

Biopolyol preparation from liquefaction of grape seeds

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ABSTRACT: The feasibility of liquefying grape seeds (GS) in the blended solvents of PEG 400 and glycerol for the production of biopolyol was investigated. Different liquefaction conditions have great influences on the residue ratio of GS. The influences of the liquefaction condition such as temperature, time, catalyst percentage, and liquid–solid ratio on the residue ratio were discussed. The optimal conditions obtained were 180 °C, 120 min, catalyst percentage (percentage of solvent mass) of 3.5%, and liquid–solid ratio of 4. The FTIR showed that the lignin, cellulose, and hemicellulose in the GS were effectively decomposed in the liquefaction process. The characteristic parameters of the biopolyol were as follows: hydroxyl number of 397.46 mg KOH/g, acid number of 1.85 mg KOH/g, viscosity of 2960 mPa·s, weight-average molecular weight of $5.18 \times 10^3 \text{ g mol}^{-1}$, and polydispersity of 3.64. These results suggest that the GS-based polyol was suitable for the production of polyurethane foams. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43835.

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INTRODUCTION

As a renewable source, biomass was regarded as a potential candidate to replace the petroleum. There are many ways to utilize biomass such as liquefaction, pyrolysis, and gasification.^{1,2} Compared to the other ways, liquefaction under the atmospheric pressure is a convenient and effective technology for converting lignocellulosic biomass into fragments of small molecules with good flow ability.³ So far, different lignocellulosic biomass, such as palm kernel cake,⁴ alkaline lignin,⁵ Kraft lignin,⁶ sugar-cane bagasse,⁷ soybean straw,⁸ bamboo shoot shell,⁹ wheat straw,¹⁰ wood,³ and acid hydrolysis residue of corncob¹¹ have been liquefied successfully for the production of biopolyol. One kind of the commonly used liquefaction solvents are phenolic compounds and the biopolyol containing abundant phenolic compounds are often used to synthesize phenolic resins.^{12,13} The other kind liquefaction solvent are polyhydric alcohols, including ethylene glycol (EG), polyethylene glycol (PEG), glycerin.^{12,14–17} The obtained biopolyol is characterized with more hydroxyl groups and is suitable for polyurethane foam preparation.^{9,11}

The grape is one of the largest fruit crops in China and with an annual production of more than 11 million tons.¹⁸ About 60% of grape production were used for wine making,¹⁹ and the wine processing can produce a large number of grape marc which consists of grape skins (50%), stalks (25%), and seeds (25%).²⁰ At present, there are three main ways to use grape seed (GS) in

the world: (1) GS oil production,^{21,22} (2) polyphenolic compounds extraction,^{23,24} (3) animal feed production.²⁵ However, the study on liquefaction of GS for the production of biopolyol and polyurethane foam is rarely reported.

Based on the aforementioned discussion, the present study aimed to study the feasibility of producing biopolyol from the liquefaction of GS. The impacts of temperature, time, catalyst, and liquid–solid ratio on the reaction were investigated. Finally, the liquefied production of GS was characterized by Fourier transform infrared spectroscopic analysis (FTIR) and gel permeation chromatography (GPC) analysis, and the characteristic parameters of biopolyol including hydroxyl number, acid number, and viscosity were determined.

EXPERIMENTAL

Materials

GS used in this study is provided by Mile Dongfeng Daxingdi Wine Industry Co., Ltd (Mile, China). They were milled and sieved. The fraction more than 40 mesh was dried at 65 °C for 24 h, then stored in a desiccator at room temperature.

PEG 400 (Tianjin Yongda Chemical Reagent Co., Ltd., Tianjin, China) and glycerol (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) were used as solvent and 98% sulfuric acid (Beijing Chemical Co., Ltd., Beijing, China) was used as the catalyst. Dioxane, phthalic anhydride, potassium hydrogen phthalate,

imidazole, potassium hydroxide (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), sodium hydroxide, methanol, hydrochloric acid (Beijing Chemical Co., Ltd., Beijing, China), pyridine (Xilong Chemical Co., Ltd., Shantou, China) were used for analyzing the properties of biopolyol. All the chemicals were reagent grade and used without further purification.

Liquefaction Procedure

Liquefaction was carried out in a 250-mL three-necked flask under atmospheric pressure with condenser pipe, thermometer, and mechanical stirrer. PEG 400 and glycerol with the ratio at 4:1 were used as liquefaction solvent due to its high liquefaction efficiency and good ability to prevent condensation reaction.²⁶ Pre-weighed GS by different liquid–solid ratios (ranging from 2 to 5, wt/wt) and 98% sulfuric acid (percentage of solvent mass ranging from 1% to 6%, wt/wt) were added when the liquefaction solvent reached the desired temperature (100–200 °C). The reaction time was set between 40 and 320 min. During the reaction, the mixture was continuously stirred to make sure the reaction system was homogeneous and an allihn condenser was used to condense the volatile components from the reactants. After a predetermined reaction time, the flask was rapidly cooled down to room temperature with tap water.

