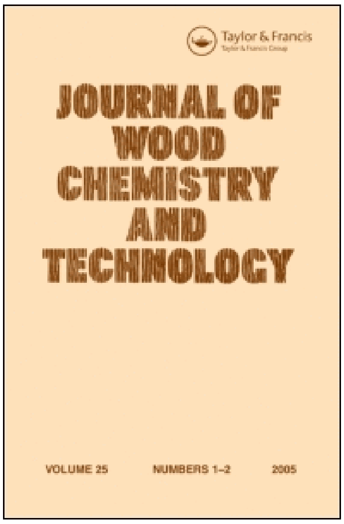

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# Reactivity Toward Phenol of Lignin from the Hydrolysis of Sweetgum Wood with Concentrated Sulfuric Acid

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# REACTIVITY TOWARD PHENOL OF LIGNIN FROM THE HYDROLYSIS OF SWEETGUM WOOD WITH CONCENTRATED SULFURIC ACID

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## ABSTRACT

Sweetgum wood was hydrolyzed at 20° and 50° C for different time periods with 68% sulfuric acid. The lignin residues obtained were subjected to a phenolation reaction. For lignin prepared at the lower temperature the maximum phenol uptake was 9.5%, and at the higher temperature only 5-6%. When wood prehydrolyzed with dilute acid was used the phenol uptake rose to 12.5%. However, all the sulfuric acid hydrolysis lignins showed much lower reactivity toward phenol than the 20% phenol uptake exhibited by lignin isolated using concentrated hydrochloric acid.

## INTRODUCTION

The prospect of deriving chemicals and fuels from woody biomass has increased interest in wood hydrolysis since the first oil crisis two decades ago. Economic considerations require that such processes be integrated to produce useful products from all the components of the wood[1].

In studies of a process for the hydrolysis of wood with concentrated hydrochloric acid it was shown that the lignin residue was quite reactive in a phenolation reaction[2], and that such phenolated lignin was very effective in the formulation of phenol-formaldehyde resin adhesives[3]. Hydrochloric acid had been chosen for these process studies because its recovery by distillation is feasible, although expensive.

Recent work has established that acids can be separated from hydrolyzate sugars and recovered by means of electrodialysis[4]. Acid volatility is no longer a requisite. Sulfuric acid may be recovered more economically by this means, allowing the cost of glucose from wood hydrolysis to approach the cost of glucose from starch hydrolysis. It was thus of interest to determine whether the lignin residue from concentrated sulfuric acid hydrolysis of wood at moderate temperatures has the same potential for utilization in resins as the hydrochloric acid lignin previously characterized[2].

The uptake of phenol in a phenolation reaction has been taken as a convenient measure of the lignin reactivity. Sulfuric acid hydrolysis lignins have been prepared under various conditions, and their reactivity evaluated.

## RESULTS AND DISCUSSION

The quantity of residue from the hydrolysis of wood with concentrated acids varies significantly with the time and temperature of exposure as well as the concentration of the acid[3,5]. Although the ultimate residue value for the sweetgum wood used in this and the previous studies would be expected to be the Klason lignin value of 22.3%, the actual values obtained are often higher. Unhydrolyzed carbohydrate contributes to residue weight, but the recondensation of hydrolyzed carbohydrate with the residual lignin can also lead to an increase in residue weight with increased time of reaction. Both situations may be seen in Table 1, which summarizes the hydrolysis results with 68% sulfuric acid at 20° and 50° C with both whole and prehydrolyzed wood.

## TABLE 1

Residues From The Hydrolysis Of Sweetgum Wood With 68% Sulfuric Acid

| Time | Whole Wood | | Prehydrolyzed Wood* | |
|---|---|---|---|---|
| | 20° C | 50° C | 20° C | 50° C |
| (h) | (% of original dry weight of wood) | | | |
| 0.5 | 97.6 | | | |
| 1.0 | 73.7 | 25.3 | 33.8 | 22.0 |
| 2.0 | 44.4 | 28.4 | | 22.0 |
| 3.0 | | 29.3 | 23.4 | |
| 3.5 | 25.5 | | | |
| 5.0 | 23.0 | | 22.9, 22.0** | |
| 6.0 | 22.0 | | | |
| 8.0 | 22.0 | | | |
| 12.0 | 21.9 | | | |

*--- 4% HCl at 100° C except **

**-- 2.4% sulfuric acid at 100°

At 20° C the loss of carbohydrate from whole wood is slow, but the amount of residue becomes constant at the Klason lignin value of 22% after 5-6 hours. At 50° C essentially all of the carbohydrate is removed within one hour. However, on continued reaction the weight of residue increases. This phenomenon had been previously observed in the hydrolysis of sweetgum wood with 43% hydrochloric acid at 40° C, but it did not occur at 30° C.[5] The weight increase was attributed to the condensation of the lignin with carbohydrates and their decomposition products in the hydrolysis mixture.

Further light is shed on this behavior by the results of the hydrolysis of prehydrolyzed wood. It can be seen from Table 1 that at both 20° C and 50° C the residue weight reaches the Klason lignin value and remains constant. The weight increase on continued reaction can thus be attributed to condensation with hemicellulose components that are absent from the prehydrolyzed wood.

## Infrared Spectra of Lignin Residues

The infrared spectra of the sulfuric acid hydrolysis lignins from whole wood showed a close resemblance to that of Klason lignin[2]. However, the spectra of the sulfuric acid hydrolysis lignins from prehydrolyzed wood showed sharper and more complicated absorption bands than those from whole wood, and were as complex as those of the HCl lignin and milled wood lignin previously described[2]. The most significant features of the spectra from prehydrolyzed wood hydrolysis residues were the much more intense, sharp and clear absorption peak at 840 $cm^{-1}$ and shoulders at 1270 and 1155 $cm^{-1}$ in comparison to those from Klason lignin and the residues from whole wood. These differences also support the conclusion that hemicellulose components can react with and modify the lignin during hydrolysis.

