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Research Article

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The optimization of biopolyol synthesis from liquefaction of rice straw using response surface method

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ABSTRACT

Polyol has been widely used as a raw material for polyurethane production which has many applications in daily life such as foam synthesis, thermoset, thermoplastic and coating materials. In general, polyol derived from petroleum based product. As the limiting amount of polyol derived from petroleum and the demand of polyol is increasing, effort is needed to find out alternative raw materials in particular potential feedstock comes from agricultural waste. However, there are limited studies focused on the use of rice straw as material for synthesis of biopolyol. Rice straw is very potential raw material for synthesis of biopolyol as it contains lignocellulose hence through liquefaction process will produce biopolyol. Response surface method was performed to determine the optimal operating condition for the liquefaction process of rice straw indicated by high content of hydroxyl group. The effect of key independent variables of liquefaction temperature, reaction time, concentration of biomass and catalyst on the hydroxyl value of product was quantified. The liquefaction process was performed in a batch reactor equipped with thermometer and reflux condenser using glycerol as a solvent and reactant. A central composite design with four independent variables and one response function was applied to determine the influence of independent variables. The concentration of biomass and acid catalyst has significant effect on the hydroxyl value of biopolyol product. The hydroxyl value is a linear function of biomass and catalyst concentration. The optimal operating condition was achieved at a temperature of 60^{o}C, reaction time of 60 minutes, 3% of biomass concentration and 0.5% of acid catalyst concentration. The viscosities of biopolyol obtained are in the range of 217.5 – 727.5 cP.

Keywords: Biopolyol; Liquefaction; Hydroxyl value; Rice straw

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INTRODUCTION

Indonesia is a tropical country with high amount of natural resources for sustainability of human being in particular agricultural sector. As a result, this sector becomes the main commodity for work and job for local community. The need of local community for food has been fulfilled by agricultural sector as a result of the increasing number of food plant production each year. However, the increasing of productivity in agriculture has resulted in a huge amount of side product agricultural waste. Rice straw is one of agricultural waste product with total number about 20 million tons per year in Indonesia. Therefore, effort is needed to convert agricultural waste product to be valuable product with various benefit for daily life.

So far, rice straw is burnt to reduce the waste but this method cause environmental problems in terms of air pollution. Waste of rice straw contains cellulose (38.48%), hemicellulose (20.51%), acid-insoluble lignin (6.42%) and ash (12.47%) [1]. Polyol has been widely used as a raw material for polyurethane production which has many applications in daily life such as foam synthesis, thermoset, thermoplastic and coating materials [2-3]. In general, polyol derived from petroleum based product. As the limiting amount of polyol derived from petroleum and the demand of polyol is increasing, effort is needed to find out alternative raw materials in particular potential feedstock comes from agricultural waste. There are some researches has utilized various bioresources through liquefaction process using appropriate solvents for the production of polyurethane and foams [4-8]. However, there are limited studies focused on the use of rice straw as feedstock for synthesis of biopolyol. Rice straw is very potential raw material for synthesis of biopolyol as it contains lignocellulose hence through liquefaction process will produce biopolyol.

Response surface method provides an efficient experimental design to study the influence of independent variables to obtain the optimal condition [9]. Furthermore, response surface method has additional benefits such as it allows determination of interaction effects between variables [10] and saves times as a reduced number of experiments are required [11].

The purpose of this research is to study the influence of independent variables (liquefaction temperature, reaction time, concentration of biomass and catalyst) on hydroxyl value (output variable) and to determine the optimal operating condition for liquefaction of biopolyol from rice straw.

EXPERIMENTAL SECTION

Materials

Materials used in this research were rice straw waste from Surabaya (size 40 mesh), glycerol (technical grade), sulfuric acid 96% as catalyst, sodium hydroxide (technical grade) and magnesium sulfate anhydrous.

Methods

Pre-treatment of Rice Straw

Rice straw was dried under sun rice then cut and mashed to reduce the size to obtain size of 40 mesh rice straw powder.

Liquefaction Process

A mixture of rice straw powder, sulfuric acid catalyst, and glycerol was added into glass reactor equipped with reflux condenser, stirrer and thermometer. The reactor was immersed into oil bath to maintain the reaction temperature. The concentration of biomass and catalyst was varied based on experimental design. Reaction was run at several isothermal conditions and several reaction times. The reaction product was then cooled at room temperature before sodium hydroxide was added to neutralize sulfuric acid in the mixture. The reaction product was then filtered to separate the liquid phase from the solid phase. Following this, magnesium sulfate anhydrous was added to reduce the water content then filtered. The final biopolyol liquid product was then analyzed in terms of hydroxyl value and viscosities.

