# EXPERIMENTS ON THE PULPING OF PERIODATE LIGNIN BY THE SULFITE PROCESS

A Thesis

by

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Submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements for the degree of Doctor of Philosophy

McGill University

Montreal, Canada

September 1951

# ACKNOWLEDGEMENTS

The author wishes to express his sincere thanks to Professor Clifford B. Purves under whose inspiring guidance this research was carried out.

Appreciation is also expressed to Dr. F. Yorston and other members of the Pulp and Paper Research Institute, Canada, for valuable assistance during this work.

Grateful acknowledgements are also made to the Allied Dye and Chemical Corporation of New York and Canadian Pulp and Paper Association for assistance in the form of a fellowship and Summer Grants.

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# GENERAL INTRODUCTION

The removal of the lignin portion of wood for the production of pulp, particularly for the manufacture of high grade paper and rayons has in the past century become of increasing technological interest. Although a considerable number of processes are known, probably the sulfite process has been the most investigated. The complexity of the structure of wood as a whole, and the lignin portion in particular has led to a large number of divergent views on the chemistry of this process. Of particular interest is the fact that thus far the lignin complex has never been separated from the holocellulose fraction entirely as a chemically unchanged product. The nearest approach is the development of periodate lignin, which stands almost alone as a preparation which can be pulped in similar manner as wood. The fact that this lignin is essentially free from carbohydrate material makes its use ideal in trying to unravel the reactions of lignin *in situ* without the complicating factors caused by either the physical or chemical properties of contaminants.

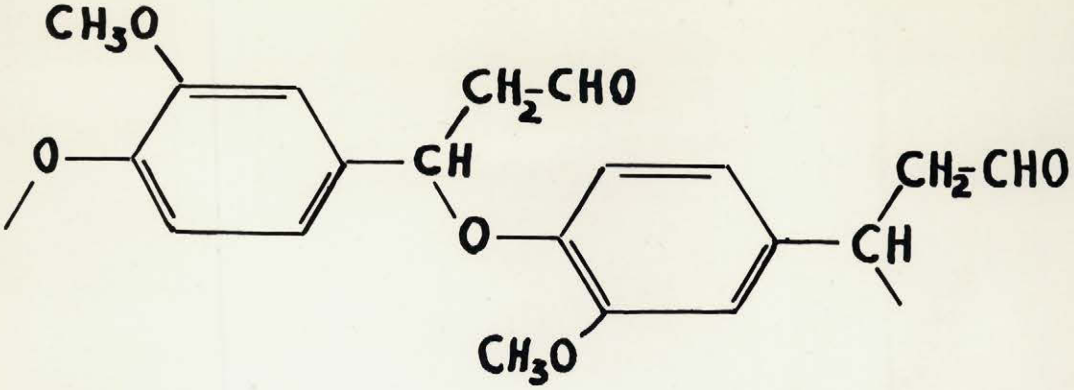
With this in mind, an investigation of the effect of alkali and acid treatments on periodate lignin has been carried out in an effort to assess their importance in the conditions of a technical sulfite cook. The "two-stage" theory offered by Hägglund as an explanation of commercial sulfite pulping has also been investigated.

# HISTORICAL INTRODUCTION

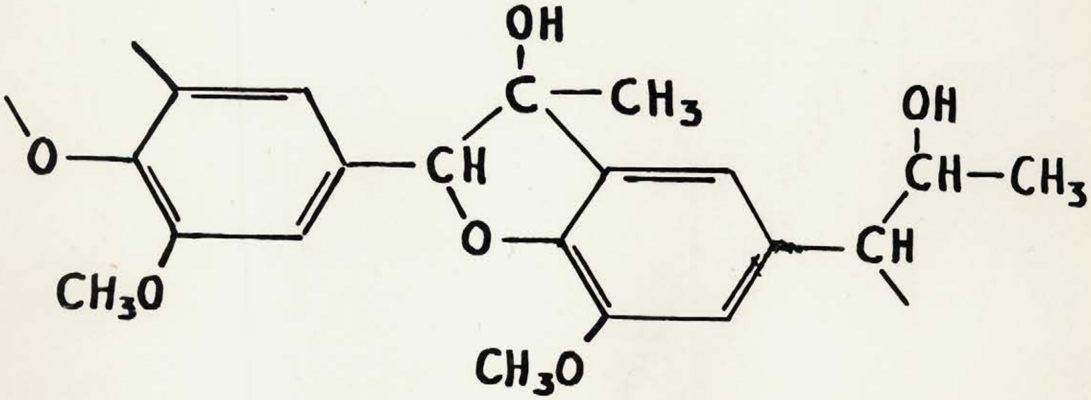
## General

The existence of several recent reviews by Phillips (1)(2), Freudenberg (3), Hibbert (4), Percival (5), Erdtman (6) and others, on the probable chemical structure of wood lignins makes it unnecessary to cover the same extensive ground in the present discussion. It is, however, generally agreed that lignin is a condensation product of unknown complexity based, at least for the most part, on oxygenated phenylpropane units. Structures I, II and III, in Plate I, which were put forward some years ago by Freudenberg (7), show the features generally attributed to the lignin molecule, although opinions still vary widely as to their accuracy in detail.

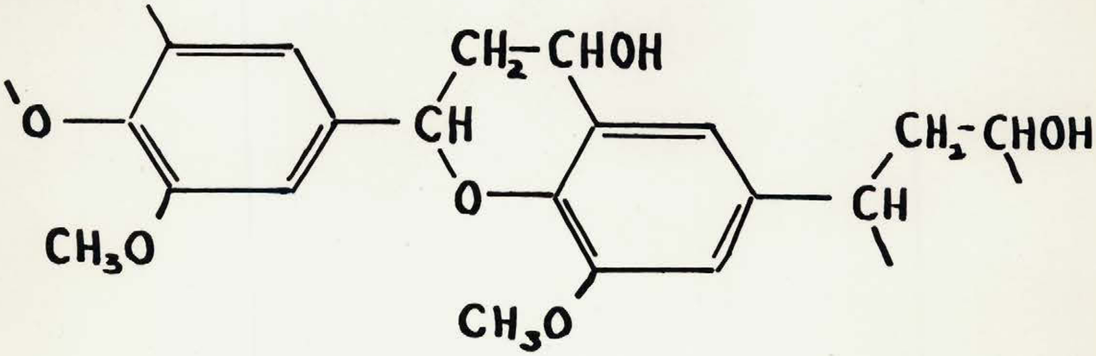
In the investigation of the behaviour and properties of lignin or non-carbohydrate portion of solvent-extracted plant tissue, workers have been forced to face the unpleasant realization that, thus far, no one has succeeded in truly separating lignin in a form that is totally comparable to the lignin *in situ*. Phillips (1) reviews a large number of methods of separation which involve the selective solution and extraction either of the lignin or the non-lignin portion. The methods of the first group, which leave most of the carbohydrates as an insoluble residue, include extractions at up to 120°C. with alcohols, thioalcohols or phenols containing small amounts of hydrogen chloride or other mineral acids; extractions with acetic acid or formic acid at similar temperatures (8)(9); extractions with technical pulping agents such as aqueous sodium hydroxide at 170°C. and aqueous



I



II



III

Plate I

sodium sulfite at 135°C. In all these cases it has been possible to show that the lignin has undergone chemical change: thus all contain structural elements derived from the extracting medium, or in the case of alkali lignins, carboxylic acid groups that were not present originally. Yields of the alcohol lignins are usually less than 50 per cent, and a repetition of extraction leads to no great improvement. As a group the extracted lignins differ sharply from lignin in situ by being more soluble in water or simple organic liquids, and by being insoluble when heated under commercial conditions in sodium or calcium bisulfite solution. The exception to this statement is the lignin obtained in 10% yield by deacetylating a product derived from wood acetylated in the presence of sulfuric acid as catalyst. This work by Suida and Titsch (10) was extended by Steeves and Hibbert (11).

In like manner, the dissolution of the carbohydrate portion of wood by cold 72% sulfuric or 43% hydrochloric acid, that is, by the Klason or Willstäter reagents, gives quantitative yields of lignin as dark, structureless, amorphous resins insoluble in all liquids including hot bisulfite liquor. The product obtained with aqueous hydrofluoric acid appears to behave similarly, although in this case the morphological structure of the wood may be retained (12). Another lignin in the same class, although apparently of greater chemical reactivity, was obtained by Freudenberg and co-workers (13)(14), who put wood meal through a cycle which consisted of alternately leaching out carbohydrates with cupraammonium and boiling the lignin enriched residue with dilute mineral acid.

The noticeable differences in chemical composition, colour, solubility, or ability to pulp normally in a bisulfite cook, that distinguish the above isolated lignins from lignin in wood, led to a research by Read (15) that is of particular interest to the writer. Read's review of the literature notes that the very drastic oxidation has thrown but little light on the structure of lignin. Early oxidations by König (16), Dorée and Hall (17), and Heuser and Samuelson (18) with 2% potassium permanganate, 32% nitric acid and 3% potassium permanganate solutions of various lignosulfonic acids yielded oxalic acids, although Dorée and Hall also obtained an unknown material believed to be hydro aromatic in nature and of the empirical formula $C_{20}H_{24}O_{12}(COOH)_6(NO_2)_2$. Fischer and co-workers (19) used air to oxidize a Willstater lignin suspended in caustic soda under pressure at 200°C. for four hours, and found small amounts of benzene hexacarboxylic acid or mellitic acid, benzene pentacarboxylic acid and a benzene tetracarboxylic acid and a benzene tricarboxylic acid among the products. The total amounts of these aromatic acids was 3.2% of the original lignin (20). On oxidation of wood under similar conditions, 0.83% of benzene polycarboxylic acids were obtained (21) - presumably from the lignin, because cellulose itself yielded negative results (22). In an oxidation process employing 5N nitric acid, Horn (23) was able to show the presence of mellitic acid in the crude product from the oxidation of a Willstäter lignin.

In an effort to determine whether cellulose or lignin in plant tissue was the precursor of coal, Bone and co-workers (24) oxidized two Willstäter lignins, peat and various coals with excess potassium permanganate in boiling potassium hydroxide. The lignins yielded up to 16 per cent of crude benzene polycarboxylic acids, whereas cellulose gave only oxalic and acetic acids and carbon dioxide. Confirmation of the failure of cellulose to yield benzene polycarboxylic acids by this method was provided by Randall, Benger and Groocock (25). These authors also oxidized about sixty aliphatic acids, aromatic hydrocarbons, aromatic substances containing carbonyl groups and aromatic acids and noted that no product was ever found that was more complex than the starting materials. In addition, substances in which one or more hydrogen atoms in the aromatic ring were substituted with hydroxyl or methoxyl groups were always completely oxidized to oxalic acid and carbon dioxide. Hence a material such as coniferyl aldehyde and similarly supposed lignin building units was always completely degraded. The occurrence of benzene polycarboxylic acids always corresponded to the presence in the original substance of benzene rings substituted several times with carbon but never with oxygen atoms. These rings were independently shown in several coal and cokes to be part of complex condensed ring systems of an obscure type (26)(27)(28). However, the presence of a carbonyl or ether link between two aromatic nucleii stabilized the molecule, as shown by the stability of diphenyl ether, diphenylene oxide, benzophenone, benzil, 1-benzonaphthone and similar substances to alkaline permanganate. If the carbon atom adjacent to the ring was substituted with oxygen, then the oxidation tended to produce an alpha keto-acid such as phenylglyoxylic from mandelic acid (29). The more complicated acids were readily reduced to benzene polycarboxylic acids by boiling concentrated nitric acid.

With the above background, the isolation of various benzene polycarboxylic acids from lignins made it very probable that they contained some benzene units substituted exclusively by carbon, and therefore not of the coniferyl aldehyde type. In each of the oxidations cited, however, the lignin had first been isolated by the drastic action of mineral acid or the oxidation had involved the use of strong nitric acid or of caustic soda under pressure. It was impossible to decide, therefore, whether the progenitors of the polycarboxylic acids were preformed in the wood lignin, or were artifacts produced during the isolation or oxidation. To resolve this doubt, Reid (15) carried out comparable oxidations of spruce wood meal, of various lignins prepared therefrom, and of alkali lignin from poplar wood. Table I reproduces the crude yields of benzene polycarboxylic acids which he recovered.

Of the above mentioned materials, lignin in situ yielded only very small amounts of benzene polycarboxylic acids. It followed that the precursors of these acids were not only practically absent from lignin in its original condition, but were formed as artifacts by the conditions of the oxidation. The yields from Willstäter, Klason and alkali lignins, which showed a general increase in that order, could therefore be taken to indicate an increasing amount of chemical change in the lignin structure caused by these methods of preparation. It was claimed that this behaviour might possibly point to the presence of a structure in the original lignin similar to that of the lignans, which are dimers of phenylpropane derivatives, linked through the beta carbon atoms of the side chains. The close structural relationships between the monomers of lignans and those isolated from lignin were pointed out by Phillips (30). Spath and co-workers (31) showed that podophyllotoxin, a lignan, when heated with fuming hydrochloric acid for twelve hours at 100-110°C., produced a dark brown substance which gave rise to benzene-1,2,4,5-tetracarboxylic acid on oxidation with alkaline permanganate (Plate II, Structure IV). If this lignan was dehydrogenated at 230-240°C. under reduced pressure with palladium catalyst, the product yielded benzene pentacarboxylic acid on oxidation (32). The isolation of these acids indicated that a structural change had occurred, which resulted in

## TABLE I

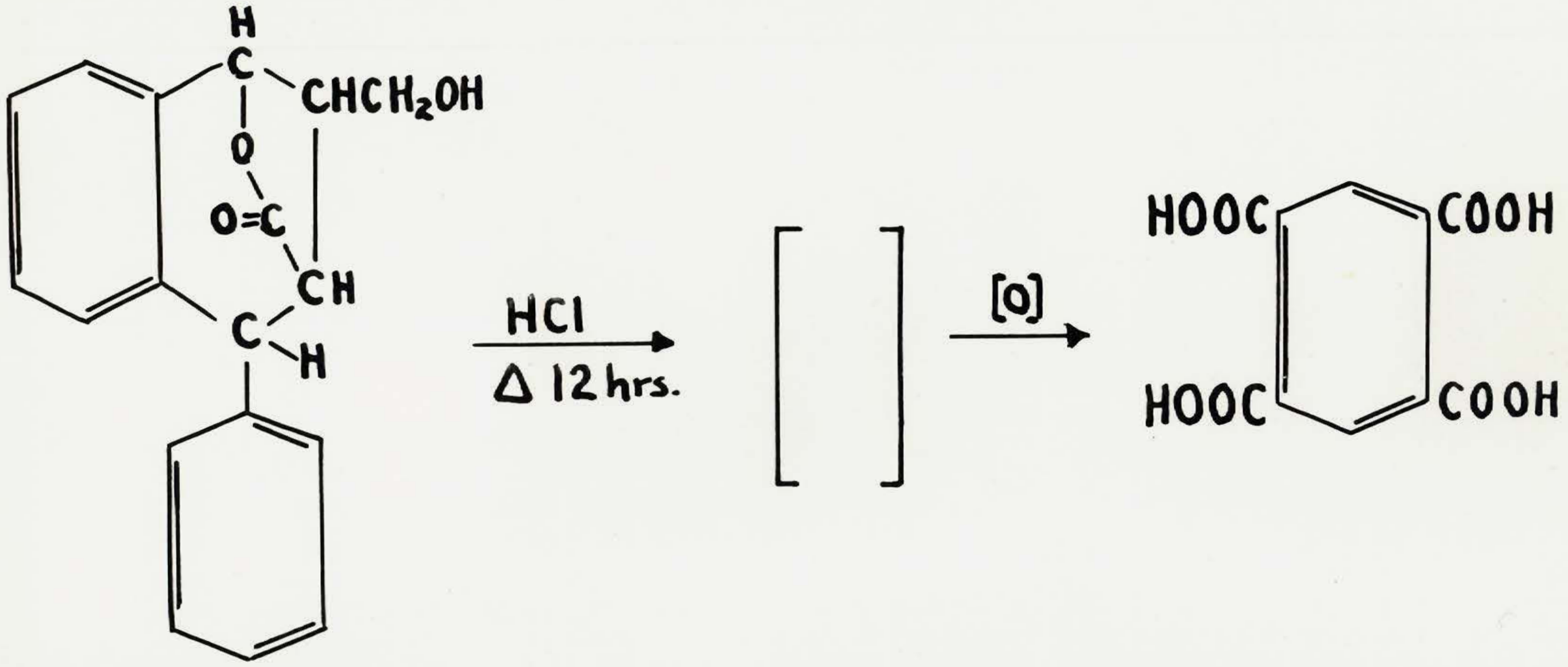
### Crude Yields of Benzene Polycarboxylic Acids[a]

| Spruce lignins | Crude 1,2,4,5 Tetra % | Crude Penta % | Crude Hexa % | Total % |
|---|---|---|---|---|
| Wood meal[b] | | 0.2 (approx.) | | 0.2 (approx.) |
| Periodate | 0.20 | 0.77 | | 0.97 |
| Willstater | 0.25 | 0.99 | | 1.24 |
| Klason | 0.45 | 2.52 | | 2.97 |
| **Poplar lignin** | | | | |
| Alkali[c] | 0.65 | 3.94 | 0.22 | 4.81 |

(a) After exhaustive oxidation with hot alkaline potassium permangante.

(b) Calculated on the basis of 27.2% Klason lignin in the spruce wood meal as the quantitative estimation of lignin *in situ*.

(c) Commercial preparation from woods not previously extracted with solvents.



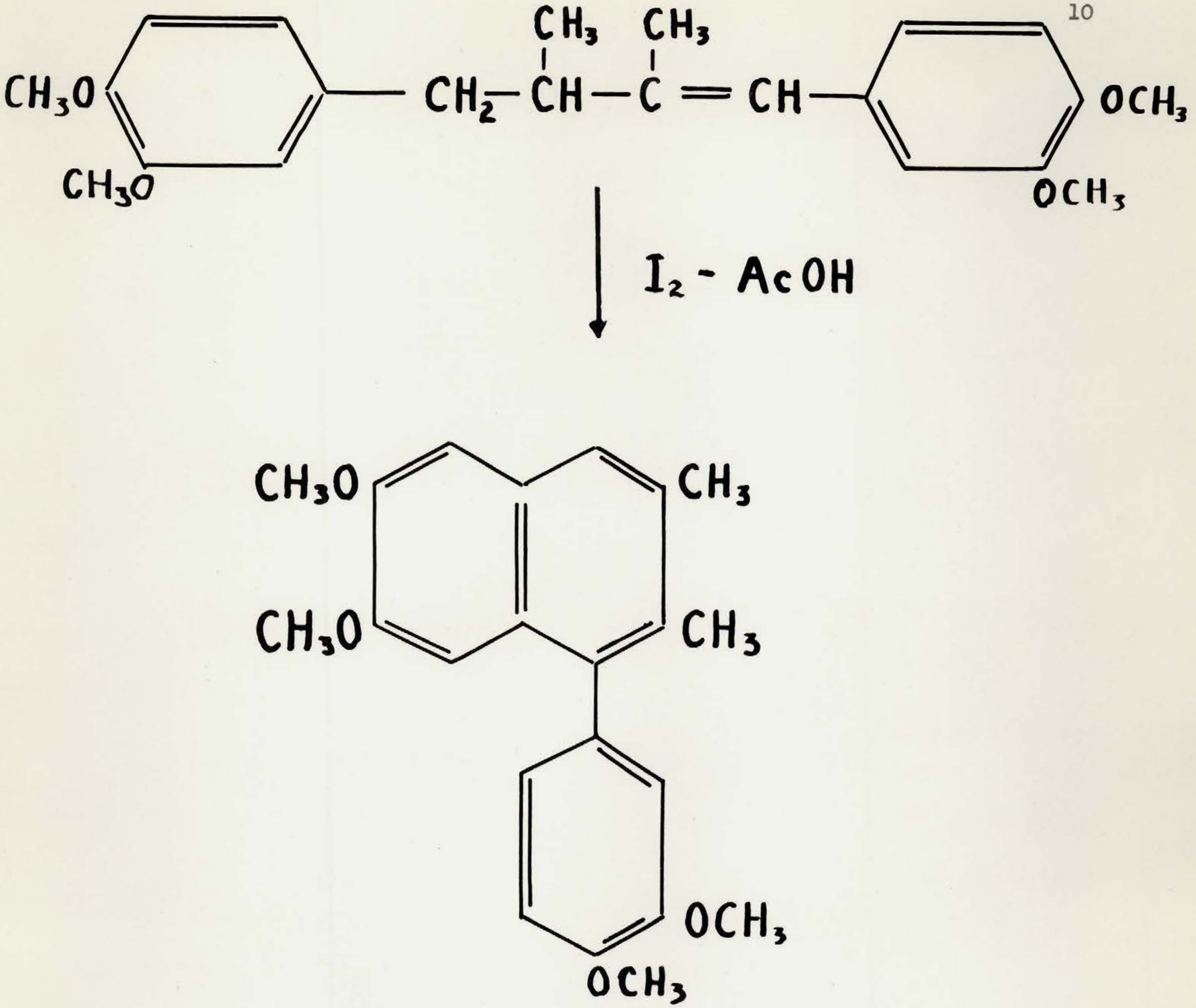
IV

Plate II

the formation of an aromatic ring substituted only by carbon. Haworth and co-workers (33) in their investigations of various lignans, showed that podophyllotoxin and conidendrin, obtained from sulfite waste liquor, were also aromatized to 1-phenylnaphthaline derivatives by the action of hot methanol containing hydrogen chloride. Even simple lignans such as quaiasetic acid were very readily cyclized in a similar way when treated with mild oxidizing agents such as iodine or lead tetraacetate (Plate III, Structure V).

Structural changes between lignin in situ and the corresponding Willstäter, ethanol and lignosulfonic acid products were also revealed by Richtzenhain (34) who oxidized fully methylated samples with boiling potassium permanganate used near neutrality, instead of in strong alkali. This milder reagent, which failed to oxidize all of the phenolic ether units, produced up to 1.3% of 4,5-dimethoxy-o-phthalic acid from lignin in wood. The conditions used to isolate the lignin had presumably caused a nuclear condensation of another carbon chain to occur in the sixth position of an oxygenated phenylpropane lignin building unit.

The above researches made it most probable that a solution of the problem of isolating lignin without change required new methods that avoided high temperatures and employed neutral chemical reagents. The methods which follow this approach include Brauns' (35) extraction of "native lignin". Brauns used 96% ethanol at room temperature and isolated about 3% of the lignin contained in spruce wood. The failure to extract the remaining 97% of the lignin suggested that his product might very well not be identical to lignin in situ. This particular objection was somewhat strengthened by the recent work of Schubert and Nord (36) who showed that


CH₃O
CH₃O
CH₃
CH₃
CH₂—CH—C = CH
OCH₃
OCH₃
I₂ - AcOH
CH₃O
CH₃O
CH₃
CH₃
OCH₃
OCH₃

V

Plate III

recovery of native lignin could be increased to 22.7% if the wood, after a pre-extraction of "native lignin", was extensively rotted by cellulose consuming fungi as Poria vaillantii and Lenzites sepiaria and re-extracted with alcohol. The suspicion that "native lignin" was a biochemical artifact was heightened not only by its solubility in ethanol, but by the ease with which it dissolved in a bisulfite cook, and by the fact that Harris (37) failed to recover any "native lignin" at all from freshly cut wood when he extracted freshly cut aspen and maple wood meals with ethanol. These same wood meals, when allowed to air dry, gave the usual yields upon alcohol extraction. In an investigation of northern pine, Wald (38) was also unable to obtain "native lignin" from freshly cut wood, even after prolonged extraction. Ploetz (39), by selective enzymatic degradation of the holocellulose fraction of wood, was able to obtain a residue rich in lignin, but his incidental use of cupriethylenediamine to remove the more resistant portions of holocellulose added the risk of chemical to biochemical changes in the lignin.

Another method which avoided the use of high temperatures and acidic or basic media resulted in the periodate lignin developed by Wald, Ritchie and Purves (40)(41). This method originated in the discovery by Jackson and Hudson (42) that cellulose, when oxidized with cold periodic acid, became soluble in hot water owing to the formation of a readily decomposed periodate oxycellulose. On the other hand, Freudenberg et al (43) stated that lignin was apparently unchanged by periodate with the exception of an observed decrease of 16% to 10% of methoxyl content in the lignin. Pennington and Ritter (44) employed periodate to remove traces of polysaccharides from lignin sulfonic acids, and were able to show that a small methoxyl containing fragment was cleaved off the sulfonic acid during the oxidation.

Ritchie and Purves (41) carried out the oxidation of wood meal at 20°C. for twenty-four hours with periodic acid buffered to pH 4.1, whereupon the oxidized meal was thoroughly washed to remove excess of the oxidant prior to boiling under reflux for three hours with 8 liters of distilled water. The residue was oxidized as before, the oxidation-extraction cycle being continued until analysis of the product showed a high (90% or more) Klason lignin content, and a negligible holocellulose content. This procedure recovered the periodate lignin from spruce wood in up to 97% yield as a light brown powder retaining the morphological structure of the wood.

