



Catalyzed Reaction with Vegetable Oil: Nucleophilic Addition of Alcohols to Soy Epoxide

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Abstract— The epoxidation of soybean oil at temperature of 60°C was provided the best result in terms of attaching the –OH functionality. Temperatures below and above 60°C it is likely the attaching reaction did not proceed sufficiently fast. The considerable yield below 40%, implies the oil is not completely converted, it is not possible by conventional methods, because the epoxide decomposes at the temperature required. The objective of this work was the development of catalyst toward the conversion of epoxide and polyol with reaction temperature at 50,60, and 70°C. The influence of different type of catalyst were studied, the effect of alcohols with different molecular configuration was determined which leads to selective addition of alcohols to the epoxide oils.

Keywords— epoxide, soybean, catalyst

I. INTRODUCTION

The preparation of polymers from renewable resources is of significant economic and scientific importance. Vegetable oils have a number of excellent properties that can be utilized in producing valuable polymeric materials. The oils are characterized by their oxirane number and hydroxyl value.¹⁻³ Vegetable oils are part of larger family of chemical compounds known as fats or lipids, which made up predominantly of triesters of glycerol with fatty acids called triglycerides. The chemical structures of lipids are combination and permutations of fatty acids that can be esterified through hydroxyl groups of glycerol. The composition of fatty acids contained in the vegetable oils determines the further use of oils; which can be transformed into polyol through double bonds epoxidation and oxirane ring opening.⁴⁻⁶

Soybean, palm, and sunflower contain mainly long chain fatty acids (C18) which are used as raw materials for polymer applications. Triglycerides offer two reactive sites, the double bond in the saturated fatty acid chain and the acid group of the fatty acid chain. The majority of derivatization reactions is carried out the carboxylic group, whereas oleochemical reactions involving the alkyl chain or double bond.⁷

The preparation of polyols from oils has been the subject of many studies, but limited attention has been paid to the effect of different alcohol of small molecular weight, used as the ring opening reagents with soy epoxide oil.⁸⁻⁹

Epoxide known as oxirane; cyclic ethers with three membered ring. The highly strained ring in the molecules makes more reactive than others ethers which highly susceptible to ring opening reactions; a cleavage of one of the carbon-oxygen bonds, which can be initiated by either electrophiles or nucleophiles, or catalyzed by either acids or bases. Epoxidation with percarboxylic acids is generally catalyzed by soluble mineral acids like sulfuric, tungstic or molybdic acids.¹⁰ The reactions catalyzed by clays are carried out under mild conditions, the separation of the spent catalyst is achieved by filtration, and the product is recovered by mere evaporation of solvent. In particular, the microporous structure and surface acidity is of great interest of carrying out reactions.¹¹

In the present work, the soy-based polyols were synthesized by using epoxy ring opening reaction with different small molecular weight alcohols. These epoxy ring opening reaction gave a range of different structures, which when converted to polyurethanes imparted different properties to the final products.

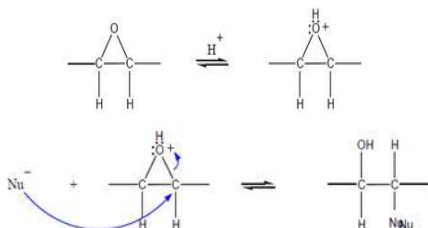
II. EXPERIMENTAL

A. Materials

Soybean oil of RBD (Refined, Bleached, Deodorized) was obtained from Variatama Jakarta with specifications of Iodine value 53,89 gram Iod/100 gr sample, viscosity

65,5278 cps, acid value 0,024 mgr KOH/ gr sample, and with atomic weight of 0.538. Hydrogen peroxide from Brataco Chemika, acetic acid from Merck Germany, and sulphuric acid from Tedia Company, Inc. All materials were used as received without further purification.

Soy polyols were synthesized from soy epoxides, with alcohols; methanol, butanol, ethylene glycol (Ethyl Gly) using acid liquid catalyst. The performance of bentonite as a catalyst for throughout the reactions; epoxidation and hydroxylation was chosen as a comparative analysis. The work was done for butanol 1 using acid catalysis named as (but 1) otherwise with bentonite was named as (but 2). The mechanism reaction of nucleophilic attack can be seen on scheme 1.



