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Polyols Production by Chemical Modification of Autocatalyzed Ethanol-Water Lignin from *Betula alnoides*

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ABSTRACT: *Betula alnoides* lignin, recovered as a byproduct in autocatalyzed ethanol-water pulping process, was converted into viscous polyether polyols through oxypropylation and liquefaction methods, with the aim of adding value to this byproduct. The oxypropylation reaction was performed by reacting autocatalyzed ethanol-water lignin (AEL) with propylene oxide under the acidic and alkaline conditions at room temperature, respectively. In contrast, the liquefaction reaction was carried out using the mixed solvents of polyethylene glycol and glycerol at 160°C with sulfuric acid as a catalyst. The resulting polyether polyols from each method was characterized by Fourier transform-infrared (FTIR), ^{1}H and ^{31}P nuclear magnetic resonance (NMR) spectroscopy, gel permeation chromatography (GPC), and thermogravimetric analysis. Quantitative ^{31}P NMR indicated that all the aliphatic hydroxyl group values of polyols increased significantly by the above two methods. More secondary hydroxyl groups (2.016 mmol/g) were obtained in the alkaline oxypropylation reaction, whereas more primary hydroxyl groups (4.296 mmol/g) were found in the liquefied product. GPC analysis showed that the alkaline oxypropylated product (M_w 3130 g/mol, M_n 2080 g/mol) and liquefied product (M_w 4990 g/mol, M_n 4630 g/mol) have higher molecular weights than AEL (M_w 2560 g/mol, M_n 1530 g/mol). Thermal stability analysis suggested that the polyether polyols have a lower degradation temperature than AEL. These polyols used as precursors in polyurethane synthesis give promising properties, which open new avenues of exploitation of AEL. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 434–442, 2013

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INTRODUCTION

In recent years, the exploitation and utilization of lignocellulosic biomass for chemicals and materials has been attracting considerable attention, mainly due to the economical and environmental problems accompanied with the use of fossil resources. Lignin is the second most abundant component in plant cell walls of lignocellulosic materials after cellulose, corresponding to an annual production of 5 × 10^7 tons.[1] It is an irregular aromatic biopolymer consisting primarily of phenylpropane units linked by ether and carbon-carbon bonds.[2]

As we known, most utilization of lignin as a macromonomer is mainly dependent on its source and subsequent isolation processes, which are closely related to the relative reactivity of both aliphatic and phenolic hydroxyl groups. Because organosolve pretreatment is considered as an environmentally friendly and promising pretreatment technology for biofuels, enormous amounts of autocatalyzed ethanol-water lignin (AEL) are produced.[3] AEL is a high-purity and sulfur-free lignin, which has less condensed structure and narrower molecular weight distribution than lignin obtained by other methods.[4] Lignin samples contain a variety of functional groups, such as hydroxyl groups and carboxylic acid groups. Hydroxyl groups are the most characteristic functions in lignin, which determine its reactivity and constitute the reactive sites in macromolecular chemistry.[5] Lignin is utilized as a sole precursor in the synthesis of polyols, and two alternative approaches have been put forward: (i) oxypropylation of lignin with propylene oxide (PO), [6,7] (ii) liquefying lignin with polyethylene glycol (PEG) and glycerol.[8]

One promising approach is the oxypropylation reaction between lignin and PO. In the initial reaction, an alkoxy group of lignin molecules react with PO, which would lead to hydroxypropylated lignin. This product can react further with PO molecules and the formation of the poly(oxypropylene) chains of various lengths, each terminated with a hydroxyl group. The resulting polyols were expected to react with isocyanate-terminated prepolymer to form polyurethane.[6,9–12] Among them, most of the oxypropylation reactions needed high temperature and pressures to work, and the reaction conditions were complex, which were conducted in the presence of potassium hydroxide as a catalyst. However, according to the literature,[13,14] the procedure for lignin oxypropylation through a relatively simple treatment with PO under mild conditions was selected. The other interesting approach is the liquefaction of lignin with PEG and glycerol. In liquefaction processes, lignocellulosic materials, such as bagasse,[15] cotton stalk,[16] wheat straw,[17] bamboo,[18] and western red cedar, are dissolved into different solvents at certain temperature with a catalyst.[19] Furthermore, the liquefaction of lignin models, such as guaiacylglycerol-β-guiacyl ether with phenol,[20] and the liquefaction of enzymatic hydrolysis lignin with PEG and glycerol has been investigated.[8] In the liquefaction process of lignin, it was firstly degraded to small fragments of lower molecular weight with sulfuric acid as a catalyst under high temperature. Then the reaction of the hydroxyl groups in the fragments with PEG form ether bonds in the liquefaction products. In the later stage, residual lignin self-polymerization occurred.[8] In these articles, the biomass is directly converted into viscous polyols in the synthesis of polymeric products. However, few articles concerning liquefying AEL into polyether polyols were reported.

Based on the above considerations, the aim of this work was to establish the feasibility of converting AEL from *Betula alnoides* using both oxypropylation and liquefaction methods into polyether polyols. These two processes were carried out in PO and PEG/glycerol reactants, respectively. The bio-based polyol products obtained under optimized conditions can be used directly for the preparation of polyurethane foams without any additional treatment. The polyols were characterized by using spectroscopic techniques, such as Fourier transform-infrared (FTIR), nuclear magnetic resonance (NMR) spectroscopy, and their thermal stability was studied in terms of thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials

Birch (*Betula alnoides*) was collected from Yunnan Province (Southern China). Wood meal (20–40 mesh) was collected. PO was used as the oxypropylation reagent. PEG (PEG-400) and glycerol were used as the liquefaction reagents. All other chemicals were reagent grade and were used without further purification.

