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Synthesis of bio-polyols by epoxide ring opening reaction with H₂O as a reagent

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Abstract

The different nucleophilic reagents have been using in epoxide ring opening reactions among which water is the most preferable. At first, the epoxide group must be protonated by water in the presence of H₂SO₄ as catalyst. The successful epoxide ring opening reaction of epoxidized soybean oil (ESO) by water in the H₂SO₄ environment was verified by FTIR and H-NMR spectroscopy. The effect of reaction parameters like the amount of reagents, catalyst, temperature and time of a polyol synthesis were studied through the hydroxyl and oxirane oxygen content of product. Moreover, the impact of the parameters on the correlation P/E was determined by comparing a hydroxyl group formation to an epoxide group consumption. When the hydroxylation reaction was carried out with ESO:H₂O mole ratio of 1:15; in 8 wt.% H₂SO₄; at temperature of 70 °C and in 5 hours, the hydroxyl content of 358.51 mgKOH/g of the obtained product was achieved.

Keywords. Epoxidized vegetable oil, biopolyol, epoxide ring-opening, epoxidized soybean oil.

1. INTRODUCTION

There are many methods to synthesize polyols from a epoxidized vegetable oil (EVO). These methods can be divided into two groups. Group 1 (indirect method) - polyols are synthesized from the epoxidized vegetable oil through the formation of intermediate compounds. This group has two methods: method 1-the epoxidized vegetable oils were first performed by ring-opening polymerization catalyst HBF₄, then reduced by catalytic LiH₄; method 2 – the epoxidized vegetable oil was initially carbonized by CO₂ and catalyst, then ring opened by agent of HR forms such as HN[R'OH]₂. Group 2 (direct method) – polyol is synthesized directly from the epoxidized vegetable oil without going through intermediate compounds. This group has also two methods: method 1 - polyol is synthesized by the hydrogenation of epoxidized vegetable oil with catalyst of Ni; method 2 - polyol is synthesized by epoxide ring opening reaction in the presence of ring-opening agent of HXR form such as HR, H₂O [1].

Biobased polyols were synthesized from reaction between epoxidized soybean oil and lactic, glycolic, or acetic acids by Sylvain Caillol and the average hydroxyl functionality of polyol were between 4 and 5 [2]. According to Zlatanić, the polyols were

synthesized from six epoxidized oils by epoxide ring opening reaction with boiling methanol in the presence of a tetrafluoroboric acid catalyst and the hydroxyl value of these polyols ranges from 163.5 mgKOH/g to 247.8 mgKOH/g [3]. A.A. Beltrán and L.A. Boyacá studied epoxide ring-opening reaction of epoxidized soybean oil with ethylene glycol and ethanol by using catalyst of H₂SO₄ in the period from 2 to 6 hours and found the optimal temperature is 70 °C with ethanol and 80 °C with ethylene glycol [4].

This work studied the influence of reaction parameters like the amount of reagents (H₂O), catalyst (H₂SO₄), temperature and time on the hydroxylation reaction in order to find the optimal conditions for synthesis of the bio-polyol with high hydroxyl content.

2. EXPERIMENTAL

2.1. Materials

Vietnam soybean oil with iodine value of 131 cgI₂/g. Sodium tungstate dehydrate and Wijs solution are from Merck, Germany. Hydrogen bromide solution (33 wt.%) is of Sigma-Aldrich, USA. Phosphoric acid H₃PO₄ (85 wt.%) and hydrogen peroxide (30 wt.%), sulfuric acid H₂SO₄ (98 wt.%), glacial acetic acid are from Xilong Chemical, China.

2.2. Methods

2.2.1. Epoxidation procedure

The reaction was performed in a 500 ml four neck flask equipped with a stirrer, thermometer, dropping funnel and reflux cooler. The Vietnam soybean oil and catalyst were added to the flask and then the 30wt.% hydrogen peroxide was dropped. After charging H_2O_2 was completed, the reaction was continued mixing for another hour. After that, the mixture was cooled down and treated with water. The final product (ESO) was dried out by heating about $60^\circ C$ in a vacuum oven.

2.2.2. Hydroxylation procedure

The reaction was carried out in the 500 ml three neck flask equipped with a stirrer, thermometer and reflux cooler. The ESO, reagent of H_2O and catalyst of H_2SO_4 were added to the flask. After charging, the reaction was continued mixing at certain temperature for a further time. After that, the mixture was cooled down and treated with water. The final product was dried out by heating at about $60^\circ C$ in the vacuum oven.

