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Optimization of Polycondensation of Polylactic Acid Using Al(DS)$_3$ Catalyst

Ahmad Musonnifin Aziz[1], Anggi Tirta Sari Br Nainggolan[1], Rossesari Nailah Syahbarakat [1], Arief Widjaja[1], Tri Widjaja[1,*]

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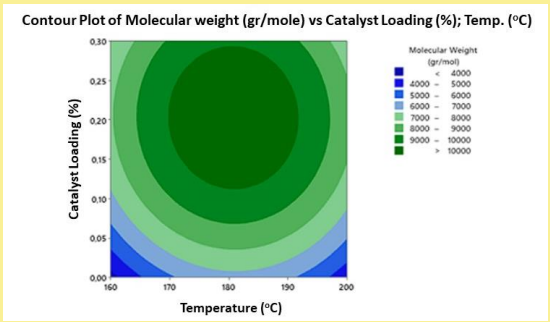
***Abstract*—** Poly(lactic acid) (PLA) is a promising candidate as a renewable resource for plastic production. The use of PLA as a plastic material helps alleviate issues associated with waste. In the production of Polylactic Acid (PLA), by-products such as water are generated, and the Lewis acid catalyst used in PLA production is susceptible to rapid decomposition and deactivation by water. This research aims to optimize PLA polymerization using a water-resistant catalyst, Al(DS)$_3$, to achieve an optimum PLA molecular weight. The synthesized PLA is then analyzed using viscometry to determine its molecular weight. Optimization is carried out using the Response Surface Methodology (RSM) with a Central Composite Design (CCD) matrix. The molecular weight of the synthesized PLA is measured through viscometry, and the data is input into Minitab to obtain the optimum point. This optimum point is further validated by calculating the error value from the optimization results. The optimized PLA results in a molecular weight of 10.313 g/mol with an error value of 4.47% at a catalyst concentration of 0.15% and an operating temperature of 180 °C.



***Keywords*—** Lewis Acid Surfactant Combined Catalyst, Polycondensation, Poly(lactic acid), Sodium Dodecyl Sulfate

I. INTRODUCTION

The waste issue, particularly plastic waste, is a global focus today [1]. Quoting data from the Ministry of Environment of the Republic of Indonesia, in 2021, the accumulation of waste in Indonesia reached 24.41 million tons per year. According to data from the Population Administration, it is predicted that the potential amount of waste in 2022 will reach 68.6 million tons, meaning it could increase by about three times compared to the previous year. Indeed, plastic plays a crucial role in modern society due to its lightweight, durable properties, relatively low cost, and long lifespan. However, a significant portion of plastic, especially conventional plastic, poses environmental problems. The production process of plastic generates pollutants and greenhouse gases, contributing to environmental pollution and global warming. Additionally, its high durability makes it biologically difficult to decompose, leading to environmental pollution. According to data from the Ministry of Environment and Forestry (KLHK) of the Republic of Indonesia, approximately 6.8 million tons of plastic waste end up in the Indonesian seas each year, with only 10 percent being recycled, 20 percent ending up in landfills, and the remainder left unmanaged.

Generally, plastic is produced from crude oil or petroleum and natural gas that has undergone further processing to become petrochemical products. Typically, crude oil is processed through refining along with natural gas to produce petrochemicals. These petrochemical products are then further processed into plastic pellets or granules. Finally, various types of plastic products can be manufactured from these plastic granules according to their intended use.Plastic waste has highly detrimental effects on the environment. Plastic pollution is considered more harmful than carbon footprint. Moreover, burning plastic can contribute to pollution by emitting harmful and toxic emissions. Additionally, this process is expensive and economically unsustainable. Hence, there is a need for biodegradable plastics, where the material can almost

[1]Departement of Chemical Engineering, Institut Teknologi Sepuluh Nopember, Sukolilo, Surabaya, 60111, Indonesia. *E-mail: triw@chem-eng.its.ac.id

entirely transform into non-hazardous waste for the environment within a few months.

Bioplastics, which functionally resemble synthetic plastics but are environmentally friendly, are touted as a promising solution to address this issue. Bioplastics are either biodegradable or produced from biological materials or renewable resources, such as starch, cellulose, vegetable oil, and plant fats [2].

