AN ABSTRACT OF THE THESIS OF

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Title: The Mechanism of the Sulfonation of Lignin as Revealed by its Reaction with Methyl Hypochlorite

Abstract Approved:

In an effort to discover information which might be of value in utilizing the waste product, lignin, through better knowledge of its structure, the mechanism of bisulfite addition to lignin during the sulfite process was studied.

The chemistry of lignin is discussed in order to give an idea of what might be expected in such a reaction. Literature information relating to chlorination of lignin is reviewed, since this reaction was employed in the study. The sulfite pulping process is described in order to make clear the conditions under which commercial sulfonation of lignin takes place.

The bisulfite reaction is supposed to occur by addition at ethylenic and active carbonyl bonds in the lignin. It is believed that the lignin molecule binds four molecules of sulfur dioxide (as bisulfite), two of which are permanently combined with ethylene groups, one less permanently combined, and one molecule of sulfur dioxide loosely combined with an active carbonyl group.

Methyl hypochlorite, formed by the reaction of chlorine and dry methanol, has been found to add at ethylenic bonds in isolated lignin. Chlorination of lignin does not remove the sulfonic acid group, according to current theories. Therefore, no methyl hypochlorite addition should occur in sulfonated lignin, if the bisulfite groups are already present at the ethylenic bonds.

Chlorination of hemlock sulfuric acid lignin, calcium lignosulfonate and magnesium lignosulfonate was carried out in dry methanol. The starting materials and chlorinated products were analyzed for methoxyl, sulfur, carbon, hydrogen, ash, moisture and chlorine content. Formulas for the various materials which gave reasonable agreement with the analytical results were set up. These formulas were used as an indication of whether methyl hypochlorite addition had occurred or not.

The chlorination products from the different starting materials varied considerably in methanol and water solubility. The hemlock lignin yielded a methanol-insoluble product. The calcium lignosulfonate produced
three residues: one methanol-insoluble; one methanol-soluble, water-insoluble; and one methanol- and water-soluble. The magnesium lignosulfonate chlorination product was composed of two residues, both methanol-soluble, one water-insoluble, and one water-soluble.

In only one case did methyl hypochlorite addition fail to occur. In one other case, it appeared that sulfurous acid instead of bisulfite was present.

It was concluded that by no means all of the ethylenic bonds in lignin are saturated during the sulfite process. A soluble product evidently results when some of the bonds have been saturated; some groups remain completely unsaturated, while others may be fully saturated.
THE MECHANISM OF THE SULFONATION
OF LIGNIN AS REVEALED BY ITS
REACTION WITH METHYL HYPOCHLORITE

by

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Utilization of lignin is one of the most serious problems confronting the modern pulp manufacturer. A potential and as yet almost untapped source of organic chemicals, it remains a waste material and an economic nuisance at the end of the pulp-making process. The waste sulfite liquor, of which lignin is the chief constituent from the wood, has been disposed of largely in natural waters, causing pollution and constituting a menace to fish and game conservation.

Some attempt has been made to utilize its physical characteristics in making road binders, to use it as a fuel, and to incorporate it with resins. Commercial plants for production of vanillin have also been built. However, all these methods have the same faults: either the product is not entirely satisfactory or the market is not sufficient to make an outlet for all the waste material. Besides, in these ways the full value of lignin's organic constituents cannot be realized.

Hence the structure of lignin has been the subject of a great deal of research and investigation. It has been felt that a knowledge of its composition and chemical properties would lead to more intelligent ways of converting lignin to use. Doubtless this belief is true. In the end, such an approach will surely lead to a satisfactory solution of the problem. However, the complexity of its structure and the fact that any known method of isolation
alters the structure of lignin suggest that the solution will not be immediate. Thus, much of the work so far done seems fruitless and contradictory, but eventually a theory will be developed to correlate the facts.

It is the purpose of this thesis to begin an investigation of the mechanism by which calcium and magnesium bisulfite are chemically added to the lignin during the sulfite process. If this fact can be ascertained, it may then be possible to determine the ease with which these groups can be removed should such be desirable in utilizing lignin.
Occurrence and Formation

The name lignin was given by Schulze (43) in 1857 to a substance which is found between the long cellulose cells in trees. In young trees and in lower plants the lignin content is much less and may be almost entirely lacking. It acts chiefly as a cementing material, and earlier investigators (31), (36) assumed that it was held between the tissues by mechanical impregnation alone. However, the fact that specific chemical reactions are necessary to separate cellulose from lignin seems to indicate that there is a chemical bond between the two. This bond may be in the form of (1) an ether linkage between lignin, cellulose, and other carbohydrates (35), (2) an ester-like union between an acidic group in lignin and an hydroxyl group of the carbohydrate material, (7), (34) or (3) an acetal-like linkage (25).

There are several theories as to the formation of lignin within the plant. The essential point of difference in these theories is the identity of the parent substance which produces lignin. Three types of parent substances which have been postulated are:

(1) Cellulose. Cross and Bevan (4), König and Rump (32), and Fuchs (15) believed the intimate association of cellulose with
lignin suggests that the latter might be produced by a chemical change in the epidermis of the cellulose tissues. Certain similarities are apparent, such as the double refraction exhibited by both under the polarizing microscope.

(2) Pentose or pentosans. Klason (29) has found that, in general, plant substances which are high in lignin content are low in pentosans and vice versa. In this group of substances could be included all soluble carbohydrates, called hemicelluloses.

(3) Pectin. Ehrlich (5) discovered that in lignified tissues, pectins are present only in traces, if any, while in non-lignified tissues large amounts are usually found. It is significant that young trees show a low lignin and high pectin content; as the tree grows the lignin content increases, apparently at the expense of the pectin. Also, the alcohol-soluble portion of pectinic materials resembles lignin in methoxyl and carbon-hydrogen content.

Physical properties

Lignin is altered by all procedures which remove it from wood either completely or partially. Freudenberg (10) states that it cannot be separated from other wood constituents unchanged because:

(1) Acid hydrolysis is necessary to break the linkage between lignin and cellulose or other carbohydrates.

(2) Lignin exists in different condensation steps according to the age and origin of the wood. Highly polymerized, sugar-free
constituents occur together with lower polymers containing sugars. Treatment with acid to separate the sugars condenses smaller units into larger ones.

(3) The swelling property of cellulose and its tendency to form colloidal solutions makes impossible its extraction from lignin by use of specific solvents.

It must therefore be remembered that the properties to be discussed are those of the altered lignin which has been removed from the wood.

Isolated lignin is light tan or brownish in color. Brauns (2) claims to have obtained a white product by neutral ethanol extraction, but probably this represents only the more soluble parts of the complex. X-ray analysis indicates that lignin is amorphous.

Other physical properties listed by Freudenberg (10) are: low tensile strength, equal in all directions; limited swelling capacity; refractive index (spruce lignin), 1.61. The latter determination was made using immersion liquids of increasing refractive index. The double refraction exhibited by lignin decreased until it disappeared with iodobenzene (n= 1.62), and then reappeared with liquids of greater refractive index.

Chemical properties and reactions

(1) Methylation (22). Two agents are employed: dimethyl sulfate and diazomethane. The former replaces all the hydroxyl groups,
while the latter reacts only with phenolic or acidic groups. The methoxyl content of spruce lignin is nearly doubled using dimethyl sulfate, but diazomethane increases it only about twenty-five percent (11). It is therefore concluded that only a small number of the hydroxyl groups are aromatic.