2.2.3. Analytical techniques

Fourier transform infrared spectroscopic analysis and nuclear magnetic resonance spectroscopic analysis were performed on the IRAffiniti-1S, Shimadzu (Japan) and Bruker Avance 500 (USA).

Iodine value is determined according to standard ASTM D5768: sample was dissolved in the solvent in the presence of Wijs solution and titrated with 0,1N $Na_2S_2O_3$ solution. Oxirane content is determined according to standard ASTM D1652: sample was dissolved in the solvent and titrated directly with HBr solution 0,1N. Hydroxyl content is determined according to standard ASTM D1957: sample was first acetylated and then titrated by KOH solution 0,5N. The density and viscosity are determined by using pycnometer 25ml (China) and Brookfield Model RVT (Germany) respectively.

3. RESULTS AND DISCUSSION

3.1. Synthesis and characteristics of ESO

Epoxidized soybean oil was synthesized according to a published procedure [5]. The characteristics of ESO are shown in table 1.

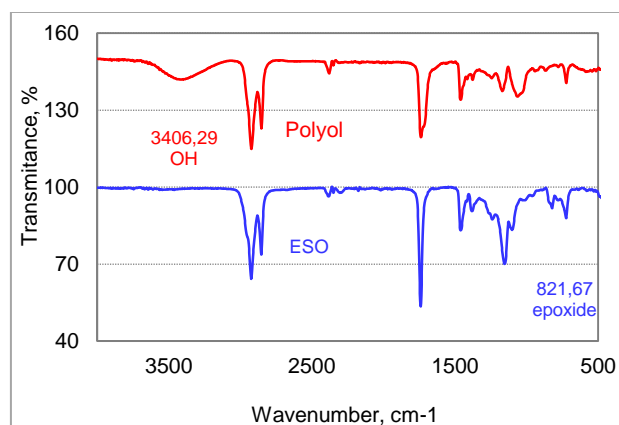
Table 1: Characteristics of ESO and biopolyol

Characteristics	ESO	Biopolyol
Hydroxyl content, mgKOH/g	18.02	358.51
Oxirane content, %	6.68	0.73
Iodine value, cgI ₂ /g	7.5	2.87
Density 20 °C, g/ml	1.02	1.02
Viscosity 20 °C, cP	375	1920

3.2. Evaluating the result of epoxide ring opening reaction

The success of the hydroxylation reaction associated with the formation of hydroxyl groups on macromolecule of the product. The FTIR spectroscopic analysis of obtained polyol and epoxidized soybean oil was studied to confirm the presence of hydroxyl groups on macromolecules.

FTIR spectra of epoxidized soybean oil and polyol are shown in figure 1. The disappearance of the band at 821.67 cm^{-1} in the spectra of polyol indicated that the epoxide group had been used up. The appearance of the band at 3406.29 cm^{-1} , which was not seen in spectra of epoxidized soybean oil (ESO), was the characteristic of the hydroxyl group that connected with carbon atom. This analysis confirmed that the hydroxylation reaction had taken place.



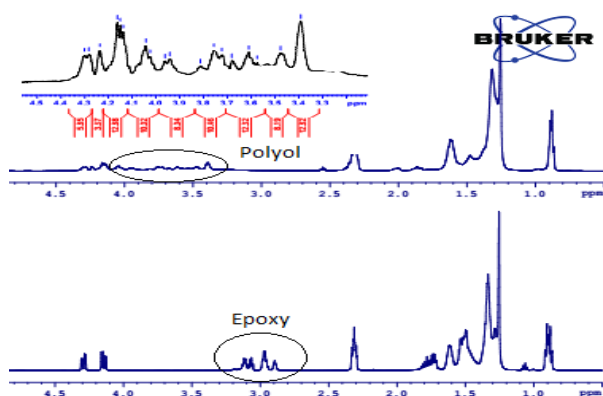
Polyol was synthesized with ESO: H_2O molar ratio of 1:10; H_2SO_4 8 wt.%; $70^\circ C$; 2000 rpm

Figure 1: FTIR spectrum of ESO and polyol

In parallel with the FTIR spectroscopic analysis, nuclear magnetic resonance spectroscopy was used as well. The 1H -NMR spectra of epoxidized soybean oil and polyol are shown in Fig. 2.

