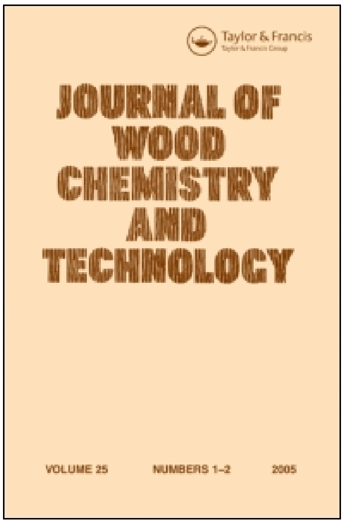
This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Wood Chemistry and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

The Attempted Depolymerization of Hc1 Lignin By Catalytic Hydrogenolysis

Tor P. Schultz[a]; Chen-Loung Chen[b]; Irving S. Goldstein[b]
[a] Mississippi Forest Products Utilization Laboratory, Mississippi State University, MS, USA [b] Department of Wood and Paper Science, North Carolina State University, Raleigh, NC, USA

To cite this Article Schultz, Tor P. , Chen, Chen-Loung and Goldstein, Irving S.(1982) 'The Attempted Depolymerization of Hc1 Lignin By Catalytic Hydrogenolysis', Journal of Wood Chemistry and Technology, 2: 1, 33 — 46
To link to this Article: DOI: 10.1080/02773818208085118
URL: http://dx.doi.org/10.1080/02773818208085118

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 2(1), 33-46 (1982)

THE ATTEMPTED DEPOLYMERIZATION OF HCl LIGNIN BY CATALYTIC HYDROGENOLYSIS

Tor P. Schultz
Mississippi Forest Products Utilization Laboratory
Mississippi State University
Mississippi State, MS 39762 USA

Chen-Loung Chen and Irving S. Goldstein
Department of Wood and Paper Science
North Carolina State University
Raleigh, NC 27650 USA

ABSTRACT

HCl lignin, prepared from sweetgum wood (*Liquidambar styraciflua* L.) by hydrolysis of the carbohydrates with superconcentrated hydrochloric acid, was reductively depolymerized in alkali using various heterogeneous catalysts. A maximum yield of 18% distillable products was obtained by this alkaline hydrolysis-catalytic hydrogenolysis treatment. Surprisingly, it was found that few covalent bonds were being cleaved by the catalysts, with the majority of the bonds having been broken by alkaline hydrolysis. GC analysis showed that a large portion of the monomeric phenolic products had been dealkylated at the para-position. A reaction scheme has been proposed to explain the alkaline-hydrolysis mechanism involved. Lignin tar, which was formed by alkaline hydrolysis of HCl lignin alone, was subjected to subsequent reduction using selected catalysts. This sequential hydrolysis-hydrogenolysis treatment caused the lignin to recondense, apparently because of the inability of the catalysts to reduce groups which are capable of polymerizing together.

INTRODUCTION

The phenolic nature of lignin has led to numerous attempts to degrade the aromatic polymer into useful chemicals by reductive techniques. Most of the results may be found in the following review articles: Schweers[1], Hrutfiord[2], and Goldstein[3]. Generally, high yields of soluble products were reported, indicating that the lignin has been extensively depolymerized by the many different catalytic processes examined. However, review of the amounts and types of monomeric compounds produced reveals significant differences among the results reported by various investigators. Para-ethylphenol derivatives are the dominant compounds reported during hydrogenolysis of lignin in alkali, with both *p*-propylphenol and *p*-hydroxyphenylpropanol derivatives predominate when a neutral or acidic solvent is used.

Recent studies on the hydrolysis of woody biomass using superconcentrated hydrochloric acid have been conducted in this laboratory. Characterization of the residual lignin formed from the hydrolysis of sweetgum wood has shown that only a small degree of internal condensation occurs during the isolation procedure[4]. Because of the similarity between HCl lignin and the "natural" lignin in wood, it might be expected that HCl lignin would have similar reactivity. The purpose of this study was to investigate the behavior of HCl lignin during reductive depolymerization.