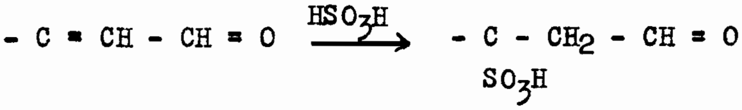
Periodate lignin also resembled lignin in wood by being insoluble in all chemically inert liquids tried, although it swelled somewhat in pyridine and 1,4-dioxane (45). When treated with ethanol containing hydrogen chloride, it yielded water-soluble and methanol-soluble fractions, and also a dark insoluble resin in roughly the same proportions as found by Hibbert and collaborators (46) for the ethanolysis of spruce wood. High pressure hydrogenation yielded 4-n-propylcyclohexanol-1, 4-n-propylcyclohexandiol-1,2, methanol, high boiling oils and a non-distillable resin in yields closely approximating those obtained by Harris (47) from the hydrogenation of spruce methanol lignin. As was expected, oxidation of periodate lignin with alkaline nitrobenzene under pressure yielded significant amounts of vanillin. Nevertheless, periodate lignin was not identical with lignin _in situ_, because its methoxyl content of 10 to 12% was substantially less than the value calculated by Wald, Ritchie and Purves (40). The inference that periodate lignin was slightly oxidized during isolation was supported by the observation that it was slowly oxidized by air when kept in boiling tetralin or caustic soda, and yielded traces of vanillin. Reference to Table I also shows that periodate lignin on drastic oxidation produced appreciable yields of benzene tetra and penta carboxylic acids, although less than those obtained from other isolated lignins. Periodate lignin had presumably not entirely escaped chemical condensation during its isolation.

The marked superiority of periodate lignin over preparations isolated by acids, alkalis or organic liquids was shown by its ability to dissolve in a sodium bisulfite cook, at a rate parallel to that observed by Corey, Calhoun and Maass (48) for the similar pulping of spruce wood chips. A systematic discrepancy in the absolute rate, however, was tentatively ascribed to the temperature lag on heating the cook. These results led Ritchie and Purves to claim that periodate lignin fulfilled to a great extent the need for an isolated lignin reasonably free from the suspicion of having suffered extensive resinification or severe chemical change during isolation, and comparable to lignin *in situ*. In particular, periodate lignin offered a promising new approach to fundamental investigations of the sulfite process without the complicating side effects of the non-lignin materials in plant tissue.

## Chemistry of the Sulfite Cooking Process

The fact that a solution of sulfurous acid containing calcium bisulfite will delignify wood and produce a satisfactory pulp was first discovered by Tilghmann (49) in 1886, and his patents form the basis of all the modifications of the sulfite process now in use. Essentially, the commercial process consists of transforming the water-insoluble lignin components of wood to water-soluble lignosulfonic acids which may be removed by washing. The material remaining insoluble is in the main a cellulose pulp. The complexity of wood, and indeed the structural complexity of lignin make it extremely difficult to state with any degree of accuracy what is occurring during the chemical pulping. Factors such as chip size of the wood, rates of diffusion, species, source and age of the tree as well as composition of the liquor at the locus of reaction only add to the difficulties mentioned. However, in spite of these obstacles, a number of theories on sulfonation have been put forward. Yorston (50), on reviewing this subject, pointed out that no true solvent is known for lignin, that all chemical processes appear to involve transformation of the lignin into soluble derivatives, and that the essential step in cooking was the introduction of lyophile groups into the lignin nucleus. Thus, alkali lignin, as shown by Brauns and Grimes (51), contains more hydroxyl groups than lignin *in situ*, a circumstance which would promote solubility of the material in caustic solutions. The presence in the lignin nucleus of additional groups from the organic liquids employed for extraction has been already noted (52) (53). As the name implies, lignosulfonic acids contain the $SO_3H$ group (54), which is known to render soluble in water numerous compounds into which it has been introduced.

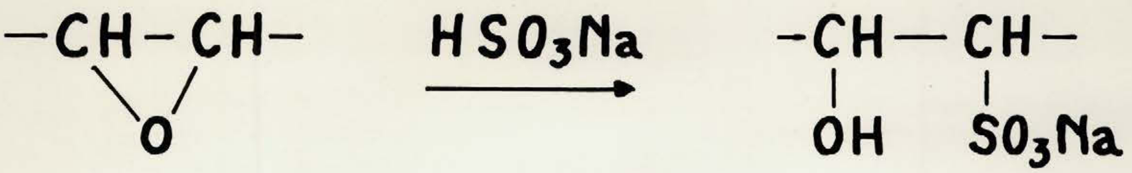
Among the early explanations of the sulfonation reaction was that submitted by Klason (55) who claimed the presence of an ethylene linkage in an acrolein group as the point of attack of the sulfurous acid liquor



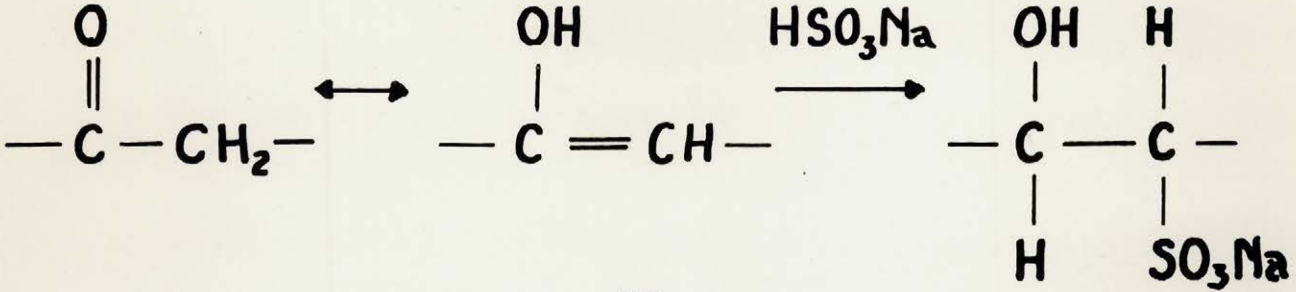
$$-\mathrm{C}=\mathrm{CH}-\mathrm{CH}=\mathrm{O}\xrightarrow{\mathrm{HSO_3H}}-\underset{\mathrm{SO_3H}}{\mathrm{C}}-\mathrm{CH_2}-\mathrm{CH}=\mathrm{O}$$

However, Klason's evidence is fragmentary and has been adversely criticized by certain investigators (56) on the fact that lignin does not behave as an unsaturated compound to hydrobromic acid (57) or lead tetraacetate (58). Hägglund and Carlsson (59) observed the formation of one hydroxyl group for every sulfonic acid group introduced into the lignin nucleus. They concluded that the reaction involves cleavage of an oxygen linkage between two carbon atoms (Plate IV, Structure VI) or addition to a keto-methylene group in the enolic form (Plate IV, Structure VII). Another explanation was put forward by Fuchs and collaborators (60) on the basis of Bucherer's (61) observation that resorcinol could be sulfonated with bisulfite solution (Plate IV, Structure VIII). However, the resulting formation of weakly bound bisulfite groups, which are due to addition of the sulfurous acid to carbonyl groups and which are easily detected by titration with standard iodine solution, and also the strongly bound sulfonic acid groups, formed by addition to the ethylenic bond does not agree in ratio with those observed in lignosulfonic acids (62). The universal failure to isolate any aromatic sulfonic acid by the oxidation of lignosulfonic acids has led to the conviction that the latter carry the substituent in the aliphatic side chain, and not in the aromatic nucleus of the phenylpropane building unit.

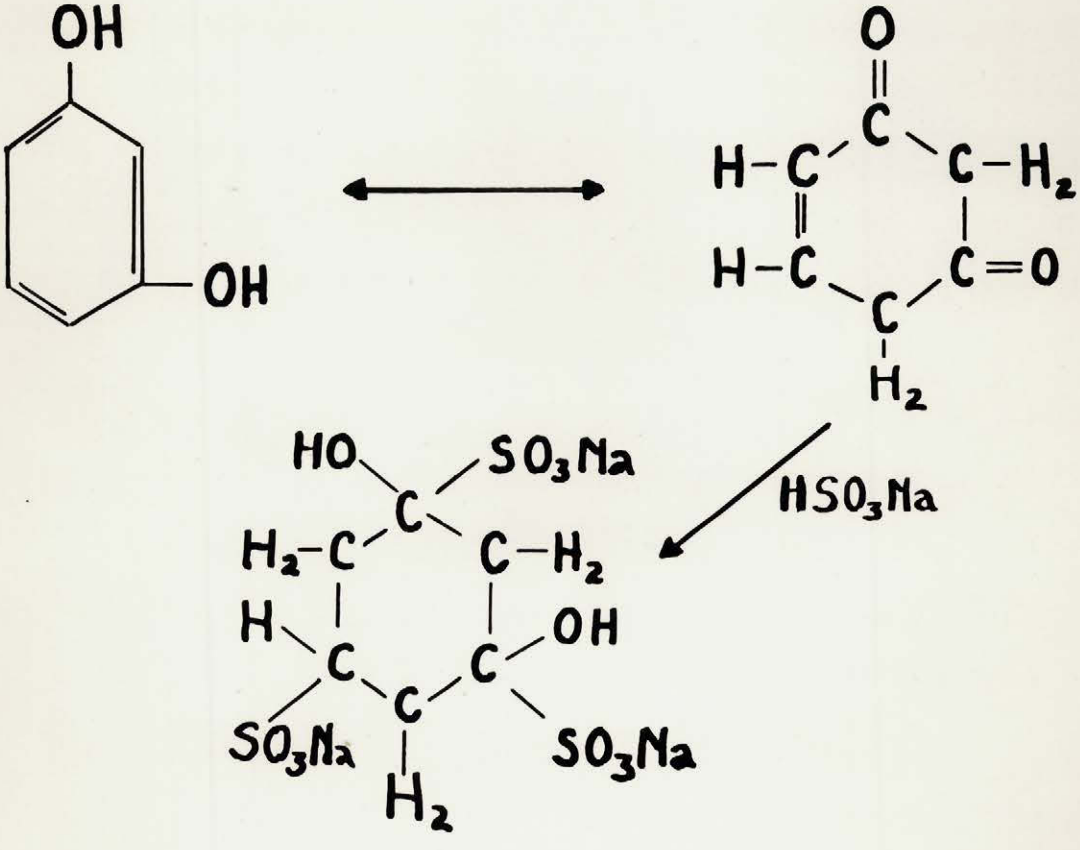
Freudenberg (58), in his investigations of lignin, proposed several explanations for the mechanism of sulfonation. To overcome the fact that lignin does not behave as an unsaturated compound, he claimed that a dehydration of a hydroxy-methylene system occurred, resulting in the formation of an ethylene group which was subsequently attacked by sulfurous acid. However, since this reaction does not account for the formation of an extra hydroxyl group as found by Hägglund (59), the proposal was abandoned. More recently, Freudenberg (63) postulated a mechanism, using his linear



VI



VII



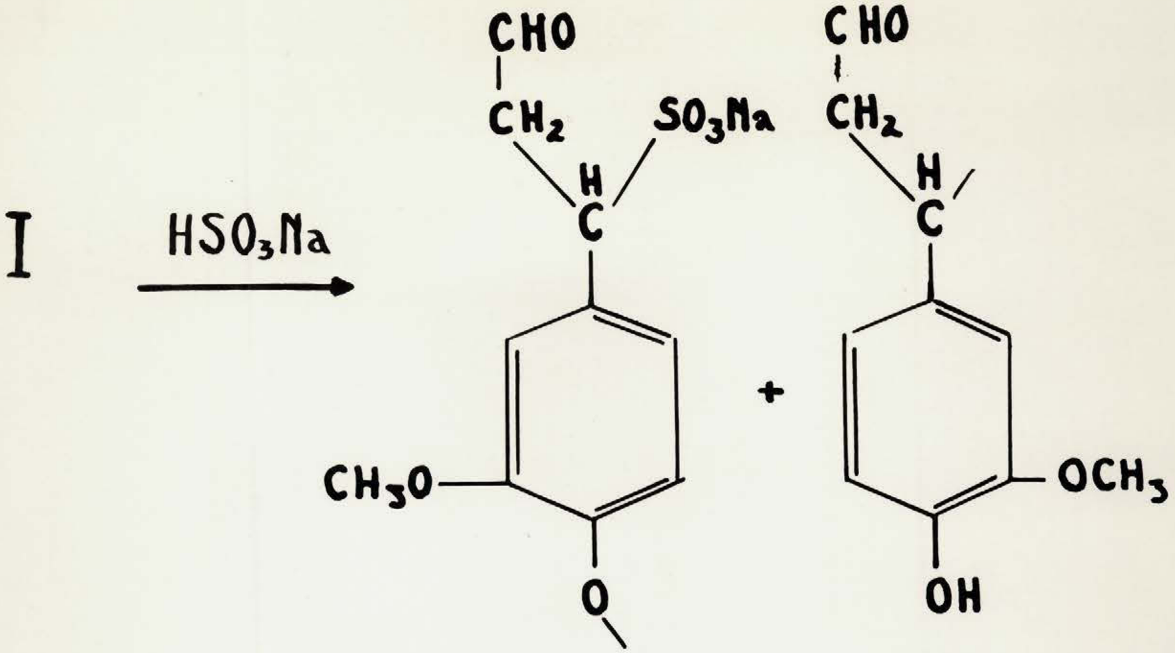
VIII

Plate IV

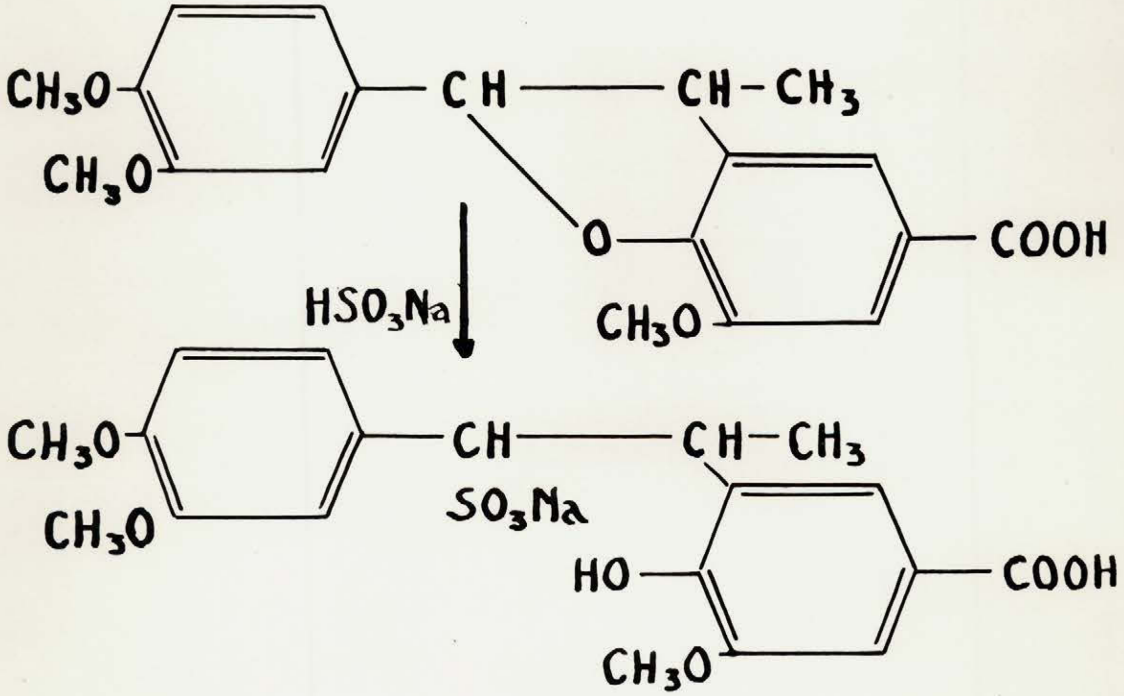
formula (Plate I, Structure I) for the structure of lignin (Plate V, Structure IX). This mechanism involves the production of a new phenolic group by sulfonation. Indirect evidence for this view is found in the behaviour of Erdtman's acid which is supposed to be structurally analogous to lignin, as Plate V, Structure X shows. The sulfonation of this acid results in the formation of a phenolic hydroxyl group (7).

Brauns and Brown (64) considered that a free hydroxyl group played a considerable part in sulfite pulping. This conclusion was based on the behaviour of methylated wood, which could not be delignified in a subsequent sulfite cook, although the wood did show an uptake of sulfur. Similar results were also obtained by Hägglund and Holmberg (65). Tomlinson and Hibbert (66) suggested that the sulfonic acid was introduced in the lignin molecule at a position alpha to the aromatic nucleus, since drastic treatment with alkali yielded substantial amounts of vanillin. Lignosulfonic acids, in contrast to lignin, do not require added oxidant to vanillin with alkali under pressure (67).

In the investigations of the nature of reactive groups in lignin responsible for its sulfonation, a number of workers employed model substances in place of lignin or lignosulfonic acids. For example, Wacek and Kratzl (68) synthesized a number of derivatives based on phenylpropane which they sulfonated at 100°C. with sodium bisulfite. According to these authors, substances such as 1-phenyl,1-hydroxypropane (Plate VI, Structure XI) yielded 25% of the corresponding sulfonic acid, while material based on an ethylenic group alpha to the aromatic ring, as in cinnamic aldehyde (Plate VI, Structure XII), reacted quantitatively. From results obtained on a series of fifteen compounds, it was claimed that the sulfonic acid group


I
HSO₃Na
CHO
CH₂
SO₃Na
H
C
CH₃O
O
+
CHO
CH₂
H
C
OCH₃
OH

IX


CH₃O
CH₃O
CH
CH–CH₃
O
COOH
CH₃O
HSO₃Na
CH₃O
CH₃O
CH
CH–CH₃
SO₃Na
HO
COOH
CH₃O

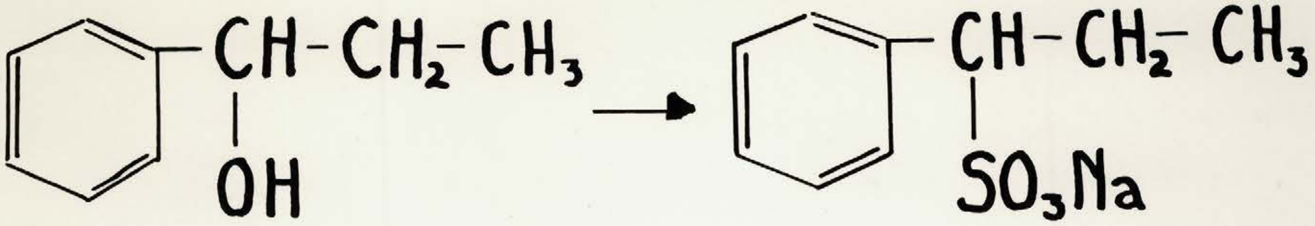
X

Plate V

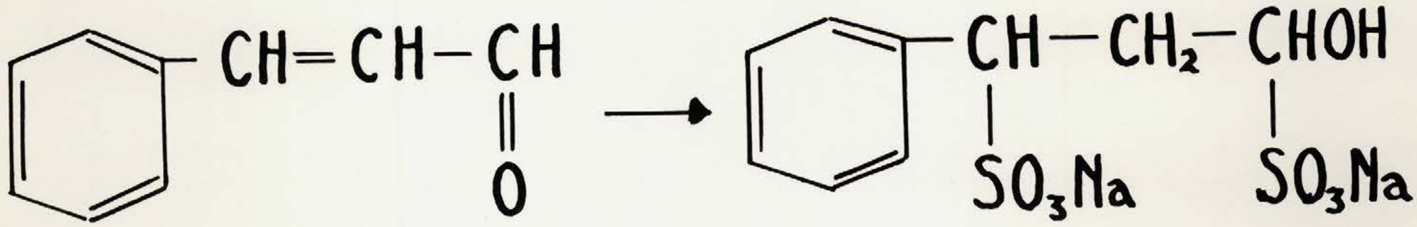
was always introduced most easily at the alpha position by either addition to an unsaturated carbon linkage, or replacement of a hydroxyl group. In addition, the presence of a carbonyl group in the beta or gamma positions of the aliphatic side chain hindered substitution of the hydroxyl group in the alpha position (phenylacetylcarbinol or 1-phenyl,1-hydroxy,2-propanone, Plate VI, Structure XIII), but accelerated addition to the ethylenic group. From a study on the alkaline oxidation of a number of these model compounds, Kratzl (69) postulated a theory of sulfonation which explained the yield of acetaldehyde and vanillin obtained upon alkaline oxidation of the sulfonated lignin (Plate VII, Structure XIV).

Erdtman and Leopold (70), working with a series of polyethers of alpha hydroxyacetoquaiacone, were able to sulfonate these materials with sulfurous acid containing varying amounts of caustic soda, and found that the production of sulfonic acids was dependent on the hydrogen ion concentration of the sulfite liquor. Lindgren (71), using a series of benzyl alcohols as model substances, found that 3,4-dimethoxyphenylethyl alcohol and veratryl alcohol could both be sulfonated under acidic conditions to almost quantitative yields of the corresponding alpha sulfonic acid, but reacted more slowly when in alkaline bisulfite liquor. Behaviour of these model substances with phenols in sulfurous acid paralleled that of lignin in failure to form soluble derivatives. In a later study (72), using diveratryl ether, a similar dependency of sulfonation on the hydrogen ion concentration of the liquor was noted. This ether could be hydrolysed under acidic conditions only.

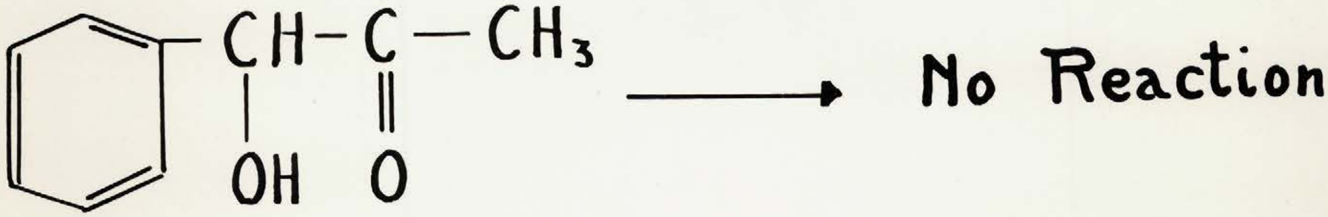
Hibbert and Sankey (73) carried out a kinetic study of the products of reaction of sulfurous acid with a series of simple compounds with



