



## Production of polyols via direct hydrolysis of kraft lignin: Effect of process parameters



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### HIGHLIGHTS

- Bio-polyols were produced via alkaline hydrolysis of kraft lignin for polyurethanes.
- A high yield of polyols up to 92% was obtained, with suitable –OH numbers and  $M_w$ .
- The  $M_w$  of lignin was reduced from 10,000 g/mol to ~3300 g/mol at low temperature.
- A higher temperature especially 350 °C favored polyols of lower  $M_w$  ~1400 g/mol.
- A longer reaction time produced polyols with lower aliphatic –OH number.

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### ABSTRACT

Kraft lignin (KL) was successfully depolymerized into polyols of moderately high hydroxyl number and yield with moderately low weight-average molecular weight ( $M_w$ ) via direct hydrolysis using NaOH as a catalyst, without any organic solvent/capping agent. The effects of process parameters including reaction temperature, reaction time, NaOH/lignin ratio (w/w) and substrate concentration were investigated and the polyols/depolymerized lignins (DLs) obtained were characterized with GPC-UV, FTIR-ATR, <sup>1</sup>H NMR, Elemental & TOC analyzer. The best operating conditions appeared to be at 250 °C, 1 h, and NaOH/lignin ratio ≈0.28 with 20 wt.% substrate concentration, leading to <0.5% solid residues and ~92% yield of DL (aliphatic-hydroxyl number ≈352 mg KOH/mg and  $M_w$  ≈ 3310 g/mole), suitable for replacement of polyols in polyurethane foam synthesis. The overall % carbon recovery under the above best conditions was ~90%. A higher temperature favored reduced  $M_w$  of the polyols while a longer reaction time promoted dehydration/condensation reactions.

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### 1. Introduction

Due to increased concerns worldwide of declining low-cost petroleum reserves, energy security, climate change and sustainability, more attention has been focused towards the exploration of renewable resources such as agricultural and industrial wastes/by-products for fuels and chemicals (Sricharoenchaikul, 2009). Lignin (20–30 wt.% in wood) (Fang et al., 2008), a natural, aromatic three dimensional high molecular weight biopolymer composed of phenyl propanol units (Tejado et al., 2007), is a potential candidate for the production of fuels, chemicals and bio-based materials. All native lignins are heterogeneous in nature and mainly composed of two types of linkages: condensed linkages (e.g., 5–5 and β-1 linkages) and ether linkages (e.g., α-O-4 and β-O-4) (Chakar and Ragauskas, 2004). The percentage of ether link-

ages in soft- and hardwood lignins are 56% and 72%, respectively (Pu et al., 2008). Aryl ether linkages can be more easily cleaved than the stable C–C linkages since the latter are stable and resistant to chemical depolymerization.

The major source of lignin (kraft lignin and liginosulfonates) is the pulp and paper industry. About one million tons/year of liginosulfonates, derived from sulfite pulping liquors, are used as dispersants for dyes, pesticides, cement, asphalt and a variety of other applications (Holladay et al., 2007). Nowadays kraft pulping accounts for 80% of the world's chemical pulp production and 50–55 million metric tons of lignin are produced annually in the form of black liquor; the liquid phase remaining after alkaline pulping has liberated the cellulose fibers (Borges da Silva et al., 2009). Black liquor is conventionally burned in recovery boilers to regenerate pulping chemicals and to produce steam and electricity for mill operations. While most kraft lignin is thus not available for isolation, a special case exists in the 60–70% of North American kraft mills that have production bottlenecks due to the thermal capacity

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of their recovery boilers. An interesting solution to this problem is to extract some of the lignin in black liquor by precipitation. In North America alone, the potential of precipitated lignin was estimated at 1.5 Mt/year. The removed lignin can be further utilized as a raw material for value-added bio-products which would diversify the mill's economic base.

Because of lignin's special phenyl propanol structure and aryl-alkyl ether bonding, lignin from kraft pulping mills can be a good source of polyols. These polymers have multiple hydroxyl groups in their structure and are one of the essential raw materials for polyurethane (PU) production (Demharther, 1998). Although with much lower reactivity (Cheng et al., 2012), even crude lignin can be directly incorporated into PU formulations due to the presence of aliphatic and aromatic hydroxyl groups in its structure as the reactive sites (Cateto et al., 2008). Polyols can be polyether or polyester polyols (Tu et al., 2008), with the most critical properties being equivalent weight and hydroxyl number/functionality. Petroleum derived polyols are typically used, but rising petroleum prices and sustainability concerns have focused attention towards bio-based polyols (Bueno-Ferrer et al., 2012) or ligno-polyols (Borges da Silva et al., 2009).

