



# Near-critical water hydrothermal transformation of industrial lignins to high value phenolics



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## ABSTRACT

A process for the production of high-value-added phenolics following hydrothermal depolymerization of black liquor lignins after acidification without catalysis was successfully deployed and is described herein. A high yield of liquid products up to 33.3 mg/mL (based on raw black liquor) was recovered at 290 °C, 30 min, and pH 6; meanwhile, only 12.6 mg/mL solid residue was obtained. GC–MS analyses of the liquid products confirmed value-added aromatic monomers, among which the yields of phenol, guaiacol, and 2,6-dimethoxy-phenol were high (~60% of the identified compounds). FT–IR of the solid residues indicated that the black liquor lignin was depolymerized through cleavage of ether bonds and decarboxylation. The results suggest that black liquor may be a new resource for aromatic products.

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## 1. Introduction

Natural gas, fossil oil, and coal are non-renewable resources that are widely used for the production of fuels and chemicals [1]. However, public awareness of environmental pollution and energy costs have prompted the consideration of biomass as a more sustainable resource. After chitin and the cellulose (including hemicelluloses), lignin is the most abundant biosynthesized biomass that is derived from the polymerization of three phenylpropane monomers, namely *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol mainly crosslinked by  $\beta$ -O-4 linkages [2,3]. Because of its unique structure and chemical properties, lignin can be considered an alternative raw material for the production of phenol, guaiacol, catechol, and syringol etc. [4,5].

Lignin has been shown to be able to be converted into smaller molecular units (phenolic compounds) by hydrothermal conversion, pyrolysis, enzymatic degradation, photocatalysed degradation, electrochemical degradation, ionic liquids degradation, microwave irradiation oxidation, etc. However, the extraction of lignin is necessary and poses a nontrivial challenge. Farag and Chaouki performed an economic evaluation of converting lignin into chemicals and found that the estimated selling price was not competitive with fossil fuel-based analogues, a result primarily

attributable to the high cost of the lignin feedstock [6]. In addition, expensive catalysts hinder further upgrading of lignin.

In chemical pulping, the separation of lignin from wood chips takes place in digesters. Lignin and other organic acids are dissolved into the digester pulping liquor and leave as black liquor at a solid concentration of 15–20 wt.-% [6]. Unfortunately, end-of-pipe discharge to receiving waters causes horrible pollution and soil contamination [7]. In fact, it has already been confirmed that alkali lignin from the black liquor can be extracted and converted into aromatic chemicals by hydrothermal treatment; a process that involves hot compressed water as a green reaction medium [8–12]. However, very little attention on direct hydrothermal decomposition of black liquor has been shown due to the complexity of the chemical constituents. If a pre-process for black liquor is added to remove adventitious impurities, using black liquor instead of lignin as feedstock for hydrothermal decomposition addresses the environmental impacts associated with papermaking and facilitates upgrading lignin for phenolic products.

First of all, the needed inorganic chemicals for the pulping process are recoverable by burning the solid product in hydrothermal decomposition [13]; it has been reported that the solid product is a high-energy char for fuel production [12]. Secondly, the needed energy for drying lignin in the precipitation and extraction process is saved. Thirdly, the inorganic salt from black liquor can play a catalytic role in the hydrothermal conversion process [14,15]. Most of all, the bio-oils which are mostly aromatics can be collected from the hydrothermal decomposition step.

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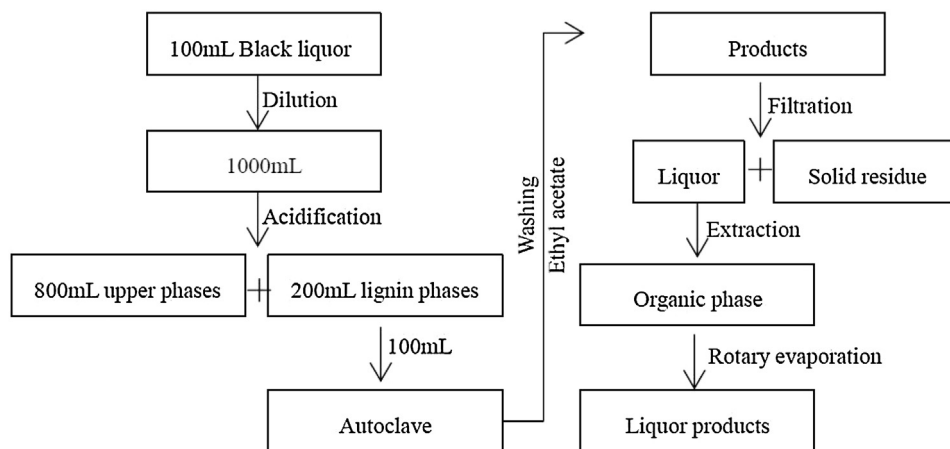


Fig. 1. Schematic representation of the process used in the current study.