(2) Acetylation (40). Lignin can be acetylated with acetic anhydride in pyridine. By this method a higher acetyl content is obtained than would be expected from methylation results.

(3) Halogenation. Reaction of lignin with chlorine is discussed more completely elsewhere in this paper (see p. 16). Bromination (13) seems to follow a similar course. Very little work has been done with iodine derivatives.

(4) Nitration (44). The ease with which nitration occurs suggests an aromatic structure in lignin. So far the reaction has yielded no products of particular value.

(5) Sulfonation. There has been considerable interest in the reaction of lignin with sulfurous acid to produce "lignosulfonic acid", since this is the treatment to which it is subjected in the sulfite processing of pulp (see p. 11). Klason (30) believes that the sulfurous acid adds at an olefinic bond as follows:

\[-C=CH + HOSO\textsubscript{2}H \rightarrow C=CH + HOSO\textsubscript{2}H\]

More recently, Freudenberg (10) proposed that the sulfonic acid group was substituted directly into the aromatic nucleus.

Hagglund (16) suggested the following type of reaction:

\[-C=OH + HSO\textsubscript{3}Na \rightarrow C=OH + SO\textsubscript{3}Na\]
Most recent work (8) suggests an enolization reaction:

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{H}
\end{align*}
\rightleftharpoons
\begin{align*}
\text{C} & \quad \text{C} \\
\text{H} &
\end{align*} + \text{HSO}_3\text{Na} \rightarrow
\begin{align*}
\text{C} & \quad \text{C} \\
\text{OH} & \quad \text{SO}_3\text{Na}
\end{align*}
\]


(7) Reduction (other than hydrogenation). Using hydriodic acid and red phosphorus, Willstätter (46) obtained a mixture of hydrocarbons, containing substances of an acidic nature. He concluded there was a similarity between lignin and carbohydrates because they reacted in the same manner with the above reagents. With zinc dust and high temperature, Phillips (38) obtained an aqueous distillate which contained catechol and an oil in which guaiacol was present.

(8) Catalytic hydrogenation (20) (21). The principal products to date have been saturated hydrocarbon derivatives. It has been necessary to work almost entirely with isolated lignin, rather than sulfite liquor itself, because of the serious poisoning effect of the sulfur upon the common nickel, copper, and platinum catalysts which would otherwise be most efficient and useful. Some of the more promising substances obtained by hydrogenation have been:
Attempts to reduce lignin to sugars with hydrochloric acid have resulted in low yields. A small amount of formaldehyde has been obtained, on the basis of which the methylene dioxide grouping (discussed later) has been postulated by Freudenberg (10).

(10) Degradation (12). Fusion with sodium or potassium hydroxide followed by acidification, dilution, and extraction with ether and benzene has yielded the following products:

Although the yields are low, this method has been applied to waste soda liquor for the commercial production of vanillin. Industrial demand is not sufficient, however, to make it feasible as a large scale operation.

(11) Cleavage of ether bonds (10). Treatment with aqueous alkali does not destroy the carbon framework; rupture occurs chiefly
at ether bonds and possibly at oxygen linkages in heterocyclic rings. In this process, free phenolic groups must be protected by methylation before alkali treatment. The following products have been isolated from the reaction mixture:

![Chemical structures](image)

**Veratric Acid**  **Isoheminic Acid**  **Dehydroveratric Acid**  **Trimethylgallic Acid**

Treatment of sulfonated lignin with thioglycollic acid and aqueous mineral acids causes the larger portion to become soluble in alkali. This is believed due to the replacement of sulfonic acid groups by \(-\text{S} \cdot \text{CH}_2 \cdot \text{COOH}\). (26)

**Structure**

Analytical evidence (8) gives the following elemental composition:

- **Carbon** - 65-66%
- **Hydrogen** - 6%
- Balance is oxygen; distribution:
  - **Methoxyl** - 15% (fir) - 22% (hardwood)
  - **Hydroxyl** - 9%, of which
    - 6-7% is secondary
    - 2% is tertiary
  - **Ether oxygen** about 7.5%
Freudenberg (10) has stated that lignin may be regarded as a product resulting from esterification and condensation of the following and similar units:

\[
\begin{align*}
\text{H}_2\text{C} \cdot \text{OH} & \quad \text{H} \cdot \text{C} = \text{O} & \quad \text{CH}_3 \\
\text{H} \cdot \text{C} \cdot \text{OH} & \quad \text{R} & \quad \text{R} \\
\text{H} \cdot \text{COH} & \quad \text{OH} & \quad \text{OCH}_3
\end{align*}
\]

The presence of aldehydic and ketonic groups has not been proved completely. Evidence (10) indicates that the tertiary hydroxyl and methyl groups are bound to the same carbon atom: methyl groups comprise 2.7 per cent of the total, which is approximately equal to the tertiary hydroxyl content.

If it is assumed that all oxygen atoms, methoxyl and piperonyl groups can be replaced with hydrogen, a nuclear hydrocarbon of empirical formula \(\text{C}_9\text{H}_{10}\) is obtained, which is phenylpropane minus two hydrogen atoms (3). Lignin could be built of such simple units linked either directly or through oxygen atoms, since there are many naturally occurring products which are derivatives of phenylpropane. However, if the structure were as simple as this, it would have been definitely established long before now.

Hibbert (24), using an ethanol-hydrochloric acid treatment, has obtained these products from spruce and maple:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CHOCH}_3 & \quad \text{CHOCH}_3 \\
\text{CH} = \text{O} & \quad \text{CH} = \text{O} \\
\text{H}_2\text{CO} & \quad \text{H}_2\text{CO} \\
\text{OH} & \quad \text{OH} \\
\text{SPRUCE AND MAPLE} & \quad \text{MAPLE}
\end{align*}
\]
He believes that these are the true building stones of lignin, but this is not necessarily true, according to Erdtman (8). In the isolation and determination of lignin these materials could polymerize into insoluble products, and these products would be included in the total lignin value. However, they are interesting in lignin chemistry because they are more characteristic of woody material than other similar compounds associated with lignin.

A structure presented by Erdtman (8) is:

\[
\begin{array}{c}
H_2CO \quad \quad \quad \quad \quad H_2CO \\
\quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad
The presence of the \( \text{C(OH)CH}_2 \) group in the above ring systems is in agreement with the formation of acetic acid by chromic acid oxidation, according to Erdtman (8).

Possibly the most satisfactory unit so far postulated for lignin structure is dehydroisoeugenol:

![Dehydroisoeugenol structure]

Erdtman (8) believes hydrolytic opening of the oxygen bridges in this compound, followed by methylation of the phenolic hydroxyl groups thus liberated, should form a product capable of yielding isohepmipinic acid (see above) upon oxidation with permanganate.

Freudenberg (10) has advanced the following lignin formula to account for the methylene dioxide linkage:

![Lignin formula]

This linkage is included because of his yield of formaldehyde. As yet this formula has not been widely accepted.

At present it is impossible to evaluate the various theories of lignin structure. There are several which have certain merits that have been excluded from this discussion. So far, no single hypothesis completely correlates all of the experimental data. However, most of them, and especially the more recent ones, are undoubtedly significant.
THE SULFITE PULP PROCESS

Theory

The principal purpose of the sulfite cooking process is to remove lignin, which imparts a dark color to the pulp due to its tendency to resinify when heated with mineral acids. Some pitch or resin and low-molecular weight carbohydrates are also removed in the process.

The main reaction in the cooking process is the combination of calcium or magnesium bisulfite with groups in the lignin molecule, forming soluble calcium or magnesium salts of lignosulfonic acid. The bisulfite is formed by the reaction of sulfur dioxide with calcium or magnesium oxide.