XI

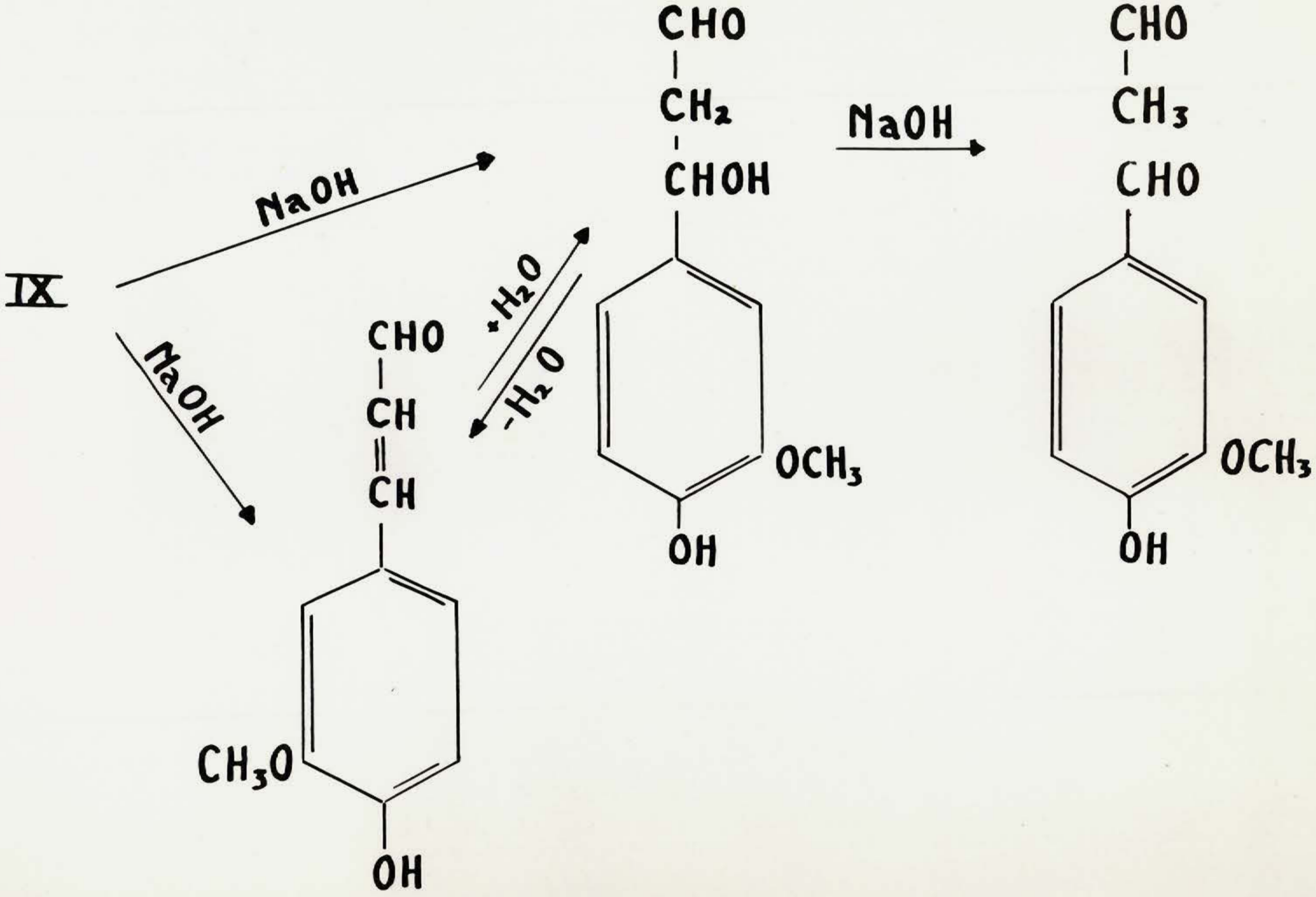


XII



XIII

Plate VI

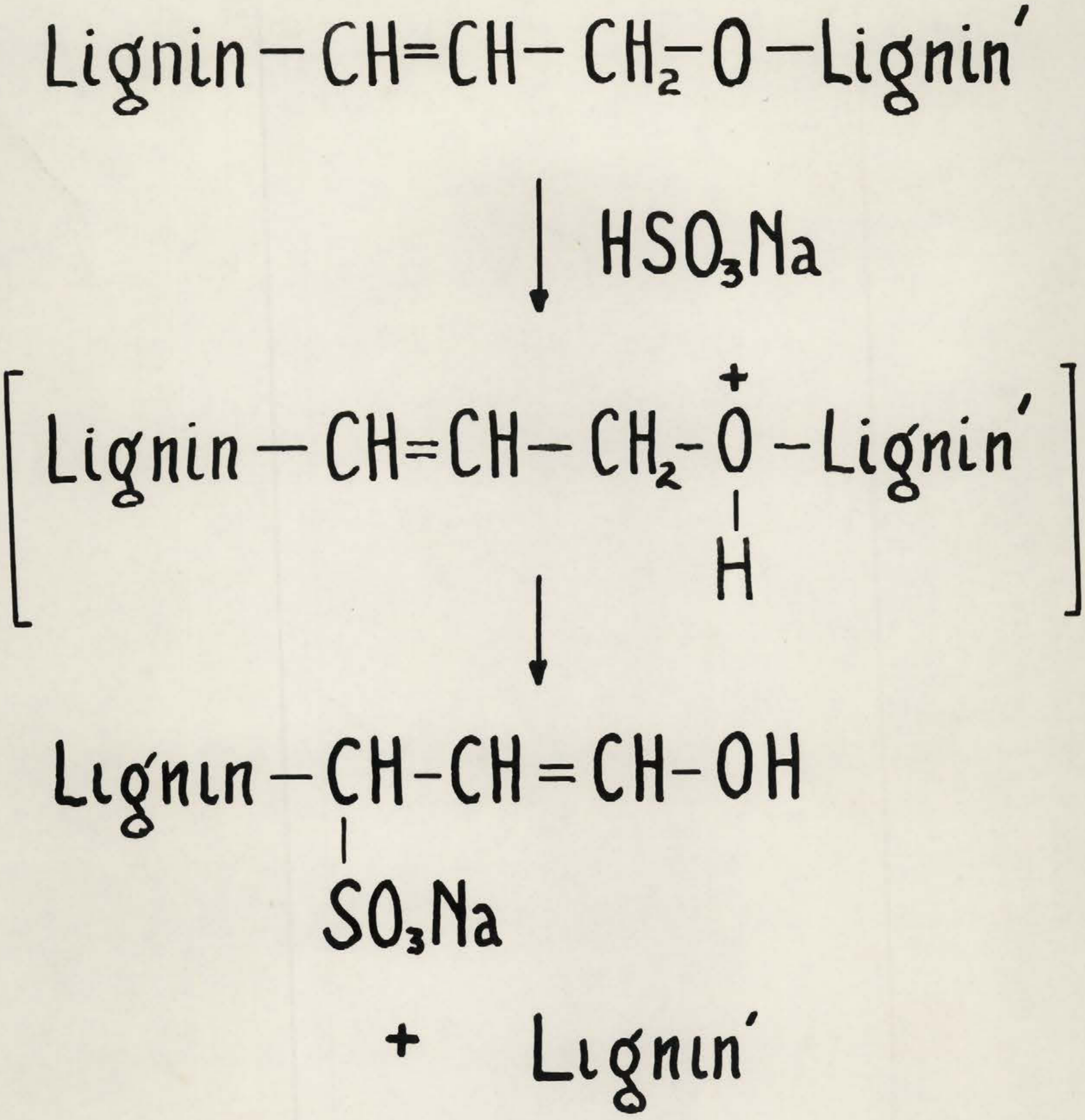


XIV

Plate VII

groupings related to lignin and lingosulfonic acids. They found that only cinnamic aldehyde, which had an ethylene group conjugated with a carbonyl group, resulted in a sulfonic acid possessing a temperature-conductivity curve similar to lignosulfonic acids. From their results, these workers postulated a sulfonation theory in which the sulfurous acid added 1,4 to either an acrolein group or an oxonium intermediate formed the opening of an oxygen ring in the lignin (Plate VIII, Structure XV).

More recently, a theory of sulfite pulping involving two stages has been put forward by Hägglund and has been widely accepted. In early work he was able to show that a solid, insoluble lignosulfonic acid was first formed during sulfonation (74). A later study (75) revealed that a wood meal cooked in sulfite liquor under mild conditions, which brought about only slight delignification, resulted in a semi-pulp containing only a few percent sulfur on the basis of the lignin content. A sodium bisulfite solution containing no excess of sulfurous acid was frequently used as the cooking liquor. Acid washing of the residual pulp to remove the sodium base left a product which readily underwent further delignification on merely heating in water at 80°C. The semi-pulp, whether acid washed or not, could be cooked down to a low lignin content in acid buffers containing no sulfurous acid, at a rate which was a function of the hydrogen ion and also the salt concentrations of the buffer. On the basis of these results, Hägglund concluded that, in the first stage, the lignin is sulfonated, but remains in the solid state, and in the second stage the sulfonated lignin is dissolved. He considered the second stage to be controlled by the hydrogen ion concentration of the cooking liquor, and regarded the reaction taking place as an acid hydrolysis. Kullgren (76), who investigated the hydrolysis



$$\text{Lignin}-CH=CH-CH_2-O-\text{Lignin}'$$

$$\Big\downarrow\ HSO_3Na$$

$$\left[\text{Lignin}-CH=CH-CH_2-\overset{+}{\underset{\substack{|\\H}}{O}}-\text{Lignin}'\right]$$

$$\Big\downarrow$$

$$\text{Lignin}-\underset{\substack{|\\SO_3Na}}{CH}-CH=CH-OH$$

$$+\ \text{Lignin}'$$

XV

Plate VIII

in both aqueous and alcoholic media, found that the lignosulfonic acids so formed contained groups derived from the solvents employed. He concluded from these observations that the solubilization was due to hydrolytic fission of linkages connecting neighbouring lignin molecules or lignin and carbohydrate molecules. Strangeland (77) studied the rates of pulping in sulfite liquors, and decided that the sulfonation reaction is so rapid in comparison with the acid hydrolysis that the latter acts as the rate-controlling factor in delignification.

The Hägglund theory has also been investigated by Yorston and Green (78) in an effort to determine what degree of cooking was necessary to result in a semi-pulp that could be delignified by subsequent acid hydrolysis, and also the hydrogen ion concentration necessary for hydrolysis. Excellent agreement with Hägglund's theory was obtained by cooking a pulp sample in bisulfite liquor for 1.5 hours at 130°C., followed by a cook in buffer solution at pH 2.0. The hydrolysis showed a rate of delignification even more rapid than in bisulfite liquor itself. When hydrolysis was carried out in a buffer solution of pH 3.0, the rate of delignification was slower than in bisulfite liquor.

In an investigation of the sulfonation step, Freudenberg and coworkers (79) fractionally pulped wood at low temperatures, and obtained a series of lignosulfonic acids of increasing sulfur content. The fractions were analysed for hydroxyl content by acetylation techniques and, contrary to expectation, the highly sulfonated acids did not contain more hydroxyl groups than the less sulfonated ones. Although these workers were hesitant to draw definite conclusions from their results, they were of the opinion that no phenolic groups were formed during these mild sulfite cooks. Erdtman and collaborators (80) later showed by spectrochemical analysis that no phenolic groups were formed during similar mild sulfonations.

In a recent review on the chemistry of lignin, Erdtman (81) accepts the sulfonation as mainly due to substitution of hydroxyl groups, and offers the theory that lignin is composed of two types of structure. The first type, "group A", is sulfonated over a large pH range and the second, "group B", has to be first cleaved by hydrolysis and may then be sulfonated. Group A is believed to be of the benzyl alcohol type, while group B is based on an acetal structure. Some support is lent to this theory by extensive work with model compounds (70)(71)(72)(82)(83)(84)(85).

To date, there has been no theory offered which fully satisfies all observations made on the sulfite cooking process. In general, Hägglund's two-stage mechanism is accepted, but the manner of sulfonation and hydrolysis is still highly controversial. Although general application of Hagglund's ideas to commercial production has not as yet been carried out, a recent paper by Howard (86) on two-stage cooks on a semi-commercial scale claims that this procedure has been satisfactory. Advantages of the process are found to be an increase in pulp yield and a substantial decrease in sulfur dioxide consumption per ton of wood.

## The Effect of Aqueous Pretreatments on Delignification in Sulfite Cooks

Operators of sulfite digesters have long noticed that excessive steaming of a charge, prior to the addition of the sulfite liquor, resulted in some physical or chemical change in the wood which made subsequent delignification difficult (50). Also, a similar phenomenon occurs if the charge is too rapidly heated in the presence of the bisulfite liquor. In this latter case, the difficulty was attributed to the more rapid penetration of the sulfur dioxide into the wood chips in preference to the base dissolved in the liquor (87)(88). The sulfonation which occurred was believed to have released active groups causing polymerization of the lignin material. This phenomenon is known as a "burnt" or "black" cook, and is, of course, avoided as much as possible in commercial operations. The effect of heating wood chips in various aqueous solutions was first studied by Klason (89), who found that pretreatment in hot aqueous systems at pH 7 resulted in a product that was not easily delignified. Corey and Maass (90) later confirmed Klason's work, but showed experimentally that pretreatment of wood chips by heating in either an atmosphere of nitrogen or in toluene at 130°C. did not change the delignification rate as compared to wood. When wood was pretreated by heating in distilled water at 130°C. for varying lengths of time, subsequent delignification in calcium bisulfite liquor became increasingly difficult. In further experiments on the pretreatment of wood chips with distilled water, it was found that the water became acidic owing to the presence of formic and acetic acids. No theory was postulated as to whether the acids formed were a result of leaching, cracking or hydrolysis processes on either the holocellulose or lignin portions of the wood. In order to discover whether or not these acids were contributing factors to the difficulty of subsequent delignification, these authors pretreated wood samples either by heating in chip form in a flow of distilled water at 130°C. for six hours, or by forcing water at 130°C. through the sample in block form for six hours. The bisulfite cook which followed showed that preheating in flowing water only slightly countered the difficulty of delignification, while removal of the pretreating liquor from the wood by pressure during pretreatment resulted in products that could be easily delignified. From these results, the authors concluded that the acids from the wood play a major part in causing the difficulty in delignification, and that the presence of water, as well as an elevated temperature, was necessary to make this action effective. The effect of hydrogen ion concentration was investigated further by pretreating wood meal samples in sealed bombs containing McIlvaine's disodium hydrogen phosphate-citric acid buffer solutions (91) ranging from pH 3 to pH 8. After the bombs had been heated for six hours at 130°C., the meal was recovered and cooked in bisulfite liquor for three hours at 140°C. The resulting pulps were analysed for lignin by the Ross-Potter method (92) which employs formaldehyde as well as 72% sulfuric acid. This series of cooks showed that the deleterious effect of the pretreatment was least at pH 4.6, while at pH values more alkaline or acidic, subsequent delignification became increasingly difficult.

During the study at various hydrogen ion concentrations, the pH values of the solutions were measured at ordinary temperatures both before and after the pretreatment, and were found to be unchanged. The possible liberation of acids would, of course, be undetected, since the ratio of buffer solution to wood meal was 30:1. Corey and Maass recognized that it was impossible to predict accurately the behaviour of the buffered solutions at the elevated temperatures used in the pretreatments. However, since that time a number of investigations have been carried out on the effect of temperature on pH values of certain buffers. Unfortunately, none have been made on the McIlvaine series specifically, although the behaviour of citric acid and sodium hydrogen phosphate have been investigated separately or in conjunction with other buffering compounds. In addition, no reported work was carried out at temperatures in the range 130°-150°C., of interest in sulfite pulping. Britton (93) pointed out that the pH value of citric acid had no appreciable temperature coefficient up to 60°C. In a later study, Britton and Welford (94) investigated the effect of temperature on the buffering action of the Britton-Robinson universal buffer (95), composed of citric, boric and diethylbabituric acids, potassium dihydrogen phosphate and sodium hydroxide, by means of a standard hydrogen electrode. Negligible changes of pH with temperature in the range of 12.5° to 90°C. were observed for pH values of 2.5 to 6.2, where the buffering action of citric acid is predominant. For pH values between 6.2 and 7.5, where the dihydrogen phosphate ion is the active buffering agent, the pH value decreased only 0.025 units for a rise in temperature of 80°C. Bates and Acree (96) carried out comparable work on a buffer composed of potassium dihydrogen and disodium phosphates. Their data showed that the change in pH for a 60°C. rise in temperature was negligible. Although no one has as yet investigated buffers at temperatures over 100°C., it may possibly be assumed from the behaviour of the components of the McIlvaine buffer at temperatures below this value that the effect of temperature is negligible in the higher range.

In conjunction with another study on the effect of hydrogen ion concentration in the pretreatment of wood, Calhoun and Maass (97)(98) noted that different buffers of the same pH value gave different results. Further work showed that the effect was due to the type of ion employed rather than to variation in the salt concentration. There existed a close similarity between the observed order of cation and anion effect in the treatment, and the lyotropic series given by Traube (99) for the hydration of ions and swelling of gelatin, and to the series by Stamm (100) for the swelling of wood. This similarity seemed to indicate that colloidal factors, such as the swelling and peptizing of the wood, are involved in the phenomenon of pretreatment, rather than a purely chemical reaction on the lignin.

In order to investigate the effect of temperature at constant hydrogen ion concentration in pretreatment, Corey, Calhoun and Maass (48) heated samples of spruce wood meal in buffer solutions of pH 3, 5 and 7 for six hours at temperatures of 100°, 110°, 120°, 130° and 140°C., and then cooked the residues for three hours at 140°C. in bisulfite liquor. The results showed that an increase in the temperature of pretreatment caused a decrease in the degree of delignification of the pulp brought about by the subsequent cook. From previous work, pretreatment at pH 5 had less effect than at other pH values. A study of the effect of temperature at pH 5 revealed that pretreatments at 100° and 110°C. corresponded to delignification in the subsequent cook of the same extent as observed with untreated samples. In addition, the pretreatment of spruce wood at any pH value and at temperatures above 120°C. substantially changed the cooking properties. Delignification also became increasingly difficult as the time of pretreatment, at various pH values and temperatures, was increased.

Richter's (101) recent results confirmed those obtained by Corey and Maass (90), inasmuch as pretreatment of western hemlock wood chips with distilled water at elevated temperatures caused the water to become progressively more acidic as the temperature was increased (Table II). In addition, the degree of delignification became smaller. The pretreatment was carried out for four hours at the temperature indicated and nitrogen

## TABLE II

## Effect of Aqueous Pretreatment of Western Hemlock

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Stage 1 - Water Pretreatment | | | | | | | |
| Maximum temperature (a) °C. | 60 | 75 | 110 | 120 | 130 | 150 | 170 | none |
| Semi-pulp yield % | 97 | 97 | 97 | 96 | 96 | 87 | 76.1 | - |
| pH at end of cook | 6.8 | 6.6 | 5.3 | 4.3 | 3.8 | 3.7 | 3.4 | - |
| | Stage 2 - Pulping with Acid Sulfite (b) | | | | | | | |
| Over-all pulp yield % | 50.6 | 51 | 49 | 51.4 | 60 | 66.4 | 69.9 | 49.9 |
| Lignin % | 7.9 | 8.1 | 7.4 | 11.5 | 17.1 | 32.9 | 38.1 | 9.9 |
| Lignin removed % | 86.7 | 86.3 | 87.9 | 80.5 | 65.8 | 27.5 | 11.0 | 83.9 |
| Non-lignin removed % | 33.5 | 33 | 35.5 | 34.5 | 29 | 36.5 | 38 | 36 |

(a) For four hours at 100 lbs. pressure of nitrogen.

(b) To 110°C. and 150 lbs. pressure during 7.5 hours.

was employed to maintain a pressure of 100 lbs. in the system. The second stage, sulfite cooking, was made with 15% sulfurous acid at a maximum temperature of 110°C. and a maximum pressure of 150 lbs. for 7.5 hours. No base was added to the cooking liquor in this study.

The effects of other aqueous solutions such as sodium sulfite, sodium hydroxide, sodium sulfide and sulfurous acid were also investigated. Sodium sulfite, in 2% concentration, was found to increase the rate of delignification in subsequent cooking even at a temperature as high as 170°C. On the other hand, sodium hydroxide, sodium sulfide and a number of other organic and inorganic solutions had a deleterious effect on the subsequent delignification of western hemlock. Pressure during pretreatment was a minor factor in hindering later delignification. Although the cooking of western hemlock, following the above pretreatments, was usually carried out in an acid sulfite system, a comparison with a series of calcium base bisulfite cooks revealed the latter to be more rapid in delignification, but capable of being hindered in similar ways.

In his review on sulfite pulping, Yorston (50) discussed the nature of the pretreatment effect. He claimed that sulfonation of the lignin in the wood was decreased as the pretreatment was made more drastic, and that the rate of solution of the lignin was retarded. He also thought that "the change in lignin, whatever its nature, must be reversible, for pretreatment for 36 hours at 140°C. did not inhibit cooking, but merely retarded the process." Corey and Maass (90) claimed that a physical was more probable than a chemical change in the wood as an explanation for pretreatment effects. They considered the cooking reaction to be heterogeneous and that the lignin existed as submicroscopic particles, on whose surface the sulfonation reaction occurred. Pretreatment was claimed to cause agglomeration of the micro particles, resulting in a decrease of exposed surface. Consequently the rate of cooking in the initial phases of the cook would be decreased. As the cooking progressed, and lignin dissolved, the lignin particles would become smaller until they approached in size to particles present in untreated wood. At this stage, the rates of delignification for untreated and treated woods would be the same. This inference was borne out experimentally, since the slope of a delignification rate curve of a pretreated sample paralleled that from untreated wood after prolonged cooking.

Richter, on the other hand, accepted Hägglund's theory of sulfonation followed by hydrolysis as the basis of the cooking reaction. However, lignin possibly reacted with secondary substances in wood to yield a complex product which remained insoluble in subsequent cooking either because it was not sulfonated or because its sulfonate was not hydrolysed. An alternate theory proposed was that lignin might have polymerized or condensed to make later cooking difficult, if not impossible. However, no final theory could be put forward until a more definite knowledge of lignin structure was obtained.

The advent of periodate lignin made it practical for the first time to study the effect of pretreatments in the absence of the complications introduced by the presence of wood carbohydrates. This was undertaken in this laboratory by Miss E. Charnley, who heated periodate lignin in solutions buffered to pH values between 2 and 8 at temperatures of 100°, 120° and 135°C. Lack of adequate experimental controls both in the pretreatment and the subsequent standard cook with calcium bisulfite introduced wide and capricious variations between duplicate runs. For this reason it seemed impossible to make a reliable review of her findings.

## EXPERIMENTAL

### Preparation of Spruce Periodate Lignin

Two samples of spruce periodate lignin were prepared according to the procedure outlined by Ritchie and Purves (41). Dry chips of Black Spruce wood, obtained from four-foot logo of a tree approximately seventy years old were ground in a Wiley mill to pass a two-millimeter screen. The resulting wood meal was extracted exhaustively with 2:1 benzene-ethanol for forty-eight hours in a large Soxhlet extractor of 200 gms. capacity, followed by a similar extraction with ethanol. The extracted material was air dried.

The first preparation of periodate lignin employed 300 gms. of air dried meal, which was oxidized with three liters of 4.5% periodic acid, buffered at pH 4.2 with sodium acetate, for twenty-four hours. The partially oxidized meal was recovered on a glass cloth sheet in a large Büchner funnel and washed in a 12-l. glass tank with fittings constructed for this purpose. The filtrate was retained for recovery and re-use. The washing process was continued until the effluent showed no trace of periodate or iodate ions to a starch-potassium iodide test. The meal was recovered by filtration and the oxidized holocellulose portion hydrolysed by adding the meal to ten liters of boiling distilled water made acid to pH 5.0 by the addition of glacial acetic acid, and contained in a 12-l. flask fitted with a reflux condenser. The hydrolysis was carried out for three hours, followed by recovery of the meal from the hydrolysate by filtration.

The treatment of the meal by successive oxidation, washing and hydrolysis steps was continued for six cycles, whereupon the finished product was air dried.

A second preparation of Spruce Periodate Lignin, with the intention of making a large quantity and applying modifications to the existing method, was carried out with the help of C. F. Brounstein. The Black Spruce wood meal, prior to oxidation, was processed as previously described. The initial oxidation utilized a series of five Erlenmeyer flasks of six liter capacity each, containing 400 gms. of prepared meal and four liters of buffered 4.5% periodate solution. After twenty-four hours, the meal was recovered by filtration, and combined and redivided to form three separate batches of similar size, which were handled separately during subsequent processing steps.

In previous preparations of periodate lignin samples, the washing stage of the processing cycle had always proven to be the most time consuming and troublesome. The original washing method of Ritchie and Purves, based on a continuous throughput of water with the effluent screened and removed by suction, generally ceased operation because the filter screen clogged due to the presence of very fine particles. Efforts to improve the continuous washing process by increasing the filter area, by employment of a series of graded screens and by decreasing the suction pressure on the screen face met with little success. As a result, a batch washing process was finally developed which, although slow, was trouble-free and efficient. This method consisted of adding the oxidized meal to a large enamelled tank containing sixty liters of water. The meal was mechanically stirred with the water for three hours and then allowed to settle. Within two hours, the meal had settled to the bottom of the tank and the supernatant liquid was siphoned into a metal cylinder 6 inches in diameter and 16 inches high, fitted with a 200-mesh copper screen base. Some of the coarse meal was carried over during the siphoning and acted as a filter mat for the fines. No clogging difficulties were experienced during siphoning. The tank was refilled with water, and the wash repeated. After washing for three days, the supernatant liquid was tested for the presence of periodate and iodate ions with starch-iodide solution and the washings continued until all the oxidants had been removed.

The hydrolyses were carried out in a stainless steel tank with thirty liters of distilled water acidified to pH 5.0 with glacial acetic acid. After five cycles of oxidation, washing and hydrolysis, the separate batches of product were individually analysed for Klason Lignin, holocellulose and methoxyl contents and solubility in a standard sulfite cook. The analyses showed that the separate batches were satisfactory and of similar quality. The three products were air dried, blended together and reanalysed as shown in Table III.

The preparation of trisodium paraperiodate was carried out according to the directions of Lange and Paris (102), by oxidizing sodium iodide dissolved in a strong sodium hydroxide solution with bromine at 80°C. The aqueous solution of periodic acid used in oxidizing the wood meal was prepared by dissolving the sodium salt in distilled water with the aid of a small amount of glacial acetic acid. The quantity of salt employed was based on calculations to prepare a solution of 6-8% strength. The resulting solution was analysed for periodate content according to Muller and

## TABLE III

## Analysis of Preparations of Spruce Periodate Lignin

| Sample | Spruce Periodate Lignin I | Spruce Periodate Lignin II |
|---|---|---|
| Wt. of air dried wood meal - gms. | 300 | 2000 |
| Wt. of air dried periodate lignin - gms. | 70 | 450 |
| Moisture - % | 1.2 | 7.1 |
| Ash - % | 1.6 | 2.5 |
| Klason lignin - %(a) | 91.5 | 90.2 |
| Holocellulose - %(a) | trace | 1.41 |
| Methoxyl - %(a) | 12.0 | 11.8 |
| Insoluble in Standard(a) Sulfite Cook - % | 8.7 | 8.7 |

(a) Values corrected for ash and moisture content.

Friedberger (103), by adding an excess of standard arsenious acid solution and potassium iodide to an aliquot portion and back titrating with standard iodine solution.

$$Na_3H_2IO_6 + 2KI + H_2O \longrightarrow 2KOH + 2NaOH + NaIO_3 + I_2$$
$$I_2 + H_3AsO_3 + H_2O \longrightarrow H_3AsO_4 + 2HI$$

In this titration the solution of arsenious acid and dissolved trisodium paraperiodate was buffered at pH 8 with a small piece of solid carbon dioxide to prevent the iodate ion, formed as a by-product in the reaction, from acting as an oxidant. After adjustment to 4.5% by dilution and acidification to pH 4.1 with glacial acetic acid, the solution of sodium periodate was filtered through a "Supercel" mat in a sintered glass filter funnel to remove suspended silaceous material. The filtered solution was employed in the oxidation of the wood meal. Recovery of periodate solutions after use was carried out by first making the solutions strongly alkaline with sodium hydroxide and then oxidizing with chlorine at 85°-90°C. The precipitate of trisodium periodate was recovered by filtration, oven dried at 115°C. for four hours and employed in the preparation of fresh periodate solution.