## Phenolation of Sulfuric Acid Hydrolysis Lignins

The reactivity of the lignin residues toward phenol may be gauged by the phenol uptake values presented in Table 2. With whole wood at 20° C a maximum phenol uptake of 9.5% was observed after five hours of hydrolysis, corresponding to complete removal of carbohydrate. Longer hydrolysis periods reduced lignin reactivity, with no reaction at all with phenol occurring after 12 hours. Whole wood at 50° C gave less reactive lignins (5-6% phenol uptake) after one or two hours.

With prehydrolyzed wood at 20° C phenol uptake as high as 12.5% was observed. Here too the reactivity of the lignin residues toward phenol fell off with increasing time of hydrolysis and increasing temperature.

The phenol uptake values in Table 2 may be compared with the previously determined values of 9% for Klason lignin and 20% for HCl hydrolysis lignin[2]. Since the value for the HCl lignin was for a whole wood residue, it is apparent that hydrolysis of wood with 68% sulfuric acid not only reduces the reactivity of the residual lignin by condensation with hemicellulose derived carbohydrate fractions, but

TABLE 2

Phenolation of Sulfuric Acid (68%) Hydrolysis Lignins

| Source | Hydrolysis Temp. (°C) | Time (h) | Residue Weight (%) | Phenol Uptake (%) |
|---|---|---|---|---|
| WW | 20 | 3.5 | 25.5 | 7.5 |
| WW | 20 | 5.0 | 23.0 | 9.5 |
| WW | 20 | 8.0 | 22.0 | 5.0 |
| WW | 20 | 10.0 | 22.7 | 2.0 |
| WW | 20 | 12.0 | 21.9 | 0.0 |
| WW | 50 | 1.0 | 25.3 | 5.0 |
| WW | 50 | 2.0 | 28.4 | 6.0 |
| HPW | 20 | 3.0 | 23.4 | 12.0 |
| HPW | 20 | 5.0 | 22.9 | 9.0 |
| HPW | 50 | 1.0 | 22.0 | 6.5 |
| HPW | 50 | 2.0 | 22.0 | 6.0 |
| SPW | 20 | 5.0 | 22.0 | 12.5 |

WW--Whole Wood
HPW--HCl Prehydrolyzed Wood
SPW--Sulfuric Acid Prehydrolyzed Wood

also by enhanced internal condensation of the lignin[5]. The sulfuric acid catalyzes this internal condensation more effectively than the hydrochloric.

Qualitative observation of the lignin residues showed differences in color that could be correlated with reactivity. The least reactive lignins prepared at 50° C were deep black in color. The more reactive lignins prepared at 20° C were lighter in color, ranging from dark brown to light black. The most reactive HCl lignins were light brown in color.

## Site of Phenolation

Phenolation of lignin under acidic catalysis leads mainly to reactions with the $\alpha$-carbon of the phenylpropane side chain[6]. Loss of reactivity at this position in the sulfuric acid hydrolysis residues might not necessarily prevent phenolation of these lignins by other techniques. Lignites and bituminous coals are readily phenolated to a high degree at 100° C with $BF_3$ as catalyst[7]. Presumably reaction occurs with the isopropyl and diarylmethane groups in coal.

### Conclusions

It had previously been believed[2,3] that the reason for the lower reactivity of Klason lignin toward phenol compared to HCl hydrolysis lignins was the higher temperature to which the former is exposed during the dilute acid hydrolysis step. This concept must be modified in the light of the present results. Prehydrolysis of the wood with dilute acid at 100° C still allowed greater reactivity than Klason lignin. But low temperature hydrolysis with 68% sulfuric acid gave lignins of equal to or lower reactivity than Klason lignin. The confounding effect of hemicellulose presence in the sulfuric acid hydrolysis must also be considered. Temperature of the concentrated acid hydrolysis also has an effect.

To summarize, sulfuric acid (68%) lignins are less reactive in phenolation than HCl (43%) lignins. Sulfuric acid lignins from prehydrolyzed wood are more reactive than those from whole wood, because of the removal of hemicellulose sugars that otherwise recondense with the lignin. And extended time or increased temperature of hydrolysis cause loss of lignin reactivity toward phenol.

## EXPERIMENTAL

Sweetgum (*Liquidambar styraciflua* L.) wood meal passing through a 40 mesh screen and preextracted with benzene-ethanol, 2/1 v/v, was used.

### Hydrolysis of Wood Meal

Hydrolysis experiments were performed using 68% $H_2SO_4$ with an acid to wood ratio of 10:1 (w/w). The acid was added to 2 g of wood in a flask, and the mixture shaken in a bath at 20° or 50° C for the desired length of time. After dilution with distilled water and filtration on a medium porosity sintered glass crucible, the residue was washed with distilled water, dried in a vacuum oven at 50-60° C and weighed.

### Prehydrolysis of Wood Meal

Wood meal (10 g) was mixed with 4% HCl or 2.4% $H_2SO_4$ (100 ml) in a round bottom flask and heated under reflux for six hours. The prehydrolyzed wood was filtered and washed with hot distilled water.

### Phenolation of Lignin

The phenolation reactions were performed as previously described[2], with the exception that 0.09 g lignin residue was reacted with 14 g phenol. Increasing the amount of lignin used to as high as 0.35 g had no effect on the yield of the reaction. The reported yields are the average of two or three replications.

Infrared spectra were obtained using a pellet made from 1 mg lignin and 400 mg KBr on a Beckman Acculab spectrophotometer.

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