ACS Sustainable Chemistry & Engineering

Research Article

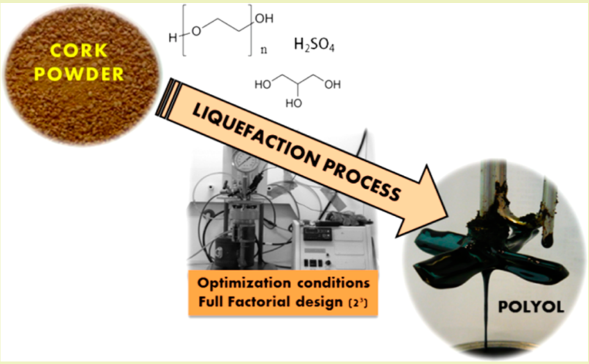
pubs.acs.org/journal/ascecg

Ecopolyol Production from Industrial Cork Powder via Acid Liquefaction Using Polyhydric Alcohols

Belinda Soares,[†] Nuno Gama,[†] Carmen Freire,[†] Ana Barros-Timmons,[†] Inês Brandão,[‡] Rui Silva,[‡] Carlos Pascoal Neto,[†] and Artur Ferreira*[,†,§]

[†]CICECO and Department of Chemistry, University of Aveiro, 3810-193, Aveiro, Portugal
[‡]Sapec-Química SA, Zona Industrial de Ovar—Lote 18, 3880 Ovar, Portugal
[§]ESTGA, University of Aveiro, 3810-193 Aveiro, Portugal

ABSTRACT: Ecopolyol production from acid liquefaction of cork powder was studied for the first time using PEG 400 and glycerol as liquefaction solvents in the presence of sulfuric acid at moderate temperature and atmospheric pressure. The effect of the temperature, concentration of catalyst, and time on the liquefaction yield has been investigated using a fixed set of reaction conditions namely, a liquefaction solvent mixture/cork powder ratio of 5/1 and a solvent mixture PEG 400/glycerol ratio of 90/10. The full-factorial design of experiments (DOE) 2^3 was applied to obtain an optimized set of liquefaction conditions aiming at minimizing the residue content. The minimum residue contents experimentally obtained in this study were 29 wt %, related to cork powder, which were achieved at 150 °C, 4 wt % of sulfuric acid, and 60 min. This value corresponds to 5 wt % of residue per total mass of reaction product. The polyols obtained under optimal conditions present similar characteristics (hydroxyl number value 219 mg_{KOH}/g_{polyol} and viscosity 2875 cP, at 25 °C) to those of petroleum-based polyols typically used in the polyurethane foam industry.



KEYWORDS: *Polyols, PEG 400, Glycerol, Liquefaction process, Cork powder, Quercus suber L., Biorefinery, Statistical design of experiments (DOE)*

INTRODUCTION

Lignocellulosic biomass residues represent a renewable, biodegradable, abundant, and cheap source of raw materials for the chemical industry without affecting food and feed supplies.[1] The polyurethane industry is aware of this trend and has been exploring the development of low-cost polyols from different biomass resources by liquefaction methodologies.[2,3] For example, Shiraishi et al.[4] patented a process to convert lignocellulosic materials into added-value products via liquefaction using polyhydric alcohols, such as ethylene glycol (EG), polyethylene glycol (PEG), and glycerol, as liquefaction solvents in the presence of sulfuric acid, at moderate temperatures and atmospheric pressure. The liquefied products, rich in hydroxyl groups, have high reactivity and can be used as starting materials in the production of several environmental friendly polymeric products, including polyurethane foams.[5,6] Since then, the valorization of lignocellulosic residues by acid liquefaction using polyhydric alcohols has been the subject of a large number of publications. Several lignocellulosic residues such as corn bran,[6] wood,[7] corn stover and rice straw,[8] wheat straw,[9] bagasse and cotton stalks,[10] lignin,[11] rapeseed cake, olive stone, and apple pomace[12] have been successfully converted into polyols suitable to produce polyurethane materials with similar characteristics to those of conventional products. However, to the best of our knowledge, the acid liquefaction of cork powder using polyhydric alcohols has never been investigated.

Cork, the bark of oak (*Quercus suber L.*), is a natural, renewable, and sustainable raw material typically composed of suberin (30−60 wt %), lignin (19−22 wt %), polysaccharides (12−20 wt %), and extractives (9−20 wt %), including aliphatic, phenolic, and triterpenic compounds.[13] The relative abundance of these elements is extremely variable, being influenced by the geographical origin, quality, or even the different parts of the tree from which the cork is harvested. Cork industry is a key sector in Portuguese economy. During the production of wine cork stoppers this industry generates residues that are then granulated and used in a variety of applications, mainly agglomerated materials. Throughout this process, cork powder, a low granulometry fraction that is not suitable for the production of agglomerates, is also generated in considerable amounts. This byproduct represents about 25% of the total cork production corresponding to about 25 000 tons per year in Portugal.[14] Due to its low economic value and high

Received: November 22, 2013
Revised: January 11, 2014
Published: January 13, 2014

dx.doi.org/10.1021/sc400488c | *ACS Sustainable Chem. Eng.* 2014, 2, 846−854

burning capacity, this byproduct is currently used for energy production.

Several studies on the valorization of cork powder for novel applications have been reported. For example, Machado et al.[15] showed that cork powder can be used as a low-cost biosorbent. Cardoso et al.[16] reported the potentialities of cork powder as raw material for the preparation of activated carbon that can be used in the control of atmospheric pollution. The conversion of cork powder into polymeric materials is another way to valorize this industrial waste[17] that has been studied in our group following two distinct approaches: (i) the isolation of the suberin components from cork powder and their subsequent use as monomers in polymer synthesis, such as polyesters and polyurethanes[18] and (ii) the bulk conversion of cork powder trough oxypropylation into liquid polyols which were then used as macromonomers in polyurethane synthesis.[19,20]

Following our interest on the valorization of cork powder, the objectives of the present study were to assess the suitability of a more environmentally friendly liquefaction reaction, specifically the acidic liquefaction using polyhydric alcohols, to convert cork powder into liquid polyols. For that purpose, a design of experiments methodology (DOE) and statistical analysis were used to optimize the liquefaction conditions (temperature, sulfuric acid concentration, and time). In this study the liquefaction solvents/cork powder and the PEG 400/glycerol ratios were fixed.

■ EXPERIMENTAL SECTION

Materials. Cork powder used in this study was kindly provided by Corticeira Amorim (Portugal). The material was air-dried (moisture content between 8 and 10 wt %), milled in a Retsch cross beater mill SK1 (Haan, Germany), and sieved and the 18−60 mesh fraction was selected for the liquefaction experiments. This fraction was oven-dried, at 105 ± 2 °C for 24 h, before the liquefaction step.