EXPERIMENTAL PROCEDURES

HCl lignin was prepared by the following procedure. Preextracted sweetgum wood meal (Liquidambar styraciflua L.) was added to superconcentrated hydrochloric acid (44-45%) in a reaction vessel cooled to -5°C. The acid to wood ratio was about 13:1 (V/W). The wood-acid mixture was left at -5°C for one hour before slowly raising the temperature. The mixture was then stirred for eight additional hours at ambient temperature. The reaction mixture was filtered at the completion of the hydrolysis and the insoluble lignin repeatedly washed with distilled water, sodium carbonate solution, and then water again. The lignin was isolated as a brown powder in 24% yield. Klason lignin determination on the same wood showed a total lignin content of 25.8%: 22.3% insoluble plus 3.5% soluble. Carbohydrate analysis showed that the HCl lignin contained less than 1% residual carbohydrates.

The reactor vessel used for the reactions was a 1-liter Parr rocking hydrogenation autoclave. For the hydrogenations, approximately 5 grams of lignin (or 20 grams wood meal) and 0.5 grams of catalyst were added together with the solvent to the reactor. After sealing, the oxygen in the reactor was purged successively with nitogran and hydrogen. The reactor was then filled with hydrogen to 1,000 psig at room temperature. The reaction time reported is the actual time at temperature, excluding any time needed for heating or cooling. At the completion of the run, the reactor was cooled overnight before the products were removed. At first, the neutrals were separated from the phenolics by continuous chloroform extraction of the alkaline solution. This procedure was discontinued when it became apparent that the lignin hydrogenation products recondensed in the presence of chloroform and alkali. For all reported results the reaction mixtures were immediately acidified with hydrochloric acid to a pH of 4, and the neutrals and phenols extracted together.

After isolation of the chloroform soluble products, the solvent was removed under vacuum and the residue vacuum distilled using a short-path distillation apparatus. The distillates from the preliminary experiments were analyzed using a Tenax-GC column[5]. For later experiments, it was found that an OV-17 column gave superior results[6].

After extraction of the soluble products, the aqueous layer was filtered and the insoluble products were determined gravimetrically. The quantity of water soluble lignin was measured by UV absorbance at 205 nm.

The procedure for the catalytic hydrogenation of lignin which had been previously depolymerized by alkaline hydrolysis was as follows. HCl lignin was hydrolyzed in dioxane-aqueous alkali (1:1) at 250°C. The chloroform soluble products were extracted after acidification, and the solvent was removed under vacuum. The residue was returned to the autoclave together with the catalyst and solvent, and the resulting mixture was hydrogenated at the conditions specified in the experimental section.

At the completion of the hydrogenation, the neutral and phenolic products were separately extracted using ether. When high yields of soluble phenolics were obtained, they were further characterized by vacuum distillation.

RESULTS AND DISCUSSION

Organization of Reaction Conditions

Preliminary experiments (Table 1) were conducted in order to determine the optimum range of operating conditions; i.e., catalyst, temperature, time, and solvent. Surprisingly, it was found that the catalyst had little apparent influence on the yield of monomers. The yield of distillates was 16 to 18% when HCl lignin was reacted in aqueous alkali:dioxane in the presence of hydrogen, and 16% from the control runs without catalyst. GC analysis of the control runs showed a high ratio of dealkylated phenols to *p*-ethylphenolic derivatives, with the ratio decreasing slightly when catalysts of moderate activity were present.

When the effect of time was examined, it appeared that HCl lignin was quickly depolymerized, but that the products slowly recondensed as shown by the low yield of distillates at 5.0 hours.

Aqueous alkali:dioxane gave higher monomeric yields than aqueous alkali alone. In addition, only a trace of distillate was observed when dioxane:water was used as the solvent, suggesting that alkaline hydrolysis was the predominant depolymerization process.

