Optimization of Lactide synthesis from Lactic Acid in biorefinery of palm oil waste using Response Surface Methodology

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Optimization of Lactide synthesis from Lactic Acid in biorefinery of palm oil waste using Response Surface Methodology

M Gozan[1,4], F Kamilah[1], Y Whulanza[2] and Rahmayetty[3]

[1] Department of Chemical Engineering, Universitas Indonesia, Kampus UI Depok 16424, Indonesia
[2] Department of Mechanical Engineering. Universitas Indonesia. Kampus UI Depok 16424, Indonesia
[3] Department of Chemical Engineering. Faculty of Industrial Technology. Universitas Sultan Ageng Tirtayasa, Banten, Indonesia

E-mail: mgozan@che.ui.ac.id

Abstract. Ring open polymerization is one of the production polylactic acid by formation of monomer before. Lactic acid is converted into lactide in two stages, polycondensation and depolymerization. Yield lactide will determine the molecular weight which produced. This study is to optimize the lactide production from lactic acid 90% by the variations of temperature (190-220^{o}C), vacuum pressure (5-15 cmHg), and zinc acetate catalyst (0,3-0,6% w/w). As the temperature, vacuum pressure, and catalyst is increased, lactide that is produced also increases. Optimum condition of lactide production is obtained by Response surface methodology at the temperature 220^{o}C, catalyst 0,45%w/w, and 10 cmHg in vacuum pressure. Equation or model from this study by using RSM is *yield* lactide = -258,75 + 7,79A + 2,90B + 3,51C + 0,48AB - 0,06AC – 3,97x10^{-3}BC – 105,42A^2 – 7,17B^2 – 0,10C^2 (A:catalyst; B:temperature; C:pressure).

1. Introduction

Utilization of conventional plastics are used as packaging materials not only get a lot of profit, but also causes serious environmental problems such as accumulation of garbage. Furthermore, plastic raw materials requires many natural resources that has declined and difficult to renewable (non-renewable). Polymer demand in 2020 is predicted to reach 7149.8 kilo ton increased by 5.6% from 2014 to 2020 [1]. Fossil resources has been reduced and the increasing concentration of carbon dioxide in the atmosphere has focused attention on the development of bio-based plastics [2].

Polylactic acid (PLA) has great potential to be developed as a replacement for conventional plastic. PLA is a multifunctional polymer biodegradable, and derived from renewable resources [3]. PLA has been widely used for various applications, especially in the fields of medicine, packaging, and textiles. In the medical field, PLA is used in the sewing thread for operating purposes (surgical implants) and wrapping materials of capsules for drug delivery systems (drug delivery) and also for repair of body tissue (mooring new cell growth). In the field of packaging, PLA is developed for the manufacture of

[4] To whom any correspondence should be addressed.

plastic bags (retail bag), containers, and edible films for vegetables and fruit. In the field of textiles, PLA is used in the manufacture of shirts and bags [4, 5].

Poly lactic acid is a plastic material that often used as a food packaging because it has the characteristics of transparency, maintaining, and biodegradability. Ester bond in the PLA can cause either naturally degraded by heat, light, or bacteria (Fusarium moniliform and Penicillium roquefort) [6].

In general, PLA is used to replace a transparent material with high density and prices. Plastic materials are replaced into the type of PET (1.4 g / cc, 1.4 usd / kg), flexible PVC (1.3 g / cc, 1 usd / kg). Polylactic acid needs in Indonesia each year is quite large, visible from export and import data in Figure 1. The increasing needs of PLA in Indonesia, make we should develop technology to produce PLA.