Analysis Methods

According to the method reported by Yao *et al.*,²⁷ about 1 g biopolyol obtained was added into 20 mL 4-dioxane aqueous solution. The mixture was placed in a thermostatic shaker (25 °C, 150 rpm) for 4 h. It was then filtered with pre-weighed filter paper. The filter paper with residue was dried at 105 °C overnight in an oven and weighed again. Liquefaction efficiency was evaluated according to the residue ratio (RR) of the biopolyol. The RR was calculated as given in eq. (1):

$$RR(\%) = \frac{(m_2 - m_1)}{m_0} \times 100 \quad (1)$$

where m_0 is the weight of biopolyol sample (g);
 m_1 is the weight of filter paper (g);
 m_2 is the weight of the filter paper with residue (g).

Hydroxyl number was determined according to the Chinese National Standard GB 12008.3-2009, the determination detail can be found in our previously published work.⁵

About 0.5 g biopolyol sample was dissolved into 20 mL 1,4-dioxane solution (80%, vol/vol). The mixture was titrated with 0.02 M potassium hydroxide solution. The acid number of the polyol was calculated based on eq. (2):

$$\text{Acid number} = \frac{(V_1 - V_2) \times N \times 56.1}{w} \quad (2)$$

where V_1 is the volume of the potassium hydroxide solution required for titration of the polyol sample (mL);

V_2 is the volume of the potassium hydroxide solution required for titration of the blank sample (mL);

N is the molarity of the potassium hydroxide solution;

56.1 is the molar mass of potassium hydroxide;

w is the weight of the polyol (g).

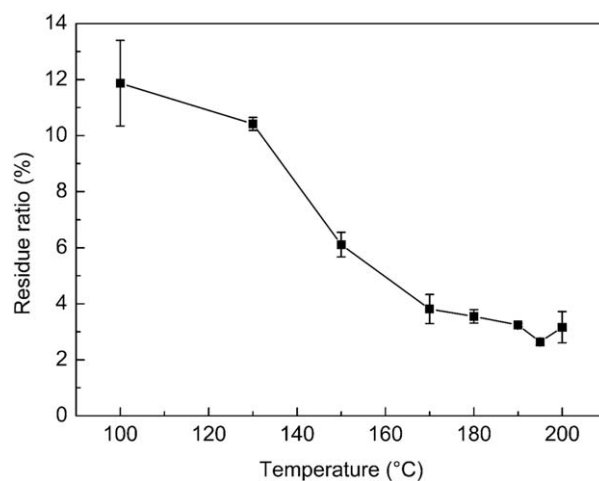


Figure 1. Effect of liquefaction temperature on the residue ratio of biopolyol (liquid–solid ratio, 4:1; H₂SO₄ wt %, 3%; Time, 80 min).

Viscosity was determined according to the Chinese National Standard GB 12008.8-92 using a digital viscometer (NDJ-8S, Weide Instrument Co., Ltd.) at 25 °C.

The molecular weight of the biopolyol was determined using a HPLC system (1260, Agilent Technology) equipped with a refractive index detector (RID, G1362A) and a GPC column (TSK G3000 PWXL).⁵

FTIR spectrum of GS and liquefied products were analyzed by FTIR spectrometer (Nicolet 6700, Thermo Scientific) using the KBr disk technique.⁵

RESULTS AND DISCUSSION

Effect of Liquefaction Temperature

The RR of the biopolyol at different temperatures is shown in Figure 1. It is obvious that the RR was decreased dramatically as temperature increased, indicating that the temperature has an important impact on GS liquefaction. When the temperature was 100 °C, the biopolyol sample had a high RR of 11.87%, this means that the degradation of GS was not sufficient. As the temperature increased to 195 °C, the RR decreased to 2.64%, which was slightly lower than that at 200 °C (3.16%). The three essential components (lignin, cellulose, and hemicellulose) in biomass are connected by complex chemical bonds.²⁸ The low temperature was insufficient to destroy these chemical bonds and GS liquefaction efficiency was low. When the temperature rose gradually, more and more chemical bonds were broken down which led to a higher biomass liquefaction ratio. On the other hand, the liquefaction reaction is a dynamic balance between degradation and condensation reaction.²⁹ The degradation reaction is dominant when the temperature is low. While, the condensation reaction begins to be dominant at a higher temperature, which could reduce the liquefaction efficiency. In the present study, when the temperature was increased to 195 °C, the condensation reaction became too severe which made the RR increase again. When the temperature was higher than 180 °C, the RR tended to be stable. Therefore, 180 °C would be the most desirable liquefaction temperature for GS.

