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Studies on the Lignin Fraction of Aspenwood Pulps Produced by Sulfite-Bisulfite Cooking Liquor Systems

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STUDIES ON THE LIGNIN FRACTION OF ASPENWOOD PULPS PRODUCED BY SULFITE-BISULFITE COOKING LIQUOR SYSTEMS

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INTRODUCTION

The neutral sulfite semichemical (NSSC) pulping process has come into favor in the last few years largely because of its ability to produce competitive commercial pulps from deciduous wood. Hardwoods in general are cheaper and more abundant than softwoods; their fiber length, lignin, and alpha-cellulose content are lower, and their hemicellulose content is higher than those of the conifers. The full chemical processes required to delignify the longer, more highly lignified softwood fibers, when applied to deciduous woods, result in a drastic loss of hemicellulose as well as lignin. The semichemical process, however, relies on a combination of mild chemical delignification and mechanical attrition to separate the papermaking fibers; therefore, a smaller proportion of each wood component is removed in pulping. The lower lignin content of the hardwoods may then be used to advantage, since hardwood pulps at any given yield exhibit lower lignin content than softwood pulps at the same yield; also, the larger proportion of hemicelluloses retained by the pulp allows improved strength properties in the resultant paper or board (1). Hardwoods yield semichemical pulps that are much stronger in relation to their fiber length than are softwood semichemical pulps, and the greater difficulty in pulping and fiberizing the longer-fibered softwoods has largely limited the process to the hardwoods (2).

Since its development in 1926 (3), the NSSC process has been the subject of relatively little fundamental work. Lea (4) studied the effect of a NSSC cook on the hemicellulose fraction of aspenwood, comparing the hemicellulose

from the final pulp with the original wood hemicellulose. Quick (5) studied the nature and order of hemicelluloses removed during a NSSC cook of aspenwood. Doriswamy (6) investigated the kinetics of sodium sulfite pulping of aspenwood to determine the cooking conditions for maximum lignin removal and minimum pentosan removal.

There is a gap in the present knowledge of the fate of lignin in a neutral sulfite cook; this thesis is submitted as a contribution to that knowledge. Most of the hypotheses cited in the literature concerning the neutral sulfite reaction mechanism are but extensions of acid sulfite pulping theory. In this thesis, a program of investigation has been followed which allows comparison to be made of the nature of the pulping reaction and its products at various times during the cook, and at various pH levels spanning the sulfite-bisulfite range. Proposed theories of neutral sulfite pulping are evaluated in the light of the chemical differences in pulps produced in the bisulfite range of pH (to which the acid sulfite pulping theory is applicable), and those produced in the neutral sulfite pH range.

HISTORICAL REVIEW

SULFITE PULPING THEORY

The literature abounds with conflicting proposals of acid sulfite pulping theory; since all of these proposals may not be extended to the neutral sulfite range of cooking, only those which are pertinent to the discussion will be treated here.

One of the most widely quoted theories on mechanism is attributed to

Hägglund (7). He postulates a two-step delignification reaction: (1) rapid sulfonation of lignin in the solid state by the bisulfite ion, with the formation of a solid, insoluble lignosulfonic acid ("sulfonated wood"), which cannot be removed by simple washing with water, and (2) a slower dissolution of the solid lignosulfonic acid to form soluble compounds by hydrolysis of lignin-lignin or lignin-carbohydrate bonds.

As the pH is increased, the rate of sulfonation decreases, and complete delignification is never reached (8). Hägglund cites this fact as evidence that the rate of sulfonation is proportional only to the hydrogen ion concentration of the cooking liquor. The solid insoluble lignosulfonic acid produced during the first stage of delignification contains some free sulfonic acid groups, but others have become neutralized by the base. Therefore, "sulfonated wood" is really a cationic ion exchanger of the sulfonic acid type, extracting sodium ions from solution and raising the hydrogen ion concentration. Kullgren (9) washed a spruce "sulfonated wood" with acid to replace all of the metal ions with hydrogen ions; after a water wash, a material was obtained from which soluble lignosulfonic acid (Kullgren's Acid) could be obtained merely by heating with water. It appears that the hydrogen ions of the solid lignosulfonic acid catalyze the breakdown of insoluble lignin complexes with the formation of soluble, low-sulfonated lignosulfonic acid; no bisulfite ion is necessary for hydrolysis. Since neither the first nor second stages of the delignification reaction are dependent on the degree of sulfonation, Hägglund states that the rate of delignification is proportional only to the hydrogen ion concentration.

Maass and co-workers (10) disagree with Hägglund on the rate-governing reaction in acid sulfite delignification. They believe that sulfonation occurs by a gradual process (and not rapidly, as does Hägglund), and conclude that the rate of delignification is controlled by the bisulfite ion concentration (rate of sulfonation) in addition to the hydrogen ion concentration (rate of hydrolysis). Recently, Häggroth, Lindgren, and Saedén (11) have confirmed Maass' theory for cooks at pH levels below 2.4; they found the rate of lignin removal to be dependent upon both the amount of applied sulfur dioxide and the hydrogen ion concentration. For values of pH greater than 3.5, however, the rate of delignification was found to be less affected by changes in the proportion of sulfur dioxide.

In addition to the two-step delignification reaction outlined above, a third reaction between acid sulfite cooking liquor and lignin is also hypothesized by Hägglund; this reaction is the further sulfonation in the liquor of the low-sulfonated "Kullgren's Acid" removed in the second stage of delignification. This continued sulfonation of the already solubilized lignosulfonate to technical lignosulfonic acid is a slow reaction which usually doubles the sulfur content of the lignin (12), although technical lignosulfonic acids have been isolated with sulfur contents as low as those normally present in "Kullgren's Acid" lignin fractions. This indicates that the degree of sulfonation ordinarily found in lignin in acid sulfite spent liquors is not a prerequisite for solubility.

From the many reactions of lignin, it is apparent that it is not a homogeneous entity. Different groups within the molecule react differently,

as noted in the two-stage sulfonation theory; a portion of the lignin may be sulfonated in the solid state, while another portion must become solubilized before it may be sulfonated. This has led many lignin chemists to agree on the presence of two reactive groups in lignin, often designated as "A" and "B" groups. "A" lignins, often thought of as benzyl alcohol types, react with sulfites at all pH levels; when they are sulfonated, Hägglund's "sulfonated wood" is formed. Mikawa and co-workers, as reported by Lindgren (13), have further subdivided the "A" group into "X" and "Z" groups. Their data indicate that "X" groups are sulfonated slightly more rapidly than "Z" groups by sulfite solutions at pH 5.9.

The other main lignin type, group "B", reacts with sulfites only at low pH; it appears to be cleaved at a rate inversely proportional to the pH in the latter stages of an acid sulfite cook, and then sulfonated in solution (the third stage of reaction). This group probably links lignin to carbohydrates or other lignin residues of moderate size to form giant "genuine lignin" molecules by bonds which are broken when "sulfonated wood" is subjected to hydrolysis. The "B" lignin group is generally thought of as being either an acetal type, which may be hydrolyzed to a hemiacetal containing a hydroxyl group replacable by a sulfonic acid radical, or a dibenzyl ether type, whose sulfonation depends on hydrolytic fission of the ether linkage, with the formation of a benzyl alcohol group identical to the "A" group (14).

Now, with this background in acid sulfite theory, it is possible to speculate on the changes which might occur if the reaction pH were raised to the level of a neutral sulfite cook. According to theory, an increase in the pulping pH results in a sharp decrease in the rate of delignification.

At pH levels greater than 7.0, no acid hydrolysis occurs, and lignin may not be removed from the pulp (15). Even the sulfonation reaction is greatly retarded, since lignin may be sulfonated only to the capacity of its "A" groups before hydrolysis must occur to liberate "B" groups for sulfonation. Lindgren and Saeden (16) calculated that the relative amount of "A" groups present in hardwood lignins is only half that present in softwood lignins; this suppresses the level of theoretical sulfonation capacity even more in deciduous woods.

Many conflicting results on rate of delignification may be cited from the literature. It is known that lignin is removed from wood under the conditions of a neutral sulfite cook, but Hägglund (8) states that complete delignification may never be reached, probably due to a low solubility of lignosulfonic acid in alkaline solutions (12). Husband (17) found that the rate of delignification falls off markedly at spent liquor pH levels greater than 8.0, and reasons that alkaline rearrangement of some part of the lignin has effectively prohibited its removal by mechanisms prevailing at the lower pH levels. Alkaline pulps may be produced at pH levels greater than 12.0, but it is unlikely that alkali lignin is formed in the NSSC pH range of pulping. Ross, Hart, Strapp and Yean (15) state that, in the buffer zone in solutions of sulfite-bisulfite, the sulfonation of lignin is not sufficient to produce soluble lignin fractions unless additional sulfonation occurs; the general reactions occurring at high and low pH (alkaline and acid cooks) are (1) inoperative, (2) only partially completed, or (3) greatly retarded in these solutions. Lindgren (13), on the other hand, cites the removal of 11 to 15% of the lignin present in spruce by sulfite solutions

at pH 6 to 7, and states that this fraction seems to be bound by easily hydrolyzable linkages such as acetal or benzyl ether types; these were the same bonds hypothesized as linking "B" lignin groups to the parent molecule. Trucano (18), in a study of the reaction between sodium sulfite and sprucewood at pH 9.5, found that a soluble, sulfonated lignin was formed. The sulfite was said to react quite drastically with the lignin, even to the extent of inducing partial demethoxylation.

The extent of sulfonation at high pH is also open to question. It is generally thought that the bisulfite ion is the pulping agent, and Han and co-workers (19) have shown that the concentration of bisulfite ion in the system

$$H_2SO_3 \rightleftharpoons H^+ + HSO_3^- \rightleftharpoons 2H^+ + SO_3^=$$

falls off to insignificance above pH 8. Nevertheless, Hägglund (12) has shown that considerable sulfur may be bound to lignin at pH levels as high as 12.0. Since sulfite ion forms the bulk of the chemical in the cooking liquor at high pH levels, it is not impossible that it may also act as a sulfonating agent. Husband (17, 20), however, believes that bisulfite ion is the active cooking chemical, and that it is produced during the cook by reaction between sodium sulfite and wood acids, in which acetic acid predominates.

Lindgren (13) found that the reaction between sprucewood and sodium sulfite liquor for 24 hours at 135°C. and pH 5 to 9 yielded lignin containing approximately the same amount of sulfur as that found in "sulfonated wood", or half as much as found in technical lignosulfonic acid; approximately

one-third of the lignin was dissolved. In a similar experiment, Hägglund and Johnson (12) confirmed these results, and found that no more sulfur was taken up on heating to sixty hours. The product was similar to Hägglund's "sulfonated wood", and yielded low-sulfonated soluble lignosulfonic acid on Kullgren hydrolysis. At pH 4, Lindgren (13) found sulfur contents only slightly lower than those of a technical lignosulfonic acid, but most of the lignin was dissolved. Lindgren (16) also investigated the sulfonation of hardwoods. He found that only a portion of birch lignin dissolved at pH 6 to 7; the sulfur content of the lignin remaining in the pulp was lower than that of softwood treated under similar conditions, due to the lower percentage of "A" lignin groups present. Other experimenters (21) found that the reaction of sulfite liquors at pH 8.5 on white birch wood at 170°C. (more nearly typical NSSC conditions than work cited previously) for three hours produced dissolved lignins with a degree of sulfonation at least as high as that of technical lignosulfonic acid produced in an acid sulfite cook on softwood. The bulk of the lignin remained in the wood, but portions were dissolved by boiling in water for three hours, and by Kullgren hydrolysis. These fractions were sulfonated to approximately the degree of a softwood "Kullgren's Acid", and appeared to be the sulfonated "A" lignin groups of Hägglund.

Husband (17, 20, 22) explains his theory of neutral sulfite delignification as follows: wood acids liberated during the cook react with sodium sulfite, producing sodium bisulfite and sodium acetate; as more and more of these acids enter the the liquor, the pH falls until it is checked by (1) the buffer system sodium sulfite-sodium bisulfite, whose capacity to absorb acid

increases continuously to pH 7.2, where their ratio is unity, and (2) the sulfonation of lignin, which serves to remove from solution the acidic salt sodium bisulfite to form the less acidic salt sodium lignosulfonate. When the amount of wood acids in the liquor is greater than the capacity of this buffer system, a further drop in pH occurs. At low pH, however, another buffer system appears to be operative; although sodium bisulfite produced as above is consumed by lignin, sodium acetate accumulates in the liquor. If the number of moles of acetic acid entering solution exceeds the number of moles of sodium sulfite, the reaction between wood acids and sodium sulfite is displaced far to the right, and the great amounts of acetate produced create, with the excess acetic acid, a buffer system of continually increasing capacity to the point at which these components are present in equal amounts--at pH 4.75. Therefore, supplementary buffer such as sodium bicarbonate is not a buffer in the true sense, but rather a source of bicarbonate ions to accept protons from wood acids, adjusting the pH level of the sulfite-bisulfite buffer system. Husband concludes that the rate of lignin removal in the pH range 4 to 8 is a function of both hydrogen ion concentration and of the relative amount of cooking chemical present. This is in agreement with Maass' theory, but at odds with the theory of Hägglund, and with the confirmatory work of Häggroth, et. al. (11). Husband did not find the removal of carbohydrate to be dependent upon the bisulfite ion concentration.

Certain of the data gathered by Husband on white birchwood (17) in support of his theory of neutral sulfite pH buffering may be rearranged to show comparisons in reaction rate between cooks made at different pH levels;

these results are important to the aims of this thesis, and many are verified or contradicted over a range of pH greater than that investigated by Husband. He found for the temperature levels 150, 160 and 170°C., that more total material, lignin and pentosan were removed from the wood in a given time in cooks at pH 4 than in cooks at pH 5; in each case, the rate of removal was greater at lower pH. At both pH levels, at given yield, the lignin content of the pulps decreased with decrease in temperature and increase in ratio of chemical to wood. At constant yield, base concentration and temperature, however, the lignin contents of pulp produced at pH 5 were slightly less than those in pulps produced at pH 4; therefore, the amount of lignin removed in pulping to a constant yield was slightly greater for cooks at high pH, even though the amount of sulfur dioxide present was lower than in lower pH liquors. The liquors of higher pH appeared to be more selective for lignin removal, but the rates of removal were greater at low pH.

Strapp (23) attempts to explain the "extraction" process of delignification by the construction of Ross Diagrams; the starting material (wood), composed of lignin and carbohydrate, is treated with a liquid reagent to remove lignin, but some carbohydrate is extracted as well, in proportions which vary with the nature of the raw material and the reagent, the temperature and the time. Each component is not extracted at a constant rate; the ratio of lignin to carbohydrate is not necessarily the same in two pulps of identical yield from the same wood, but varies with change in the other variables listed above. The destruction of carbohydrate during the cook may be kept in perspective by the use of the Ross Diagram, which is basically a

graph of lignin to carbohydrate ratio vs. yield; lines of constant residual lignin and constant residual carbohydrate are plotted, and the pulping area is defined as that area within lines of maximum possible residual lignin (that present in the wood), maximum residual carbohydrate, and minimum possible residual carbohydrate (cellulose content). When the lignin/non-lignin ratio is plotted vs. yield for sulfite cooks, the ratio increases slightly with the first increment of yield loss, due to the early extraction of acetyl, resins, protein, and water solubles. After this initial rise, the ratio remains constant with decrease in yield, showing that lignin and carbohydrate are removed in proportion to the amounts originally present in the wood, and then decreases with additional loss in yield; this decrease indicates a greater proportional removal of lignin, but is due to a decrease in the rate of carbohydrate removal. The curves for kraft and soda cooks show greater lignin/nonlignin ratios at any given yield than do sulfite curves; the soda cook is least selective for lignin removal.

