

# Second Generation of Biodiesel Production from Indonesian Jatropha Oil by Continuous Reactive Distillation Process

Arief Budiman<sup>a</sup>

Ratna D. Kusumaningtyas<sup>a</sup>

Sutijan<sup>a</sup>

Rochmadi<sup>a</sup>

Suryo Purwono<sup>a</sup>

<sup>a</sup>Department of Chemical Engineering, Faculty of Engineering, Gadjah Mada University, 55281 Yogyakarta, Indonesia

Email : abudiman@ugm.ac.id

The batch process of biodiesel production deals with problems related to the labor and separation cost since it is slow, entailing several separation steps, labor intensive, and not suitable for a very large-scale production. Therefore, a second generation process technology for biodiesel should be developed. In this work, a continuous transesterification using reactive distillation was proposed. The goal was to bring in a more efficient reactor system by combining chemical reactions and separation simultaneously in one unit. In this work, a laboratory-scale Reactive Distillation was applied for the biodiesel synthesis from the Indonesian refined jatropha oil in the presence of NaOH catalyst. The experimental investigation demonstrated the effects of the temperature, catalyst loading, and molar ratio of the reactants. The best result was achieved on the process conducted at the reaction temperature of 65 °C with molar ratio of methanol to triglycerides of 10:1 and catalyst loading of 0.75% w/ w oil. The reaction conversion was 94.83% and methyl ester content of the product was 99.27%. The fuel characteristic of biodiesel agreed with the Indonesian national standard and ASTM specification.

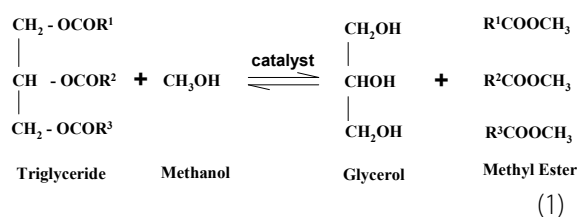
**Keywords:** biodiesel, reactive distillation, transesterification, jatropha oil

## INTRODUCTION

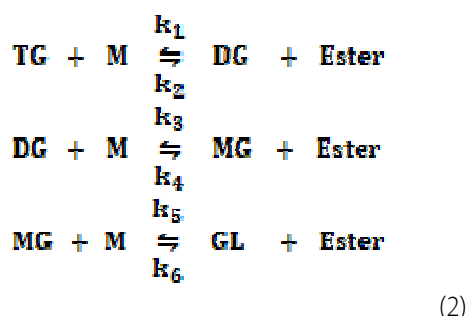
Environmental pollution and diminishing of fossil fuels reserves has raised the concern on the search for the alternative energy sources. Among the available alternative energy sources, biodiesel has drawn significant attention since it holds various advantages compared with fossil fuel in terms of renewability, non-toxicity, and biodegradability characteristic. Biodiesel also has

high cetane number and low sulfur content, hence it will prolong the machine's lifetime (Mittelbach and Remschmidt, 2008).

Biodiesel is commonly synthesized by transesterification of vegetable oils with short chain alcohols, such as methanol or ethanol, in the presence of alkaline catalyst. General equation for transesterification of triglycerides with methanol for producing biodiesel is:



Previous studies have revealed that transesterification reaction consists of a number of consecutive, reversible reactions (Sharma, *et al.*, 2008; Om Tapanes, *et al.*, 2008). While reacting with methanol, triglyceride (TG) is converted stepwise to diglyceride (DG) and subsequently monoglyceride (MG). Finally, monoglyceride forms methyl ester (biodiesel) and glycerol (GL). A mole of ester is released at each step, hence three moles of methyl ester are yielded from one mole of triglyceride. The three stages of the transesterification reaction of vegetable oil with alcohol to esters and glycerol are pointed out on the following equation:



The more indepth study on the reaction mechanism proves that the base-catalyzed transesterification was formulated as three steps. In a pre-step the basic catalyst reacts with the alcohol, producing an alkoxide anion. The first step is a nucleophilic attack of the alkoxide anion on the carbonyl group of the glyceride to form a tetrahedral intermediate (intermediate I). In the second step, the tetrahedral intermediate reacts with a second alcohol molecule (methanol) to regenerate the anion of the alcohol (methoxide), and form another intermediate (intermediate II). In the last step, rearrangement of the tetrahedral intermediate results in the formation of a fatty acid ester and glycerin. All these steps are reversible. In the pre-step the basic catalyst is mixed with the alcohol, the actual catalyst, and the alkoxide group

is formed (Berchmans and Hirata, 2008).

Transesterification reaction commonly proceeds in batch reactor with the retention time of approximately one to several hours. After being settled within several hours, the reaction products will clearly form two layers (Demirbas, 2008a). The upper layer is biodiesel (methyl ester) and the lower layer is glycerol. These two layers are then separated by using decanter to obtain high purity biodiesel. Batch reactor for biodiesel production is simple, but it is only effective for the production capacity of 500 – 10.000 tons biodiesel/ year. For the capacity over 30.000 ton biodiesel/ year, it will be more economical if the preparation conducted via a continuous process.

Among the various vegetable oil sources, non-edible oils are suitable for biodiesel production, because edible oils are already in demand and too expensive than diesel fuel. As non edible oil, jatropha oil is considered to be the wonder biodiesel feed stock because of rapid in growth, higher seed productivity, suitable for tropical regions. Reaction kinetics and separation process for biodiesel preparation in batch reactor from jatropha oil have been discussed by several authors (Sahoo and Das, 2009; Lu *et al.*, 2009; Jain and Sharma, 2010). Thermodynamic analysis has been applied to the process of biodiesel production by Talens *et al* (2007) and they used Exergy Flow Analysis as an environmental assessment tool to account wastes, emission and determined the exergetic efficiency.