Scheme 1. Acid catalyzed nucleophilic attack
a. Epoxide activation b. Nucleophilic attack

The reaction conditions were summarized in Table 1.

TABLE I
THE COMPOSITION of POLYOL SYNTHESIS

No	Methanol (ml)	Butanol (ml)	Ethyl Gly (ml)	Catalyst	
				Liquid (ml)	Solid (ml)
1	13.08	-	-	0.25	-
2	10.9	-	-	0.26	-
3	-	14.8	-	0.3	-
4	-	4.935	-	0.19	-
5	-	-	10.1	0.25	-
6	-	-	16.84	0.25	-
7	-	24.6	-	-	0.39
8	-	16.84	-	-	0.3

The reaction duration is 2 hr with temperature 117⁰C
The ratio of epoxy/alcohols based on stoichiometric calculations (mol/mol)

III. RESULTS AND DISCUSSIONS

The preliminary work was to determined the optimal catalyst concentration which was done in three variables. It was found the optimal concentration was 1% of the

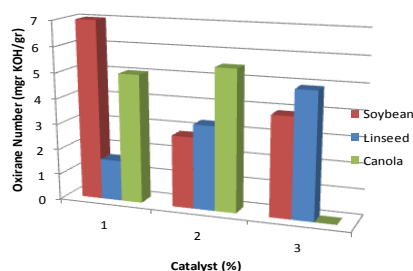


Fig. 1. Catalyst for epoxidation at 60°C

total weight of epoxide and alcohol, but the result differ to other edible oil; canola and linseed oil which is related to the composition of unsaturated fatty acid in the oil.

Synthesis of Epoxide

A. The Effect of time reaction and temperature

The reaction of alcohols with soybean were done at temperature of 50,60, and 70⁰C. It was found reaction temperature of 60⁰C was the best result in terms of attaching the -OH functionality to the soybean oil which was confirmed through the oxirane number of epoxide. Temperatures below and above 60⁰C it is likely the polymerization/attaching reaction did not proceed sufficiently fast. It is clearly approved by 30 minutes and 150 minutes of reaction either 50 and 60⁰C mostly a lower -OH functionality can be attributed to the further reaction of -OH group. In the case of the reaction of alcohol with soybean oil, a temperature 60⁰C with 90 minutes of reaction of CH₃COOH/H₂O₂ 1:6.5 (mol/mol) was selected for the study, which was confirmed through FTIR analysis. From the spectrum occurs at a wavelength band widening 3388.93 and 3356.14 cm⁻¹ after the formation of polyols.

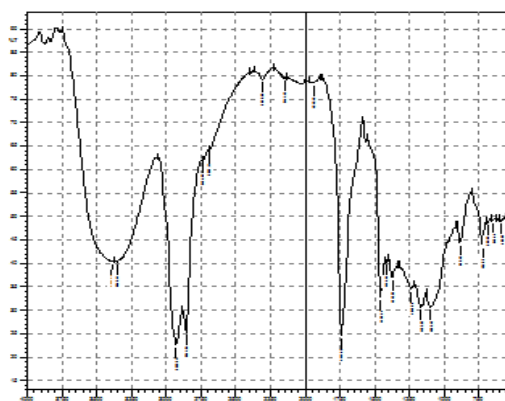


Fig 2. Spectrum IR soy polyol

In the figure below compares the conversion of epoxide using a concentration equal to three variables namely the reaction temperature 50,60,70⁰C. The indicator used was oxirane number (%). It is clearly can be seen that the conversion of epoxides was best at reaction temperature of 50⁰, otherwise epoxide conversion at temperature of 70⁰ C tends to be low.

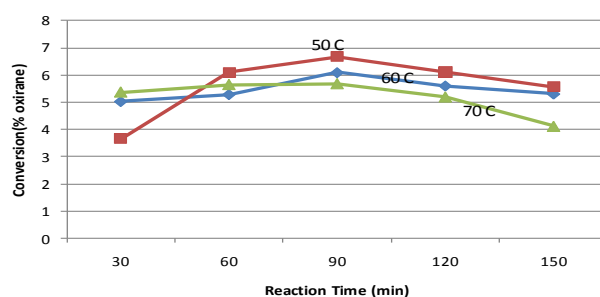


Fig 3. Epoxidation with peracetic acid with temperature reaction 50, 60, and 70°C

The catalytic results of homogeneous acids for the epoxidation conversion using three variable concentrations

were 1:4.3, 1:4.4, and 1:6.4 at temperature 50°C. The concentration ratio of 1:6.4 and 1:4.3 was the maximum conversion achievement at reaction time 150 minutes.