It is not only possible to graphically portray a sequence of stages in a single cook, as shown above, with a Ross Diagram, but also the results of a series of cooks in which some parameters are held constant, while others are varied. Strapp (23) describes a series of four-hour spruce-balsam cooks using liquor composed of constant concentrations of sodium hydroxide sulfited to varying degrees with sulfur dioxide; four temperatures from 125 to 170°C. were also investigated. In general, as the temperature of the cook was increased, greater amounts of both lignin and carbohydrate were removed, but relatively more lignin was extracted from the pulp. As sulfur dioxide was added to the cooking liquor, both the lignin/nonlignin

ratio and the yield increased, indicating a lower degree of removal of both components, but proportionally greater removal of carbohydrate than in cooks using pure sodium hydroxide. As more sulfur dioxide was added, the pH of the cooking liquor approached neutrality, the yield increased still further, and the lignin/nonlignin ratio decreased slightly along lines of constant residual carbohydrate. Thus, lignin was removed at a higher rate than carbohydrate, but both components approached the points of minimum removal. As the pH was decreased still more by addition of sulfur dioxide, both the lignin/nonlignin ratio and the yield decreased fairly regularly. In this acid pH range, relatively more lignin than carbohydrate was removed, and both components approached the points of maximum removal.

A Ross Diagram of a poplar cook produced under the same conditions as the spruce-balsam cook cited above showed similar changes in yield and ratio with change in pH, except for one incongruity. Whereas the carbohydrate retained at any given delignification in the acid spruce-balsam cooks increased with increase in temperature, that of the poplar series decreased. Strapp's data also indicate the greater efficiency of sulfite pulping liquor for the removal of lignin from hardwood than from softwood.

HOMOGENEITY OF LIGNIN

Bailey (24, 25), working with Douglas-fir, found that lignin was not homogeneously distributed across the cell wall. An analysis of the middle lamella revealed a lignin content of abount 71% and a pentosan content of 14%; wood rays were found to contain 41% lignin, and differing percentages were reported for isolated springwood and summerwood areas.

Studies on lignin homogeneity are reported in the literature for at least two other bases of comparison. When homogeneity is considered in respect to reactant ("A" and "B") groups, the relative proportion of these subgroups in any isolated wood or pulp fraction is dependent upon the original proportions present in different portions of the wood structure, if these different cell areas are separated in isolation. The proportions isolated probably depend mainly, however, on the selectivity of the isolating agent for any subgroup. Sulfite liquor in the alkaline pH range is selective for "A" groups only; according to theory, no "B" groups may be cleaved and sulfonated unless acid conditions exist. Therefore, the pulp and liquor products contain different proportions of "A" and "B" groups, even though they may be homogeneously distributed in the original wood.

The homogeneity of lignin with respect to structural groups, such as guaiacyl and syringyl nuclei in hardwood lignins, is a different case. Here the isolating agent is not expected to be selective for either of these groups, since the reactive nature of the syringyl nucleus is probably not affected by the presence of one extra methoxyl group. Therefore, the relative amounts of these structural subgroups in a given pulp or liquor fraction may be dependent on the heterogeneity of distribution of these groups in the cell structure of the original wood, if the pulping liquor preferentially attacks and removes components in different areas of the cell at different times during the cook.

Bixler (26), in a series of pulping studies on 20-micron wood cross sections, found the alkali processes to be more selective for middle lamella lignin than the acid sulfite process. When all of the middle lamella lignin

had been removed by the kraft process, very little cell wall lignin had reacted. In the sulfite process, however, the reaction was seen to proceed with greater homogeneity across the whole cell wall. This does not conflict with the views of Strapp (23), who states that alkaline processes are less selective for total lignin than the sulfite process. Bixler found the nature of kraft and soda cooks on softwood to be similar, but the kraft process was faster. With hardwoods, the effects were not so obvious visually, but were generally the same as for softwoods, except that the soda digestion was found to be more rapid than the kraft. The secondary walls of poplar seemed less heavily and more uniformly lignified than those of softwoods; the distinct band of heavily lignified material around the periphery of the cell was not apparent.

Alkaline pulping liquors are said to penetrate wood uniformly in all directions, with greater ease than acid sulfite liquors (27). Acid liquors are more harmful to the carbohydrate portion of the wood, due to hydrolytic degradation. When dry softwood chips first encounter acid sulfite liquor they swell considerably in the radial and tangential direction, but little in the longitudinal direction. Liquor penetration, however, is up to one hundred times faster in the longitudinal plane than in either of the transverse planes, and up to ten times faster in the summerwood than the springwood, due to differences in capillary pore size (27). According to Howard (27), liquor penetration in softwoods proceeds up the tracheid lumens, through the fiber wall by means of simple or bordered pits, and through the middle lamella to more lumens. Lange (28) points out that the middle lamella lignin reacts in the early stages of an acid sulfite cook; it is probable

that the liquor attacks the middle lamella at its point of contact with the edge of the pit, and then penetrates in all directions within the middle lamella, as well as through the pit into the next lumen. The rate and ease of penetration of acid sulfite liquor through the cell wall is decreased if no pits are present, or if the pits are closed by torus structures, as is very often the case in heartwood. Holzer and Booth (29) hypothesize that the difference in selectivity of acid and alkaline liquor for various wood components may be due to pulping characteristics (kraft liquor may be less able to penetrate the cell wall due to swelling or absorption of alkali on cellulose), or to pH differences (lignin-cellulose bonds in the cell wall or lignin-hemicellulose bonds in the middle lamella may be more easily split by acid or alkaline liquors, respectively).

In hardwoods, morphological differences in cell structure probably cause differences in liquor penetration. Vessels, due to their large lumen area, are probably the chief means of liquor conduction within the chip; large vessel to vessel and vessel to ray cell pits may allow liquor to flow both longitudinally and radially. Hardwood fibers contain pits which are much smaller and less numerous than those in softwood tracheids, so it is not unreasonable to assume that interfiber liquor flow proceeds mainly by diffusion through the cell wall. Torus structures are nonexistent or less pronounced in hardwood pits than in those of softwood. Hardwood vessels frequently contain tyloses, which hinder the flow of liquor and cause a marked decrease in penetration rate. On the whole, it would seem that penetration of cooking liquor into hardwood chips might begin at the vessel lumens on the chip edge, proceed through pits to more vessel and ray cells,

and to fibers through cell wall diffusion, and, to a minor extent, pit flow.

Since diffusion, penetration, and preferential attack of pulping liquor serve to roughly fractionate the wood structure according to cell morphology, isolating components from the same part of many cells at similar times during a cook, the relative proportions of structural subgroups present in isolated fractions may be considered an indication of the homogeneity of distribution of these groups in the original wood structure. Larsson (30) found that aspen lignin was homogeneous as to "A" group and methoxyl distribution; reaction with sulfite pulping liquors yielded lignin fractions with identical sulfur to methoxyl ratios throughout. Other experimenters (21) have isolated lignin fractions with different ratios of sulfur to methoxyl from the same wood. Stone (31), plotting the nitrobenzene oxidation aldehyde content of lignin in NSSC spent liquors vs. time, found the concentration of syringaldehyde to increase from zero to 24% during the cook while the vanillin content of the lignin in the liquor remained constant at about 12%, indicating that different portions of the cell wall contain different relative amounts of syringyl and guaiacyl groups. Larsson (32) reasoned that if lignin is a mixture of two distinct subgroups (guaiacyl and syringyl), the molecular fractions should also be component fractions, with syringyl lignin in lower weight fractions. No such distribution was found to occur, so he hypothesized that only one lignin is present in aspenwood, composed of alternating syringyl and guaiacyl nuclei. Aaltio and Roschier (33) extracted aspen repeatedly with neutral buffered solutions of butanol and water; over a total of nine cooks, in which 92.6% of the lignin was removed, the lignin to pentosan ratio in the dissolved fraction was

found to drop from 1.35 (Cook one) to 0.87 (Cooks two to five) to 0.64 (Cooks six to nine). When the ratio dropped at Cook six, the methoxyl content of the lignin also dropped from 21 to 15%, and defiberization was seen to occur. They explain these phenomena as follows: in the first cook, the "loosely bound" lignin was removed, increasing the lignin to pentosan ratio. In the next series of cooks, the lignin from the middle lamella was removed, in the last cooks, the lignin from the cell wall was removed, accompanied by a substantial removal of cellulose. Thus, lignin is not homogeneous in its combination with pentosans, but forms two distinct complexes. The methoxyl content of one of these complexes indicates the presence of very few syringyl groups; therefore lignin is heterogeneous with respect to syringyl-guaiacyl distribution in the cell wall. These results show decreasing proportions of syringyl groups in the lignin as the cook progresses, and appear to be in disagreement with Stone's results, which indicate increasing syringaldehyde to vanillin (S/V) ratios with increase in time of cooking. These differences may be explained on the basis of the amount of lignin removed; Aaltio and Roschier removed 40% of the wood lignin in the first cook, with additional removal in the subsequent cooks, whereas Stone studied delignification only in the range of zero to 40% removal. It is possible that S/V ratios change in different directions for different ranges of delignification, especially since different isolating agents were employed in the two investigations.

PRESENTATION OF THE PROBLEM

The literature review has summarized the present state of knowledge of hardwood lignin and sulfite pulping theory. The nature of a pulping problem is such that a well-planned, unified program of sample preparation and

analysis allows basic information to be obtained in many diverse fields. Many of the basic data are pertinent to more than one area of study; new interpretations result in many cases when these data are referred to new bases.

In general, it is the purpose of this thesis to study the fate of lignin during the pulping of aspenwood by sulfite-bisulfite solutions, and to evaluate conflicting opinions in the literature and advance new ideas on the theory of neutral sulfite pulping. The following broad areas are investigated over a wide range of cooking liquor pH, so that comparisons of the results in each area may be translated into differences between acid sulfite and neutral sulfite pulping:

(1) the rate and extent of sulfonation of lignin

(2) the rate and extent of removal of lignin and total woody material

(3) the homogeneity of lignin with respect to structural groups

(4) the selectivity of cooking liquor for lignin

(5) the path of liquor movement within the cell structure.

APPROACH TO THE PROBLEM

Liquors of constant sodium hydroxide content, but with sulfur dioxide equivalence ranging from solutions of pure sulfite to pure bisulfite, were reacted with aspenwood under constant cooking conditions for varying lengths of time. By analysis of the resultant pulp samples, comparative studies of reaction rate and product were made at different pH levels of pulping; the pulping interval in which a given variable changed was observed and related to a corresponding time at a different pH level. Only by the use of

incremental cooks may each step in the pulping process be followed from its inception to its completion.

The experimental work required for the development of standard procedures for each of the analyses performed on pulp and liquor samples is outlined in the APPENDIX. In a few isolated cases, this work uncovered relationships important to the understanding of pulping theory; where this occurs, the results of the investigation are given, and reference is made to the complete discussion and development in the APPENDIX. A summary of the relationship between each of the analyses performed and the areas of investigation cited above follows.

Yield determinations on each pulp allow the rate and extent of loss of total wood material to be characterized for cooks of differing initial liquor pH. Also, the use of this parameter as an independent variable uncovers relationships between other variables at constant yield, which are often more important than relationships at constant cooking time. Lignin determinations on pulps allow evaluations to be made of differences in rate and extent of lignin removal and selectivity of liquor for lignins isolated at different pH levels. Sulfur determinations show differences in rate and extent of sulfonation of different reactant groups in cooks of different pH. Aldehyde yields from nitrobenzene oxidation of pulp and liquor samples indicate homogeneity of lignin fractions and selectivity of liquor for different structural groups at different times and pH levels during the cook.

The path of liquor movement, and the reaction between liquor and lignin within the cell structure at different pH levels of pulping may be deduced

from the microscopic examination of stained longitudinal chip cross sections. The use of stains showing those cell areas containing (1) lignin in any form, and (2) sulfonated lignin, allow changes to be observed in these areas with increase in cooking time for cooks at any experimental pH level. Where the nitrobenzene oxidation or sulfur data indicate a heterogeneous distribution of structural or reactive lignin groups in isolated pulping fractions, the original positions of these groups in different parts of the cell wall may be identified at each cooking time interval. Thus, the selectivity of cooking liquor may be investigated with respect to both particular cell areas and particular lignin subgroups.

NOMENCLATURE

Because 35 cooks have been produced at varying levels of pH and total pulping time, a unified system of pulping product designation is followed, so that reference to the data from one particular cook sample may be made concisely with a minimum of explanation and qualification. Cooks are in general identified by the prefix "C", followed by the series number, the initial liquor pH, and finally the time of pulping. Thus, a series one cook at pH 7.2 for 90 minutes is designated CI 7.2-90. The single large-scale cook produced for the experimentation in analytical procedure may be identified by the symbol XC 9.0-90, and the cooks incorporating radioactive sulfur in the liquor are prefixed XRC.

SAMPLE PREPARATION

WOOD

Aspen (Populus tremuloides) was chosen as the basic raw material because of its widespread use in NSSC pulping. Sapwood only was used in the experimentation, because heartwood is more difficult to penetrate, more variable in composition, and more susceptible to undetectable rot than sapwood. If mixtures of sapwood and heartwood are used in pulping, either the size of the cook must be large, or the particle size of the wood small to insure that each cook is run on a constant proportion mixture of the two. In this thesis, data are presented for cooks of relatively small scale, and the particle size, while necessarily small enough to minimize burning and penetration problems, had to be chosen large enough that woody structure cross sections could be taken and viewed microscopically.

Consequently, two aspen trees were felled on June 11, 1956 in the Rhinelander Paper Co. Experimental Forest near Eagle River, Wisconsin. Three logs were cut from these trees and trimmed to 48-inch lengths, barked, and disks were saved for wood analysis. The sapwood was veneered from these logs at a wet thickness of 0.097 inches, and the veneer sheets were stacked vertically to dry. On reaching air-dry equilibrium, they were cut free of all knots and heartwood; half-inch squares cut from the sheets from only one of the three logs formed the raw material for all the cooks made in this thesis. This log was found to be 45 years old, with a ring density of 6.85/in. and a specific gravity of 0.511 g. ovendry/ml. water. Air-dry wood meal produced in the Wiley mill was extracted according to Institute Method 11 and

air dried once more before wood analyses were made.

LIQUOR

The cooking liquor consisted of unbuffered sodium sulfite-bisulfite solutions produced by the reaction between a constant amount of base ion (sodium in sodium hydroxide) with sulfur dioxide gas until the desired pH level was attained. To further minimize the problems of burning and penetration, the concentration of sodium hydroxide was calculated so that the amount of liquor initially taken up by the wood contained approximately enough cooking chemical for complete pulping, even in solutions of the highest experimental pH (corresponding to the least amount of sulfur dioxide introduced).

This calculation follows, for solutions of pure sodium sulfite. If ovendry aspen takes up 230% liquor on soaking (34), a wood sample with moisture content as great as 15% would still be expected to absorb 215%; dividing the 17% chemical generally needed for an easily bleached pulp by 215%, it is found that the chemical concentration of sodium sulfite in the cooking liquor must be 7.9%, corresponding to 2.8% sodium ion and 5.0% sodium hydroxide. At liquor-to-wood ratios of 10:1, the total chemical based on the wood equals 79% for sulfite liquors and 130% for bisulfite liquors.

The possibility of buffer interference in the pulping reaction is questionable; Richter (35) states that pulp is little affected by kind or degree of buffer, but Husband (17, 20) asserts that pulp quality is improved if no buffer is used. His theory indicates that sodium sulfite

reacts with wood acids to form buffer systems which hinder the decrease of pH during the cook without the addition of separate buffer. At the high chemical-to-wood ratios used in the experimental cooks, the liquor solutions tend to buffer themselves, and burning may be prevented with little circulation. Therefore, no extra buffer was added to the cooking liquor.

One purpose of this thesis is to compare the reaction products of cooks made under the same conditions, but with liquor of different sulfite contents. The pH values 4.5 and 9.0 were taken from a dissociation curve cited by Han, et. al. (19) as representing solutions of pure bisulfite and 97.50% sulfite, respectively. However, this curve is drawn for dilute solutions; its applicability at the high liquor concentrations used here is open to question. Therefore, two preliminary experiments were run to determine the pH of pure sodium sulfite and bisulfite solutions at sodium normality equal to 1.25. In the first experiment, 100 ml. 1.25N sodium hydroxide were sulfited with gaseous sulfur dioxide to pH 1.1; this mixture was titrated with 1.25N hydroxide, and the pH was taken at each interval of base addition. These data may be seen in Table IA. In the second experiment, 500 ml. 1.25N hydroxide were sulfited to pH 2.10; then small increments of 1.25N hydroxide were added. After each addition, the pH was taken, and the sulfur dioxide concentration in g./l. was determined by Institute Method 110 (below pH 4.6) or Pulping Group Procedure 5 (above pH 4.98). This latter procedure is a simple back titration with thiosulfate of the excess iodine remaining after reaction with dilute acidified cooking liquor. These data may be seen in Table IB.