Several types of continuous-flow processes for biodiesel preparation have been introduced (Leevijit *et al.*, 2000; Bisowarno *et al.*, 2004). However, most existing continuous processes still employ conventional configuration in which reaction and product separation occurs separately. This conventional configuration is not economical since it requires high capital as well as operation and energy cost. Hence, to acquire a more effective and efficient process system, development of a novel configuration of biodiesel production which enables the integration of the chemical reaction and product purification in a single equipment is

necessary. In this research, a second generation process technology using continuous reactive distillation technique was proposed to produce biodiesel from jatropha oil. RD offers benefits by integrating distillation and reaction in one unit. It reduces separation steps, lower the capital and operating cost, and shift the equilibrium towards the products (Kusumaningtyas, 2009).

This work features an experimental

investigation of biodiesel synthesis from jatropha oil using laboratory-scale reactive distillation system. Effects of main parameters, including column temperature, catalyst loading, and molar ratio of methanol to triglyceride were examined to determine the optimal operation condition resulting best reaction conversion. This finding was compared with the reaction performed via batch process.

**Table 1.** Fatty Acid Composition of Refined Jatropha Oil

Fatty acid	Formula	Systemic name	Structure	Molecular weight	wt %
Myristic	C <sub>14</sub> H <sub>28</sub> O <sub>2</sub>	Tetradecanoic	14:0	228.37	0.9137
Palmitic	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	Hexadecanoic	16:0	256.43	3.4507
Palmitoleic	C <sub>16</sub> H <sub>30</sub> O <sub>2</sub>	<i>cis</i> -9-Hexadecenoic	16:1	254.4	2.7247
Stearic	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	Octadecanoic	18:0	284.48	8.7925
Oleic	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	<i>cis</i> -9-octadecenoic	18:1	282.46	42.2836
Linoleic	C <sub>18</sub> H <sub>30</sub> O <sub>2</sub>	<i>cis</i> -9, <i>cis</i> -12-octadecadienoic	18:2	280.45	37.6266
Linolenic	C <sub>18</sub> H <sub>28</sub> O <sub>2</sub>	<i>cis</i> -6, <i>cis</i> -9, <i>cis</i> -12-octadecatrienoic	18:3	278.44	0.5672

## EXPERIMENTAL METHODS

### Material

The feedstocks of this biodiesel synthesis were the refined Indonesian jatropha oil and methanol, whereas sodium hydroxide was utilized as catalyst. Refined jatropha oil used in this research was obtained from the PT Energi Hijau Lestari, Indonesia. Chemical analysis shown the density at room temperature (ASTM D 1298), and kinematic viscosity (ASTM D 445 Method) of this refined palm oil were 907 kg/ m<sup>3</sup>, and 40.7925 mm<sup>2</sup>/s, respectively. Fatty acid composition of this oil was determined by Gas Chromatography as shown in Table 1. An HP 5890 gas chromatograph (series II) with a flame ionization detector was used under the following experimental conditions: a HT-5 fused silica capillary GC columns (6 meters), helium as the carrier gas, an injection temperature of 370 °C, a column temperature of 120 - 370 °C (20 °C/min), and a detector temperature of 370 °C. Based on the

fatty acid profile, the average molecular weights of the oil was calculated and it was found as 838.7919 g/ gmol. This value was used in data processing and process evaluating parameter calculation.

Methanol (technical grade, 99% purity) was obtained from PT Kaltim Methanol Indonesia (Bontang, Indonesia) and NaOH (99% purity, certified) was from Merck (Darmstadt, Germany). Other analytical reagents and standard chemicals were all analytical grade and purchased from Merck (Germany).

### Experimental Procedure

A laboratory-scale continuous reactive distillation (RD) system applied in this research is illustrated in Figure 1. The main apparatus was a single 120 cm length glass-column with outer diameter of 5.1 cm. This column was filled up by glass raschig ring packing with diameter of 0.5 cm and 1 cm in length. This RD column was equipped with condensor, reflux control, reboiler, feed tanks

of palm oil and methanol-NaOH, heater, peristaltic pump, and thermometer. Jatropha oil, methanol, and NaOH catalyst had to undergo pretreatment step prior to the biodiesel synthesis process. Jatropha oil was primarily preheated at moderate temperature for an hour before each experiment in order to remove water and other impurities. Methanol and NaOH solution were then prepared in a certain composition with the intention that the corresponding amount of catalyst would provide the desired methanol-to-triglyceride molar ratio once mixed with the oil. In this work, the influence of catalyst loading was investigated at 0.25, 0.5, 0.75, 0.875, and 1%.

