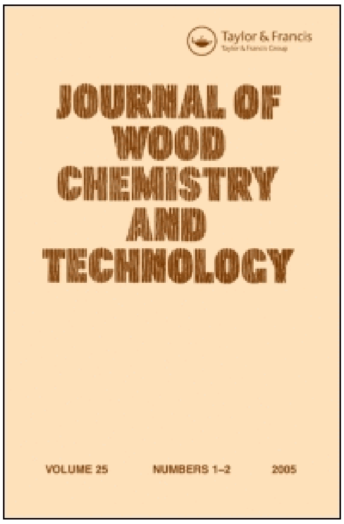

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LIGNIN AND RELATED COMPOUNDS XII. CATALYTIC DEGRADATION OF PROTO AND ISOLATED ASPEN LIGNINS UNDER INITIALLY ALKALINE CONDITIONS

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ABSTRACT

Catalytic degradation of aspen lignin under initially alkaline conditions has been studied as a method of selective conversion of the lignin polymer into potentially valuable phenolic chemicals. In contrast to initially neutral conditions, degradation is not dependent on the presence of molecular hydrogen and relatively larger amounts of C_6-C-C over C_6-C-C-C degradation products are obtained. The addition of anthraquinone to a typical soda pulping process results in a twofold increase in the yield of monomeric lignin products.

INTRODUCTION

Catalytic hydrogenolysis of the lignin of aspen wood gives low molecular fragments as a potential source of aromatic (phenolic) chemicals (1). Under the initially neutral conditions of that study the four major products were 4-n-propylguaiacol, 4-n-propylsyringol, dihydroconiferyl alcohol and dihydrosinapyl alcohol, all C_6-C-C-C fragments. It was reported that the relative abundance of these derivatives varied with conditions of the hydrogenolysis procedure thus providing a degree of selective degradation of the lignin. A more significant variation in the nature of the products occurs if the hydrogenolysis is effected under initially alkaline conditions. Earlier work in these laboratories (2), using spruce wood, revealed that C_6-C-C fragments, namely 4-ethylguaiacol and 4-(2-hydroxyethyl)guaiacol predominated at the expense of the C_6-C-C-C derivatives. This alternate mode of selective lignin degradation has now been further studied using aspen lignin.

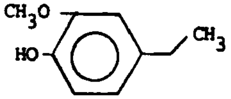
With the increasing interest in alkali-anthraquinone pulping it was of interest to determine the effect of anthraquinone addition on the catalytic hydrogenolysis of the lignin. Indeed if, as had been shown earlier (2), catalytic lignin degradation could be achieved under alkaline conditions without the need for added molecular hydrogen, the possibility existed for direct use of the alkaline pulping liquors for subsequent degradation to lignin chemicals of the type referred to above.

The cleavage of the β-γ carbon-carbon linkage under the alkaline conditions requires a particular structure of the original lignin. The data obtained in this study on aspen wood together with that obtained using model substances permit a discussion of this structural requirement and the postulation of a possible mechanism for the degradation.

DISCUSSION OF RESULTS

The monomeric hydrogenolysis products obtained from aspen wood under initially alkaline conditions are shown in Table 1. A number of previously recognized dimeric lignin derivatives representing 1,2-diarylethane, 5,5'-diaryl and diarylmethane structures were also identified. These represented only 7.7 percent of the total area of the identifiable chromatogram peaks. The most abundant was 1,2-disyringylethane comprising 3.2 percent. Confirming the observation made earlier in the case of spruce wood (2) was the appearance of the relatively larger amounts of the C_6-C-C compounds (a total of 39.2 percent) over the C_6-C-C-C compounds (a total of 17.4 percent). The two major lignin derivatives were 4-ethylguaiacol(I) and 4-ethylsyringol(II).

For the purpose of this research the relative abundance of these two compounds was used to monitor the effect of the changes in reaction conditions.