It is found that the peaks at 2.9÷3.3 ppm which are the characteristic of epoxide group protons

existed clearly on the $^1\text{H-NMR}$ spectra of the ESO but these peaks did not appear in the $^1\text{H-NMR}$ spectra of the polyol. Also the peaks at 3.4–4.1 ppm were assigned to the protons of methine $-\text{CH}-$ and hydroxyl groups connected to carbon atom (HC-OH) were absent from the $^1\text{H-NMR}$ spectra of ESO but appeared on the $^1\text{H-NMR}$ spectra of the polyol. This proves the epoxide groups in the ESO were converted to hydroxyl groups in the polyol. The results of the nuclear magnetic resonance spectroscopic analysis once again confirmed the success of hydroxylation reaction.



Polyol was synthesized with ESO:H₂O molar ratio of 1:20; 8 wt.% H₂SO₄; 70°C; 2000 rpm

Figure 2: $^1\text{H-NMR}$ spectrum of ESO and polyol

3.3. The impact of reaction parameters on the hydroxylation reaction

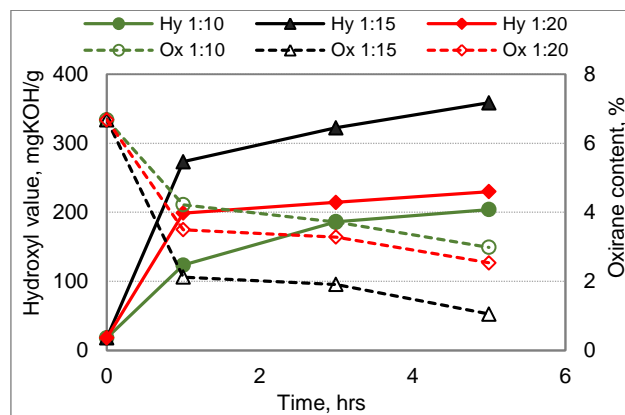
3.3.1. The effect of reagent content

A series of hydroxylation reactions were carried out at 70 °C temperature, 2000 rpm stirring speed, the molar ratio of the epoxide group of ESO to water (ESO:H₂O) in the range of 1:10 to 1:20 and the concentration of H₂SO₄ was fixed at 8 wt.%. The progress of reaction was monitored by measuring the oxirane and hydroxyl content of products.

As can be seen from Fig. 3, prolonging reaction time decreased the oxirane content of polyol while increased the hydroxyl content. When raising the amount of H₂O from molar ratio of 1:10 to 1:15, the oxirane content of polyol declined remarkably, indicating that the ability to open epoxide ring increased strongly and consequently the hydroxyl content of polyol grew remarkably as well.

Increasing further the amount of H₂O to 1:20, the oxirane content of polyol had greater value than the reaction with molar ratio of 1:15 but smaller value than the one with molar ratio of 1:10. This demonstrated the ability to open the epoxide ring in this case was lower than the case of 1:15, but higher

than the one of 1:10. The inevitable result of the hydroxyl content of the polyol in this case also followed the same trend. The ESO:H₂O ratio of 1:15 has the highest ability to either open the epoxide ring or form the hydroxyl group.



Hy: hydroxyl content, Ox: oxirane content

Figure 3: The effect of H₂O content on the oxirane and hydroxyl contents of polyol

The correlation between hydroxyl group formation (P) and the epoxide group consumption (E) (it was called correlation P/E) allows to evaluate the presence of site reaction, in which:

$$P = \frac{\text{Hydroxyl content}_{exp} - 18,02}{\text{Hydroxyl content}_{th}} \times 100 \quad (1)$$

$$E = \frac{6,68 - \text{oxirane content}_{exp}}{6,68} \times 100 \quad (2)$$

(exp: experiment; th: theory)

From the oxirane content of ESO (6.68%), it is easy to calculate theoretical hydroxyl content of the polyol (468.435 mgKOH/g). The effect of H₂O content on the correlation P/E is presented in Fig. 4.