After the preparation, both the reactants were poured into the feed tanks of the reactive distillation reactor system. Column and reboiler were heated by electrical heating coil and mantel, respectively, and maintained at the desired temperature. Column temperature was varied from 45 to 75 °C and considered as the reaction temperature. The methanol/ catalyst premix and jatropha oil were fed into the mixer and subsequently entering the RD column. Flow rates of the feed were set-up based on the desired molar ratio of triglyceride and methanol (4:1, 6:1, 8:1, and 10:1). Each segment of the reaction zone in the RD column functioned as a reactor. Hence, both methanol and triglyceride gradually flowed to the bottom and reacted in the liquid phase to produce ester and glycerol, with the residence time of 6.34 minutes. A reboiler (500 ml three-neck flask with 200-300 ml) was fitted to the bottom of the column to drive methanol off the product mixture before discharging to the decanter. On the other hand, unreacted methanol vapor that rose to the top part of the column were condensed by a water-cooled condenser and refluxing back to the column directly from the top. The product mixture was withdrawn from the reboiler to the decanter, where glycerol and ester were separated by gravity (Kusumaningtyas, 2009). Each experiment was carried out continuously for a period of 1-5 hours. During the continuous operation, samples were periodically taken at the reboiler. Samples were

collected only after steady state operation had been reached.

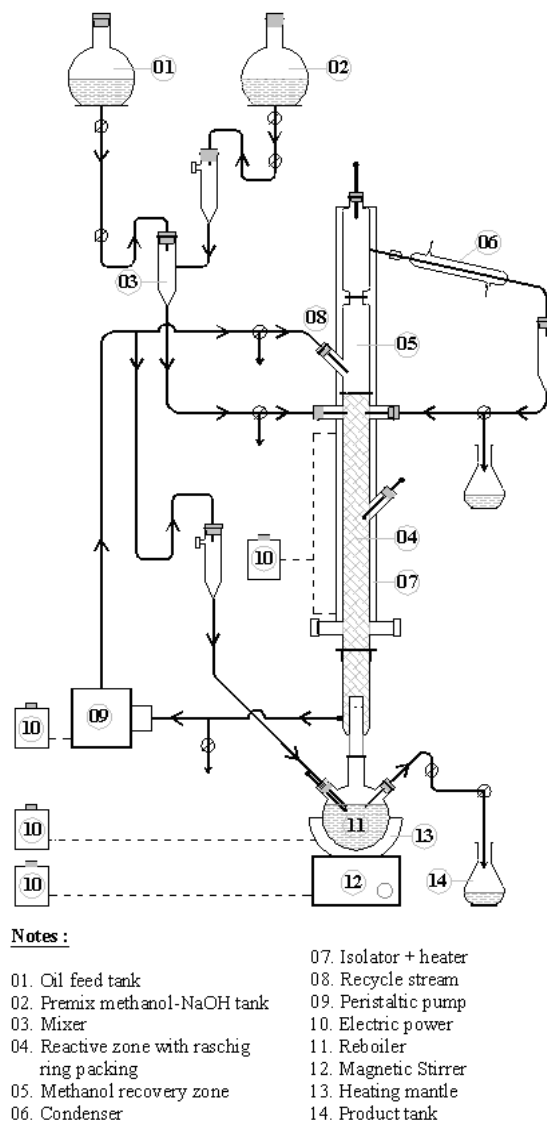
### Chemical Analysis

The completeness of the reaction (reaction conversion) was measured by the wet-chemical American Oil Chemists' Society (AOCS) method for determining glycerol, *i. e.* AOCS official method Ca 14-56 entitled "Total, Free, and Combined Glycerol Iodometric-Periodic Acid Method" (Van Gerpen, *et al.*, 2004; Canakci and Van Gerpen, 1999). This difference was stated as a percentage of the original total glycerin amount. Biodiesel yielded on the optimum condition was also analyzed using Gas Chromatography (HP 5890 gas chromatograph series II) and GC-MS (Shimadzu QP2010S with Rtx-5MS column) for the superior information obtained, including chemicals composition and methyl ester content. This product was furthermore tested to determine its fuel properties, including the values of specific gravity at 60/ 60 °F, kinematic viscosity at 40 °C, flash point PMCC, Pour point, copper strip corrosion (3 hours/ 50°C), water content, Conradson Carbon Residue in original sample, and 90% distillation temperature. The properties of this fuel was then compared with the standard of ASTM D 6751 and Indonesian National Standar (SNI 04-7182-2006) on biodiesel product.

### RESULTS AND DISCUSSION

Biodiesel is traditionally produced by batch process using well-mixed stirred tank and a series of separation equipments. Though simple, batch process is slow, labor intensive, and costly for a very-large scale process (Kiss, *et al.*, 2006; Singh, *et al.*, 2004). In view of that, biodiesel manufacturing at large scale asks for the development of the more ground-breaking and efficient processes, particularly the continuous process which able to reduce post reaction cleaning and total processing time. An innovative transesterification of Indonesian jatropha oil based on the continuous reactive distillation process is among the promising alternative to batch transesterification for some reasons.

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**Figure 1.** scheme of Reactive Distillation Column for Biodiesel Synthesis