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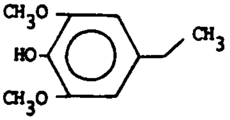
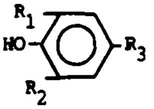


II

Effect of Temperature and Nature and Pressure of Gaseous Atmosphere

The hydrogenolysis of spruce wood indicated that under alkaline conditions, the presence of molecular hydrogen was much less important than if

TABLE 1 Monomeric Compounds Obtained from Hydrogenolysis of Aspen Woodmeal Under Alkaline Conditions[a]



Ret. Time min.	R_1	R_2	R_3	Relative Abundance %[b]
4.2	H	H	H	5.0
6.1	H	OCH_3	H	3.0
7.4	H	H	CH_2CH_3	1.4
8.3	H	OCH_3	CH_3	2.2
10	H	H	$CH_2CH_2CH_3$	0.2
11	H	OCH_3	CH_2CH_3	11
12	OCH_3	OCH_3	H	4.5
13	H	OCH_3	$CH_2CH_2CH_3$	4.0
15	OCH_3	OCH_3	CH_3	5.5
17	H	OCH_3	$COCH_3$	2.4
18	OCH_3	OCH_3	CH_2CH_3	21
19	H	OCH_3	$COCH_2CH_3$	0.2
20	OCH_3	OCH_3	$CH_2CH_2CH_3$	7.2
22	H	OCH_3	$CH_2CH_2CH_2OH$	0.6
24	OCH_3	OCH_3	$COCH_3$	2.4
26	OCH_3	OCH_3	CH_2CH_2OH	1.0
27	OCH_3	OCH_3	$COCH_2CH_3$	2.4
29	OCH_3	OCH_3	$CH_2CH_2CH_2OH$	2.8

a. Run 1: Aspen wood (10g), Rh-C (5%, 1g), NaOH (4.5g), dioxane-water (150 mL, 1:1 V/V), 195°C, 5h, hydrogen (500 psi, initial pressure).

b. Percentage of total area of peaks of chromatographable compounds.

TABLE 2 Hydrogenolysis of Aspen Woodmeal Under Initially Alkaline Conditions [a,b]

Run	Condition	Chloroform-Dioxane Soluble Fraction g	4-Ethyl-guaiacol[c] %	4-Ethyl-syringol[c] %
1.	Standard conditions at 195°C	1.9	4.0	16
2.	Same at 150°C	1.1	2.0	9.0
3.	Atmospheric hydrogen initial pressure	1.7	4.0	17
4.	50 Psi nitrogen initial pressure	1.2	4.3	16
5.	500 Psi nitrogen initial pressure	1.7	3.5	13
6.	No Rh-C	2.0	0.0	0.0

a. All reactions under standard conditions unless indicated otherwise. Standard conditions; aspen wood (10 g), Rh-C (5%, 1 g), NaOH (4.5 g), dioxane water (150 mL, 1:1 v/v), hydrogen (500 psi, initial pressure), 195°C, 5 h.

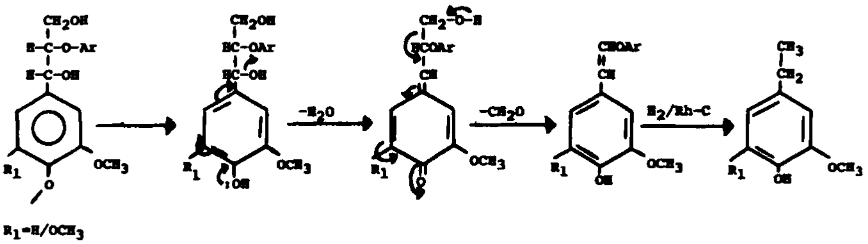
b. Percentage of propyl side chain compounds is less than one.

c. Weight percentage on the basis of total chloroform-dioxane soluble fraction.

the reaction were done under initially neutral conditions (2). A series of experiments using aspen wood meal was designed to study the role of the gaseous atmosphere under different conditions of pressure and temperature. A description of these runs, along with data on the nature of the lignin products obtained, is given in Table 2. Run 6 in which no catalyst was used has been included for comparison and to assess if any of the lignin derivatives were the result of alkaline hydrolysis and/or reaction with hydrogen gas.

It is clear that in the absence of the catalyst, even though a significant amount of lignin is removed as the chloroform-dioxane soluble fraction, no degradation to the smaller fragments, I and II, occurs. The previously recommended (3) temperature of 195°C has again been shown to be more suitable (Runs 1 and 2) for this degradation process. Of greater interest is the recognition that for aspen wood lignin also, degradation to the C_6-C-C monomeric units is not dependent on the presence of molecular hydrogen as a reactant. In nitrogen atmosphere, lignin removal and subsequent degradation to the monomeric units may be accomplished but the yields, if effected under similar conditions, are reduced (Runs 1 and 5). A further degree of selectivity may be seen in comparing the products obtained from a standard run (Run 1 and Table 1), using hydrogen at an initial pressure of 500 psi and that using nitrogen gas at an initial pressure of 50 psi (Run 4 and Table 3). In the latter case only eight monomeric compounds and no dimeric units were detected but again the two major products were I and II.