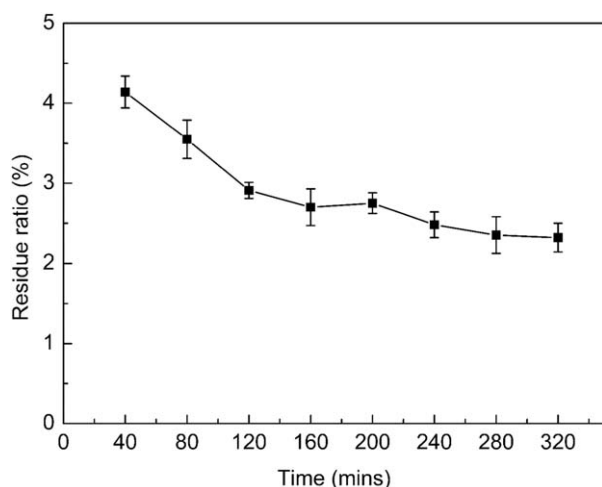


Figure 2. Effect of liquefaction time on the residue ratio of biopolyol (liquid–solid ratio, 4; H_2SO_4 wt %, 3%; liquefaction temperature, 180°C).

Effect of Liquefaction Time

The RR of biopolyol at the different time is shown in Figure 2. At the initial stage (<120 min), the RR of the polyol decreased rapidly, indicating that the liquefaction reaction was rapid. With the extension of liquefaction time, the decrease of the RR gradually slowed down and tended to be stable after 280 min. As mentioned above, degradation and condensation reaction coexist in the liquefaction of GS. The degradation reaction dominated in the initial reaction and the GS degraded rapidly, making the RR decrease rapidly. But in the later stage of reaction, the condensation reaction between small molecules became increasingly intense, making the decrease of the RR became slow.³⁰ When the liquefaction time was longer than 120 min, the change of the RR was not obvious. Therefore, 120 min was chosen as the optimal liquefaction time.

Effect of Catalyst Percentage

The liquefaction reaction could be catalyzed by different catalysts including hydrochloric, phosphoric, and sulfuric acids. In the present study, sulfuric acid was chosen as the catalyst in the lique-

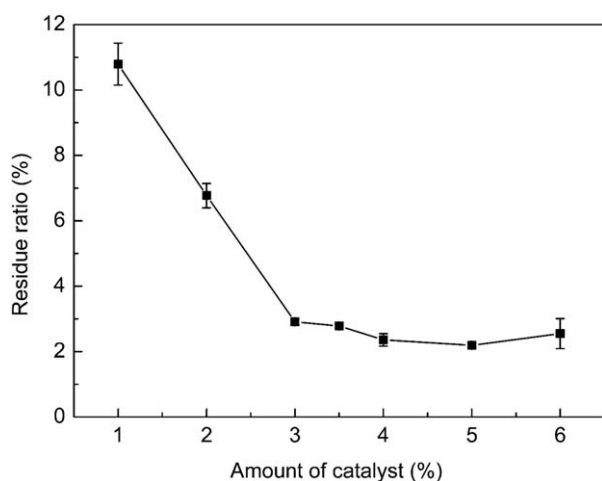


Figure 3. Effect of the catalyst percentage on the residue ratio (liquid–solid ratio, 4; liquefaction temperature, 180°C ; Time, 120 min).

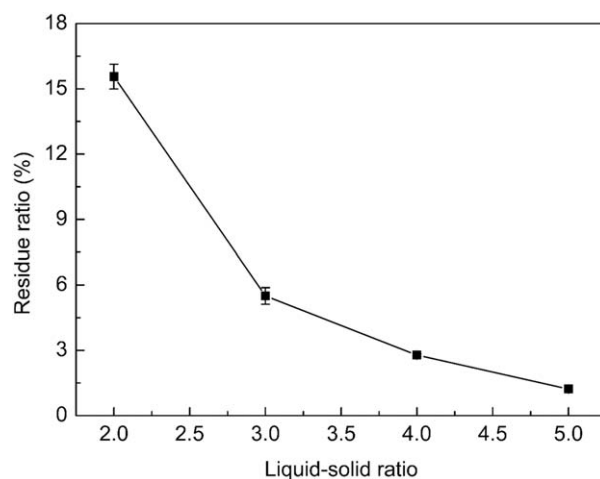


Figure 4. Effect of liquid–solid ratio on the residue ratio (H_2SO_4 wt %, 3.5%; liquefaction temperature, 180°C ; Time, 120 min).