Experimental Design

Full factorial Central Composite Design (CCD) was used to determine he total number of expeiments applying the equation $2^k + 2k + n_o$ [11] where $2.^k$ is factorial design, $2k$ is star point, k is totl number of independent variables, and n_o is total number of rplication at central point.

This research focused on the effect of four independent variables liquefaction temperature (X_1), reaction time (X_2), concentration of biomass (X_3), and concentration of catalyst (X_4) on response variable of hydroxyl value of biopolyol product. The central value of independent variables was used is liquefaction temperature 80^{o}C; reaction time 120 minutes; concentration of biomass of 5%; and sulfuric acid catalyst concentration of 1.5%. Four independent variables were studied and optimized in the form of coded value X_1, X_2, X_3, and X_4 at five levels (-2, -1, 0, 1, 2) using equation:

$$X_i = \frac{x_i - x_0}{\Delta x_i}$$

where X_i is coded value of independent variable, x_i is real value of independent variable, x_0 is real value of independent variable at central point, and Δx_i is interval. The distribution of coded values $X_1, X_2, X_3,$ and X_4 as described in Table 1.

Table 1. Range and Level Variables

Variables	Coded value	Range dan levels				
		-2	-1	0	1	2
Liquefaction temperature(^{o}C)	X_1	60	70	80	90	100
Reaction time (minutes)	X_2	60	90	120	150	180
Concentration of biomass (%)	X_3	3	4	5	6	7
Concentration of catalyst (%)	X_4	0.5	1.0	1.5	2.0	2.5

RESULTS AND DISCUSSION

Statistical Analysis

A second order polynomial model was performed to fit the experimental data presented in Table 2 using the equation below:

$$Y_1 = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{44} X_4^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{14} X_1 X_4 + \beta_{23} X_2 X_3 + \beta_{24} X_2 X_4 + \beta_{34} X_3 X_4$$

where Y_1 is the response, β_0 is constant; $\beta_1, \beta_2, \beta_3, \beta_4$ represent linear coefficients; $\beta_{11}, \beta_{22}, \beta_{33}, \beta_{44}$ are the quadratic coefficients; $\beta_{12}, \beta_{13}, \beta_{14}, \beta_{23}, \beta_{24}, \beta_{34}$ are interaction coefficients.

The correlation of the response Y_1 to coded value was estimated by multiple linear regressions. The regression coefficients are presented in Table 3.The experimental data from the central composite design was fitted with second order polynomial model by performing multiple linear regressions. The correlation between hydroxyl value of biopolyol and four input variables (liquefaction temperature, reaction time, concentration of biomass and catalyst) in coded unit after applying of response surface method can be represented by the equation:

$$Y_1 = 587.09 - 11.88X_1 - 9.55X_2 - 14.53X_3 - 22.40X_4 + 4.07X_1^2 + 1.77X_2^2 - 3.37X_3^2 - 0.59X_4^2 + 18.58X_1X_2 + 4.98X_1X_3 - 8.24X_1X_4 + 3.20X_2X_3 + 9.27X_2X_4 + 10.55X_3X_4$$

