Synthesis of bio-lubricant from *Jatropha curcas* oils

M.I.M. Zamratul, M.T.S. Syaima, I.M. Noor, Rifdi, W.M.W.T

***Abstract*—** *Jatropha curcas* oil is one of the most versatile plant oils. With the rising environmental concerns, the need for bio-based lubricant is an alternative to replace fossil-based lubricant. In this paper, bio-lubricant was synthesized from Jatropha curcas oil through hydrolysis reaction using lipase enzyme (Polipazyme$^{TM)}$ followed by non- catalytic esterification reaction. In hydrolysis reaction, the effect of oil to buffer ratio was studied. While the influence of fatty acids to alcohol (2-propanol) during esterification was investigated. Results show that the optimum rate of hydrolysis was achieved with 16% V/V ratio of Jatropha to buffer at temperature of 40°C, agitation speed of 650 rpm and pH of 7. Likewise, the same value (16% V/V) of fatty acids to 2-propanol is needed for complete conversion of fatty acids to propyl esters. The optimal conditions for esterification process occurred at 75°C and 950 rpm of agitation.

Keywords— Bio-lubricant, *Jatropha curcas*, Polipazyme^{TM}, enzymatic hydrolysis, esterification

I. INTRODUCTION

LUBRICANTS basestocks may be of petroleum, vegetable or synthetic nature .The most usual type of lubricant is petroleum based (Jain and Suhane, 2012). Lubricants manufactured conventionally from non-renewable mineral oil resources are not biodegradable and are liable to cause adverse environmental impacts. *Jatropha curcas*, a non-edible oil present a promising biolubricant feedstock alternative (Avisha, et al., 2012). A method was developed by using the two-step process of lipase-mediated hydrolysis of JO followed by esterification of FFA with2-propanol .Two essential processes namely hydrolysis and esterification are required to synthesize bio-lubricants from JO. Enzyme or chemicals are used in hydrolysis reaction, while lower chain alcohols such as ethanol, methanol and propanol are used in esterification reaction.

From the literature, there are few studies about the applications of a biocatalyst or a chemical catalyst for hydrolysis process (Whittal and Sutton, 2012; Bowman et al, 2010; Jin et al., 2008, Zhou et al., 2008). In addition, it has been proven that the application of an enzyme, for instance lipase, in hydrolysis reaction followed by esterification can yield maximum production of bio-lubricant (Al-Zuhair et al., 2003; Avisha et al., 2012).

Furthermore, enzymatic reaction could be performed at mild pH and ambient temperature (Salimon, 2011). Therefore, in this work, lipase is selected as a biocatalyst to catalyze the hydrolysis of Jatropha oil. Since lipase functions at the water-oil interface, the interfacial area between oil and the aqueous phase is one of the factors that affects the rate of hydrolysis (Noor et al., 2003). Therefore, the ratio of Jatropha oil to buffer solution is one of the significant parameters that has to be optimized to obtain an optimum hydrolysis rate. In the literature, different ratios of oil to buffer solution are reported to achieve an optimum hydrolysis reaction (Wang, 2010;Rathod and Pandit, 2009; Goswami et al., 2009).

Hydrolysis reaction will be followed by esterification reaction to convert the FA to fatty acid methyl esters (FAME), which is a bio-lubricant. In this step, the ratio of fatty acid to alcohol plays an important role in optimum production of FAME. The amount of alcohols to be added is a crucial. parameter since a very high alcohol concentration may inhibit enzymatic (Gogoi and Dutta, 2009; Dörmő et al., 2004) esterification. Therefore, alcohols must be added in stepwise manner in order to avoid the presence of excessive alcohols (Deng, et al., 2003). Many studies on the esterification of vegetable oils at various fractions of fatty acids to alcohols has been conducted (Avisha et al., 2012; Bokade, 2009).

In this work, the effect of JO to buffer solution ratio in the hydrolysis process as well as the effect of FA to alcohols ratio in the esterification process were examined

II. EXPERIMENTS

A. Materials

Jatropha curcas oil (JO) used in this study was obtained from Trades Wings Resources, Malaysia. Lipase enzyme (Polipazyme^{TM}) was produced at Department of Chemical Engineering, University of Malaya. All the fine chemicals used in the experiment (oleic acid, phenolphthalein, acetate acid, sodium hydroxide, diethyl ether, 2-propanol, glycerin), calibration buffer solutions (pH 4, pH7 and pH 10) were obtained from Fisher Scientific (M) Sdn. Bhd.

B. Bio-lubricant production

The development process of bio-lubricant was carried out using bioprocess method (Polipazyme^{TM}). The reaction took place in a beaker, which was immersed in a temperature controlled water bath and were maintained at a desired stirring

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speed using a motor-driven laboratory impeller stirrer. After the solution reached 40°C, lipase diluted in buffer was added to start the reaction. Samples were withdrawn at every 5 minutes time intervals to determine the initial maximum rate of hydrolysis. The experiments were repeated using different JO to buffer (aqueous solution) ratio.