The requirement of the catalyst to effect lignin degradation and liberation of the monomeric units implies that such a process is not one of a simple alkali-catalyzed hydrolysis. In the presence of hydrogen a proposed mechanism for the β-γ cleavage, involves the production of the quinone methide intermediate and is illustrated as follows:



In the absence of molecular hydrogen a question arises with respect to the mechanism of the reductive step. One possibility could be a catalyzed redox

TABLE 3 Compounds Obtained from the Hydrogenolysis of Aspen Woodmeal Under Alkaline Conditions Using no Hydrogen Gas (Run 4, Table 2)

Name of Compounds	Relative Abundance %[a]
4-Methylguaiacol	1.2
4-Ethylguaiacol	16
Syringol	5.9
Unknown	1.1
4-Methylsyringol	11
4-Ethylsyringol	57
4-n-Propylsyringol	2.8
4-Hydroxy-3,5-dimethoxyphenyl methyl ketone	4.4

[a] Percentage of total area of peaks of chromatographable compounds.

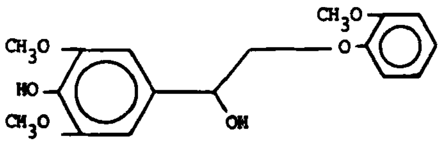
process. It has been shown by Rao and Perlin (4) that, in the presence of a Pd-C catalyst, the following reactions occurred:

$$Ph_2CHOH \xrightarrow[\text{reflux, 48 h}]{\text{Pd/C, dioxane}} \underset{(1:1\ \text{ratio})}{PhCH_2Ph + PhCOPh}$$

and

$$PhCH{=}CHPh \xrightarrow[\text{reflux, 48 h}]{\text{Pd/C, }CH_3CHOHCH_3} PhCH_2CH_2Ph + CH_3COCH_3$$

The above reactions were repeated using the Rh-C catalyst in place of the Pd/C catalyst. The same results were obtained. Furthermore the model compound, III, (1.0 g) was reacted with a



III

three percent solution of sodium hydroxide in 50 mL of water-dioxane (1:1 v/v) in the presence of Rh-C(5%)(0.1 g) for 5 hours at 195°C under an initial pressure of nitrogen of 50 psi. The following compounds along with their percentage of the areas of all peaks of chromatographable compounds were detected in the product: 4-ethylsyringol (21%), acetosyringone (15%), guaiacol (19%) and syringaldehyde (24%). The formation of the ethyl derivative as had occurred under similar conditions from spruce wood lignin, supports the presence in the lignin macromolecule of α-hydroxy groups. The role of the rhodium-charcoal would appear to be that of a hydrogen carrier, possibly through formation of a rhodium hydride species, which catalyzes the reduction and simultaneous formation of an α-keto derivative.

Effect of addition of anthraquinone

The addition of a small amount of anthraquinone (AQ) has been found to increase the yield and improve the quality of the pulp in alkaline pulping (5,6,7,8,9,10). Little research has been reported on the nature of the alkali lignin released by this process. It was therefore of interest to study the catalytic degradation of an isolated AQ- lignin to determine any significant changes in the fragmentation products compared to those from soda lignin. In light of the the results discussed above the interesting possibility existed whereby the alkaline liquors from a pulping process could be used directly to convert the solubilized lignin, in the presence of a catalyst, with or without molecular hydrogen, into potentially valuable phenols. To permit these studies to relate as closely as possible to industrial application, the conditions that were used simulated those of the soda pulping process. The GC-MS analyses of the lignin derivatives obtained under initially alkaline conditions and with or without added anthraquinone and Rh-C catalyst are given in Table 4. Data are given for only the six components identified in the products which were the major monomeric compounds of each run.