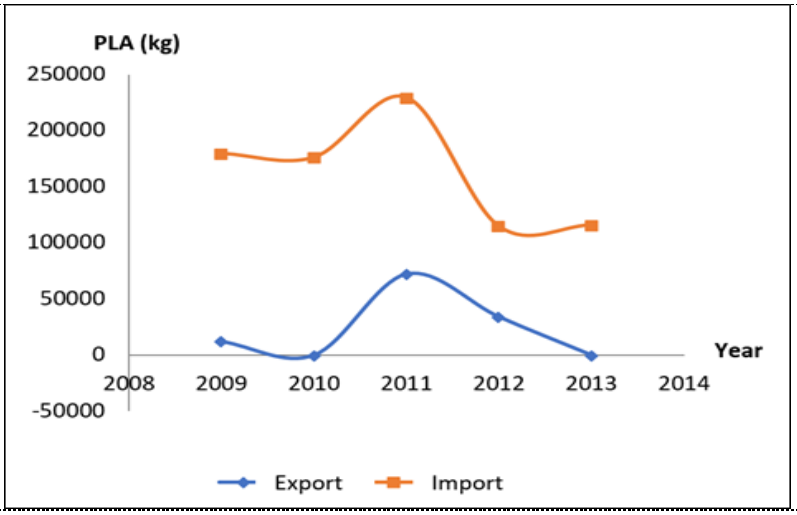

Figure 1. Export and import of PLA.
Source: www.bps.go.id, 2013

Poly lactic acid is synthesized in two stages, with fermentation process to produce lactic acid and ring opening polymerization of a cyclic dimer (lactide) of lactic acid-based polycondensation [7]. In the ring-opening polymerization process, there are three steps are being taken, namely polycondensation of lactic acid, depolymerization thus forming a cyclic dimer (lactide) and ring-opening polymerization to obtain poly lactic acid with a high molecular weight. The third process is crucial to the molecular weight of poly lactic acid produced.

Depolymerization reactions which produce compounds cyclic dimer (lactide), resulting from molecular weight between 100-5000 [8]. To produce poly lactic acid with a high molecular weight lactide monomer required a high yield. The monomer forming reaction is an equilibrium reaction which depends on operating conditions and the presence or absence of a catalyst. We have had a lot of research done on the production of lactide using a metal catalyst to obtain a high yield of lactide. But no one has done to optimize lactide formation process. Zinc acetate is one of the metal catalysts that has not been much research done on the results obtained lactide yield. This catalyst is more secure than other zinc-based catalysts. Zinc acetate as a catalyst in the thermal degradation of poly lactic acid [6]. Zinc acetate is able to accelerate the OH groups in attacking the C = O group on the oligomer chains so as to obtain lactide yield 65-70% [9].

Optimization point will be done by using statistical analysis method, Response Surface Methodology (RSM). To obtain an optimum process is influenced by a number of variables and necessary experimental data in large quantities and take a long time, automatically also will require a great cost. By using the RSM through Expert design software will get high accuracy, reducing the time and cost of research and minimize the occurrence of errors than using conventional methods.

2. Methods

In this research, we have stages such as preparation, polycondensation, and depolymerization.

2.1 Design with response surface methodology

To determine the optimize point using the matrix, first, decide temperature range, the amount of catalyst, and vacuum pressure of forming lactide to proceed to the stage of optimization. That researcher use experimental design is the design matrix Central Composite Design (CCD).

Table 1. Matrix Design of CCD.

	Satuan	**-alpha**	**-1**	**+1**	**+ alpha**
Katalis	%	0,198	0,3	0,6	0,702
Suhu	^oC	179,773	190	220	220,227
Tekanan	cmHg	1,591	5	15	18,409

After these parameters are determined, the experimental matrix by the Design-Expert software is turned up.

2.2 Poly condensation of Lactic Acid

Merck lactic acid 90% by volume of 50 ml put in a four neck flask and heated gradually at 120-180^o C for 5 hours, and nitrogen flowed.

2.3 Depolymerization of Oligomer PLA

Poly lactic acid oligomers which have been formed through polycondensation stage, then catalyst added 0.3 to 0.6% w/w to weight oligomers. The catalyst variations according to RSM design optimization. Oligomers have been added catalyst then heated at 190-220^o C and vacuum pressure by 5-15 cmHg until the oligomer doesn't produce steam again. After the depolymerization process is complete, the vacuum valve is closed slowly. Then lactide is collected on the sample container.

2.4 Analysis of Lactide Concentration

High-Performance Liquid Chromatography (HPLC) analysis is used to determine the concentration of lactide. The column is used Agilent eclipse XDB C18 Two Agilent 1200 series (Agilent, USA). Mobile phase or eluent is water/acetonitrile. Water mobile phase starting with 98% vol, after 2 minutes streamed acetonitrile concentration increased linearly up to 100% vol. Solvents for diluting the sample in the form of ethanol. A total of 0.05-0.1 grams of lactide dilute into 25 mL ethanol. H_3PO_4 buffer used is 0.03 M. The ratio of Buffer-to-eluent of 88:12. Lactide concentration can be calculated using by equation (1)

$$\text{Concentration lactide} = \frac{\text{Sample area}}{\text{Standard area}} \text{X C} \dots (1)$$

where,

C : concentration lactide standard (ppm)

3. Results and Discussion

3.1. Bonding test with FTIR

Bonding test with Fourier Transform Infrared (FTIR) on the first sample to confirm that the depolymerization process produce lactide or not.

