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SYNTHESIS OF POLYOL FROM EDIBLE OIL WASTE WITH OZONOLYSIS TECHNOLOGY

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Abstract

Polyol is a chemical compound that contains many hydroxyl groups. Polyol can be made from petroleum, nevertheless petroleum's price is increasingly high and petroleum itself is a non-renewable resource, so it may be gone someday. Alternatively, synthesis of polyol can use other material that is renewable, in case it can use waste from edible oil.

In experiment, polyol is made from edible oil waste (used palm cooking oil) through ozonolysis reaction. Beside ozone, as reactant are also used a mixture of methanol, isopropanol and water in certain ratio and sulphuric acid as catalyst. Mechanism of reaction will start at ozone attack and break the double bonds (C=C) of unsaturated fatty acid in the waste, and then hydroxyl groups of alcohol can made contact to produce polyol.

The main purpose of experiment is to determine the optimum condition for making polyol with ozonolysis technology. The experiment will be carried out by vary temperature of ozonolysis reaction, mol ratio of oil-alcohol, reaction time and ozone concentration.

The result of experiment show that hydroxyl number values of polyol vary from 92.75 to 265.62 and viscosity values vary from 9.228 to 20.403 cp. The optimum condition determined by response optimization program, and from experiment show that converting edible oil waste to polyol will be efficient with temperature 25 °C, 3 hours reaction time, 1:7 for oil and alcohol mol ratio and ozone concentration 6.3 %.

Keywords: polyol, ozonolysis, hydroxyl number, viscosity

INTRODUCTION

Polyol is a carbohydrate but it is not sugar, polyol is a derived product of sugar. At this time, the use of polyol increase, more than as a raw material of polyurethane, as a synthesis sweeter, and the caloric value of polyol smaller than sugar, and it can reduced respon insulin to sugar and because of the reason there is a statement "polyol is a sugar free". Otherwise, polyol is also as raw material for production of foam. But at this year, total of polyol production in the regional market is very low.

Other material to yield polyol is petroleum, but now the price of petroleum is high and beside that petroleum is non-renewable natural resource, so it may be gone someday. Alternatively, synthesis of polyol can use other material that is renewable, in case it can use waste from edible oil. Synthesis polyol from edible oil waste really can make improvement the use of itself. The synthesis through ozonolysis reaction, which is in this reaction ozone (O_3) have cracked double bonds of un-saturated fatty acid (oleat acid, and linoleat acid) in the waste. At the next step, hydroxyl groups (OH-) in the alcohol mixture merge with the single bonds C-C to produce the polyol.

Objectifs

1. Producing polyol from used palm cooking oil with the ozonolysis reaction.
2. Find the optimum condition to produce polyol from used palm cooking oil.

MATERIALS AND METHODS

Materials

Materials was used in this research are used palm cooking oil, alcohol mixture consist of 10% methanol 99%, 80 % isopropanol and 10% water, sulfuric acid 96% as catalyst. Ozone was generated from oxygen gas with purity 99.5% through ozone generator. KI, $MgSO_4$ anhydrate, KOH, HCl, and acetate anhydrate.

Methods

Prior to the ozonolysis reaction, used palm oil was analyzed for its fatty acid content. The experimental method for this reaction is as follows: A mixture of used palm cooking oil, alcohol mixture (10% methanol, 80% isopropanol, 10% water) and sulfuric acid catalyst is added into a stainless steel reactor equipped with cooling/heating system, stirrer, tube sparger and thermocouple. The molar ratio of methanol to used palm cooking oil is varied according to the experimental design. Ozone was produced from oxygen gas using ozone generator. The exit port of the ozone generator is connected with deep tube and the mixture of ozone and oxygen gases is delivered to the reactor through tube sparger at the bottom. The reactor outlet is connected to a potassium iodide solution trap hence excess ozone will be decomposed. The reaction was run at several isothermal conditions and at certain reaction times. After ozonolysis reaction, the generator was turned off and the product of reaction was then flushed for about 10 minutes with oxygen gas to remove ozone excess. Following this, the reaction product was allowed to attain room temperature and then neutralized using sodium carbonate solution. The solution is then decanted into a separator funnel then warm water was added to attain pH neutral.