According to Klason's theory (30), the lignin complex binds four molecules of sulfur dioxide, two of which are permanently combined with ethylene groups, one less permanently combined, and one molecule of sulfur dioxide loosely combined with an active carbonyl group. For each sulfur dioxide group added to the lignin as bisulfite, naturally one-half atom of calcium or magnesium will be used.

The lignin appears to be in chemical combination with the carbohydrates, since dissolved lignin compounds do not appear in the cooking liquor until higher temperatures are reached. Carbohydrates also pass into solution at these higher temperatures. However, addition of bisulfite begins early in the process.
Hagglund therefore assumes that bisulfite is added to a lignin-carbohydrate complex, forming an insoluble compound which is hydrolyzed at higher temperatures into lignosulfonic acid and carbohydrates. The soluble sulfonic acid is stronger than the sulfurous acid of the cooking liquor, and it reacts with the bisulfite to form a lignosulfonic acid salt. The dissolved carbohydrates (hemicelluloses) are hydrolyzed to soluble sugars.

If the bisulfite becomes depleted near the end of the process, that which is loosely combined (to the carbonyl group) may be transferred to the ethylenic groups in more permanent combination, to supply the deficiency.

Method

Two cooking processes are now used commercially, the Ritter-Kellner, or direct-cooking process, and Mitscherlich, or indirect process. The first, or direct-cooking process is so named because the digester charge is heated with direct steam. The steam condenses in the digester, constantly diluting the acid, which must be added in high concentration for this reason. The digester charge can be heated rapidly by this method, making possible a cooking time of eight hours or even less. For this reason, the method is also known as the "quick-cooking" process.

In the Mitscherlich (indirect, slow-cooking) process, the digester charge is heated by means of steam-heated copper or lead
coils placed inside the digester. No acid dilution results, since the steam condenses in the coils; consequently the acid does not have to be so strong. The cooking time is about 20 to 30 hours, at a maximum temperature of 125 to 135° C. In the direct process, the temperature is usually about 140 to 150° C, and may be as high as 155 to 160° C.

* Figure 1 represents the flow-sheets of the two processes. Referring to (a), sulfur is burned in a sulfur burner, forming sulfur dioxide gas; the burning is completed in a combustion chamber. The gas is cooled and passed into the bottom of the strong tower, and is mostly absorbed there by combination with limestone in the presence of weak acid that trickles over the stones, forming strong acid. The remaining gas escaping from the strong tower enters the weak tower, also charged with limestone, where it combines with the limestone in a shower of water, forming weak acid which then passes to the strong tower. The strong acid goes to the reclaiming tower and from there to an absorption tank to be fortified with sulfur dioxide that is relieved from the digester during cooking. The relief gas is cooled before it enters the absorption tank, and the unabsorbed portion (or overgas) goes to the reclaiming tower. The relief liquor is sometimes passed through a separator, which separates the gas from the liquor, returning the gas and sometimes the liquor, after cooling, to the acid system. The fortified or

FLOW SHEETS OF SULFITE PROCESS

Tower System and Direct Cooking

Sulfur → Sulfur Burner → Combustion Chamber
Water → Weak Tower → Gas Coolers
Limestone → Strong Tower → Gas Fan
Steam → Reclaiming Tower → Relief Coolers
Chips → Acid Storage Tanks → Separator
Digester → Direct - Cooking

 Blow-Pit → Gas → Waste Liquor (Spent Acid)

(a)

Raw Materials - Gas -

(b)

Milk of Lime System and Indirect Cooking

Sulfur → Sulfur Burner → Combustion Chamber
Water → Soaking Tower → Gas Coolers
Lime → Absorption Tanks → Gas Fan
Steam → Reclaiming Tower → Relief Coolers
Chips → Acid Storage Tanks → Separator
Acid Storage Tanks → Digester → Indirect - Cooking

Condensed Steam → Digester

 Blow-Pit → Gas → Waste Liquor (Spent Acid)

Fig 1
cooking acid is then stored in tanks for use in the digester. The proper amount is fed into the digester along with wood chips. When the cooking is finished, excess pressure is relieved and the sulfur dioxide handled as described above. The pulp, waste liquor and gas are forced into a blow-pit. Steam and gas escape by a vent, waste liquor drains through a perforated false bottom, and the pulp is washed and pumped to screens for separation of coarse material and fiber.

The method just described is the "normal" or "cold-acid" system; in this process the heat in the relief liquor and gas is wasted because of the necessity of cooling in order to absorb the sulfur dioxide in a recovery system that operates at atmospheric pressure. By operating under pressure, the "Chemipulp" process eliminates this disadvantage. It involves modification of equipment to withstand pressures of about 75 lbs. per square inch and contact with hot acid solutions.

Figure 1 (b) differs from (a) in that lime is used instead of limestone. The lime is treated with water in a slaking tank to make milk of lime, which is used in an absorption tank or tower system to make strong acid. In this flow-sheet, indirect cooking is assumed, and the steam enters a coil in the digester. In actual processes, various combinations of the above features are encountered.
An alternative method for the removal of lignin from wood pulp during processing utilizes its combination with chlorine to form a product which upon alkaline hydrolysis becomes soluble and can be washed out of the pulp. For this reason, considerable work has been done in studying the reaction of lignin and lignosulfonic acid with chlorine.

Literature Review

Heuser and Sieber (14) studied the chlorination of spruce wood. They measured the course of the reaction quantitatively by determination of the hydrochloric acid formed. The chlorinated product was isolated by extracting with alcohol, concentrating the alcoholic solution, and pouring into ice-water.

Powell and Whittaker (39) suspended finely powdered lignin in carbon tetrachloride through which a slow stream of chlorine was passed. The color of the suspended material changed from dark brown to red, with evolution of much hydrochloric acid. The product was isolated by dissolving it in acetone and precipitating with hydrochloric acid. They described the product as a brick-red solid, soluble in cold alkali, and capable of being reprecipitated by addition of dilute acid. The reprecipitated substance seemed to have a lower chlorine content than the original.
Phillips (14) confirmed the results of Powell and Whittaker, using lignin isolated from corncobs with a 2 per cent alcoholic sodium hydroxide solution. This method was believed least likely to alter the lignin.

Waentig (45) has stated that the reaction between chlorine and lignified fibers is exothermic to the extent of 120 to 150 calories per gram. The mechanism of aqueous chlorination is suggested as being similar to that assumed for the sulfite process: formation of an addition compound with the lignin-carbohydrate complex, and subsequent hydrolytic separation. Lignin chlorides isolated from spruce, beech, poplar, bamboo and wheat straw contained about 27 per cent chlorine and gave molecular weights (by boiling point in acetone) of 1000 to 1200.

Kress and Voigtman (33) studied the chlorination of Mitscherlich sulfite pulp. Their method of preparation from isolated lignin was the same as that used by Powell and Whittaker. Water was used as the chlorinating medium, and also carbon tetrachloride. The water-chlorinated material was found to be more soluble than that produced in carbon tetrachloride, but had a lower chlorine content. Mitscherlich sulfite blowoff liquor was dialyzed in a parchment paper bag for two weeks, evaporated to a thick liquid, and dried in air. The lignosulfonic acid thus isolated was chlorinated in both carbon tetrachloride and water. The effect of chlorinating medium was again noticed, and the chlorinated lignosulfonic acids
were found, in general, to be more soluble than the corresponding products from lignin. The possibility of chlorination on both a benzene ring and side-chain was mentioned, and selective chlorination in the two solvents was suggested as an explanation of the differences in properties.