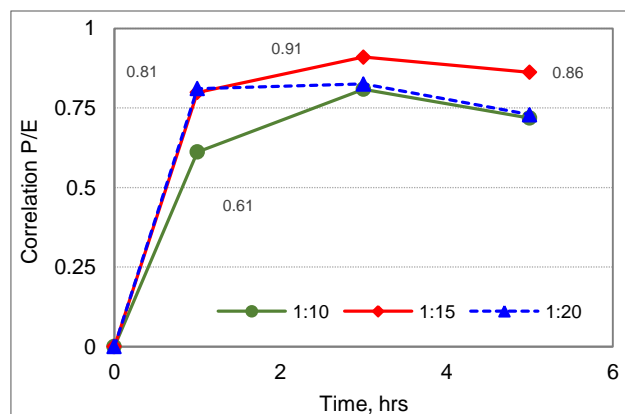


Figure 4: The effect of H₂O content on the correlation P/E

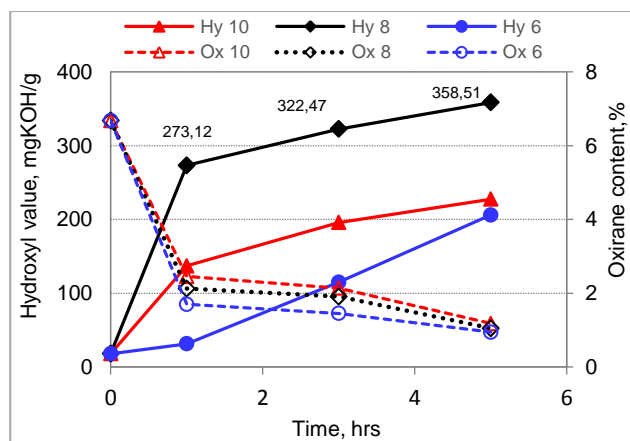
As can be noticed from Fig. 4, when the amount of H₂O was small (1:10 and 1:15), along with the prolongation of reaction time, the correlation P/E increased and reached the maximum value (for three hours) and then decreased with further increase in reaction time. When the amount of H₂O increased from 1:10 to 1:15 molar ratio, the correlation P/E increased from 0.61 to 0.81 (for one hour) and from 0.81 to 0.91 (for three hours).

Increasing the amount of H₂O to the molar ratio of 1:20, the correlation P/E for one hour reaction (0.81) showed the same value with that of the molar ratio of 1:15. However, the correlation P/E in three or five hours declined obviously to the same value with that of the molar ratio of 1:10.

Therefore, the ESO:H₂O ratio of 1:15 showed the highest in either the hydroxyl group or the correlation P/E, indicating that this reaction had the lowest degree of side reactions.

3.3.2. The effect of catalyst content

Three hydroxylation reactions were carried out at 70 °C temperature, 2000 rpm stirring speed, the molar ratio of ESO:H₂O was fixed at 1:15 and the concentration of catalyst H₂SO₄ changed from 6 wt.% to 10 wt.%. The progress of reaction was monitored by determining the oxirane and hydroxyl contents of products. The results are shown in Fig. 5.



Hy: hydroxyl content, Ox: oxirane content

Figure 5: The effect of H₂SO₄ content on the oxirane and the hydroxyl content of polyol

The oxirane content declined and the hydroxyl content of polyol increased along with the prolongation of reaction time. When the content of catalyst increased from 6 wt.% to 10 wt.%, the oxirane content had trend of slightly increasing, suggesting that the ability to open epoxide ring reduced gently (Fig. 5).

Unlike the oxirane content, the hydroxyl content of polyol seems to depend noticeably on the content of catalyst. The results indicated that increasing the catalytic content from 6 wt.% to 8 wt.%, the hydroxyl content of polyol increased sharply (from 31.33 mgKOH/g to 273.12 mgKOH/g in one hour and from 206.05 mgKOH/g to 358.51 mgKOH/g in five hours). Further increasing the amount of catalyst to 10 wt.%, the hydroxyl content of polyol was greater than that of 6 wt.% catalyst but much smaller than that of 8 wt.% catalyst (Fig. 5). These results demonstrated that the catalyst of 8 wt.% is optimum content for hydroxylation reaction.

With different catalyst contents, the ability to open ring of epoxide group was not much different but the ability to form hydroxyl group was greatly different so that the correlation P/E was also large different. The effect of H₂SO₄ content on the correlation P/E is described in Fig. 6.