The highest yield of distillates was obtained at a reaction temperature of 250°C, with lower reaction temperatures producing

Table 1
Results from the Preliminary Hydrogenation of Sweetgum Lignins

Reaction	Lignin	Catalyst	Solvent	Temperature °C	Time hr.	Hydrogen	Distillable, weight %
1-A	HCl	--	Dioxane:3% NaOH[1]	250	1.5	+	16
1-B	HCl	--	Dioxane:3% NaOH	250	1.5	-	16
1-C	Wood[2]	--	Dioxane:3% NaOH	250	1.5	-	53[3]
1-D	HCl	--	1.5% NaOH	250	1.5	-	9
2-A	HCl	Fe_2O_3	3% NaOH	200	2.0	+	0
2-B	HCl	"	3% NaOH	250	1.5	+	1
2-C	HCl	"	3% NaOH	300	1.5	+	6
2-D	HCl	"	3% NaOH	350	1.5	+	11
2-E	HCl	"	Dioxane:3% NaOH	175	1.5	+	1
2-F	HCl	"	Dioxane:3% NaOH	250	1.5	+	18
2-G	Wood	"	Dioxane:3% NaOH	250	1.5	+	38[3]
2-H	HCl	"	Dioxane:Water	250	1.5	+	0
2-I	HCl	"	Dioxane:3% NaOH	250	5.0	+	3
2-J	HCl	"	Dioxane:3% NaOH	250	0.5	+	17
2-K	Klason	"	Dioxane:3% NaOH	250	1.5	+	2
3-A	HCl	$CoOMoO_3$	3% NaOH	250	1.5	+	8
3-B	HCl	"	3% NaOH	350	0.75	+	5
3-C	HCl	"	Dioxane:3% NaOH	250	1.5	+	16
3-D	Wood	"	Dioxane:3% NaOH	250	1.5	+	34
3-E	HCl	"	Water	250	1.5	+	0

[1] 1:1, 200 ml.

[2] 25.8% lignin.

[3] Based on the original lignin content, probably contains some carbohydrate-derived materials.

only traces of monomers. Moderate amounts of distillates were obtained at higher temperatures, but GC analysis was able to identify only a small fraction. This suggests that any phenols which may have been formed had been further degraded at the higher reaction temperatures.

Alkaline Hydrolysis-Catalytic Hydrogenolysis

The preliminary experiments suggested that alkaline hydrolysis, rather than catalytic hydrogenolysis, was responsible for depolymerizing the lignin. In order to verify this conclusion, direct comparison of alkaline hydrolysis and hydrogenolysis was carried out (Table 2). The catalyst ($CoOMoO_3$) which had been shown by the preliminary runs to give the highest yield of phenols without alkyl groups (lowest activity) was used. The results obtained are given in Table 2, with Table 3 showing the products identified using GC.

The addition of the catalyst had almost no influence on the yield or type of monomers produced. A slight difference in the ratio of dealkylated to p-ethylphenolic derivatives can be seen in the noncatalytic runs. This slight difference was also noted in the preliminary experiments.

These findings seemed contradictory to past lignin hydrogenolysis experiments. However, when the authors reviewed past studies, it was found that few researchers had run a controlled experiment (no catalyst or hydrogen). Thus, what prior researchers had thought was catalytic hydrogenolysis may simply have been the hydrolytic depolymerization of lignin. Cyclohexanol derivatives, which have been found in some studies, could have been formed by the exhaustive catalytic hydrogenation of previously hydrolyzed phenolic compounds.

Yields of both chloroform-soluble and distillable products were much larger when "natural" wood lignin was hydrolyzed than when hydrolyzing HCl lignin. The high yield of distillates obtained from wood (32%) may be ascribed to the presence of carbo-

Table 2
Reaction Conditions and Results for the Alkaline Hydrolysis of Sweetgum Lignins.