As time progresses, global awareness of environmental issues caused by human activities is increasing. One manifestation of this awareness is the growing production of biodegradable plastics from year to year. Poly(lactic acid) (PLA) holds tremendous potential as a renewable resource for plastic production. Therefore, the use of PLA as a plastic material is beneficial in addressing issues caused by waste. However, due to its relatively high cost, the application of PLA as a substitute for conventional plastics has not yet reached its maximum potential. Thus, simplification and optimization in the production of PLA are needed to reduce the manufacturing cost. The production of PLA can be carried out through various methods, including polycondensation of lactic acid in solution under atmospheric and reduced pressure conditions, Ring Opening Polymerization (ROP), melt polycondensation, and direct polycondensation of lactic acid [3]. The method employed in this research is the direct polycondensation of lactic acid, which includes dehydration, polycondensation, and recrystallization [4-5].

This research begins with the preparation of the Lewis Acid Surfactant Combined Catalyst (LASC) [6-8]. LASC is chosen because it is a catalyst that is water-compatible, allowing heavy metals or traditional Lewis acids to react without worrying water which lead to decomposition and deactivation that causing increasment of PLA production cost. In this study, Aluminium (Fe) metal is used, reacted with Sodium Dodecyl Sulfate (SDS), and will be compared with the $AlCl_3$ catalyst [9-12]. The next step involves polycondensation by adding 200 mL of L-lactic acid to a three-necked flask, supplemented with the LASC catalyst. The resulting PLA will undergo viscometry analysis to determine its molecular weight, followed by optimization to obtain the optimum operating conditions then validating optimization result by re-run polycondensation step [13-16].

II. METHOD

A. Optimization Design

Optimization was performed on PLA with the addition of the LASC $Al(DS)_3$ catalyst using Response Surface Methodology (RSM) and the Central Composite Design (CCD) matrix in Design Expert 13 software (trial version). There are two independent variables in the polycondensation experiment: X1, representing the temperature in Celsius, and X2, representing the catalyst loading in percentage. The alpha (α) value is set at 1. Alpha represents the distance of each axial point (star point) from the center point in the central composite design. Three levels (-1, 0, +1) are used for each parameter to obtain response surfaces for each significant variable and optimal values. The variables and their levels are indicated in Table 1. Level zero (0) is the expected value, level -1 is the lower limit, while level +1 is the upper limit. Subsequently, these parameter values are generated into the Design Expert software, as stated in Table 2.

TABLE 1.
DETERMINATION OF THE CENTRAL COMPOSITE DESIGN (CCD) EXPERIMENT

Variable	Unit	Range and Level		
		-1	0	+1
X1 (Temp.)	Celcius	160	180	200
X2 (Cat. Conc.)	(%)	0	0.15	0.3

TABLE 2.
EXPERIMENT MATRIX OF RSM

Run	Variable	
	X1 (Temperature)	X2 (Catalyst Concentration)
1	180	0.15
2	180	0.00
3	180	0.15
4	160	0.30
5	180	0.15
6	200	0.00
7	200	0.30
8	180	0.15
9	180	0.15
10	160	0.00
11	160	0.15
12	180	0.30
13	200	0.15

In a Central Composite Design with 2 factors, there are 13 points that need to be experimented with [1]. The obtained PLA is subjected to molecular weight measurement and entered into Minitab. Subsequently, Minitab will provide various forms of analysis, allowing us to assess the points of the Independent Variable Unit Range and Level -1 0 1 X1 (Temperature) Celsius 160 180 200 X2 (Catalyst Loading) Percent (%) 0, 0.15, 0.3 to determine which one is the best and optimum. Then, it is validated to determine the error value of the optimal PLA [17].

B. Materials and Equipment

The materials used in this research include $AlCl_3$, Sodium Dodecyl Sulfate, L-Lactic Acid, Distilled Water (Aquades), Methanol, and Chloroform.

The equipment used in this research includes a Vacuum Pump, Condenser, Erlenmeyer Flask, Graduated Flask, Magnetic Stirrer, Thermometer, Oven, Desiccator, Filter Paper, and Heater.