TABLE I

pH VERSUS MILLILITERS OF SODIUM HYDROXIDE AND GRAMS PER LITER OF SULFUR DIOXIDE FOR SOLUTIONS OF 1.25N SULFITE AND BISULFITE

A				B			
pH	$NaOH$, ml.	pH	$NaOH$, ml.	pH	Total SO_2	Free SO_2	Comb. SO_2 (By Difference)
1.10	0.0	7.50	170.0	2.10	90.6	51.8	38.8
1.60	25.0	7.75	176.0	2.65	83.8	45.7	38.1
1.75	30.0	8.00	180.0	3.00	79.4	40.9	38.5
1.97	35.0	8.22	182.0	3.46	76.8	39.0	37.8
2.32	40.0	8.50	184.0	3.99	75.5	37.4	38.1
2.53	42.0	8.76	185.0	4.40	75.3	37.1	38.2
3.00	44.0	9.00	185.5	4.60	75.0	37.4	37.6
3.40	45.0	9.40	186.0	4.98	74.0		
4.10	46.5	10.10	186.5	5.48	67.9		
4.38	47.5	11.00	187.0	6.23	55.1		
4.63	49.0	11.40	187.5	7.00	45.2		
4.75	50.0	11.57	188.0	7.60	41.9		
5.00	53.0	11.75	189.0	8.07	40.3		
5.51	64.0	11.90	191.0	8.59	39.7		
6.00	84.0	12.10	195.0	9.30	39.4		
6.25	100.0	12.20	200.0	10.05	39.4		
6.50	115.0	12.30	217.0	10.90	39.0		
7.00	147.0	12.40	230.0	11.50	37.5		
				12.00	27.8		

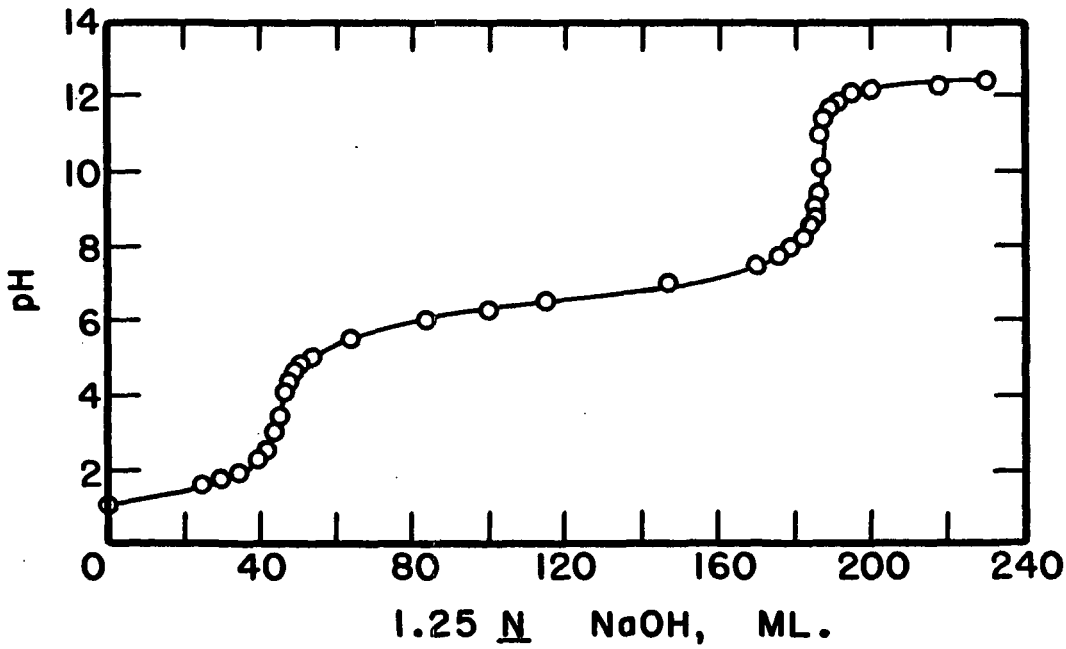
Figures 1A and 1B are graphic representations of the data presented in Table I. The sulfur dioxide concentration at both pH 4.5 and 9.0 was found to be very close to that at the experimental inflection points, so these values of pH were used in all thesis cooks. In the first series of cooks, a set of experiments was also run with a cooking liquor of pH 7.2; this value was chosen to slow the effect of neutral liquors on pulping products, and to determine whether liquor of intermediate pH would give products of intermediate characteristics.

Standard sodium hydroxide solutions of 50 g./l. concentration in distilled water were prepared and analyzed by titration of a known amount of potassium acid phthalate to the phenolphthalein end point; these solutions were then sulfited to the required pH, and used as cooking liquor in the pulping experiments.

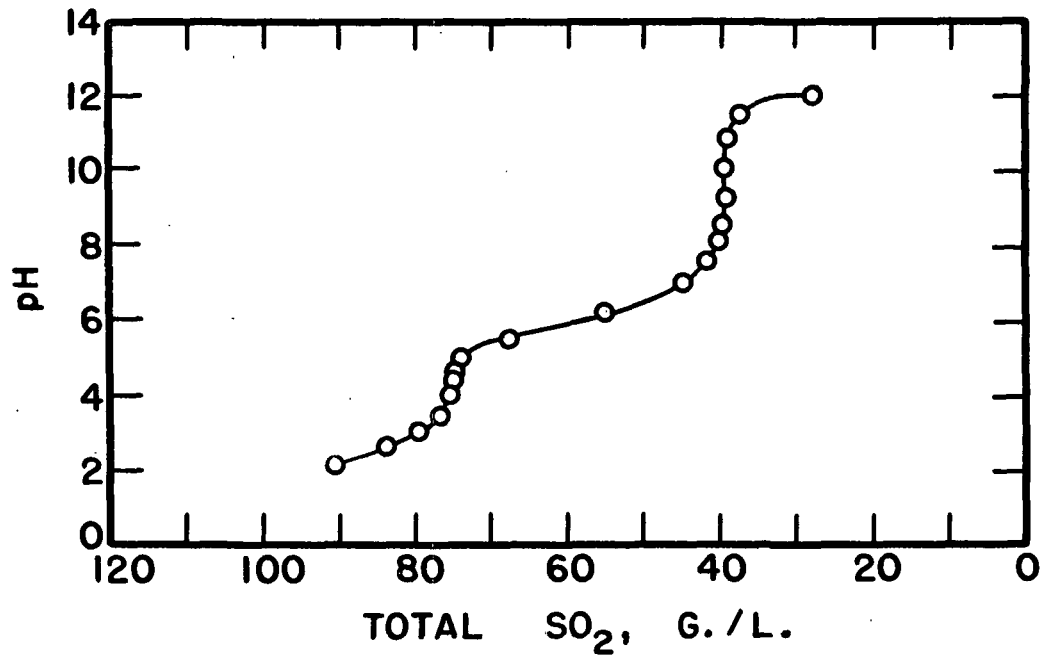
PULP

A total of thirty-five experimental cooks were made under similar conditions, with only pulping liquor pH and pulping time as controlled variables. Of these cooks, thirty-one were prepared for analysis of pulp and liquor fractions ("data" cooks), and four were prepared for investigation of analytical procedures. The following discussion treats only the "data" cooks; the others will be discussed in the APPENDIX.

Wood chips (15 g. ovendry equivalent) and liquor (150 ml.) of appropriate pH were placed in 200-ml. bombs; the theoretical volume occupied within the bombs equalled 150 ml. liquor minus 32 ml. taken up by the wood plus 45 ml. wood (at 0.33 g. ovendry/ml. green volume), or 163 ml. The bombs were sealed, placed in an externally heated rocking jacket and cooks were made according to the following schedule: time to temperature, 90 minutes; time at temperature (170°C.), 120 minutes for a complete cook. A thermocouple was placed in one bomb head well, and temperature was constantly indicated on a control potentiometer. The small digesters were not relieved; gas relief might tend to give inconsistent results, since the data obtained for the longer cooks would be affected by the amount of carbon dioxide and acetic acid formed and removed by relief, whereas those from the



A : Titration of 100 ml. of Solution, pH vs. ml. NaOH



B : pH vs. Determined SO_2 Concentration During the Addition of 1.25N NaOH to 500 ml. of Solution

Figure 1. Addition of 1.25N NaOH to Sulfited 1.25N NaOH Solutions

shorter cooks (in which the temperature does not become great enough to cause appreciable gas pressure) would not. The above conditions were maintained constant for all of the experimental cooks.

Four series of experimental pulp runs, totalling 31 cooks, were made to gather data for this thesis. The first and fourth series are complete sets, each containing pulps and liquors produced at all experimental pH levels and pulping times. The second series cooks are repeat runs on the first series, at only a few of the experimental pulping times. The third series extend the data for cooks at one pH level beyond the proposed range of cooking time.

Twelve Series I cooks were made, four of cooking time 30, 90, 150 and 210 minutes at each of the three pH levels 4.5, 7.2, and 9.0. These cooks are designated CI 4.5-30, etc. The temperature at the time of removal of the 30 and 90-minute cooks was approximately 100° and 170°C., respectively. All of the cooks at a single pH level were made simultaneously, with one bomb in each of the four receptacles in the heating jacket.

At the completion of each set of cooks, the bombs were cooled rapidly in cold running water; the contents were removed, and the liquor was separated from the chips on a Büchner funnel. The chips were then disintegrated in a Waring Blendor, suction filtered, placed in approximately one liter of distilled water, mixed, and filtered again; this procedure was repeated until each pulp had been washed with three one-liter volumes of water. These cooks were made before the washing procedure as noted in the APPENDIX had been developed. Each pulp was then oven dried, disintegrated in the micro-Wiley mill, and redried before analysis; no extraction was performed on the pulps.

Six Series II cooks were made according to the procedures given above. These repeat cooks were produced at 30 and 210-minute time intervals for each of the three liquor pH levels.

Three Series III cooks were produced at pH 9.0 for times greater than 210 minutes, according to the general procedure outlined above; samples were withdrawn from the heating jacket at 360, 480, and 600 minutes. The longest cook was at temperature for 510 minutes, but no burning was observed. After the bombs had been cooled in running water and the liquor had been separated from the chips, a few chips were withdrawn and saved for microscopic analysis. The remainder were disintegrated and washed in four additional volumes of water. Each pulp was oven dried and disintegrated in the micro-Wiley mill as before, and was not pre-extracted before analysis.

Ten Series IV cooks were produced under the closest possible control of pulping variables; due to changes in the mechanical and electrical structure of the rocking heating jacket and the substitution of a new potentiometer-controller, the rate of temperature rise for these cooks was slightly different from that of the early series cooks. It was also discovered that the temperature within two bombs in the heating jacket was more often dissimilar than alike, especially during the temperature rise at the beginning of the cook. For this reason, the temperature of each of the bombs in the heating jacket was continuously adjusted to a common value during the Series IV cooks. In the Series I cooks, all of the pulps of the same liquor pH level were produced simultaneously in the heating jacket, with individual bombs being removed at the proper time intervals. Because of the probability

of temperature differences in these bombs, and of rate differences in the rise to temperature between cooks of different pH, the data obtained in the Series I cooks are not very reliable when plotted against time. They are quite useful, however, when compared at constant yield, lignin content, etc., for these relationships might be expected to hold for any cooking schedule. In the Series IV cooks, two bombs containing liquors of different pH, but of the same total cooking time, were pulped simultaneously in the heating jacket, with continuous temperature adjustment, as noted previously. This also guaranteed a uniform rate of temperature rise for any two cooks of equal pulping time.

Five Series IV cooks were produced at pH 4.5 and five at pH 9.0, with the following common pulping times: 30, 60, 90, 150, and 210 minutes. All other cooking conditions were the same as those of the early series cooks. After pulping, the bombs were cooled rapidly in running water, opened, and chip samples were withdrawn for microscopic examination and placed in distilled water. The remainder of each pulp was disintegrated in the Waring Blendor, filtered, slurried with distilled water, and filtered again until the washing step had been repeated ten times. The pulps were then air dried, disintegrated in the micro-Wiley mill, and air dried again. All Series IV pulps were extracted with alcohol-benzene according to Institute Method 11 prior to analysis.

The liquor analyses and spent liquor pH data for all four series of cooks may be seen in Tables 2 and 3, together with the analytical data.

EXPERIMENTAL RESULTS

Tables in this section contain the raw and calculated analytical data for each of the thirty-one "data" cooks in tabular form; the next section will show these data graphically and discuss their application to the aims of the thesis as outlined in the INTRODUCTION.

It has been stated that the data from Series IV cooks are more reliable than those from Series I and II cooks; this is due in part to the differences in pulping procedure already mentioned, and in part to differences in analytical procedure, especially in the lignin determination. The early series cooks were produced during the period of intense experimentation in analytical techniques; their analysis is not governed by the findings of the experimental work summarized in the APPENDIX.

ANALYSIS OF PULP AND LIQUOR SAMPLES

The slightly modified Klason lignin procedure used in the first three series cooks follows: one gram of disintegrated, nonextracted, ovendry pulp was treated with 72% sulfuric acid for 3.5 hours at 18 to 22°C. The reaction mixture was then diluted to 800 ml., boiled four hours and filtered through two sheets of Whatman no. 40 filter paper of known weight difference. After washing free of acidity and sulfate ion, the nested papers were separated, dried at 105°C. overnight, cooled and reweighed. Since both papers are subjected to the same acid and wash treatment, the weight of lignin may be calculated by subtraction if neither sheet is charred due to residual sulfuric acid. No soluble lignin determinations were run on the Klason filtrates. The sulfur content of each pulp was taken by the Leco method

outlined in the APPENDIX, and nitrobenzene oxidation was performed on each liquor only (except those of the Series III cooks, where pulp oxidations were also run) according to the method of Stone and Blundell (36). Microscopic examinations were run on Series III pulps only.

The Series IV cooks were made under closely controlled conditions, and the analytical data were taken on the basis of the conclusions derived from the experimental work cited in the APPENDIX. The analytical data from the early series cooks were partly or wholly deficient in soluble lignin determinations, microscopic examination, and nitrobenzene oxidation; these data are complete in the Series IV cooks. The Klason lignin determination procedure used in the Series IV cooks follows: disintegrated, extracted airdry pulp (1.0 g. equivalent) was treated as above for 3.5 hours with sulfuric acid, diluted to 800 ml. and boiled four hours. The reaction mixture was filtered through two sheets of Whatman no. 42 filter paper or exactly the same weight, washed, dried, and weighed. Three methods of soluble lignin determination were run for comparison: (1) UV spectrophotometry of the whole Klason lignin filtrate, using the specific extinction data of Buchanan, Brauns, and Leaf (37), (2) UV spectrophotometry of the alcohol eluate of a column of Zeo-Karb 215 resin after passage of the Klason lignin filtrate through such a column, according to the method of McKenzie, McPherson, and Stewart (38), and (3) weight of the evaporated ion-exchange column eluate. The sulfur content of each pulp was taken by the Leco method, and nitrobenzene oxidation was performed as above on both pulp and liquor fractions from each cook. Microscopic examination was made of stained pulp chip cross sections from each cook according to the method

outlined in the APPENDIX. Residual sulfur dioxide in the spent liquor was determined for the Series IV cooks only.

Klason and soluble lignin determinations were run on the wood according to the general procedures outlined for the Series IV cooks, using both 20 ml. sulfuric acid for 3.5 hours and 15 ml. acid for 3.0 hours, after Institute Methods 428 and 13, respectively. The results of these determinations agreed within 0.1% lignin. Sulfur determination, nitrobenzene oxidation, and microscopic examination were all run according to the methods outlined in the APPENDIX.

Liquor analyses, Klason and soluble lignin, sulfur and nitrobenzene oxidation data may be seen in tabular form for the wood and all of the experimental cooks in Tables II and III.