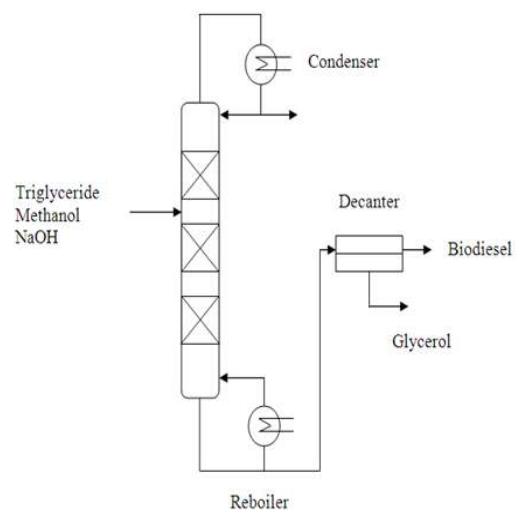
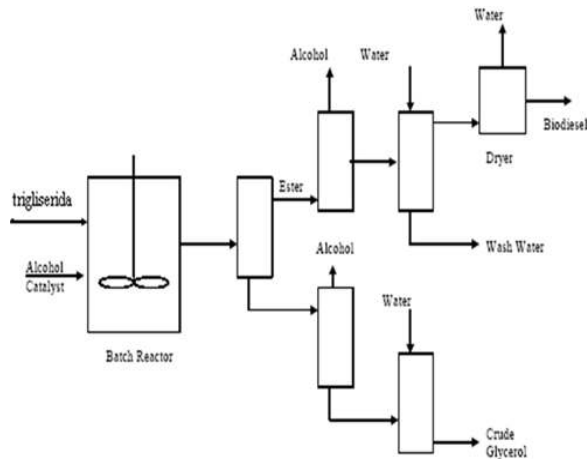
Reactive Distillation (RD) combines a simultaneous function of reaction and product purification in a single equipment (Budiman, 1999; Budiman *et al.*, 2006). Beheld from the technology perspective RD provides great advantage in terms of reaction equilibrium. Combining reaction and separation into a single unit can shift the reaction equilibrium towards the desired products by continuous removal of the products (Kiss *et al.*, 2006). Lee and Westerberg (2000) suggest that RD is also considered efficient since the heat of reaction can reduce the heat load of a condenser or reboiler. For the exothermic

reaction, the heat released in the reaction process can be utilized for fulfilling the energy demand on the separation zone. The other benefit, this configuration will results in the lower capital cost due to the reduced number of reactor, piping, and instrumentation. Hence, reactive distillation is an attractive alternative to the classical batch reactor for biodiesel production. The comparison of the batch and RD configuration is presented in Figure 2.

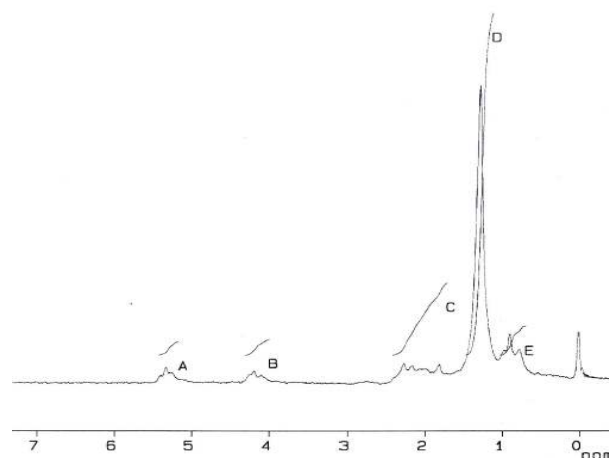
This work examined the possibility of RD application on the biodiesel production from jatropha oil through an experimental investigation at the laboratory-scale. In this proposed

configuration, the function of the reactor on the conventional configuration was shifted within the middle part of the column, which was then called as reactive zone. On the contrary, the top and the bottom part of the column were named separation zone. Enriching and stripping section were located above and below the reactive section. The Rd column was equipped with condenser on top part of the column, which worked for condensing methanol and returning it to the column as recovery. This reflux of the methanol resulted in the high ratio of methanol to oil in the column that helped to displace the reaction to the right (Kusumaningtyas *et al.*, 2009; Sutijan, *et al.*, 2008).

The start-up material selected for this process was non-edible refined *jatropha* oil. This *jatropha* oil had the free fatty acid (FFA) content of 0.67% (AOCS Official Method Ca 14-56), which was less than the 1% limit for satisfactory transesterification reaction using alkaline catalyst (Berchmans and Hirata, 2008). Hence, it was suitable feedstock for a base-catalyzed process and could be directly applied for the transesterification reaction. Due to its low FFA content, the oil pretreatment or either the FFA removal or the conversion of the FFA to esters before beginning the base catalyzed reaction was not crucial (Van Gerpen, *et al.*, 2004). The FFA profile of the *jatropha*



**2.a** **2.b**  
**Figure 2.** Comparison of: a. Batch Process and b. Reactive Distillation



**Figure 3.** Spectrum of H-NMR of Refined *Jatropha* Oil

oil feedstock is also presented by the H-NMR 60 MHz spectrum in Figure 3. It shows the low content of FFA, as identified by the peak at the 2.3 ppm representing the triplet peak of  $\alpha$ -CH<sub>2</sub> group.

The RD process in this work was performed in a packed column filled up by glass raschig ring type packing with diameter of 0.5 cm and 1 cm in length. Porosity of the packing was determined by an experimental investigation. It was exhibited that the total volume of the column (74 cm long with an ID of 5.1 cm) was 1450.4840 cm<sup>3</sup> and the total void volume of the column was 746.6667 cm<sup>3</sup>. Porosity of the packing was therefore 51.47%. A computer simulation using ASPEN Plus Version 11.1 was also carried out to examine the vapor/ liquid phase ratio of the stages in the column. It was revealed that the average vapor/ liquid phase ratio along the column is 0.3800 (volumetric base) or 0.7693 (molar base) or 0.3971 (mass base). A reflux total setup was operated in this reactive distillation. The residence time of the reaction was derived via a specific experiment and it was found to be 6.34 minutes. This residence time is considered adequate compared with the work conducted by Singh *et al.* (2004), which applied the residence time of about 5 minutes in reactive distillation column. Besides, one among the advantages of the RD application is to greatly increase the biodiesel production per unit reactor volume per time at much-shortened reaction time (Lee and Westerberg, 2000).