C. Titration

The initial maximum rate of hydrolysis and esterification were determined by titration with 0.1N sodium hydroxide (NaOH). The samples from both processes (hydrolysis and esterification) were homogenized with buffer and diethyl ether. They were then titrated with 0.1N sodium hydroxide using Metrohm 719 S Titrino auto-titration system. The amounts of NaOH required to neutralize the samples were recorded. Distilled water was used as blank (Noor, et al., 2003). The initial rate of hydrolysis was calculated using (1)

$$\mathbf{r_0} = \frac{(m - m0)}{t} \quad (1)$$

Where, r0 is the initial rate of hydrolysis (g/ s.l.), m is the weight of acid per volume of sample (g/l), m0 is the weight of acid per volume of the control sample (g/l), and t is the time when the sample was withdrawn (s). For esterification, the same equations were used. However, the initial rate of esterification is in the unit of mol/s.l.

D. Enzymatic hydrolysis

The hydrolysis reactions were carried out in a beaker, which was immersed in a temperature controlled water bath and were maintained at a desired stirring speed using a motor-driven laboratory impeller stirrer. The ratio of Jatropha oil (JO) to buffer solution used was from 5%V/V. Initially, JO was dispersed in of buffer solution in a beaker. The beaker was immersed in a water bath and stirred at 650 rpm. After the solution reached 40°C, lipase diluted in buffer was added to start the reaction. Samples was withdrawn at every 5 minutes time intervals to determine the initial maximum rate of hydrolysis. The experiments were repeated using different JO to buffer (aqueous solution) ratio. The obtained FA was then undergoing further esterification reaction.

E. Non-catalytic esterification

The alcohol used in esterification process was 2-propanol. The esterification experiment was performed at ratios of FA to alcohol (5%V/V). Reactions were carried out at 75°C, and agitation speed of 950 rpm.. Firstly, 5% V of fatty acid (FA) was dispersed in 2- propanol solution in a beaker. The beaker was immersed in a 75°C water bath and stirred at 950 rpm. Samples were withdrawn at regular time with the interval of 5 minutes to determine the initial rate of esterification. The experiments were repeated at different ratios of fatty acid to 2-propanol.

III. RESULTS AND DISCUSSION

Fig. 1 shows the initial rate of hydrolysis for all samples at different ratios of JO: buffer. According to Fig. 1, the initial maximum hydrolysis rate started to increase from the beginning to a maximum point at 16% V/V JO: buffer. After this point, the rate of hydrolysis started to decrease gradually. The reason for this observation is that the interfaces between the oil and water will be saturated by the oil phase with the continuous increment of the Jatropha oil substrate, and subsequently the active sites of lipase will be limited (Dörmő, et al., 2004; Noor, et al., 2003; Murty, 2002). Therefore, JO: buffer ratio of 16% V/V is considered to be the optimum ratio for the hydrolysis reaction. This result (16% V/V JO: buffer) was quite similar to the determined value (20% V/V JO: buffer) which had been reported by the previous research works in the literature (Goswami, et al., 2009; Rathod & Pandit, 2009; Wang, 2010).

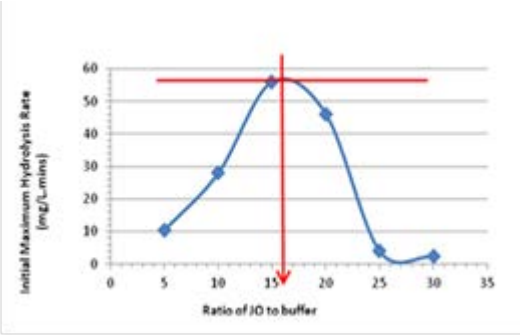

Fig. 1 Initial maximum hydrolysis rate versus ratio of JO: buffer

According to Fig. 2, the optimum ratio of FA: 2-propanol is 16 V/V%, at agitation speed of 950 rpm and 75°C. As expected, at FA: 2-propanol ratios above the optimum value the reaction started to level off. The reason for this observation is that when the concentration of propanol has exceeded a desired amount, it may slow down and subsequently completely inhibits the reaction (Deng, et al., 2003). Based on Fig. 2, it is concluded that the ratio of 16% V/V FA: 2-propanol is sufficient to obtain the maximum initial rate of esterification.

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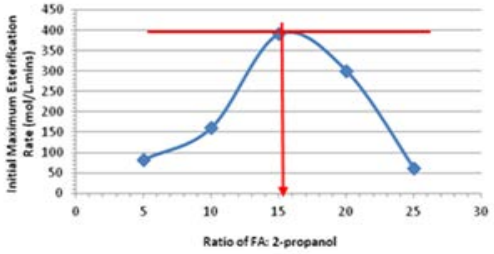

Fig. 2 Initial maximum esterification rate versus ratio of fatty acid to 2-propanol

IV. CONCLUSION

Increasing attention to environmental issues has driven the lubricant industry toward ecofriendly products from renewable sources, which is non-edible *Jatropha curcas*. In this work, biolubricant was successfully synthesized using fatty acid of Jatropha curcas oil in the presence of Polipazyme™ as

catalyst. The results obtain suggest that at the following temperature: 75 °C, agitation speed: 950 rpm and ratio of JO: buffer : 16% V/V are sufficient for the hydrolysis of JO as biolubricant base. Esterified jatropha oil also has been successfully produced at the following temperature: 75 °C, agitation speed: 950 rpm and ratio of FA: 2-propanol 16% V/V .

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