Arnold, Simmons and Curran (1) chlorinated long-leaf pine wood in an aqueous medium, extracted their product with alcohol, concentrated the solution, and precipitated the chlorolignin by pouring into 10 volumes of water. In this way they obtained a light buff-colored product amounting to about 3 per cent of the original wood weight. The product had no melting-point, but noticeable decomposition occurred at 140°C. It had a chlorine content of 14.2 per cent and was soluble in alkaline solutions, alcohol, acetone, glacial acetic acid, fusel oil, ethyl acetate, dioxane, and benzaldehyde. It was only slightly soluble in carbon tetrachloride, chloroform, ether, and glycerol.

Pederson and Benson (37) studied the chlorine derivatives of butanol lignin, sulfite waste liquor lignin, and wood. They discovered differences in chlorine content but almost identical properties. Chlorination was carried out in carbon tetrachloride; all of the products were insoluble in this medium. The chlorination reaction did not remove the sulfonic acid group. Chlorolignin was assertedly best prepared by first removing the sulfonic acid group by caustic fusion.
Karateev et al. (27) investigated the chlorination of lignosulfonic acid and sulfite alkali liquor. They obtained derivatives which could be divided, after drying, into fractions insoluble and soluble in water. The chlorine derivatives of lignosulfonic acid contained more chlorine in the soluble than in the insoluble portion, whereas with those from sulfite liquor the reverse was true. The chlorine derivatives of lignosulfonic acid contained 10.4 to 32.2 per cent chlorine, depending on the conditions of chlorination. The removal of methoxyl groups occurred in the chlorination, and the amount of demethoxylation increased with the increase in reacted chlorine, but not equally for the soluble and insoluble portions. On the average, one methoxyl group was substituted for each 2.6 atoms of chlorine in the insoluble portion, and for each 3.8 atoms of chlorine in the soluble portion.

Sarkar (41) observed the effect of dry chlorine on dry jute, and reported the formation of a chlorolignin containing the same per cent of chlorine as when treated with moist chlorine. Light was stated to have no effect on the reaction. In the presence of iodine, ferric chloride or antimony trichloride, the maximum chlorine content was 17.7 per cent. When lignin was chlorinated in the presence of methyl alcohol, methylation and chlorination were believed to occur. By careful chlorination of finely powdered lignin for four hours, a compound containing 25.8 per cent chlorine was always formed. The chlorine content fell to 17.7 per cent when the chlorolignin
was treated with dilute sodium hydroxide. Sarkar believed that hydrochloric acid lignin contained no double bonds, from estimation of the chlorine in combination as hydrochloric acid. Chlorolignin boiled with 12 per cent hydrochloric acid gave carbon dioxide, even in an atmosphere of hydrogen. A molecular weight of 816 was assumed for lignin in the calculations.

Hibbert et al. (23) postulated a mechanism for the chlorination of lignin from a kinetic standpoint. With isolated alkali lignin, they found that treatment with chlorine in aqueous solution results in almost equivalent chlorination and demethoxylation, the degree being dependent on the amount of chlorine added and the acidity of the reaction mixture. Literature was cited to indicate that methoxyl grouping in lignin are probably attached to guaiacyl nuclei, and that halogenation should occur in the 5- or 6- position. Their experimental results were interpreted as indicating that chlorine did occur in these positions, and that the presence of the chlorine atoms induced instability in the methoxyl groupings. They believed the methoxyl groups then cleaved with the formation of quinone or diketo structures which could react further to yield acidic groupings in the lignin.

Kinetically, the rate of chlorine consumption by lignosulfonic acid was treated by assuming that the process involved two major reactions, an initial, rapid one and a slow, time-determining second order reaction.
Harris (19) made a study of the reaction of methyl hypochlorite with lignin. The methyl hypochlorite was formed by the interaction of chlorine with dry methanol. A product was obtained with higher methoxyl content than would be expected if the methanol did not enter into the reaction. It was believed that the methyl hypochlorite, which is known to add to ethylenic linkages, had added to olefinic bonds in the lignin. The hypochlorite, prepared in various ways, reacted with maple lignin to give compounds containing two methoxyl groups in excess of those in the starting material; with spruce lignin, to produce compounds with two or three excess methoxyl groups.

Summary and Theory

The process of chlorination is believed to be one of substitution and/or addition (37). Postulated reactions are shown:

\[
\begin{align*}
RH + Cl_2 &\rightarrow RCl + HCl \\
RCH = CH R' + Cl_2 &\rightarrow RCHCl - CHCl R'
\end{align*}
\]

The second reaction may proceed further, accompanied by the splitting off of hydrochloric acid.

In aqueous solution, chlorination appears to be principally by substitution, with some addition, and with demethoxylation occurring. In methanol, the formation of methyl hypochlorite seems to suppress the demethoxylation reaction, probably due to the fact that here chlorination is primarily of the additive rather than the substitutional type.
STATEMENT OF PROBLEM

In his paper concerning reaction of lignin with chlorine in methanol, Harris (19) postulates the formation of methyl hypochlorite, \( \text{CH}_3\text{OCl} \), in a manner analogous to the reaction of chlorine with water to form hypochlorous acid:

\[
\begin{align*}
(1) \quad & \text{Cl}_2 + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCl} + \text{HCl} \\
(2) \quad & \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCI} + \text{HCl}
\end{align*}
\]

Harris then undertakes to show that the addition of methyl hypochlorite to the ethylenic bonds in lignin occurs as follows:

\[
\text{CH}_3\text{OCl} + \begin{array}{c}
\text{H} \\
\text{Cl}
\end{array} \rightarrow \begin{array}{c}
\text{H} \\
\text{Cl}
\end{array} \begin{array}{c}
\text{C} \\
\text{OCH}_3
\end{array} \begin{array}{c}
\text{Cl} \\
\text{C}
\end{array}
\]

In all of his experiments, some additional chlorine was introduced by substitution, in spite of precautions taken to remove the hydrochloric acid formed in reaction (1). However, making allowance for the substituted chlorine, the results seem reasonable.

As already discussed, it is believed that addition of calcium and magnesium bisulfite also occurs at ethylenic bonds, as well as at the carbonyl group. If methyl hypochlorite is not active enough to replace the calcium (magnesium) bisulfite (see p. 18), then no addition of methyl hypochlorite should take place at bonds to which bisulfite groups have been added.

It was felt that this method could be applied quantitatively enough to determine the number of ethylenic bonds in sulfite lignin
to which calcium (magnesium) bisulfite had been added. From the amount of sulfur originally present, the number of substituted carbonyl groups could also be calculated. Such a determination would be of value in (1) verifying the ethylenic structure in lignin, and (2) showing the mechanism of lignin sulfonation.
Materials Used

Lignin was isolated from ground hemlock wood (60-mesh) by treatment with 72 per cent sulfuric acid. The acid was added slowly to the dry wood. The mixture was contained in an ice-bath, and the acid was added at such a rate that the temperature did not rise above 20° C. The mixture was allowed to stand for about six hours at the same temperature, and was then diluted with enough water to reduce the acid concentration to 3 per cent. The dilute solution was boiled under a reflux condenser for 5 or 6 hours. The product was filtered with suction and washed with water until free from acid. It was then dried, first in air and then in a vacuum desiccator over phosphorus pentoxide. The material was tested for complete hydrolysis by the method of Schorger (41) (Herzberg iodine stain). Absence of a blue color (negative test) was observed when the solid material was stained with the iodine solution. The product was brown in color.