The resulted product was then dried with magnesium sulfate anhydrous and then filtered. The polyol product was then analyzed for hydroxyl number, alkali number, and viscosity.

The experiment will be conduct by the variables temperature, reaction time, ratio used palm cooking oil to alcohol (1:3; 1:4; 1:5; 1:6; 1:7), and ozone concentration.

Experimental Design

This research focused on the effect of four independent variables temperature (X_1), reaction time (X_2), molar ratio of oil to alcohol mixtures (X_3), ozone concentration (X_4), and on response variables of hydroxyl number of polyol product (Y). The central value of independent variables was used is temperature of reaction

25°C; reaction time 3 hours; molar ratio of oil to alcohol mixtures 1:5; and ozone concentration 5.8% mol. 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 Variable

Variables	Coded value	Range dan level				
		-2	-1	0	1	2
Temperature (°C)	X_1	15	20	25	30	35
Reaction time (h)	X_2	1	2	3	4	5
Molar ratio	X_3	1:3	1:4	1:5	1:6	1:7
C_{ozone}	X_4	4.8	5.3	5.8	6.3	6.8

RESULTS AND DISCUSSIONS

The characterization of used palm cooking oil using Gas Chromatography shows various fatty acids content as described in Table 2.

Table 2
Fatty Acid Composition of Used Cooking Oil

Saturated fatty acid	Composition (wt %)
Lauric acid	1.78
Myristic acid	1.80
Palmitic acid	39.1
Stearic acid	4.42
Unsaturated fatty acid	**Composition (wt %)**
Oleic acid	36.6
Linoleic acid	12.2

Synthesis of polyol with ozonolysis reaction.
In the experiment, synthesis polyol took place through ozonolysis reaction. Mechanism of the reaction is started by ozone (O_3) attacked and cracked double bonds in un-saturated fatty acid (oleat and linoleat) in used cooking oil.

$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH + O_3 \rightarrow$
(oleic acid-double bond)

$CH_3(CH_2)_7CH\text{-}CH(CH_2)_7COOH$
(oleic acid-single bond)

$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH + O_3 \rightarrow$
(linoleic acid-double bond)

$CH_3(CH_2)_4CH\text{-}CHCH_2CH\text{-}CH(CH_2)_7COOH$
(linoleic acid-single bond)

After the severance of double bonds, the hydroxyl groups (-OH) in the alcohol mixture attach to C-C single bond to formed polyol.

$H_3(CH_2)_7CH\text{-}CH(CH_2)_7COOH + CH_3OH + C_3H_7OH + H_2O$
(oleic acid-single bond) (methanol) (isopropanol)

↓

$CH_3(CH_2)_7CH(OH)\text{-}CH(OH)(CH_2)_7COOH$
(polyol)

$CH_3(CH_2)_4CH\text{-}CHCH_2CH\text{-}CH(CH_2)_7COOH + CH_3OH$
(linoleic acid-single bond) (methanol)

$+ C_3H_7OH + H_2O$
(isopropanol)

↓

$CH_3(CH_2)_4CH(OH)\text{-}CH(OH)CH_2CH(OH)\text{-}CH(OH)(CH_2)_7COOH$
(polyol)

At the observation, the reaction to produced polyol was showed under change of colour of solution.
At beginning, the used cooking oil appeared as a brown colour. After ozonolysis for 2 hours, the colour has changed to brown pale as appeared at figure 3. If the reaction would have continued for 4 hours, the colour would have changed to browner pale. The change of colour was an indication that the reactions between used palm cooking oil and alcohol mixture have formed polyol.