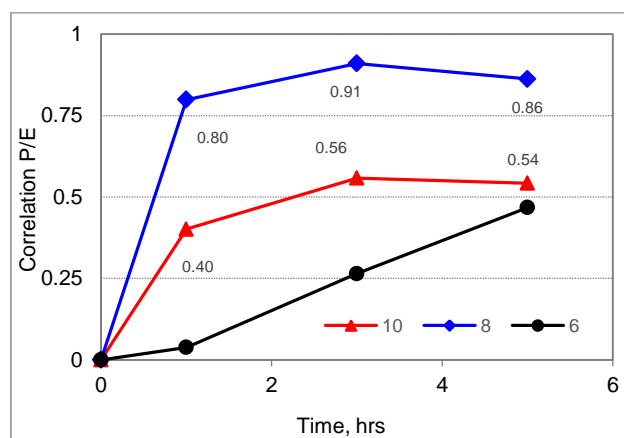


Figure 6: The effect of H₂SO₄ content on the correlation P/E

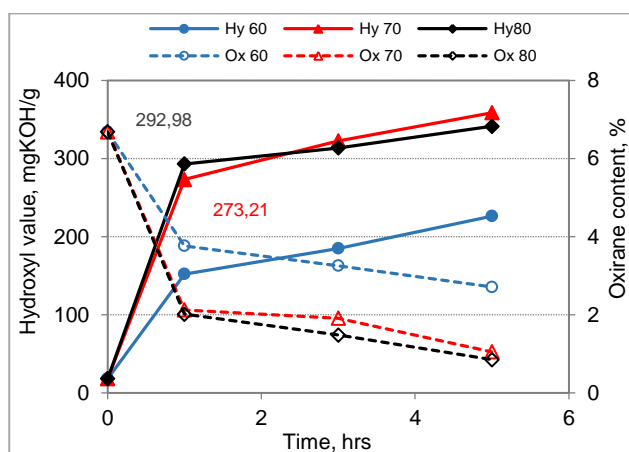
When the amount of catalyst was 6 wt.%, the ability to open ring of epoxide group was the highest but the ability to form hydroxyl group was the lowest (Fig. 5). Thus, the correlation P/E was the lowest (Fig. 6). This illustrated that when the amount of catalyst was small, many side reactions took place. The oxirane content of polyols decreased sharply within the first hour of the reaction and slightly in the following hours. However, the hydroxyl content of polyol increased marginally within the first hour of the reaction and remarkably in the next hours (Fig. 5). These results suggested that the correlation P/E also increased in parallel with the increase of the reaction time (Fig. 6).

When the amount of catalysts was at 8 wt.% and 10 wt.%, the oxirane content of polyol also decreased exceptionally within the first hour of the reaction and gently in the next hours. However, the hydroxyl content of polyol increased strongly within

the first hour of the reaction and lightly in the following hours (Fig. 5). So the correlation P/E increased and reached the maximum value for the reaction in three hours. The correlation P/E decreased with the elongation of the reaction time to five hours. It was indicated that the highest correlation P/E was 0.91 for the reaction in three hours when the amount of catalyst was in 8 wt.% (fig.6).

3.3.3. The effect of temperature reaction

A series of hydroxylation reactions were carried out at 60, 70 and 80 °C temperature, 2000 rpm stirring speed, the molar ratio of ESO:H₂O and the concentration of catalyst H₂SO₄ were fixed at 1:15 and 8 wt.% respectively. The progress of reaction was monitored by measuring the oxirane and hydroxyl contents of products. The results are shown in Fig. 7.



Hy: hydroxyl content, Ox: oxirane content

Figure 7: The effect of temperature on the oxirane and the hydroxyl content of polyol product