Table 2. CCD and Response Variable

Run	Temperature (X_1) (°C)	Reaction time (X_2) (minutes)	Concentration of Biomass (X_3) (%)	Concentration of Catalyst (X_4) (%)	Hydroxyl value (Y_1) (mg KOH/g sample)
1	80(0)	120(0)	5(0)	0.5(-2)	607.26
2	90(1)	90(-1)	6(1)	2(1)	548.83
3	80(0)	120(0)	5(0)	2.5(2)	567.80
4	90(1)	150(1)	4(-1)	1(-1)	641.09
5	70(-1)	90(-1)	6(1)	1(-1)	625.33
6	60(-2)	120(0)	5(0)	1.5(0)	632.70
7	70(-1)	90(-1)	4(-1)	1(-1)	718.77
8	80(0)	120(0)	3(-2)	1.5(0)	592.08
9	80(0)	120(0)	7(2)	1.5(0)	560.72
10	70(-1)	150(1)	6(1)	1(-1)	554.72
11	80(0)	180(2)	5(0)	1,5(0)	598.14
12	70(-1)	150(1)	6(1)	2(1)	548.82
13	90(1)	150(1)	6(1)	2(1)	533.91
14	90(1)	90(-1)	4(-1)	2(1)	524.45
15	80(0)	120(0)	5(0)	1.5(0)	547.28
16	70(-1)	90(-1)	4(-1)	2(1)	609.00
17	80(0)	120(0)	5(0)	1.5(0)	589.52
18	70(-1)	90(-1)	6(1)	2(1)	574.77
19	70(-1)	150(1)	4(-1)	1(-1)	577.95
20	80(0)	120(0)	5(0)	1.5(0)	564.97
21	80(0)	120(0)	5(0)	1.5(0)	590.27
22	90(1)	90(-1)	4(-1)	1(-1)	640.89
23	80(0)	120(0)	5(0)	1.5(0)	605.24
24	90(1)	150(1)	6(1)	1(-1)	595.68
25	70(-1)	150(1)	4(-1)	2(1)	580.74
26	90(1)	90(-1)	6(1)	1(-1)	575.55
27	90(10	150(1)	4(-1)	2(1)	550.75
28	100(2)	120(0)	5(0)	1.5(0)	579.59
29	80(0)	120(0)	5(0)	1.5(0)	557.16
30	80(0)	60(-2)	5(0)	1.5(0)	595.80
31	80(0)	120(00	5(0)	1.5(0)	655.20

Table 3. Significance of regression Coefficients for Y_1

	Coefficients	t statistics	p-value
Intercept	587.09	50.175	0.000
X_1	-11.88	-1.880	0.078
X_2	-9.55	-1.512	0.150
X_3	-14.53	-2.300	0.035*)
X_4	-22.40	-3.545	0.003*)
X_1^2	4.07	0.702	0.493
X_2^2	1.77	0.306	0.763
X_3^2	-3.37	-0.582	0.569
X_4^2	-0.59	-0.101	0.920
X_1X_2	18.58	2.401	0.029*)
X_1X_3	4.98	0.643	0.529
X_1X_4	-8.24	-1.065	0.303
X_2X_3	3.20	0.414	0.685
X_2X_4	9.27	1.197	0.249
X_3X_4	10.55	1.363	0.192

*) *Significant at 5% (<0.05)*

The result indicated that biomass and acid catalyst concentration have significant effect on the hydroxyl value of biopolyol from liquefaction of rice straw (significant at $p<0.05$). The hydroxyl value is linear function of biomass and acid catalyst concentration. Furthermore, the interaction of variables (liquefaction temperature and reaction time) has significant effect on the hydroxyl value of biopolyol ($p<0.05$).

The Influence of Temperature on Hydroxyl Value of Biopolyol

Temperature has different effect when the liquefaction process was run at different reaction time. As can be seen from Figure 1, the hydroxyl value of biopolyol decreased from about 720 to 550 mg KOH/ g sample with the increasing of reaction temperature from 60^oC to 100^oC at lower reaction time (60 min).In contrast to this, at higher reaction time (180 min) the hydroxyl value of biopolyol increased with the rise of liquefaction temperature.

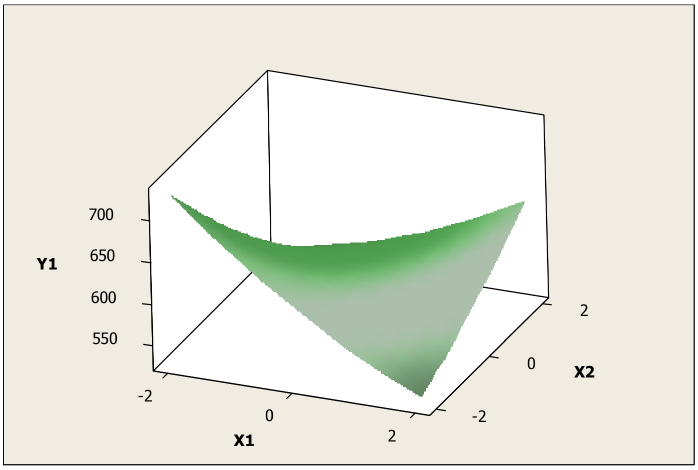
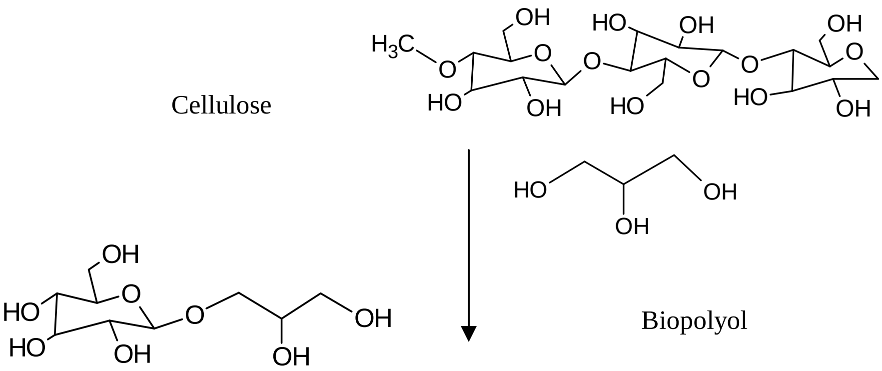