TABLE II

PULPING DATA AND ANALYSES OF SERIES I AND II PULPS

	CI 4.5-30	CII 4.5-30	CI 4.5-90	CI 4.5-150	CI 4.5-210	CII 4.5-210	CI 7.2-30	CII 7.2-30	CI 7.2-90
White Liquor									
Total sodium as NaOH, g./l.	—	50.2	—	—	—	50.2	—	50.2	—
Total sulfur as SO_2, g./l.	64.0	73.2	64.0	64.0	64.0	73.2	—	42.7	—
Spent Liquor									
pH	3.65	4.51	3.50	3.41	2.30	3.02	7.12	6.89	6.90
Yield									
% of wood, o.d. basis	94.8	95.6	73.5	54.6	49.1	54.8	91.2	93.1	79.0
Lignin									
Klason, % of pulp[1]	18.6	17.2	11.3	4.1	2.2	1.9	18.0	16.9	12.3
Klason, % of wood	17.6	16.5	8.3	2.2	1.1	1.1	16.4	15.7	9.7
Nonlignin/lignin ratio[2]	4.4	4.8	7.9	23.4	44.4	51.6	4.6	4.9	7.1
Original wood Klason remaining in pulp[3], %	100.0	93.8	47.2	12.5	6.3	6.3	93.2	89.3	55.1
Original wood Klason in liquor[4], %	0.0	6.2	52.8	87.5	93.7	93.7	6.8	10.7	44.9
Mg. Klason/ml. liquor[5]	0.0	1.1	9.3	15.4	16.5	16.5	1.2	1.9	7.9
Sulfur									
% in pulp, pulp basis	0.198	0.172	0.352	0.243	0.304	0.177	0.236	0.188	0.357
% in pulp, Klason lignin, calc.[6]	1.06	1.00	3.11	5.91	13.80	9.30	1.31	1.11	3.22
Nitrobenzene Oxidation of Liquor									
Mg. syringaldehyde/ml. liquor	0.07	0.04	0.97	2.84	4.27	3.54	0.08	0.05	0.71
Mg. vanillin/ml. liquor	0.06	0.04	0.57	1.31	1.91	1.64	0.09	0.06	0.47
% Syringaldehyde in Klason lignin in liquor, calc.[7]	—	3.3	10.4	18.5	25.8	21.4	6.4	2.8	9.0
% Vanillin in Klason lignin in liquor, calc.[7]	—	3.6	6.1	8.5	11.6	9.9	7.2	3.1	6.0
Syringaldehyde/vanillin ratio (By weight)[13]	1.11	0.91	1.70	2.17	2.23	2.16	0.87	0.93	1.50

TABLE II (Continu

PULPING DATA AND ANALYSES OF SERIES I

	CI 7.2-150	CI 7.2-210	CII 7.2-210	CI 9.0-30					I 210
White Liquor									
Total sodium as NaOH, g./l.	--	--	50.2	--					
Total sulfur as SO_2, g./l.	--	--	42.7	40.9					
Spent Liquor									
pH	6.90	6.90	6.70	7.90	7.90	7.41	7.49	7.60	7.29
Yield									
% of wood, o.d. basis	73.0	71.1	73.8	91.4	91.8	79.6	70.3	64.6	75.1
Lignin									
Klason, % of pulp	9.0	8.8	9.5	17.8	16.9	12.5	8.0	6.0	9.5
Klason, % of wood[1]	6.6	6.3	7.0	16.3	15.0	9.6	5.6	3.9	7.1
Nonlignin/lignin ratio[2]	10.1	10.4	9.5	4.6	4.9	7.0	11.5	15.7	9.5
Original wood Klason remaining in pulp[3], %	37.5	35.8	39.8	92.6	85.3	54.5	31.8	22.2	40.3
Original wood Klason in liquor[4], %	62.5	64.2	60.2	7.4	14.7	45.5	68.2	77.8	59.7
Mg. Klason/ml. liquor[5]	11.0	11.3	10.6	1.3	2.6	8.0	12.0	13.7	10.5
Sulfur									
% in pulp, pulp basis	0.377	0.363	0.408	0.164	0.161	0.350	0.326	0.311	0.295
% in pulp, Klason lignin, calc.[6]	4.18	4.13	4.29	0.92	0.95	2.79	4.07	5.18	3.10
Nitrobenzene Oxidation of Liquor									
Mg. syringaldehyde/ml. liquor	1.54	1.61	1.74	0.12	0.07	0.69	1.77	2.35	1.73
Mg. vanillin/ml. liquor	0.80	0.82	0.92	0.11	0.07	0.47	1.03	1.14	0.88
% Syringaldehyde in Klason lignin in liquor, calc.[7]	14.0	14.2	16.5	8.9	2.7	8.6	14.8	17.1	16.5
% Vanillin in Klason lignin in liquor, calc.[7]	7.3	7.2	8.6	8.7	2.7	5.9	8.6	8.3	8.4
Syringaldehyde/vanillin ratio (By weight)[13]	1.92	1.97	1.90	1.06	1.02	1.46	1.72	2.06	1.98

TABLE III

PULPING DATA AND ANALYSES, WOOD, SERIES III AND IV PULPS

	Wood	CIII 9.0-360	CIII 9.0-480	CIII 9.0-600	CIV 4.5-30	CIV 4.6-60	CIV 4.5-90	CIV 4.5-150	CIV 4.5-210	CIV 9.0-30	CIV 9.0-60	CIV 9.0-90	CIV 9.0-150	CIV 9.0-210
White Liquor														
Total sodium as NaOH, g./l.	--	50.0	50.0	50.0	50.1	50.1	50.1	50.1	50.1	50.1	50.1	50.1	50.1	50.1
Total sulfur as SO_2, g./l.	--	37.8	37.8	37.8	75.3	76.0	75.3	75.3	76.0	38.7	39.5	37.8	37.8	39.5
Spent Liquor														
pH	--	7.20	7.20	7.10	3.90	3.42	3.15	3.00	2.67	7.60	7.17	7.03	7.05	7.12
Sulfur dioxide consumed, % of wood[8]	--	--	--	--	3.9	3.8	10.1	22.5	59.8	1.2	2.5	4.1	7.4	12.4
Yield														
% of wood, c.d. basis	100.0	69.2	64.1	56.8	95.0	84.0	64.1	48.0	46.8	94.0	87.3	79.3	70.1	67.2
Extractives														
% of pulp	3.01	--	--	--	1.56	0.81	0.72	1.13	1.75	0.99	0.52	0.35	0.50	0.53
% of unextracted wood	3.01	--	--	--	1.48	0.68	0.46	0.54	0.82	0.93	0.45	0.28	0.35	0.36
Lignin														
Klason, % of pulp	17.6	7.8	5.2	2.1	17.8	15.0	7.3	1.3	1.0	16.9	15.0	12.5	8.6	6.7
Klason, % of unextracted wood[1]	17.6	5.4	3.3	1.2	16.7	12.5	4.7	0.6	0.5	15.7	13.0	9.9	6.0	4.5
UV soluble, % of pulp[9]	3.2	5.2	3.8	1.9	3.8	5.1	5.9	2.9	1.4	4.2	5.3	6.0	5.7	5.1
UV soluble, % of unextracted wood[1]	3.2	3.6	2.4	1.1	3.6	4.3	3.8	1.4	0.6	3.9	4.6	4.7	4.0	3.4
Total, % of pulp[10]	20.8	13.0	9.0	4.0	21.6	20.1	13.2	4.2	2.4	21.1	20.3	18.5	14.3	11.8
Total, % of unextracted wood[1,10]	20.8	9.0	5.7	2.3	20.3	16.8	8.4	2.0	1.1	19.6	17.6	14.6	10.0	7.9
Nonlignin/lignin ratio[2]	4.7	11.8	18.2	46.6	4.6	5.7	11.9	75.9	99.0	4.9	5.7	7.0	10.6	13.9
UV soluble/total lignin ratio	0.154	0.400	0.421	0.478	0.175	0.254	0.447	0.700	0.583	0.197	0.260	0.322	0.400	0.430
Original wood Klason remaining in pulp[3], %	100.0	30.7	18.8	6.8	96.0	71.6	26.7	3.4	2.8	90.3	74.4	56.2	34.1	25.6
Original wood Klason in liquor[4], %	0.0	69.3	81.2	93.2	4.0	28.4	73.3	96.6	97.2	9.7	25.6	43.8	65.9	74.4
Original wood total remaining in pulp[3], %	100.0	43.2	27.4	11.1	98.6	81.3	40.8	9.6	5.8	95.2	85.1	70.2	48.0	37.0
Original wood total in liquor[4], %	0.0	56.8	72.6	88.9	1.4	18.7	59.2	90.4	94.2	4.8	14.9	29.8	52.0	63.0
Mg. Klason/ml. liquor[5]	--	12.2	14.3	16.4	0.9	5.1	12.9	17.0	17.1	1.9	4.6	7.7	11.6	13.1
Mg. total/ml. liquor[11]	--	11.8	15.1	18.5	0.5	4.0	12.4	18.8	19.7	1.2	3.2	6.2	10.8	12.9

TABLE III (Continued)

PULPING DATA AND ANALYSES, WOOD, SERIES III AND IV PULPS

	Wood	CIII 9.0-360	CIII 9.0-480	CIII 9.0-600	CIV 4.5-30	CIV 4.6-60	CIV 4.5-90	CIV 4.5-150	CIV 4.5-210	CIV 9.0-30	CIV 9.0-60	CIV 9.0-90	CIV 9.0-150	CIV 9.0-210
Sulfur														
% in pulp, pulp basis	0.0	0.332	0.253	0.177	0.089	0.302	0.305	0.151	0.318	0.127	0.285	0.362	0.360	0.319
% in pulp Klason lignin, calc.[6]	0.0	4.26	4.86	8.43	0.50	2.01	4.18	11.61	31.80	0.75	1.90	2.90	4.18	4.76
% in pulp total lignin, calc.[6]	0.0	2.56	2.81	4.42	0.41	1.50	2.31	3.60	13.25	0.60	1.40	1.96	2.52	2.70
Nitrobenzene Oxidation of Liquor														
Mg. syringaldehyde/ml. liquor	—	—	—	—	0.03	0.35	2.01	3.60	4.33	0.11	0.40	0.82	1.67	2.38
Mg. vanillin/ml. liquor	—	—	—	—	0.03	0.24	1.05	1.70	1.97	0.12	0.32	0.54	0.91	1.17
% Syringaldehyde in Klason lignin in liquor, calc.[7]	—	—	—	—	4.0	7.0	15.6	21.2	25.3	6.5	8.8	10.7	14.4	18.2
% Vanillin in Klason lignin in liquor calc.[7]	—	—	—	—	4.0	4.8	8.1	10.0	11.5	6.8	7.2	7.0	7.9	8.9
% Syringaldehyde in total lignin in liquor, calc.[7]	—	—	—	—	9.3	9.0	16.3	19.1	22.1	11.1	12.7	13.3	15.5	18.5
% Vanillin in total lignin in liquor calc.[7]	—	—	—	—	9.3	6.2	8.5	9.0	10.0	11.6	10.2	8.8	8.4	9.1
Syringaldehyde/vanillin ratio (By weight)[13]	—	—	—	—	1.00	1.46	1.91	2.10	2.20	0.96	1.26	1.52	1.83	2.03
Nitrobenzene Oxidation of Pulp														
% Syringaldehyde in pulp, pulp basis	6.12	—	—	—	6.54	5.13	2.74	0.45	0.39	6.09	5.14	4.49	3.13	2.37
% Vanillin in pulp, pulp basis	2.56	—	—	—	2.74	2.29	1.29	0.24	0.23	2.58	2.32	2.05	1.49	1.22
% Syringaldehyde in pulp, unextracted wood basis[1]	6.12	—	—	—	6.12	4.28	1.75	0.21	0.18	5.67	4.47	3.56	2.18	1.59
% Vanillin in pulp, unextracted wood basis[1]	2.56	—	—	—	2.56	1.91	0.82	0.11	0.11	2.40	2.02	1.62	1.04	0.82
% Syringaldehyde in pulp Klason lignin, calc.[12]	34.8	—	—	—	36.2	34.2	37.5	34.6	39.0	36.0	34.4	35.9	36.4	35.4
% Vanillin in pulp Klason lignin, calc.[12]	14.6	—	—	—	15.4	15.2	17.7	18.5	23.0	15.3	15.5	16.4	17.3	18.2
% Syringaldehyde in pulp total lignin calc.[12]	29.4	—	—	—	29.8	25.5	20.8	10.7	32.4	28.9	25.3	24.2	21.8	20.1
% Vanillin in pulp total lignin, calc.[12]	12.3	—	—	—	12.7	11.4	9.8	5.7	19.2	12.2	11.4	11.1	10.4	10.3
Syringaldehyde/vanillin ratio (By weight)[13]	2.39	—	—	—	2.39	2.24	2.12	1.87	1.69	2.36	2.22	2.19	2.10	1.94

KEY TO CALCULATIONS, TABLES II AND III

[1]Wood basis data = (pulp basis data)(yield/100)(100 - % extractives)

[2]Nonlignin/lignin ratio = $\frac{\text{yield - wood basis Klason lignin}}{\text{wood basis Klason lignin}}$

$= \frac{\text{100 - pulp basis Klason lignin}}{\text{pulp basis Klason lignin}}$

[3]% of original wood lignin remaining in pulp = (wood basis lignin)(100/17.6)

[4]% of original wood lignin in liquor = 100 - % remaining in pulp

[5]Mg. Klason lignin/ml. liquor = (17.6 - wood basis Klason)(15/100)(1000/150)

[6]% Sulfur in lignin = $\frac{\text{\% sulfur in pulp, pulp basis}}{\text{\% lignin in pulp, pulp basis}}$

[7]% Aldehyde in lignin in liquor = $\frac{\text{mg. aldehyde/ml. liquor}}{\text{mg. lignin/ml. liquor}}(100)$

[8]Sulfur dioxide consumed, % of wood =

(white liquor g./l. SO_2 - spent liquor g./l. SO_2)(150/1000)(100/15)

[9]UV soluble lignin, % of pulp = $\frac{(\text{Optical density})_{230\ \text{mmu}}(\text{liters dilution})}{(\text{specific extinction})_{230\ \text{mmu}}(\text{weight sample})}$

where liter's dilution = 2.5 and specific extinction = 42

[10]% Total lignin = % Klason lignin + % UV soluble lignin

[11]Mg. total lignin/ml. liquor = (20.8 - wood basis total)(15/100)(1000/150)

[12]% Aldehyde in pulp lignin = $\frac{\text{\% aldehyde in pulp, pulp basis}}{\text{\% lignin in pulp, pulp basis}}(100)$

[13]Syringaldehyde/vanillin ratio (by weight) = $\frac{\text{mg. syringaldehyde}}{\text{mg. vanillin}}$

DISCUSSION OF RESULTS

It was found that the collection and comparison of data from four sets of experimental pulp runs were necessary for the development of the conclusions presented in this thesis. The conditions of the first series of cooks were rather arbitrarily chosen so that pulps with a fairly wide spread of yield and lignin content might be obtained at each of three liquor pH levels spanning the sulfite-bisulfite range. Although soluble lignin, microscopic examination, and nitrobenzene oxidation determinations were not performed on these pulps, the analyses run were representative of those proposed for the final cooks. An evaluation was made of the suitability of these arbitrary conditions for the production of pulps whose analyses adequately indicate (1) progressive chemical changes in pulp structure with increase in cooking time, and (2) chemical differences at different pH levels. The results of this evaluation were used in fixing the pulping conditions of the later series cooks. Repeat (Series II) cooks were produced under the same conditions as the Series I cooks at the shortest and longest time intervals for each of the experimental pH levels so that certain inconsistent data obtained in analysis of the earlier cooks might be checked.

The Series III cooks were the first affected by the evaluation of cooking conditions; it may be noted in the tabular data that the lignin content and yield of pulp CI 4.5-210 are much lower than those of pulp CI 9.0-210, indicating a higher rate of reaction at pH 4.5. This difference is so pronounced that comparisons at constant yield and lignin content cannot be made between these two pulps. Therefore, longer cooks than originally scheduled were produced at pH 9.0 for the purpose of obtaining

pulps at this pH with chemical characteristics closely akin to those of pulp CI 4.5-210. It may be seen in Tables II and III that in most cases the analytical data from pulp CIII 9.0-360 indicate a lower degree of reaction than even those of pulp CI 9.0-210. This is due to inconsistencies in the cooking schedule brought about by changes in the mechanical and electrical structure of the heating apparatus, and does not detract from the importance of the Series III cook results. The data obtained for pulp CIII 9.0-600 allowed comparisons to be made between cooks of different pH at the low levels of yield and lignin content found in pulp CI 4.5-210.