Calcium lignosulfonate was separated from the other constituents of a waste sulfite liquor by dialysis of the liquor in a cellophane bag for two weeks. Water was removed by evaporating under reduced pressure. The product was dried, first in the air and then in a vacuum oven.

Magnesium lignosulfonate was also obtained from a waste sulfite liquor. It was purified by countercurrent dialysis. The product was then dried in the same manner as the calcium lignosulfonate.
The calcium and magnesium lignosulfonates were kept in stoppered bottles. The moisture content was determined, and analytical samples were corrected to a moisture-free basis (with the exception of samples for combustion analysis, which were dried over phosphorus pentoxide). The material was ground to approximately 100-mesh before use.

Chlorination

Chlorinations were carried out in an ordinary three-necked, 500-ml. balloon flask equipped with a motor stirrer, thermometer, and a perforated inlet tube for chlorine. The stirrer shaft was fitted with a mercury seal, the mercury being covered with a layer of carbon tetrachloride to prevent reaction between mercury and chlorine. Commercial dry chlorine was introduced through the inlet tube after drying by bubbling through concentrated sulfuric acid. The exit chlorine passed through a dilute sodium hydroxide solution, which also served as a rough bubble counter to indicate completion of the reaction. The flask was surrounded with cracked ice, and the chlorine rate adjusted so that the temperature was held below 10°C throughout the chlorination.

Five-gram samples were placed in the flask with 200 ml. of methanol which had been dried by distillation through a modified Fenske column and collected in a flask containing anhydrous calcium sulfate. Chlorine was passed through the mixture at a fairly rapid rate for three to six hours, depending on the type of lignin.
Magnesium lignosulfonate gave a completely soluble product at the end of three hours; the calcium lignosulfonate became partially soluble at the end of five hours, and practically all the hemlock lignin remained insoluble in methanol at the end of six hours.

Harris (19), in his work with methyl hypochlorite and lignin, suggested methods for removal of hydrogen chloride as it was formed, including chlorination in the presence of barium carbonate. His object was to prevent substitution reactions between lignin and the hydrochloric acid. Preliminary experiments were conducted using 25 grams (an excess) of anhydrous (oven-dried) barium carbonate in the reaction flask, but no appreciable difference in chlorine content was found upon analyses of the products. The barium carbonate was not used in later experiments, therefore, since it introduced an additional complication, that of separating the insoluble chlorinated product from the excess carbonate. In the preliminary experiments, this separation was accomplished by dissolving out the excess carbonate with hydrochloric acid, at a low temperature.

At the end of the chlorination, the mixture was allowed to warm slightly (to about 15° C) to increase the solubility of the product in methanol. Rise in temperature above about 20° C caused a rather vigorous reaction to occur, with the evolution of heat and gas. The insoluble residue, if any, was removed by filtration. With hemlock lignin, this residue was the principal product. With calcium lignosulfonate, a material hereafter designated as Ca-Residue l
was obtained. With magnesium lignosulfonate, there was no appreciable amount of residue at this point. The residue was washed free of chlorine (starch-iodide test paper).

The filtrate (filtrate I) was poured on to about one-half liter of cracked ice and allowed to stand for approximately an hour, after which any precipitate present was filtered. In the case of hemlock lignin, no precipitate was obtained; calcium lignosulfonate produced a light yellow residue (Ca-Residue 2 below); magnesium lignosulfonate yielded a product of similar appearance (Mg-Residue 1 below).

The filtrate (filtrate II) in each case was evaporated to dryness in a vacuum evaporator surrounded by a water bath. Temperature was maintained at 45 to 50° C. Hemlock lignin yielded no residue of consequence; considerable difference was evident in the residues obtained from the calcium and magnesium lignosulfonates. The former gave a light yellow powder (Ca-Residue 3), while that from the magnesium lignin (Mg-Residue 2) was extremely hygroscopic, gelatinous and sticky while moist, and slightly darker in color than the calcium lignin residue when dry. Considerable difficulty was encountered in drying the last-mentioned product; it was finally accomplished by placing the sample in a vacuum desiccator over phosphorus pentoxide for several days.

Methods of Analysis

Chlorine. The procedure of Arnold, Simmons and Curran (1),
which they found comparable to standard methods, was used. 0.5 gram samples were refluxed for five hours with 1:1 nitric acid and an excess of 0.1 N silver nitrate (standardized against pure sodium chloride with chromate indicator). The silver chloride was filtered off from the solution, and the precipitate was washed several times with water. The filtrate was titrated with 0.1 N potassium thiocyanate, using ferric alum indicator. The thiocyanate was standardized against the standard silver nitrate in a nitric acid medium, using ferric alum indicator.

**Methoxyl.** The apparatus developed by Christensen, Friedman, and Sato (3) was used. This method, a micro determination, is based upon the conversion of methoxyl groups to methyl iodide by hydriodic acid. The volatile methyl iodide distills out of the reaction flask, which is maintained at a temperature of 135 to 140° C in a phosphoric bath heated by a micro burner, and is then collected in an evacuated flask containing (1) a 10 per cent sodium acetate-glacial acetic acid solution, and (2) an excess of bromine. After removal of excess bromine with formic acid, the iodide is titrated in the usual way with standard thiosulfate, using a micro-burette.

**Sulfur.** A Parr fusion bomb was used for the oxidation of sulfur to sulfate. 0.5-gram samples were mixed with an excess of sodium peroxide, 1 gram of potassium perchlorate, and 0.5 gram of sucrose. The bomb was electrically fired with a storage battery, the current
of which passed through a high-resistance nichrome wire in contact with the bomb charge. The sulfate was determined gravimetrically.

Carbon-Hydrogen. A combustion apparatus of the type described by Fisher (9) was used. The samples were burned in a stream of dry oxygen in a tube containing cupric oxide, cerium dioxide (as a catalyst), and lead peroxide for the absorption of sulfur and halogens. The lead peroxide was not used in combustion of the original hemlock lignin, since preliminary combustions on succinic acid and sucrose indicated that the peroxide absorbed appreciable quantities of carbon dioxide even at temperatures close to 300° C. Since lead carbonate decomposes at 315° C, a temperature slightly above that value was maintained in this section of the furnace when the peroxide was used. The water produced in the combustion was absorbed by magnesium perchlorate (Anhydrole), the carbon dioxide by ascarite.

Ash. Platinum crucibles were used for the calcium and magnesium lignosulfonate samples. All other samples, including chlorinated products, were ashed in porcelain crucibles. In correcting sample weights for ash, the residues from the calcium and magnesium lignosulfonates were considered as calcium sulfate and magnesium oxide, respectively.

Moisture. The original hemlock lignin and all of the chlorinated products were dried and kept in a desiccator over phosphorus pentoxide. Instability toward heat did not permit oven-drying of these materials.
The calcium and magnesium lignosulfonate samples were dried at 110° C for several hours, and a moisture correction was applied in calculations, except for combustion samples, which were dried over phosphorus pentoxide. All other materials were considered moisture-free.
DATA

Table I is a summary of analytical information obtained for the various derivatives of lignin studied.

Table II contains the same information converted to an ash-free, moisture-free basis. These values were used in subsequent calculations.

Tables III - X show correlations between observed and computed analyses for individual fractions.

Table XI gives a comparison of calculated and observed results for all materials studied.

Chlorination yields: Based on 5-gram samples of starting materials.