	Conditions					
Reaction	4-A	4-B	4-C	4-D	5-A	5-B
Lignin	HCl	Klason	Wood	HCl	HCl	Wood
Catalyst	None	None	None	None	$CoMoO_3$	$CoMoO_3$
Solvent	Dioxane; 3% NaOH[1]	Dioxane; 3% NaOH[1]	Dioxane; 3% NaOH[1]	1.5% NaOH[2]	Dioxane; 3% NaOH[1]	Dioxane; 3% NaOH[1]
Time, hr.	1.0	1.0	1.0	1.0	1.0	1.0
Atmosphere, psig	N_2, 15	N_2, 15	N_2, 15	N_2, 15	H_2, 1000	H_2, 1000
Temperature, °C	250	250	250	250	250	250
	Products, Weight %					
Residue	6	23	116[3]	38	5	126[3]
Chloroform soluble Nondistillable	55	50	85[3]	22	58	90[3]
Distillable	18	Trace	32[3]	13	15	35[3]
Water soluble	3	ND[5]	ND[5]	4	ND[5]	ND[5]
Demethylation loss	3	--	--	4	3	--
Dealkylation loss	9	--	--	9	9	--
Material balance	94			90	90	

[1] 1:1, 200 ml.

[2] 200 ml.

[3] Excess yield, probably caused by carbohydrate-derived materials.

[4] Estimated by GC data.

[5] Not determined.

hydrate-derived products. GC analysis of the distillates showed similar yields in the identified phenolics from both HCl lignin and the "natural" lignin in wood. High yields from wood hydrogenation reactions reported by previous investigators probably include some by-products formed from the carbohydrates.

Examination of the GC analyses (Table 3) shows a much higher ratio of syringyl to guaiacyl derivatives than is present in the original lignin. Because of the blocked 5 position, syringyl units in the lignin would be expected to have a lower degree of interunit carbon-carbon bonding than guaiacyl units. Thus, the observed ratio indicates that the portion of the lignin which has a higher degree of condensed

Table 3
GC Analysis of Hydrolysis Reactions, Weight Percent of Original Lignin

Reaction	4-A	4-C	4-D	5-A	5-B
% Distillates	18	32	13	15	35
% of Distillates Identified	63	36	69	60	38
Compound[1]					
Phenol	tr	tr	0.1	tr	tr
Methylphenol	--	--	0.1	tr	--
Ethylphenol	tr	tr	tr	tr	tr
Propylphenol	--	--	--	tr	0.3
2-(4-Hydroxyphenyl)-1-ethanol	--	--	--	--	--
3-(4-Hydroxyphenyl)-1-propanol	--	--	--	--	--
Guaiacol	1.2	0.8	1.4	0.9	0.8
Methylguaiacol	0.1	--	0.1	0.2	--
Ethylguaiacol	0.2	0.7	0.2	0.2	0.5
Propylguaiacol	--	--	--	--	--
2-(4-Hydroxy-3-methoxy-phenyl)-1-ethanol	--	--	--	tr	--
3-(4-Hydroxy-3-methoxy-phenyl)-1-propanol	tr	tr	tr	tr	tr
Syringol	5.4	6.6	4.2	4.1	6.0
Methylsyringol	1.3	0.5	0.8	0.5	0.7
Ethylsyringol	1.1	1.5	0.5	1.7	1.8
3-(4-Hydroxy-3,5-dimethoxy-phenyl)-1-propanol	tr	tr	tr	tr	tr
Catechol	0.3	0.7	0.2	0.3	0.8
Methylcatechol	0.3	0.4	0.1	0.2	0.9
Ethylcatechol	0.2	--	0.1	0.3	0.9
1,2-dihydroxy-3-methoxybenzene	1.0[2]	0.4[2]	1.1[2]	0.9[2]	0.6[2]
Total[3]	11.1	11.6	8.9	9.3	13.3

[1] The alkyl substituent is para to the phenolic hydroxy group.