AEL Preparation

The lignin preparation was carried out using a 1.0 L stainless steel reactor (Parr, USA). Before autocatalyzed ethanol-water pulping process, the reactor was filled with excess nitrogen to remove the air. The reactor was loaded with the raw material (10 g) and 60% ethanol solution with a solid to liquid ratio of 1 : 10 (g/mL), and then heated up to 200°C for 2 h. After treatment, the reactor was cooled down rapidly, and the pulp was recovered by filtration using nylon and washed repeatedly by 60% aqueous ethanol. Next, the filtrate and the washing liquor were combined and then concentrated to about 20 mL under reduced pressure. Subsequently, the concentrated liquor was poured into three volumes of water and the lignin precipitate was collected by filtration. The lignin preparation obtained was freeze-dried for further use.

Oxypropylation of AEL

Oxypropylation reactions were conducted according to Ahvazi et al.[14] with slight modifications. Briefly, AEL (200 mg) and 100 mL of 37% PO were mixed in a 250 mL beaker under constant magnetic stirring for 30 min. Two different batches were carried out at room temperature under constant agitation for 5 days, 5 mL of 0.1 N NaOH and 5 mL of 1 M H_2SO_4 were added as catalysts, respectively. After the reaction was complete, the product was oven dried at 105°C to a constant weight before analysis.

Liquefaction of AEL

Liquefaction experiment was performed according to the literatures.[8,15] The optimal liquefaction conditions were liquefying reactants by weight ratio of PEG-400 : glycerol : sulfuric acid of 90 : 10 : 3, AEL/liquefying reactants at a ratio of 0.2, reaction temperature: 160°C, and reaction time: 60 min. Liquefying reactants were added into a three-necked glass flask (250 mL) immersed in an oil bath and heated, which was equipped with reflux condenser and thermometer under constant magnetic stirring at nitrogen atmosphere. When the temperature reached 160°C, AEL was added gradually, and the liquefaction reaction was carried out for 1 h to obtain a homogeneous liquefied product. Then the flask was cooled down rapidly in ice-bath, and the liquefied products were oven dried at 105°C to a constant weight before further analysis.

Characterization of AEL and Polyols

Measurement of Reaction Extent. Reaction extent of oxypropylated and liquefied products was determined as following: 1 g of the product was weighed and diluted with 20 mL 1, 4-dioxane-water mixture (80/20, w/w). The dilution was adequately stirred over 2 h and filtered with filter paper. The filter residue was oven dried at 105°C to a constant weight. The yield of the residue was calculated as follows:

$$\text{Yield} = [1 - M/M_0] \times 100\%$$

where M_0 is the mass of AEL and M is the mass of unreacted residue dissolved in 1, 4-dioxane after oxypropylation or liquefaction reaction.

FTIR Analysis. FTIR spectra were recorded using a Thermo Scientific Nicolet iN10 FTIR Microscope (Thermo Nicolet Corporation, Madison, WI) equipped with a liquid nitrogen cooled MCT detector. Samples were ground and pelletized using BaF_2 and their spectra were recorded in the range from 4000 to 700 cm^{-1} at 4 cm^{-1} resolution and 128 scans per sample.

^{1}H, HSQC and ^{31}P NMR Analysis. ^{1}H NMR spectra were recorded after 128 scans. Samples (20 mg) were dissolved in 1 mL of deuterated dimethylsulfoxide (DMSO-d_6, 99.8% D). A repetition time of 3.98 s for acquisition time and 1 s for relaxation time were used. ^{1}H-^{13}C correlation 2D (HSQC) NMR spectrum was recorded with a *z*-gradient double resonance probe. Sample (25 mg) was dissolved in 1 mL of DMSO-d_6 (99.8% D). The spectral widths were 8000 and 20,000 Hz for the ^{1}H- and ^{13}C- dimensions, respectively.

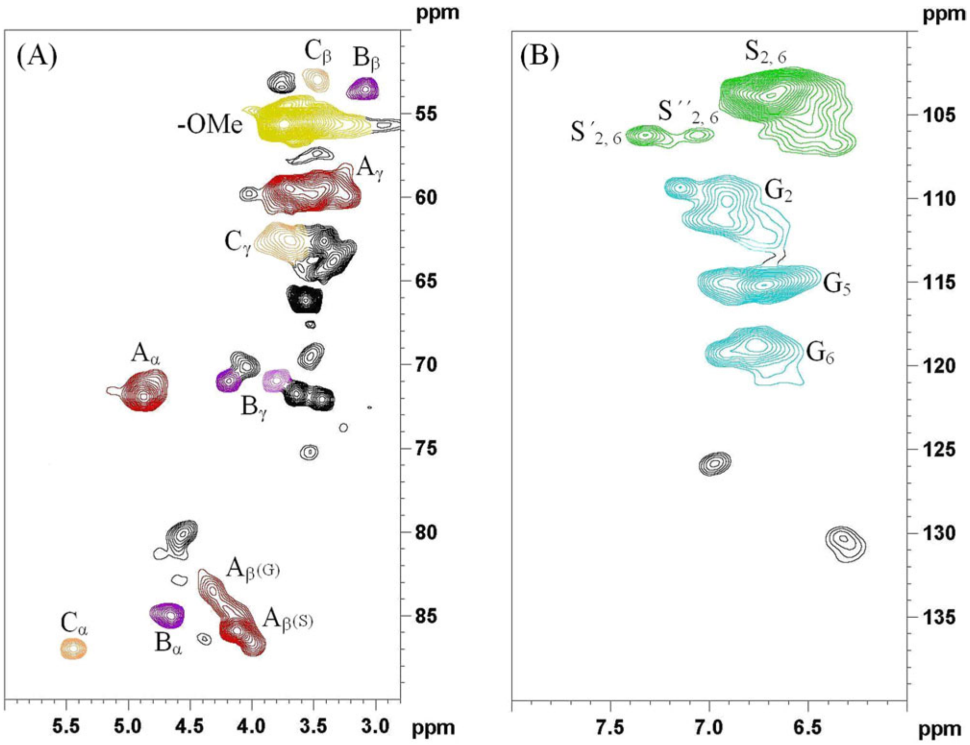

Figure 1. HSQC spectra of AEL from Betula alnoides: (A) oxygenated aliphatic region (δC/δH 50–90/2.8–6.0 ppm), and (B) aromatic region (δC/δH 100–140/6.0–8.0 ppm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