faction of GS. Because the sulfuric acid has been proved to be the best among these catalysts.³⁰ As shown in Figure 3, when the loading of sulfuric acid was less than 3%, the RR of the biopolyol decreased sharply. The decrease of the RR became slower and slower with the increasing amount of sulfuric acid. It could be seen that sulfuric acid with proper concentration enhanced the liquefaction efficiency of GS effectively. However, the condensation reaction of small molecules was promoted when a higher amount of sulfuric acid was used.³¹ To keep a higher liquefaction rate while preventing the occurrence of condensation reactions at the same time,¹⁵ the optimal loading of sulfuric acid was chosen as 3.5%.

Effect of Liquid–Solid Ratio

The RR of liquefied products at different liquid–solid ratio is shown in Figure 4. When the liquid–solid ratio was set as 2.0, the RR of biopolyol was relatively high. With the increase of the liquid–solid ratio, the RR decreased rapidly. As the liquid–solid ratio was increased to 4.0, the RR of 2.78% was reached. The

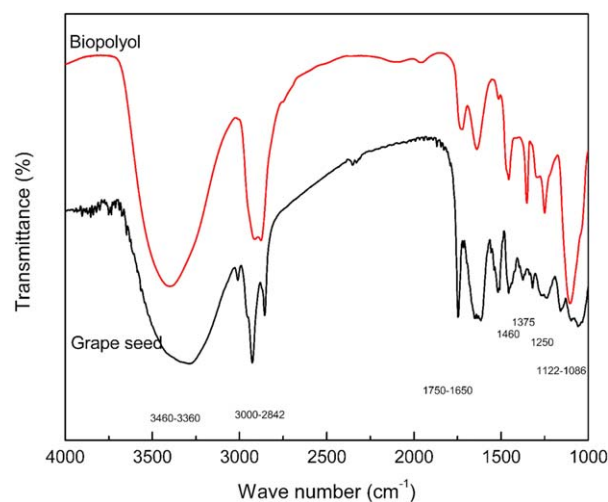


Figure 5. FTIR spectra of grape seed and biopolyol (liquid–solid ratio, 4; H_2SO_4 wt %, 3.5%; liquefaction temperature, 180°C ; Time, 120 min). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Summary of Infrared Key Bands Observed in Grape Seeds and Biopolyol

Grape seed		Biopolyol ^a		Assignment
Band position (cm ⁻¹)	Transmittance (%)	Band position (cm ⁻¹)	Transmittance (%)	
3292	10.00	3399	16.16	Stretching vibration of hydroxyl groups
2927	10.34	2914	33.08	C–H stretching of CH ₃ , CH ₂ and CH groups
1747	28.52	1725	72.54	Stretching vibration of C=O in ketone, aldehyde, carbonyl acid and ester
1456	37.92	1456	54.52	C–H deformation in lignin, cellulose and hemicellulose
1375	43.15	1375	67.27	
1250	32.78	1250	42.52	Stretching vibration of ether bonds
1097	26.98	1104	10.00	

^aLiquid–solid ratio, 4; H₂SO₄ wt %, 3.5%; Liquefaction temperature, 180 °C; Time, 120 min.

RR decreased to 1.22% with the liquid–solid ratio at 5.0, indicating the GS was nearly completely liquefied.

When the liquid–solid ratio was low, the viscosity of the reaction system accordingly became higher.⁴ This would reduce the fluidity of the GS and the contact between the biomass and liquefied agent was also not sufficient. These all contributed to the condensation of the small molecules of GS, leading to a lower liquefaction efficiency. By increasing the liquid–solid ratio, the viscosity of the reaction system could be decreased and GS were dispersed in the liquid more homogeneously. The contact between biomass and liquefaction agent was thus improved which promoted the liquefaction reaction. However, an excessive liquid–solid ratio was not observed to decrease the RR obviously and more reactants used would increase the production cost. Therefore, the liquid–solid ratio of 4:1 was chosen.