[2] The methyl and ethyl derivatives of 1,2-dihydroxy-3-methoxybenzene may also be present in the distillates. Compounds which may be present but which are not eluted from the OV-17 column include 1,2,3-trihydroxybenzene and its methyl and ethyl derivatives.

[3] The internal standard used was syringaldehyde. The presence of any unreduced syringaldehyde among the alkaline hydrolysis products would introduce a relative error.

aromatic structures gives a lower monomeric yield. This was confirmed when highly condensed Klason lignin was hydrolyzed, with only traces of monomers detected.

A possible mechanism to explain these results has been postulated (Figure 1). It is probable that the phenolic anion 1 initially reacts via the quinone methide intermediate 2 to give the vinyl derivative 3. If an active catalyst is present, the vinyl derivatives of the type 3 would undergo hydrogenolysis of

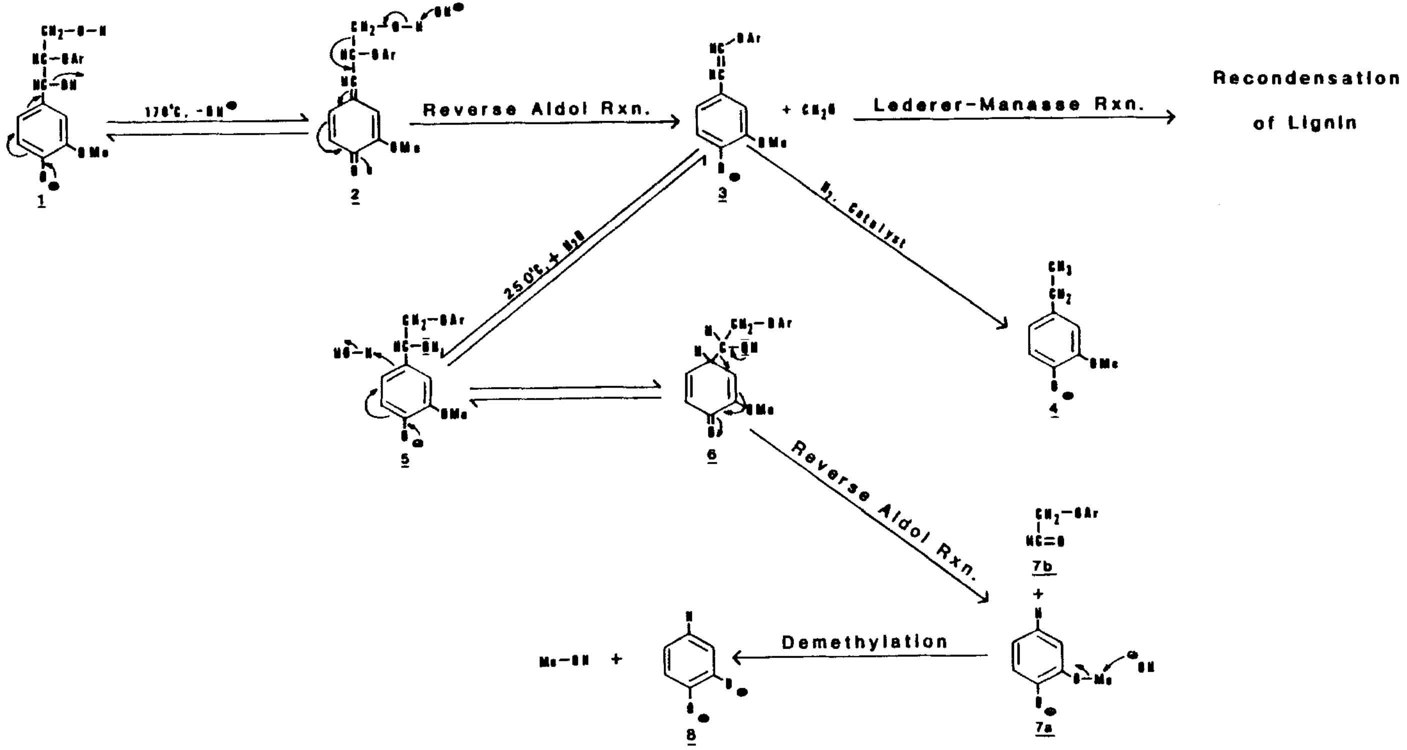


Figure 1. Proposed mechanism for the dealkylation of lignin at 250°C in aqueous alkali.