Polyethylene glycol (PEG, 99% purity, supplied by Merck) with average molecular weight of 400 and glycerol (99.5% purity, supplied by Sigma-Aldrich) were used as solvents and sulfuric acid (H_2SO_4, 95−97% purity, supplied by Fluka) was used as catalyst. All other chemicals were reagent grade and were used without further purification.

Liquefaction Reaction. The acid liquefaction reactions were carried out in a 300 cm^3 stainless steel vessel (PARR, model 4566) equipped with an independent controller (PARR, model 4842), stirring (200 rpm), heating resistance (1000 W), internal water cooling system, and temperature sensor. The typical procedure consisted in introducing weighed amounts of dried cork powder, solvent mixture (PEG 400/glycerol, 90/10 wt/wt), and sulfuric acid (3 and 4 wt %) in the reactor. The concentration of sulfuric acid was calculated as the weight content based on the amount of the liquefaction solvent mixture. The reaction mixture was then stirred at atmospheric pressure and room temperature for 5 min allowing the impregnation of the cork powder with the solvents. The temperature and reaction time were studied from 150 to 170 °C and from 60 to 120 min, respectively. The time countdown started when the temperature of the reaction reached the defined set point. After a preset reaction time, the heater was turned off and the stirrer kept running until the mixture cooled down to room temperature, using a cold-water bath to quench the reaction. The polyols obtained upon recovery from the reactor were a mixture of liquefied cork powder and residue. In order to optimize the liquefactions conditions (temperature, sulfuric acid concentration, and time), the liquefaction solvents/cork powder ratio of 5/1 (w/w) and the solvent mixture PEG 400/glycerol ratio of 90/10 (w/w) were fixed. These parameters were selected based on the suitable values found in previously published liquefaction studies for several lignocellulosic agricultural crop residues.[8−11,21,22] All experiments and analyses were performed at least in duplicate and the data were expressed as mean ± standard deviation.

Determination of Residue Content Related to Cork Powder. Following the procedure reported by Hu et al.[23] approximately 2 g of polyols (with residue) were weighed and well-dispersed in 30 mL of ethanol in a 250 mL Erlenmeyer flask, at 30 °C and under magnetic stirring, for 10 min. Then, the solid residues were separated by vacuum-filtration using a 50 mL predried fritted glass filtering crucible with a layer of cellulose filter paper (grade 1, Whatman) placed at the bottom. Deionized water was used to rinse the residue in the crucible until the filtrate became colorless. The crucible was dried in an oven at 105 ± 2 °C for 24 h to ensure complete drying. The residue content, related to the initial cork powder and obtained in liquefaction process, was calculated using eq 1.

$$\text{residue content (wt\%)} = [((W_1 - W_2)/W_3) \times W_4 \times 100]/W_5 \tag{1}$$

where W_1 is the total dry weight of the filtering crucible with residue (g); W_2 is the net weight of filtering crucible without residue (g); W_3 is the weight of polyols' sample (reaction product) used for determination of residue content related to cork powder (g); W_4 is the total weight of polyols obtained from liquefaction process (reaction product) (g); and W_5 is the weight of cork powder used in the liquefaction process (g).

The residue content is the average value of at least two consistent replicates (less than 5 wt % deviations).

Experimental Design. A second-order full-factorial design (2^3) was developed to optimize the liquefaction conditions. Table 1 shows the design of experiments used in this study. The temperature, sulfuric acid concentration, and the liquefaction time were the selected independent variables. These three factors were picked based on previous studies found in literature.[6,9−11,21,24,25] The influence of temperature (X_T, 150−160 °C), sulfuric acid concentration (X_{SA}, 3−4 wt %), and liquefaction time (X_t, 60−80 min) on the dependent variable or system response (Y) (residue content) were studied for optimal liquefaction conditions and estimated by the use of MINITAB 16 and Design-Expert 7.0 software, according to the design of experiments using a full-factorial design with two replicates involving a total of 16 experiments. Experimental results were modeled according to a cubic polynomial described by eq 2.

Table 1. Statistical Full-Factorial Design (2^3) for Acid Liquefaction Experiments

factors	low level	high level
temperature, X_T (°C)	150	160
sulfuric acid concentration, X_{SA} (wt %)	3	4
liquefaction time, X_t (min)	60	80

$$\begin{aligned} Y = \beta_0 + \beta_T X_T + \beta_{SA} X_{SA} + \beta_t X_t + \beta_{T,SA} X_T X_{SA} + \beta_{T,t} X_T X_t \\ + \beta_{SA,t} X_{SA} X_t + \beta_{T,SA,t} X_T X_{SA} X_t \end{aligned} \tag{2}$$

The predicted responses are designated as Y associated with each factor level combinations; β_0 is the model constant, β_T to $\beta_{T,SA,t}$ represent the model coefficients for the linear interaction and cubic effects of the independent variables respectively. X_T, X_{SA}, and X_t are the coded factors between −1 (lower limit) and +1 (upper limit).

The coefficients in eq 2 were calculated by multiple regression analysis, based on the experimental data, using analysis of variance methods (ANOVA). The models were validated comparing the predicted values obtained by the model with the experimental data. Two-dimensional contour plots and three-dimensional response surface curves were plotted in order to study the interaction between the various parameters in the liquefaction reaction and to determine the optimum levels of each factor required to obtain minimum residue content, i.e. the maximum cork powder conversion into liquid polyol.

Preliminary Characterization of Polyols, Cork Powder, and Residues. The polyols without residues were characterized by different analytical techniques: chemical analysis (hydroxyl and acid numbers and viscosity) and structural analysis (Fourier transform infrared spectroscopy (FTIR)). The cork powder and the residues were characterized by FTIR.

The acid number of the polyols was determined in accordance with the ASTM D4662-08 standard.[26] Approximately 2 g of each polyol were dispersed in 50 mL of ethanol in a 100 mL Erlenmeyer flask. Titrations were conducted using 0.1 N NaOH solution and the end point determined by a digital pH meter (HI 2211 pH/ORP−Hanna Instruments), equipped with a HI 1043B probe. The number of milligrams of KOH required to neutralize the acid of one gram of sample was calculated using eq 3.

$$\text{acid number } (\text{mg}_{\text{KOH}}/\text{g}_{\text{polyol}}) = [(A - B)56.1N]/W \tag{3}$$

where A is the volume of NaOH solution required for titration of the sample (mL); B is the volume of NaOH solution required for titration of the blank (mL); N is the normality of the NaOH solution; and W is the weight of the sample (g).