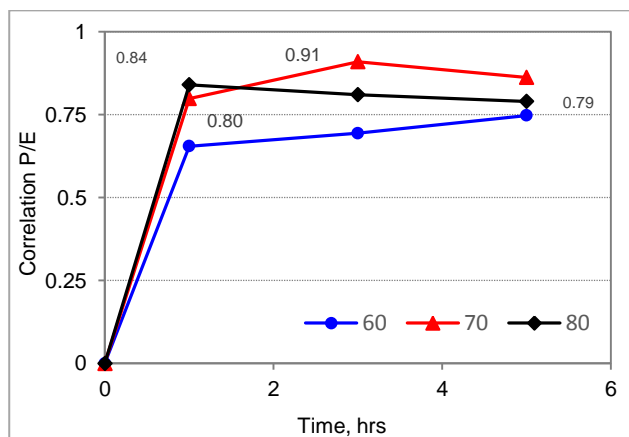


Figure 8: The effect of temperature on the correlation P/E

It was found that when the reaction was carried out at 60 °C, the oxirane content of polyol product remained quite high and the hydroxyl group was low. Raising the temperature to 70 °C, the ability to open epoxide group increased. Moreover, the oxirane contents of polyol product of reaction at 70 °C and 80 °C gave almost the same. However, the hydroxyl group of the product at one hour and 80 °C (292.98 mgKOH/g) was higher than that at 70 °C (273.21 mgKOH/g). Therefore the correlation P/E at one hour and at 80 °C (0.84) was also higher than at 70 °C (0.8 %) (Fig. 8). For the reaction in three hours and five hours, the hydroxyl group of the polyol product at 70 °C was higher than that of at 80 °C. As the result the correlation P/E at 70 °C (0.91 in three hours) was higher than that at 80 °C (0.81 in three hours) (Fig. 8).

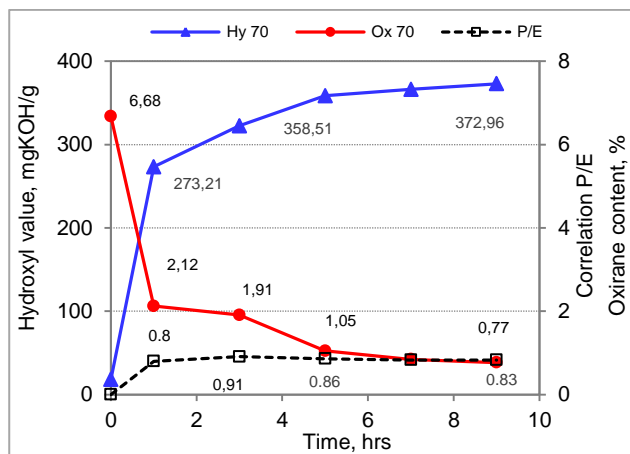
With the temperature of 60 °C, the correlation P/E was likely to increase from one hour to five hours but at 70 °C the correlation P/E increased and reached the maximum value for the reaction in three hours then decreased if further extending the reaction time up to 5 hours. However, when the reaction was carried out at 80 °C, the correlation P/E dropped immediately after the first hour reaction (Fig. 8). That result indicated that prolonging reaction time led to more side reactions.

3.3.4. The effect of reaction time

The hydroxylation reaction was carried out in 9 hours at 70 °C temperature, 2000 rpm stirring speed, the molar ratio of ESO:H₂O and the concentration of catalyst H₂SO₄ were fixed at 1:15 and 8 wt.% respectively. The progress of reaction was monitored by measuring the oxirane and the hydroxyl content of the product. The results are shown in Fig. 9.

As can be seen from Fig. 9, the oxirane content of polyol dropped strongly from 6.68 to 2.12 % for the reaction in one hour and continued to go down 1.05 % for that of five hours but decreased very slowly to 0.77 % when further extending the reaction up to 9 hours. However, the hydroxyl content of polyol raised to 358.51 mg KOH/g at five hours and increased gradually to 372.96 mg KOH/g when further prolonging the time to nine hours. These results indicated that after five hours both the epoxide ring-opening and the hydroxyl group forming reactions took place very slowly.

The correlation P/E reached 0.8 in one hour reaction and increased to 0.91 in three hours but went down 0.86 in five hours and remained unchanged up to nine hours.



Hy: hydroxyl content, Ox: oxirane content
P/E: correlation P/E

Figure 9: The effect of time on the oxirane and the hydroxyl content of polyol and the correlation P/E

4. CONCLUSIONS

The success of hydroxylation reaction of epoxidized soybean oil was confirmed by FTIR and H-NMR spectrum.

The optimal conditions for the hydroxylation reaction of epoxidized soybean oil was found: the ESO:H₂O molar ratio of 1:15, the H₂SO₄ of 8 wt.%, at temperature of 70 °C. The hydroxyl content of bio-polyol which received after 5 hours reached to 358.51 mgKOH/g and other characteristics of this bio-polyol have been determined.

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