The conditions of the Series IV cooks were also affected by the evaluation mentioned above. The great differences in analytical results between the 30 and 90-minute cooks at each pH level resulted in the addition of 60-minute cooks to the Series IV schedule, the evaluation of proposed pH levels indicated that the production of Series IV cooks at pH 7.2 was not warranted by the amount of information expected. In the Series I cooks, the pulps produced at pH 7.2 exhibited trends when graphed against time that were very similar to those of the pH 9.0 pulps, except for slight inconsistencies which were minimized or nullified by the Series II cooks. It will be seen that the pH 7.2 pulps yielded data virtually identical to those of the pH 9.0 pulps, but different from those of the pH 4.5 pulps, when plotted at constant yield or lignin content. Therefore, Series IV cooks were produced at only two pH levels, 4.5 and 9.0, but with five cooking time intervals.

The data obtained for the early series cooks do not conflict with those

of the Series IV cooks in any case; the same trends may be seen in graphical representation of these data, even though the absolute values may not be identical at any given time. Data from the early series cooks are of little consequence when plotted against time, because cooks of the same pH, but different time, were produced simultaneously in the heating jacket; this allowed slight differences in the cooking schedule of pulps of the same theoretical time, due to inconsistencies in the rate of heat application at the beginning of the cook. Only in the Series IV cooks were pulps of the same pulping time heated simultaneously, under carefully controlled conditions of temperature. Therefore, only the final series cook data are presented graphically in this section when time is the independent variable; when the pulps are compared at constant yield or lignin content, however, the data from all four series of cooks are plotted. In this case, the absolute value of data from any series cook at given pH might be expected to agree at given yield or lignin content even if the cooking conditions were slightly different.

SOLUBLE LIGNIN

It may be noted that whenever the Series IV data alone are plotted against time in this discussion, the lignin content is defined by the sum of Klason plus UV-soluble lignin. Also, where some parameter is plotted against yield or lignin content (with the consequent inclusion of the early series cook data) that lignin content is defined by the Klason lignin value only. This is done because soluble lignin determinations were not made on the Series I and II Klason lignin filtrates, and might justifiably be open to serious question were it not for the relationship between Klason and

UV-soluble lignin shown in Figure 2. This curve indicates that at any given Klason lignin content, the amount of UV-soluble lignin derived from the filtrate is the same for cooks at either pH 4.5 or 9.0; if soluble lignin data were added to the Klason lignin data for all points on the curves plotted against yield or lignin content, the relationships shown would hold at any experimental pH level. Therefore, when data from all pH levels of pulping fall on a single curve, that curve would still be unique if Klason lignin data were replaced with those of total lignin.

Soluble lignin determinations were run on Series IV Klason lignin filtrates by three methods, so that the results of the standard UV determination might be compared with two variations of an ion-exchange method proposed by McKenzie, McPherson and Stewart (38) for the determination of soluble lignin in eucalyptus wood and holocelluloses. The development work cited in the APPENDIX concerning ion-exchange fractionation shows that a portion of the Klason lignin filtrate may be sorbed on Zeo-Karb 215 resin columns, and removed by elution with ethanol; a material balance run on this fractionation is fairly precise for both pulp and wood filtrates.

Because of the rather large variation in alcohol blank values from these columns, the agreement between duplicate determinations of per cent soluble lignin on any given sample was poor. The trends that may be observed in these data, however, are very interesting when contrasted against those of the method of soluble lignin determination by UV spectrophotometry of the whole Klason lignin filtrate (designated as the "standard" method). McKenzie, et. al. (38) suggest that the alcohol eluate be evaporated to dryness so that the amount of soluble lignin might be obtained by simple weighing. When

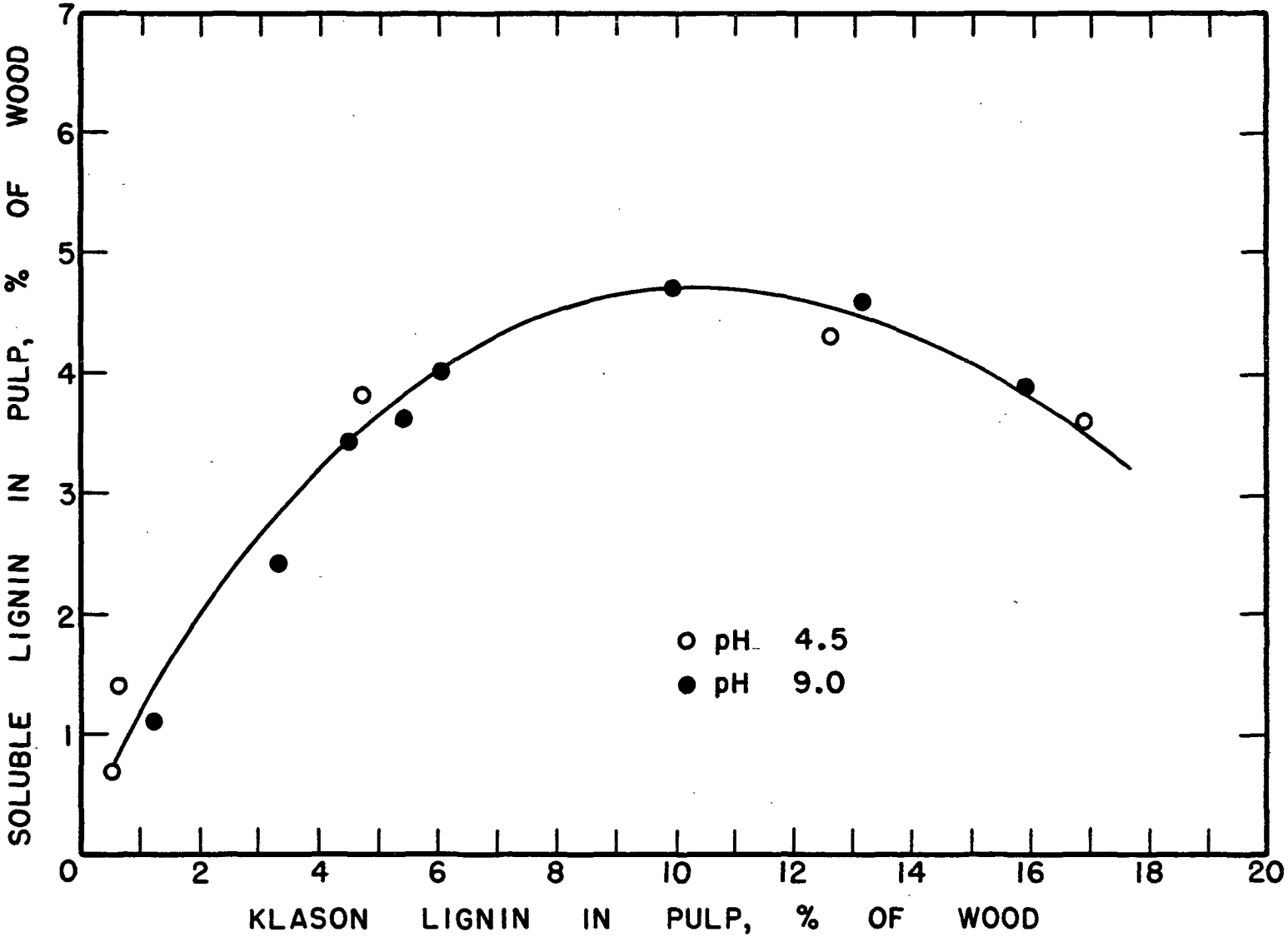


Figure 2. Relationship Between Klason and UV Soluble Lignin Content, Series IV Pulps

alcohol blanks were made on the columns, however, the amount of resin entering solution was in many cases greater than the amount of soluble lignin expected from the Klason lignin filtrate; thus, the blank values were not only variable, they were also too great. For this reason, lignin in the alcohol eluate was also estimated by UV spectrophotometry at 230 mmu, using the specific extinction data given by Buchanan, et. al. (37). Since the dissolved resin also absorbs in the UV range, blank values were taken once more.

Summaries of the data from the ion-exchange method of soluble lignin determination by weight and by absorption may be seen in Table IVA and IVB, respectively. The values obtained by both methods are roughly comparable, and remain much more constant during the cook than do the results of the UV data given in Table III, especially for the CIV 9.0 cooks. In general, the percentage of the "standard" UV-soluble lignin represented by the ion-exchange soluble lignin is higher at the beginning and end of the cook than at the middle; in most cases it is much less than 100%. Only a portion of the total UV-absorbing material in a Klason lignin filtrate was held on Zeo-Karb 215; the remainder may be accounted for by UV measurement of the "through-fraction". If this resin selectively isolates lignin or ligninlike materials, leaving carbohydrate degradation products in the filtrate, as stated in the literature (38), the soluble lignin determination by UV spectrophotometry on the whole Klason lignin filtrate may well give high results, especially in the middle Klason lignin ranges, where the amount of apparent soluble lignin increased, as seen in Figure 2.

All in all, the ion-exchange method looks promising for the determination of soluble lignin in Klason lignin filtrates, but its use at the present time may not be justified over the "standard" UV spectrophotometric determination, because of the following deterrents: (1) the alcohol column blanks were found to be too great, and show too much variation for precise determinations to be made, and (2) it has not been conclusively established that Zeo-Karb 215 removes all soluble lignin from solution, and allows all nonlignin to pass through the ion-exchange column.

REACTION RATE AND SELECTIVITY

Figure 3 shows a plot of pulp yield vs. time of pulping for the Series IV cooks; at any given time after approximately 40 minutes, the yield of pulps produced at pH 4.5 was lower than that of pulps produced at pH 9.0. It appears that the rate of pulping was slightly greater at pH 9.0 in the very early portion of the cook, perhaps within the range of possible experimental error. The rate at pH 4.5 soon exceeded that at pH 9.0, resulting in pulps of much lower yield at long cooking times. These trends are borne out in the Series I and II cooks, even though the absolute values of yield are not identical with those of the Series IV cooks at any given time; the yield values of the CI 7.2 pulps checked closely with those of the CI 9.0 pulps until about 150 minutes cooking time, when the rate of reaction at pH 7.2 appeared to decrease slightly, resulting in pulps of greater yield at pH 7.2. These data agree with those of Strapp (23), who shows that in a given time of pulping, less total woody material is removed at neutrality in the sulfite system than at higher or lower pH levels.

TABLE IV

ION-EXCHANGE METHOD OF SOLUBLE LIGNIN DETERMINATION

Pulp Sample (Series IV Cooks)	Col. No.	A. SOLUBLE LIGNIN BY WEIGHT: Evapd. Alc. Eluate, Wt. Sol. Lig. + Blank	Evapd. Alc. Blank Wt. Resin Blank	Diff. Wt. Sol. Lignin	100 x Diff. / Wt. Lig. Sample	Sol. Lig., %	UV Sol. Lig. on Whole Klason Filtr., %	Av.	B. SOLUBLE LIGNIN BY UV ABSORPTION: Alc. Eluate Opt. Dens./L. Diln.	Alc. Blank Opt. Dens./L. Diln.	Diff.= Sol. Lig. Opt. Dens./L. Diln.	100 x Diff. / Wt. Lig. Sample	Sol. Lig., %	UV Sol. Lig. on Whole Klason Filtr., %	Av.
4.5-30	1	.0932	.0621	.0311	3.13	3.33	82.0	87.2	2.00	.72	1.28	3.09	3.40	80.8	88.8
	2	.0920	.0569	.0351	3.53		92.5		2.34	.79	1.55	3.70		96.8	
4.5-60	1	.1241	.0021	.0620	5.96	5.25	117.7	103.7	2.48	.72	1.76	4.05	3.52	79.9	69.5
	2	.1004	.0569	.0435	4.55		89.8		1.98	.79	1.19	2.99		59.0	
4.5-90	1	.1093	.0621	.0472	4.89	4.36	83.5	74.5	2.50	.72	1.78	4.39	3.86	75.0	66.0
	2	.0939	.0569	.0370	3.84		65.5		2.14	.79	1.35	3.34		57.0	
4.5-150	3	.0805	.0579	.0226	2.31	2.20	78.6	74.7	1.76	.88	0.88	2.15	1.98	73.2	67.6
	4	.0804	.0603	.0201	2.08		70.8		1.46	.72	0.74	1.82		62.0	
4.5-210	5	.0628	.0462	.0166	1.71	1.88	121.2	133.3	1.24	.63	0.61	1.55	1.24	110.0	88.0
	6	.0740	.0540	.0200	2.05		145.3		0.92	.54	0.38	0.93		66.0	
9.0-30	3	.0941	.0579	.0362	3.73	3.72	89.5	89.4	2.44	.88	1.56	3.82	3.70	91.6	88.6
	4	.0963	.0603	.0360	3.72		89.3		2.18	.72	1.45	3.57		85.6	
9.0-60	3	.0924	.0579	.0345	3.50	3.77	66.3	71.4	2.44	.88	1.56	3.78	3.73	71.6	70.6
	4	.0990	.0603	.0393	4.04		76.5		2.22	.72	1.50	3.68		69.7	
9.0-90	1	.0936	.0621	.0315	3.17	3.56	53.0	59.5	2.28	.72	1.56	3.73	3.91	62.4	65.3
	2	.0962	.0569	.0393	3.95		66.0		2.50	.79	1.71	4.09		68.3	
9.0-150	5	.0888	.0462	.0426	4.38	3.86	76.8	67.7	2.20	.63	1.57	3.84	3.59	67.4	63.0
	6	.0868	.0540	.0328	3.34		58.7		1.90	.54	1.36	3.34		58.6	
9.0-210	5	.0859	.0462	.0397	4.11	3.61	80.5	70.7	2.20	.63	1.57	3.87	3.55	75.8	69.5
	6	.0848	.0540	.0308	3.11		60.9		1.88	.54	1.34	3.23		63.2	
Wood	3	.0884	.0579	.0305	3.01	2.91	91.5	88.5	2.00	.88	1.12	2.64	2.95	80.3	89.5
	4	.0887	.0603	.0284	2.81		85.5		2.10	.72	1.38	3.25		98.7	
Wood	5	.0682	.0462	.0220	2.19	2.20	68.6	69.1	1.82	.63	1.19	2.82	2.95	88.4	92.4
	6	.0763	.0540	.0223	2.22		69.6		1.84	.54	1.30	3.07		96.3	

Just as the cooks at pH 4.5 removed more woody material per unit time than the cooks at pH 7.2 or 9.0, the rate of delignification was also greater for cooks in the bisulfite range of pH. This confirms the work of Husband (17) over a wider range of initial pH. It may be seen in Figure 4 that both the Klason and total lignin contents of the pulps at pH 4.5 were lower than those at pH 9.0 for any cooking time greater than 50 minutes. The amount of lignin removed at any given time was greater for CIV 9.0 pulps up to 50 minutes, and greater for CIV 4.5 pulps after this time. Once more, the CI 7.2 pulps exhibited lignin contents very close to those of the CI 9.0 pulps until 150 minutes cooking time, where the residual lignin in the pulp was greater for cooks at neutrality, indicating a slightly decreased rate of delignification at these long cooking times. Figure 4 also effectively shows the increased importance of soluble lignin data at low levels of Klason lignin content; in general, as the cooks progressed, the ratio of soluble lignin to total lignin in the pulp increased almost linearly through 210 minutes cooking time (see Table III). In any case, a substantial amount of lignin may be removed from wood in the neutral sulfite range of pH.