The hydroxyl number of the polyols was determined in accordance with the ASTM D4274-05 standard[27] in which the esterification process is catalyzed by imidazole. Titrations were conducted using 0.5 N NaOH solution and the end point determined by a digital pH meter. The hydroxyl number was corrected and calculated according to eq 4.

$$\text{hydroxyl number } (\text{mg}_{\text{KOH}}/\text{g}_{\text{polyol}}) = [(B - A)56.1N]/W + C \tag{4}$$

where A is the volume of NaOH solution required for titration of the sample (mL); B is the volume of NaOH solution required for titration of the blank (mL); N is the normality of the NaOH solution; W is the weight of the sample (g); and C is the acidity of the sample ($\text{mg}_{\text{KOH}}/\text{g}_{\text{polyol}}$).

The viscosity of the polyols was determined according to the ASTM D4878-08 standard method A[28] using a Visco Star R viscometer. Measurements were conducted at 25 ± 0.1 °C. The equipment was calibrated using a range of silicone viscosity standards (RT500, RT1000, RT5000, RT12500) provided by Cannon Instrument Company.

The FTIR spectra of the polyols, cork powder, and residues were collected on a Mattson 7000 FTIR spectrometer, equipped with a single horizontal Golden Gate ATR cell (attenuated total reflectance), and a diamond crystal. All data were recorded at room temperature, in the 4000−500 cm^{-1} range by accumulating 64 scans with a resolution of 4 cm^{-1}.

■ RESULTS AND DISCUSSION

On the basis of the biorefinery concept, the main focus of our work was to increase the value of cork powder which due to its characteristics is normally just used as fuel despite of its chemical richness. Indeed, cork powder is a residue of one of the most relevant Portuguese industries which can be transformed into liquid polyols and later be used as macromonomers in polyurethane foam formulations.[19,20] In this work, the possibility of converting cork powder into liquid polyols via acid liquefaction using polyhydric alcohols at atmospheric pressure and moderate temperatures was studied. Initially the effect of temperature, sulfuric acid concentration, and liquefaction time were investigated. Next, using the design of experiments combined with statistical analysis, the liquefaction conditions were optimized.

Effect of Liquefaction Conditions. *Temperature.* The effect of temperature was studied by carrying out the reaction at three different temperatures (150, 160, and 170 °C). These temperature levels were selected according to suitable results reported in the literature.[4,6,9−11,21] Figure 1 shows the influence of temperature on the residue content of the liquefied cork powder using a solvents mixture of PEG 400/glycerol (90/10 wt/wt), liquefaction solvents/cork powder ratio of 5/1 (w/w), and sulfuric acid as catalyst (3 and 4 wt %) at 60 and 80 min of liquefaction time. As observed, the temperature is an important factor on the conversion of cork powder into polyols. In the case of sulfuric acid concentration of 3 wt %, the residue content decreased from 41 ± 0.4 to 38 ± 2.5 wt % when the liquefaction temperature was increased from 160 to 170 °C, independently of the reaction time. Previous studies had reported the same behavior for the liquefaction of other lignocellulosic agricultural residues (cotton stalks and bagasse) under the same reaction conditions.[10] At 150 °C and 3 wt % of sulfuric acid concentration, the residue content increased by 10 wt % with the liquefaction time. This result is also consistent with the literature.[9] In the case of 4 wt % of sulfuric acid concentration, the residue content increased from 29 ± 1.9 to 45 ± 0.2 wt % as the liquefaction temperature increased from 150 to 170 °C, independently of liquefaction time. Indeed, raising the temperature may promote the decomposition of cork compounds (mainly suberin, lignin, and cellulose) and polycondensation of the liquefaction intermediates simultaneously.[9] The lowest residue content was achieved at 150 °C; therefore, it can be concluded that 150 °C is considered the most suitable temperature for acid liquefaction of cork powder, within the studied range.

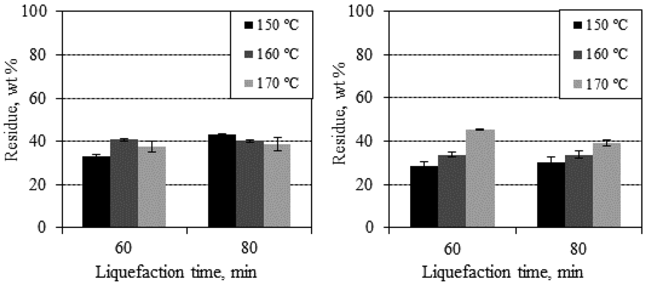


Figure 1. Effect of temperature on the residue content. Liquefaction time, 60 and 80 min; sulfuric acid concentration, 3 (left) and 4 wt % (right); solvents mixture, PEG 400/glycerol, 90/10 (w/w); liquefaction solvents/cork powder, 5/1 (w/w).

Sulfuric Acid Concentration. It has been established that the decomposition of lignocellulosic raw material during acid liquefaction proceeds mainly via a series of hydrolysis and solvolysis reactions[10] and the presence of a catalyst is crucial to improve the extent of liquefaction. Previous studies showed that sulfuric acid exhibited the best catalytic effect compared with hydrochloric and phosphoric acids, in the range of 1−5 wt %.[24] However, a high concentration of sulfuric acid has a strong oxidation effect and may cause other secondary reactions.[10,24] Figure 2 shows the influence of sulfuric acid concentration (3 and 4 wt %) on the residue content of the liquefied cork powder at 150 °C for 60 and 80 min, using solvents mixture PEG 400/glycerol ratio of 90/10 (w/w) and liquefaction solvents/cork powder ratio of 5/1 (w/w). For 60 min of reaction, the increase of the sulfuric acid concentration from 3 to 4 wt % resulted in a slight decrease of the residue content from 33 ± 0.7 to 29 ± 1.9 wt % while for 80 min of reaction, a more remarkable decrease of residue content from 43 ± 0.1 to 30 ± 2.5 wt %, was observed. As expected, the increase of the sulfuric acid concentration had a positive effect on the conversion of cork powder into liquid polyol. The lowest residue content (29 ± 1.9 wt %) was achieved at 4 wt %. From these results, it can be concluded that 4 wt % is the most suitable sulfuric acid concentration for acid liquefaction of cork powder.

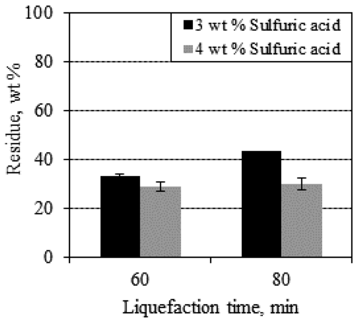


Figure 2. Effect of sulfuric acid concentration on the residue content. Liquefaction temperature, 150 °C; liquefaction time, 60 and 80 min; solvents mixture, PEG 400/glycerol, 90/10 (w/w); liquefaction solvents/cork powder, 5/1 (w/w).