Hydroxyl Number

Hydroxyl numbers refers to number of hydroxyl groups (-OH) in the chemical compound. The reaction between polyol and di-isosianat formed polyurethane as raw material of foam. One of parameters to classified polyol in a good quality is depend on the hydroxyl number, it means higher hydroxyl number, the quality is better because polyol with higher hydroxyl number could easier formed cross link with diisosianat to yields polyol. Base on the data, hydroxyl number is a important parameter to be analyzed. The values of hydroxyl numbers of polyol is shown as follow:

Table 3.
Hydroxil number of polyol

Observation	Time (hour)	Mol Ratio	% [O_3]	Temp. (°C)	Hydroksil Number
	x_2	x_3	x_4	x_1	
1	2	1 : 4	4.8	20	183.3181
2	4	1 : 4	4.8	20	233.3141
3	2	1 : 6	4.8	20	185.3129
4	4	1 : 6	4.8	20	236.3312
5	2	1 : 4	5.8	20	255.0111
6	4	1 : 4	5.8	20	257.8537
7	2	1 : 6	5.8	20	262.1757
8	4	1 : 6	5.8	20	265.6214
9	2	1 : 4	4.8	30	115.0608
10	4	1 : 4	4.8	30	119.5931
11	2	1 : 6	4.8	30	127.6513
12	4	1 : 6	4.8	30	127.9513
13	2	1 : 4	5.8	30	126.9793
14	4	1 : 4	5.8	30	129.0875
15	2	1 : 6	5.8	30	127.0233
16	4	1 : 6	5.8	30	129.5371
17	1	1 : 5	5.3	25	130.3682
18	5	1 : 5	5.3	25	153.8018
19	3	1 : 3	5.3	25	139.0150
20	3	1 : 7	5.3	25	151.6910
21	3	1 : 5	4.3	25	137.4228
22	3	1 : 5	6.3	25	157.6109
23	3	1 : 5	5.3	15	145.8878
24	3	1 : 5	5.3	35	92.7497
25	3	1 : 5	5.3	25	142.2484
26	3	1 : 5	5.3	25	143.4061
27	3	1 : 5	5.3	25	141.7285
28	3	1 : 5	5.3	25	143.4208
29	3	1 : 5	5.3	25	142.8178
30	3	1 : 5	5.3	25	142.1902

From table 3 above, it is known that hydroxyl number would increased by the time of reaction, for example : from the data number 1 and 2, hydroxyl number of polyol produced in reaction time 4 hours higher than hydroxyl number of polyol produced in reaction time 2 hours. The results can be explained as follow: longer time of reaction caused contact between used cooking oil and alcohol in the reactor is more intense and so more amount of polyol produced.

In table 3, it is also known that increase of ozone concentration caused increase of hydroxyl number. Ozone concentration gives an effect to conversion of used palm cooking oil. Ozone is a reagent that promote the severance of double bonds C=C at unsaturated fatty acid in used cooking oil. Higher ozone concentration, more amount of the severance of double bonds C=C unsaturated fatty acid, so more amount of hydroxyl groups (-OH) in alcohol mixture inserted and attached to single bonds C-C to formed a polyol. For example, it is shown in observation number 1 and 5, the data have shown that raising ozone concentration promote raising of hydroxyl number of polyol .

For the temperature, the use of higher temperature of reaction gave a significant effect to hydroxyl number too. At high temperature, alcohol mixtures will be vaporized and as result amount of alcohol mixture reacted with used palm cooking oil decreased and polyol product from the reaction has a lower hydroxyl number. Other reason why hydroxyl number of polyol decreased at high temperature is at high temperature solubility of ozone is small. Upon the data observation number 9 until number 16 (for temperature 30 °C), hydroxyl number at

these variables is lower than hydroxyl number at other data observation. At the data observation number 24 (for temperature 35 °C), hydroxyl number at these conditions is lowest than hydroxyl number at other data observation. At lower temperature, solubility of ozone in used palm cooking oil went up and so ozone concentration in oil phase went up too, and as consequence rate of reaction to yield polyol will increase. For this reason why hydroxyl number of polyol at temperatures of reaction 15 °C, 20 °C, and 25 °C more than hydroxyl number polyol at other temperatures of reaction as 30 °C and 35 °C.