^{31}P NMR spectra were recorded with 32,768 data points and a spectral width of 60606.06 Hz. A relaxation delay of 5 s was used, and the number of scans was 512. Samples (30 mg) were weighed into 2 mL a volumetric flask, 500 μL of a solvent mixture containing anhydrous pyridine and deuterated chloroform (1.6 : 1, v/v) were added. This was followed by the addition of 100 μL of cyclohexanol (10.85 mg/mL), as an internal standard, and 50 μL of chromium (III) acetylacetonate solution (5.6 mg/mL in anhydrous pyridine and deuterated chloroform 1.6 : 1, v/v), as a relaxation reagent. Finally, the mixture was treated with 100 μL of phosphitylating reagent (2-chloro-1, 3, 2-dioxaphospholane) and then transferred into a 5 mm tube for subsequent NMR analysis. All NMR experiments were carried out on a Bruker AV III NMR spectrometer at 400 MHz at 25°C. Spectra were processed and analyzed using the Bruker Topspin 2.1 software package.

GPC Analysis. Gel permeation chromatography (GPC, Agilent 1200, Shropshire, UK) was carried out on a PL-gel Mixed Bed HPLC Column (Inner Diam: 7.5 mm; Length: 300 mm; Particle Size: 10 um; Mid-Weight range: 500–10 M). Detection was achieved with a Knauer differential refractometer. The column was eluted with tetrahydrofuran at a flow rate of 1.0 mL/min. Samples (4 mg) were dissolved in 2 mL tetrahydrofuran. Monodisperse polystyrene was used as the standard for calibration.

Thermal Analysis. Thermal stability was determined using TGA and differential thermal analysis (DTA) on a simultaneous thermal analyzer (DTG-60, Shimadzu, Japan). The apparatus was continually flushed with nitrogen at a flow of 30 mL/min. Each sample was weighed between 8 and 12 mg, and then heated from room temperature to 600°C at a rate of 20°C/min.

RESULTS AND DISCUSSION

Lignin Characterization

With the purpose of obtaining high purity and yields of lignin, the lignin preparation (AEL) was isolated from autocatalyzed ethanol-water pulping process. Meanwhile, for a more complete structural characterization of *Betula alnoides* lignin, AEL was subjected to 2D-HSQC-NMR analysis.[21–23] 2D-HSQC spectrum of AEL in the side chain region (δ_C/δ_H 50–90/2.8–6.0 ppm) is shown in Figure 1(A). The main substructures present are depicted in Figure 2. The *β-O-4′* substructure (A) was prominent signals, their C_α—H_α correlations being at δ_C/δ_H 72.1/4.88 ppm. Similarly, C_β—H_β correlations were observed at δ_C/δ_H 83.6/4.32 and 86.2/4.13 ppm for *β-O-4′* structures linked to guaiacyl (G) and syringyl (S) lignin units, respectively. The C_γ—H_γ correlations in *β-O-4′* substructures observed at δ_C/δ_H 59.8/3.25 and 3.68 ppm partially overlapped with other signals. Besides *β-O-4′* aryl ether substructures, other linkages were also observed. Obvious signals for resinol (*β*—*β′*/*α*—O-*γ*/*γ*-*O*-*α*) substructures (B) were also observed, as shown by their C_α—H_α, C_β—H_β and the double C_γ—H_γ correlations at δ_C/δ_H 85.1/4.68, 53.8/3.1, and 71.1/3.81 and 4.18 ppm, respectively. The C_α—H_α, C_β—H_β, and C_γ—H_γ correlations of phenylcoumaran (*β-5′*/*α-O-4′*) substructures (C) were observed at δ_C/δ_H 87.5/5.45, 53.1/3.49, and 62.8/3.68 ppm, respectively. The main cross-signals of the lignin in the aromatic region (δ_C/δ_H 100–140/6.0–8.0 ppm)