Liquefaction Time. On the basis of the previous results, the temperature of 150 °C and 4 wt % of sulfuric acid concentration were fixed in order to study the effect of the liquefaction time on the residue content, as shown in Figure 3.

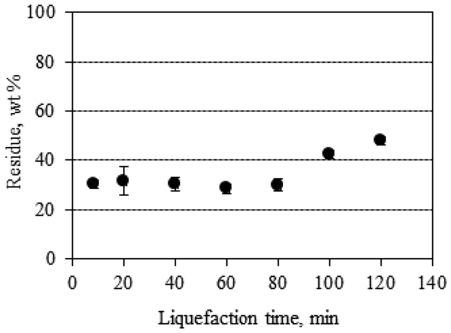


Figure 3. Effect of reaction time on the residue content. Liquefaction temperature, 150 °C; sulfuric acid concentration, 4 wt %; solvents mixture, PEG 400/glycerol, 90/10 (w/w); liquefaction solvents/cork powder, 5/1 (w/w).

A significant decrease in the residue content (30 ± 1.8 wt %) was observed during the first 10 min of reaction. Previous studies have also reported a significant decrease of residue content at the initial stages of liquefaction of biomass due to the occurrence of depolymerization and hydrolysis reactions of its components (lignin, hemicelluloses, and amorphous zones of cellulose).[6,9,10,21,29] After this first stage, the residue content decreased slowly over time until 60 min of reaction (29 ± 1.9 wt %), probably due to the degradation of the crystalline regions of cellulose.[30] From 60 to 120 min of reaction, a remarkable increase of residue content from 29 ± 1.9 to 48 ± 1.6 wt % was observed. This increase of the residue content in the last stage of liquefaction was also reported by other research groups.[9,21,31−33] The formation of condensed residues may be associated with the occurrence of polycondensation reactions between degraded compounds from suberin, lignin, and cellulose resulting from the lack of liquefaction reagents. Indeed, Min et al.[32] concluded that the polycondensation reaction occurs in the process of biomass liquefaction under conditions of insufficient liquefaction solvents combined with longer liquefaction times. The lowest residue content of 29 ± 1.9 wt % was achieved at 150 °C, 4 wt % of sulfuric acid and 60 min of reaction. Previous studies on liquefaction of lignocellulosic materials (bagasse and cotton stalk,[10] lignin,[11] and rapeseed cake[21]) using polyhydric alcohols showed biomass conversions around 90 wt % (10 wt % of residue) for a liquefaction time less than 100 min and under the same conditions of liquefaction solvents/biomass ratio of 5/1 (w/w). The relatively lower conversion obtained in our study with cork might be explained by the different chemical composition (presence of suberin in cork powder) or the pretreatment used in referred studies. In this present study, the cork powder was used without any pretreatment. Furthermore, from the industrial point of view, this process revealed to be adequate, generating only 5 wt % of residue per total mass of polyol obtained (i.e., reaction product). Moreover, as it will be discussed later, the solid residue may find applications, for example as filler in the preparation of composite materials.

The suitable liquefaction conditions to reduce the polycondensation reaction and to obtain the maximal conversion of cork powder into liquid polyol around 70 wt % (30 wt % of residue, based on the amount of initial cork powder used in the liquefaction process) were temperature of 150 °C, sulfuric acid concentration of 4 wt %, and 60 min of liquefaction time. However, statistical analyses were applied in order to confirm these results using mathematical models.

Statistical Analysis and Optimization of the Liquefaction Conditions. In order to optimize the liquefaction conditions three factors were studied: temperature (X_T), sulfuric acid concentration (X_{SA}), and liquefaction time (X_t). On the basis of the previous results of the effect of these parameters on the residue content, two levels were selected for each one: temperature, 150 and 160 °C; sulfuric acid concentration, 3 and 4 wt %; and liquefaction time, 60 and 80 min. Table 2 shows the experimental matrix for the full-factorial design (2^3) and the corresponding results.

Table 2. Experimental Matrix of Full-Factorial Design (2^3) and Results

run	standard order	factors X_T (°C)	X_{SA} (wt %)	X_t (min)	residue (wt %) (mean ± standard deviation)
1	(1)	150	3	60	33.0 ± 0.7
2	x_T	160	3	60	40.7 ± 0.4
3	x_{SA}	150	4	60	28.7 ± 1.9
4	$x_T x_{SA}$	160	4	60	33.8 ± 0.9
5	x_t	150	3	80	43.2 ± 0.1
6	$x_T x_t$	160	3	80	40.2 ± 0.6
7	$x_{SA} x_t$	150	4	80	30.0 ± 2.5
8	$x_T x_{SA} x_t$	160	4	80	33.7 ± 1.6

The statistical analysis of the experimental results was carried out, and all the main effects and the interactions were estimated using the YATES algorithm. The analysis of variance (ANOVA) and the estimated coefficients for the polynomial model are presented in Table 3. From Table 3, it is possible to conclude that all the main effects and given interactions were significant on residue content, at 95% confidence level, except for temperature/sulfuric acid concentration interaction. The sulfuric acid concentration proved to be the factor with more effect on the residue content (60%), followed by temperature (11%), temperature/time interaction (9%), time (7%), temperature/sulfuric acid concentration/time interaction (5%), and sulfuric acid concentration/time interaction (4%), representing a total of 95% of significance. This study proved that the sulfuric acid concentration factor is the parameter with more

Table 3. Analysis of Variance (ANOVA) and Coefficients for Polynomial Model Obtained from Experimental Design[a]

constant	effects	coefficients	DF	SS	MS	F-test	% SS/total
β_0	35.38	35.38					
β_{SA}	−7.76	−3.88	1	241.03	241.03	134.23	58.65
β_T	3.36	1.68	1	45.23	45.23	25.19	11.00
$\beta_{T,t}$	−3.04	−1.52	1	36.91	36.91	20.55	8.98
β_t	2.72	1.36	1	29.43	29.43	16.39	7.16
$\beta_{T,SA,t}$	2.34	1.17	1	21.86	21.86	12.17	5.32
$\beta_{SA,t}$	−2.12	−1.06	1	17.85	17.85	9.94	4.34
$\beta_{T,SA}$[b]	1.04	0.52	1	4.31			
residual error			8	14.36	1.80	$F_{\text{Distribution}}$ (0.05; 1; 9) = 5.12	
total			15	410.96			

[a] DF degree of freedom; SS sum of squares; MS mean square. [b] Indicates insignificant value at 95% confidence level.

influence on residue content, representing about 60% of significance within the studied range.