Figure 1. Temperature and reaction time vs hydroxyl value

Another figure indicated that temperature has a negative effect on the hydroxyl value of biopolyol product according to Figure 2 for all biomass concentration. The hydroxyl value of biopolyol dropped from 660 to 560 mg KOH/g sample for higher reaction temperature. It can be explained that biopolyol is a chemical compound contains hydroxyl groups from lignocellulose biomass. Through the liquefaction process, solvolysis and hydroalkylation reaction occurred. At first stage, cellulose materials will be degraded by glycerol to produce biopolyol according to the following solvolysis reaction mechanism:



At higher reaction time and temperature, biopolyol can be degraded to produce side reaction product called levulinic acid through hydroalkylation reaction hence biopolyol with lower hydroxyl value resulted [12]. Research by Celigbak et al. (2011) have also reported similar behavior for the liquefaction of bio-oil from loblolly pine [13].

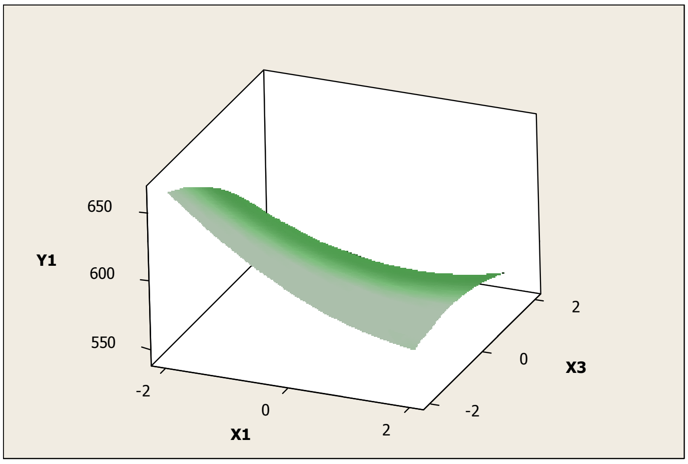


Figure 2. Temperature and biomass concentration vs hydroxyl value

Another important finding is the liquefaction temperature has no effect on the hydroxyl value of polyol indicated by the hydroxyl value remained the same at 640 mg KOH/g sample when the liquefaction was run at lower acid catalyst concentration of 0.5%. In contrast, liquefaction temperature has significant effect if the liquefaction was conducted at higher 2.5 % of catalyst concentration resulted in the hydroxyl value dropped from 650 to about 500 mg KOH/g sample.