Hydrolysis of lignin can produce a multitude of high value products via acid- or base-catalyzed cleavage of ether bonds (Fang et al., 2008). Hydrolysis is a milder process than pyrolysis, but wide structural heterogeneity of the products remains a great challenge (Roberts et al., 2011; Xu et al., 2008). Lignin hydrolysis under acidic conditions has been extensively studied (Lundquist, 1976; Matsushita and Yasuda, 2005); its major drawback is the unavoidable repolymerization/condensation of intermediate products formed during the reaction (Yuan et al., 2010). Alkaline catalysis or organic solvents are preferable in this regard; however, organic solvents have the disadvantage of increased costs and process complexity arising from the need to recover spent solvent. Depolymerization of lignin in alkali also occurs through the rupture of ether bonds (Nenkova et al., 2011); however, the alkaline catalyst not only hinders coke/char formation but also increases the yield of depolymerized products. Miller et al. (1999) observed high conversions during kraft lignin depolymerization using KOH in supercritical methanol or ethanol at 290 °C. Later, Yuan et al. (2010) produced oligomers/polyols ( $M_w \approx 1000$  g/mol and  $M_n \approx 450$  g/mol) through hydrolytic degradation of alkaline lignin ( $M_w \approx 60,000$  g/mol and  $M_n \approx 10,000$  g/mol) using NaOH in a water-ethanol mixture and phenol as a capping agent (lignin to phenol ratio = 1:1 (w/w)). Under optimal conditions (260 °C and 1 h), char and gas production was negligible. Further studies by Yoshikawa et al. (2012) indicated that strong bases like KOH or NaOH gave superior conversion and were effective in reducing char formation. Recently, Beauchet et al. (2012) carried out base-catalyzed de-polymerization of KL (10 wt.% concentration) in a continuous flow reactor over 270–315 °C and 130 bar for the production of a monomers-rich fraction as well as fractions of gas, small organic compounds and oligomers. Monomers can be suitable precursors for the production of L-Chemicals, and oligomers for L-fuels.

Nowadays, kraft lignin has gained more attention as a potential non-food, biopolyols (Cateto et al., 2008). Proposed reactions include oxypropylation (Li and Ragauskas, 2012), oxidation followed by membrane/ultra-filtration (Borges da Silva et al., 2009) and hydrolytic degradation using organic solvents and a petroleum derived capping agent (phenol) (Yuan et al., 2010). These approaches may be insufficiently "green" or economic due to the use of large amount of petroleum-derived products (phenols, polypropylene glycol, polyethylene glycol etc.) or costly separation techniques.

The major objective of this work is thus to produce polyols via direct hydrolysis of kraft lignin (KL) of  $M_w \approx 10,000$  g/mol, in water. This process is expected to produce renewable polyols from kraft lignin (or simply black liquor) with desirable characteristics

for rigid polyurethane foam synthesis like low  $M_w$ , moderately high aliphatic hydroxyl number/functionality, and high yields. This work presents the preliminary results from a parametric study to determine the key process factors, while detailed process optimization will be reported in our future work.

## 2. Methods

### 2.1. Materials

Softwood kraft lignin (KL) used in this study was kindly provided by FPInnovations-Thunder Bay Bioeconomy Technology Centre and was completely soluble in aqueous alkali (pH > 10). It is a yellow-brown powder with weak odor and specific gravity of 0.80. The relative weight-average molecular weight ( $M_w$ ) of KL is  $\approx 10,000$  g/mol (PDI  $\approx 2.0$ ) based on our GPC-UV analysis. The proximate and ultimate analysis of KL is given in Table 1. The dried sample contained 0.57 wt.% ash and 5.2 wt.% sulfur (on dry ash free basis). The ash content of lignin was determined gravimetrically in a muffle furnace at 700 °C for 4 h. The ultimate analysis was done on a CHNSO Elemental Analyzer and reported on a dry and ash free basis. Other chemicals used include NaOH (96%), sulfuric acid (99%), acetone (99.5%),  $d_6$ -DMSO and  $d$ -chloroform, tetrahydrofuran (THF, HPLC grade), pyridine, acetic anhydride and dibromomethane, all CAS reagent grade, purchased from Sigma-Aldrich and used without further purification.

### 2.2. Kraft lignin hydrolysis experiments

The hydrolysis experiments were carried out in a 100 mL Parr Model 4848 reactor, equipped with a pressure gauge, thermocouple, stirrer, gas line and sampling line. In a typical run, 12 g KL, 33 g NaOH (10 wt.% solution in distilled water) and 15 g of distilled water were loaded into the reactor. The reactor was sealed, evacuated and purged thrice with  $N_2$  to ensure complete removal of residual air. The reactor was then finally pressurized with  $N_2$  to a cold pressure of 2 MPa and tested for leaks. The reactor was heated under a fixed stirring rate (390 rpm) and allowed to run over a pre-specified length of reaction time after reaching the required temperature. During the reaction the pressure of the reactor system will increase depending on the temperature mainly due to the water vapor pressure (e.g., 5 MPa at 250 °C, 8 MPa at 300 °C up to 16 MPa at 350 °C). After the pre-set reaction time elapsed, the reactor was immediately quenched with water to stop further reaction. After the system reached a low temperature (near room temperature), the gas was collected in a gas cylinder of known volume (2800 mL) and the pressure of the gas cylinder was adjusted to 1.0 atm (abs.) using high purity nitrogen as a makeup gas. The gaseous products were analyzed using a Micro-GC-TCD analyzer and the overall gas yield was determined. The gaseous products are mainly composed of  $H_2$ , CO,  $CH_4$  and  $C_2$ – $C_3$ . Each experiment was conducted 2–3 times to ensure that the relative experimental errors in DL yield be within  $\pm 10\%$ .

The reactor contents were then completely rinsed into a beaker using distilled water. The pH value of the washed reactor contents (varying from 11.0 to 9.5 depending on the reaction conditions) was adjusted to approximately 2.0 using 1.0 M  $H_2SO_4$  solution to precipitate the DL products. The acidified reaction mixture was then filtered through a Buchner funnel. The aqueous (Aq) phase was analyzed by TOC-analyzer. As the gas yield was found to be very low ( $\leq 1$  wt.%) in all tests, a lumped yield of (Gas + Aq) phase was reported in this study for simplicity. The solid cake containing depolymerized KL was dissolved in acetone (20–25 mL) under sonication and then filtered under vacuum with Buchner funnel to get acetone soluble depolymerized lignin (DL) or polyols and solid res-

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