From these results, the prediction model obtained was a cubic polynomial described by eq 5.

$$\text{residue content}_{\text{predicted}}\ (\text{wt }\%) = 35.38 - 3.88X_{SA} + 1.68X_T - 1.52X_TX_t + 1.36X_t + 1.17X_TX_{SA}X_t - 1.06X_{SA}X_t + 0.52X_TX_{SA} \quad (R^2 = 0.9650) \tag{5}$$

In order to validate the model, the experimental residues versus the predicted residues were plotted. As shown in Figure 4, the prediction of the cubic polynomial model is satisfactory.

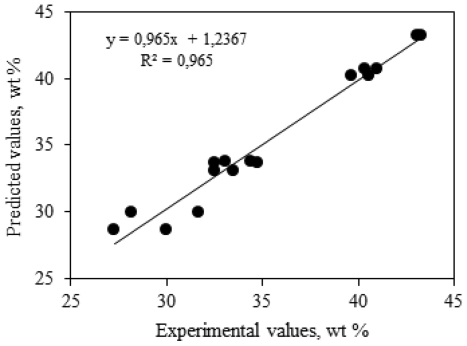


Figure 4. Predicted residue as a function of experimental residue obtained by a polynomial model.

Figure 5 shows the optimal response surface and contour plots of the sulfuric acid concentration effect, temperature, and liquefaction time on residue content to obtain the minimum response. Figure 5a and b shows the sulfuric acid concentration and temperature effects at 60 and 80 min, respectively. For optimal system response, the sulfuric acid concentration should be kept at high value (4 wt %) and the temperature at low value (150 °C) to obtain the minimum residue content regardless of liquefaction time as observed in Figure 5c. Indeed, according to the plot in Figure 5d, the minimum was obtained when the temperature was kept constant at the lowest value (150 °C), short liquefaction times, and highest sulfuric acid concentration. The minimum residue content predicted of 30 wt % was achieved at 150 °C, 4 wt % of sulfuric acid concentration, and 60 min of liquefaction, for the studied range.

These statistical results showed that the suitable liquefaction conditions to maximize the conversion of cork powder into polyol were the liquefaction temperature of 150 °C, the sulfuric acid concentration of 4 wt %, and 60 min of liquefaction time, for the studied range. On the basis of the biorefinery concept, this polyol production process allowed the replacement of about 12 wt % of the mixture liquefaction solvents (PEG 400 and glycerol) by cork powder. In order to maximize the incorporation of cork powder into polyol one parameter that should be studied in detail is the liquefaction solvent/cork powder ratio. Moreover, the range of reaction parameters namely, temperature and time, needs to be further expanded and the sampling intervals narrowed in order to take full advantage of the DOE tool and thus optimize the reaction conditions.

Characterization of the Obtained Polyols, Cork Powder, and Residues. A preliminary characterization of the obtained polyols was performed to evaluate their suitability as precursors in formulations of polyurethane foams. In that sense, the hydroxyl and acid numbers and the viscosity are the most important parameters to evaluate the potentialities of the polyols. FTIR analyses were also carried out to have a first insight into the chemical structure of the polyols.

Hydroxyl and Acid Numbers. The effect of liquefaction time on the hydroxyl and acid numbers of the liquefied cork powder obtained under optimal liquefaction conditions (150 °C and 4 wt % of sulfuric acid concentration) is shown in Figure 6. The hydroxyl number (OH) of liquefaction solvents (mixture PEG 400 and glycerol) was used as the starting point in the plot because the hydroxyl groups in solid cork powder are inaccessible.[34] The hydroxyl number decreased significantly from 419 to 160 $\text{mg}_{\text{KOH}}/\text{g}_{\text{polyol}}$, during the first 20 min of liquefaction. This behavior can be attributed to the occurrence of dehydration and thermal-oxidative degradation of the liquefaction solvents and cork compounds (suberin, lignin, hemicellulose, and amorphous zones of cellulose), as reported in the literature.[10,35] In the following 60 min, the hydroxyl number increased to 223 $\text{mg}_{\text{KOH}}/\text{g}_{\text{polyol}}$ probably due to the cleavage of ester or ether linkages between the suberin or lignin units.[9] With the increase of the liquefaction time, the hydroxyl number decreased again from 223 to 130 $\text{mg}_{\text{KOH}}/\text{g}_{\text{polyol}}$. The rapid decrease in hydroxyl number associated with the increase of the residue content in the later stage of liquefaction, as observed above (see Figure 3) can be due to the occurrence of polycondensation reactions and the dehydration reactions between the acid substances derived from the decomposed cork powder components and the polyhydric alcohols that might contribute to the consumption of hydroxyl groups.[34]

As regards the acid number, the liquefied cork powder has an acidic character due to the sulfuric acid used as catalyst in the liquefaction process and the acidic substances generated by the decomposition of the cork powder components, mainly

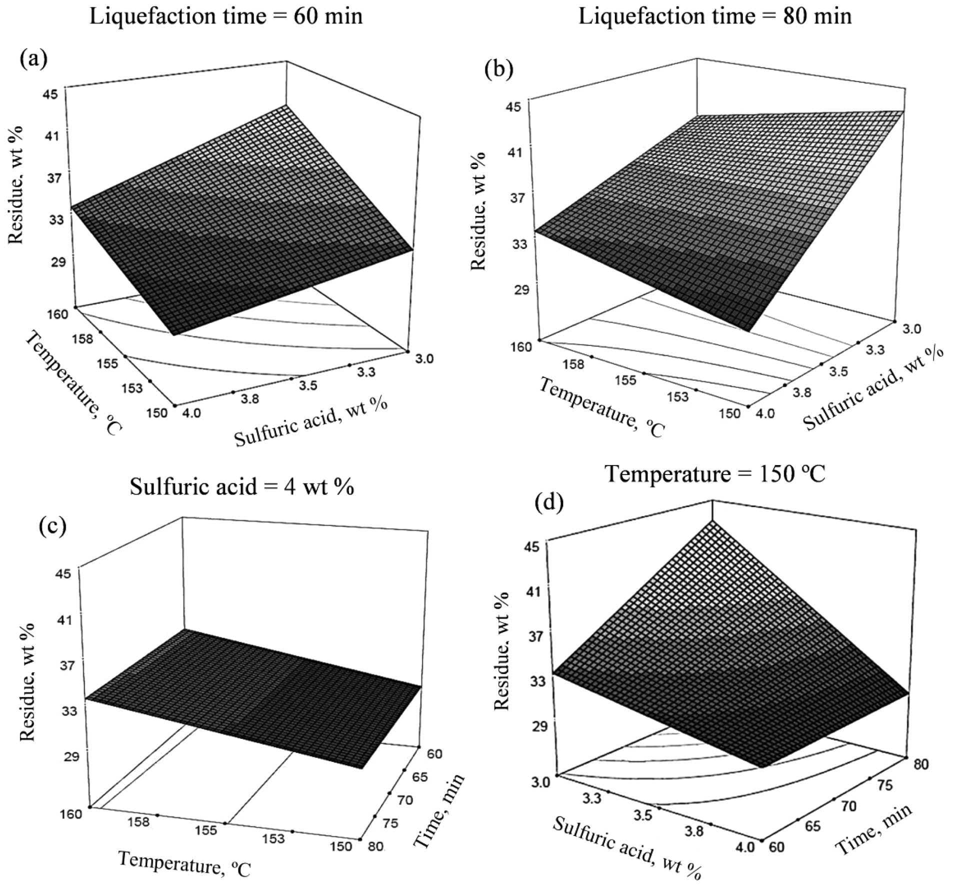


Figure 5. Surface response plots of the effect of temperature, sulfuric acid concentration, and time on the residue content: (a) fixed liquefaction time at 60 min; (b) fixed liquefaction time at 80 min; (c) fixed sulfuric acid concentration at 4 wt %; (d) fixed temperature at 150 °C.