Bixler (26) found that alkaline processes, such as kraft and soda cooks, were more selective for middle lamella lignin than the acid sulfite process, but Strapp (23) states that alkaline processes are less selective for the removal of total lignin than the acid sulfite process. The data presented in Figure 5, lignin content *vs.* yield, and Figure 6, nonlignin/lignin ratio *vs.* yield, show that cooking liquor in the bisulfite range of pH was less selective for lignin removal than liquor in the neutral sulfite range of pH, even though the rate of reaction was found to be greater for cooks at lower

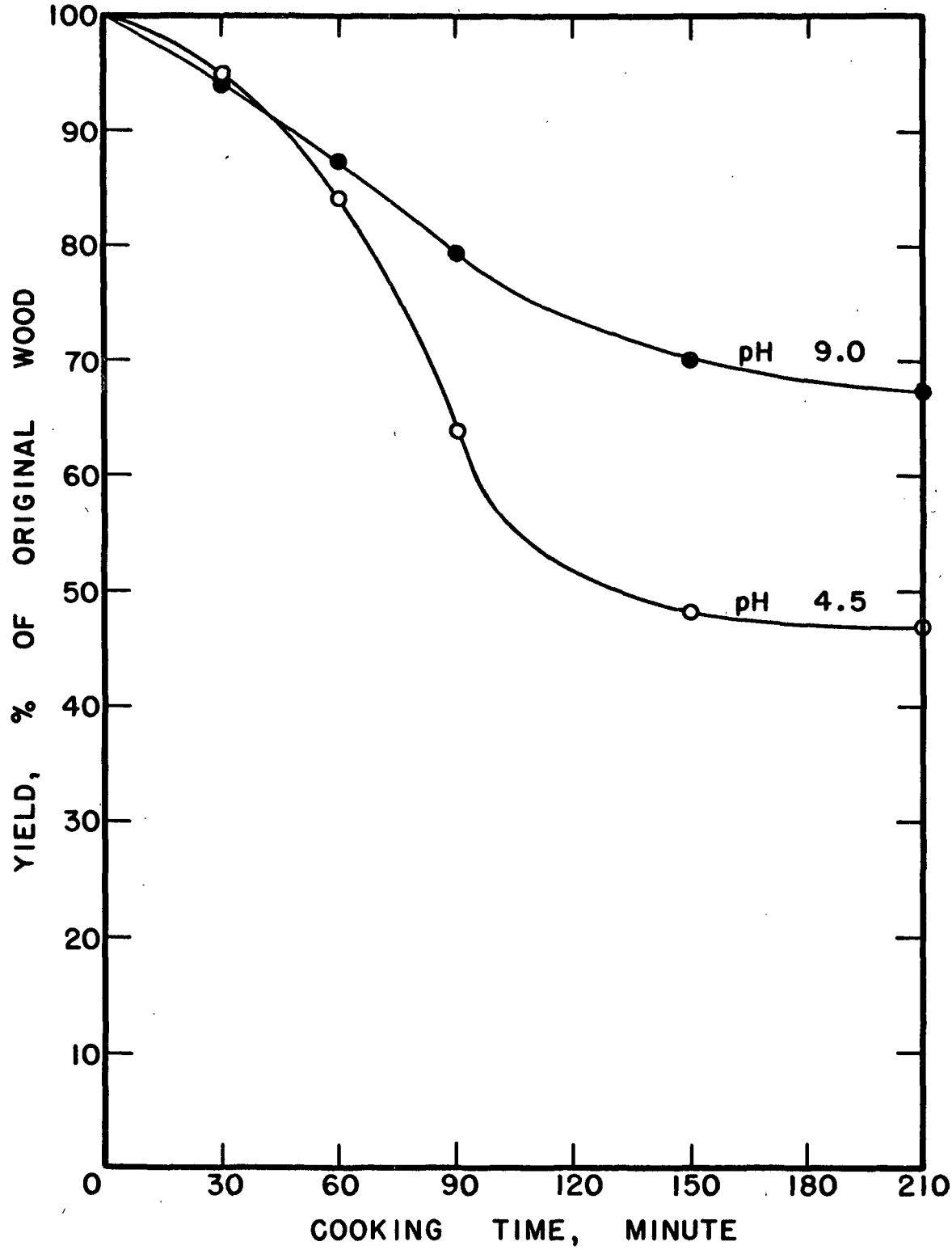


Figure 3. Pulp Yield vs. Time of Pulping, Series IV Cooks

pH. In these graphs, data from all four series of cooks have been plotted; the precision of these data is great enough that smooth line curves may be drawn for any cook at given pH, notwithstanding small differences in cooking conditions. These graphs also illustrate the importance of the Series III cooks to the conclusions; without long cooks at pH 9.0, valid comparisons could not be made at low yield values. At any given yield, the amount of residual Klason lignin present in the pulp was always lower, and the non-lignin/lignin ratio was always higher for cooks at pH 7.2 or 9.0 than for cooks at pH 4.5. The curves of the pH 7.2 pulps could not be distinguished from those of the pH 9.0 pulps. Therefore, proportionately more carbohydrate and less lignin was removed at pH 4.5 than at either pH 7.2 or 9.0 when aspenwood was pulped to a given yield, and the selectivity of the liquor for lignin was greater for cooks in the neutral sulfite range of pH than for cooks in the bisulfite range, even though the rate of reaction was greater at low pH.

It may be noted that Figure 6 is an inverse plot of the variables of a Ross Diagram. When these variables are plotted as in Strapp's work (23), the resultant curves appear very similar to those in Figure 5, with the pH 4.5 pulps exhibiting greater lignin/nonlignin ratios at any given yield. These results disagree with those of Strapp, who showed that this ratio decreased with increase in sulfur dioxide applied, even at constant yield, for four-hour cooks of poplar at 170°C. Figure 6 is so plotted because a more informative curve shape is obtained; the nonlignin/lignin ratio may be extrapolated to 100% yield, and checks with the ratio obtained for the wood. This ratio only doubled in the yield range 100 to 70%, as seen in the slightly

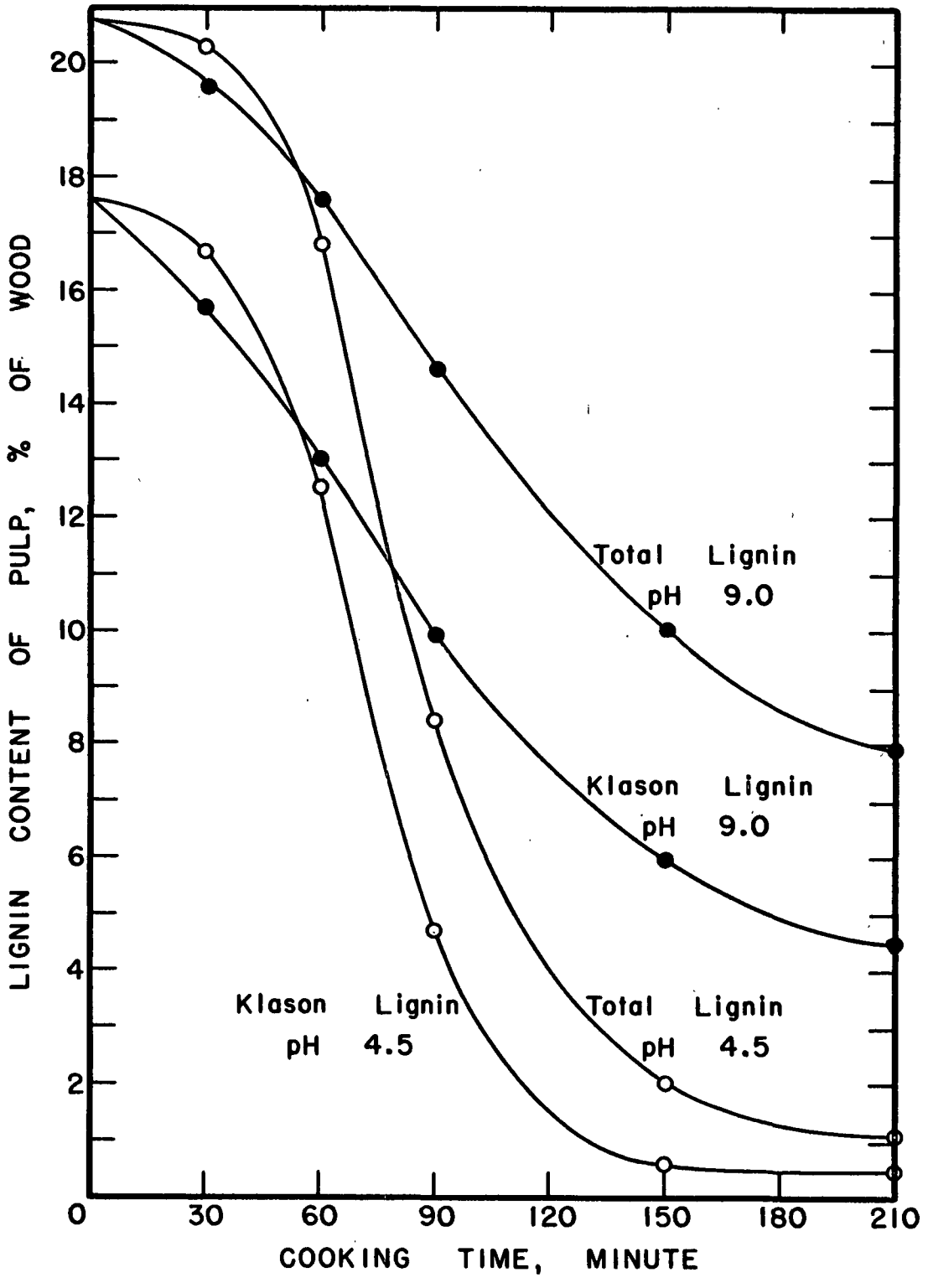


Figure 4. Lignin Content of Pulp vs. Time of Pulping, Series IV Cooks

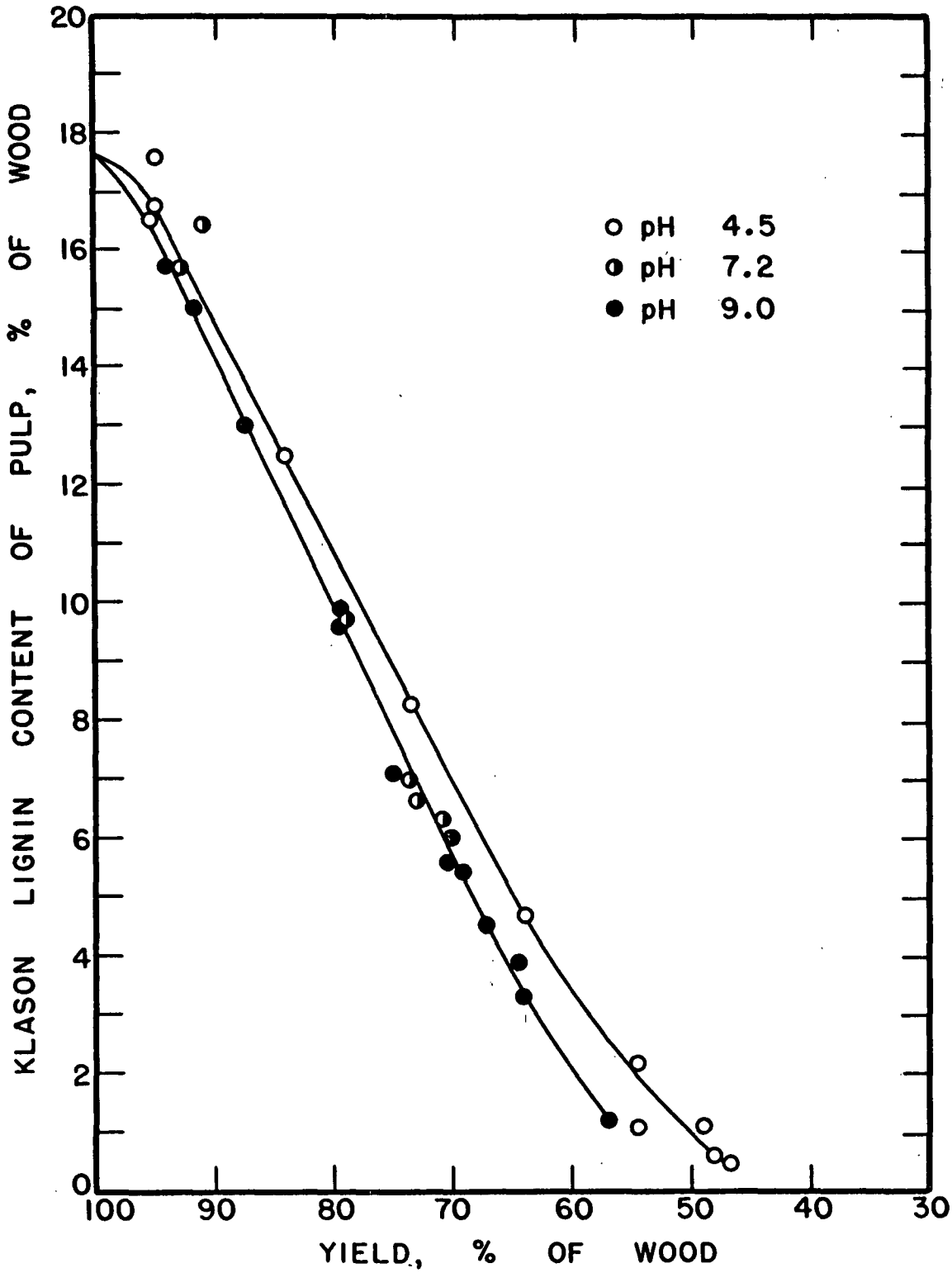


Figure 5. Relationship Between Klason Lignin Content and Yield, Series I-IV Pulps

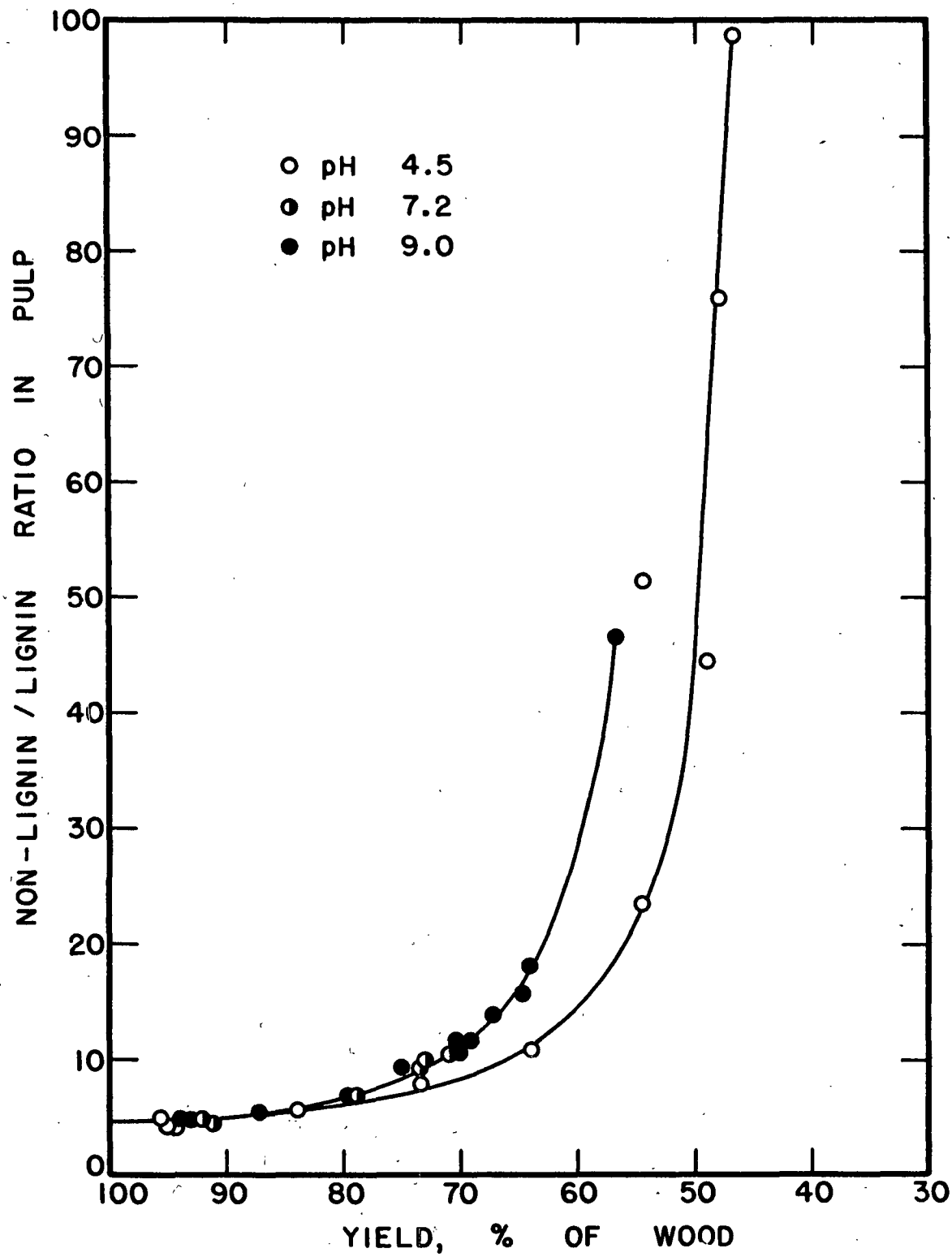


Figure 6. Relationship Between Nonlignin/Lignin Ratio and Yield, Series I-IV Pulps

increasing curves at both pH levels in Figure 6. Below 70%, however, both curves rise sharply, indicating that the liquors had become much more selective for lignin removal. This is probably due not to a sudden increase in the rate of lignin removal (note Figure 4), but rather to a decrease in the amount of carbohydrate material available for removal. It is probable that most of the hemicelluloses have been removed by this time, leaving cellulose as the main carbohydrate residual in the pulp; this cellulose resists the attack of cooking liquor and allows more lignin to be removed per unit yield loss than in the early portion of the cook. If this curve is plotted as lignin/nonlignin ratio vs. yield, the values decrease for both pH levels of pulping from 0.213 in the wood to almost zero at about 50% yield; the interval of constant ratio cited by Strapp in the high yield ranges is not nearly so pronounced as in the curve depicted in Figure 6.