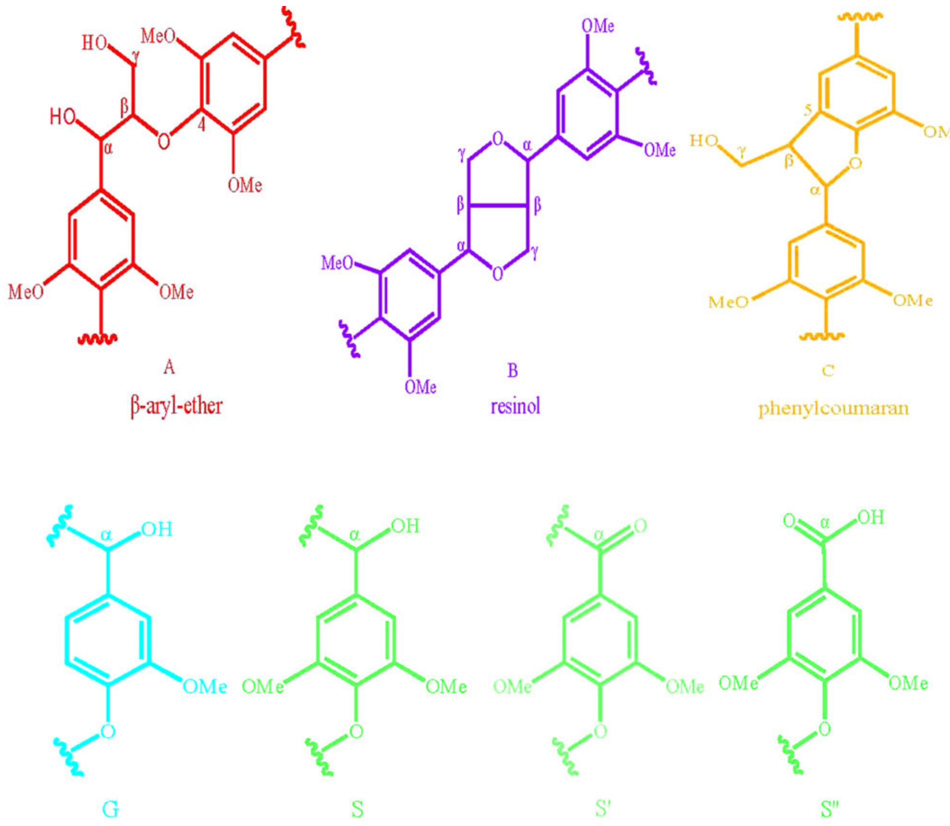

Figure 2. Main structures present in AEL: (A) β-O-4́ linkages; (B) resinol (β-β́/α-O-γ́/γ-O-ά) structures; (C) phenylcoumarane (β-5́/α-O-4́) structures; (G) guaiacyl unit; (S) syringyl unit; (S′) oxidized syringyl unit with a carbonyl group at C_α (phenolic); (S″) oxidized syringyl unit with a carboxyl group at Cα. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

are shown in Figure 1(B). The S units showed a prominent signal for the $C_{2,6}$—$H_{2,6}$ correlation at δ_C/δ_H 103.9/6.68 ppm, whereas the G units showed different correlations for C_2—H_2 (δ_C/δ_H 110.2/6.91 ppm), C_5—H_5 (δ_C/δ_H 115.2/6.71), and C_6—H_6 (δ_C/δ_H 118.8/6.76 ppm). Signals corresponding to $C_{2,6}$—$H_{2,6}$ correlations in C_α-oxidized S units (S′ and S″) were observed at δ_C/δ_H 106.5/7.31 and 106.5/7.04 ppm. All the above results indicated that AEL is a typical hardwood lignin.

Preparation of Polyol Products

In the present work, AEL-based polyol products were prepared through oxypropylation and liquefaction for the purpose of preparing polyurethane foams. By comparing oxypropylation with liquefaction method, an appropriate one for the conversion of AEL into polyol products was chosen. The extent of both oxypropylation and liquefaction reactions was high as expressed by the amount of unreacted lignin residue that was barely present in the polyol products. An oxypropylated product yield of 93% was obtained at an AEL : PO ratio of 2 by using 37% PO at room temperature for 5 days under the alkaline condition, whereas a corresponding yield of 80% was obtained under an acidic condition.[14] In the case of the liquefaction process, a yield of 97% was obtained at AEL : liquefying reactants ratio of 0.2 at 160°C for 1 h. The results indicated that the efficiency of liquefaction reaction was higher than oxypropylation method under the optimal conditions for the conversion of AEL into polyols.

FTIR Analysis

FTIR spectroscopy was used to investigate the structural discrepancies of the lignin and its derivatives. As can be seen from the spectra (Figure 3), the peaks at about 3600–3100 cm^{-1} are attributed to OH groups stretching absorption, 2939–2847, 1458, and 1370 cm^{-1} are assigned to CH_3, CH_2, and CH aliphatic groups, respectively.

The bands at 1593, 1508, 1458, and 1421 cm^{-1} are due to aromatic skeletal vibrations of sample (a). Furthermore, the syringyl absorption around 1323 cm^{-1}, weak band at 1262 cm^{-1}, strong band near 1215 cm^{-1}, and its maximum absorbance at 1119 cm^{-1} are attributed to characteristic absorption peaks of sample (a). All these characteristics suggested that AEL was a typical hardwood lignin, which were well in agreement with the 2D-HSQC-NMR analysis.[21,22] Sample (b) exhibited more increase in the peak intensity of OH groups than the corresponding OH groups from sample (c). This phenomenon suggested that AEL was more liable to oxypropylation under the alkaline condition than under the acidic condition, which is in agreement with the literature.[6,14] Sample (d) showed that the absorption intensity of OH groups increased significantly, which might be due to the structure of PEG and glycerol. Additionally, the increase in the peak intensity of methyl groups was probably due to two reasons, according to Jin et al.,[8] one was that the bonds between the coupling of benzene ring units ruptured and

