

Stability Patterns of Methoxy Phenols under Alkaline Hydrolysis Conditions

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It has long been recognized that lignin is a potential renewable source of chemicals, however, there has been only limited success in the commercialization of processes for converting lignin into chemicals [1,2]. Alkaline hydrolysis of lignin has received considerable attention because the reagents are relatively inexpensive and the phenolic products obtained are of potential value [1]. The most successful process for commercial production of a low molecular weight chemical from lignin was the alkaline hydrolysis of mostly lignosulfonates into vanillin [3,4]. With addition of air or oxygen yields increase into the 10–30% range. Several groups have studied the production of phenols and methoxy phenols from cooking kraft black liquor at higher temperatures (260–310 °C) [5,6]. The main chemicals identified were guaiacol and catechol plus their methyl and ethyl analogs, and phenol. The yield of ether-solubles was reported to reach a maximum of about 30% on a weight basis. The yield of identifiable phenolics was about 10% with catechol the largest product (~5%). Thring and co-workers studied the alkaline hydrolysis of lignins isolated with organic solvents, ethylene glycol [7] and ethanol [8]. At a treatment severity equivalent to a reaction temperature of 300°C for 1 hour, 20% of ethylene glycol lignin was recovered as ether-solubles. The yield of identifiable phenolics was about 11% with catechols being the largest components. Similar yields and products were observed when ALCELL lignin was used as the feedstock.

In all of this work relatively low yields of monomeric phenolics were observed. This may be due to the inability of the hydroxyl group to cleave any but the most labile ether linkages in lignin. Gierer and Noren [9] observed that hydroxyl groups cleaved only certain types of ether linkages. However, little attention has been paid to examining the stability of the desirable phenolic products that can be produced from lignin. The purpose of this paper is to examine the stability of methoxy phenols under standard lignin alkaline hydrolysis conditions. We are attempting to improve our understanding of the chemistry involved in the degradation of methoxy phenols by identifying the products formed and measuring the kinetics of the degradation reactions. By improving our understanding we hope to learn how to increase the yields of desirable phenolic products from lignin.

Reactions were performed in a 75 mL stainless steel reaction vessel. A leak test was performed using N₂ at 1800 psi, thus removing air. The reaction vessel was heated in a fluidized sand bath maintained approximately 10 °C above the desired reaction temperature. A thermocouple inside the vessel was used to measure the reaction temperature. A pressure transducer was used to monitor the reaction pressure. After the desired reaction time the vessel was removed from the sand bath and quenched in an ice-water bath. The heat up and cool down of the reactor was recorded so that their contribution to the reaction severity could be included. The reaction products were initially analyzed by high-pressure liquid chromatography (HPLC) on a reversed-phase C18 column. Samples were prepared for analysis by acidifying with sulfuric acid and then diluting 1 ml to 25 ml with 50% methanol. Products and starting compounds were identified by comparison with the UV spectra and retention times of pure compounds. The products and starting compounds were quantified using external standard calibration. The formation of polymeric products was determined using gel permeation chromatography (GPC). Three columns (30 x 0.8 cm each, Polymer Laboratories PL-Gel) each containing styrene-divinyl benzene copolymer gel beads (10 µm diameter) with nominal pore diameters of 10⁴, 10³ and 50 Å, respectively, were connected in series. The solvent used was HPLC grade tetrahydrofuran at a flow rate of 1ml/min. Prior to analysis the samples were quantitatively acetylated by a method similar to that of Gierer and Lindberg [10] to

minimize non-size exclusion effects. Prior to acetylation the product was isolated from the product solution by first acidifying it to a pH < 2 with sulfuric acid, and then extracting the acidified solution with diethyl ether (3 x 60 ml). The extract was freed of ether by evaporation and then dried under vacuum.

Reaction of simple methoxy phenols, such as guaiacol and syringol, show that the C-O bond in the methoxy group is the most labile. Thus guaiacol is converted to catechol and syringol is converted first to 3-methoxy catechol and then pyrogallol. However, in none of our experiments were the methoxy phenols converted stoichiometrically into the corresponding hydroxy phenols. Methyl guaiacol behaved similarly. A high conversion (~90%) of methyl guaiacol was observed, however, the yields of methyl catechol (11-23%), catechol (4%) and guaiacol (2%), were relatively small. About 60% of the methyl guaiacol remained unaccounted for. Propyl guaiacol was converted to propyl catechol and catechol, but a significant amount remained unidentified in the product. Homovanillyl alcohol was completely converted, but identified products only accounted for about 30 – 40% of the starting material. The main products were catechol and guaiacol plus their methyl and ethyl homologues. Similarly vanillic acid was completely converted under alkaline hydrolysis conditions. Decarboxylation was complete even under

the mildest conditions. Guaiacol was the main product under mild conditions with catechol increasing as the conditions became more severe. Small amounts of 1,2-dimethoxy benzene were also observed under moderate conditions.

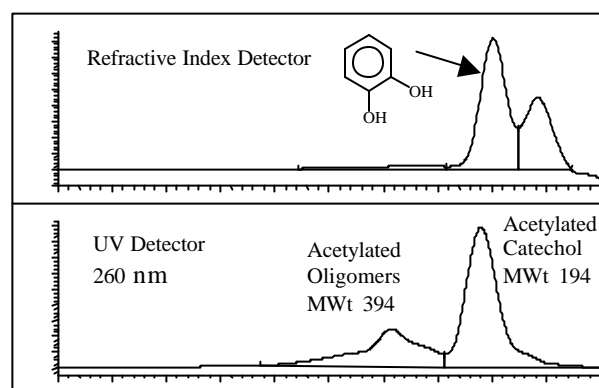


Figure 1. GPC of Catechol Reaction Product

When catechol, the simplest product formed in alkaline hydrolysis of lignins, was treated with 1% NaOH, about 10–15% of the catechol was converted. At higher base levels (3%), up to 30% of the catechol was lost. As can be seen from Figure 1, the loss of catechol is caused by its conversion into oligomeric material. The molecular weight of the oligomers indicates that

they are mostly dimeric. The oligomer peak is much smaller in the refractive index detector, indicating that the oligomers are more chromophoric than catechol. This could be explained if catechol were oxidized into quinones. This possibility will be examined further.

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