The shape of the curves in Figure 5 is also of interest; the graph of Klason lignin vs. yield may also be extrapolated to the wood value at 100% yield. At both low and high pH it is a straight line in the yield range 95 to 65%, but above and below these limits, the slope of the curve decreases, indicating that a greater amount of total wood material was removed with less change in the lignin content than within the limits. This was to be expected, since many nonlignin materials may be removed in the early portion of the cook by extraction, and since the small amount of residual lignin difficultly removed by pulping probably approaches zero asymptotically with great decrease in yield.

SULFONATION AND HYDROLYSIS

It may be seen in the tabular data that, in general, the sulfur content of each pulp rose to a maximum at about 90 minutes cooking time, and decreased thereafter; the sulfur contents of the pH 4.5 pulps decreased most rapidly, followed by those at pH 9.0 and 7.2. The lignin content of these pulps, however, decreased even faster, as shown in Figure 7, the sulfur content of the lignin vs. time of pulping. This sulfur content was calculated as the quotient of the sulfur content of the pulp divided by the total lignin content of the pulp, and is submitted as the most reasonable estimate of the sulfur content of all of the lignin as it exists in the pulp. The direct determination of sulfur in Klason and soluble lignin residues is hindered by the great mass of sulfur introduced as sulfuric acid in the Klason determination since the sulfur contents of the fractionated lignins were found to be unequal, and proportionately greater in the soluble fraction, it would also be necessary in a direct determination to accurately determine the amount of soluble lignin present, so that a weighted average sulfur content could be calculated. The thorough discussion of this problem in the APPENDIX concludes that the simply calculated percentage is the most accurate method presently available. The estimation of the sulfur content of the sulfonated lignin fraction in the pulp by analysis of the whole Kullgren extract is clouded by the presence of carbohydrate material in this extract, as noted in the APPENDIX. A Klason lignin determination on the Kullgren extract yields no insolubles, making determination of the exact amount of lignin in this fraction difficult. Therefore, no direct accurate sulfur determination may presently be made on isolated total or sulfonated lignin fractions.

Figure 7 shows that the sulfur content of the lignin in the CIV 9.0 pulps increased to 150 minutes cooking time, then levelled off at a fairly constant value of 2.6% through 210 minutes; at pH 4.5, however, the sulfur content increased continuously throughout the cook. This same phenomenon was apparent in the plotted data for the Series I and II cooks, and the CI 7.2 pulps showed values of sulfur content very close to those of the CI 9.0 pulps. At any time greater than 60 minutes, the sulfur content of the pulps produced at pH 4.5 was greater than that of the pulps produced at pH 9.0, but in the early portion of the cook, the same greater degree of reaction already shown in yield and lignin content curves appeared for the cooks at pH 9.0. Over most of the cook, however, the rate of sulfonation of lignin appeared to be greater at lower pH.

At first glance, these curves appear to support the classical theory of sulfonation, i.e., that in the neutral sulfite range of pH (7 to 9), only the "A" lignin groups are sulfonated, and that equilibrium may be reached (1) when all of these groups have become sulfonated (if no lignin is being removed), or (2) when the rate of lignin removal equals the rate of sulfonation. Since it is apparent from Figure 4 that lignin is being removed at this stage of the neutral sulfite cook, explanation (2) must be the correct one. Bisulfite and acid sulfite systems, on the other hand, are able to sulfonate "B" groups as well as "A" groups, resulting in the corresponding rise in sulfur content seen in Figure 7. If this theory may be applied, it appears that the sulfonation of "B" groups did not begin until the cook had progressed 60 minutes, since up to this point the extent of sulfonation at pH 4.5 was no greater than that at pH 9.0 or 7.2.

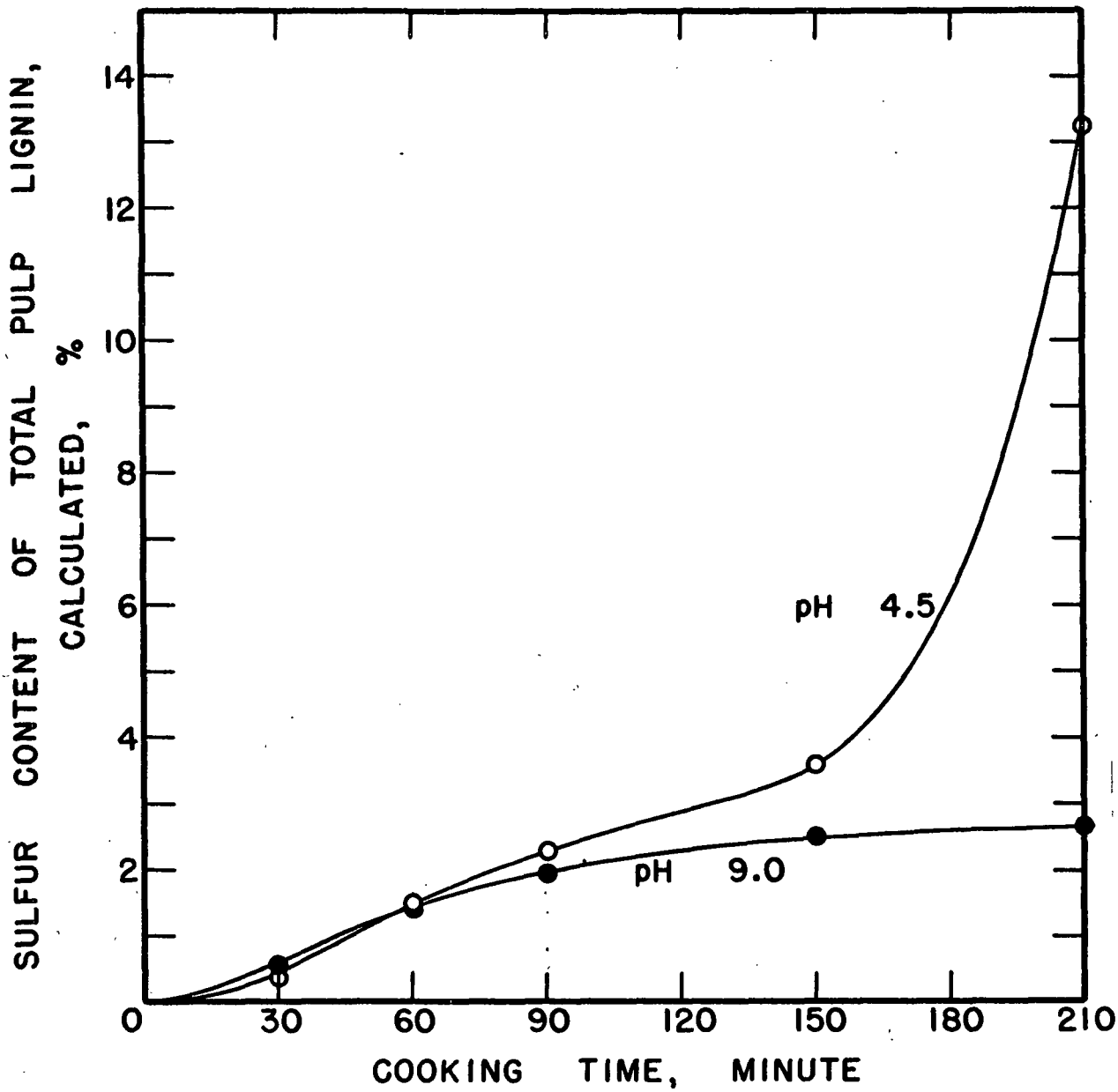


Figure 7. Sulfur Content of Pulp Lignin vs. Time of Pulping, Series IV Cooks

The only inconsistency in this reasoning concerns the sulfonation of "B" lignin groups in acid sulfite solutions; pulping theory maintains that these groups must be cleaved before they may be sulfonated. If it were not necessary to cleave them, their sulfonation might be accomplished by liquors at any pH, and if they were cleaved, their sulfonation would not be indicated on a graph of the sulfur content of the lignin in the pulp. It appears from the data presented in Figure 7, however, that additional sulfonation occurred in the solid state in acid sulfonation cooks, but not in alkaline cooks. Sulfonation may also occur in solution in pulping liquors of initial pH 4.5 and not in those at pH 9.0, but the shape of the curves of sulfur dioxide consumed vs. time for the two pH levels is very similar to those in Figure 7; the amount of sulfur dioxide consumed at pH 4.5 increased in proportion to the increase in sulfur content of the lignin in the pulp, while the consumption at pH 9.0 levelled off to a constant value. The similarity of the sulfur dioxide consumption curves and the lignin sulfur content curves may be taken as an indication that a large proportion of the total sulfonation occurs in the solid state, and according to the relationships shown in Figure 7.

It might be expected that the sulfur content of the lignin in pulps produced at pH 4.5 might level off at some cooking time greater than 210 minutes, due to the sulfur saturation of sulfonatable groups or to an equalization between the rates of sulfonation and lignin removal, since the hydrolysis capacity of these liquors is much greater than those at pH 9.0. This is unlikely, for the sulfur content of the lignin increased regularly up to 210 minutes cooking time, where approximately 95% of the lignin present in

the wood had been removed. It might also be expected from theory that the sulfur content of the lignin in pulps produced at pH 9.0 might increase at some greater pulping time, for although theoretical sulfur saturation may be reached at this pH level long before all of the lignin in the pulp is sulfonated, the theoretical hydrolysis capacity of these liquors is so low that all of the sulfonated lignin may not be removable. This is contradicted by the CIII 9.0-600 data, however; 89% of the original wood lignin was solubilized by alkaline sulfite cooking liquor. Taking the more realistic outlook that these liquors are able to remove the bulk of the wood lignin, it might then be theorized that the sulfur content of the pH 9.0 pulp lignins would be expected to remain constant, or even decrease, due to the removal of all of the sulfonated "A" lignin groups. The series III cooks indicated, however, that the sulfur content of this lignin rises at longer cooking time, indicating the same type of additional sulfonation seen in the pH 4.5 lignins. According to Hägglund's theory, only "A" lignin groups may be sulfonated unless the pH of the cooking liquor at that late time and high temperature is low enough for hydrolysis to occur. The cold spent liquor pH in the CIII cooks never dropped below 7.0; it may be, however, that the local pH of the liquor at certain points in the hot digester was below the neutral point. No attempts were made at pH evaluation at the elevated temperatures and pressures of the cooks. Whether or not hydrolysis occurs in neutral sulfite solution cannot be answered at this point; the data indicate, however, that similar mechanisms of lignin removal existed at both low and high pH, and that sulfonation of pulp lignin in the solid state seemed to proceed at both pH levels beyond the plateau of "A" group sulfonation.

One other explanation may be proposed for the rise in sulfur content at low lignin contents of pulps produced by both bisulfite and neutral sulfite cooking liquors. It is known that a small portion of the lignin in pulp is difficultly removed by pulping methods, due either to its high state of condensation or to physical inaccessibility; if this fraction were to become increasingly sulfonated, so that the rate of sulfonation exceeds the rate of delignification, the sulfur content of the lignin might rise as pictured in Figure 7. It is unlikely, however, that a highly condensed or inaccessible lignin fraction could become highly sulfonated and degraded without being subsequently removed.

A rearrangement of the data to more suitable bases for comparison yields supporting evidence to the hypotheses proposed above. Figure 8 is a plot of calculated percent sulfur in the pulp lignin vs. the percentage of the original lignin remaining in the pulp; data from all four series of experimental cooks fall well on this curve, but the rather sharp break in the curve at 6% sulfur is verified for the pH 9.0 cooks only by cook CIII 9.0-600. Figure 8 shows that for any given amount of delignification, the amount of sulfur in the lignin remaining in the pulp was the same for cooks at any pH level. Although the rate of delignification was greater at pH 4.5, the rate of sulfonation was also greater; thus, the amount of sulfur necessary to produce a given amount of delignification was the same for cooks at any pH level within the sulfite-bisulfite range.

The curve presented in Figure 8 would agree with sulfite pulping theory if all the experimental points fell on a straight line of increasing slope;

the sharp increase in sulfur content at low lignin content may be drawn as another straight line intersecting the first, however, indicating that two sulfonation reactions occurred in the solid state at both pH levels of pulping. If only one lignin group reacted with cooking liquor, and the increase in sulfur content were due to the increasing difficulty of removal of a portion of this lignin, as previously theorized, the break in the curve would not be expected to be as sharp as that shown in Figure 8. If this curve indicates the sulfonation of "B" lignin groups, starting at about 90 minutes cooking time for the pH 4.5 cooks, these groups appear to have been sulfonated in the solid state as well as in solution, and by pulping liquors in the alkaline pH range. It seems reasonable that if "B" groups may be sulfonated without first being solubilized by hydrolysis, they may be sulfonated by alkaline sulfite liquors as well as acid sulfite liquors. Mikawa and co-workers (13) have split the "A" lignin group into two other groups by differences in rate of sulfonation; it may also be possible that the differences shown in Figure 8 indicate the sulfonation of two different "A" type groups, but it must be remembered that in the range of sulfur content increase, the great bulk of the lignin originally present in the wood has been removed. If "B" lignin groups do exist, it appears that they may be sulfonated and removed by liquors of original pH 9.0 as well as those at pH 4.5. The data do not indicate that hydrolysis was necessary before sulfonation occurred, unless hydrolysis also occurred to a great extent at pH levels of neutrality or greater. If these premises are true, the same sulfonation reaction or reactions occurred at all experimental pH levels of pulping in the sulfite-bisulfite range; only the rate of this reaction varied with pH.

The identity of the rate-governing reaction is open to question; the sulfur content of the CIV 4.5 pulps increased at a much faster rate than that of the CIV 9.0 pulps, even though the theoretical hydrolysis capacity is much greater at pH 4.5. This indicates that the hydrolysis reaction was slower than the sulfonation reaction, and therefore governed the rate. Conversely, the difference in rate of reaction between cooks at pH 4.5 and 9.0 appears to be more closely proportional to the difference in bisulfite ion concentration between these two liquors than the difference in hydrogen ion concentration. Since alkaline sulfite liquors may effect the removal of the bulk of the wood lignin, it is possible that acid hydrolysis plays a minor role in delignification, and that differences in reaction rate at different pH levels may be explained on the basis of the difference in bisulfite ion concentration alone, employing a concept of equal rates of lignin removal at any pH level due to simple solubility of degraded molecules rather than hydrolysis.