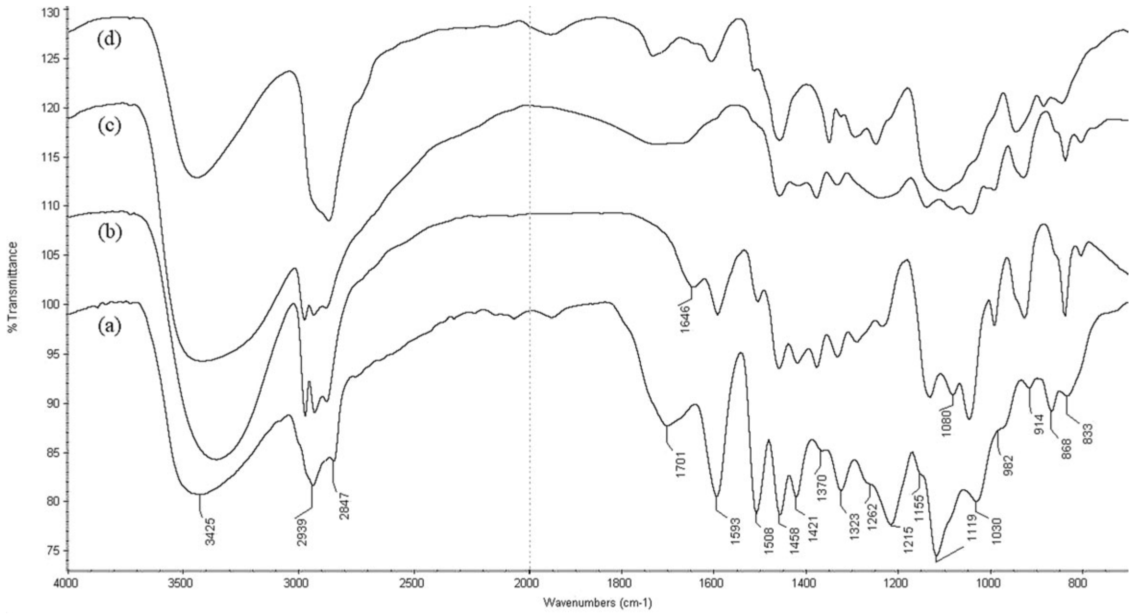

Figure 3. FTIR spectra of (a) AEL, (b) oxypropylated lignin with PO under the alkaline condition, (c) oxypropylated lignin with PO under the acidic condition, (d) liquefied lignin with glycerol and PEG.

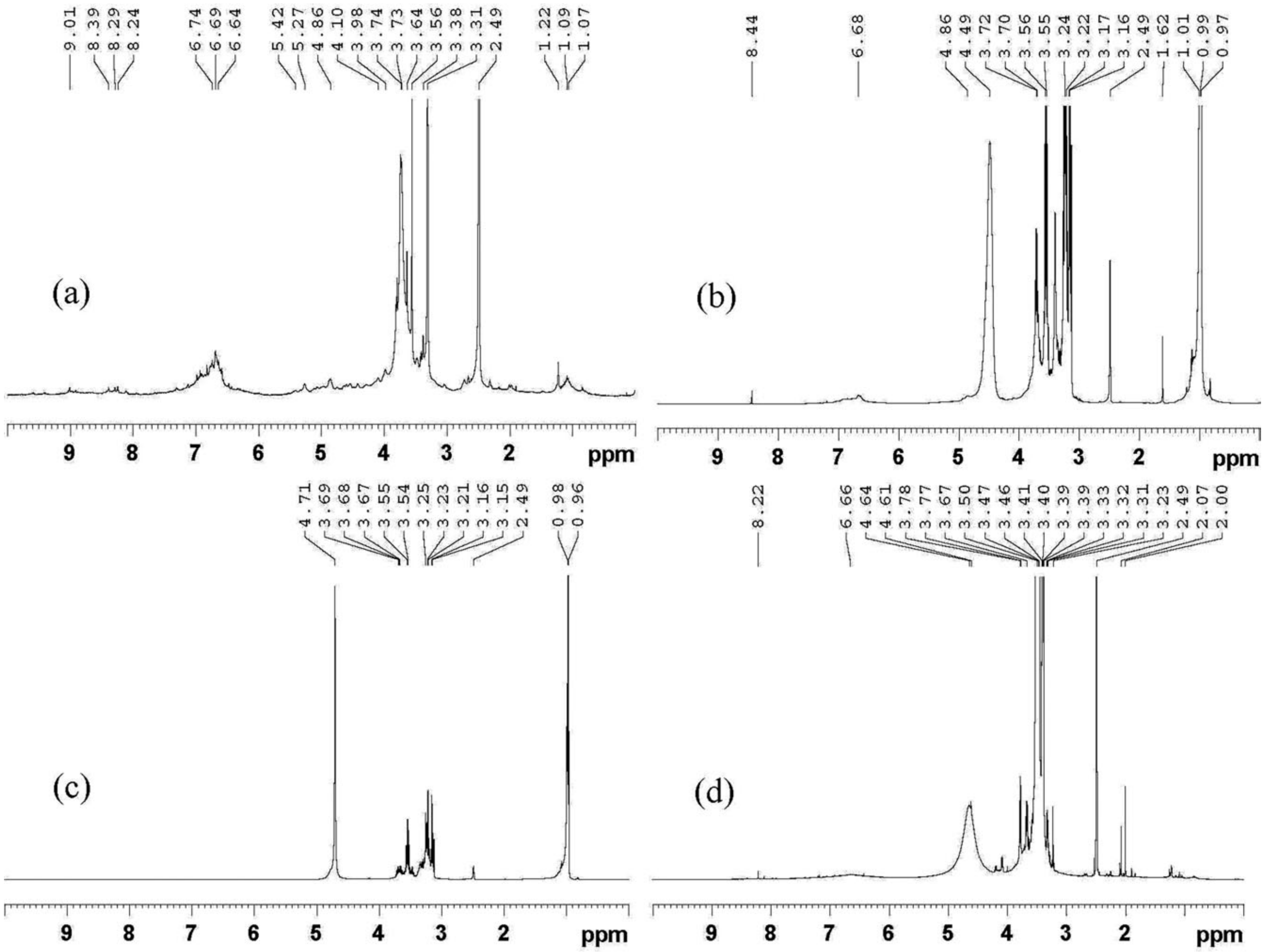

Figure 4. ^{1}H NMR spectra of (a) AEL, (b) oxypropylated lignin with PO under the alkaline condition, (c) oxypropylated lignin with PO under the acidic condition, (d) liquefied lignin with glycerol and PEG.