Two significant observations may be made from these data. The addition of the anthraquinone in a typical soda pulping process permits of a marked, about twofold, increase in the yield of the isolated lignin products in the chloroform-dioxane soluble fraction. Since there is no significant change in the relative abundance of the six major lignin products in this fraction, the recoverable yield of these compounds is essentially doubled. Should these types of chemicals be shown to have value on an industrial scale, it would clearly be advantageous to use the alkali-anthraquinone pulping process as their source. Furthermore, and of more structural interest, are the results reported in Tables 2 and 4. As shown in Runs 4 and 5 (Table 2) the direct treatment of the wood in alkaline conditions in the presence of the catalyst at

TABLE 4 Delignification of Aspen Wood Meal Under Different Alkaline Conditions[a]

Run	Additive	Temp	Pulp	$CHCl_3$-dioxane	Major Lignin Products, %[b]						
				solubles	guaicol	syringol	vanillin	syringaldehyde	acetoguaiacone	acetosyringone	Total
	(g)	°C	g	g							
7	-	170	5.0	0.6	0.67	2.9	2.0	6.7	0.67	3.5	16
8	AQ(0.035)	170	5.2	1.3	1.4	6.2	4.7	13.0	1.6	5.8	33
9	Rh-C(1.0) AQ(0.035)	170	5.3	1.3	2.2	8.3	6.8	11.0	0.90	3.1	32
10[c]	Rh-C(1.0)	195	-	1.0	4.0	13.0	0.11	0.21	1.6	4.6	24

a. Aspen wood meal (10 g), water (100 mL), NaOH (2.8 g), 2.5 h.

b. Weight percentage of lignin.

c. Black liquor from Run 8.

195° in a nitrogen atmosphere gives rise to the ethyl derivatives as the major products. However in a two-stage reaction whereby the major products from an initial treatment under alkaline conditions but without the catalyst (Run 8, Table 4) are treated in the presence of the catalyst at 195° only the same types of initial products (phenols, aldehydes and ketones) result and no ethyl derivatives are formed. This implies that the mechanism of the lignin degradation by direct catalytic conversion under alkaline conditions follows a different course to that involving the two-step process of degradation followed by the final catalytic procedure. From the point of view of the selective conversion of lignin into potentially useful derivatives it is significant to note that the alkali anthraquinone pulping process produces mainly syringol, vanillin, syringaldehyde and acetosyringone whereas treatment of this black liquor with the catalyst at 195°C leads primarily to guaiacol, syringol and acetosyringone.

EXPERIMENTAL

Aspen wood (Populus tremuloides, Michx.), about 30 years old, was ground to a meal (20 mesh) in a Wiley mill and air-dried to a moisture content of 4.6 percent. The lignin content was 18.7 percent.

All reactions were carried out in a Model 4560 Parr reactor of 1.1×10^3 mL capacity equipped with a magnetic stirrer. Details of the reaction conditions of each run are reported as footnotes to the tabulated data. In each case the reactor was cooled, the contents were filtered and the filtrate acidified with dilute hydrochloric acid. The filtrate was extracted exhaustively with chloroform. The chloroform-dioxane extract was washed with water, dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure to yield a product referred to as the chloroform-dioxane soluble fraction.

Capillary gas chromatographic-mass spectroscopic identification of the chloroform-dioxane soluble fractions was done using a Finnigan Model 400 system interfaced to an INCOS Model 2300 data acquisition system. The column was DB-5 fused silica 60 m x 0.32 mm, film thickness 0.25 nm; temperature programmed 50-100°C at 40°/minute; then at 100-300°C at 4°/minute.

Quantitative analyses of the major lignin degradation products were made using a Hewlett Packard Model 5750 gas chromatograph, fitted with a 6 ft., 1/8 in. O.D. stainless steel column packed with 20% SE-30 on Chromosorb W (A.W. , D.M.C.S. treated, 80/100 mesh). Temperature was programmed for 100°-270°C at 10°C/minute with a flow rate of 40 mL/minute. Calibration curves were made using authentic samples of compounds that were available in the laboratory.

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REFERENCES

1. J.M. Pepper and M.D. Rahman, Cell. Chem. Technol., 21, 233 (1987).
2. James M. Pepper and Punsei Supathna, Can. J. Chem., 56, 899 (1978).
3. James M. Pepper and Reginald W. Fleming, Can. J. Chem., 56, 896 (1978).
4. V.S. Rao and A.S. Perlin, Can. J. Chem., 61, 652 (1983).
5. B.I. Fleming, G.J. Kubes, J.M. Macleod and H.I. Bolker, TAPPI, 61, 44 (1978).
6. G.J. Kubes, B.I. Fleming, J.M. Macleod and H.I. Bolker, TAPPI, 61, 46 (1978).
7. L.L. Landucci, TAPPI, 63, 95 (1980).
8. J. Gierer, O. Lindeberg and I. Noren, Holzforschung, 33, 213 (1979).
9. J.R. Obst, L.L. Landucci and N. Sanyer, TAPPI, 61, (1980).
10. J.R. Obst and N. Sanyer, TAPPI, 63, 111 (1980).