the β-aryl ether linkage and concomitant reduction to give ethyl derivatives of the type 4. This would explain the high yields of p-ethylphenol derivatives reported in previous studies. However, if an active catalyst is not present and at a higher reaction temperature, i.e., 250°C, water can add to the double bond to form the benzylic hydroxy compounds of the type 5. As shown by Miksche[7], p-hydroxybenzyl alcohol derivatives can undergo C_1-C_α cleavage via a reverse aldol addition by protonation of the quinone methide intermediate 6. Of special interest are the various carbonyl compounds which are formed; i.e., 7b. these compounds can condense with an available phenolic compound, thus decreasing the yield of monomeric products if excessively long reaction times are employed. Concurrently, some C-3 methoxy groups can undergo demethylation by hydroxyl ion, a weak nucleophile, thus forming catechol compounds of the type 8.

Some cleavage of carbon-carbon bonds may also occur via a homolytic cleavage. Turunen[8], after heating propylguaiacol in alkali at 250°C, found traces of guaiacol and catechol. This homolytic cleavage was also noted by Domburgs[9], who reported that a few C_1-C_α bonds were thermally cleaved at 250°C.

The experiments have shown that dioxane-aqueous alkali gave higher yields than aqueous alkali alone. Some possible explanations for this are:

(1) Increased lignin solubility.

(2) Protic solvents form hydrogen bonds to the benzylic hydroxy group of 6. An aprotic nonpolar solvent, such as dioxane, could reduce the extent of this hydrogen bonding. If a protic solvent does form such hydrogen bonds, dealkylation via the reverse aldol addition involving C_1-C_α becomes less likely.

Sequential Hydrolysis-Hydrogenolysis

Since the HCl lignin had already been extensively depolymerized by alkaline hydrolysis with cleavage of C_1-C_α bonds, further hydrogenation of this alkali-hydrolyzed lignin tar seemed of potential utility. To investigate this approach, several catalysts and temperatures were employed. The reaction conditions and results are given in Table 4.

It is evident from Table 4 that the yields of distillable phenolics after catalytic hydrogenation of prehydrolyzed HCl lignin tar were lower than the amount which was present initially (18%). While preliminary hydrogenations had shown that the lignin did recondense in the presence of alkali, it was expected that the groups which were causing the recondensation to occur; i.e., β-carbonyl groups in compounds of the type 7b (Figure 1), would be reduced. In addition, those reactions run in a neutral solvent would not be expected to recondense. However, the yields of monomers from hydrogenation reactions run in a neutral solvent were also low.

The yield of neutral products was also lower than had been anticipated from the known ability of the catalysts used to saturate aromatic rings at high temperatures. This suggests that either the solubility of hydrogen in water was insufficient, or that the catalyst was deactivated in some manner by the lignin or solvent. Lignin oligomers, which are too large to diffuse into the minute inner pores of the catalyst, could also block the pores and prevent smaller molecules from diffusing into the catalyst.

SUMMARY

The depolymerization of HCl lignin by various reductive methods has been studied. Initially, the catalytic hydrogenolysis of lignin using heterogeneous catalysts in an alkaline solvent was examined. Previous investigators have reported that this method was successful for producing monomeric compounds in moderate yields. The present study has shown that the lignin was mainly depolymerized by the alkali, with the catalyst having only a very minor effect. Analysis of the products showed that the dominant products formed were dealkylated phenolic deriva-

Table 4
Reaction Conditions and Products Obtained by the Catalytic Hydrogenation of Depolymerized Lignin Tar. The Initial Hydrogen Pressure was 1,000 psig at Ambient Temperature.