At table 3, it is shown that raising of mol ratio between used palm cooking oil and alcohol mixtures promote raising of hydroxyl number. The phenomenon could be explained that if mol ratio oil phase -alcohol mixtures rose, total of mol ester polyol increased too. At higher concentration of alcohol mixtures consist of methanol, isopropanol and water, the reaction between used palm cooking oil – alcohol mixtures will produces polyol with characteristic higher hydroxyl number.

The experiment has produced polyol with hydroxyl number in the range 92.75 – 265.62. The highest hydroxyl number is reached at condition: reaction time 4 hours, mol ratio oil phase-alcohol mixtures 1:6, ozone concentration 5.8 % and temperature of reaction 20 °C. By the statistic test (response optimization), optimum point is in condition: reaction time 3 jam, mol ratio oil phase – alcohol mixtures 1 : 7, ozone concentration 6.3 %, and temperature of reaction 25 °C. At this point, the hydroxyl number is 220.

Viscosity

There are several factor influenced the viscosity of polyol product, one of them is molecular weight. The products of polyol in experiment have the difference characteristic in hydroxyl number, the difference of hydroxyl number made the difference of structure of molecules, and as result the molecular weight is also difference. The difference of molecular weight influenced the viscosity of product. Polyol from experiment have viscosity in the range 9.228 cp - 20.403 cp. The highest viscosity is reached at condition: reaction time 4 hours, mol ratio oil phase – alcohol 1: 6, ozone concentration 4.8% and temperature of reaction 30 °C. Further, the viscosity will influenced the characteristic product of polyurethane if the process will be continued. When the polyol is viscous, so it will formed rigid foam, and in the other condition when the polyol has lower viscosity, so it will formed flexible foam.
This is the value of viscosity of polyol at several conditions:

Table 4.
Viscosity of polyol from experiment

Obser-vation	Time (hour)	Mol Ratio Reactant	(%) [O_3]	Temp. (°C)	Viscosity (cp)
	x_2	x_3	x_4	x_1	
1	2	1 : 4	4.8	20	14.7012
2	4	1 : 4	4.8	20	17.1446
3	2	1 : 6	4.8	20	8.4704
4	4	1 : 6	4.8	20	15.5156
5	2	1 : 4	5.8	20	10.7510
6	4	1 : 4	5.8	20	12.7057
7	2	1 : 6	5.8	20	9.5700
8	4	1 : 6	5.8	20	13.1537
9	2	1 : 4	4.8	30	11.3211
10	4	1 : 4	4.8	30	18.0405
11	2	1 : 6	4.8	30	13.9274
12	4	1 : 6	4.8	30	20.4025
13	2	1 : 4	5.8	30	15.5075
14	4	1 : 4	5.8	30	14.9048
15	2	1 : 6	5.8	30	12.2985
16	4	1 : 6	5.8	30	18.3256
17	1	1 : 5	5.3	25	13.2351
18	5	1 : 5	5.3	25	19.0586
19	3	1 : 3	5.3	25	10.2623
20	3	1 : 7	5.3	25	14.1717
21	3	1 : 5	4.8	25	13.0722
22	3	1 : 5	6.3	25	14.9048
23	3	1 : 5	5.3	15	16.7373
24	3	1 : 5	5.3	35	9.2279
25	3	1 : 5	5.3	25	14.6604
26	3	1 : 5	5.3	25	15.1084
27	3	1 : 5	5.3	25	14.4568
28	3	1 : 5	5.3	25	14.4975
29	3	1 : 5	5.3	25	14.4161
30	3	1 : 5	5.3	25	14.4161

In order to make clear the correlation between variables of the experiment to hydroxyl number,

it is shown the figure 2; figure 3; and figure 4 below.