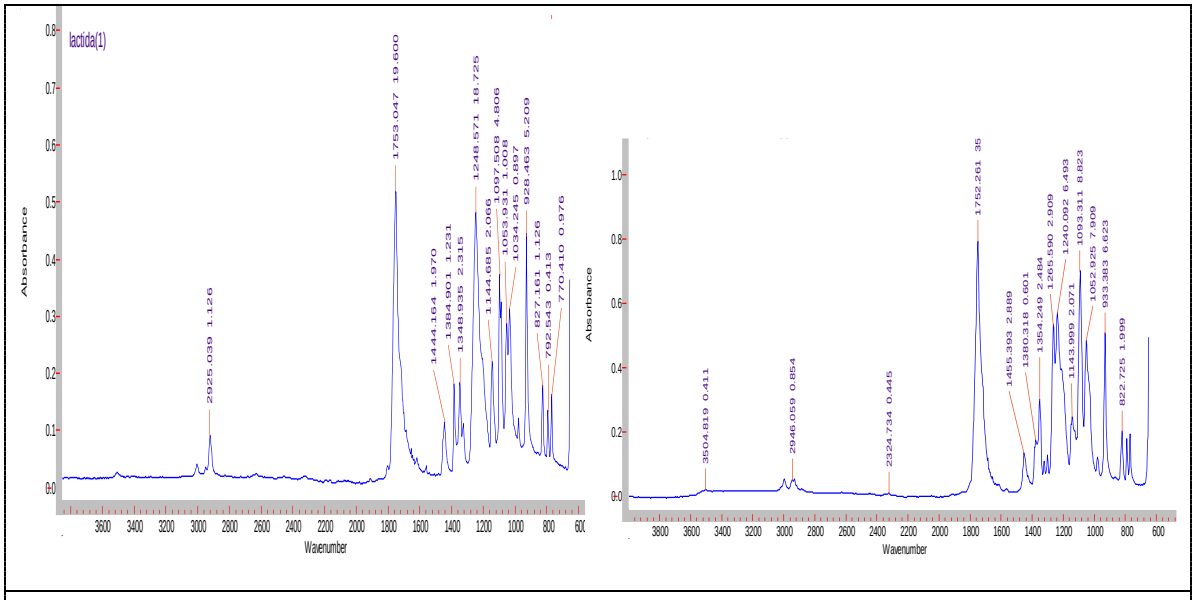

Figure 2. Chromatogram of Lactide, Standard Chromatogram (left); Sample Chromatogram (right)

On the spectrum can be seen that the OH bond in water in the area of 3504.819 cm-[1]. Ester structure, a cyclic -C = O very strong look at the area 1752.261 cm-[1]. Then four substituents -CO appear on the area 1265.590; 1240.092; 1093.311; 1052.925 cm-[1]. Three substituents -CH appear on 1455.393; 1380.318; 1354.249 cm-[1]. Spectrums with the bond -C = O, -CO, and -CH indicate that there is a ring-shaped compound (lactide).

3.2. Optimization of temperature, zinc acetate catalyst and pressure using Response Surface Methodology (RSM)

Research with response surface methodology to get an optimum condition of lactide formation is getting results with optimum operating conditions at 220^{o} C temperature, amount of catalyst is 0.45% w/w and vacuum pressure is 10 cmHg. In this condition lactide is produced which is 78.469%. At the contours of response, there is a central point experiment conducted 3 points. While the optimum point at the high response. This point is the alpha value +1 of the draft model of central composite design (CCD). This value is not different from the predicted values which use the equation.