## Construction of Bombs for Small Scale Cooks

From preliminary experiments, it was found that satisfactory results could be obtained from a standard sulfite cook with a lignin charge as low as 300 mgms. Since slightly larger pretreatment cooks in the order of 500 mgms. would also be necessary, special bombs and glass liners were designed and constructed to handle samples within these limits.

The completed reaction bomb consisted of two parts, a sealed glass liner and a tubular metal container. The glass liner, constructed separately for each reaction, was made from 6-inch lengths of 22 mm. O.D. Pyrex tubing. Before charging, one end of the tube was sealed and blown smooth in an oxygen torch and was then numbered with an engraving pencil followed by cleaning and rinsing with distilled water. In general, the loading procedure was to charge the dry material with a weighing stick and constrict the tube to an opening of 1/4 inch at a point 5 to $5\frac{1}{2}$ inches from the sealed end. The liquor charge was then pipetted into the bomb and the tube sealed at the point of constriction. The maximum capacity of this bomb was 35 cc. (Figure I)

The metal container for the liner consisted of a piece of 1-inch heavy duty pipe, $7\frac{1}{2}$ inches in length. At one end, the pipe was internally threaded with a standard pipe thread, and a standard $\frac{3}{4}$-inch pipe plug fitted and sealed. The opposite end of the pipe was externally threaded to a length of 2 inches with standard pipe thread to allow a 1-inch pipe cap to be fastened without seizing. The open face of the container was smoothed on a lathe to permit a tight seal to be made when the cap was fastened. The gasket for the container consisted of a lead casting poured into the cap to a depth of about $\frac{1}{2}$ inch. When the lead had solidified, the cap was threaded onto the bomb and tightened by force until the pipe had entered the lead to a depth of 1/8 inch. The cap and pipe were numbered and kept as a set throughout the investigation. In operation, the cap was fastened with a pipe wrench using light pressure and was found to retain its seal throughout numerous runs. Ten containers were constructed. (Figure I)

In carrying out a run, the charged and sealed liner was carefully placed in the metal container and about 10 cc. of distilled water was added to exert an even back-pressure at the elevated temperature. A small amount of glass wool was added to cushion the liner against the end over end agitation during the run. The cap was finally fastened and the bomb inserted in the carrier rack of the heating bath. After completion of a run, the bombs were removed from the bath and allowed to cook for about ten minutes before being slowly opened. The glass liner was slipped out by inverting the bomb and cooled to room temperature before opening. In a few cases where the liner stuck in the container, the plug at the other end of the container could also be removed and the liner gently forced out.

## Bombs for Large Scale Cooks

In the design and construction of a large scale bomb for this investigation, the limiting factors were the maximum size of tubing available for the glass liner and the over-all length of the finished container which, of necessity, had to fit between the steel supports of the bath. (See below). The maximum size of Pyrex glass tubing commercially available was 100 mm. O.D., and two liners were made from this material by Mr. D. Lorimer, Radiation Laboratory, McGill University, according to the plan shown in Figure II. One end of the liner was completely sealed and blown slightly round for structural strength. The other end was shaped to match the seal and a length of 22 mm. O.D. Pyrex tubing was fused into the center of this end. Charging of the periodate lignin was carried out with a powder funnel placed in the extended small tubing. The liquor was then added

Completed Bomb

Glass Liner

Bomb (unassembled)

Figure I - Bomb for Small Scale Cook

and the small tube sealed at a point not more than one inch from the body of the bomb. Extreme care was taken to prevent cracking or formation of a strain in the glass liners, which had a capacity of 1.2 liters.

The metal container for these liners was designed and built by Mr. K. Webb, Machine Shop, Pulp and Paper Research Institute, and consisted of a section of 4-inch steel pipe 9¾ inches in length. The internal and external sides were machine turned and a circular plate of 1/4-inch steel was welded on to seal one end. An external steel axle was welded to the center of the circular plate. The opposite end of the pipe was machine threaded to fit a standard 4-inch pipe cap, and turned internally to form a step 1/4 inch deep and 1/8 inch in width. A circular plate, to which an axle was welded, was machined to fit snugly into the step. A 4-inch pipe cap, in which a 2½-inch hole was bored, was used to seal the circular plate to the pipe. The pipe cap was fitted with six Allen type setscrews, placed radially around the bored hole in the flat portion of the cap. A photograph of the assembly is shown in Figure III. Sealing of the container involved placing the machined plate into the top of the pipe, axle outwards, followed by attaching the cap to hand tightness. The setscrews were then tightened with a wrench. Although no gasket was employed, this seal was found to withstand pressures up to 75 pounds gauge.

The operation of these larger scale bombs involved charging and sealing the glass liner, which was then gently inserted into the metal container. Approximately 50 to 100 ml. of distilled water were added to effect back-pressure on the liner during the heating of the container.

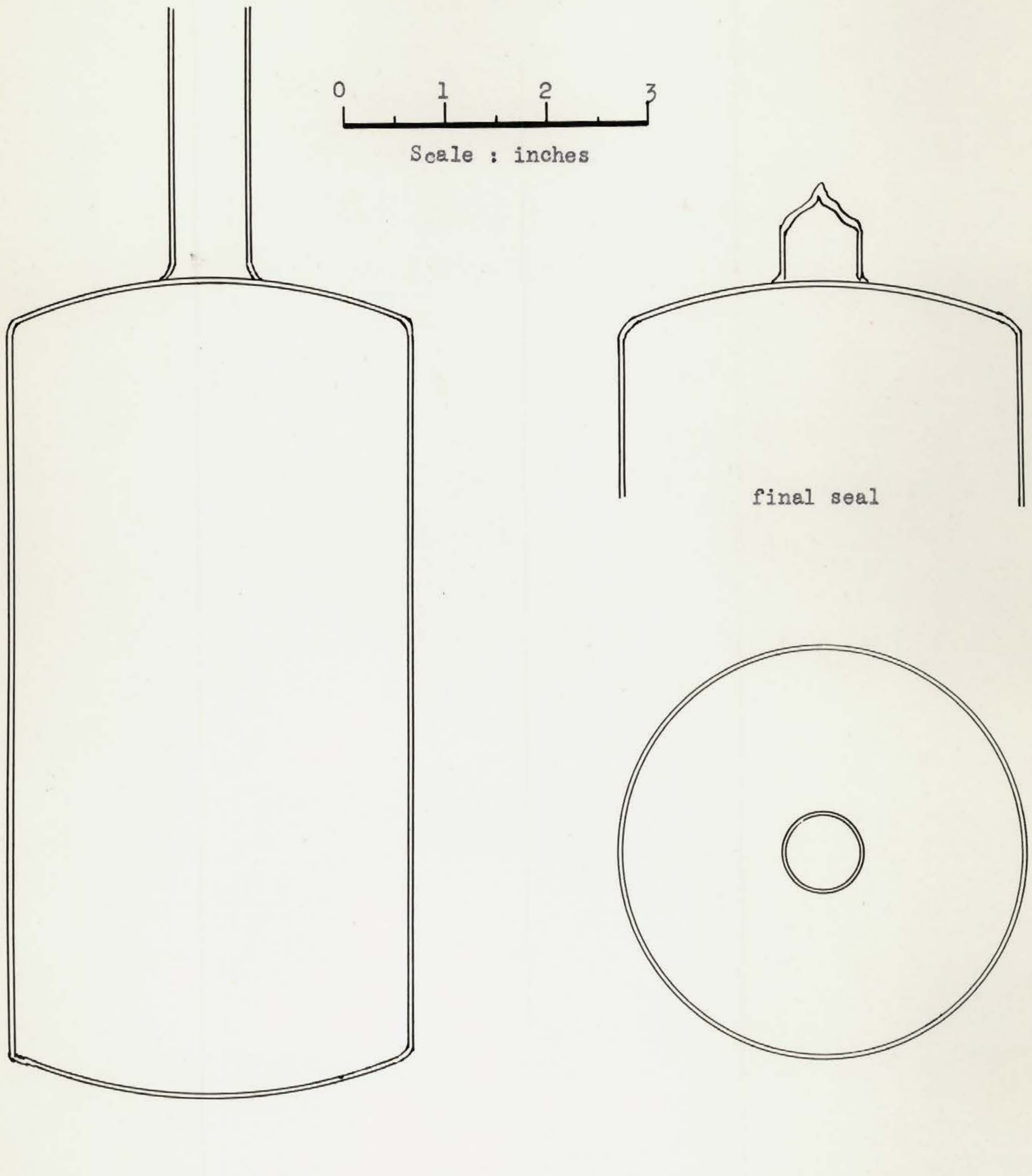


Figure II - Glass Liner for Large Scale Cooks

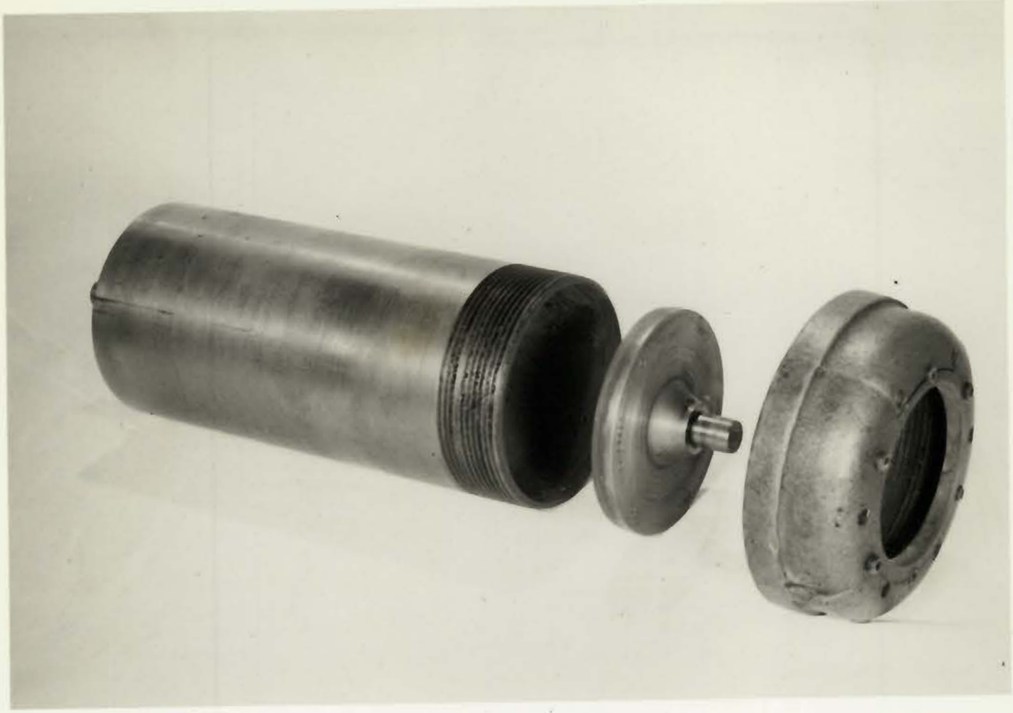


Figure III - Metal Container for Large Scale Cooks

## Construction of the Oil Bath

The heating and agitation of both the large and small scale bombs was carried out in a specially constructed oil bath maintained at a constant temperature throughout the various runs. The bath itself consisted of a tank 15 x 15 x 15 inches in size, constructed of 1/8-inch steel plate in which all seams were welded to be leakproof. A wooden container 21 x 21 x 18 inches in size surrounded the tank, which was centered by wooden stringers, so that its open top was flush with the top of the box. As insulation, the outside of the tank was covered with 1/16-inch asbestos sheet, and granular vermiculite was packed into the air space between the tank and container.

The operating equipment of the bath was fitted to a wooden lid fastened to the container by means of a pair of heavy steel hinges. The bottom of the lid was insulated with 1/16-inch asbestos sheet, and faced with #20 gauge galvanized sheet iron. The agitation of the bombs was carried out with a 1/8-horsepower electric motor operating through a 100:1 ratio speed reducer, which were connected by means of two pulleys and an endless "V" belt. Power from the speed reducer was transmitted to either the bomb rack or the large scale bomb by means of sprocket wheels and an endless chain. Constant temperature control was maintained using a Cenco-DeKhotinsky thermoregulator connected to a Cenco A.C. relay. The relay, in turn, controlled a 1500-watt General Electric "Calrod" heater. The heater unit was also mounted to the lid and bent to protrude into the tank down the side near the hinges, along the bottom and across the center of the tank when the lid was in the closed position. A photograph of the completed bath is shown in Figure IV.

Operation of the oil bath with the small bombs previously described required a specially constructed rack as shown in Figure V. The rack consisted of two matched plates of 1/8-inch aluminum sheet, $9\frac{3}{4}$ x $7\frac{1}{2}$ inches in size, through which twelve holes of $1\frac{1}{2}$-inch diameter were drilled. These plates were fastened at both ends to aluminum plates $7\frac{1}{2}$ x $7\frac{1}{2}$ x 1/8 inches so as to form a rack for twelve bombs. A hinged lid was fastened to the rack which, when closed, held the bombs in position by their caps during the end over end agitation. The lid locked into position with two cupboard clasps which were found to be satisfactory for all runs carried out. The carrier rack was fitted with axles held to the end plates with flanges, and held in position in the oil bath by two supports 10 inches long of $\frac{1}{2}$-inch steel and fastened to the underside of the lid. A slot 5/8 inch in width and $1\frac{1}{2}$ inches in depth was cut horizontally in each of the steel supports so that either the carrier rack or the large bomb could be slipped into position with ease during changeovers for reactions of either scale. The rack or large scale bomb was locked into position with wing bolts. Rotation of the rack was carried out by means of a chain drive to the speed reducer on the lid, and no other agitation of the oil bath was required. During operation of the large scale bomb, a laboratory type 1/10-horsepower stirring motor was fitted to the lid and used to drive a shaft with a 2-inch propeller inserted into the oil. The large scale bomb was mounted by attaching a sprocket wheel (removed from the rack) to the axle on the removable circular plate. After the bomb was placed on the steel supports, the endless chain was fitted to the sprocket wheel and the assembly moved along until it gently fell into the

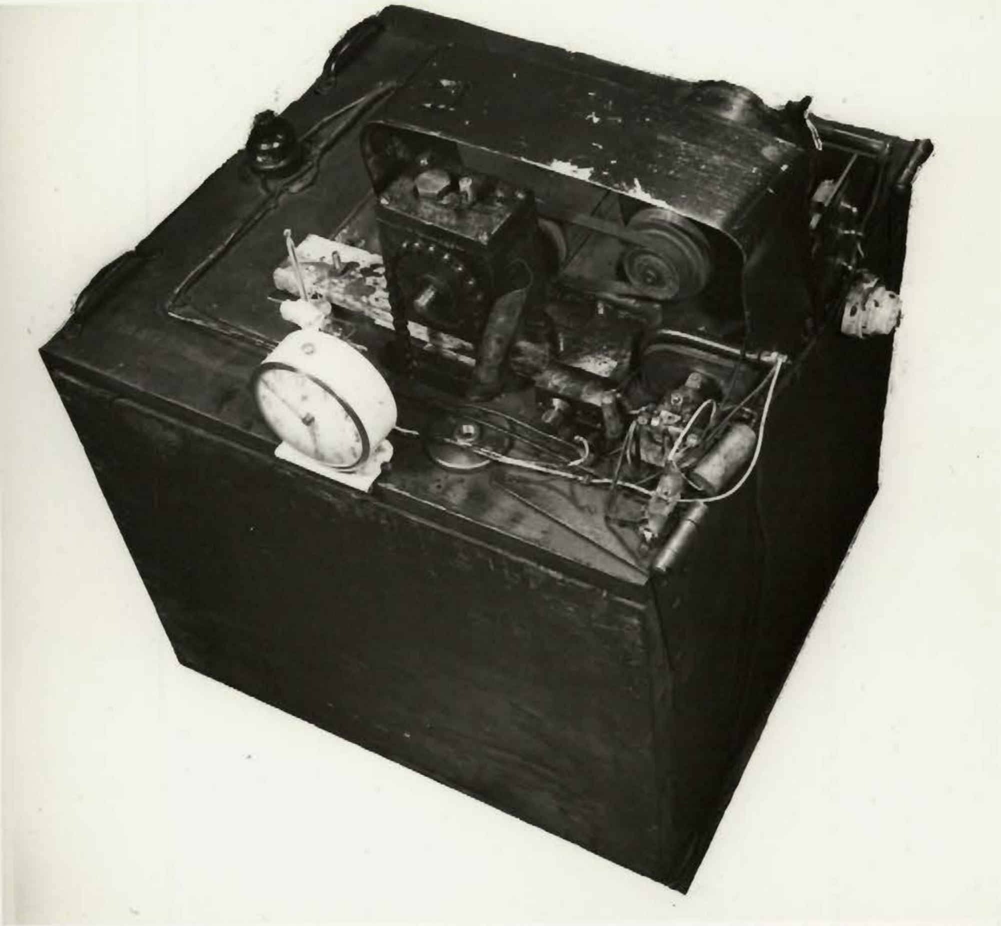


Figure IV - Constant Temperature Oil Bath

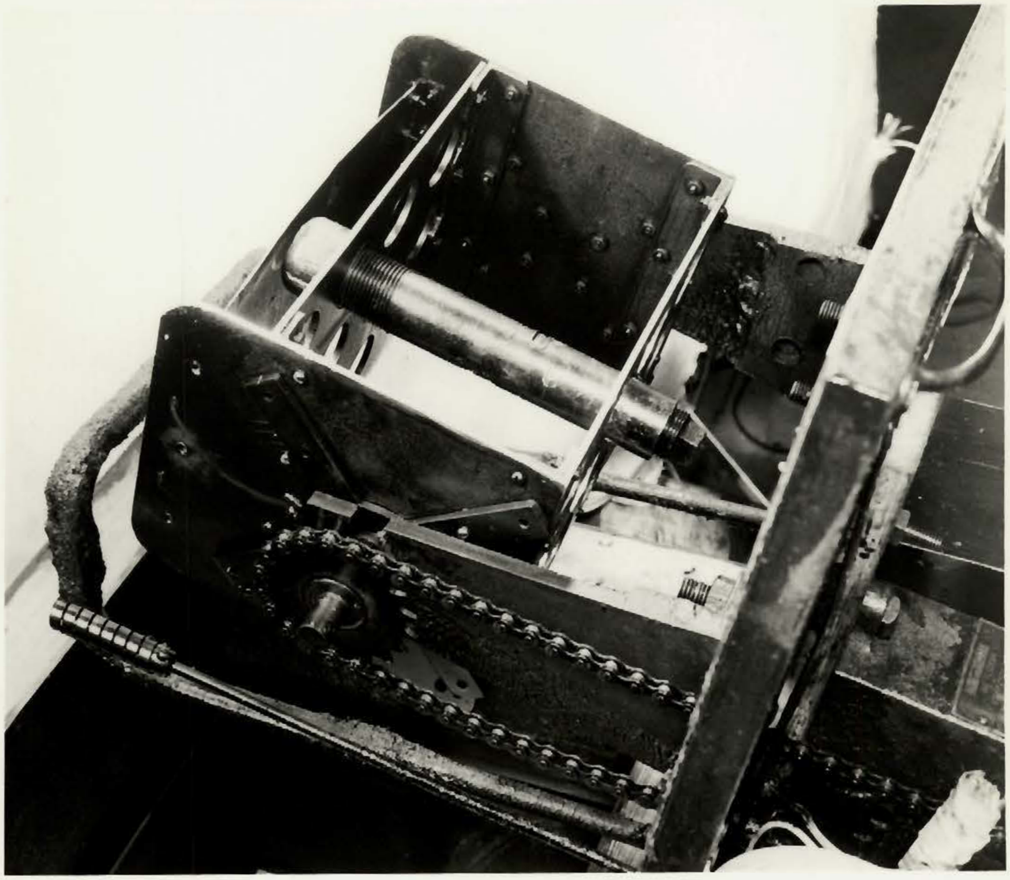


Figure V - Carrier for Small Scale Bomb

solids at the end of the steel supports. The axles were locked into position with wing bolts.

A master switch and switch panel were installed as controls for the electrical units of the bath. The switch panel controlled the agitator motor, the stirring motor and a timer which started operation for preheating before a run. A diagram of the wiring circuit is shown in Figure VI.

When completed, the tank was charged with 6 Imperial gallons of Sturbinol 65 petroleum based oil, obtained from Imperial Oil Ltd., Montreal, Que. This oil proved to be very satisfactory up to a temperature of 160°C., but after eighteen months of more or less continuous operation showed a tendency to decompose and fume. In use, the bath was kept at the preset temperature within ±1°C., and the agitation was 10 R.P.M. end over end for the small bombs, and 10 R.P.M. around the horizontal axis of the large bomb. The bath required three to five minutes to regain the preset temperature after the small bombs were loaded and eight to ten minutes after the large bomb.

## Pretreatments of Periodate Lignin

The aqueous pretreatment of spruce periodate lignin at 100°C. employed a 100-ml. flask having a standard taper neck and fitted with a reflux condenser. A sample of the order of 1 gm. was accurately weighed into the flask, and a liquor charge of 50.0 milliliters of buffer solution added. The flask was heated to boiling with a Glas-Col unit, and the contents kept under reflux for four hours before being rinsed and filtered into a tared sintered glass crucible of coarse porosity, and the residue

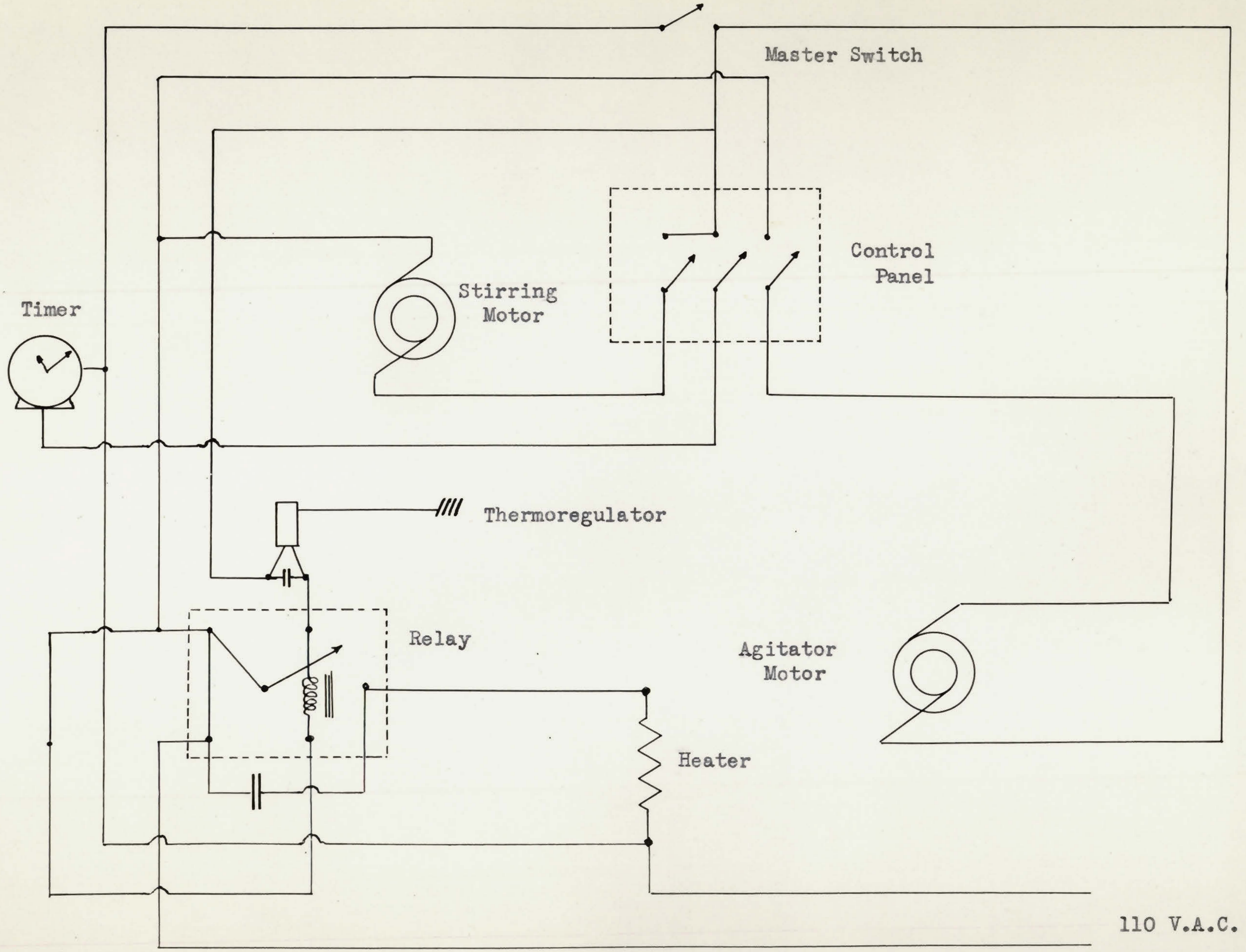


Figure VI - Wiring Circuit of Oil Bath

washed with 150 milliliters of distilled water. The crucible was dried in vacuo at 50°C. over phosphorous pentoxide for four hours, and weighed.