The RD ation system was continuously operated for 3 – 5 hours and it required about one hour reaching steady state before any sampling or observations could be taken. The reactor performance was assessed based on the conversion of triglycerides to methyl esters obtained. Among the key reactor variables that dictated conversion and selectivity are temperature, catalyst loading, and the molar ratio of methanol to triglyceride. Effect of the reaction temperature was studied at 45, 55, 65, and 75 °C, effects of the catalyst amount was investigated in range of 0.25, 0.5, 0.75, 0.875, and 1 weight % of oil, and the influence of molar

ratio of methanol to oil was examined at 4:1, 6:1, 8:1, and 10:1. For all the experiments run, the overall flow rate of the column was 4.1 ml/ min and the average residence time in the reactive distillation column was 6.34 minutes. The best condition was determined based on conversion of oil to ester attained in each experiment. Biodiesel produced at the optimum condition was further analyzed using GC and GC-MS to identify its methyl ester content and chemical composition, and went through several ASTM tests to determine its fuel characteristic. Additionally, the highest conversion accomplished by the RD process at the optimum condition was then compared with the conversion achieved through batch process, which was conducted in this work according to the optimum condition advocated by Meher *et al.* (2006) and Van Gerpen, *et al.* (2004).

## The Influence of the Reaction

### Temperature

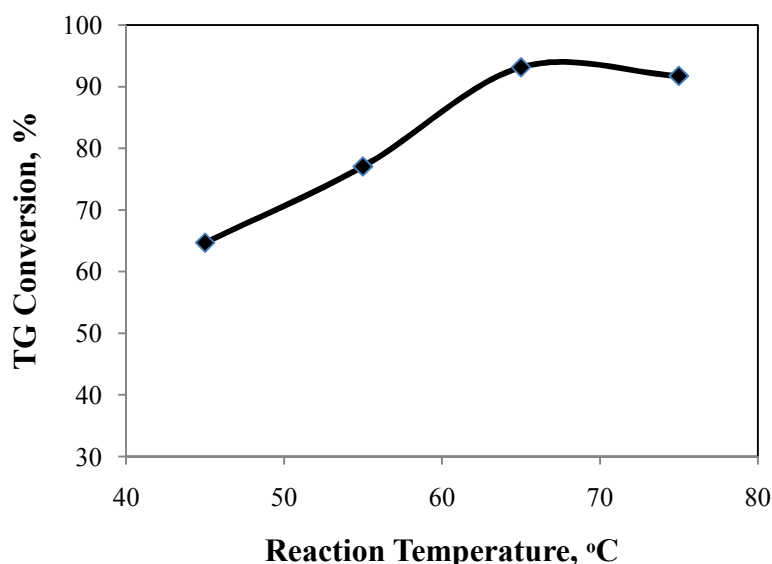
Figure 4 shows the influence of reaction temperature on jatropha oil conversion to methyl ester at a catalyst amount of 0.75% w/ w oil and molar ratio of methanol to oil of 8:1. Column temperature, which was considered identical with the reaction temperature, was employed in the range of 45 - 75 °C. It was demonstrated that the reaction conversion increased with increasing reaction temperature up to 65 °C with the conversion of 93.12%. It is not unpredictable since the use of higher reaction temperatures can improve both kinetic and mass transfer stages (Darnoko and Cheryan, 2000). As those usually occur in any reactions, the increase in temperature will enhance reaction rate exponentially. An increase in reaction temperature will also let the reactants to be more miscible. It is remarked that the solubility of alcohols increases in the triglyceride phase as the temperature increased, making possible the reaction to take place and leading to the higher reaction rate (Behzadi and Farid, 2009).

However, in this work, it was observed that the reaction conversion then decreased with the

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further increase of temperature above 65 °C. It was given that the reaction took place in a liquid/liquid phase, and therefore the reaction temperature would be limited to methanol boiling point of around 65 °C at atmospheric operating pressure. The decrease on the conversion at the higher reaction temperature might be caused by the

vaporization of methanol into, leaving the liquid phase. The reduced of methanol concentration in liquid phase accordingly lowered the reaction rate. Thus, the most favorable reaction temperature was considered to be around 65 °C for the atmospheric column operating pressure.



**Figure 4.** Effect of Reaction Temperature on the Triglycerides (TG) Conversion

### The Influence of Catalyst Loading

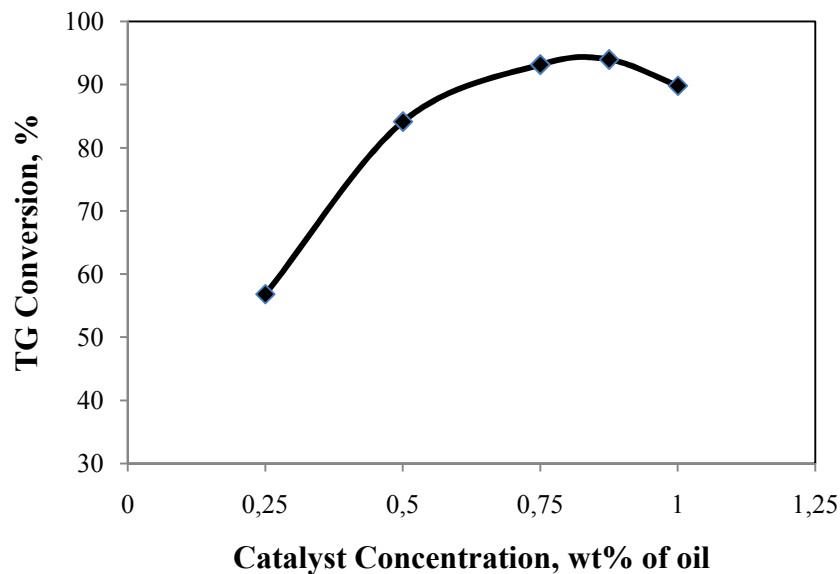
A catalyst is generally used to enhance the reaction rate and yield. It gives a lower activation energy, thus, more products will be formed in the same amount of time. For the equilibrium-limited reaction as transesterification, the optimized condition is generally determined by its reaction rate rather than by its equilibrium conversion. In view of that, catalyst plays an important role in transesterification reaction, which runs very slowly in the absence of catalyst.