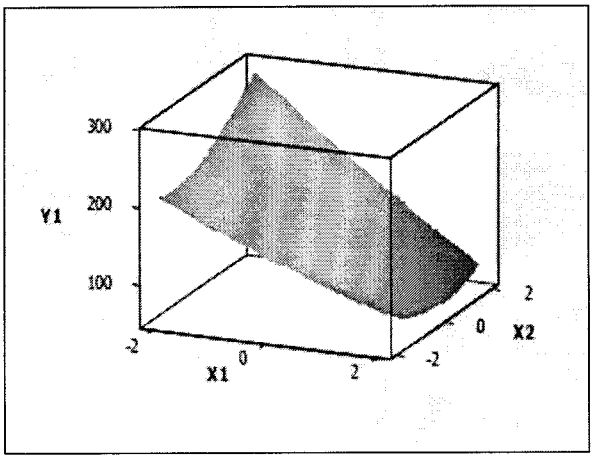

Figure 2. The effect of temperature (x_1) and time of reaction (x_2) to hydroxyl number

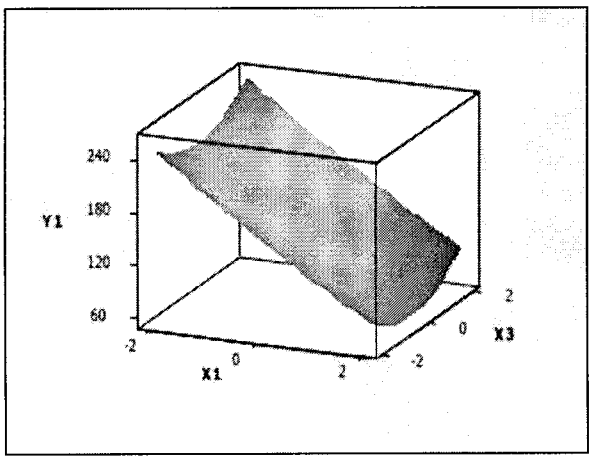

Figure 3. The effect of temperature (x_1) and mol ratio-reactant (x_2) to hydroxyl number

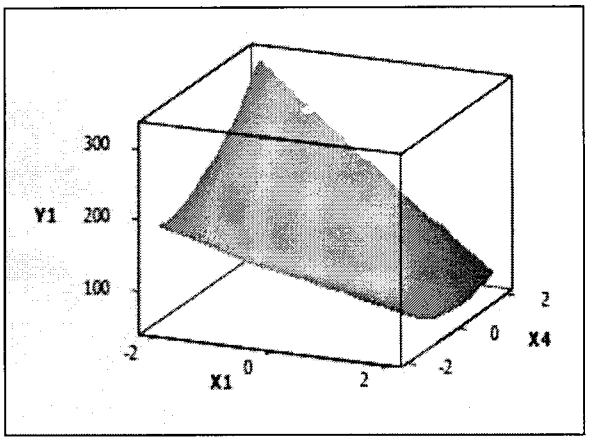

Figure 4. The effect of temperature (x_1) and ozone concentration (x_4) to hydroxyl number

From the figures above, it is shown that hydroxyl number is increasingly by the time of reaction, ozone concentration, and mol ratio between oil phase – alcohol, and as other result shown that hydroxyl number is decreasingly by higher temperature of reaction. The information is the same with the previous explanation.

CONCLUSIONS

1. At the condition is as below: longer time of reaction, higher ozone concentration, lower temperature of reaction, and higher mol ratio between used palm cooking oil-alcohol mixtures, the hydroxyl number will increased.
2. Polyol from the experiment have hydroxyl number is in the range of 92.75 – 265.62. The highest of hydroxyl number is reached at condition: reaction time 4 hours, mol ratio used palm cooking oil – alcohol mixtures 1:6, ozone concentration 5.8 %, and temperature of reaction 20 °C. The optimum result is in condition: reaction time 3 hours, mol ratio used palm cooking oil-alcohol mixtures 1: 7, ozone concentration 6.3 %, and temperature of reaction 25 °C. The optimum hydroxyl number is 220.
3. Polyol from the experiment have viscosity is in the range of 9.228 – 20.403 cp. The highest viscosity is

reached at condition: reaction time 4 hours, mol ratio used palm cooking oil–alcohol mixtures 1:6, ozone concentration 4.8 % and temperature of reaction 30 °C.

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