Pretreatments at temperatures greater than 100°C. were carried out in the small scaled bombs (described above) with the exception of four large scale runs. For all small scale pretreatments, a charge in the order of 0.5 gm. of periodate lignin, accurately weighed, and 25.0 milliliters of buffer solution was used. The charged bombs were heated at the required temperature in the oil bath for four hours, removed from the bath and the container opened. The liner was immersed in water for fifteen minutes and then opened. Initially, an oxygen torch was used as in the opening of Carius bombs, care being taken to prevent the boiling or charring of the contents in the liner. A later technique, which was very successful, involved scoring a line around the liner with a file, at a point 1/4 to 1/2 inch below the constricted end, which was then neatly cracked off with a hot glass rod. The contents of the bomb were transferred and filtered through a tared sintered glass crucible with the aid of 100 milliliters of distilled water. The crucible was dried in vacuo at 50°C. over phosphorous pentoxide for four hours and weighed.

Large scale pretreatments, which were carried out to obtain big samples for oxidation with alkaline permanganate, were based on the results from small scale bomb runs. The amount of periodate lignin charged was chosen to give a total dry residue of close to 15 gm. in one run, and the buffer solution added gave a liquor to solids ratio of 50:1. After completion of the run, the liquor was filtered through a Buchner funnel and the liner rinsed with 1.5 liters of distilled water. The washings were filtered, and the total recovered solids dried in vacuo at 50°C.

for four hours and weighed.

The buffer solutions employed for pretreatments between pH 2 to 8 inclusive were based on 0.M. citric acid and disodium hydrogen phosphate, according to McIlvaine (91). For pH values of 1, 9 and 10, solutions of 0.2N hydrochloric acid, 0.2N potassium chloride, 0.1N sodium hydroxide and 0.1M boric acid were used after the method of Clark and Lubs (105). Prior to charging of the solution into the liner, the hydrogen ion concentration of the buffer was checked with a Beckman 3A pH meter. Buffer solutions with pH values of 0.1 unit difference from the specified hydrogen ion concentration were discarded; otherwise the buffer was adjusted by the addition of appropriate stock solution. After completion of a run, the residual liquor was rechecked with the pH meter to note any change in pH value which might have occurred.

Solubility data collected from a study of various buffered pretreatments on a series of runs at 100°, 120° and 150°C. are shown in Table IV. A later study of the effect of pretreatment temperature up to 160°C. on solubility, and also its effect on subsequent delignification, is summarized in Table V.

## Standard Sulfite Cooks

The preparation of sulfite liquor for standard cooks was simplified to permit the production of solutions of constant composition with ease. A slurry of 8.175 gm. of calcium oxide (reagent grade) in 50 milliliters of distilled water was transferred into a 1-liter volumetric flask with 100 milliliters of hot water. A flask containing about 750 milliliters

## TABLE IV

## Solubility of Periodate Lignin During Pretreatment(a)

| Temperature 100°C. (a) | | | | Temperature 120°C. (b) (c) | | | | Temperature 150°C. (b)(d) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| pH of Pretreatment | Soluble in Liquor % | | pH of Residual Liquor % | pH of Pretreatment | Soluble in Liquor % | | pH of Residual Liquor % | pH of Pretreatment | Soluble in Liquor % | | pH of Residual Liquor % |
| | | Mean | | | | Mean | | | | Mean | |
| 1.1 | 9.9<br>9.8 | 9.9 | 1.2 | 1.0 | 14.7<br>15.8 | 15.2 | 1.2 | 1.1 | 22.2<br>21.9 | 22.0 | 1.2 |
| 2.2 | 5.7<br>5.8 | 5.8 | 2.3 | 2.2 | 11.5<br>11.0 | 11.2 | 2.3 | 2.2 | 20.7<br>19.3 | 20.0 | 2.6 |
| 3.0 | 5.1<br>5.0 | 5.0 | 3.2 | 3.0 | 10.3<br>10.9 | 10.6 | 3.1 | 3.0 | 19.9<br>17.3 | 18.6 | 3.0 |
| 4.0 | 4.0<br>3.9 | 3.9 | 4.0 | 4.0 | 9.9<br>9.9 | 9.9 | 4.0 | 4.0 | 16.6<br>16.2 | 16.4 | 3.9 |
| 5.0 | 3.3<br>3.2 | 3.2 | 4.8 | 5.0 | 8.0<br>9.2 | 8.6 | 4.9 | 5.0 | 16.2<br>16.3 | 16.3 | 4.6 |
| 6.0 | 5.1<br>4.8 | 4.9 | 5.4 | 6.0 | 9.6<br>10.3 | 10.0 | 5.8 | 6.0 | 18.1<br>17.4 | 17.3 | 5.5 |
| 7.0 | 5.8<br>6.0 | 5.9 | 6.4 | 7.0 | 10.2<br>11.7 | 10.9 | 6.6 | 7.0 | 17.8<br>17.7 | 17.7 | 6.3 |
| 8.0 | 6.8<br>8.1 | 7.4 | 7.3 | 8.0 | 9.6<br>10.6 | 10.1 | 7.2 | 8.0 | 18.5<br>18.3 | 18.4 | 6.9 |
| 9.0 | 8.8<br>9.9 | 9.3 | 8.0 | 9.0 | 13.1<br>13.1 | 13.1 | 7.8 | 9.0 | 20.5<br>20.0 | 20.2 | 8.0 |
| 9.8 | 9.8<br>10.2 | 10.0 | 8.4 | 10.0 | 15.1<br>14.3 | 14.7 | 8.1 | 9.8 | 23.7<br>24.6 | 24.2 | 8.5 |

(a) 1 gm. samples and 50 ml. buffer solution.
(b) 0.5 gm. samples and 25 ml. buffer solution.
(c) Samples of periodate lignin SPL I.
(d) Samples of periodate lignin SPL II.

of distilled water was cooled in a brine tank to 0°C. and sulfur dioxide gas (Commercial grade, 99.9% minimum $SO_2$, obtained from Canadian Industries Limited, Montreal) bubbled through the liquid until the concentration amounted to approximately 10%, as determined by a titration with N potassium iodate in presence of excess potassium iodide. From calculations based on the method of mixtures, the appropriate amount of sulfurous acid solution was added to the volumetric flask containing calcium hydroxide, such that addition of distilled water to the mark resulted in a solution of 6% total sulfur dioxide. Analysis of the finished liquor by the Palmrose method (104) revealed the composition to be 6.00 ±0.05% total and 1.00 ±0.02% combined sulfur dioxide in all cases.

Loading of the glass liners for standard sulfite cooks required an accurately weighed lignin sample of the order of 0.30 gm. and 15.0 milliliters of liquor added by pipette. Before sealing, the bomb and contents were frozen in a brine tank at -10°C. until solid, since the vapour pressure of the liquor at room temperature tended to blow out the seal while it was still molten. The liners were then heated in containers in the oil bath for six hours at 135°C. After completion of the cook, the liners were removed from the containers and frozen at -10°C., since opening of the bombs when even slightly warm caused violent ebullition of the liquor with accompanying loss of material. The contents of the liners were washed into two 15-ml. tapered centrifuge tubes with distilled water, and, after being centrifuged for five minutes, the supernatant liquid was decanted and filtered through a tared sintered glass crucible. Distilled water was added to the centrifuge tubes and the solid residue triturated. The solids were again centrifuged to the base of the tubes and the remaining clear liquid filtered through the crucible. The washing step was repeated four times, and the final residue transferred to the crucible with absolute alcohol by means of a wash bottle. The crucible was dried *in vacuo* at 50°C. for four hours and weighed.

$$\%\ \text{Solubility in Standard Sulfite Cook} = \frac{\text{Weight of charge} - \text{Weight of residue}}{\text{Weight of charge}}$$

The standard cooks were applied in analysis of lignin preparations and also in a study of the effect of aqueous pretreatment on periodate lignin. A summary of the investigation of the effect of temperature of pretreatment on subsequent delignification under standard cooking conditions is shown in Table V. Data from a study of solubility in standard cooks of periodate pretreated at 100°, 120° and 150°C. in a pH range of 1 to 10 is shown in Table VI.

## Isolation of Lignosulfonic Acids

A series of small scale cooks used samples of about 0.5 gm., accurately weighed, and 25 milliliters of 9% sodium bisulfite solution. The cooks were operated at 100°C. for seventy-two hours and yielded almost 90% of the original charge in the form of insoluble material. Charging and opening of the bomb liners were carried out according to standardized procedures mentioned earlier. The method of recovery, however, was changed in order to retain known weights of material and thus permit further reactions to be undertaken in the same liner. The bomb liner was fitted into an adapter cup and whirled in a large centrifuge for fifteen minutes; the liquid content was discarded, the residue triturated with 20 milliliters of distilled water and recentrifuged for fifteen minutes. The wash was

## TABLE V

### Effect of Temperature of Pretreatment on Periodate Lignin (a)

| Temperature of Pretreatment °C. | Solubility in Buffer solution (b) % | | Insolubility in Standard Bisulfite cook (c) % | |
|---|---|---|---|---|
| | | Mean | | Mean |
| 100 | 5.7<br>5.8 | 5.8 | 9.3<br>7.4 | 8.4 |
| 120 | 11.5<br>11.0 | 11.2 | 73.2<br>75.7 | 74.5 |
| 130 | 16.5<br>20.2 | 18.3 | 80.2<br>82.2 | 81.2 |
| 140 | 19.5<br>19.2 | 19.3 | 86.2<br>84.5 | 85.3 |
| 150 | 20.7<br>19.3 | 20.0 | 94.0<br>95.4 | 94.7 |
| 160 | 25.0<br>25.4 | 25.2 | 103.8<br>102.8 | 103.2 |

(a) Periodate lignin sample SPL II.

(b) Four hours in buffer solution - pH 2.2 (see Table III).

(c) Calcium base with 6% total, 1% combined $SO_2$ at 135°C. for six hours.

## TABLE VI

## Solubility of Pretreated Periodate Lignin in a Standard Sulfite Cook [(a)]

| Temperature 100°C. [(b)] | | | Temperature 120°C. [(b)] | | | Temperature 150°C. [(c)] | | |
|---|---|---|---|---|---|---|---|---|
| pH of Pretreatment | Solubility % | | pH of Pretreatment | Solubility % | | pH of Pretreatment | Solubility % | |
| | | Mean | | | Mean | | | Mean |
| 1.1 | 83.8<br>83.7 | 83.8 | 1.0 | 22.4<br>24.1 | 23.0 | 1.1 | 5.3<br>4.2 | 4.7 |
| 2.2 | 90.7<br>92.6 | 91.6 | 2.2 | 26.8<br>24.3 | 25.5 | 2.2 | 6.0<br>4.6 | 5.3 |
| 3.0 | 91.3<br>93.2 | 92.2 | 3.0 | 31.8<br>27.4 | 29.6 | 3.0 | 7.4<br>6.8 | 7.1 |
| 4.0 | 90.4<br>92.2 | 91.2 | 4.0 | 32.6<br>29.2 | 30.9 | 4.0 | 8.4<br>7.5 | 7.9 |
| 5.0 | 90.0<br>87.2 | 88.6 | 5.0 | 33.4<br>29.6 | 31.5 | 5.0 | 7.2<br>8.3 | 7.7 |
| 6.0 | 90.0<br>91.6 | 90.8 | 6.0 | 26.0<br>27.2 | 26.4 | 6.0 | 8.1<br>6.0 | 7.1 |
| 7.0 | 82.6<br>79.8 | 81.2 | 7.0 | 36.2<br>30.8 | 33.5 | 7.0 | 7.3<br>5.6 | 6.4 |
| 8.0 | 77.5<br>74.8 | 75.1 | 8.0 | 28.3<br>27.4 | 27.9 | 8.0 | 6.8<br>6.2 | 6.6 |
| 9.0 | 78.3<br>76.2 | 77.1 | 9.0 | 30.1<br>28.6 | 29.3 | 9.0 | 8.3<br>7.1 | 7.7 |
| 9.8 | 71.1<br>72.2 | 71.7 | 10.0 | 31.0<br>27.8 | 29.4 | 9.8 | 8.1<br>7.5 | 7.8 |

(a) Calcium base with 6% total, 1% combined $SO_2$ at 135°C. for six hours. Liquor Ratio 50:1.

(b) Sample of periodate lignin SPL I.

(c) Sample of periodate lignin SPL II.

repeated twice with distilled water, and twice with cold normal hydrochloric acid, followed by two more water washes. When analysed at this stage, the material was essentially ash-free (Found 0.0-0.3%).

In order to investigate phenolic and acidic groups in the solid lignosulfonic acids, the ash-free solids were transferred with dioxane from the liner into two 15-ml. tapered tubes which were centrifuged and the supernatant liquid decanted. Fresh dioxane was added and triturated with the solid residue and the tubes again centrifuged. Five washings were required to obtain a supernatant liquid of the same refractive index as the original dioxane. The solid residue was then dried _in vacuo_ at 50°C. for four hours and used for the methylations with diazomethane.

Acid hydrolyses of the lignosulfonic acids were carried out with the residue from the deashing treatment. The liquor charge of 15.0 milliliters was added to the liner, which was then resealed. After cooking, the contents were washed into a tared sintered glass crucible with 50 milliliters of distilled water, were dried _in vacuo_ at 50°C. for four hours and weighed.

To isolate a hydrolysed lignosulfonic acid, the contents of the liner, after the hydrolysis, were filtered and the liner washed with 5 milliliters of distilled water. The filtrate and washings from two liners were combined and transferred into a 35 x 150 mm. test-tube fitted with a 29/42 standard taper neck. The test-tube was arranged for a distillation in which a jet passed nitrogen over the surface of the liquor. Approximately 30 milliliters of water was distilled from the liquor by heating over a steam bath under partial vacuum, but evaporation to dryness in this way was liable to cause formation of an unmanageable resin. The test-tube was therefore removed, and, after the contents had been frozen in an ice-salt mixture, was connected by an all glass system through a vapour trap to an oil pump capable of maintaining a vacuum of 0.05 mm. The test-tube was kept immersed in a Dewar flask containing a salt-ice mixture maintained at -5° to -8°C., while the vapour trap was held in a solid carbon dioxide-acetone mixture. All the ice had evaporated after the system had been kept _in vacuo_ for forty-eight hours and the residue of solid lignosulfonic acid was stored for further use.

## Oxidations with Alkaline Potassium Permanganate

Samples of alkali lignin from poplar wood (obtained from Howard Smith Paper Mills Limited, Cornwall, Ontario), and spruce periodate lignin before and after various treatments, were oxidized separately after the manner of Read and Purves (15). The oxidation was carried out at 75°C. with mechanical agitation in 0.25N sodium hydroxide which contained 6.25 gm. of the lignin per liter. Solid potassium permanganate was added in small increments over a period of nine hours until the total addition was ten times the weight of the original lignin, which was 30 to 50 gm. After the addition of the permanganate, the solution was kept at 75°C. and stirred for fifteen hours. It was convenient to use a constant levelling device during the oxidation. The device consisted of an 8-l. Erlenmeyer flask stoppered with a rubber plug through which was inserted an 18-inch length of 15-mm. glass tubing. After the flask had been filled with distilled water, it was inverted and supported over the oxidation bath with the tube immersed to a point just below the surface of the solution. This reservoir was found to contain sufficient water to maintain the bath at a constant level for twenty-four hours.

After the oxidation had become very slow, ethanol was added to reduce excess permanganate, and the solution was filtered to remove the manganese dioxide formed during oxidation. The residue from the filtration was triturated with hot water and the mixture refiltered, filtrate and washings being combined and the residue discarded. The combined solution was acidified with concentrated hydrochloric acid to pH 2.2 and was distilled under reduced pressure in an atmosphere of nitrogen until the volume was reduced from perhaps 8 or 9 to approximately 1.5 liters. The liquor, now free from carbonate, was made alkali to pH 10.2, heated to 60°C., and treated with a strong solution of 120 gm. of barium chloride dihydrate in water. This addition caused the precipitation of barium salts which were allowed to digest for thirty minutes at 60°C. and then cooled to room temperature. The precipitate was recovered by filtration, dried at 110°C. for four hours and weighed.

## Separation of Benzene Polycarboxylic Acids

The dried crude barium salts, obtained from the oxidation process, were reoxidized for twelve hours by being heated under reflux with 300 milliliters of concentrated nitric acid. This oxidation removed oxalic acid and reduced any aromatic keto-acids to the corresponding carboxyl group. The nitric acid was removed by distillation under vacuum and the solid material remaining was dried in vacuo at 50°C. over sodium hydroxide pellets. The residual dried barium salts were boiled for twenty minutes in 100 milliliters of distilled water, made alkaline to pH 10.2 with potassium hydroxide, to dissolve any barium nitrate, and after recovery the insoluble portion was dissolved in 100 milliliters of N hydrochloric acid.

A solution of 2N sulfuric acid was added slowly with agitation until all barium had been precipitated, and was followed by the addition of a few milliliters of 2.5% barium chloride solution to avoid the presence of even traces of sulfuric acid during subsequent evaporation of the filtrate to dryness. The near white crystalline mixed benzene polycarboxylic acids were finally dried *in vacuo* at 50°C. over phosphorous pentoxide and were separated exactly as described by Read (15). This separation depended on the facts that mellitic acid failed to form an ester when boiled with methanolic hydrogen chloride; benzene 1,2,4,5 tetracarboxylic (pyromellitic) acid yielded the neutral tetramethyl ester, while acidic esters were obtained from the two isomeric tetracarboxylic (which were absent) and from the pentacarboxylic acids. Figure VII summarizes the details of the separation.

## Methylation Procedures

*Diazomethane.* The preparation of diazomethane was based on the method of Arndt and Amende (106). Nitrosomethylurea was synthesized according to directions given in "Organic Synthesis" (107) and successful results were obtained for the three preparations carried out. The production of diazomethane by the following reaction

$$CH_3NNOCONH_2 + KOH \longrightarrow CH_2N_2 + KCNO + 2H_2O$$

utilized the procedure described in "Organic Synthesis" (108) for the preparation of a diazomethane solution. However, absolute dioxane, prepared according to Vogel (109), was substituted for ether as the solvent. This change was advantageous, since dioxane was one of the few organic liquids capable of wetting periodate lignin thoroughly (45).

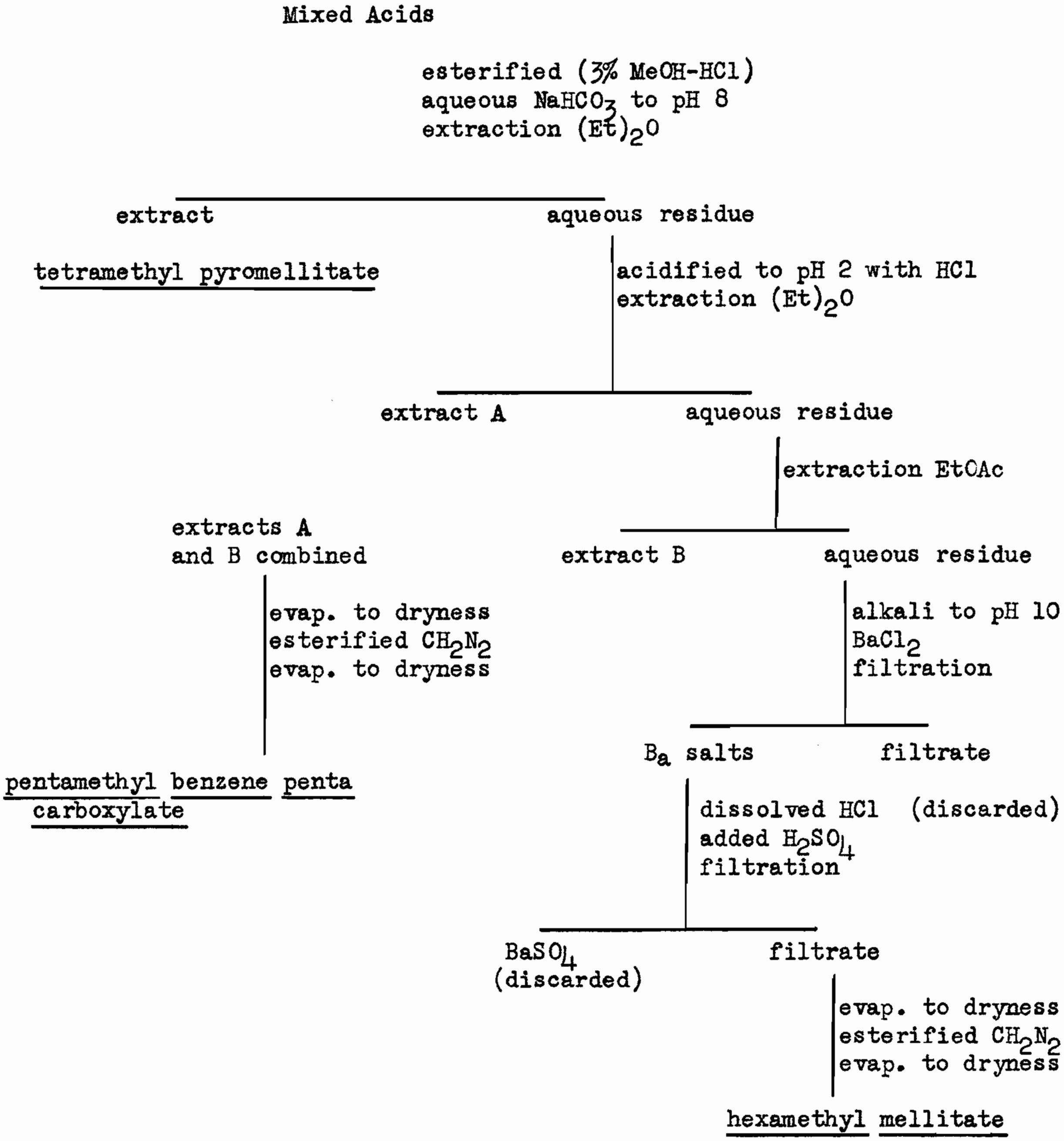


Figure VII

Flow Sheet for Separation of Mixed Benzene Polycarboxylic Acids

In the investigation of phenolic groups developed by pretreatments of periodate lignin, the diazomethane was employed in 10% solution. Approximately 1 gm. of the periodate lignin, pretreated or not, was washed, vacuum dried and placed in a glass reactor tube shown in Figure VIII. A few milliliters of absolute dioxane was added and the system sealed. A vacuum from a water aspirator was applied through the stopcock lead until the dioxane was brought to a boil. By this means, the lignin sample was freed of air and was thoroughly wetted before 10 milliliters of dioazomethane in dioxane was added. The system was sealed with elastic bands and shaken on a rocker table for two hours. An additional 10 milliliters of diazomethane solution was added and the system shaken overnight. The lignin residue was washed out of the reaction tube with absolute dioxane, was recovered on a small Buchner funnel and was extracted with 10 milliliters of petroleum ether. The solid residue was vacuum dried and the methoxyl content determined. Methylations were repeated until the methoxyl content of the product ceased to increase.