Characterization of Liquefied Product

The FTIR spectra of the GS and the biopolyol are shown in Figure 5. The peak positions of the key infrared bands and their relative transmittance (the intensity of the transmittance peak normalized to unity) are summarized in Table I respectively. The broad band at about 3460–3360 cm⁻¹ was the characteristic

stretching vibration of hydroxyl group.³² It showed an increase in the spectrum of biopolyol, indicating the presence of a large number of hydroxyl groups. The peak at 3000–2842 cm⁻¹ of LGS for the C–H stretching of CH₃, CH₂, and CH groups was increased, indicating that some chemical bonds in GS were destroyed and some hydroxyl groups were generated.¹⁶ Both GS and biopolyol had broad absorption bands at about 1750–1650 cm⁻¹, they were attributed to the stretching vibration of C=O in ketone, aldehyde, carbonyl acid, and ester.¹⁶ The waves of biopolyol at 1460 cm⁻¹ and 1375 cm⁻¹ corresponding to C–H deformation in lignin, cellulose, and hemicellulose showed an increase, which may be due to the degradation of GS in the liquefaction process.^{33,34} The biopolyol also had an increase in the peak intensity at 1250 cm⁻¹ and 1110 cm⁻¹ due to the ether bonds, indicating the ether bonds were formed in the liquefaction reaction.^{33,35} All these absorption bands showed that the lignin, cellulose, and hemicellulose in GS were effectively solvated in the liquefaction reaction.

At the optimal conditions (liquid–solid ratio, 4; H₂SO₄ wt %, 3.5%; liquefaction temperature, 180 °C; Time, 120 min), the RR of biopolyol of was 2.78%, and the characteristic parameters of the biopolyols are listed in Table II.

Table II. General Properties of Biopolyols

Lignocellulosic biomass	Biomass conversion ratio (%) ^a	Hydroxyl number (mg KOH/g)	Acid number (mg KOH/g)	Viscosity (mPa·s)	M _w (g mol ⁻¹)	References
Rapeseed cake pellets	93	505	—	400	—	16
Bagasse and cotton stalks	93.1 and 87.9	223–253	25–28	—	—	15
Waste paper	60–90	336–396	19.0–29.7	2609–3899	650–900	37
Wheat straw	96	352	28	1500	1270	10
Soybean straw	65–75	440–540	<5	16,000–45,000	—	8
Palm kernel cake	92.8	236	19	750	—	4
Grape seed	85.7	397	1.85	2960	5180	present study

^aBiomass conversion ratio(%)=100(1 - $\frac{(m_2 - m_1) \times m_3}{m_0 \times m_4}$), where m₀ is the weight of biopolyol weighed for analysis (g), m₁ is the weight of filter paper (g), m₂ is the weight of the filter paper with residue (g), m₃ is the weight of total weight of polyols obtained from liquefaction process (g), m₄ is the weight of biomass added in the liquefaction process (g).

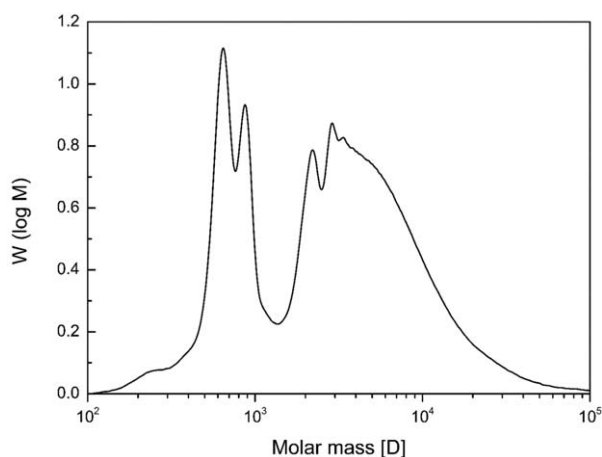


Figure 6. The GPC analysis of the biopolyol (H_2SO_4 wt %, 3.5%; liquefaction temperature, 180 °C; Time, 120 min).

The GPC analysis of the biopolyol is shown in Figure 6. The weight-average molecular of the biopolyol was $5.18 \times 10^3 \text{ g mol}^{-1}$, the number-average molecular weight was $1.42 \times 10^3 \text{ g mol}^{-1}$, and the polydispersity was 3.64. For the synthesis of rigid polyurethane foam, the hydroxyl value of polyol is generally between 300 and 800 mg KOH/g, and the viscosity should be less than 300 Pa s.³⁶ As exhibited in Table I, the properties of the produced biopolyol was similar to those obtained from other biomass. Generally, the biopolyol based GS was suitable for the synthesis of polyurethane foams.

CONCLUSIONS

GS were effectively liquefied in the liquefying solvent of PEG 400 and glycerol by the catalysis of sulfuric acid under atmospheric pressure. Four factors including temperature, time, catalyst percentage, and liquid–solid ratio were optimized. The GS-based biopolyol was suitable for the synthesis of polyurethane foams due to the characterization results. And due to its biodegradability, it is also an environmentally friendly product which can be a candidate for petroleum-based polyol.

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