The common types of transesterification catalyst are alkaline, acid, enzyme, and solid/heterogeneous catalysts (Meher, 2006). Among these classes, base-catalyzed transesterification is found to be the best alternative to produce biodiesel (Om Tapanes, 2008). In fact, for the application of the alkaline catalysts, the starting material should have low FFA concentration (less

than 1% w/w) and all material should be substantially anhydrous. Regardless of these drawbacks, alkaline catalyst, such as sodium methoxide, potassium hydroxide, potassium methoxide, is effective, much faster than the acid one, and most often used commercially for transesterification. Comparing the two popular alkaline-catalysts, NaOH is significantly better in the performance than NaOMe since it is cheaper, easily dissolved in methanol, and can readily react with triglycerides (Meher *et al.*, 2006; Ma and Hanna, 1999). For this reason, NaOH is selected as the catalyst in this investigation.

Figure 5 shows the effect of catalyst loading on the triglyceride (TG) conversion. The catalyst concentration employed were 0.25, 0.5, 0.75, 0.875, and 1 wt% of oil, whereas the reaction temperature, molar ratio of methanol to oil, and residence time were kept at 65 °C, 8: 1, and 6.34 minutes, respectively.





**Figure 5.** Effect of Catalyst Loading on the Triglycerides (TG) Conversion

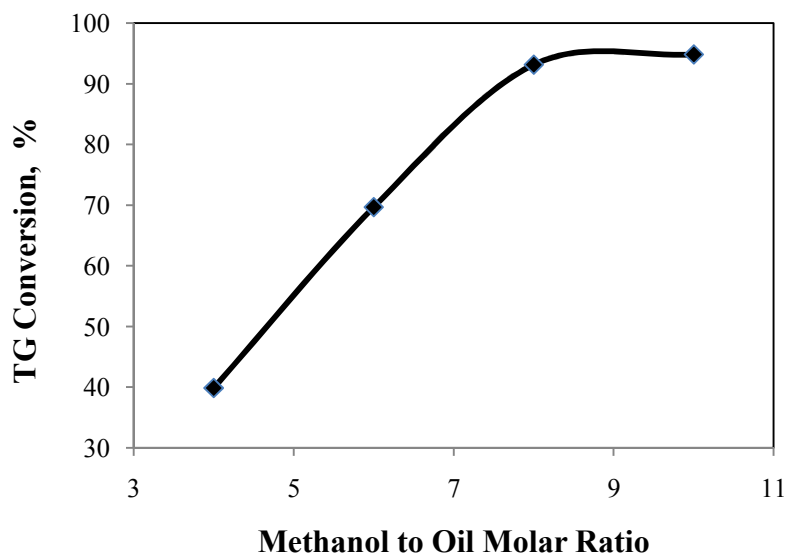
It was exhibited that oil conversion to biodiesel was increased firstly with an increase of catalyst from 0.25 to 0.75 wt%. With a further increase of the catalyst loading, the conversion leveled off. In addition, when the catalyst concentration was over 0.875, the conversion was seemed to reduce. It might be attributed to the formation of sodium soaps. The similar phenomenon was also described by Behzadi and Farid (2009). It was reported that with sodium hydroxide as a catalyst, high yield losses are subjected to the undesired saponification reaction and methyl ester dissolution in the glycerol phase. On the other words, the resulting soap causes an increase in formation of gels that inhibits the desired reaction and the glycerol separation. This sodium soaps formation came across to increase with catalyst concentration. Based on this finding, subsequent experiments were then conducted using 0.75 wt% of NaOH/ wt of oil.

### The Influence of Molar Ratio of the Reactants

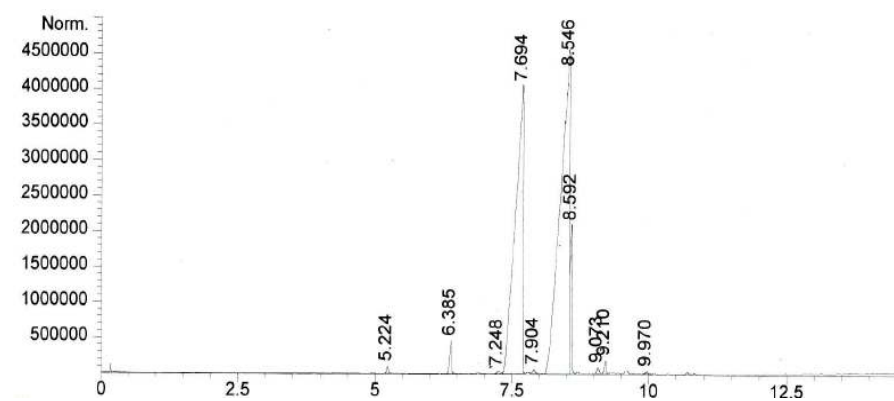
Molar ratio of alcohol to triglyceride is one of the most important variables affecting the yield of ester. Stoichiometrically, transesterification of vegetable oil only requires three moles of alcohol and one mole of triglyceride to yield biodiesel.