<table>
<thead>
<tr>
<th>Lignin/Residue</th>
<th>Grams Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hemlock lignin</td>
<td>7-8 grams</td>
</tr>
<tr>
<td>Calcium lignosulfonate</td>
<td>1.3 grams</td>
</tr>
<tr>
<td>Residue 1</td>
<td>1.3 grams product</td>
</tr>
<tr>
<td>Residue 2</td>
<td>3.9 grams product</td>
</tr>
<tr>
<td>Residue 3</td>
<td>2.5 grams product</td>
</tr>
<tr>
<td>Total</td>
<td>8.7 grams product</td>
</tr>
<tr>
<td>Magnesium lignosulfonate</td>
<td>2.5 grams</td>
</tr>
<tr>
<td>Residue 1</td>
<td>2.5 grams product</td>
</tr>
<tr>
<td>Residue 2</td>
<td>1.9 grams product</td>
</tr>
<tr>
<td>Total</td>
<td>4.4 grams product</td>
</tr>
<tr>
<td>Sample</td>
<td>Moisture</td>
</tr>
<tr>
<td>-------------------------</td>
<td>----------</td>
</tr>
<tr>
<td>Hemlock Lig.</td>
<td>---</td>
</tr>
<tr>
<td>Chlorinated Hemlock Lig.</td>
<td>---</td>
</tr>
<tr>
<td>Calcium Lignosulfonate</td>
<td>3.14%</td>
</tr>
<tr>
<td>Ca-Residue 1</td>
<td>---</td>
</tr>
<tr>
<td>Ca-Residue 2</td>
<td>---</td>
</tr>
<tr>
<td>Ca-Residue 3</td>
<td>---</td>
</tr>
<tr>
<td>Magnesium Lignosulfonate</td>
<td>3.84</td>
</tr>
<tr>
<td>Mg-Residue 1</td>
<td>---</td>
</tr>
<tr>
<td>Mg-Residue 2</td>
<td>---</td>
</tr>
</tbody>
</table>

* For methoxyl sample

** Not determined
### TABLE II - ANALYTICAL RESULTS ON MOISTURE AND ASH-FREE BASIS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chlorine</th>
<th>Methoxyl</th>
<th>Sulfur</th>
<th>Carbon</th>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hemlock Lign.</td>
<td>---</td>
<td>14.5%</td>
<td>---</td>
<td>61.6%</td>
<td>5.68%</td>
</tr>
<tr>
<td>Chlorinated Hemlock Lign.</td>
<td>14.9%</td>
<td>16.6</td>
<td>---</td>
<td>**</td>
<td>**</td>
</tr>
<tr>
<td>Calcium Lignosulfonate</td>
<td>---</td>
<td>12.4</td>
<td>7.38%</td>
<td>54.4</td>
<td>5.58</td>
</tr>
<tr>
<td>Ca-Residue 1</td>
<td></td>
<td></td>
<td></td>
<td>Incomplete analysis</td>
<td></td>
</tr>
<tr>
<td>Ca-Residue 2</td>
<td>18.1</td>
<td>15.9</td>
<td>2.88</td>
<td>38.1</td>
<td>3.96</td>
</tr>
<tr>
<td>Ca-Residue 3</td>
<td>21.3</td>
<td>12.7</td>
<td>7.46</td>
<td>**</td>
<td>**</td>
</tr>
<tr>
<td>Magnesium Lignosulfonate</td>
<td>---</td>
<td>8.29</td>
<td>8.26</td>
<td>43.2</td>
<td>5.66</td>
</tr>
<tr>
<td>Mg-Residue 1</td>
<td>18.3</td>
<td>14.25</td>
<td>3.39</td>
<td>36.7</td>
<td>4.01</td>
</tr>
<tr>
<td>Mg-Residue 2</td>
<td>15.8</td>
<td>6.93</td>
<td>7.10</td>
<td>29.9</td>
<td>4.55</td>
</tr>
</tbody>
</table>

**Not determined**
TABLE III

ORIGINAL HEMLOCK LIGNIN

Formula: (1) $C_{40}H_{36}O_{13}(OCH_3)_4$

(2) $C_{40}H_{36}O_{14}(OCH_3)_4$

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Found</th>
<th>Calc'd. (1)</th>
<th>Calc'd. (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methoxyl</td>
<td>14.5%</td>
<td>14.6%</td>
<td>14.4%</td>
</tr>
<tr>
<td>Carbon</td>
<td>61.1</td>
<td>62.2</td>
<td>61.2</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5.64</td>
<td>5.66</td>
<td>5.56</td>
</tr>
<tr>
<td>Ash</td>
<td>0.59</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Agreement is about the same for either formula; therefore (1) is adopted, since it conforms more closely to the accepted structure for sulfuric acid lignin.
TABLE IV

CHLORINATED HEMLOCK LIGNIN

Formula: \( \text{C}_{40,33,0,13}(\text{OCH})_{3,6,5} \text{Cl} \)

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Found</th>
<th>Calc'd.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine</td>
<td>14.9%</td>
<td>16.4%</td>
</tr>
<tr>
<td>Methoxyl</td>
<td>16.5</td>
<td>17.2</td>
</tr>
<tr>
<td>Ash</td>
<td>0.50</td>
<td>0</td>
</tr>
</tbody>
</table>

Decrease in the number of hydrogen atoms occurs because one is removed from each chlorine introduced by substitution.
TABLE V

CALCIUM LIGNOSULFONATE

Formula: (1) \( C_{40} H_{36} O_{13} (OCH_3) (SO_4^{2-}Ca)_{3/2} \)

(2) \( C_{40} H_{36} O_{13} (OCH_3) (SO_4^{2-}Ca)_{3/3} \)

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Found</th>
<th>Calc'd. (1)</th>
<th>Calc'd. (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methoxyl</td>
<td>11.1%</td>
<td>11.9%</td>
<td>10.8%</td>
</tr>
<tr>
<td>Sulfur</td>
<td>6.64</td>
<td>6.11</td>
<td>8.35</td>
</tr>
<tr>
<td>Carbon</td>
<td>49.0</td>
<td>50.5</td>
<td>46.0</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5.02</td>
<td>4.58</td>
<td>4.19</td>
</tr>
<tr>
<td>Ash</td>
<td>10.0</td>
<td>12.9</td>
<td>19.5</td>
</tr>
</tbody>
</table>

(as CaSO₄)

Formula (1) is adopted, since it gives better agreement with the experimental data.
TABLE VI

Ca-RESIDUE 2

Formula: \( C_{40}H_{32}O_{13}(OCH_3)_4(SO_3H)(CH_3OCl)_2Cl_4 \)

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Found</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine</td>
<td>18.0%</td>
<td>17.9%</td>
</tr>
<tr>
<td>Methoxyl</td>
<td>15.8</td>
<td>15.6</td>
</tr>
<tr>
<td>Sulfur</td>
<td>2.37</td>
<td>2.69</td>
</tr>
<tr>
<td>Carbon</td>
<td>37.9</td>
<td>46.4</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>3.94</td>
<td>4.28</td>
</tr>
<tr>
<td>Ash (as CaSO_4)</td>
<td>0.59</td>
<td>0</td>
</tr>
</tbody>
</table>
TABLE VII