In the study of phenolic groups formed by sulfonation and posthydrolysis, a modification of technique was employed which permitted the use of as little as 0.3 gm. of lignosulfonic acid and used much less nitrosomethylurea. The sample was placed in a 25 x 220 mm. test-tube, and 10 milliliters of absolute dioxane added. The tube was sealed with a stopper and evacuated until the dioxane boiled. The test-tube was opened and placed under the outlet tube of a specially constructed small scale diazomethane generator, see Figure IX, and the gas bubbled through the dioxane suspension. When the diazomethane was completely removed from the generator charge, the test-tube was attached through a mercury seal to a

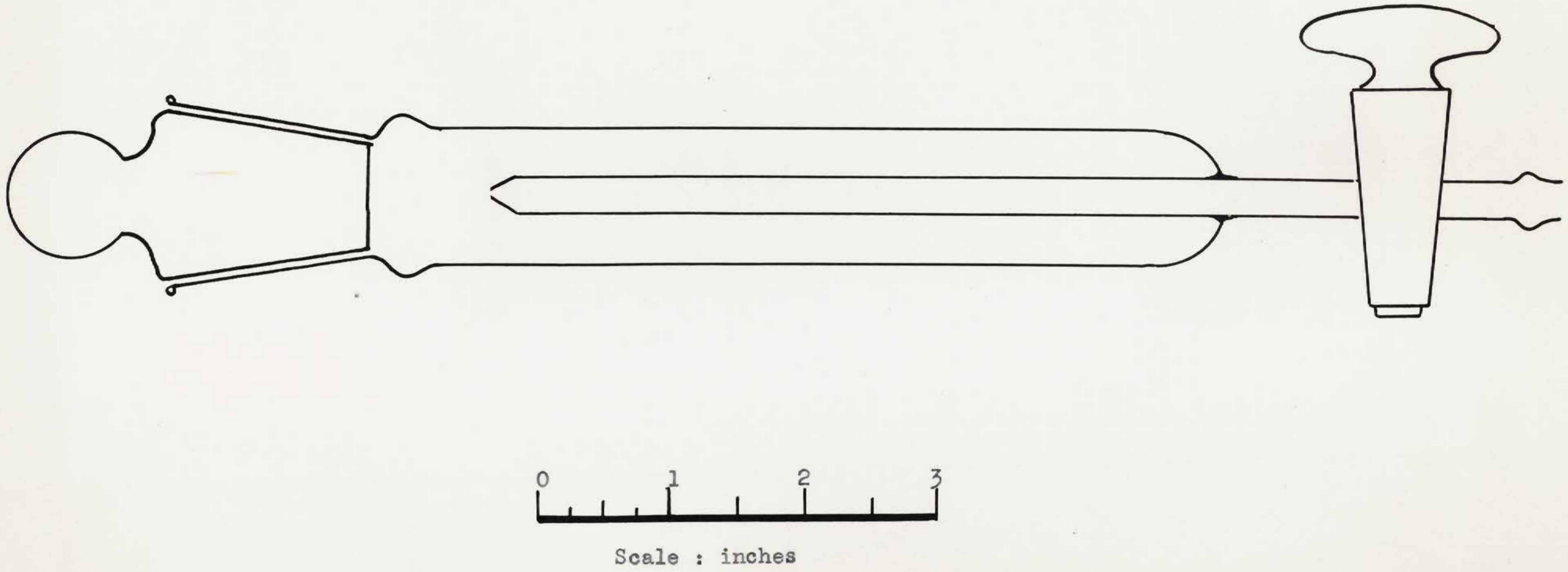


Figure VIII - Methylation Reactor Vessel

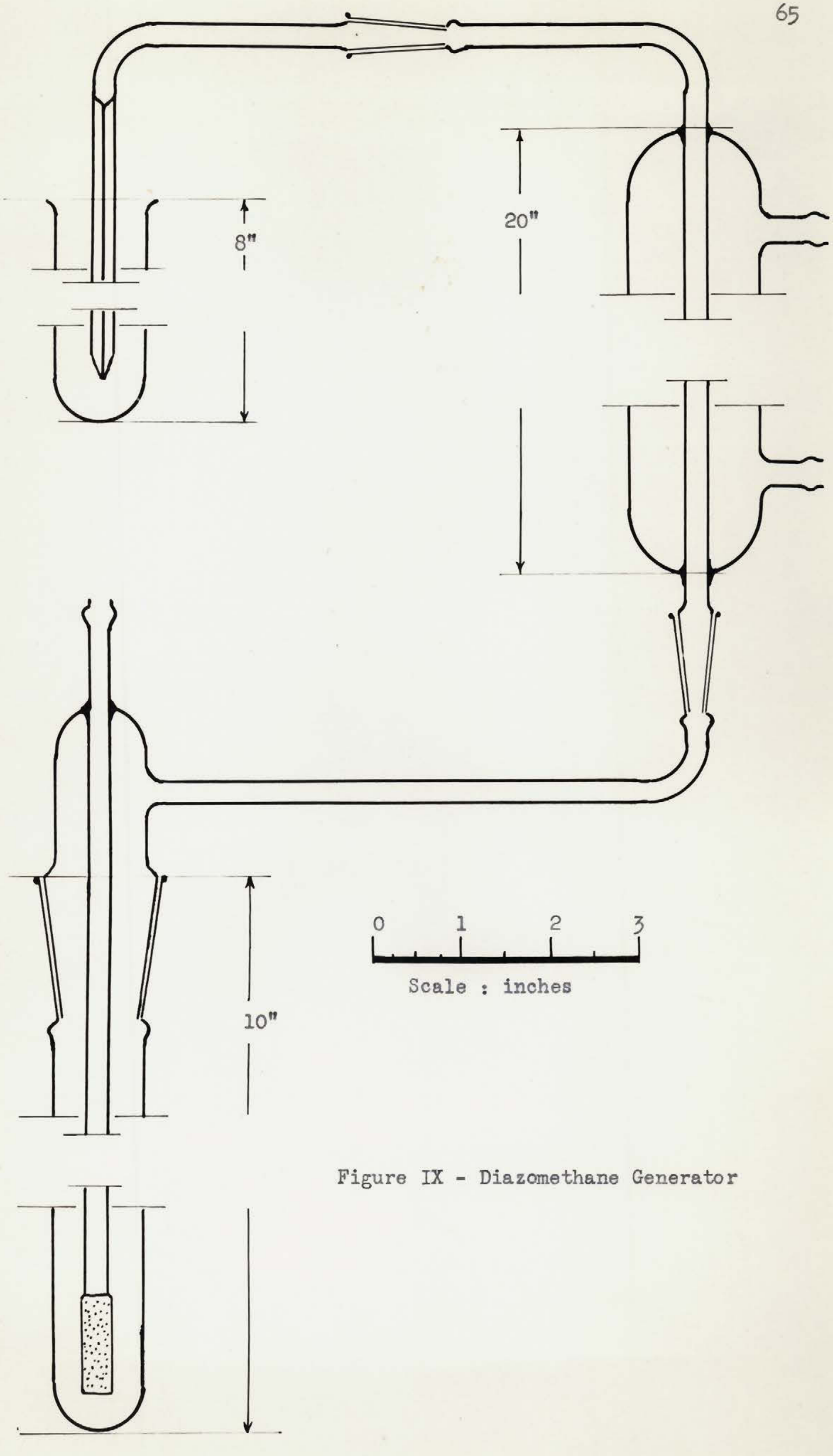


Figure IX - Diazomethane Generator

mechanical stirrer and the contents were agitated for twelve hours. The contents of the test-tube were then filtered in a small Buchner funnel and washed with 10 milliliters of dioxane and 10 milliliters of petroleum ether. The solid residue was vacuum dried and analysed for methoxyl content. Methylations were repeated until two successive methylations yielded products of similar methoxyl content.

The small-scale generator for the production of diazomethane was constructed from a 25 x 220 mm. Pyrex test-tube to which a 24/40 standard taper joint was sealed. A 24/40 standard taper joint with an inner sealed tube ending in a glass fritted dispenser was fitted into the test-tube for the passage of nitrogen gas through the system. A reflux condenser was connected to the side of the inner seal through a 12/30 standard taper joint. The opposite end of the reflux condenser was connected to a capillary bubbling tube by means of a 12/30 joint. The test-tube containing the sample to be methylated was placed below the bubbler tube during operation. The quantities of materials employed were 5 gms. of nitrosomethylurea, 9 ml. of 50% potassium hydroxide, and 20 ml. of ether. Approximately one gram of diazomethane was produced during each run.

<u>Dimethyl Sulfate.</u> The methylation was based on a general procedure outlined by Vogel (110), depending on the reaction

$$ROH + (CH_3)_2SO_4 + NaOH \longrightarrow ROCH_3 + CH_3NaSO_4 + H_2O$$

where R is an aliphatic or aromatic system, but was scaled down to 0.5 gm. samples. The sample was placed in a 25 x 220 mm. test-tube and 5 milliliters of distilled water was added. After bringing the liquid to a quick boil by reducing the pressure, a mechanical stirrer was arranged to agitate the contents of the test-tube. The caustic soda solution, 0.2N, was added dropwise by burette until 0.5 milliliter was released, at which time a 30% solution of dimethyl sulfate in dioxane was added at an equal rate until 5 milliliters of each solution were added. The agitation was continued for thirty minutes before the product was recovered on a filter, washed and dried *in vacuo*.

## Analytical Methods

*Methoxyl.* Methoxyl contents were determined by the method of Viebock and Schwappach (111) and Viebock and Brecher (112) as modified by Penniston and Hibbert (113). Approximately 20 mgm. of accurately weighed dry sample was employed.

*Klason Lignin.* The two samples of spruce periodate lignin were analysed by the method outlined in "TAPPI Standards" T-222-M-42 (114). Approximately 200 mgm. of accurately weighed dry sample was employed. Values obtained are shown in Table III.

*Holocellulose Analysis.* The method used was that of Kurth and Ritter (115) and was based on the exhaustive extraction of a 300-mgm. sample with alcohol-pyridine alternated with a series of brief chlorinations.

*Moisture and Ash.* Samples of 1.0 gm. of the air dried lignin were heated for four hours at 110°C. in a porcelain crucible and the loss in weight was considered as the moisture content. The ash content of periodate lignin was determined by heating the crucible and residue from the moisture determination at 750°C. for four hours. The weight of the residue was considered as the ash content of the original charge.

Ash values, as determined during the sulfonation studies, were carried out according to the micro method outlined by Pregl (116), but the low ash content of the samples required the use of 20-mgm. samples.

Sulfur Analyses. The determination of the sulfur content of lignosulfonic acids, produced by the cooking of periodate lignin with 9% sodium bisulfite solution, was according to the method of Grote and Krekler (117), modified according to Ramberge and Bäcklund (118). The method was based on the combustion in air of a 100-mgm. sample in a specially constructed quartz tube. The sulfur dioxide formed was caught in a scrubbing tower and oxidized with dilute hydrogen peroxide to sulfuric acid, which was titrated with dilute standard sodium hydroxide. A blank allowed for the presence of acid in the hydrogen peroxide reagent.

During the investigation of phenolic groups formed in lignosulfonic acids the analyses for sulfur were made by peroxide fusion in a micro Paar bomb. The procedure was that indicated in the operating instructions published by the Paar Instrument Company, Moline, Ill. (119). The barium sulfate formed during the analysis was collected, ignited and weighed in a micro Gooch crucible, using asbestos as the filtering medium. Sample size was increased to 20 mgm. because of the low sulfur content.

Micro Carius determinations for sulfur, according to the method outlined by Pregl (120), were attempted, but in all cases where periodate lignin was present the tubes exploded on heating to 280°C.

A titrimetric method described by Mahoney and Michel (121) based on a tetra hydroxy quinone indicator for barium ion was attempted, but found to be unsuitable for the low sulfur content of the sample and subject to a number of inaccuracies.

Active Hydrogen. The determination of active hydrogen groups in samples of periodate lignin altered by pretreatment was carried out in micro scale on the basis of a procedure outlined by Niederl and Niederl (122). The analysis employed methyl magnesium iodide as the active reagent. A sample of known weight, about 60 mgm., was charged into the reaction chamber and 1 milliliter of absolute dioxane was added. The chamber, after being evacuated to boil the dioxane and wet the sample, was attached to the manometer, and the determination carried out.

# DISCUSSION AND RESULTS

## The Effect of Pretreatments on Solubility of Periodate Lignin in a Standard Sulfite Cook

The research started with two preparations of periodate lignin, the second of which was on a larger scale than heretofore, and involved technical difficulties in washing the partly oxidized wood. These difficulties were successfully overcome, and the satisfactory nature of the product was shown by a relatively high methoxyl content, by a negligible holocellulose fraction, and by the ability to dissolve almost completely in a standard bisulfite cook (Table III).

In the initial investigation, the samples, when heated in buffered aqueous solutions at 100°C. and higher, lost weight to a degree that depended on both the hydrogen ion concentration and the temperature. It soon became apparent that a quantitative study of the effect required a close control of the operating conditions, especially at the higher temperatures. Special equipment was therefore constructed so that twelve small glass bombs could be heated and cooled, with gentle agitation, under exactly the same conditions in an oil bath kept to within 1°C. of the desired temperature. The determinations, which were carried out in duplicate, were closely reproducible at 100°C. (Table IV) but at 120°C. and particularly at 150°C. reproducibility was somewhat impaired. Nevertheless, it was obvious that there was a well marked minimum solubility in hot aqueous solutions having a pH of about 5, and that this minimum was independent of the temperature (Table IV, Figure X). In addition, the aqueous liquor was

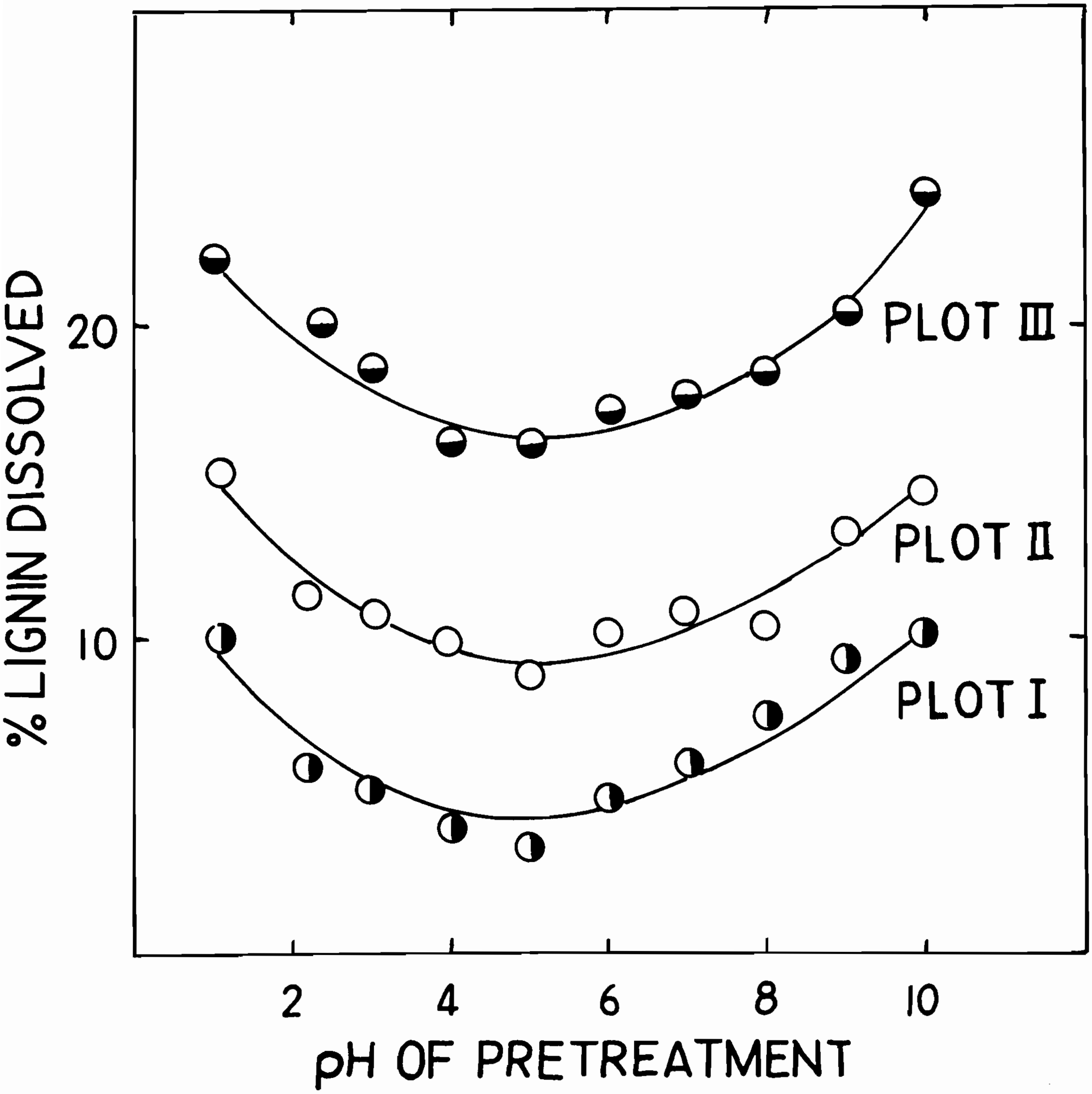


Figure X - Solubility of Periodate Lignin on Pretreatment

Plot I - Periodate Lignin SPL I for four hours at 100°C.
Plot II - Periodate Lignin SPL I for four hours at 120°C.
Plot III - Periodate Lignin SPL II for four hours at 150°C.

found to have changed its hydrogen ion concentration during the cooks. Although the changes were slight, they always made the solution more acidic after pretreatments in buffer solutions of pH values higher than 4, and more alkaline for solutions of pH 3 and lower. The lignin itself, or material derived from it, therefore acted as a buffer to pH 3 to 4 in these experiments. The colour of the undissolved periodate lignin gradually changed from the original pale brown, retained after acid treatments, to a dark black-brown shade as the pretreating solutions were made more and more alkaline. The liquors also exhibited a similar gradual colour change from a pale strat at pH 1 to a deep dark brown at pH 10.

The effect of hydrogen ion concentration on the solubility of lignin in superheated water had heretofore not been reported. However, some workers (123)(124) observed a sparing solubility of lignin, particularly in hot acid solutions. The slight changes in the pH values of the buffers before and after cooking were not in agreement with the absence of change found by Corey and Maass (90), who treated spruce wood meal in McIlvaine's buffers at a liquor to solids (as lignin) ratio of 30:1. A difference in experimental conditions, however, might explain this discrepancy. Richter (101), who cooked western hemlock with distilled water, observed that the solutions became acidic, especially as the temperature increased. From his data, shown in Table II, hydrogen ion concentration of the solution, after pretreatment at 170°C., was 3.5 and, as the temperature increased to 170°C., the value appeared to reach an equilibrium value in this range. Hence, it was possible that some weakly ionizing acid was produced during the cook which altered the pH to the observed values, depending on the concentration. Since similar treatments showed that periodate lignin also tended to buffer the liquor to pH 3 or 4, a similar acid might have been produced by the periodate lignin alone. Although it has been claimed that acetic acid was produced during the hydrolysis of wood, an acetyl determination on spruce periodate lignin was found to be negative. This determination was made by the method of Ost (125) as modified by Lemieux (126), in which the sample is distilled with aqueous phosphoric acid and acetic acid recovered in the distillate.

A cursory investigation was made of the liquor obtained by a pretreatment of periodate lignin at pH 1 and 150°C. for four hours. The liquor was exhaustively extracted with ether and n-butanol, which removed the brown colour. Evaporation of the extracts left 18% of the lignin as a brown tar with a methoxyl content of 3.3, 3.7%. Another portion of the original liquor (pH 1 and 150°C.) yielded the ultra-violet absorption curve shown in Figure XI. Before this examination, the sample was diluted 1:100 with distilled water, and the estimated lignin content calculated from the loss in weight during the pretreatment was 0.0529 gm. per liter. The slit-width for this determination was 0.662 mm. throughout. The inflections in the absorption plot corresponded to a minimum at 250 Å and a maximum at 280 Å. Many workers (127)(128)(129) claimed that the general shape of this plot, and particularly a minimum and maximum in the exact positions found, were characteristic of lignosulfonic acids, other lignin derivatives and definitely of phenols or other benzene rings substituted by oxygen. The slender evidence available therefore suggested that acidic treatments separated a soluble phenolic compound of low methoxyl content from the periodate lignin. Analysis of the residual lignin showed that

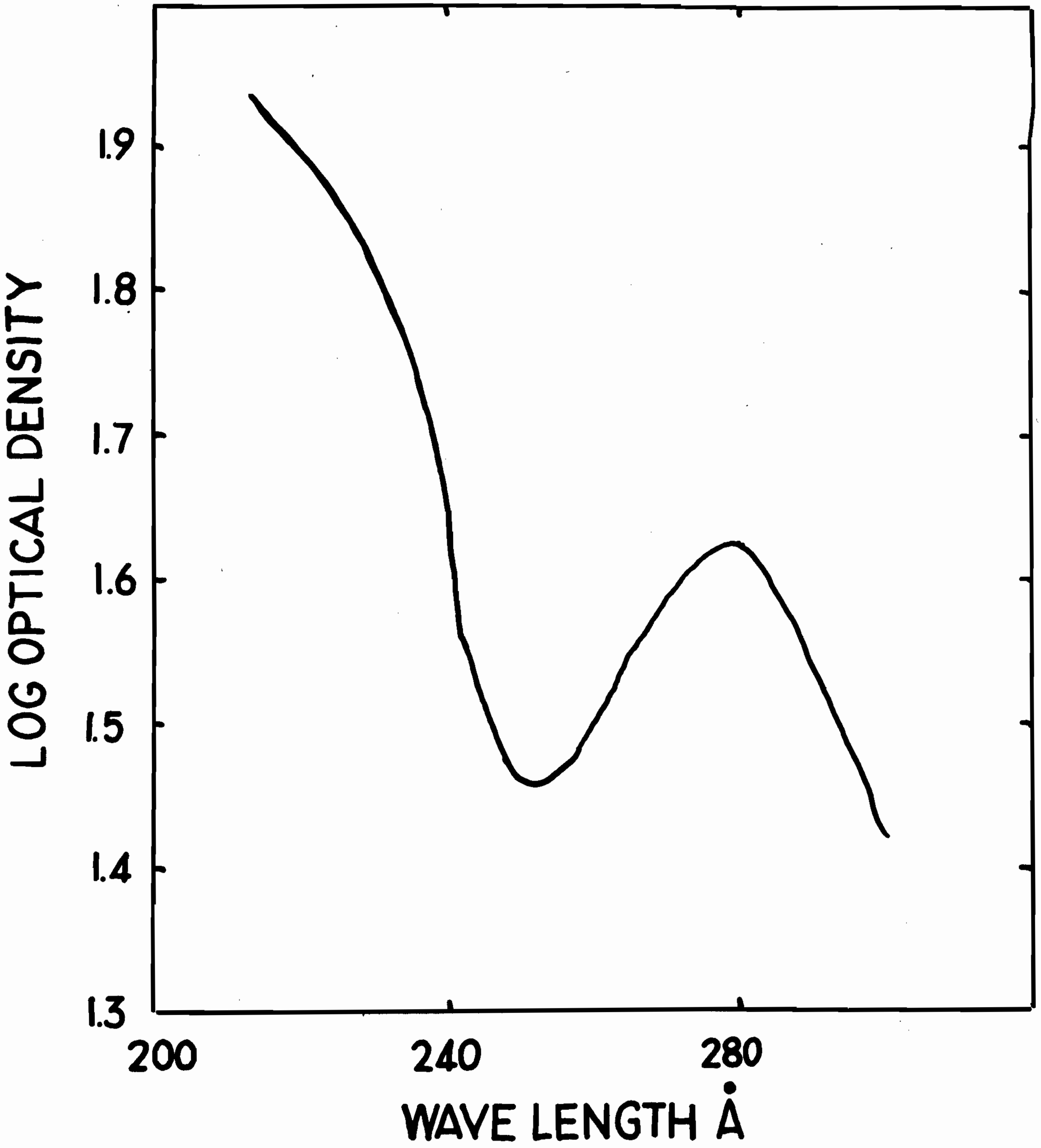


Figure XI - Ultra-violet Absorption Spectrum of Residual Pretreating Liquor(a)

(a) Pretreatment at pH 1 and 150°C. for four hours, sample diluted 100:1.

the methoxyl contents remained the same (Table VII, column 3) with the exception of pretreatments at pH 1. In this case, the initial value was increased from 11.3 to 12.4% after treatments at 120°C. and to about 13.1% at 150°C. It was interesting to note that, since the 22% dissolved at 150°C. had a methoxyl content of 3.5%, and the 78% residue had 13%, calculation by the rule of mixtures gave 10.9% for the original lignin. The near concordance of this with the value of 11.3% actually found suggests that almost all methoxyl units were recovered. If 18% of the lignin was assumed to be dissolved (i.e. the amount recovered by the extraction of the liquor) and 82% undissolved, the calculated value for the methoxyl content of the original sample was indeed 11.3%.

Heuser and co-workers (130), by using 5% hydrochloric acid at 170-180°C. for a long time, succeeded in reducing the methoxyl content of a lignin sample to only 5.79%. However, Phillips (123) found no decrease from the original value when he subjected a Willstater lignin alternately to fuming hydrochloric acid at 8 to 10°C. for twenty-four hours and to boiling 5% hydrochloric acid for one hour. As the cold and hot extractions were repeated, Phillips was able to detect a loss in weight of the lignin and tentatively explained this behaviour as a degradation of the lignin complex which had proceeded without creating a difference in the methoxyl contents of the soluble and insoluble portions. The opposite result observed in the present case might be connected with the probability that periodate lignin had been somewhat oxidized during its isolation. Oxidation of phenolic ethers is frequently attended by loss of alkoxyl groups and the formation of quinones (131) and such an occurrence would explain the fact that the methoxyl content of periodate lignin was less than the

## TABLE VII

## Methoxyl Contents of Pretreated Lignins(a)

| Pretreatment(b) | | |
|---|---|---|
| pH | Temp. °C. | Methoxyl % |
| nil | nil | 11.3, 11.3 |
| 1.0 | 120 | 12.4, 12.4 |
| 5.0 | 120 | 11.5, 11.5 |
| 9.0 | 120 | 11,2, 11.1 |
| 1.0 | 150 | 13.4, 12.8<br>13.1, 12.8 |

(a) Sample SPL II.

(b) Cooked for four hours.

calculated value of about 15% (41). These oxidized portions of the complex might be more prone to hydrolysis and would be preferentially removed to leave a residue of higher methoxyl content. Such a process would also account, in part at least, for the high losses of lignin during acid treatment. Table V and Figure XII show that at pH 1 these losses increased linearly or nearly so with the temperature of the pretreatment, which as usual was for four hours. No similar study was undertaken at pH 4 to 5, where the losses and the solubility were at a minimum.

For the purpose of comparing the effects of various pretreatments on the ability of periodate lignin to pulp in a sulfite cook, its solubility in hot sulfite liquor was determined under rigorously standardized conditions. These conditions, which were similar to those employed in commercial bisulfite pulping procedures and by a number of workers in the laboratory (41)(48), required heating the sample for six hours at 135°C. in a calcium base sulfite liquor of 6% total and 1% combined sulfur dioxide, with a liquor to solids ratio of 50:1. The development of a semi-micro technique, which could control the various operating conditions, made it possible to investigate periodate lignin residues in quantities as small as 0.250 mgm. with reasonable accuracy.