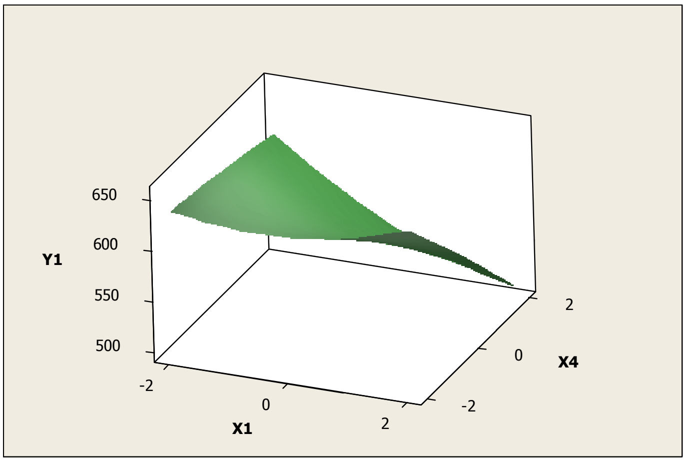


Figure 3. Temperature and catalyst concentration vs hydroxyl value

The Influence of Reaction Time on Hydroxyl Value of Biopolyol

The result illustrated that reaction time has a negative effect on the hydroxyl value of biopolyol product (Figure 4). This because higher reaction time will result in undesired product of levulinic acid hence lower hydroxyl value of biopolyol product obtained [12]. This result is occurred at all range of biomass concentration (3% to 7% biomass concentration). To prove the formation of hydroxyl groups from the conversion of lignocellulose biomass of rice straw, a FTIR analysis was performed. Figure 6 showed the profile of FTIR analysis of biopolyol obtained from liquefaction process.

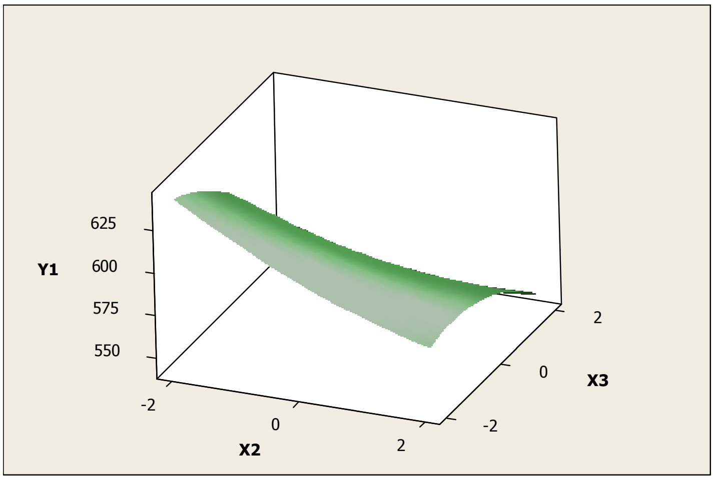


Figure 4. Reaction time and biomass concentration vs hydroxyl value

Reaction time has different effect on the hydroxyl value of biopolyol for different acid catalyst concentration. At lower catalyst concentration (0.5%), temperature has a negative effect on hydroxyl value decreased from 700 to 570 mg KOH/g sample. Different effect shown if the liquefaction was run at higher catalyst concentration (2.5%) resulted in the hydroxyl value remained constant at 570 mg KOH/g sample (Figure 5).