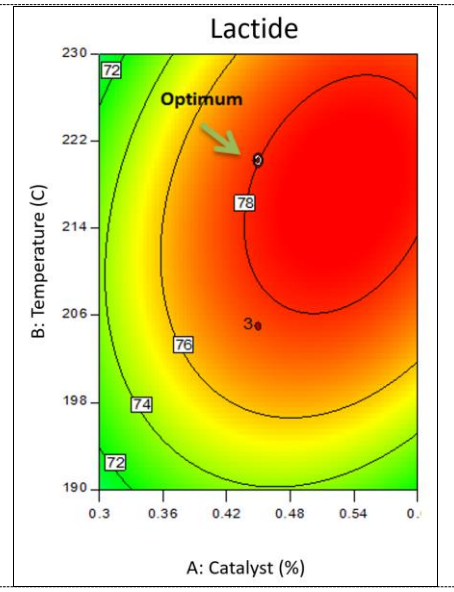

Figure 3. Response 2D of lactide yield

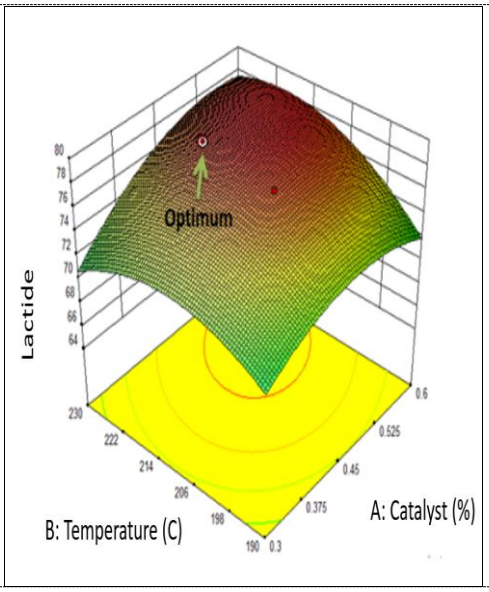

Figure 4. Response 3D of Laktide yield

The highest response (red area) is the highest yield of lactide. But the optimum point is in the region shown in arrows and aren't on the highest response (red). This is because the lowest point in the response seen imprecise. At low catalyst percent, response decreases drastically than at high catalyst. So that the optimum point shifted toward with smaller catalyst and not be in the highest response (red entirely).

When the pressure vacuum is increased and the catalyst is added more, the production of lactide is increased. According to the reference auras, 2010, that the increase of catalyst concentration and vacuum pressure will increase the production of lactide. However, increasing catalyst is not always linear to increase production of lactide, it is linked to the rate of mass transfer between the catalyst with the substrate [8]. Moreover, when the temperature is increased, the reaction rate will be increased so that the reaction goes to the right. The amount of catalyst will also accelerate the rate of reaction this is due to the increased surface area of contact between the PLA oligomers with a catalyst.

3.3 Lactide Analysis by HPLC

Lactide analysis by HPLC method used to determine the concentration of lactide.

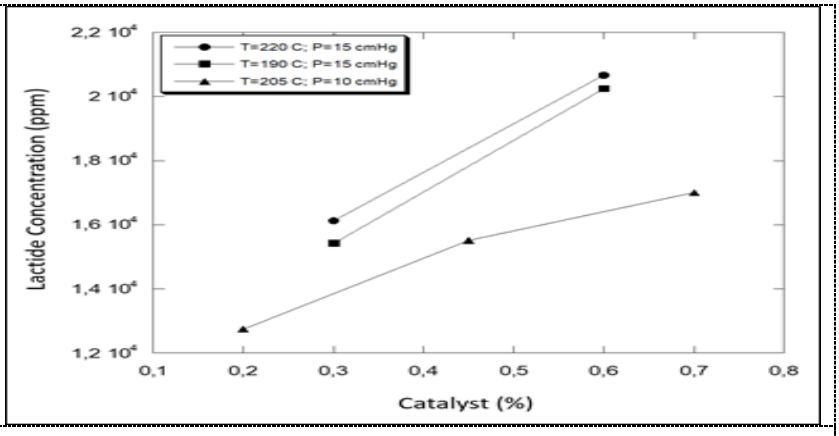

Figure 5. Effect of catalyst zinc acetate on lactide concentration.

From figure 5, show that when the catalyst is increased, lactide concentration is also increased. From that figure also seen that the curve with conditions of 190^{o} C and vacuum pressure 15 cmHg and the curve with conditions of 220^{o}C and vacuum pressure 15 cmHg, have the same precision visually. Both of these curves differ only in the temperature conditions where the temperatures are higher at 220^{o} C was resulted in higher concentrations as well. The relationship between the amount of catalyst added to the linear lactide concentration also occurs on other research [10], which found the addition of catalyst will increase yield lactide and increase conversion of depolymerization reactions.

