UTILIZATION OF WASTE LIGNIN
Current Chemical Research
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UTILIZATION OF WASTE LIGNIN

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The utilization of lignin in the wastes incurred in the logging, milling, and conversion of the forest crop has been a problem for many years. Sulfite liquors have not only been a waste but a nuisance in the national waterways. Pulping liquors alone are capable of supplying annually 1,500,000 tons of lignin. Forest and sawmill wastes constitute an additional lignin source of several million tons annually.

Such conditions have stimulated extensive research directed toward finding methods of utilizing lignin. A few sulfite pulp mills have in recent years worked out means for the disposal or recovery of this waste; the sulfate and soda pulp mills dispose of lignin waste by evaporating and burning. Current recovery or disposal methods at pulp mills entail the installation of equipment at considerable expense to precipitate the lignin or to evaporate the pulping liquor preparatory for conversion into other products or for burning.

More than 100 years have passed since lignin was first recognized as a constituent of plant material, but its structure is still unknown. This is because lignin does not readily split up into identifiable building units, as is the case with its associate cellulose. Because of the lack of adequate means of identifying lignin, a great deal of time was consumed in seeking a satisfactory method for the isolation of unchanged lignin. Within the last decade lignin investigators have succeeded in finding the number and types of reactive groups and certain cleavage products. This knowledge has made it possible to correlate many of the conflicting ideas about lignin and to carry out a more definite program of research for its utilization.

A review of some of the characteristics of lignin gives us a picture, somewhat incomplete in places, but nevertheless helpful in the solution of the problem of what to do with lignin.

For isolating lignin, wood or other plant material is subjected to a hydrolytic reaction aided by the use of any one of the following agents: sulfuric acid (13); hydrochloric acid (23); other mineral acids

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(22); organic acids, either those present in the wood (15) or added (6) pulping chemicals; bases (18); fungi (1) or hydrolytic enzymes present in wood (2). There is no example known where lignin has been isolated without the application of hydrolytic reactions.

"Native lignin" (12), the alcohol-soluble lignin obtained from wood without the use of added acid, has been thought by some investigators to exist as such in wood. Table 1 contains the results of experimental work to determine the amount of native lignin that can be obtained from wood treated to prevent the action of hydrolytic enzymes, as compared with the amount obtained from air-dried wood or wood attacked by blue stain, both of which promote hydrolysis. One sample was placed in 95 percent alcohol and extracted immediately after cutting, the other was allowed to air-dry and then was extracted. Blue stain developed in one sample that was being stored under normal conditions before extraction. Fats and oils were removed from the dried extract by ether and carbon tetrachloride. The residue was triturated with 70 percent sulfuric acid at 15°C, for 4 hours and otherwise treated as in the lignin determination. The dried residue was considered the lignin yield. It is recognized that compounds other than lignin may be present which would make these values higher than the actual lignin yield. Green wood contained only a small amount of native lignin. Storage or the action of fungi increased the amount. This increase may be attributed to hydrolysis.

Table 1.—Extraction of green and air-dried wood with ethanol

<table>
<thead>
<tr>
<th>Material</th>
<th>Total extract</th>
<th>Lignin</th>
<th>Percent&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Percent&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green aspen</td>
<td>5.8</td>
<td>0.006</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air-dried aspen</td>
<td>13.2</td>
<td>2.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Green maple</td>
<td>4.1</td>
<td>0.033</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air-dried maple</td>
<td>8.6</td>
<td>1.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aspen sawdust attacked by blue stain</td>
<td>16.0</td>
<td>3.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Based on the weight of the dry wood.

The utilization of lignin depends entirely on the reactive groups of the molecule. Hardwood and softwood lignins differ somewhat in their reactions, but to avoid too much detail this discussion will include only hardwood lignin. Table 2 illustrates the reactions of maple lignin as isolated with 70 percent sulfuric acid from completely extracted green wood and having a methoxyl content of 20.3 percent, carbon 63.3 and hydrogen 5.7. Calculated on the basis of the reactions, the smallest molecular
weight of this lignin is 910. Its reactions indicate that this molecule would contain 6 methoxyl groups, 4 hydroxyl groups, and 2 ethylenic double bonds. This lignin corresponds to the formula

\[ \text{C}_{128}\text{H}_{300}\text{O}_{8}(\text{OCH}_3)_6(\text{OH})_4 \]

Eight oxygens are unidentified. They may exist in ether linkages, lactone rings, or a part of a ring such as in furan.