However, in practice, the molar ratio of methanol to oil is supposed to be higher than the stoichiometric requirement in order to drive the reaction towards methyl esters formation. The molar ratio is also associated with the type of catalyst used. Ma and Hanna (1999) report that An acid catalyzed reaction for biodiesel production needs a 30:1 ratio of alcohols to oil, on the other hand, Meher *et al.* (2006) suggest that the optimum molar ratios of methanol/oil to give the best conversion of oil to methyl ester are between 9:1 and 12:1.

Figure 6 denoted the influence of methanol to oil molar ratio on the conversion of the reactions conducted at 0.75 wt%/ wt oil catalyst amount and temperature of 65 °C via the RD process. The reaction conversion increased noticeably with increasing the molar ratio from 4 to 10. The conversion of 94.83% could be achieved with the residence time of 6.34 minutes. However, a further increase of the molar ratio is not recommended since it could possibly diminish the reaction conversion. In fact, too high reactants molar ratio can hinder the separation of glycerol from biodiesel products. It is because methanol is completely soluble in both methyl ester and glycerol, but insoluble in oil.



**Figure 6.** Effect of Methanol to Oil Molar Ratio on the Triglycerides (TG) Conversion



**Figure 7.** GC Chromatogram of Jatropha Oil Biodiesel via Reactive Distillation Process

Conversely, glycerol has a low solubility in both oil and methyl esters (Zhou *et al.*, 2006). Thus, too high molar ratio of alcohol to vegetable oil will increase the solubility of glycerol in ester phase (Behzadi and Farid, 2009). When a large amount of glycerol exists in product solution, it facilitates to drive the equilibrium to reverse to the left, leading to the decreased biodiesel yield (Meher *et al.*, 2006). Hence, in this work, the ratio molar of 10:1 was considered to be the optimum one, that offered a nearly complete reaction conversion and let the easy separation of glycerol from the final product of biodiesel.

The experimental results have shown the effects of temperature, catalyst loading, and

reactants molar ratio on the laboratory-scale RD performance. It was confirmed that the best RD performance was reached at the following operating condition: reaction temperature of 65 °C, catalyst loading of 0.75% wt/ wt oil, and molar ratio methanol to oil of 10:1, giving the oil conversion to jatropha biodiesel of 94.83%. This high yield of methyl ester has proved that RD is prospective for the commercial application. However, it is often asserted that methyl ester product is not biodiesel until it meets the ASTM D6751 standard. To verify this biodiesel product as legal fuel for sale and distribution, a set of advanced tests should be run to ascertain the biodiesel's purity, chemical composition, and physical properties.

### Quality of Produced-Jatropha Biodiesel

Following the above-mentioned optimized process, reactant conversion of 94.83% was obtained from jatropha oil by the RD reactor. The product mixture was then gravitationally separated to obtain biodiesel and glycerol. Subsequently, biodiesel produced was washed with hot distilled water, with the temperature of 80 °C, to remove the excess methanol, the leftover catalyst, traces of glycerol, and possible soap. The washed ester layer was dried at 110 °C to eliminate the moisture and methanol. This product was further analyzed using Gas Chromatography and GC-MS to find its ester content and chemical composition. The fuel characteristic of this jatropha oil biodiesel was also examined and compared with the ASTM D6751 as well as the Indonesian National Standard specification (04-7182-2006).

GCMS-QP2010S Shimadzu instrument equipped with the 30 length Rtx-5MS column with internal diameter of 0.25 mm was utilized for the initial determination of fatty ester composition. This instrument used helium as carrier gas and was operated under these conditions: pressure of 16.5 kPa, column oven temperature of 80 °C, injection temperature of 300 °C, total flow of 80 mL/min, column flow of 0.5 ml/ min, linear velocity of 26.1 cm/sec, purge flow of 3 ml/ min, and split ratio of 152.9. Oven temperature program was 80-120 °C with the rate of 5 °C/ min, held for 5 minutes. Furthermore, methyl ester content of jatropha oil biodiesel was found out using An HP 5890 gas chromatograph (series II) with a flame ionization detector. This instrument was used under the following experimental conditions: a HT-5 fused silica capillary GC columns (6 meters), helium as the carrier gas, an injection temperature of 370 °C, a column temperature of 120 – 370 °C (20 °C/min), and a detector temperature of 370 °C. Analysis on the standard pure compounds of methanol, glycerol, biodiesel, and jatropha oil has revealed that those compounds gave retention time of 0.0162, 6.488, 7-10, and 14-18.8 minutes, respectively.

Chromatogram of jatropha oil biodiesel

presented in Figure 7. It is shown that high alkyl ester content of 99.27% has been acquired, meaning that almost all triglyceride has been converted into methyl ester (biodiesel). According to the Indonesian national standard and European biodiesel quality standard EN 14214, the minimum purity is 96.5 wt%. Hence, this biodiesel product has fulfilled those limits (Moser and Vaughn, 2010). The fatty acid methyl esters composition of this jatropha biodiesel in details is given in Table 2. Furthermore, fuel characteristic of this jatropha oil biodiesel, compared with the ASTM D 6751 and Indonesian National Standar No. 04-7182-2006 specification, are summarized in Table 3. It is exemplified that it meets the specification of American society of Testing Material and Indonesian standard in terms of specific gravity, kinematic viscosity, flash point PMCC, pour point, copperstrip corrosion, water content, carbon residue (100%), 90% distillation temperature, and methyl ester purity were. This jatropha oil biodiesel from RD process is therefore potential for market and commercialization.