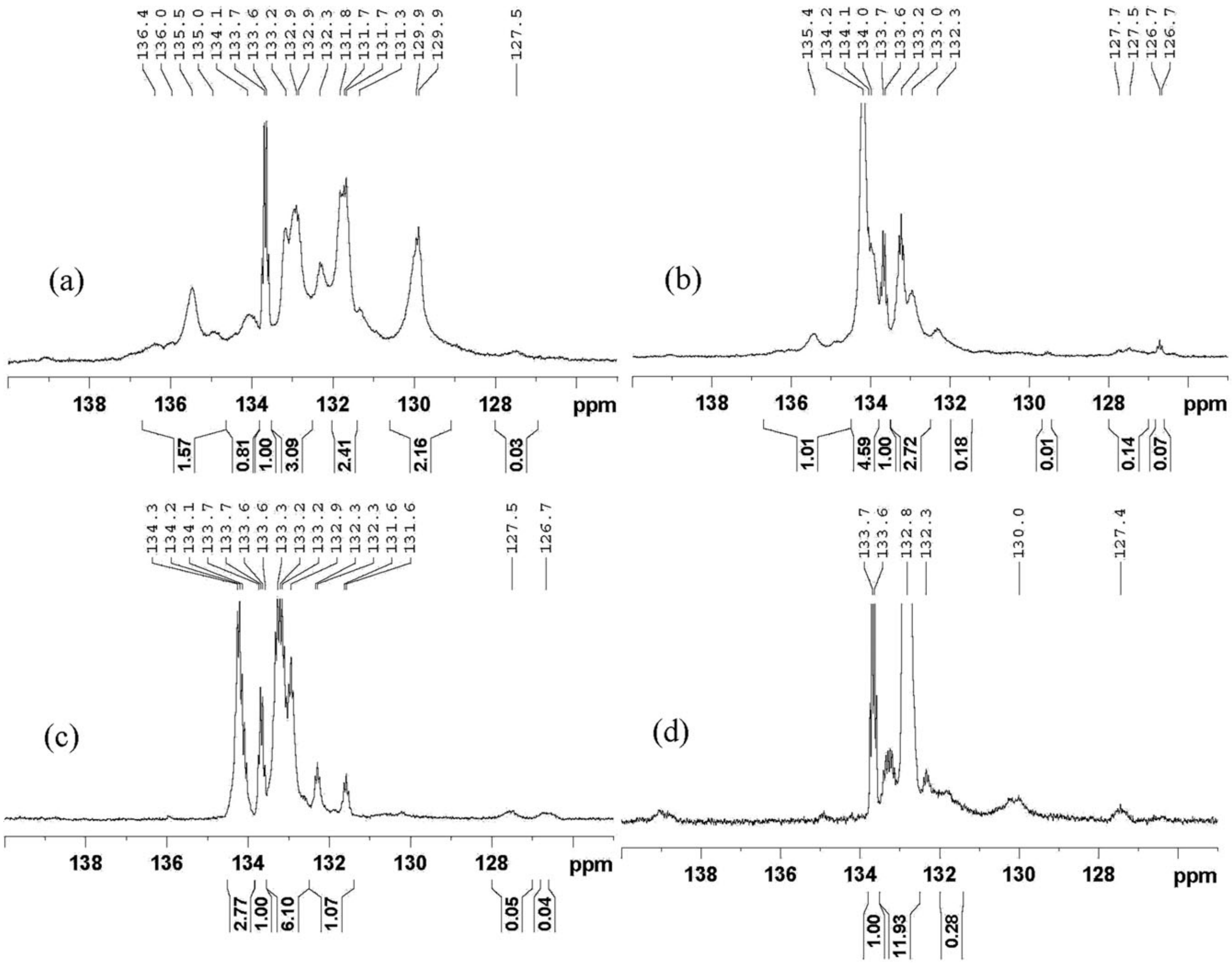

Figure 5. ^{31}P NMR spectra of (a) AEL, (b) oxypropylated lignin with PO under the alkaline condition, (c) oxypropylated lignin with PO under the acidic condition, (d) liquefied lignin with glycerol and PEG.

smaller benzene ring units formed, the other was that the alkylation reaction of the phenol hydroxyl units of the lignin occurred. All the above results indicated that oxypropylation and liquefaction reactions induced a successful chain extension reaction for the conversion of AEL into polyether polyols.

^{1}H NMR Analysis

^{1}H NMR spectra of different samples are shown in Figure 4, in which most of the peaks were consistently similar, apart from some different signals. The peaks around 3.8, 3.5, and 1.1 ppm are attributed to CH_3, CH_2, and CH groups of PO homopolymer of sample (b) and (c), respectively. Furthermore, it should be noted that the doublet in the case of the methyl signal of PO could not be observed probably due to the broadening effect of the PO homopolymer chains.[6] In addition, strong peaks in the region of 6.5–7.5 ppm are assigned to aromatic ring of sample (a) whereas these peaks in other samples (b-d) were quite weak. All these signals confirmed that polyols were indeed synthesized through oxypropylation and liquefaction methods. These observations corroborated the conclusion drawn from the comparison of the corresponding FTIR spectra.