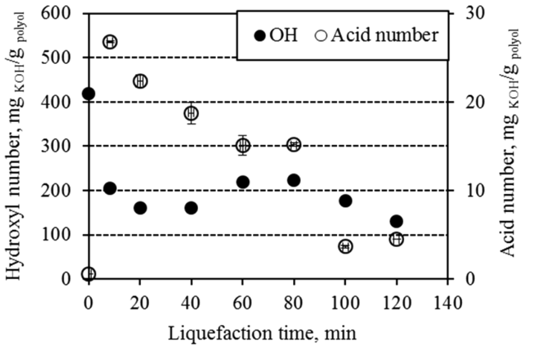


Figure 6. Effect of liquefaction time on the hydroxyl and acid numbers. Liquefaction temperature, 150 °C; sulfuric acid concentration, 4 wt %; solvents mixture, PEG 400/glycerol, 90/10 (w/w); liquefaction solvents/cork powder, 5/1 (w/w).

cellulose and hemicelluloses. The significant decrease of the acid number from 27 to 4 mg_{KOH}/g_{polyol} observed with the increase of the liquefaction time (shown in Figure 6) can be associated with the occurrence of esterification reactions between the acidic groups of the products resulting from the degraded cork compounds and alcohols (PEG 400 or glycerol).[34]

The hydroxyl numbers obtained in this study (130−223 mg_{KOH}/g_{polyol}) were relatively low when compared to those reported for other polyols obtained from several lignocellulosic agricultural residues, using PEG 400 and glycerol under similar liquefactions conditions. This may be due to the lower hydroxyl content of cork powder. The acid numbers (4−27 mg_{KOH}/g_{polyol}) were almost in the same range of those reported in the literature.[9,10,12,25] Nevertheless, the polyols from cork powder obtained in this study presented adequate hydroxyl numbers values to be used in polyurethane foam formulations. However, before use in that type of synthesis the high acid number of polyols needs to be reduced because the presence of the residual acid groups reduces the catalytic activity of tertiary amines via the formation of ammonium salts in the production of polyurethane foams.[36]

Viscosity. The viscosity is an important fluid property when studying the rheological behavior of the polyols and their suitability for the preparation of polyurethane foams. Figure 7 shows the effect of the liquefaction time on the viscosity of the liquefied cork powder obtained under optimal conditions (150 °C and 4 wt % of sulfuric acid concentration). The viscosity remained almost constant (around 3000 cP) until 100 min of liquefaction time. In the later stage, a rapid increase of viscosity from 3576 to 23 420 cP (100−120 min) was observed. Worth noting is the fact that this remarkable increase of viscosity follows the evolution of residue content observed in Figure 3. Thus, it is thought to be associated with the formation of compounds with higher molecular weight associated with the polycondensation reactions discussed before. Moreover, at this stage the hydroxyl and acid numbers also dropped suggesting that, as previously discussed, polycondensation reactions occurred between acid groups of the lignocellulosic degradation compounds and hydroxyl groups of the solvents. In the future more studies need to be carried out in order to understand the

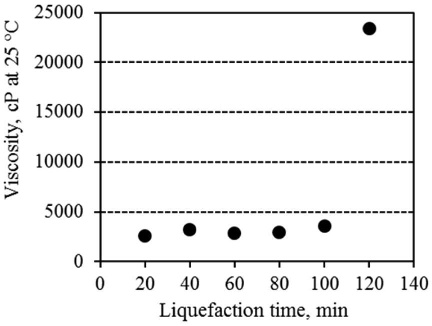


Figure 7. Effect of liquefaction time on the viscosity. Liquefaction temperature, 150 °C; sulfuric acid concentration, 4 wt %; solvents mixture, PEG 400/glycerol, 90/10 (w/w); liquefaction solvents/cork powder, 5/1 (w/w).

polycondensation process and the mechanism of biomass liquefaction in the presence of polyhydric alcohols and acid catalysts under moderate temperature and atmospheric pressure.

FTIR. The ATR FTIR technique was employed to investigate the functional groups of the obtained products (polyol and residue) and thus demonstrate the success of liquefaction of cork powder. Figure 8 shows the ATR FTIR normalized spectra of the polyols obtained from liquefied cork powder at different liquefaction times and under optimal conditions (150 °C, 4 wt % of sulfuric acid concentration, solvents mixture of PEG 400/glycerol of 90/10 (w/w) and liquefaction solvents/cork powder ratio of 5/1 (w/w)). The spectra display a broad band around 3400 cm^{-1} which is the typical band arising from the OH stretching vibration, a broad band between 2800 and 3000 cm^{-1}, typical of C–H stretching vibrations and a sharp band near 1112 cm^{-1}, attributed to the C–O stretching vibrations. All these functional groups are present in the liquefactions solvents (mostly PEG 400). Additionally, a peak near 1741 cm^{-1} that increases modestly with the reaction time, arising from the C=O stretching vibration, typical of ester groups, confirms the occurrence of the reaction between the liquefaction solvents (PEG 400 and glycerol) and the cork powder compounds or derivatives formed during liquefaction.

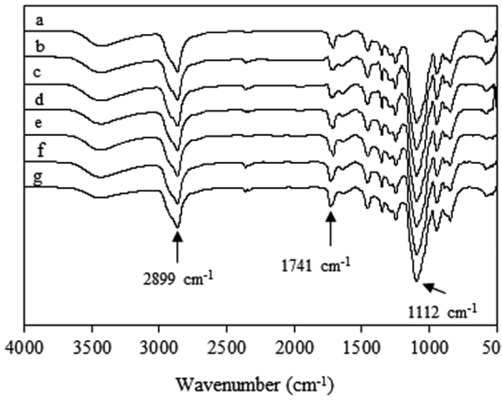


Figure 8. ATR FTIR normalized spectra of the polyol from cork powder at different liquefaction times: (a) 10, (b) 20, (c) 40, (d) 60, (e) 80, (f) 100, (g) 120 min. Liquefaction temperature, 150 °C; sulfuric acid concentration, 4 wt %; solvents mixture, PEG 400/glycerol, 90/10 (w/w); liquefaction solvents/cork powder, 5/1 (w/w).