Table 2.—Reactions of maple lignin

<table>
<thead>
<tr>
<th>Four hydroxy groups</th>
<th>Calculated: Cl₂</th>
<th>Six methoxy groups</th>
<th>Calculated: Cl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>One secondary alcohol</td>
<td>8 : 3</td>
<td>One methylated hemiacetal</td>
<td>2 : 0</td>
</tr>
<tr>
<td>( \text{CH}_3\text{-C-}\text{OH} )</td>
<td></td>
<td>( \text{CH}_3\text{-OCH}_3 )</td>
<td></td>
</tr>
<tr>
<td>Two hemiacetal</td>
<td>4 : 0</td>
<td>One methylated enolic</td>
<td>2 : 1</td>
</tr>
<tr>
<td>( \text{C-OH} )</td>
<td></td>
<td>( \text{C-OCH}_3 )</td>
<td></td>
</tr>
<tr>
<td>One tautomeric</td>
<td>2 : 1</td>
<td>Three methoxyls attached to ring linkages as</td>
<td>6 : 0</td>
</tr>
<tr>
<td>( \text{C-C-}\text{OH} \leftrightarrow \text{C-C-}\text{=O} )</td>
<td></td>
<td>( \text{C-OCH}_3 )</td>
<td></td>
</tr>
<tr>
<td>Two double bonds</td>
<td>4 : 4</td>
<td>One methoxyl attached to tertiary carbon atom</td>
<td>0 : 0</td>
</tr>
<tr>
<td>( \text{C}\text{-}\text{OCH}_3 )</td>
<td></td>
<td>( \text{R} )</td>
<td></td>
</tr>
<tr>
<td>( \text{R'}\text{-C-OCH}_3 )</td>
<td></td>
<td>( \text{R''} )</td>
<td></td>
</tr>
<tr>
<td>( \text{R}'' )</td>
<td></td>
<td>( \text{R}'' )</td>
<td></td>
</tr>
<tr>
<td>Total...</td>
<td>28 : 9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

One of the hydroxy groups is a secondary alcohol group with a methyl group on the central carbon atom. This group, on treatment with an alkaline iodine solution, gave iodoform equivalent to 1 mole for each molecular weight (910) of lignin. With bleaching powder it gave chloroform. If

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-3-
the hydroxyl group is first methylated, it does not react with bleaching powder to give chloroform. On oxidation with chromic acid, lignin gave a 6 percent yield of acetic acid, which indicated the presence of a \( \text{CH}_3\text{C} \) grouping. The amount obtained by oxidizing lignin agrees with the amount that should be obtained from a compound containing one such secondary alcohol group.

Two other hydroxyl groups react as hemiacetals and are similar in reactivity to the glucosidic hydroxyl group in glucose. These are methylated by treating lignin or wood with methanol containing dry hydrogen chloride. The resulting compound contains 27.5 percent methoxyl groups. These new methoxyls are stable in alkaline solution but are removed by heating with 36 percent hydrochloric acid or acetic acid containing hydrochloric acid. It may be that lignin is bound to other cell components by means of these hemiacetal groups.

Another hydroxyl group is acidic in nature and may account for the solubility of lignin in alkali. It may be methylated with diazomethane. Certain color changes occurring in the lignin molecule may be accounted for by the reactions of this group. This group exhibits tautomeric reactions. Its keto form reacts with hydrazine and semicarbazide. If this group is methylated, which stabilizes the enol configuration, lignin becomes insoluble in alkali, is lighter in color and less reactive, and no longer shows the reactions of a keto form. The most characteristic reactions of lignin may be attributed to this group.

All hydroxyl groups can be methylated with dimethyl sulfate and give a compound containing 32.2 percent methoxyl groups. In case lignin is methylated in solvents such as acetone, that react with lignin in the presence of alkali, a higher value may be obtained due to formation of new hydroxyl groups.

One of the methoxyl groups on lignin as it occurs in wood is easily removed by hydrochloric acid, sulfuric acid, acetic anhydride, and pulping reactions. With sulfuric acid, methanol is produced. In these respects it behaves as a glucosidic or hemiacetal group. The loss of this group may account for the low methoxyl values found in lignin which had been isolated without temperature control.