C. Research Procedure

a. $Al(DS)_3$ synthesize

Approximately 3.4 grams (11.8 mmol) of SDS is mixed with 100 mL of distilled water (heated to a temperature of 60 °C). The dissolved SDS is then combined with $FeCl_3$ metal, dissolved in 20 mL of distilled water (heated to a temperature of 60 °C), with a mass of 0.6384 grams (5.9 mmol). The metal is then mixed with SDS in an Erlenmeyer flask and stirred for 30 minutes. The solid

catalyst obtained is filtered, washed with distilled water, and then dried in an oven for 24 hours.

b. Polycondensation

The polycondensation process is carried out by adding a catalyst. The reaction begins with a dehydration process and polycondensation. The reaction involves adding 20 mL of L-lactic acid to a three-necked flask along with 0.15% or 0.3% by weight of LASC or metal. The flask is connected to a fractional column and a condenser to separate water vapor. The dehydration stage starts by raising the temperature to 130 °C under a vacuum of 20 kPa for 1 hour, and the three-necked flask is tightly closed. This process facilitates water removal, and the resulting concentration of L-lactic acid is approximately 96%. The next stage is polycondensation, conducted by increasing the temperature according to the desired variable under a vacuum of 20 kPa while stirring with a magnetic stirrer at 250 rpm for 6 hours. The produced PLA is then used to calculate the molecular weight using the Viscosity Method. The Measurement of PLA molecular weight and input submitted into Minitab for analysis. Then we conducted assessment of the points of the Independent Variable Unit Range to determine the best and optimum points. Finally, validation was conducted according to optimization to determine the error value of the optimal PLA.

III. RESULTS AND DISCUSSION

A. Optimization Result

The combination of the experimental design obtained from the Central Composite Design (CCD) was then investigated with a total of 13 samples. Based on the research referring to the CCD design table, the optimization treatment combinations and response data are presented in Table 3. According to Table 3, the optimization results with the response of PLA molecular weight from the CCD design are apparent. Operating conditions of 160°C with 0% catalyst (without catalyst) on PLA resulted in the smallest molecular weight, which is 3,323.2 g/mol. Meanwhile, the largest molecular weight of PLA occurred under operating conditions of 180°C with a catalyst loading of 0.15%, with a molecular weight of 11832.7 g/mol. Temperature and catalyst loading significantly affect the molecular weight of the produced PLA. From Table 3, it can be seen that the optimum condition is at an operating temperature of 180°C with a catalyst loading of 0.15%, marked by an increase in molecular weight. Longer polymerization time is required to achieve the desired molecular mass, accompanied by inevitable degradation due to the additional time at high temperatures containing the catalyst. This is demonstrated by PLA at 200°C experiencing a decrease [18-20].

Table 4 explains the influence of temperature and catalyst loading on the CCD Design model. A design is considered significant if it has a P-Value < 0.05. The Probability Value (P-Value) can be interpreted as the observed probability level from the statistical test. Temperature*Temperature, Catalyst Loading*Catalyst Loading, and Catalyst Loading are significant parameters. However, the Temperature parameter and Temperature*Catalyst Loading are not significant because they are > 0.05.

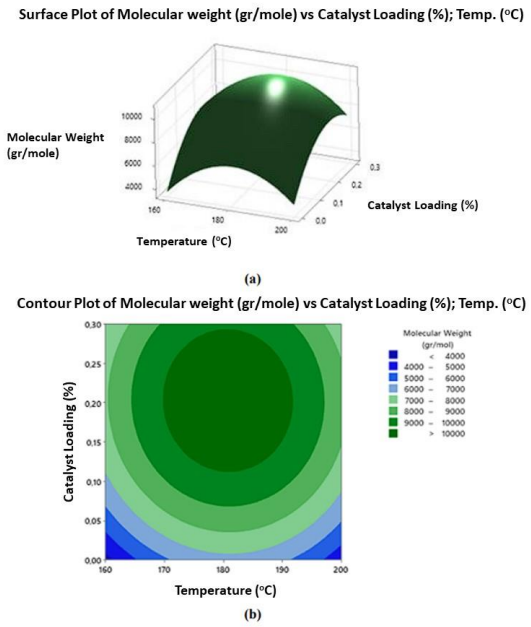


Figure 1. (a) Surface Plot dan (b) Countour Plot Desain CCD

According from Table 4 the equation generated for this optimization was:

$$Y1 = -217563 + 2477\ X1 + 45550\ X2 - 6.84\ X1^2 - 101474\ X2^2 - 25X1X2 \quad (1)$$

TABLE 3.
PLA MOLECULAR WEIGHT RESPONDS

STD ORDER	RUN ORDER	PT TYPE	BLOCKS	T (°C)	CAT. CONC. (%)	MW (GRAM/MOLE)
11	1	0	1	180	0.15	10,889.6
7	2	-1	1	180	0.00	6,937.4
9	3	0	1	180	0.15	11,832.7
3	4	1	1	160	0.30	7,504.6
12	5	0	1	180	0.15	10,464.9
2	6	1	1	200	0.00	4,267.5
4	7	1	1	200	0.30	8,151.98
10	8	0	1	180	0.15	11,153.4
13	9	0	1	180	0.15	9,529.5
1	10	1	1	160	0.00	3,323.2
5	11	-1	1	160	0.15	7,383.5
8	12	-1	1	180	0.30	8,459.3
6	13	-1	1	200	0.15	7,108.3