The FTIR normalized spectra of cork powder and the residues obtained from liquefied cork powder at different liquefaction times and under optimal conditions (150 °C, 4 wt % of sulfuric acid concentration, solvents mixture of PEG 400/glycerol of 90/10 (w/w) and liquefaction solvents/cork powder ratio of 5/1 (w/w)) are shown in Figure 9. The spectrum of cork powder shows the typical peaks characteristics of the suberin-containing material, displaying a broad band around 3400 cm^{-1} assigned to the OH stretching vibration, the peaks at 2930 and 2863 cm^{-1} corresponding to the CH_2 stretching vibrations and the peaks at 1744 cm^{-1} and the band at 1170–1057 cm^{-1} arising from the ester C=O and C—O stretching vibrations, respectively. The spectra of residues obtained at different reactions times preserved almost the typical absorption bands of cork powder. The principal differences are the decrease in intensity of the peaks at 2950 and 2906 cm^{-1}, corresponding to the C—H stretching vibration and the increase in intensity of the sharp band around 1110 cm^{-1}, attributed to the C—O stretching vibration. The increase of the intensity of the latter band could be attributed to the solvent mixture indicating that during the liquefaction it was incorporated into the residue.

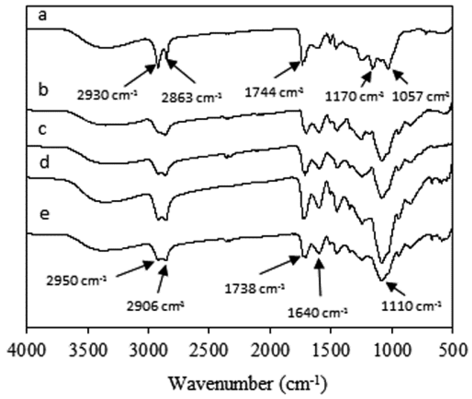


Figure 9. FTIR normalized spectra of cork powder (a) and residue obtained from liquefied cork powder at different liquefaction times (b) 10, (c) 40, (d) 60, (e) 80 min. Liquefaction temperature, 150 °C; sulfuric acid concentration, 4 wt %; solvents mixture, PEG 400/glycerol, 90/10 (w/w); liquefaction solvents/cork powder, 5/1 (w/w).

Notice should be made that the residues were thoroughly washed with water prior to analyses hence, the increase of intensity of the C–O stretching band implies that the polyhydric alcohols were indeed incorporated in the residue. The band around 1640 cm^{-1} is assigned to residual water. Furthermore, these results suggest that the solid residue may be used as fillers in the preparation of homogeneous polyurethane composite foams due to the compatibility between fillers and matrix.

■ CONCLUSIONS

It was shown that it is possible to convert cork powder into liquid polyols via acid liquefaction, at atmospheric pressure and moderate temperatures, in the presence of PEG 400 and glycerol as liquefaction solvents and sulfuric acid as catalyst. The second-order full-factorial design (2^3) was successfully applied to obtain an optimized set of liquefaction conditions (temperature, sulfuric acid concentration, and time) to minimize the residue content (29 wt %, cork powder basis), i.e. maximize the conversion of cork powder into liquid polyol, in the studied range. As a result, the optimal conditions leading to the minimum residue content that have been determined were the following: 150 °C, 4 wt % of sulfuric acid concentration, and 60 min of liquefaction time. Indeed, the relevance of the role of sulfuric acid concentration on the residue content (at 95% of confidence level) was clearly supported by the mathematical model developed in this study. From the industrial point of view, this process proved to be adequate generating only 5 wt % of residue per total mass of polyol obtained (i.e., reaction product). Finally, these polyols have high potential in the formulation and production of polyurethane foams being an alternative to the existing commercial polyols made with 100% petrochemical raw materials as they have similar characteristics. However, additional work will need to be carried out in order to optimize the process, in particular to maximize the incorporation of cork powder in new materials such as polyurethane foams both as liquid polyol as well as filler in the case of the solid residue. Indeed, due to the chemical nature of this type of residue, the ensuing composites are expected to be rather homogeneous.

AUTHOR INFORMATION

Corresponding Author

*Telephone: +351 234 611 500. Fax: +351 234 611 500. E-mail: artur.ferreira@ua.pt.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank QREN/FEDER for funding the Ecopolyols project (No. 11435). Amorim group is gratefully acknowledged for supplying cork powder. CICECO acknowledges FCT for the Pest-C/CTM/LA0011/2013 project. C.F. acknowledges FCT/MCTES for a research contract under the Program “Investigador FCT 2012”.

REFERENCES

(1) Fernando, S.; Adhikari, S.; Chandrapal, C.; Murali, N. Biorefineries: current status, challenges, and future. *Energy Fuels* **2006**, *20*, 1727−1737.

(2) Alma, M. H.; Basturk, M. A. New polyurethane-type rigid foams from liquefied wood powders. *J. Mater. Sci. Lett.* **2003**, *22*, 1225−1228.

(3) Hakim, A. A.; Nassar, M.; Emam, A.; Sultan, M. Preparation and characterization of rigid polyurethane foam prepared from sugar-cane bagasse polyol. *Mater. Chem. Phys.* **2011**, *129*, 301−307.

(4) Shiraishi, N.; Shirakawa, K.; Kurimoto, Y. *Method for preparing a liquefied solution of lingo-cellulose substance with polyhydric alcohols*. EP0472 474 B1, 1992.

(5) Kurimoto, Y.; Takeda, M.; Koizumi, A.; Yamauchi, S.; Doi, S.; Tamura, Y. Mechanical properties of polyurethane films prepared from liquefied wood with polymeric MDI. *Bioresour. Technol.* **2000**, *74*, 151−157.

(6) Lee, S.-H.; Yoshioka, M.; Shiraishi, N. Liquefaction of corn bran (CB) in the presence of alcohols and preparation of polyurethane foam from its liquefied polyol. *J. Appl. Polym. Sci.* **2000**, *78* (2), 319−325.

(7) Kurimoto, Y.; Koizumi, A.; Doi, S.; Yamauchi, S.; Ono, H. Wood species effects on the characteristics of liquefied wood and the properties of polyurethane films prepared from the liquefied wood. *Biomass Bioenergy* **2001**, *21*, 381−390.