### Comparison between RD Reactor and A Well-Mixed Batch Reactor

The highest conversion of jatropha oil transesterification performed using laboratory-scale RD was 94.83% at 65 °C with catalyst loading of 0.75 wt% of oil and 10:1 molar ratio of methanol to oil. The above mentioned result was compared with the conversion attained by transesterification process carried out by a well-mixed batch reactor. The batch jatropha oil transesterification was carried out in this study according to the formula suggested by Meher *et al.* (2006) and Ma and Hanna (1999). It was recommended that, for the maximum conversion, the batch transesterification process in the present of homogeneous alkaline catalyst should be conducted under the condition of methanol-oil ratio 6:1, 0.5 – 1 wt% NaOH catalyst and 65 °C. Thus, in this work, the batch process was carried out at 65 °C (the temperature of about the boiling point of methanol) using methanol-oil molar ratio of 6:1 and NaOH catalyst in the range of 0.5-1 wt%. However, for the NaOH catalyst usage of

**Table 2.** Fatty Ester Composition of Jatropha Biodiesel via Reactive Distillation Process

No	Fatty Acid Methyl Ester	Structure	Wt%
1	Methyl myristate	14:0	0.188
2	Methyl palmitate	16:0	1.0635
3	Methyl palmitoleate	16:1	0.1519
4	Methyl Stearate	18:0	3.7912
5	Methyl oleate	18:1	39.447
6	Methyl linoleate	18:2	54.255
7	Methyl linolenate	18:3	0.3687
	Total		99.2653

**Table 3.** Physical Properties of Jatropha Oil Methyl Ester via Reactive Distillation Process

Property	Unit	Jatropha Oil Methyl Ester via RD Process	Limits		Test Method
			Indonesian National Standar 04-7182-2006	ASTM D 6751	
Specific gravity at 60/ 60 °F		0.8791	0.850 - 890	NA	ASTM D 1298
Kinematic viscosity at 40 °C	mm <sup>2</sup> /s	4.6980	2.3-6.0	1.9 - 6.0	ASTM D 445
Flash point	°C	180.5	Min. 100	Min 130	ASTM D 93
Pour point	°C	9	NA	NA	ASTM D 97
Copperstrip corrosion (3 hr/ 50 °C)		1a	Max. No 3	Max. No 3	ASTM D 130
Conradson Carbon Residue, in original sample	% wt	0.03	Max. 0.05	Max. 0.05	ASTM D 4530
Water content	% vol	trace	Max. 0.05	Max. 0.05	ASTM D 95
Vacuum distillation end point	°C	337.5 °C, at T-90	360 °C max, at T-90	360 °C max, at T-90	ASTM D 86
Alkyl Esters content	Mass %	98.85%	96.5% min	NA	

greater than 0.5%, the soap formation seemed to be dominant. Thus, the performance evaluation only conducted towards the batch reactor run in the presence of 0.5 wt% NaOH catalyst. It was revealed that after the reaction proceeded for 10 minutes and 1 hours, the reaction conversion of the batch process reached 39.28% and 70.99%, respectively, which was lower than that obtained by the process run by RD reactor at the optimum

condition (temperature 65 °C, catalyst loading of 0.75 wt% , reactant molar ratio of methanol to oil of 10:1, and residence time of 6.34 minutes. Indeed, the batch process (65 °C, 6:1 reactants molar ratio, 0.5–1 wt% NaOH catalyst, and residence time of 10 minutes) resulted in the lower conversion compared with the conversion of the RD process run at the lower residence time and molar ratio of methanol to oil (65 °C, 4:1 reactants molar ratio,

0.75wt% NaOH catalyst, and residence time of 6.34 minutes), which was 39.26 as compared to 39.88% using RD process. Therefore, based on the reaction conversion achieved, this experimental investigation verified that the performance of the continuous RD system proposed in this work was superior to the conventional batch process for the biodiesel preparation from palm oil.

## CONCLUSIONS

Second generation biodiesel production process by using continuous-flow RD system has been intensively studied. It was revealed that this reactor was superior to the batch one. The laboratory-scale RD for biodiesel provided the best conversion of 94.83% at the residence time of only 6.34 minutes at the mild reaction condition: 65 °C column temperature, 0.75% w NaOH catalyst/ w oil, 10:1 metanol:jatropha oil molar ratio, and retention time of. Methyl ester content of the product was 99.27%, which was higher than the Europe quality standard EN 14214 (96.5%). Test on the fuel characteristic of biodiesel product showed that it satisfied the standard of ASTM D 6751 and Indonesian National Standar on biodiesel in terms of the values of specific gravity, kinematic viscosity, flash point PMCC, pour point, copperstrip corrosion, water content, carbon residue (100%), and 90% distillation temperature. For the comparison, the reaction performed via batch process at the operating condition of 65 °C, 0.5% w NaOH/ w oil, and 1:6 metanol:palm oil molar ratio resulted in a reaction conversion of 70.99% and 39.28% in 1 hours and 10 minutes reaction time, respectively. It has proved that the RD reactor posses an enhanced performance on the biodiesel production than batch reactor, and thus it is viable for the future commercial application.

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