Ca-RESIDUE 3

Formula: (1) $C_{40}H_{29}O_{13}(OCH_3)_4(SO_3Ca)_3(CH_3OCl)Cl_6$

(2) $C_{40}H_{29}O_{13}(OCH_3)_4(SO_3Ca)_3(CH_3OCl)_2Cl_7$

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Found</th>
<th>Calc'd. (1)</th>
<th>Calc'd. (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine</td>
<td>17.8%</td>
<td>17.5%</td>
<td>21.0%</td>
</tr>
<tr>
<td>Methoxyl</td>
<td>10.6</td>
<td>10.9</td>
<td>12.2</td>
</tr>
<tr>
<td>Sulfur</td>
<td>6.25</td>
<td>6.75</td>
<td>6.30</td>
</tr>
<tr>
<td>Ash</td>
<td>16.1</td>
<td>14.3</td>
<td>13.4</td>
</tr>
</tbody>
</table>

(ash CaSO₄)

Formula (1) gives the better agreement of the two, and therefore it is adopted.
TABLE VIII

MAGNESIUM LIGNOSULFONATE

Formula:  
(1) \( C_{40}H_{36}O_{13}(OC\text{H}_3)_{\frac{3}{3}}(\text{SO}_3\text{Mg})_4 \)  
(2) \( C_{40}H_{36}O_{13}(OC\text{H}_3)_4(\text{SO}_3\text{Mg})_3 \)

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Found</th>
<th>Calc'd. (1)</th>
<th>Calc'd. (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methoxyl</td>
<td>7.25%</td>
<td>8.50%</td>
<td>10.2%</td>
</tr>
<tr>
<td>Carbon</td>
<td>39.4</td>
<td>47.2</td>
<td>43.4</td>
</tr>
<tr>
<td>Sulfur</td>
<td>7.54</td>
<td>8.80</td>
<td>10.5</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5.16</td>
<td>4.12</td>
<td>3.95</td>
</tr>
<tr>
<td>Ash (as MgO)</td>
<td>8.63</td>
<td>5.48</td>
<td>6.58</td>
</tr>
</tbody>
</table>

Agreement here is rather poor; the high ash value suggests the possibility that considerable impurity was present in the material.

Formula (1) is in better agreement with experimental values in some respects. It is to be noted that one methoxyl group appears to have been split off during sulfonation, if this assumption is correct. Formula (1) is used in the calculations below.
TABLE IX

Mg-RESIDUE 1

Formula: (1) $\text{C}_{40}\text{H}_{32}\text{O}_{13}(\text{OCH}_3)_3(\text{SO}_3^2\text{Mg})(\text{CH}_3\text{OCl})_2\text{Cl}_4$

(2) $\text{C}_{40}\text{H}_{32}\text{O}_{13}(\text{OCH}_3)_3(\text{SO}_3^2\text{Mg})(\text{CH}_3\text{OCl})_3\text{Cl}_4$

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Found</th>
<th>Calc'd. (1)</th>
<th>Calc'd. (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine</td>
<td>18.1%</td>
<td>18.1%</td>
<td>19.9%</td>
</tr>
<tr>
<td>Methoxyl</td>
<td>14.1</td>
<td>13.1</td>
<td>14.9</td>
</tr>
<tr>
<td>Sulfur</td>
<td>3.34</td>
<td>2.71</td>
<td>2.56</td>
</tr>
<tr>
<td>Carbon</td>
<td>36.2</td>
<td>45.7</td>
<td>44.2</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>3.96</td>
<td>3.98</td>
<td>4.01</td>
</tr>
<tr>
<td>Ash (as MgO)</td>
<td>1.36</td>
<td>2.80</td>
<td>2.24</td>
</tr>
</tbody>
</table>

Even though agreement is not good in either case, it is slightly better for formula (1). The indication of a single bisulfite group is interesting: it suggests the possibility that the lignosulfonate sample varied considerably with respect to bisulfite content.
TABLE X

Mg-RESIDUE 2

Formula: $\text{C}_{40}\text{H}_{30}\text{O}_{13}(\text{CCH}_3)_3(\text{SO}_3\text{Mg})_3\text{Cl}_6$

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Found</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine</td>
<td>14.1%</td>
<td>16.4%</td>
</tr>
<tr>
<td>Methoxyl</td>
<td>6.19</td>
<td>7.15</td>
</tr>
<tr>
<td>Sulfur</td>
<td>6.34</td>
<td>7.39</td>
</tr>
<tr>
<td>Carbon</td>
<td>26.7</td>
<td>39.7</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>4.07</td>
<td>3.00</td>
</tr>
<tr>
<td>Ash</td>
<td>10.55</td>
<td>4.62</td>
</tr>
<tr>
<td>(as MgO)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The poor agreement here may be due to the fact that any soluble impurities in the original material would be present as contaminants in this residue from evaporation. However, it would seem that no methyl hypochlorite could be introduced into part of the sulfonated lignin, and this is perhaps significant. The assumption that even one methyl hypochlorite was introduced gave a unit weight of 1790, which appeared unreasonable in light of the smaller increase in unit weight for other residues.
## TABLE XI
COMPARISON OF OBSERVED AND CALCULATED RESULTS (MOISTURE-FREE BASIS)

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Hemlock Lignin</th>
<th>Chlorinated Hemlock Lig.</th>
<th>Ca Lignosulfonate</th>
<th>Ca-Res.*</th>
<th>Ca-Res.</th>
<th>Mg Lignosulfonate</th>
<th>Mg-Res.</th>
<th>Mg-Res.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chlorine</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Found</td>
<td>--</td>
<td>14.9%</td>
<td>--</td>
<td>13.0%</td>
<td>18.0%</td>
<td>--</td>
<td>18.1%</td>
<td>14.1%</td>
</tr>
<tr>
<td>Calc'd.</td>
<td>--</td>
<td>16.4</td>
<td>--</td>
<td>17.9</td>
<td>17.5</td>
<td>--</td>
<td>18.1</td>
<td>16.4</td>
</tr>
<tr>
<td><strong>Methoxyl</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Found</td>
<td>14.5%</td>
<td>16.1</td>
<td>11.1%</td>
<td>15.8</td>
<td>10.6</td>
<td>7.25%</td>
<td>14.1</td>
<td>6.19</td>
</tr>
<tr>
<td>Calc'd.</td>
<td>14.6</td>
<td>17.2</td>
<td>11.9</td>
<td>15.6</td>
<td>10.9</td>
<td>8.50</td>
<td>13.1</td>
<td>7.15</td>
</tr>
<tr>
<td><strong>Sulfur</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Found</td>
<td>--</td>
<td>--</td>
<td>6.64</td>
<td>2.87</td>
<td>6.25</td>
<td>7.54</td>
<td>3.34</td>
<td>6.34</td>
</tr>
<tr>
<td>Calc'd.</td>
<td>--</td>
<td>--</td>
<td>6.11</td>
<td>2.69</td>
<td>6.75</td>
<td>8.80</td>
<td>2.71</td>
<td>7.39</td>
</tr>
<tr>
<td><strong>Carbon</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Found</td>
<td>61.1</td>
<td>**</td>
<td>49.0</td>
<td>37.9</td>
<td>**</td>
<td>39.4</td>
<td>36.2</td>
<td>26.7</td>
</tr>
<tr>
<td>Calc'd.</td>
<td>62.2</td>
<td>51.1</td>
<td>50.5</td>
<td>46.4</td>
<td>38.0</td>
<td>47.2</td>
<td>45.7</td>
<td>39.7</td>
</tr>
<tr>
<td><strong>Hydrogen</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Found</td>
<td>5.64</td>
<td>**</td>
<td>5.02</td>
<td>4.15</td>
<td>3.94</td>
<td>**</td>
<td>5.16</td>
<td>3.96</td>
</tr>
<tr>
<td>Calc'd.</td>
<td>5.66</td>
<td>4.70</td>
<td>4.58</td>
<td>4.28</td>
<td>3.16</td>
<td>4.12</td>
<td>3.98</td>
<td>3.00</td>
</tr>
<tr>
<td><strong>Ash</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Found</td>
<td>0.59</td>
<td>0.50</td>
<td>10.00</td>
<td>0.59</td>
<td>16.1</td>
<td>8.63</td>
<td>1.36</td>
<td>10.55</td>
</tr>
<tr>
<td>Calc'd.</td>
<td>0</td>
<td>0</td>
<td>13.0</td>
<td>14.3</td>
<td>5.48</td>
<td>2.80</td>
<td>4.62</td>
<td></td>
</tr>
</tbody>
</table>

*Incomplete analysis
**Not determined
CALCULATIONS

General Outline of Calculations

1. Assuming four methoxyl groups per lignin unit (not necessarily a mole), a formula for the original hemlock lignin was derived from methoxyl and carbon-hydrogen data.

