and after esterification process is shown in Table 1. It was shown that Initial *Jatropha curcas* oil from Indonesia had the highest unsaturated fatty acid content oil compared to other sources such as Nicaragua, Cape Verde and Malaysia, thus making it more vulnerable to oxidize to an oils with a high Free Fatty Acid content. This is probably the reason why the free fatty acid found on initial *Jatropha curcas* oil from Indonesia was as high as 16.45% wt corresponding to an acid value of 32.9 mg KOH.

Further analyses of the oil composition showed a decrease of the unsaturated oil content after the esterification process, except for the Oleic Acid. The changes on the oil composition probably occurred during Sulfuric Acid addition in the esterification process. As it is a strong acid, there is the possibility of some destruction reaction as side reaction between Sulfuric Acid and Unsaturated Oil.

B. Free Fatty Acid Value

The objective of the esterification process was to decrease the FFA content on the oil, in this research the FFA was decreased from 16.45 % wt to 0.9 %, wt, therefore 94.5% FFA on initial *Jatropha Curcas* oil was converted to FAEE. The conversion of the reaction quite similar to other research that using the methanolic route [18], other research by Lu [19] found that in the operation condition 1 % wt H_2SO_4, 70 ^{O}C, 2 hours and 12 % wt of methanol 92.5% FFA was converted. Free Fatty Acid was converted into Fatty Acid Ethyl Ester

TABLE I
JATROPHA CURCAS OIL COMPOSITION

		This experiment		Foidl [3]		Emil Akbar [17]
		Before Esterification	After Esterification	Capo Verde	Nicaragua	Malaysia
Palmitic	C16:0	7.1	10.5	15.1	13.6	14.2
Palmitoleic	C16:1	8.8	4.5	0.9	0.8	0.7
Stearic	C18:0	3.4	5.2	7.1	7.4	7
Oleic	C18:1	20.1	32.2	44.7	34.3	44.7
Linoleic	C18:2	40.9	37.5	31.4	43.2	32.8
Linolenic	C18:3	19.7	10	0.9	0.2	0.2
Saturated Oil		10.5	15.7	22.2	21	21.2
Unsaturated Oil		89.5	84.3	77.8	79	78.8

(FAEE) and in the end of the esterification reaction it was found 47 % wt FAEE on the Oil. The high percentage of FAEE in the oil is reasonable when a part of the oil also converted into FAEE, thus in this case esterification and transesterification reaction occurred simultaneously in the esterification step.

C. Transesterification

Transesterification reaction was conducted in an Oscillatory Flow Reactor. The oil containing 47% FAEE was used as feedstock. The maximum conversion, 91 % wt occurred in the first 5 minutes reaction, after it stabilized in around 89%., therefore no conversion was further verified. The 47% FAEE from the previous reaction seem affect the transestrification reaction because this FAEE more soluble in ethanol and slightly displaced it, making it "less available" for use on the reaction with the oil, also ethanol itself is less reactive than methanol [20]. Fig.2 shows the conversion of the oil into biodiesel during the 60 minute of transesterification reaction.

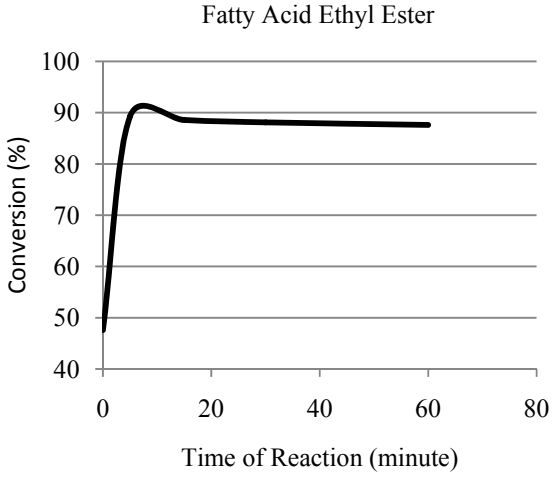


Fig. 3 Conversion of reaction in OFR

IV. CONCLUSION

Jatropha Curcas Oil with high FFA could be used as feedstock for biodiesel production. The process was performed into 2 steps, the first was the acid esterification reaction for decreasing the free fatty acid content by converted into biodiesel, and the second one was an alkaline transesterification reaction to convert the rest of the oil into biodiesel. Side reaction seemed to have occurred during the esterification reaction leading to changes in the oil composition especially the unsaturated fatty acids. Oscillatory Flow Reactor presented a good performance for the transesterification process, leading to a final product conversion of around 90% wt.

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