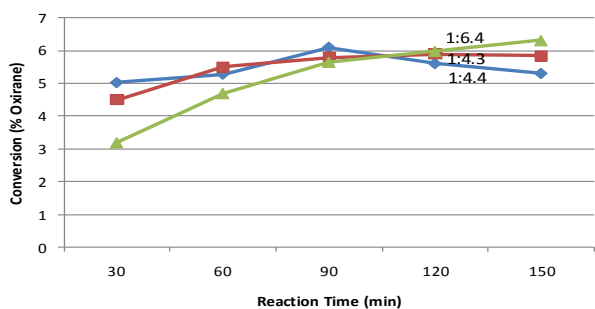


Fig. 4 Epoxidation with peracetic acid at 50°C. The concentration was a ratio of acetic acid to H₂O₂.

The activity of the acid liquid catalyst on epoxide conversion are presented in figure 5, the reaction was carried out at 60°C using three variable concentrations. At all concentrations the best conversion was achieved at 90 minutes of reaction.

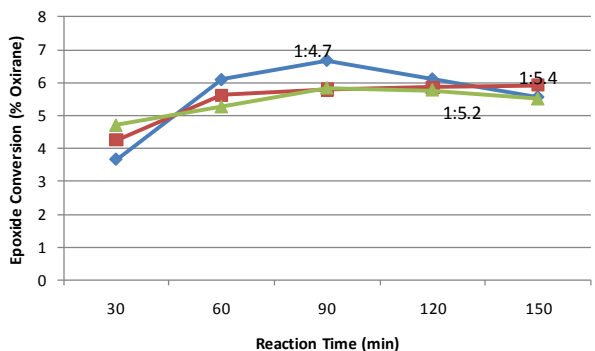


Fig. 5. Epoxidation with peracetic acid at 60°C. The concentration was a ratio of acetic acid to H₂O₂.

The comparative result of fig 4 to fig 5 above, has made up a conclusion the reaction occur for epoxide conversion with the same liquid acid catalyst was the best at 60°C.

B. Effect of concentration

The table 1 summarizes the various ratios of alcohols taken previously in terms of volume (ml) of the oil taken. From the analysis of the products obtained it can be concluded that the reaction either reaches equilibrium or completion after a certain point and does not proceed any further in spite of having a larger concentration of alcohols in the oil.

One possible explanation for this is that there might be a steric hindrance after a point which does not allow the further interaction between the double bonds of the oil and the double bond present both in alcohols.

The considerable yield below 40%, this implies that the oil is not completely converted, it is not possible by conventional methods, because the epoxide decomposes at the temperature required. The higher activity of butanol 2 compared to butanol 1 can be rationalized in terms of the higher acid strength of bentonite to acid liquid catalyst.

The poor selectivities obtained with the bentonite is important to remark, it can be either because of the small pore size of solid catalyst or forming by-product exist from the epoxide ring opening reactions; quantitatively ketone production by temperature condition at 110°C, presented in fig 6.

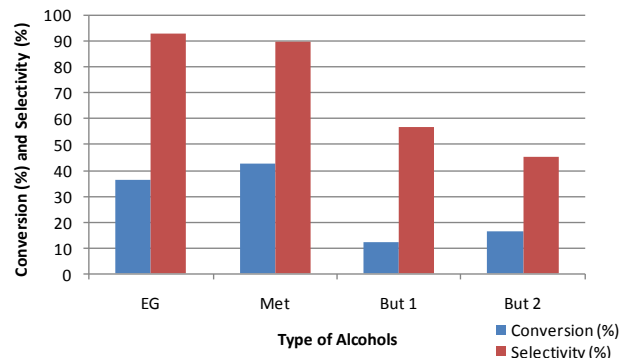


Fig 6. Hydroxylation of epoxide with alcohols. Reaction time 120 minutes

In table 2 shows the time reaction were significantly influence to the polyols oxirane number. Logically all epoxides reactions will cause the open nucleophilic ring which formed a decreased oxirane number. In the polyol (but 1) and (but 2) even it was synthesized by using NÚ butanol, but it has different response in the reaction scheme because the role of the two catalysts.