Based on Equation 1, an R-squared value of 90.84% is obtained, as shown in Table 5. The coefficient of determination (R-squared, R^2) indicates the quality of the

generated model. The minimum acceptable value for R^2 should be 0.8 or 80% (in this case, the model is acceptable). Nevertheless, this experiment can be accepted because it has an R-squared value of 90.84%. Therefore, it can be concluded that PLA with operating conditions of 180°C and a catalyst loading of 0.15% is PLA with the highest target, achieving a molecular weight of 11,832.7 g/mol.

TABLE 4.
ANALYSIS OF VARIANCE (ANOVA)

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	5	72026100	14405220	13.88	0.002
Linear	2	15609797	7804899	7.52	0.018
Temp. (Celcius)	1	28844	288844	0.28	0.614
Cat. Conc. (%)	1	15320953	15320953	14.76	0.006
Square	2	56394249	28197125	27.17	0.001
Temp. (Celcius)* temp. (Celcius)	1	20669339	20669339	19.91	0.003
Cat. Conc. (%)*Cat. Conc. (%)	1	14397374	14397374	13.87	
2-Way Interaction	1	22054	22054	0.02	0.888
Temp. (Celcius)* Cat. Conc. (%)	1	22054	22054	0.02	0.888
Error	7	7265404	1037915		
Lack-of-fit	3	4342790	1447597	1.98	0.259
Pure Error	4	2922614	730653		
Total	12	79291504			

TABLE 5.
SUMMARY OF OPTIMIZATION PLA+AL(DS)$_3$

S	R-sq	R-sq (Adj)	R-sq (Pred)
1,018.78	90.84%	84.29%	46.74%

The R-squared value (0.9084) indicates a good relationship between the experimental and predicted values of the response. A high R-squared value approaching 100% suggests that the data analyzed through Response Surface Methodology (RSM) approximates the actual values, meaning the experimental data is consistent. The standard deviation (S) measures the difference between sample values and the mean value [21]. The obtained value of S in this research is relatively small, amounting to 1,018.78.

TABLE 6.
RESULTS OF OPTIMIZATION DATA VALIDATION

T (°C)	Power Rate (%)	Molar Mass (10^3 gr/mol)				Error
		I	II	Avg.	Expected	
180.6	0.203	10.1	10.5	10.3	10.8	0.0477

In this CCD Optimization Design, PLA with optimal conditions was obtained at an operating temperature of 180.6°C and a catalyst loading of 0.2030%, resulting in a molecular weight of 10,830.5 g/mol. After obtaining the optimal results, the next step is to validate the optimization outcomes.

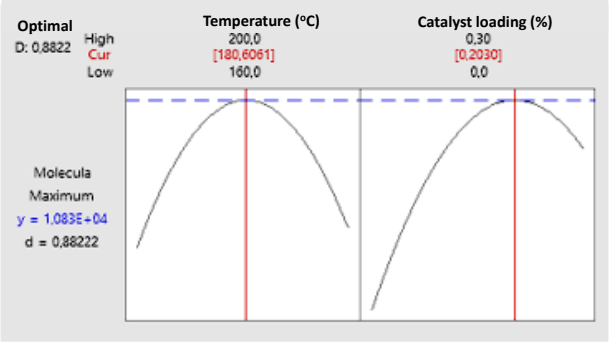


Figure 2. Response Optimization for maximum molecular weight (gr/mol)

The data was retested between the theoretical data from the optimization results and the experimental data, and the results obtained are as shown in Table 6. The percentage error obtained is 4.77%, which is less than 5%, the error limit for experiment replication. It can be concluded that the optimum points from the Response Surface Methodology (RSM) obtained are accurate.

IV. CONCLUSION

The optimization of the PLA synthesis operating conditions using the polycondensation method with LASC catalyst was carried out by conducting 13 runs and then optimizing using the Response Surface Methodology (RSM) with a CCD matrix. The optimization results indicate that a temperature of 180°C with a catalyst loading of 0.2% w/w is the optimum condition for PLA synthesis. This is supported by validation results with an error of 4.7%, and an average molecular weight of 10.83 x 10^3 g/mol was obtained.

V. ACKNOWLEDEGMENT

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