Reaction	Reaction Conditions				Ether Soluble Products Weight %[1]		Distillable Phenolics Weight %[1]
	Temperature °C	Solvent	Time hr.	Catalyst	Neutrals	Phenolics	
6A	250	0.75% NaOH	1.5	Copper chromite, nonstabilized	1	17	5
6B	325	0.75% NaOH	1.0	Copper chromite, nonstabilized	3	23	7
6C	250	0.75% NaOH	1.5	Copper chromite, stabilized	2	31	11
6D	325	0.75% NaOH	1.0	Copper chromite, stabilized	0	16	2
6E	250	0.75% NaOH	1.5	Pd/C	4	17	4
7A	250	Water	1.5	Copper chromite, nonstabilized	1	29	ND[2]
7B	325	Water	1.0	Copper chromite, nonstabilized	Trace	6	ND[2]
7C	250	Water	1.5	Copper chromite, stabilized	1	24	ND
7D	250	Water	1.5	Raney Nickel	Trace	32	11

[1] Based on the original HCl lignin.
[2] Not determined.

tives, with the ratio of dealkylated to ethyl derivatives decreasing if catalysts were present. The total yield of distillable phenolics produced by an alkaline hydrolysis reaction (16-18%) was similar to the yields reported by other researchers who catalytically reduced lignin in alkali.

A reaction scheme has been postulated to explain the observed results. It is believed that the lignin polymer first undergoes alkaline depolymerization reactions by way of an intermediate quinone methide. At higher reaction temperatures, water can add to the intermediate, leading to the elimination of the alkyl group by a reverse aldol mechanism. Hydrogenation of the vinyl group intermediate in the presence of active catalysts increases the yield of ethyl derivatives formed and prevents dealkylation via C_1-C_α cleavage of the phenolic compounds present in the reaction mixture.

Attempts were made to further depolymerize the alkaline-hydrolyzed lignin tar by catalytic hydrogenolysis. This treatment caused recondensation of the lignin hydrolysis fragments in both alkaline and neutral solutions. It is believed that the catalysts were unable to reduce the reactive groups in the hydrolyzed lignin, leaving these groups free to participate in recondensation reactions.

ACKNOWLEDGEMENTS

This work was performed with the support of the National Science Foundation, Problem-Focused Research Grant No. PFR 77-12243 A01. This paper is based on the senior author's Ph.D. research while he was at North Carolina State University.

LITERATURE CITED

1. W. Schweers, Papper och Trae, 4a, 1 (1966).
2. B. F. Hrutfiord, In Lignins - Occurrence, Formation, Structure and Reactions, Chap. 12, K. Sarkanen and C. Ludwig, Eds., J. Wiley and Sons, New York, NY, 1971.
3. I. S. Goldstein, Applied Polymer Sym., 28, 259 (1975).

4. M. H. Winston, C. L. Chen, J. S. Gratzl, and I. S. Goldstein, "Characterization of the Lignin Residue from Hydrolysis of Sweetgum Wood with Superconcentrated Hydrochloric Acid," 181st National ACS Meeting, Atlanta, Georgia, March 31, 1981.

5. F. Scaringelli, T. P. Schultz, and I. S. Goldstein, Analy. Letters, 13 (A4), 261 (1980).

6. T. P. Schultz, C. L. Chen, I. S. Goldstein, and F. P. Scaringelli, J. of Chrom. Sci., 19 (5), 235 (1981).

7. G. E. Miksche, Acta Chem. Scand., 26, 3275 (1972).

8. J. Turunen, Soc. Scient. Fennica, 28, 9 (1963).

9. G. Domburgs, Latv. PSR Zinat. Akad. Vestia, Kim. Ser., 6, 734 (1975). Also see Chem. Abst., 83, 81604p.