(8) Liang, L.; Mao, Z.; Li, Y.; Wan, C.; Wang, T.; Zhang, L.; Zhang, L. Liquefaction of crop residues for polyol production. *Bioresources* **2006**, *1* (2), 248−256.

(9) Chen, F.; Lu, Z. Liquefaction of wheat straw and preparation of rigid polyurethane foam from the liquefaction products. *J. Appl. Polym. Sci.* **2009**, *111*, 508−516.

(10) Hassan, M.; Shukry, N. Polyhydric alcohol liquefaction of some lignocellulosic agricultural residues. *Ind. Crops Prod.* **2008**, *27*, 33−38.

(11) Jin, Y.; Ruan, X.; Cheng, X.; Lü, Q. Liquefaction of lignin by polyethyleneglycol and glycerol. *Bioresour. Technol.* **2011**, *102*, 3581−3583.

(12) Briones, R.; Serrano, L.; Labidi, J. Valorization of some lignocellulosic agro-industrial residues to obtain biopolyols. *J. Chem. Technol. Biotechnol.* **2012**, *87* (2), 244−249.

(13) Silva, S. P.; Sabino, M. A.; Fernandes, E. M.; Correlo, L. F.; Boesel, L. F.; Reis, R. L. Cork: properties, capabilities and applications. *Int. Mater. Rev.* **2005**, *50* (6), 345−365.

(14) http://www.apcor.pt/artigo/anuario-apcor-2012.htm (accessed Nov 18, 2013).

(15) Machado, R.; Carvalho, J.; Correia, J. Removal of trivalent chromium (III) from solution by biosorption in cork powder. *J. Chem. Technol. Biotechnol.* **2002**, *77*, 1340−1348.

(16) Cardoso, B.; Mestre, A.; Carvalho, A.; Pires, J. Activated carbon derived from cork powder waste by KOH activation: preparation, characterization, and VOCs adsorption. *Ind. Eng. Chem. Res.* **2008**, *47*, 5841−5846.

(17) Silvestre, A. J.; et al. Cork and suberin: major sources, properties and applications. In *Monomers, polymers and composites from renewable resources*; Belgacem, M. N., Gandini, A., Eds.; Elsevier: Amsterdam, Boston, 2008.

(18) Sousa, A.; Gandini, A.; Silvestre, A. J.; Pascoal Neto, C. Synthesis and characterization of novel biopolyesters from suberin and model comonomers. *ChemSusChem.* **2008**, *1*, 1020−1025.

(19) Evtiouguina, M.; Barros-Timmons, A.; Cruz-Pinto, J. J.; Pascoal Neto, C.; Belgacem, N.; Pavier, C.; Gandini, A. Oxypropylation of cork and the use of the ensuing polyols in polyurethane formulations. *Biomacromolecules* **2002**, *3*, 57−62.

(20) Gandini, A.; Cruz-Pinto, J. J.; Pascoal Neto, C. University of Aveiro. Process for the production of liquid polyols of renewable origin by the liquefaction of agro-forestry and agro-food biomass. WO2010020903, 2010.

(21) Briones, R.; Serrano, L.; Llano-Ponte, R.; Labidi, J. Polyols obtained from solvolysis liquefaction of biodiesel production solid residues. *Chem. Eng. J.* **2011**, *175*, 169−175.

(22) Yan, Y.; Pang, H.; Yang, X.; Zhang, R.; Liao, B. Preparation and characterization of water-blown polyurethane foam from liquefied cornstalk polyol. *J. Appl. Polym. Sci.* **2008**, *110*, 1099−1111.

(23) Hu, S.; Wan, C.; Li, Y. Production and characterization of biopolyols and polyurethane foams from crude glycerol based liquefaction of soybean straw. *Bioresour. Technol.* **2012**, *103*, 227−233.

(24) Wang, H.; Chen, H.-Z. A novel method of utilizing the biomass resource: rapid liquefaction of wheat straw and preparation of biodegradable polyurethane foam (PUF). *J. Chin. Inst. Chem. Eng.* **2007**, *38*, 95−102.

(25) Zheng, Z.; Pan, H.; Huang, Y.; Chung, Y. H.; Zhang, X.; Feng, H. Rapid liquefaction of wood in polyhydric alcohols under microwave heating and its liquefied products for preparation of rigid polyurethane foam. *Open Mater. Sci. J.* **2011**, *5*, 1−8.

(26) ASTM D 4662-08. *Standard Test Methods for Testing Polyurethane Raw Materials: Determination of Acid and Alkalinity Numbers of Polyols*; ASTM International. 2011; DOI: 10.1520/D4662-08R11E01.

(27) ASTM D 4274-05. *Standard Test Methods for Testing Polyurethane Raw Materials: Determination of Hydroxyl Numbers of Polyols*; ASTM International. 2005; DOI: 10.1520/D4274-05.

(28) ASTM D4878−08. *Standard Test Methods for Polyurethane Raw Materials: Determination of Viscosity of Polyols*. ASTM International, 2008; DOI: 10.1520/D4878-08.

(29) Zhang, H.; Ding, F.; Luo, C.; Xiong, L.; Chen, X. Liquefaction and characterization of acid hydrolysis residue of corncob in polyhydric alcohols. *Ind. Crops Prod.* **2012**, *39*, 47−51.

(30) Jasiukaityte, E.; Kunaver, M.; Strlič, M. Cellulose liquefaction in acidified ethylene glycol. *Cellulose* **2009**, *16* (3), 393−405.

(31) Kobayashi, M.; Asano, T.; Kajiyama, M.; Tomita, B. Analysis on residue formation during wood liquefaction with polyhydric alcohol. *J. Wood Sci.* **2004**, *50* (5), 407−414.

(32) Min, N.; Guang-jie, Z.; Alma, M. H. Polycondensation reaction and its mechanism during lignocellulosic liquefaction by an acid catalyst: a review. *Forestry Stud. China* **2011**, *13* (1), 71−79.

(33) Pan, H.; Shupe, T. E.; Hse, C. Y. Characterization of liquefied wood residues from different liquefaction conditions. *J. Appl. Polym. Sci.* **2007**, *105*, 3739−3746.

(34) Pan, H.; Zheng, Z.; Hse, C. Y. Microwave-assisted liquefaction of wood with polyhydric alcohols and its application in preparation of polyurethane (PU) foams. *Eur. J. Wood Wood Prod.* **2012**, *70* (4), 461−470.

(35) Zhang, H.; Pang, H.; Shi, J. S.; Fu, T.; Liao, B. Investigation of liquefied wood residues based on cellulose, hemicellulose, and lignin. *J. Appl. Polym. Sci.* **2012b**, *123*, 850−856.

(36) Ionescu, M. *Chemistry and Technology of Polyols for Polyurethanes*; Rapra Technology Limited: Shrewsburty, Sheopshire, UK., 2005.