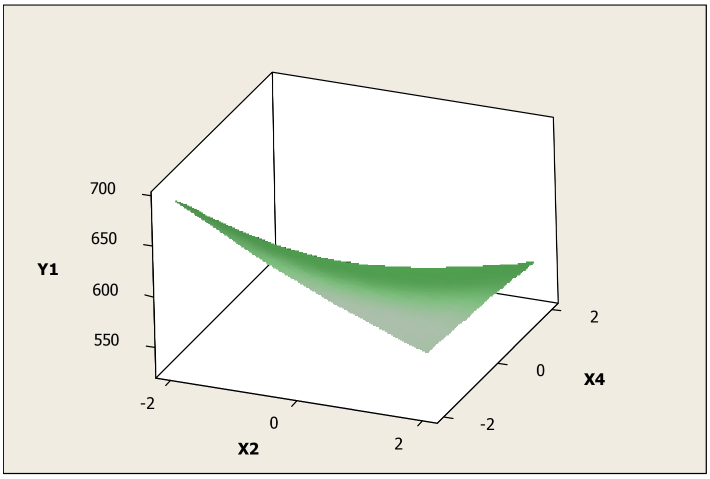


Figure 5. Reaction time and catalyst concentration vs hydroxyl value

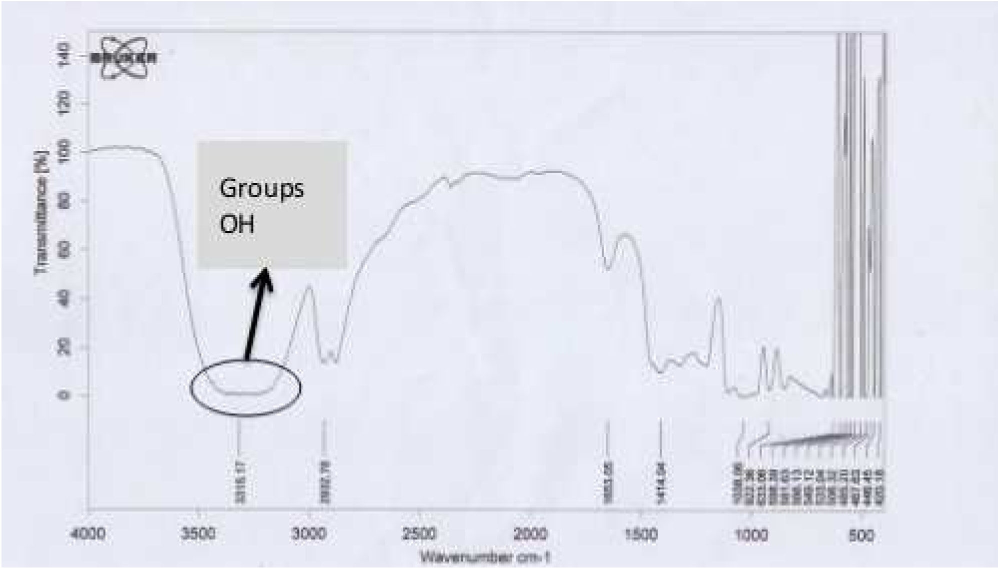


Figure 6. FTIR spectra of biopolyol

The Influence of Biomass and Catalyst Concentration on Hydroxyl Value of Biopolyol

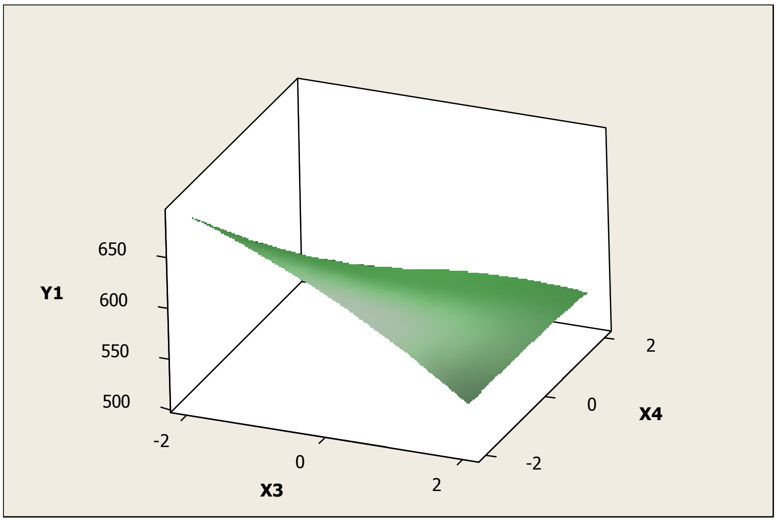


Figure 7. Biomass and catalyst concentration vs hydroxyl value

As illustrated in Figure 7, the hydroxyl value of biopolyol decreased slightly with the increasing amount of biomass concentration for the use of 0.5% acid catalyst concentration. However, at higher acid catalyst concentration (2.5%) the result shown different trend and indicated no effect of the increasing amount of biomass concentration on hydroxyl value accounted for about 550 mg KOH/g sample biopolyol produced. Similar trend has shown by the effect of catalyst concentration on the hydroxyl value of biopolyol product. At lower biomass concentration (3%), the hydroxyl value of biopolyol decreased with the increasing amount of catalyst concentration whereas the hydroxyl value of biopolyol remained the same with the rise of catalyst concentration at higher biomass concentration (7%) as shown in Figure 7. The viscosities of biopolyol obtained in this research were in the range 217.5 – 727.5 cP.

The Optimization of Polyol Synthesis from Liquefaction of Rice Straw

The optimal operating condition for synthesis of biopolyol was indicated by high number of the hydroxyl value. The optimal condition achieved at liquefaction temperature of 60^{o}C, reaction time 60 minutes, biomass concentration 3%, and acid catalyst concentration 0.5% and the hydroxyl value possibly achieved with value 864.71 mg KOH/g sample.

CONCLUSION

This study indicated that biopolyol could be obtained from the liquefaction of rice straw using glycerol as a solvent and reactant and four independent variables have different effect on the hydroxyl value of biopolyol. Biomass and acid catalyst concentration have significant negative effect on the hydroxyl value. Liquefaction temperature and reaction time have different effects depend on the level of other independent variables. The optimal operating condition obtained at a liquefaction temperature of 60^{o}C, reaction time 60 minutes, biomass concentration 3% and acid catalyst concentration of 0.5%.

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