TABLE 2
THE EFFECT of TIME of REACTION to REDUCTION POLYOL OXIRANE NUMBER

Epoxide*/ alcohol (mol/mol)	Oxirane Number (mgr KOH/gr sample)							
	Methanol		Butanol 1		Ethyl Gly		Butanol 2	
	1 hr	2 hr	1 hr	2 hr	1 hr	2 hr	1 hr	2 hr
0.042	2.47	1.95	0.17	0.12	0.47	1.03	0.45	1.03
0.043	0.36	0.65	0.19	0.09	0.46	0.33	0.46	0.33
0.045	0.11	0.27	0.2	0.18	0.25	0.3	0.25	0.3
0.046	0.17	0.14	0.17	0.14	0.38	0.6	0.38	0.6

*oxirane number of epoxide is 6.7 mgr KOH/gr

Hydroxylation of butanol 1 and butanol 2 result a polyol; which were distinguished by the use of catalysts; acid liquid and acid solid. From this results it is clearly the decrease in oxirane number using bentonite catalyst is greater than liquid acid catalysts. This imply the bentonite which is a solid acid catalyst also took part in the reaction, thus forming more active site of OH.

In summary, in conjunction of fig 6 and table 2 these results indicate the conversion epoxidation of vegetable oils using mono alcohol: methanol and butanol with peracetic acid and catalyzed by homogeneous acids, has to minimize the contact of the newly formed polyol with the acidic centers of the catalyst because it may be assume will produce epoxide rearrangement as second by-product which can influence to misintreppettation, of the inclining of oxirane number.

IV. CONCLUSIONS

The higher activity of butanol 2 compared to butanol 1 can be rationalized in terms of the higher acid strength of bentonite to acid liquid catalyst. The poor selectivities obtained with the bentonite is important to remark, it can be either because of the small pore size of solid catalyst; The considerable yield below 40%, implies the oil is not completely converted, it is not possible by conventional methods, because the epoxide decomposes at the temperature required.

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REFERENCES

- [1] S.S.Narine, X. Kong X, Bouzidi L, Sporns Physical Properties of Polyurethanes produced from Polyols from seed oils: I. Elastomers. *J.Am.Oil Chem Soc* 84:55-63, 2007
- [2] S.S Narine, X Kong, L Bouzidi, Sporns, Physical Properties of Polyurethanes produced from Polyols from seed oils: II. Elastomers. *J.Am.Oil Chem Soc* 84: 65-72, 2007
- [3] B Lin, LYang, H Dai, A Yi, Kinetic Studies on oxirane cleavage of epoxidized soybean oil by methanol and characterization of polyols, *J. Am Oil Chem Soc* 85:113-117, 2008
- [4] Y Hong Hu., Y Gao, D.N Wang, C.P Hu, S Zu, L. Vanoverloop and D Randall, *Journal of Applied Polymer Science*, 84, p. 591; 2005
- [5] K.H Badri, S.H Ahmad and S Zakaria, *Journal of Applied Polymer Science*, 81, p.384, 2001
- [6] A Zlatanic, C Lava, W Zhang. and Z Petrovic, *Journal of Polymer Science, Part B: Polymer Physics*, 42, p.9, 2004
- [7] H Bauman, M Bühler, H Fochen, F Hirsinger, H zoebelien *Angew. Chem. Int. Ed Engl.*, 27, p.41-62, 1998
- [8] VV Goud, AV Patwardhan, NC Pradhan, Studies on the Epoxidation of Mahua Oil (*Madhumica Indica*) by Hydrogen Peroxide. *Bioresource Technol* 97: 1364-1371, 2006
- [9] D Honghai, Y Liting, L Bo, W Chengsuang and S Guang, Synthesis and Characterization of the Different soy-based polyols by ring opening of epoxidized soybean oil with methanol, 1,2 ethanadiol and 1,2 propanediol, *J. Am Oil Chem Soc*, 86:261-267, 2009
- [10] NS Trahanovsky: *Oxidation in Organic Chemistry*, 5, Part C, Chapter 3, Academic Press, New York, pp. 211-294, 1978
- [11] K Inui., T Kurabayashi, S Sato, N Ichikawa, *J. Mol Catal. A*, 216; 147, 2006