In agreement with the results of Ritchie and Purves (41), the untreated samples of spruce periodate lignin could be pulped to a residual yield of less than 10%. The resulting deep brown "waste" sulfite liquor yielded a precipitate with $\beta$-naphthylamine, which is a reaction characteristic of lignosulfonic acids. The solid portion that remained from the cook was a brown, flocculent gel that in no way retained the morphological structure of the original material. Filtration of this solid was difficult

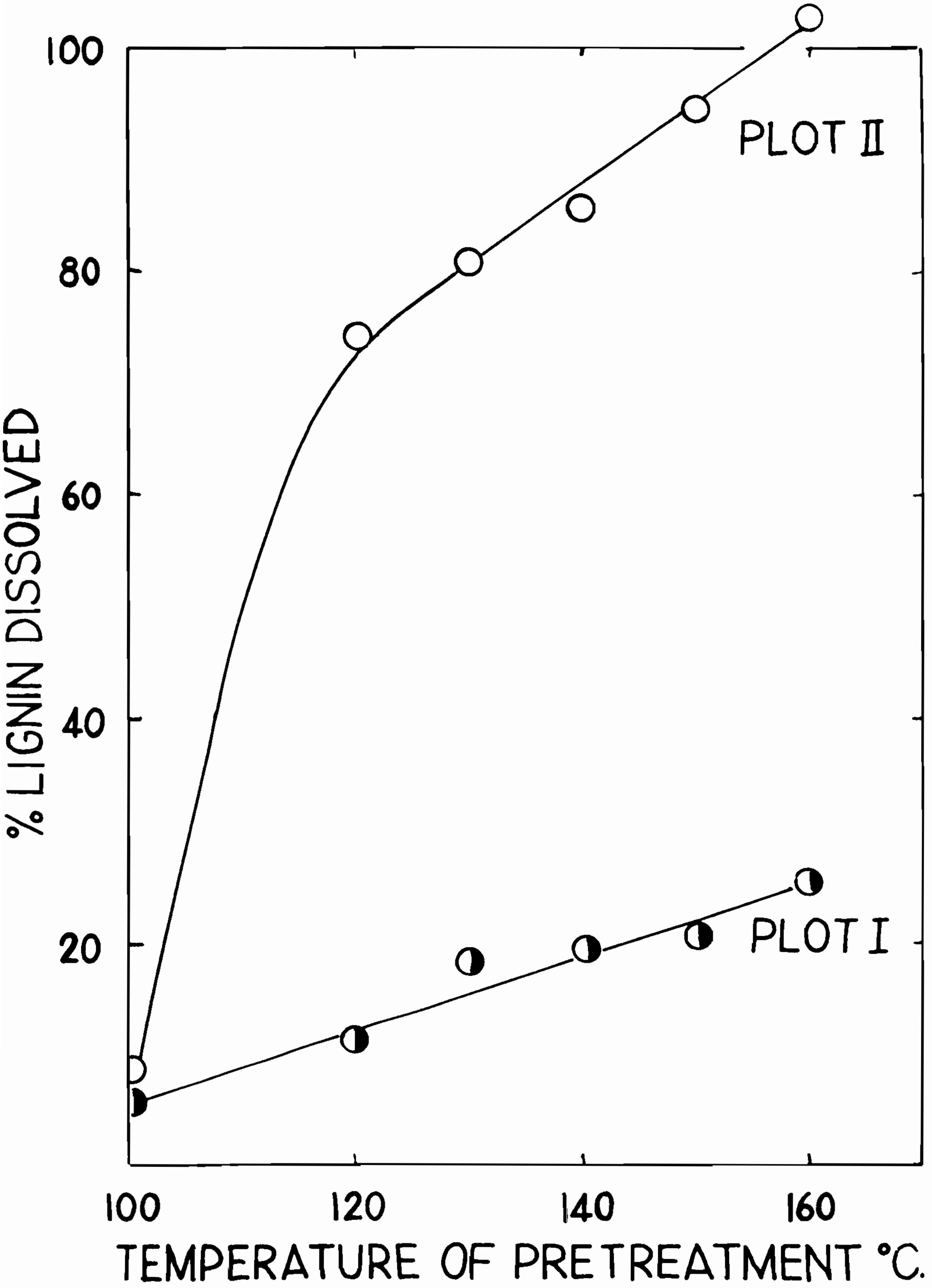


Figure XII - Effect of Temperature of Pretreatment on Solubility in Buffer and Subsequent Insolubility in a Standard Sulfite Cook

Plot I - Solubility of periodate lignin SPL II at pH 1 for four hours.
Plot II - Insolubility of the pretreated residues in a standard cook at 135°C. for six hours (calcium base, 1% combined and 6% total sulfur dioxide, liquor ratio 50:1).

because of complete clogging of the filter. By centrifuging and finally using 95% ethanol, the gel could be collapsed and recovered. The solid residue when dried became dark brown in colour and very brittle. The application of the standard cook to the pretreated lignins resulted in liquors which varied in shade from pale brown from lignins pretreated at a high temperature to deep brown from treatments at 100°C., the latter liquor being quite similar to that obtained from the original periodate lignin. These sulfite "waste" liquors were on the whole considerably lighter in colour than those obtained in commercial operations. It was also noted that, as the temperature of pretreatment was increased, the resulting residues became less swollen, until at 160°C. they were of the same granular appearance as the original material, but much darker in colour and more friable.

The standard cook revealed that the effect of hydrogen ion concentration during pretreatment of the periodate lignin was most marked at a temperature of 100°C. (Figure XIII, Plot I), while results with lignin pretreated at 150°C. were independent of this factor (Plot III). Although the curve in Plot II for 120°C. was less pronounced than in the one for 100°C., it confirmed the tendency for maximum solubility to be retained after pretreatments at pH 4 to 5.

The effect of pretreatments on the subsequent ability to pulp was also explored by heating different samples of the lignin, buffered to pH 1, for four hours at the temperatures plotted as the abcissae in Figure XII. As already mentioned, the amount of lignin dissolved in the pretreatment increased almost linearly with the temperature (Plot I), but when the residues were subsequently submitted to the standard cook,

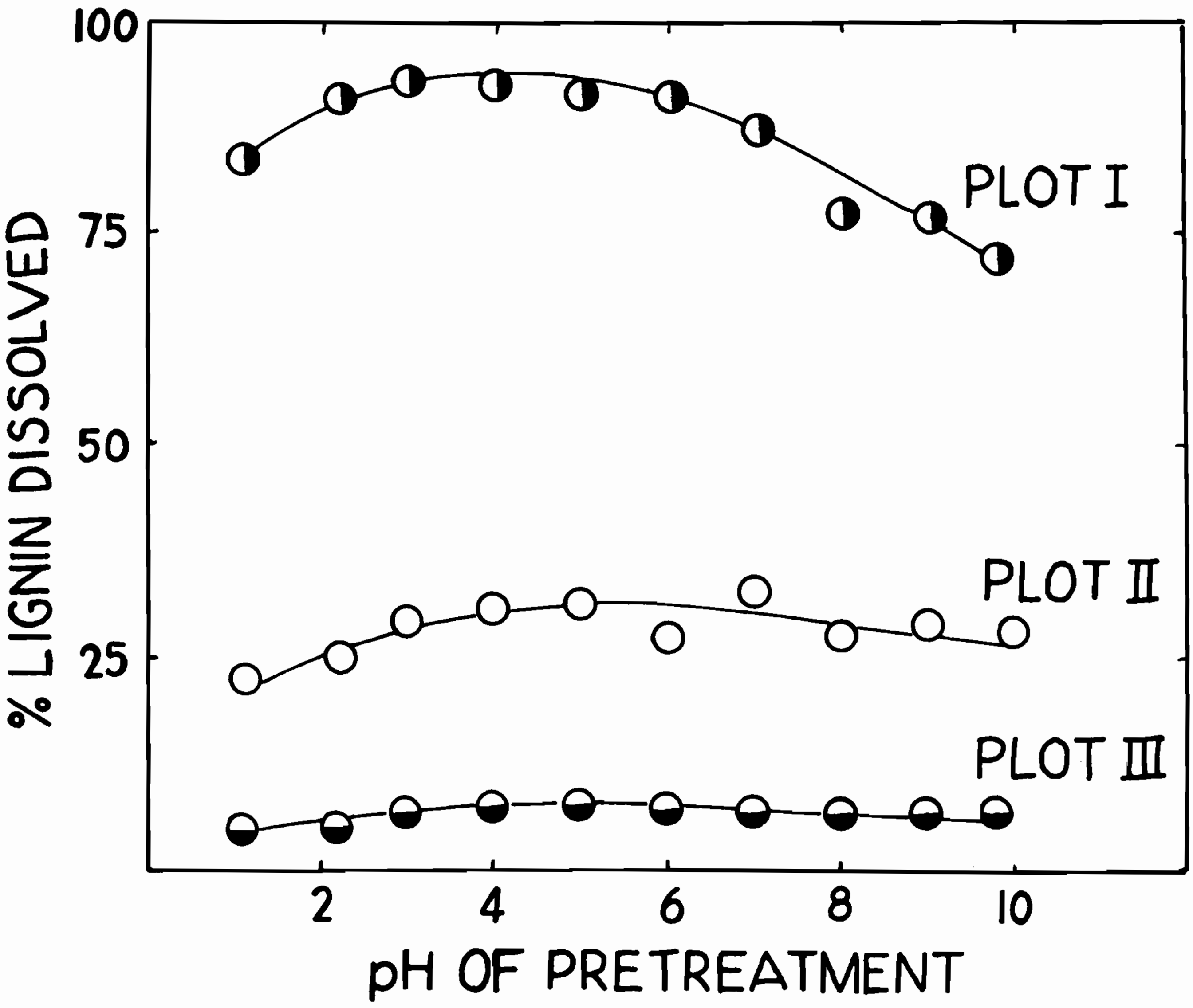


Figure XIII - Solubility of Pretreated Lignins in a Standard Sulfite Cook

Plot I - Pretreated at 100°C. for four hours.
Plot II - Pretreated at 120°C. for four hours.
Plot III - Pretreated at 150°C. for four hours.

the amount dissolved decreased very sharply between 100° and 120°C. The periodate lignin had apparently undergone a marked change in this temperature range. It was interesting to note that when 160°C. was reached, the amount dissolved had an apparent negative value because the residues in duplicate experiments were 102.8, 103.8% of the original weight pulped. Analysis by the Grote-Krekler method (117), however, revealed that this sample contained 6.62, 6.53% of sulfur, which would amount to about 20% of calcium lignosulfonate units if present in this form. The high yield was therefore quite understandable.

The results for the effect of pretreatments at various hydrogen ion concentrations on the subsequent solubility of periodate lignin in a standard cook agreed in general with the observations of Corey, Calhoun and Maass (48), who noted that wood meal was most easily delignified in a bisulfite cook after pretreatments between pH 4 to 5. Their claim that this behaviour was independent of the temperature in the range 100° to 135°C. was not entirely supported in the present work, because the effect of an increase of temperature was found to override that of hydrogen ion concentration until the latter virtually disappeared at 150°C. Richter (101), in his investigation of the pulping of western hemlock pretreated at various temperatures, also observed that delignification became increasingly difficult with increase in the temperature of pretreatment. Since the lignin content of the pretreated wood was not given, and considerable amounts of holocellulose were dissolved as well as some lignin, it was impossible to make an assessment of his results in other than a qualitative way.

In reviewing the results for the aqueous pretreatments of periodate lignin, it appeared that two factors were in operation. The first of these was the solubilizing of a minor portion of the lignin complex. Although the low methoxyl content of the portion cleaved suggested that a previously oxidized fraction had been lost, any prior oxidation was probably not an essential factor, since the unoxidized lignin in wood behaved in qualitatively the same way. The fact that the reaction occurred in alkaline solution tended to eliminate the possibility that cleavage concerned acetal bonds, which are usually stable to alkali. Ester bonds were unlikely because none were detected in periodate lignin. The probability therefore seemed to be that the bonds cleaved were ethers of complex phenols or of unsaturated derivatives produced by side reactions. The second factor concerned the failure of pretreated lignins to be successfully solubilized in the standard cook. If Hägglund (75) was correct in his assumption that the pulping reaction was sulfonation of the lignin complex, by either substitution or addition, followed by hydrolytic cleavage to soluble fragments, then failure to pulp involved a blockage of both or either of these stages. From the observation that drastically pretreated periodate lignin contained 6% sulfur, presumably as sulfonic acid, it would appear that the hydrolytic stage was the one not operating according to theory. It thus appeared that the pretreatments caused some sort of molecular rearrangement or condensation in the undissolved residue, that kept it insoluble even when cooked in the standard way. As their severity increased, the pretreatments therefore rendered the periodate lignin more and more analogous to Klason, Willstätter, alkali and other common types of isolated lignin. Since the presence of condensed ring structures in these lignins was made probable by the increased amounts of crude benzene carboxylic acids they yielded when oxidized drastically with alkaline potassium permanganate (15), the pretreated lignins were submitted to the same procedure.

## Oxidations of Pretreated Periodate Lignins with Alkaline Permanganate

To ensure that the procedure used would produce results comparable to those of Read (15) another sample of the alkali lignin which he examined was again oxidized. An untreated sample of periodate lignin (SPL II) was oxidized as a control and then two samples of the same lignin which had been pretreated at pH 2.2 for four hours at temperatures of 135°C. and 160°C., respectively. The pretreatment at 135°C. was chosen to be comparable with commercial pulping conditions, while that at 160°C. was found by previous experiment to result in a lignin residue that was virtually insoluble in a standard sulfite cook. As Table VIII shows, these large scale pretreatments caused losses in weight owing to dissolution, and conferred insolubilities in a subsequent cook, to degrees that checked well with those previously observed on the semi-micro scale.

The samples, of weights noted in Table VIII, were oxidized by hot alkaline permanganate as described in the Experimental portion, but when the manganese dioxide was recovered at the end of the process, it was observed to contain small particles resembling the original lignin in appearance. The manganese dioxide was therefore redissolved in sulfurous acid and caustic soda, and a residue, amounting to less than 5% by weight of the original lignin, was recovered. This residue was separately reoxidized in a manner similar to the large scale operation, but in standard laboratory equipment, and the products added to the original

## TABLE VIII

### History of Samples for Alkaline Permanganate Oxidation

| Sample | Material | Pretreatment[a] Temp. °C. | Pretreatment[a] Loss % | Insolubility[b] in Standard Cook % | Weight[c] of Sample gm. |
|---|---|---|---|---|---|
| A | Alkali Lignin | - | - | - | 50 |
| B | Periodate[d] Lignin | - | - | 8.7 | 50 |
| C | Periodate[d] Lignin | 135 | 17.6 | 84.8 | 29.3 |
| D | Periodate[d] Lignin | 160 | 25.6 | 103.1 | 29.8 |

(a) In buffer solution pH 2.2 for four hours.

(b) Cooked in 6% total, 1% combined calcium base sulfite liquor, 135°C. for six hours; liquor to solids ratio, 50:1.

(c) Air dried.

(d) Sample SPL II.

oxidation liquor. Oxalic acid, benzene polycarboxylic acids and unidentified substances were then precipitated as insoluble crude barium salts (Table IX), which were then boiled in concentrated nitric acid. This treatment destroyed oxalic acid, and complete evaporation recovered the other barium salts in a purified condition.

After the acids had been isolated from these salts, they were esterified by boiling in methanolic hydrogen chloride, and the separation of the unesterified mellitic acid, the partially esterified benzene penta carboxylic acid and the completely esterified benzene 1,2,4,5-tetracarboxylic acid carried out as described by Read (15), as shown in the flow sheet (Figure VII), and as quantitatively as possible. The yields, by weight, of the crude esters are recorded in Table IX, together with those of the pure neutral esters obtained from them by methylation with diazomethane. The identity of the pure esters was checked by means of their melting points, which were correct and undepressed by admixture with authentic samples prepared by Read. As Read noted, only the alkali lignin yielded mellitic acid in the form of a crystalline neutral ester, and the traces of uncrystallised gum isolated in other cases were not claimed as consisting essentially of this ester. The neutral methyl ester of the penta acid on first separation remained as a syrup, but crystallised when remethylated with diazomethane and seeded.

Since isolation of the pure neutral esters by crystallisation of the crude products of the diazomethane methylations was very wasteful, the results in Table X were rexpressed in percentages based on the crude yields, but corrected from methyl ester to free acid. This course made them comparable to Read's figures. As Table X shows, Read's results with his

# TABLE IX

## Oxidations to Benzene Polycarboxylic Acids

| | Sample of Lignin | | | |
|---|---|---|---|---|
| | A | B | C(a) | D(b) |
| $KMnO_4$ used - gm. | 500 | 500 | 300 | 300 |
| Crude Ba Salts - gm. | 69.1 | 106.7 | 49.2 | 31.3 |
| Crude Mellitic acid - gm. | 0.643 | 0.381 | 0.381 | 0.322 |
| Neutral ester - gm. | 0.099 | 0.010 | 0.025 | 0.035 |
| M. Pt. - °C. | 178-182 | (c) | (c) | (c) |
| Crude Partial ester - gm. penta acid | 1.545 | 0.360 | 1.992 | 2.323 |
| Neutral ester - gm. | 1.500 | 0.365 | 1.721 | 1.835 |
| M. Pt. - °C. | 146-148 | 147-148 | 147-149 | 146-148 |
| Crude 1,2,4,5-tetra methyl ester - gm. | 0.371 | 0.185 | 0.212 | 0.195 |
| M. Pt. - °C. | 141-142 | 141-143 | 142-143 | 142-143 |

(a) pretreated at pH 2.2 and 135°C. for four hours.

(b) pretreated at pH 2.2 and 160°C. for four hours.

(c) no crystalline material observed.

## TABLE X

### Crude Yields of Benzene Polycarboxylic Acids[a]

| Sample | Lignin | Crude[b] 1,2,4,5-tetra % | Crude[b] penta % | Crude[b] hexa % | Total % |
|---|---|---|---|---|---|
| | Alkali[c] | 0.65 | 3.94 | 0.22 | 4.81 |
| A | Alkali[d] | 0.74 | 3.00 | 0.20 | 3.94 |
| | Periodate[c] | 0.20 | 0.77 | nil | 0.97 |
| B | Periodate[e] | 0.37 | 0.73 | nil | 1.10 |
| C | Periodate[f] | 0.60 | 4.91 | nil | 5.51 |
| D | Periodate[g] | 0.57 | 5.15 | nil | 5.72 |

(a) After exhaustive oxidation with hot alkaline potassium permanganate.

(b) Corrected from yields of neutral methyl esters.

(c) Values obtained from Read (15), Table I.

(d) Repeated oxidation of same sample of lignin.

(e) Oxidation on untreated SPL II sample.

(f) SPL II sample pretreated at pH 2.2 and 135°C. for four hours.

(g) SPL II sample pretreated at pH 2.2 and 160°C. for four hours.

alkali lignin were satisfactorily duplicated, and the data from his periodate lignin were comparable with those from the present sample. It is apparent that the pretreatments, even that at 135°C., increased the yields of the benzene tetra and penta carboxylic acids to values comparable to those observed for lignins isolated by strongly acid or alkaline treatments. The results therefore showed that such changes were promoted by relatively mild conditions similar to those encountered in a technical sulfite cook.

There are, however, a number of criticisms which cast some doubt on the meaning of the results of this method of this oxidation. In the first place, the mere formation of benzene polycarboxylic acids did not necessarily mean that the nucleii from which they were obtained were directly connected with the later insolubility of the lignin. Similar oxidation studies on soluble lignosulfonic acids would tend to clarify this point, since they would reveal the presence or absence of soluble derivatives containing the nucleii producing the benzene polycarboxylic acids. A second criticism was that the conditions of oxidation were probably not sufficiently controlled, either in the present work or in those of Read (15) and Bone and his collaborators (24). Even at best, the oxidation of the various polyalkylated benzenes and naphthalenes studied by Read gave yields of the corresponding acids that fluctuated between 20% and 80% of theory. For this reason, the yields in Table X provided no information about the abundance of the precursors of the acids in the lignins oxidized; these amounts might be less than 5%, or more than perhaps 30% by weight. One of the first improvements, then, would be to keep a uniform excess of oxidant at all times, and a more closely regulated temperature and alkalinity. In addition, the materials undergoing oxidation should be of similar particle size, since they were insoluble and the rates of oxidation in the heterogeneous system might vary with consequential changes in yields. A final criticism concerned the involved and non-quantitative method used to separate the individual benzene polycarboxylic acids. An immense improvement would be the application of a simple method to isolate in a clear cut way the barium salts of the mixed poly acids, as oxidation with nitric acid, followed by removal of barium through ion exchange on a suitable resin. The pure mixed acids might then be separated by some adsorption method which would be absolute and quantitative.

## Hydroxyl Groups in Pretreated Lignins and Lignosulfonic Acids

A preceding section showed that acidic treatments of periodate lignin caused the solution of a minor portion, perhaps by the hydrolysis of phenolic ether bonds. If this guess was correct, the insoluble portion might have retained some free phenolic groups in spite of the nuclear condensations that the acidic treatments were also supposed to promote. To test this hypothesis, samples of periodate lignin were heated at pH 1 for four hours at either 120°C. or 150°C. and were thoroughly methylated either with diazomethane or with dimethyl sulfate and alkali. Some determinations of active hydrogen were also carried out. Unfortunately, the insolubility of periodate lignin, both before and after treatment, in chemically indifferent liquids made it impossible to determine molecular weights and to calculate substitutions of methoxyl groups and active hydrogen atoms on a molar basis. The best that could be done was to assume that periodate lignin, like the soluble methanol lignin exhaustively examined by Brauns (35), had a base molecular weight of 840 containing 5 methoxyl groups, corresponding to a methoxyl-free weight of 770. The results in Table XI were calculated from the formula

$$\% \ OCH_3 = \frac{3100\ x}{770 + 14\ x}$$

where x represented moles of methoxyl group in the base molecular weight. For active hydrogen, of course, the atoms per base mole were calculated from the base molecular weight plus the methoxyl content of the sample. For untreated periodate lignin, this value was 812 and for lignin treated at 150°C., 817. Even the relative value of the calculated substitutions was impaired by the fact that the acidic treatments gave a non-quantitative yield of the lignin and also probably altered the true molecular weight.

The original periodate lignin (Table XI, column 1) was methylated not at all with diazomethane and presumably contained no phenolic or carboxylic groups, a result that agreed well with the insolubility of the lignin in strong cold alkali. Similar treatment of periodate lignin samples which had first been treated in a buffered solution at pH 1 for four hours at temperatures of 120° and 150°C. showed increases in per cent methoxyl content (Table XI, columns 2 and 3) which, on the above basis, corresponded to 1.2 and 1.1 groups, respectively. Since these samples, like the original periodate lignin, were insoluble in alkali prior to methylation, it was assumed that the hydroxyl groups, indicated by the diazomethane methylation, were phenolic in nature.

In an effort to determine the presence of hydroxyl groups other than phenolic, samples of periodate lignin, one untreated and the other cooked at pH 1 and 150°C. for four hours, were methylated with dimethyl sulfate to constant methoxyl values. This method methylated aliphatic

## TABLE XI

### Production of Hydroxyl Groups in Pretreatments

| Samples | Pretreatment[a] none | 120°C. | 150°C. |
|---|---|---|---|
| Periodate Lignin SPL II | | | |
| $OCH_3$ - % | 11.3, 11.8 | 12.4, 12.4 | 13.4, 12.8 |
| Moles[b] | 3.0 | 3.2 | 3.4 |
| Methylated with Diazomethane | | | |
| $OCH_3$ - % | 11.2, 11.2 | 16.6, 16.6 | 16.5, 17.2 |
| Moles[b] | 3.0 | 4.4 | 4.5 |
| Moles increase | 0 | 1.2 | 1.1 |
| Methylated with Dimethyl Sulfate | | | |
| $OCH_3$ - % | 17.6, 18.1 | - | 24.3, 25.2 |
| Moles[b] | 4.7 | - | 7.0 |
| Moles increase | 1.7 | - | 3.6 |
| Zerewitinoff Active Hydrogen | | | |
| % | 0.66, 0.63 | - | 0.90, 0.92 |
| Atoms/base mole[c] | 5.1 | - | 7.1 |

(a) For four hours at pH 1 and temperature stated.

(b) Calculated on basis of molecular weight 770 for methoxyl free lignin.

(c) Calculated on a molecular weight of 770 plus the methoxyl content of the sample.

plus phenolic hydroxyl groups, and the result for the untreated lignin showed the total present was 1.7 moles. Since the diazomethane methylation had not revealed phenolic groups, it was believed that the hydroxyl groups were aliphatic. The periodate lignin, treated at 150°C., showed when methylated with dimethyl sulfate an increase of 3.6 methoxyl groups. By subtraction of the value obtained by similar methylation of the untreated sample, pretreatment had caused the formation of 1.9 new hydroxyl groups. Of these new groups, 1.1 were phenolic, while the remaining 0.8 was aliphatic in nature; that is, about one additional aliphatic and one additional phenolic group was formed by the acidic treatment.