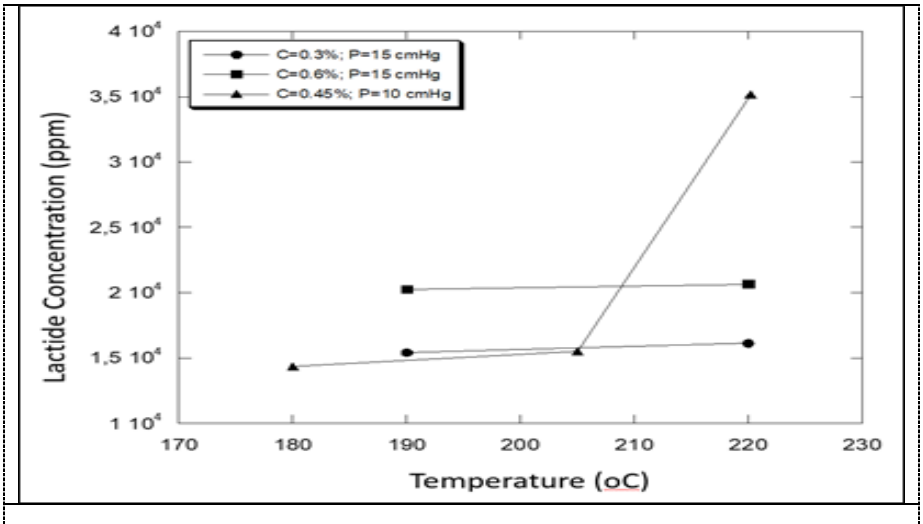

Figure 6. Effect of temperature depolymerization on lactide concentration.

From the Figure 6 show that the increasing temperature accompanied by increasing concentration of lactide. Same as in Figure 5, there are two curves which have the same precision visually. The curve a condition of 0.3% catalyst and a pressure of 15 cmHg with the curve a condition of 0.6% catalyst and the vacuum pressure of 15 cmHg. These curves have the same pressure, but have the difference in the amount of catalyst is used. The catalyst that is increased will generate a lot of lactide concentration. However, the significant increase in concentration occurs 220^{o} C to 205^{o} C temperature, with a concentration of 0.45% catalyst and 10 cmHg vacuum pressure. So, the increasing of temperature causes increasing concentration of lactide [10]. Increasing temperature cause deprotonation process of PLA oligomers faster. Deprotonation is the process of releasing a proton of oxygen atom to a carbonyl carbon groups due to the addition of a catalyst.

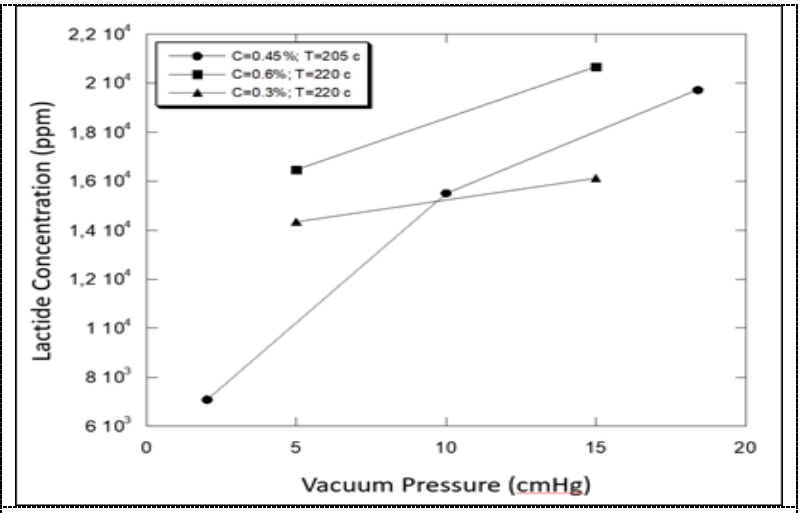

Figure 7. Effect of vacuum pressure on lactide concentration.

In Figure 7, can be seen that the higher vacuum pressure was given or more vacuum pressure in the system, due to higher concentration of lactide. However, 0.45% of catalyst, and 205° C of temperature, and 2 cmHg vacuum pressure, a concentration of lactide is decreased. This is because the vacuum pressure hasn't been able to attract steam in the flask to flow to the condenser.

It also happens in research conducted by Yoo et al, 2006. The concentration of lactide is increased when the pressure is lowered (preferably vacuum). This is due to the lower pressure, monomer and dimer are more volatile than long-chain [11]. In addition to lower pressure, the concentration of impurities such as water also decreases [11].

4. Conclusion

Optimal conditions for Lactide production from lactic acid was obtained at temperature 220°C; 0.45%w/w zinc acetate catalyst; and a vacuum pressure is 10 cmHg. The model from RSM is,

$$\text{Yield lactide (\%)} = -258{,}75 + 7{,}79A + 2{,}90B + 3{,}50C + 0{,}48AB - 0{,}06AC - 3{,}97.10^{-3}BC - 105{,}42A^2 - 7{,}17B^2 - 0{,}10C^2$$

with A: %zinc acetate catalyst; B: temperature (°C); C: vacuum pressure (cmHg)

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