# Lewis-acid catalyzed depolymerization of Protobind lignin in supercritical water and ethanol

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ABSTRACT

The use of metal acetates, metal chlorides and metal triflates as Lewis acid catalysts for the depolymerization of soda lignin under supercritical conditions was investigated. The reactions were carried out at 400 °C in water and ethanol. Lignin conversion in supercritical water led to formation of insoluble char and resulted in low yields of monomeric products. When the reaction was performed in supercritical ethanol, char formation was inhibited and higher yields of low molecular-weight organic products were obtained. The ethanol solvent was also converted in two ways. Firstly, the lignin depolymerization products were alkylated by ethanol. Secondly, ethanol was converted into a range of higher hydrocarbons including paraffins and olefins. Possible mechanisms of the lignin and ethanol conversion reactions are discussed.

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## 1. Introduction

Lignin is attractive as a renewable source of aromatics [1,2]. The cleavage of the different types of linkages in lignin is particularly challenging, making it difficult to obtain aromatics in reasonable yield. To develop an economically viable route for the upgrading of lignin into fuels and chemicals, efficient catalysts need to be identified. Among the many approaches, also the use of base [3–8] and acid catalysts [9–16] for lignin depolymerization has been addressed. For example, Labidi and co-workers recently reported about base-catalyzed depolymerization of various types of lignin in water [4,5]. Depolymerization of organosolv lignin in aqueous NaOH at 320 °C and 250 bar yielded about 11 wt% oxygen-containing aromatic products such as phenols, catechols and guaiacols. The main disadvantage of base catalysts is the extensive repolymerization of the products into insoluble char [3–8]. To prevent condensation reactions, the use of additives such as boric acid and phenol has been explored [3,5]. For instance, char formation can be suppressed by the addition of phenol at 300 °C [5]. Boric acid, however, promoted formation of condensation products, mainly di-aromatic species, in water [3]. Base catalysis was also explored in combination with organic solvents such as

alcohols (methanol, ethanol, propanol and butanol) and acetone [7,8]. In ethanol, the base-catalyzed depolymerization of organosolv-derived lignin at 290 °C resulted in high conversions with only 7 wt% ether insolubles [7]. This high lignin conversion could only be reached when large amounts of strong bases such as CsOH, KOH, and NaOH were used.

Brønsted acid catalysts, extensively used in oil refineries, have also been considered for the conversion of biomass [9–11]. For example, amorphous silica-alumina [9] and zeolites [10,11] have been evaluated as catalysts for lignin depolymerization. An early study showed that hydrocracking of Alcell lignin in tetralin by NiW supported on silica-alumina at 400 °C in 30 min resulted in a lignin conversion of 25 wt% and 5 wt% dichloromethane-solubles [9]. Catalytic fast pyrolysis has also been investigated as a technology to upgrade lignin. The use of ZSM-5, BEA, mordenite, and USY (ultrastabilized Y) zeolites provided high aromatic yields [10]. For instance, USY zeolite yielded 75 wt% liquids of which about half were aromatics [11].

So far, few studies have investigated the role of Lewis acid catalysts for the depolymerization of lignin. Davoudzadeh et al. studied the degradation of Kraft lignin in tetralin by the Lewis acid $BF_3$ [12]. The reaction was carried out in the presence of phenol as the proton donor. The yield of distillable products was found to be 25 wt% at 155 °C and atmospheric pressure. During the liquefaction of Kraft lignin in methanol, $ZnCl_2$ increased char formation at relatively low temperatures (250–350 °C) [13]. At higher

temperatures (400–420 °C), the use of $ZnCl_2$ or $FeCl_3$ led to 24 wt% monomeric products, mainly phenolics and cresols [14]. In another study, the use of $FeCl_3$ and $NiCl_2$ salts in water afforded 18 wt% ether solubles (mainly phenolics) from Alcell lignin at 300 °C [15]. Iron-based catalysts such as Fe-sulfides and Fe-sulfate, which were earlier employed in the liquefaction of coal, have also been used for the conversion of lignin [16]. Recently, such iron-based catalysts have again been used for the conversion of lignin [7]. In ethanol, a maximum oil yield of 63 wt% was obtained at 350 °C using Fe-sulfate in an atmosphere of 5 bar $H_2$. Under these conditions, no deoxygenation of the products was observed.

In a recent study, we explored the use of Lewis acid salts for the decomposition of dimer compounds that contain representative α−O–4, 5−O–4, β–1 (methylene bridges) and 5–5′ linkages present in lignin [17]. We showed that the yield of monomeric products was higher in ethanol than in water. This is due to the extensive alkylation of the mono-aromatic products that inhibits their condensation into larger products. The highest yields of deoxygenated mono-aromatics were obtained using Lewis acid catalysts at 400 °C in supercritical ethanol. The preferred Lewis acid catalysts were Fe, Cu, Ni and Al chlorides. In the present study, metal chlorides ($Fe^{+2}$, $Co^{+2}$, $Cu^{+2}$, $Ni^{+2}$ and $Al^{+3}$), acetates ($Fe^{+2}$, $Co^{+2}$, $Cu^{+2}$, $Ni^{+2}$) and triflates ($Cu^{+2}$, $Ni^{+2}$, $Al^{+3}$ and $Sc^{+3}$) were used as catalysts for the conversion of Protobind lignin. The reactions were carried out in water and ethanol under supercritical conditions at 400 °C.