Determinations of the active hydrogen present in the untreated periodate lignin, and in the lignin treated at 150°C., were carried out by the Zerewitinoff method described in the Experimental portion. This method of analysis tended to give discordant results and repeated analyses were required before satisfactory duplication was obtained. The factor which caused the most difficulty was the insolubility of the samples in the 1,4-dioxane employed as carrier for the Grignard reagent and the heterogeneous reaction was slow. The value of 5.1 atoms found for untreated periodate lignin was much higher than the 1.7 moles of hydroxyl groups found to be present by methylation technique. However, other structures give rise to active hydrogen groups, such as dibenzofuran, indene and fluorene. Consequently the difference might be ascribed to the presence of these or other structural units in the complex. But the 7.1 atoms of active hydrogen found in the sample treated at 150°C. was 2.0 moles greater than in the untreated lignin, a value in excellent agreement with that of 1.9 mole found by methylation with dimethyl sulfate and alkali. The difference between the analyses for active hydrogen was therefore attributed to the presence of an additional phenolic and hydroxyl group in the treated lignin, even though the absolute values of the estimations were inconsistent with the methylation data.

In an effort to determine whether periodate lignin formed phenolic and aliphatic hydroxyl groups at pH values greater than 1, samples of the preparation SPL II were pretreated at pH 5 and pH 9 at 120°C. for four hours and the undissolved residues methylated with a diazomethane-dioxane solution. Analyses before and after the methylation showed that the sample treated at pH 5 increased its methoxyl value from 11.5, 11.5% to only 12.0, 12.1%, while the sample treated at pH 9 changed from 11.2, 11.1% to 11.7, 11.8%. These changes were insignificant and the above treatments were regarded as having failed to produce phenolic groups. Unfortunately, the sample treated at pH 9 was not washed in acid before methylation and any phenolic groups might have been present, as sodium phenolate. In this case the negative result with diazomethane was not very conclusive.

To sum up, the acidic pretreatments at pH 1 and 150°C., which dissolved a substantial portion (20%) of the periodate lignin, produced a residue almost entirely insoluble in a subsequent sulfite cook, and containing about one additional phenolic and one additional aliphatic hydroxyl group for each base molecular weight of roughly 810. Milder treatments at pH 5 and 120°C., which dissolved less (11.2%) of the lignin, left the remainder partially soluble in the cook, and almost free of phenolic groups.

In order to study any production of free phenolic groups during sulfonation effectively, it seemed desirable to carry out the sulfonation at a temperature and pH which would in themselves promote the minimum amount of change in the periodate lignin. These conditions were shown to be a pH of 4 to 5 and not more than 100°C. (Figures X, XII and XIII, and Tables IV, V and VI). A 9% sodium bisulfite solution was used since the pH of 5.2 was near the desired range and since the total sulfur dioxide concentration approximated the strength used in the standard sulfite cook of previous studies. A series of runs, in which samples of periodate lignin were cooked for varying lengths of time at 100°C., was carried out. The sulfonated residues, when removed from the reaction liner, were all found to be highly swollen to 5 or 6 times the initial volume, but all collapsed slightly when deashed on the centrifuge with N hydrochloric acid followed by distilled water. Vacuum drying of these deashed products resulted in a dark brittle material which was unmanageable, but drying by solvent exchange through dioxane gave satisfactory products in the form of insoluble light brown powders. On the basis of Kullgren's (76) work with similar types of lignosulfonic acids, each sample was then hydrolysed in a Clark-Lubs (105) buffer mixture at pH 2.0, using 0.2N potassium chloride and 0.2N hydrochloric acid at 135°C. for six hours. Results from these sulfonations and post-hydrolyses are shown in Table XII and Figures XIV and XV. If no allowance was made for the uptake of sulfur, the yield of insoluble lignosulfonic acids was close to 90%. It was interesting to note that the recovery of periodate lignin from treatment at pH 5 and 100°C. for four hours was 3.2% or close to this value. The loss of approximately 10% might possibly be attributed, therefore, to the hydrolytic

## TABLE XII

### Rate of Sulfonation[a] of Periodate Lignin and its Effect on Post-Hydrolysis[b]

| Time Hrs. | Yield % | Sulfur[c] in residue % | | Solubility of residue at 135°C. % |
|---|---|---|---|---|
| | | | Mean | |
| 0.5 | 90.8<br>91.3 | 1.79<br>1.77 | 1.78 | - - |
| 1.0 | 90.1<br>90.9 | 2.35<br>2.44 | 2.40 | 24.5<br>24.2 |
| 4.0 | 91.2<br>90.4 | 2.79<br>2.65 | 2.72 | 57.2<br>55.3 |
| 24.0 | 89.1<br>89.6 | 2.96<br>3.14 | 3.05 | 77.2<br>78.1 |
| 48.0 | 89.1<br>88.5 | 2.98<br>2.81 | 2.88 | 82.2<br>88.5 |
| 72.0 | 87.6<br>88.8 | 3.41<br>3.51 | 3.46 | 99.4<br>99.5 |

(a) cooked in 9% sodium bisulfite at 100°C.; liquor to solids ratio 50:1.

(b) residue cooked at 135°C. in buffer mixture pH 2.2 for six hours.

(c) determined by method of Grote and Krekler (117).

action of the acidity and temperature alone. In Figure XIV, the sulfonation, on the very probable assumption that the sulfur found was present as sulfonic acid groups only, proceeded rapidly during initial phases of the cook, and then very slowly during the later stages. The reason for the decrease was not investigated, although it might have been connected with the heterogeneous nature of the reaction or a slow molecular rearrangement in the original lignin. Also from Figure XV, it appeared that the solubility of the lignin residue was sharply dependent on the extent of sulfonation and became complete when a sulfur content of 3.5% was reached. This figure, which corresponded to about one sulfur atom in a molecular weight of 840, or in one assumed lignin building unit, was somewhat lower than 6.1% found by Green and Yorston (78). The black liquor from the hydrolysis of a seventy-two hour sulfonation (3.5% S) was almost as dark brown as commercial sulfite waste liquor and the lignosulfonic acids could be precipitated with $\beta$-naphthylamine, or as their calcium salts in alcohol.

A brief investigation of the hydrolysis of sulfonated lignin was carried out to determine the effects of temperature, time and hydrogen ion concentration, the buffer being used in a liquor-solids ratio of 30:1. Since only three runs were carried out for each variable, the results were not plotted, but summarized in Table XIII. The Table shows that at 135°C. and pH 2, conditions resembling those in a commercial sulfite cook, the hydrolysis was rapid and was about 95% complete in two hours. This observation was in contradiction to Strangeland's (77) results on the cooking rates of wood, but in the present case, many of the complicating factors due to working with lignin _in situ_ were eliminated. A decrease in temperature from 135° to 100°C., however, reduced the figure of 95%

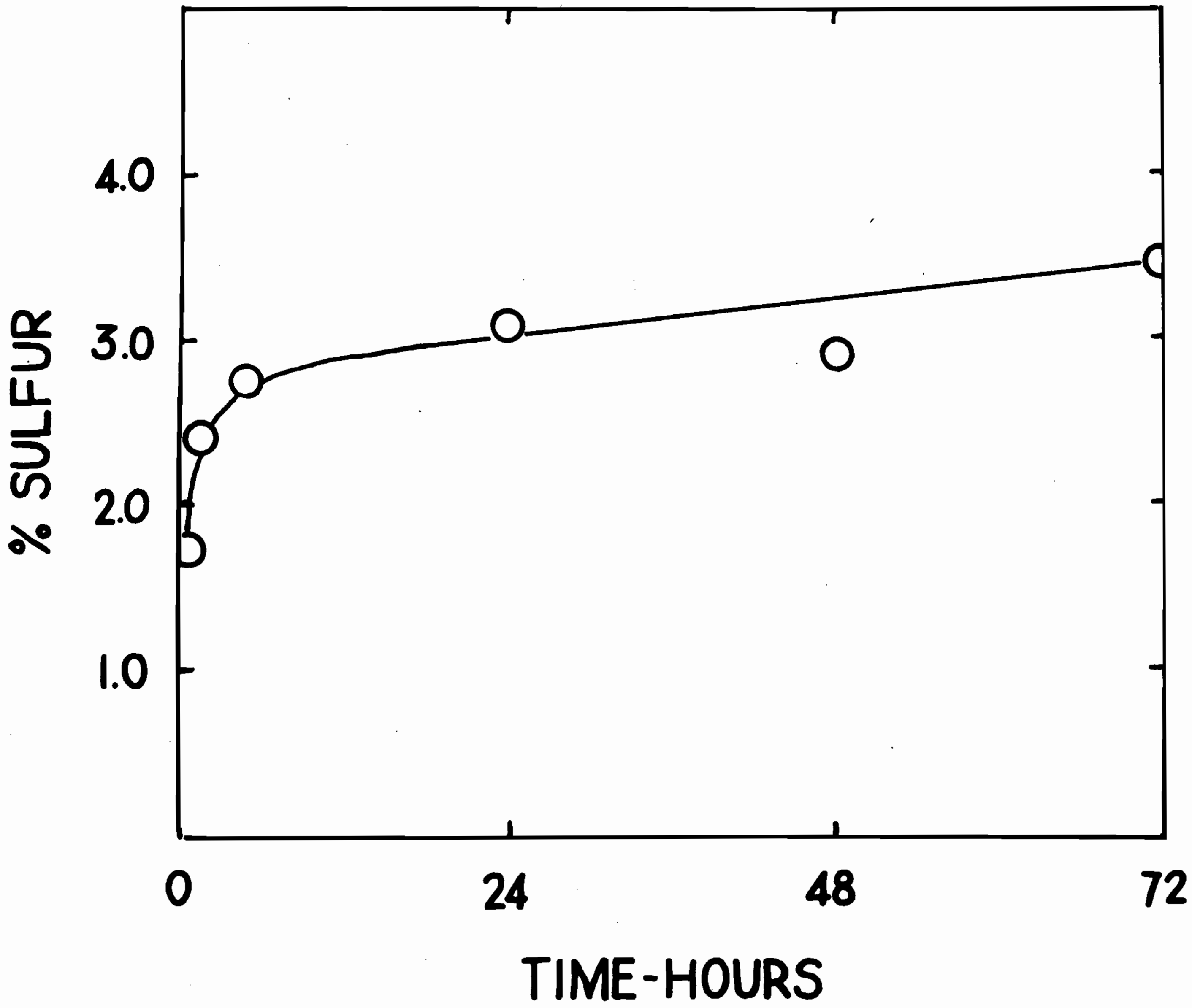


Figure XIV - Rate of Sulfonation of Periodate Lignin in 9%
Sodium Bisulfite at 100°C.

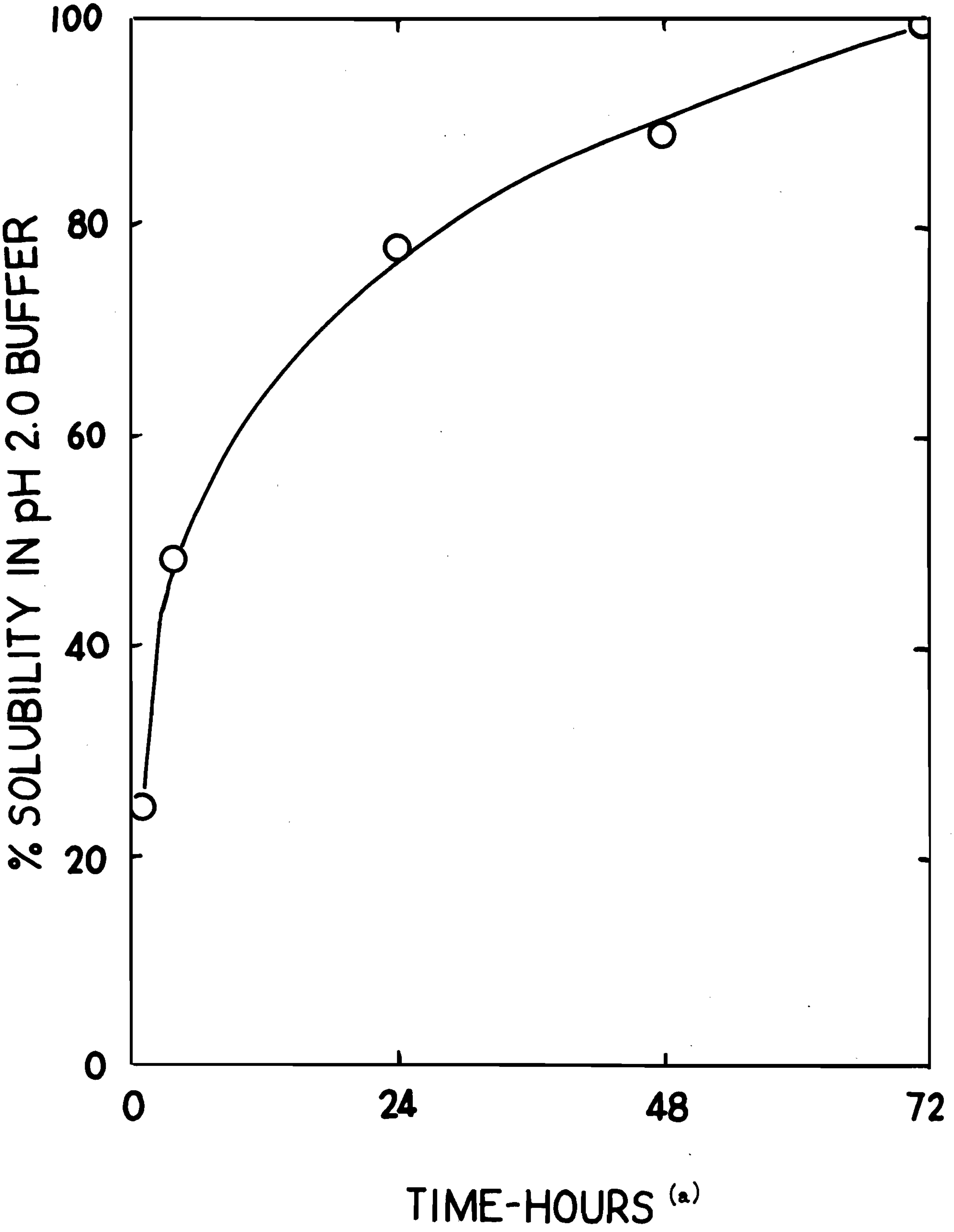


Figure XV - Solubility of Lignosulfonic Acids in Buffer Solution at 135°C. and pH 2.0 for Six Hours

(a) Time in sulfonation cook.

## TABLE XIII

## Post-Hydrolysis of Insoluble Lignosulfonic Acids

| | % Dissolved |
|---|---|
| Hydrolysis at pH 2 and 135°C. | |
| 2 hrs. | 94.9<br>94.4 |
| 4 hrs. | 98.0<br>98.0 |
| 6 hrs. | 99.4<br>99.5 |
| Hydrolysis at pH 2.0 for 2 hours | |
| 100°C. | 54.8<br>53.7 |
| 120°C. | 77.5<br>76.2 |
| 135°C. | 94.9<br>94.4 |
| Hydrolysis at 120°C. for 2 hours | |
| pH 1.0[(a)] | 69.9<br>71.2 |
| pH 2.0[(b)] | 77.5<br>76.2 |
| pH 3.0[(c)] | 54.8<br>53.0 |

Final pH values (a) pH 0.8
(b) pH 1.7
(c) pH 2.4

to about 54% in the duplicate estimations. The effects of pH at 120°C. for two hours appeared anomalous because the extent of hydrolysis at pH 1 was somewhat less than under the apparently milder conditions of pH 2. Although slight changes in pH occurred during the hydrolysis, because the strong lignosulfonic acids tended to overcome the rather dilute buffer, these changes were towards increased acidity and appeared incapable of explaining the effect.

The investigation of phenolic groups formed during these reactions employed periodate lignin which had been sulfonated for seventy-two hours (3.5% S), and rendered ash free by acid washing. This sample was methylated with diazomethane in dioxane solution, and the products analysed for ash, sulfur and for methoxyl groups (Table XIV). A comparison of mole ratios revealed that 1.2 methoxyl units had been added for each sulfur atom, and it therefore was very probable that the diazomethane had methylated the strongly acidic sulfonic acid group. On this basis, few, or perhaps even no, phenolic groups were formed during sulfonation at 100°C. and pH 5 for seventy-two hours.

Since early attempts to isolate the soluble lignosulfonic acids from hydrolysis in buffers encountered severe technical difficulties owing to the presence of salts, the insoluble, ash free, lignosulfonic acid was finally suspended in distilled water and heated for two hours at 135°C., the sulfonic acid groups themselves providing the requisite acidity of about pH 1.2. This auto hydrolysis gave a dark brown liquor and direct evaporation to dryness, even <u>in vacuo</u> at low temperature, produced a brown resin. Isolation was successfully accomplished by freezing the concentrated aqueous solution and evaporating the ice in high vacuum. This technique

## TABLE XIV

### Methylation of Lignosulfonic Acids with Diazomethane

| | Ash<br>% | S<br>% | $OCH_3$<br>% | Moles $OCH_3$ per atom S |
|---|---|---|---|---|
| Insoluble Lignosulfonic Acids | | | | |
| Before methylation | 0.5 | 3.61, 3.41 | 13.0, 13.8 | 4.0 |
| | trace | 3.49, 3.59 | 13.4, 14.0 | |
| | | mean 3.50 | mean 13.5 | |
| After methylation | 6.1 | 3.42, 3.31 | 16.9, 16.9 | 5.2 |
| | 6.5 | mean 3.37 | mean 16.9 | |
| Soluble Lignosulfonic Acids(a)(b) | | | | |
| Before methylation | 0.2 | 3.45, 3.45 | 10.1, 10.8 | 3.1 |
| | trace | | 10.6, 10.6 | |
| | | mean 3.45 | mean 10.5 | |
| After methylation | 0.2 | 16.9, 16.5 | 15.6, 15.6 | 9.5 |
| | trace | 16.8, 17.5 | | |
| | | mean 17.0 | mean 15.6 | |

(a) by auto hydrolysis of insoluble acids at 135°C. for 2 hours; yield - 85%.

(b) part of sulfur present as sulfuric acid.

left the solid lignosulfonic acids as a light brown water soluble powder in nearly quantitative yield (85%).

The sulfur content of these soluble acids, 3.45% (Table XIV) checked that of the original insoluble acids (3.5%) very well, but a noticeable decrease in the methoxyl content lowered the ratio of methoxyl groups to sulfur atoms from 4.0 to 3.1. A 50% drop in sulfur content after methylation with diazomethane, however, required further study. A weighed sample of the soluble lignosulfonic acid was dissolved in distilled water, and "Acriflavine" (a mixture of 2,8-diamino, 10-methyl acridinium chloride and 2,8-diamino acridinium chloride, obtained from E. R. Squibb and Sons, Montreal) was added. The solution was stirred and then centrifuged to settle the precipitated lignosulfonic acid salts and the liquor was decanted and retained. After washing the precipitate twice with distilled water, the washings were combined with the decanted liquor. Aqueous barium chloride was added to the combined liquor, and the precipitate that formed was collected by filtration through a tared micro-Gooch crucible which was ignited at 750°C. for four hours. The precipitate, which was barium sulfate, indicated a 10.2, 0.94% sulfur content as sulfate ion in the soluble lignosulfonic acid. Repeated analyses showed that the methylated sample contained only 1.69% and even when the sulfur present as sulfate was included the total recovery of 2.7% left 0.80% unaccounted. Whether this loss was due to the cleavage of volatile sulfur compounds during the methylation or recovery of the material cannot be stated with any degree of certainty. It was, however, quite clear that many of the sulfonic acid groups in the insoluble lignosulfonic acid were recovered in the soluble autohydrolysed product as free sulfuric acid, which was probably lost as volatile dimethyl sulfate after the methylation with diazomethane.

The analysis of the final methylated lignosulfonic acid gave a methoxyl to sulfur ratio of 1 to 9.5, so that 8.5 methoxyl groups, apart from the sulfonic ester group, were present. If it was assumed that half of the sulfur was present as free sulfuric acid, the ratio of moles methoxyl to sulfur atoms (3.1:1) corresponded to 6.2:1 for mole methoxyl to sulfonic acid groups. Even on this conservative estimate, 8.5-6.2, or about 2.3 hydroxyl groups of a phenolic nature had been produced during the autohydrolysis of the insoluble lignosulfonic acid. The production of one of these groups might possibly have been connected with the decrease in methoxyl content from 13.5% to 10.5%, and the other with the loss of sulfonic acid groups as sulfuric acid. The latter possibility seemed most unlikely, for aromatic substitution of sulfonic acid groups has hitherto not been observed with lignin. It was much more probable that a phenolic group was formed by the autohydrolysis at 135°C. and a pH of about 1 for two hours, since similar conditions, not involving sulfonic acid groups, produced a similar effect on periodate lignin itself.

As a result of the present study of sulfonation, practically no phenolic groups were formed from periodate lignin under the above conditions. This observation was in good agreement to recent views by Erdtman (80) who claimed that phenolic groups in lignosulfonic acids were not formed during sulfite cooking under similar mild conditions. However, one of the most important phenomena shown during the present investigation was the ability of periodate lignin to be sulfonated and yet remain, for the most part, insoluble in the cooking liquor. Acid hydrolysis and even auto-hydrolysis, when carried out on the sulfonated material, led to almost quantitative solution. That is, periodate lignin was pulped in a two-stage process based on sulfite liquor and water. This behaviour agreed in a qualitative manner with the theory by Hagglund (75) that commercial pulping of wood involved a two-stage process, sulfonation followed by hydrolysis. In addition, the behaviour of sulfonated lignin to auto-hydrolysis was quite similar to results by Kullgren (76) on similarly sulfonated lignins in wood.

It appeared therefore that periodate lignin was able to duplicate, to a notable extent, the behaviour attributed to lignin *in situ* towards sulfonation, without the presence of the holocellulose fraction of wood as a complicating factor.

## SUMMARY AND CLAIMS TO ORIGINAL RESEARCH

1. Carbohydrate-free spruce periodate lignin, when heated for four hours in aqueous buffers covering the pH range 1 to 10 and at temperatures of 100°, 120° and 150°C., dissolved to an extent (5-22%) that was dependent on both the pH and the temperature. Minimum solubility at all three temperatures occurred at pH 4 to 5. A cursory examination of the dissolved portion suggested that it was phenolic in nature, and after acid treatments the undissolved portion had a slightly higher methoxyl content than the original periodate lignin.
2. The original lignin failed to be methylated to a substantial extent with diazomethane and presumably contained no free phenolic groups. Treatment in an aqueous buffer at pH 1 and 150°C. for four hours, however, produced in 8.0% yield a residue containing approximately one free phenolic and one free aliphatic hydroxyl group for an assumed base molecular weight of 810. Methylation with dimethyl sulfate also suggested the presence of about one aliphatic hydroxyl group in the original lignin. The difference between the active hydrogen contents also suggested the production of an additional phenolic hydroxy group by the treatment, but the actual values were much higher than expected from the methylation data.
3. When exhaustively oxidized with hot alkaline potassium permanganate followed by boiling concentrated nitric acid, the original lignin yielded only 0.37% and 0.73%, respectively, of crude 1,2,4,5-benzene tetracarboxylic acid and benzene pentacarboxylic acids. Pre-treatments

of the lignin for four hours at pH 1 and 135° and 160°C. increased these figures to 0.60, 0.57% and 4.91, 5.15%, respectively. It was inferred that the nuclear condensations of the lignin structure assumed by Read to explain similar increases in the series spruce wood, periodate, Willstater, Klason and alkali lignins were also brought about by the above pretreatments.

4. Although over 90% of the periodate lignin dissolved when cooked at 135°C. for six hours in sodium sulfite containing 1% combined and 6% total sulfur dioxide, the lignins recovered after pretreatments in buffers were in general much less soluble. At 100°C. for four hours the original (and maximum) solubility was retained only in the pH range 4 to 5; at 120°C. the diminished solubility was only slightly dependent on the pH, and at 150°C. the greatly diminished solubility was independent of pH.

5. Choosing conditions in which the effects of temperature and pH were at a minimum, samples of periodate lignin were heated at pH 5.2 and 100°C. in 9% sodium bisulfite solution. About 90% of the lignin remained undissolved, although its sulfur content increased at first rapidly and then slowly. Complete solution of the residue when subsequently heated in a potassium chloride-hydrochloric acid buffer at pH 1 for six hours was only attained after the sulfur content reached 3.5%. A pulping period of seventy-two hours was required. A brief study showed that the above insoluble lignosulfonic acid (S, 3.5%) was quantitatively hydrolysed in water under its own acidity or in a buffer at pH 1, in two hours at 135°C. An observation that buffering

to pH 2 would be more advantageous required to be confirmed.

6. The above insoluble lignosulfonic acid (S, 3.5%) when methylated with diazomethane underwent an increase in methoxyl content that closely corresponded to the sulfonic acid groups present. No phenolic hydroxyl groups were found. Auto-hydrolysis of the sample in water at 135°C. for two hours gave a nearly quantitative yield of soluble lignosulfonic acids, which had to be isolated by evaporating ice from their frozen aqueous solution. Up to half of the sulfur content of the soluble acids was present as free sulfuric acid and a portion of the original methoxy groups had been lost. Methylations with diazomethane suggested that 2 phenolic hydroxyl groups had been introduced for each sulfonic acid group remaining.

7. Items 5 and 6 afforded direct experimental support to the two-stage theory of Hägglund and Kullgren, which was derived from experiments on the pulping of whole wood. Items 1 to 4 demonstrated that in the conditions of temperature and pH prevailing in technical sulfite cooking must have a marked effect on the progress of the cook. These experiments give direct support to the views of earlier workers who studied the effect of pretreatments on the pulping of whole wood.

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