^{31}P NMR Analysis

^{31}P NMR spectroscopy was used to identify and quantify several different classes of hydroxyl groups in lignin and its derivatives. The ^{31}P NMR spectra of the samples phosphitylated by 2-chloro-1, 3, 2-dioxaphospholane are presented in Figure 5. Distinction between the primary and secondary aliphatic hydroxyl groups is summarized in Table I.

The content of hydroxyl groups was obtained by integration of the following region: *erythro* (136.7–134.5 ppm), *threo* (134.5–133.8 ppm), primary hydroxyl units (133.5–132.5 ppm), syringyl phenolic units (132.0–131.4 ppm), guaiacyl phenolic units (129.7–129.5 ppm), *p*-hydroxyphenyl phenolic units (128.0–127.0 ppm), and carboxylic acids (126.8–126.6 ppm).[14] As can be seen from the spectra (Figure 5), sample (a) showed typical features for a hardwood lignin, which mainly included syringyl and guaiacyl units; a minor amount

Table I. ^{31}P NMR Spectroscopy Analysis of (a) AEL, (b) Oxypropylated Lignin with PO Under the Alkaline Condition, (c) Oxypropylated Lignin with PO Under the Acidic Condition, and (d) Liquefied Lignin with Glycerol and PEG (mmol/g)

Sample	(a)	(b)	(c)	*(d)*
COOH	ND	0.026	0.013	*ND*
Phenolic-OH				
G[a]	0.778	0.003	ND	*ND*
S[b]	0.909	0.067	0.160	*0.101*
H[c]	0.012	0.052	ND	*ND*
Aliphatic-OH				
Primary	1.113	0.980	2.194	*4.296*
Secondary (*erythro* and *threo*)	0.859	2.016	0.997	*ND*
Total-OH	*3.671*	*3.144*	*3.364*	*4.397*

[a]Guaiacyl-OH, [b]Syringyl-OH, [c]*p*-hydroxyphenyl-OH.
ND, not detectable.

of *p*-hydroxyphenyl units was detected. These signals were in accordance with the aforementioned results of FTIR and NMR analysis. Comparison of sample (b) and (c), it was observed that large amounts of aliphatic hydroxyl groups changed obviously during the oxypropylation reaction, the secondary hydroxyl groups of sample (b) increased to 2.016 mmol/g whereas the primary hydroxyl groups of sample (c) added up to 2.194 mmol/g. Faix[24] showed that the signals of secondary hydroxyl groups were probably assigned to the *erythro* and *threo* configurations of the *β-O*-aryl ether structures in lignin. Argyropoulos[25] demonstrated that the formation of predominantly secondary alcohols probably occurred at Cα-aryl structure. In the oxypropylation reaction under alkaline condition, resulting in the formation of secondary hydroxyl groups, whereas primary hydroxyl groups were detected under the corresponding acidic condition. With regard to the liquefaction process, the content of primary hydroxyl groups significantly increased from 1.113 to 4.296 mmol/g, indicating that polyols were formed by the introduction of PEG and glycerol into the lignin structure. However, the interesting phenomenon was that the content of secondary hydroxyl groups became zero. Based on the conclusion of Jasiukaityte et al.[26], the increased amounts of primary hydroxyl groups were probably due to the introduction of PEG and glycerol molecule at C_α position of lignin. As for the results of secondary hydroxyl groups, the reason may be interpreted in terms of lignin self-polymerization. Accordingly, the higher primary hydroxyl groups were obtained in the liquefaction process. By contrast, the higher secondary hydroxyl groups were found during the oxypropylation reaction under alkaline condition. During the production of bio-based polyurethanes, the majority of aliphatic hydroxyl groups were used as available and more reactive functional groups, and these hydroxyl groups could not only enhance the polycondensation process but also reduce the steric and electronic constraints in the chain extension process.[15]

GPC Analysis

The effects of oxypropylation and liquefaction reaction on lignin structure were evaluated by the changes in molecular weight. Weight-average (M_w) and number-average (M_n) molecular weights and polydispersity (M_w/M_n) of the samples for GPC analysis are shown in Table II. Compared with the sample (a) (M_w, 2560 g/mol and M_n, 1530 g/mol), the increase of M_w and M_n after oxypropylation reaction occurred under the alkaline condition (M_w, 3130g/mol and M_n, 2080 g/mol). More importantly, a greater increase of M_w and M_n was observed after liquefaction reaction (M_w, 4990g/mol and M_n, 4630 g/mol). The molecular weights of sample (d) had a greater increase than samples (b) and (c). The increase of molecular weights of the polyol products indicated that condensation reactions between the lignin and multifunctional alcohols occurred. Lai and Sarkanen[27] have reported that residual lignin self-polymerization reaction occurred during the liquefaction reaction of the dissolved lignin by glycerol and PEG. Jasiukaityte et al.[26] have suggested that the high molecular weight of sample (d) was mainly due to the condensed structures formed by the incorporation of the aliphatic glycerol and PEG moieties into the lignin structure. Furthermore, it should be noted that the molecular weights of sample (b) was not increased remarkably, indicating that lignin was less prone to oxypropylation under the acidic condition than that in the alkaline condition. In addition, a similar low value of polydispersity (M_w/M_n 1.08–1.67) indicated that all the samples had a narrow molecular weight distribution.