## 2. Experimental

### 2.1. Materials

Protobind 1000 lignin, which is obtained from wheat straw by soda pulping, was used as received from GreenValue (Switzerland). Deionized water with a pH value of 5.5 and absolute ethanol (Sigma Aldrich, ≥99.8%) was used as reaction solvents. Iron(II) acetate (Aldrich, 95%), copper(II) acetate (Aldrich, powder, 98%), cobalt(II) acetate tetrahydrate (Merck, ≥98.0%), nickel(II) acetate tetrahydrate (Aldrich, 98%), iron (II) chloride tetrahydrate (Aldrich, ≥99.0%), copper(II) chloride dihydrate (Aldrich, ≥99.0%), cobalt(II) chloride (Aldrich, anhydrous, ≥98.0%), nickel(II) chloride (Aldrich, anhydrous, 98%), aluminum(III) chloride hexahydrate (Fluka, ≥99.0%), scandium(III) triflate (Aldrich, 99%), aluminum(III) triflate (Aldrich, 99.9%), copper(II) triflate (Aldrich, 98%), nickel(II) triflate (Aldrich, 96%) were used without further purification. Ethyl acetate (VWR, 99.5%) was used as the extraction solvent. n-Decane (Aldrich, anhydrous, ≥99%) and di-n-butyl ether (Aldrich, anhydrous, 99.3%) were used as external standards during GC analysis. Samples were diluted by tetrahydrofuran (Aldrich, anhydrous, ≥99.9%) ten times prior to GC × GC analysis and thirty times prior to GPC analysis.

### 2.2. Catalytic activity measurements

All the experiments were performed in stainless-steel batch reactors with an internal volume of 13 mL. Reactions were carried out at 400 °C with a reaction time of 4 h. The reactors were filled with either 8 mL of water or 6.5 mL of anhydrous ethanol. In a typical run, 150 mg of lignin and 0.025 mol/L of Lewis acidic salt were loaded to each reactor. The reactors were sealed by the use of Swagelok o-rings. Reactions were carried out by placing the reactors in a preheated fluidized sand bath that allowed for rapid heating to the desired reaction temperature. No additional gas was used and reactions took place under autonomous pressure developed under these conditions.

In our system, ten parallel reactions could be run simultaneously. After the reaction was completed, the reactors were quenched in an ice bath. When char was formed or lignin residue remained, the solids were separated from the liquid products by filtration. For the experiments in water, the organics were extracted by adding ethyl acetate in a 1:1 volume ratio with water. For the experiments in ethanol, the liquid products were collected after filtration and weighed. In case metal chlorides and triflates were the catalysts, the liquid phase consisted of two layers—an organic and an aqueous layer. The aqueous and organic layers were separated by decantation. The liquid organic phases were further analyzed by GC/MS-FID, GC × GC and GPC methods.

### 2.3. Product analysis

Gas Chromatography (GC) analysis—For the identification and quantification of the reaction products, GC/MS-FID analyses were performed on a Shimadzu GC/MS-QP2010 SE series. The GC was equipped with a Restek RTX-1701 capillary column (60 × 0.25 mm i.d. and 0.25 μm film thickness). The column flow was split in a 1:10 volume ratio to the MS and FID. The injector temperature was set at 250 °C. The oven temperature was kept at 45 °C for 4 min, followed by heating to 280 °C at a rate of 4 °C/min and then held at 280 °C for 5 min. Identification of products was done using the NIST11 and NIST11s libraries. For product quantification in ethanol-mediated reactions, GC × GC analysis was performed on an Interscience Trace GC × GC equipped with a cryogenic trap system and two columns: a 30 m × 0.25 mm i.d. and a 0.25 μm film of RTX-1701 capillary column connected by a meltfit to a 120 cm × 0.15 mm i.d. and a 0.15 μm film Rxi-5Sil MS column. An FID detector was used. A dual jet modulator was applied using carbon dioxide to trap the samples. Helium was the carrier gas at a flow rate of 0.6 mL/min. The injector and FID temperatures were set at 250 °C. The oven temperature was kept at 40 °C for 5 minutes then heated up to 250 °C at a rate of 3 °C/min. The pressure was set at 0.7 bar at 40 °C. The modulation time was 6 s.

To perform a qualitative analysis of the gas-phase products, ethanol conversion was carried out in a 100 mL Parr stainless steel stirred high-pressure autoclave. Upon the completion of the reaction, the autoclave was cooled to room temperature and the built-up pressure was released by collecting the gaseous products in a separate stainless steel vessel. The products were then analyzed with Interscience Compact GC. Molsieve 5 Å and Porabond Q columns were coupled with a thermal conductivity detector (TCD), and the $Al_2O_3$/KCl column with a flame ionization detector (FID).

Gel Permeation Chromatography (GPC) analysis—GPC analysis was performed on a Shimadzu apparatus equipped with two columns connected in series (Mixed-C and Mixed-D, polymer Laboratories) and a UV-Vis detector at 254 nm. The column was calibrated with polystyrene standards. Analyses were carried out at 25 °C using tetrahydrofuran (THF) as eluent at a flow rate of 1 mL/min. Samples were dissolved with the concentration of 2 mg/mL and filtered using a 0.45 mm filter membrane prior to injection.

## 3. Results and discussion

### 3.1. Lignin conversion in sc-water and sc-ethanol

Table 1 shows that the hydrothermal conversion of Protobind lignin resulted in very low yields of low-molecular weight organic products. The main product was a black-colored char residue, which was insoluble in water and THF. The total organics yields for the catalytic reactions were around 6–8 wt% (Table 1). The yield in the blank reaction was higher. The monomers were grouped into mono-aromatics, mono-aromatic oxygenates (phenolics, catechols and guaiacols), saturated mono-oxygenates (ketones, carboxylic acids) and non-oxygenated mono-cyclic products (cyclopentanes