Herein, it is demonstrated that (Fig. 1) black liquor lignin can be used as the substrate feedstock without extra catalysts. The object of the work, therefore, is to obtain high-value-added phenolics from black liquor under hydrothermal conditions. This study investigated the effect of reaction temperature (200–380 °C), reaction time (0–120 min), and pH (2–12) on product distributions and yields. Products were characterized by gas chromatography mass spectroscopy (GC–MS) and fourier transform infrared spectroscopy (FT–IR).

## 2. Materials and methods

### 2.1. Materials

All starting materials were purchased from Sinopharm Chemical Reagent Co., Shanghai (China) and used as received without further purification, unless otherwise noted. Black liquor was obtained from in-house poplar sulfate pulping. The chemical composition of products from poplar-based pulping has been previously reported [16]. In summary, its density is 1.005 g/mL and the total solids content, organic substances, inorganic substances, total alkali content, and total available alkali are 15.43%, 8.39%, 6.32%, 3.87%, and 1.54%, respectively. In addition, 1 mL of raw black liquor gave 63 mg alkali lignin and 24 mg polysaccharide, which was determined by the method described by Crawford and Pometto [17]. After cooking, black liquors were collected from the reaction vessel. Then black liquor was filtered through a Buchner funnel under vacuum to facilitate solid impurities removal, of which 100 mL was diluted to 1000 mL. Later, 50% (wt.-%) sulfuric acid was slowly added until pH = 2 was reached causing the lignin to precipitate. After precipitation, the black liquor had two distinct phases: aqueous phase and lignin phase. The visual appearance of the former was light yellowish whereas the latter was brown. The upper layer (800 mL, contained 300 mg acid-soluble lignin and 1950 mg polysaccharide) and the lignin phase (200 mL, contain 5700 mg lignin and 370 mg polysaccharide) were the substrate feedstock for subsequent experiments.

### 2.2. Hydrothermal conversion

The experiments were performed in a high-pressure autoclave with a 4848 Reactor Controller (Parr Instrument Company, America). The 250 mL batch reactor was equipped with a pressure gauge (0–5000 psi), a pressure relief valve, and a thermocouple. Typically, 100 mL lignin phase were transferred into the reactor. The system was vented with nitrogen three times to remove air. For

each experiment, the reactor was heated at a rate of 10 °C/min from ambient to 200–380 °C, after which the experiment was continued for 0–120 min. The accuracy of the temperature controller was  $\pm 5$  °C. The content was stirred continuously at 100 rpm during hydrothermal treatment. Because the acid nature of the lignin phase could pose metallurgical issues, this study investigated the effect of pH on the distribution and yield of various products. Herein, different substrate feedstocks (acidic, neutral, and alkaline conditions by the addition 2 mol/L sodium hydroxide to lignin phases) were examined.

### 2.3. Products separation

The products can be separated into a liquid product (LP), a solid residue (SR), and gas. At the end of the experiment, the gas was removed from the reactor after the autoclave cooled. Gas products, mainly CH<sub>4</sub>, CO<sub>2</sub>, CO and H<sub>2</sub>, were collected by a latex rubber inflatable device for a GC with a Flame Ionization Detector (FID) and Thermal Conductivity Detector (TCD). Gas compositions were similar, and the yields (<5%) were not discussed. The mixture of liquid contents was filtered with a pre-weighed G3 funnel, and filtered with a polytetrafluoroethylene (PTFE) membrane. A solid residue was oven dried at 105 °C overnight before weighing. This water-ethyl acetate liquid fraction was subjected to an extraction process. Sodium sulfate anhydrous was added to the obtained ethyl acetate liquid to remove water. Then the ethyl acetate liquor was filtered and the solvent was removed by rotary evaporation. The conversion yields of various products were calculated based on raw black liquor. The term ‘LP’ was used to represent the liquid products after rotary evaporation and ‘SR’ represented the solid residue after hydrothermal conversion.

### 2.4. Solid contents and residues analysis

Elemental analyses of C, H, N, O and S contents in black liquor, lignin phases, and alkali lignin samples were performed in a Vario Micro analyzer (EL III, Germany). Metal elemental analyses of Cu, Fe, Mg, K, Na, Ca were determined on inductively coupled plasma (Optima 2000DV, American PE) using the HNO<sub>3</sub>–HClO<sub>4</sub> digestion method [18].

FT-IR spectroscopy were recorded on a SHIMADZU FTIR spectrophotometer (IR Prestige–21, Japan) using a KBr pellet containing ~1% sample over a range of 4000–500 cm<sup>-1</sup>.

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