One methoxyl is removed by reactions that involve the double bond, such as chlorination or sulfite reactions. This property is that of a methoxyl group next to a double bond such as is found in methyl vinyl ether or \( \beta \)-methoxyfurans.

Three other methoxyl groups are stable to the action of hydrochloric acid at ordinary temperatures and to the action of dry chlorine gas, but are removed by oxidizing agents such as chlorine water, chlorine dioxide in water, or dilute nitric acid. The groupings to which the three are attached are so changed by oxidation that they lose the methoxyl groups. This reaction is characteristic of hydroaromatic groupings or methylated secondary alcohols.
The sixth methoxyl is resistant to chlorination and oxidation reactions, but is removed by hydriodic acid. This grouping appears to have no hydrogen on the same carbon to which the methoxyl is attached and seems not to be adjacent to an active double bond; this indicates that the methoxyl group is attached to a tertiary carbon atom.

When lignin is treated with chlorine or bromine in methanol solution under conditions that give methyl hypochlorite or hypobromite addition compounds with ethylenic double bonds, two such bonds are found to be present (3) as indicated in the following reaction:

\[ \text{RC} = 
\begin{array}{c}
\text{C-R} + \text{CH}_3\text{OCl} \\
\end{array} 
\rightarrow 
\begin{array}{c}
\text{RC} = \\
\text{C-R} \\
\text{Cl OCH}_3
\end{array} \]

The chlorination of lignin in water gave reactions and products that agreed with the foregoing suggestions on the nature of the reactive groups of lignin. Theoretically, 8 chlorine atoms would react with the first hydroxyl and 3 would remain. The 3 chlorines would form chloroform when the chlorinated lignin is treated with an alkali. Four chlorine atoms would react with the glucosidic groups to form 2 carboxyl groups, and none would remain in the molecule. Two chlorine atoms would react with the pseudo acid, and 1 would remain in the molecule; the other would split off as hydrochloric acid.

The glucosidic methoxyl grouping would require 2 chlorine atoms, and none would remain. A carboxyl would be formed, the methoxyl-ethylenic grouping would require 2, and 1 would remain. Three methoxyl hydroaromatic or secondary alcohol groupings would require 6 chlorine atoms, and none would remain. The tertiary grouping would not react. The double bonds would require 4 chlorine atoms. In all, 28 chlorine atoms would be used and 9 would remain in the lignin molecule. This agrees with the findings of Mitchell (16). All the hydroxyl and 5 of the methoxyls would be removed as found by Harris, Sherrard, and Mitchell (8).

In the foregoing chlorination process 4 carboxyl groups would be formed if the preceding assumptions are correct. Some of these would be decomposed during the chlorination; others might be split off by boiling with hydrochloric acid. The 4 carboxyl groups would yield 19.3 percent carbon dioxide; actually 18.7 percent carbon dioxide was found (3).

The foregoing reactions apply to the external groups of lignin, but the building units are not revealed. Oxidation (2), destructive distillation (12), and fusion in alkali (5) have been employed as a means of studying this part of the molecule. Recently attempts were made to cause a cleavage of the lignin molecule during isolation (10). In all these the yield of identifiable products that have a structural significance is very low. In the case of alkali fusion and destructive distillation, rearrangements occur so that products having no relation to lignin structure may be obtained.
Hydrogenation of lignin offers a new method of attack. Some molecular rearrangement may accompany the hydrogenation and account for the product formed. Lignin heated in air was found to decompose at about 170° C., whereas the lowest temperature at which successful hydrogenation takes place is approximately 250° C. The high yield of reaction products recovered (Table 3) indicates that extensive decomposition has not occurred during hydrogenation.