Thermal Stability Analysis

The thermal decomposition of different samples is commonly determined by thermal stability analysis under nitrogen atmosphere. TG curves showed the weight loss in relation to the temperature of thermal degradation whereas DTG curves revealed the corresponding rate of weight loss. As shown in Figure 6, the thermal decomposition temperature of all the samples (a-d) was in the region ranging from 200 to 400°C. Sample (a) displayed a typical single weight loss and a maximum thermal decomposition temperature at 240–300°C, which is characteristic of lignin. Compared with sample (a), other samples (b-d) were more thermal labile. Sample (b) and (c) showed significantly different thermal stability, indicating that the polyol products obtained in the oxypropylation process under the alkaline condition were essentially different from those obtained under the acidic condition. Samples (c) and (d) showed similar features of the weight loss and maximum decomposition temperature, which were a combination of the corresponding polyols and reactants, with two main losses at 200–270 and 370–410°C. Moreover, the

Table II. Molecular Weight Analysis of (a) AEL, (b) Oxypropylated Lignin with PO Under the Alkaline Condition, (c) Oxypropylated Lignin with PO Under the Acidic Condition, and (d) Liquefied Lignin with Glycerol and PEG

Sample	(a)	(b)	(c)	*(d)*
M_w	2560	3130	2960	*4990*
M_n	1530	2079	1860	*4630*
M_w/M_n	*1.67*	*1.51*	*1.59*	*1.08*

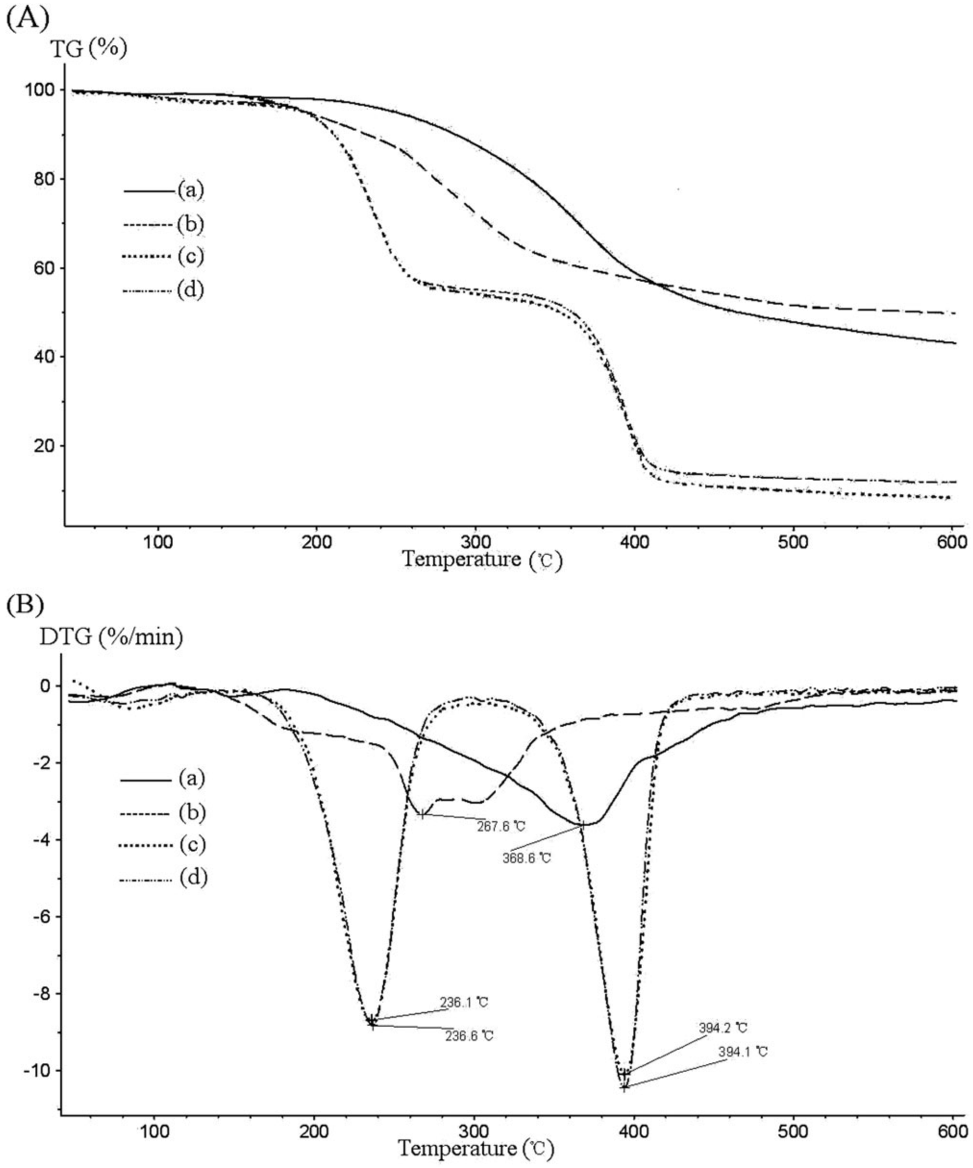

Figure 6. Thermograms analysis of (a) AEL, (b) oxypropylated lignin with PO under the alkaline condition, (c) oxypropylated lignin with PO under the acidic condition, (d) liquefied lignin with glycerol and PEG.

peaks at 236 and 394°C observed in sample (d) were partly produced by the thermal decomposition of reactants (glycerol and PEG). Sample (d) gave profiles, which were a combination of the corresponding reactants and polyether polyols; introduction of the reactants made the mixture slightly less thermal liable.[28] Accordingly, after the oxypropylation or liquefaction reactions, it was observed that the polyether polyols showed differences with respect to AEL.

CONCLUSIONS

Oxypropylation and liquefaction techniques have been used as possible ways of utilizing AEL from the autocatalyzed ethanol-water pulping process. The efficiency of liquefaction reaction was higher than oxypropylation method for the conversion of AEL into polyols. The polyether polyols obtained from two methods could be used directly as precursors in manufacturing polyurethane. Additionally, the research of preparing polyurethane with the polyether polyols generated from oxypropylation and liquefaction reactions will be further illustrated.

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