2. The effect of chlorination on the hemlock lignin was calculated to determine the number of methoxyl groups and chlorine atoms added, and also the amount of chlorine introduced by substitution.

3. Assuming that the hemlock lignin was not substantially altered during sulfonation (except for bisulfite addition), formulas for the calcium and magnesium lignosulfonates were calculated on the basis of the original hemlock lignin formula.

4. The effect of chlorination on the calcium and magnesium lignosulfonates was evaluated to determine the number of methoxyl groups introduced, also the amount of chlorine introduced by addition and by substitution. Calculations were carried out independently for each of the chlorinated residues except Ca-Residue 1. Time did not allow complete analysis of this residue, but the lower chlorine content and insolubility in methanol suggested that it consisted principally of partially chlorinated calcium lignosulfonate.
All unit weights and formula calculations were based upon methoxyl content, since this appeared to be the most reliable data obtained.

Sample calculation: Ca-Residue 2

Method for arriving at the formula postulated.

Analyses indicate a fairly high methoxyl and chlorine content; therefore the preliminary assumption is made that two methoxyl groups (and hence two chlorine atoms) have been added to the calcium lignosulfonate.

MeO content, ash-free basis = 15.9%
Unit weight = 186/0.159 = 1170
Chlorine = \((1170) \times (0.181) / 35.5 = 5.96 = 6\) atoms per unit
Sulfur = \((1170) \times (0.0283) / 32 = 1.05 = 1\) atom per unit
Carbon = \((1170) \times (0.381) / 12 = 37.1 = 37\) atoms per unit
Hydrogen = \((1170) \times (0.0396) / 1.008 = 46.3 = 46\) atoms per unit

This type of chlorination should not result in extensive demethylation or cleavage of the lignin molecule. Therefore the carbon and hydrogen values must be considerably in error.

Since the ash content is very low, it is logical to assume that the sulfur is present as \(-\text{SO}_3\text{H}\) rather than as \(-\text{SO}_3\text{Ca}\).

Formula on basis of original calcium lignosulfonate:

\[C_{40}H_{32}O_{13}(O\text{CH}_3)_4(\text{SO}_3\text{H})_2(\text{CH}_2\text{OCI})_2\text{Cl}_4\]
DISCUSSION OF RESULTS

Before the results indicated in the calculations can be accepted, their reliability must be considered. It will be noted that agreement of calculated and observed results is not more than fair, particularly in the case of carbon and hydrogen values. Perhaps these discrepancies can be clarified by a consideration of errors in the methods used. Briefly, the errors can be classified under the headings of materials and technique. Some of the more apparent of these errors are:

A. Materials

1. The starting materials were not all from the same wood sample. Also, the action of strong sulfuric acid may conceivably have altered the hemlock lignin considerably.

2. The lignosulfonates were evidently heterogeneous, even after dialysis. The calculated formulas seem to indicate that the sulfite process produced a material of varied composition.

3. The chlorinated residues were not purified extensively and some extraneous material may have been present, particularly in the case of those obtained by evaporation to dryness of the water filtrate.

B. Technique.

1. It is quite possible that chlorination was incomplete.

However, preliminary experiments on a Douglas fir sulfuric acid
lignin indicated that the rate of chlorination decreased rapidly after an hour:

<table>
<thead>
<tr>
<th>Time, hr.</th>
<th>Chlorine, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.1</td>
</tr>
<tr>
<td>3.5</td>
<td>16.8</td>
</tr>
</tbody>
</table>

Pederson and Benson (37) were able to increase the chlorine content only slightly by rechlorinating their product successively. The lignosulfonates appeared to chlorinate more readily than the sulfuric acid lignin.

2. The method of chlorine analysis was not a standard one, but gave good results when checked with a sample of amylene chlorohydrin. The chlorine content had been determined as 29 per cent by the standard micro-bomb method. By the method used in this work, a value of 28.4 per cent was obtained.

3. The carbon-hydrogen values are quite apparently in error. Insufficient sample was at hand to check determinations on the lignosulfonate residues. However, the results obtained on the original hemlock lignin are considered fairly reliable, and this value is the most essential one. It was observed that more consistent results could be obtained when the lead peroxide (necessary for absorption of sulfur and chlorine) was absent, even when this part of the furnace was maintained at a temperature well above 300°C.
Even after allowance for error is made, however, the calculations indicate that with one exception (Mg–Residue 2) it was possible to obtain methyl hypochlorite addition in all cases. Thus, the purpose of the investigation may be considered as accomplished, even though the data obtained were not accurate enough to formulate conclusively the structures of the materials studied.
CONCLUSION

From the results of analysis of the various lignin samples and residues, it would appear that commercial sulfonation does not completely saturate the ethylenic bonds in lignin. In reaching this conclusion, it is assumed that no desulfonation is produced by chlorination in methanol. The mechanism of lignin sulfonation is, therefore, postulated as follows: bisulfite addition occurs, probably at ethylenic and carbonyl bonds, until a product results which is sufficiently soluble to be washed out of the cellulose fibers. This condition may result before any of the ethylenic bonds have been saturated, but part of the lignin may be completely saturated with respect to bisulfite. Addition of sulfurous acid instead of bisulfite may occur.
BIBLIOGRAPHY


(2) Brauns, F.E. Native lignin. J. Am. Chem. Soc. 61: 2120 (1939)


(5) Ehrlich, E. Chemistry of pectin and its relation to the formation of incrustations in cellulose. Cellulosechem. 2: 161 (1931)


(15) Fuchs, W. Genuine lignin (1) acetylation of pine wood. Biochem. Z. 192: 165 (1928); C.A. 22: 2744 (1928)


(17) Högglund, E. Saccharification of wood. Ber. 56: 1866 (1923); C.A. 17: 2048 (1923)


(20) Harris, E.E., and Adkins, H. Reactions of lignin with hydrogen. Paper Trade J. 107: 56 (Feb. 15, 1938)


(22) Heuser, E., Roesch, H., and Gunkel, L. Formation of oxalic acid from sulfite cellulose waste liquors and from lignin. Cellulosechem. 2: 13-19 (1921)


(28) Klason, P. Chemical composition of deal (I) fir wood. 

(29) Klason, P. Chemical structure of pine-wood lignin. 


(36) Payen, A. Compt. rend. 7: 1052, 1125 (1838); 8: 51, 169 (1839); 9: 149 (1839); 10: 941 (1840). As quoted in article, Phillips, M. Chemistry of lignin. Chem. Rev. 14: 103-170 (1934)