Table 3.—Hydrogenation of lignin

<table>
<thead>
<tr>
<th>Material</th>
<th>Percentage of products recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Methanol</td>
</tr>
<tr>
<td>Aspen lignin by CH₃OH..................</td>
<td>26.5</td>
</tr>
<tr>
<td>Soluble aspen lignin by H₂SO₄.........</td>
<td>19.1</td>
</tr>
<tr>
<td>Aspen lignin by soda process...........</td>
<td>10.5</td>
</tr>
<tr>
<td>Insoluble aspen lignin by H₂SO₄.......</td>
<td>15.0</td>
</tr>
<tr>
<td>White spruce lignin by CH₃OH and HCl...</td>
<td>15.0</td>
</tr>
<tr>
<td>Black gum lignin by soda process......</td>
<td>11.0</td>
</tr>
</tbody>
</table>

Hydrogenation has now been applied to lignin isolated or recovered from a number of sources. Harris, D’Ianni, and Adkins (7) reported the hydrogenation of a soluble lignin obtained from hardwood by the action of methanol and hydrochloric acid. Methanol, 3 derivatives of propylcyclohexane, and a colorless high-boiling resin were obtained from the lignin. The combined yield of these, plus the water obtained as a by-product, accounted for all of the lignin. The identified products in this case amounted to almost 80 percent of the starting material. The remainder is a mixture whose general formula is (C₆H₁₀)ₓ. It is only a matter of time until this also will be identified. Both lignin isolated from soda pulping liquor and lignin isolated by sulfuric acid from either softwoods or hardwoods have been found to hydrogenate. The products vary somewhat, depending on the material used. Table 3 gives a summary of these products.

In the first report (7) and also some of the subsequent work on other lignin materials, the hydrogenation was carried out in anhydrous dioxane solution or suspension. The water formed in the reaction slowed up the process so that it was difficult to work in larger quantities. Later work has been carried out in water solution and found to give somewhat similar products.
Until recently research on the structure of lignin and that directed toward the commercial utilization of waste lignin have yielded few results. In some cases it is apparent that the attempt to use the lignin in the relatively dilute liquors resulting from the pulping of wood was a search for ways of disposing of the material without reference to its value as a source material for new products. This effort, however, was also worth while when the extentiveness of the amount not being used in any way is considered. In this class are the use of sulfite liquors for fertilizers, either as obtained directly from the pulping process or combined with ammonia, their use as road binder for secondary roads (20), and their use as fuel to furnish steam for the pulping process. The utilization of pulping liquors of the carbohydrate portion for the production of alcohol or yeast has looked promising, but up to the present time has been considered to give a poor return on the investment needed.

The development of uses somewhat more closely allied to the function of lignin in the tree as a bonding agent has resulted in several types of new plastics. One of these (4) utilizes sawdust or other finely divided wood which has been hydrolyzed to remove the less stable carbohydrates and to increase the ratio of lignin to cellulose. The resulting material is ground to a fine powder, mixed with a plasticizer, and then molded under pressure and heat into dark-colored lustrous articles. A second process (11) uses as a starting material a product resulting from the action of alkali and heat on calcium salt of lignin sulfonic acid as obtained in the Howard process. This product, when compounded with wood fiber, can be made into laminated sheets which, when assisted by a bonding or plasticizing material can be pressed into a hard, strong board. A third material (14) is obtained from the liquors resulting from the pulping of hardwoods by the soda process. Lignin is precipitated from these liquors by the use of carbon dioxide. This last material has been studied less but shows considerable promise because of its reactivity. In each of these processes use is made of the tendency of lignin to condense with itself in the presence of heat.

The tendency of lignin to show acidic or phenolic properties, coupled with its relatively high molecular weight, has resulted in its use as a substitute for tannins in the tanning of leather and as an aid in the softening of boiler water. These same properties account for the property of removing iron (17) from water and, under certain conditions, lime. This property may also be responsible for the change in water-holding characteristics of clay or cement when lignin is applied to them.

Some property, as yet unknown, causes lignin and certain lignin derivatives to act as depolarizers in the negative plates of storage batteries with a great increase in the output at temperatures below zero.

More closely related to the structure of lignin are vanillin and other phenolic substances which are obtained as cleavage products from sulfite liquor lignin by the action of heat and sodium or potassium hydroxide (21). The most important of these is vanillin. The yield is low (about 4 percent), but the commercial output of vanillin can exceed the present demand for it.
A study of the products obtained by hydrogenation of lignin is contributing to our knowledge of the structure of lignin. If ways can be found to hydrogenate lignin cheaply, it may become the source of a whole new series of organic compounds.

Advances in the utilization of lignin are encouraging but fall short of showing a way of using this vast amount of available material. Perhaps this problem will be solved when we have a better knowledge of the structure of the lignin molecule.

Literature Cited

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(10) Hibbert, H., Ibid., 61, 725 (1939).