The relative efficiency of cooking liquors at different pH for the removal of total lignin has already been discussed; the selectivity of each liquor for sulfonated lignin may be characterized by a comparison of the relative amounts of sulfur dioxide consumed at each pH level. For a given amount of delignification, the amount of sulfur dioxide consumed was not the same for both pH levels of pulping, as was the case for the sulfur content in Figure 8; Figure 9 shows that the amount of sulfur dioxide consumed was slightly greater at any given lignin content for cooks at pH 4.5 than for those at pH 9.0. Therefore, the same amount of delignification was obtained at pH 9.0 as at pH 4.5 with a slightly lower expenditure of

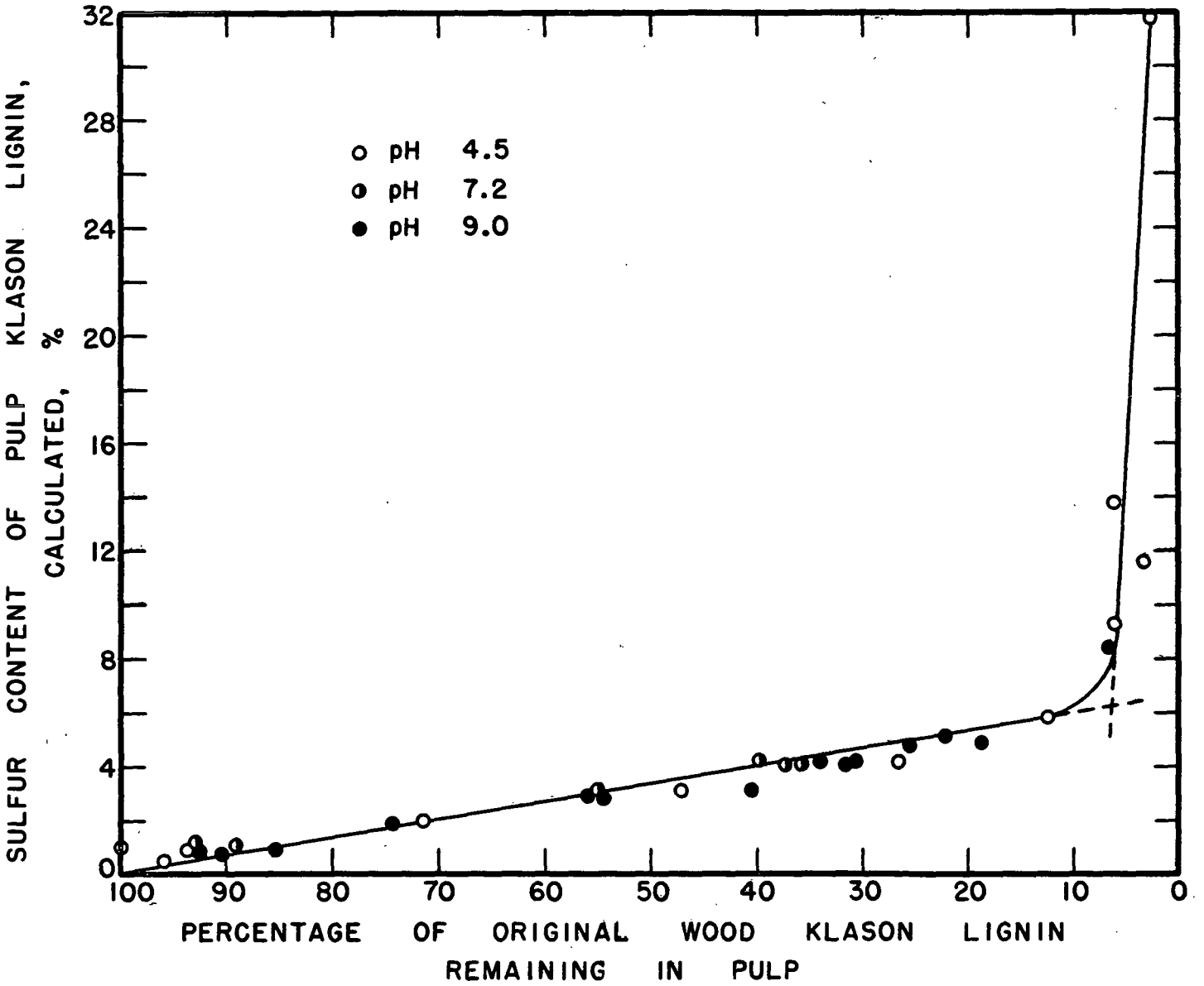


Figure 8. Relationship Between Sulfur Content of Pulp Lignin and Amount of Original Wood Lignin Remaining in Pulp, Series I-IV Cooks

sulfur dioxide; this means that cooking liquor at high pH was more efficient than liquor at low pH in its use of available sulfur for lignin removal.

This conclusion may be further substantiated by the curves presented in Figure 10, percent sulfur in total lignin vs. percent sulfur dioxide consumed. The degree of sulfonation increased with increase in sulfur dioxide consumption for both pH levels of cooking, but in the range of consumed sulfur dioxide found in the CIV 9.0 cooks, the sulfur content of the lignin remaining in the pulp was always greater (at any given amount of sulfur dioxide consumption) at pH 9.0 than at pH 4.5. Therefore, not only was the amount of lignin removed greater at any given sulfur dioxide consumption at pH 9.0, but the efficiency of the sulfonation reaction was also greater, producing greater lignin sulfur contents for any given amount of sulfur dioxide consumption. This supports the general conclusions presented previously that liquors at high pH were more selective than liquors at low pH for lignin removal.

GUAIACYL AND SYRINGYL GROUPS

The nitrobenzene oxidation of pulping reaction products is not a quantitative test for the absolute number of syringyl and guaiacyl nuclei present in any ligninlike material, but rather a measure of the amounts of these nuclei which are in such a state of availability that they may be easily oxidized to syringaldehyde and vanillin, respectively. The procedure is not a supplementary method of lignin determination; the amount of aldehyde liberated from any given sample is not necessarily equivalent to the total lignin content in that sample. Rather, the yield of aldehyde decreases with

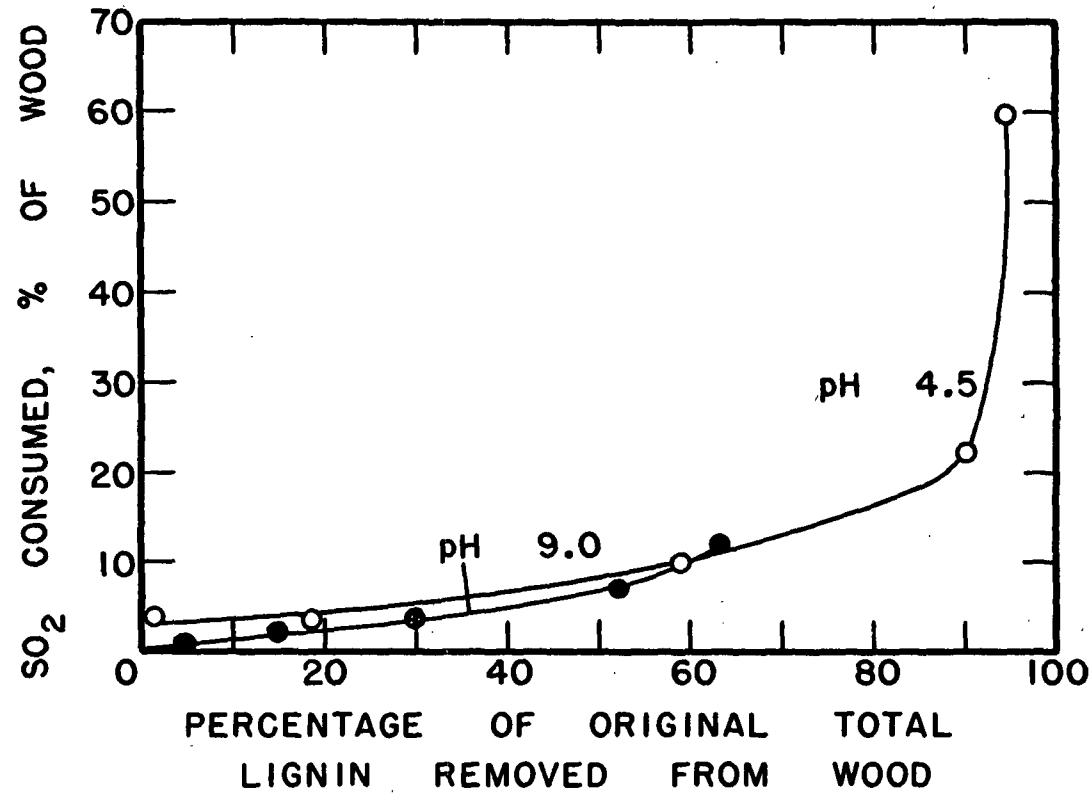


Figure 9. Relationship Between SO_2 Consumed and Amount of Original Wood Lignin Removed, Series IV Cooks

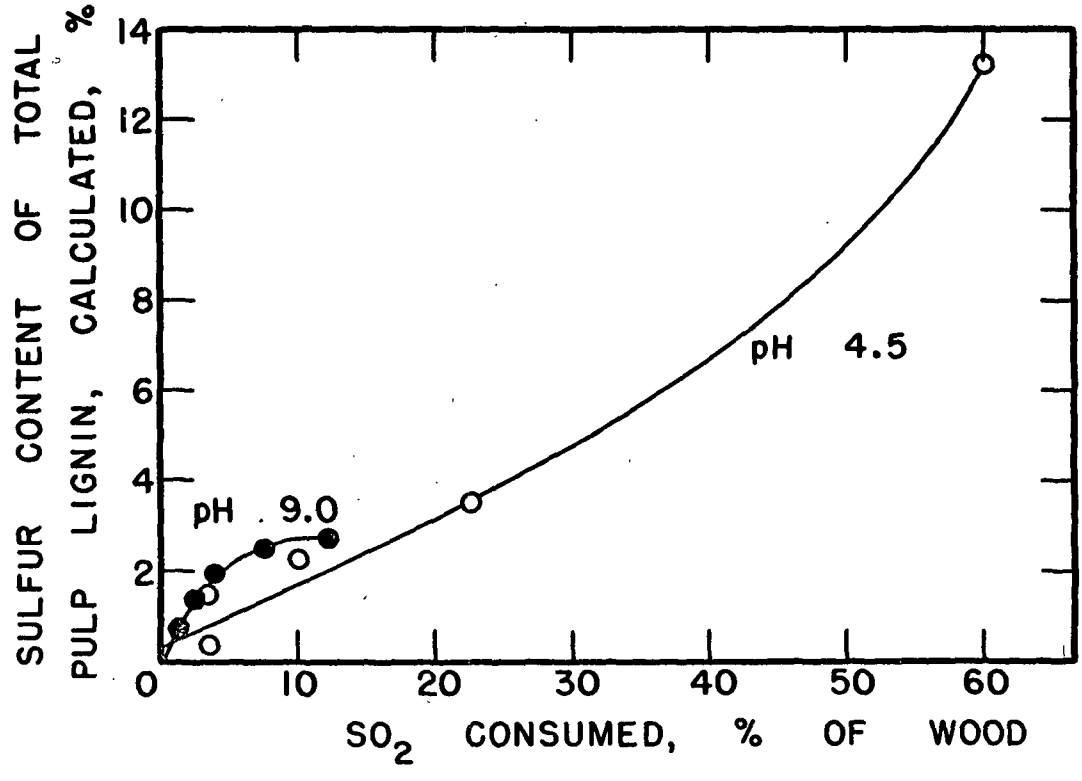


Figure 10. Relationship Between Sulfur Content of Pulp Lignin and SO_2 Consumed, Series IV Cooks

increase in the number and severity of some of the reactions to which the lignin in the sample may be subjected; the Klason lignin precipitate yields virtually no aldehyde on nitrobenzene oxidation. Direct measurement of the amount of lignin present in any spent liquor sample is difficult; because the sum of the pulp and liquor lignin content is expected to equal the amount of lignin present in the original wood, the lignin in the liquor may be determined by difference. This is not the case in aldehyde balances, however. It may be seen in Table XII in the APPENDIX that percent recovery in a pulp-liquor aldehyde balance was about 84%, and that in a Kullgren extract-residue balance was about 79%. These recovery figures may be clouded by interference from extractives originally present in the wood which probably entered the liquor during the cook. Even if the balance includes data on oxidizable nuclei in extractives as well as lignin, the percent recovery was well below 100%. Therefore, the amount of aldehyde in pulp or liquor samples may not be determined by difference, but must be measured directly, if valid comparisons are to be made. It is fortunate that nitrobenzene oxidation of spent liquor is not subject to the interfering factors present in the direct determination of lignin in these liquors. Nitrobenzene oxidations were run on both pulp and liquor samples according to the method of Stone and Blundell (36) in the Series IV cooks; these data may yield information on the relative amounts and ratio of guaiacyl and syringyl nuclei present in any sample, and show differences in composition of the lignins isolated from and remaining in the pulp at different stages of the neutral sulfite reaction.

The data given in Tables II and III show that the amount of aldehyde

per ml. liquor increased from zero with time for all series cooks, but the rate of increase was greater at pH 4.5 than at pH 9.0 or pH 7.2, paralleling the rates of lignin removal at these respective pH levels. The aldehyde content of the Series IV pulps decreased with time at both pH levels, but the decrease was gradual at pH 9.0 and fairly rapid at pH 4.5; at this latter pH, the low values of mg. aldehyde/g. pulp were virtually identical for both the 150 and 210-minute cooks. The weight ratio of syringyl to guaiacyl groups found as aldehyde (S/V ratio) in the CIV liquors increased from about one at 30 minutes time to a little over two at 210 minutes, with a slightly faster initial rise at pH 4.5; these curves may be seen in Figure 11A. It must be noted that all S/V ratios given in this thesis are on a weight basis; to calculate these ratios on a molar basis, which indicates the relative number of each type of nucleus available for oxidation, the weight ratios must be multiplied by the factor 0.831. The data from the Series I cooks are in agreement with the Series IV cook data; the curve of S/V for the CI 7.2 liquors was intermediate between those of the CI 9.0 and the CI 4.5 liquors, with the shape of the latter and values more nearly in the range of the former. The S/V ratios in the CIV pulp are plotted against cooking time in Figure 11B; the values at pH 9.0 decreased linearly from 2.4 in the wood to 1.94 in Cook CIV 9.0-210, while the ratio at pH 4.5 remained constant for 30 minutes, then decreased more rapidly to a lower value of 1.7 at 210 minutes.

The changing S/V ratios in Figure 11 and the varying ratios noted in the APPENDIX for differently isolated Kullgren hydrolysis fractions from pulp and aspenwood may be explained by either (1) differences in the relative

amounts of guaiacyl and syringyl groups which are actually present in each of these isolated lignin fractions, or (2) differences in the nature of the oxidizable bonds joining these groups to parent nuclei. Stone (31) oxidized a series of NSSC spent liquors of original pH 8.3 with nitrobenzene and found that the percent vanillin in the lignin in the liquor (lignin determined by UV spectrophotometry) remained at a constant value of 12% throughout the cook, while the percentage of syringaldehyde varied from zero at the beginning of the cook to 23% at the end. He states that methoxyl contents of preferentially soluble lignin fractions such as native lignin have in general been found to be lower than that of the original whole lignin fraction; this theory is also supported by the low S/V ratio (1.02) found in nitrobenzene oxidation of an alcohol-benzene extract of aspenwood (see APPENDIX). Nitrobenzene oxidation data may not show the true number or ratio of syringyl and guaiacyl groups in a sample because of their dependence on the nature of oxidizable bonds holding these groups to the parent molecule; in many cases, however, the oxidation technique yields results which show the same trends as the methoxyl determination. The assumption may be made that the relative number of syringyl and guaiacyl groups present in the lignin fraction of pulp or liquor samples which have undergone very similar treatment may be characterized by nitrobenzene oxidation data. Then, if the number of syringyl groups in the lignin in the liquor actually increases during the cook, the polymers containing these groups have probably become more soluble than those containing guaiacyl groups, either because of structural differences or differences in accessibility due to their location in the cell wall.

The data presented in Table III and Figure 11A agree in general with the results of Stone's work; Figures 12A and 12B, percent aldehyde based on the total lignin which has entered the liquor vs. time for the Series IV cooks at pH 4.5 and 9.0, respectively, are shown for purposes of comparison with the curves given in (31). The percent vanillin in the liquor lignin remained fairly constant throughout the cook at pH 4.5, but decreased slightly at pH 9.0; the percent syringaldehyde increased during the cook from a low value to a ratio near that present in the wood at both pH levels of pulping. The only point of conflict between this work and that presented by Stone is the value of extrapolated percent syringaldehyde at zero cooking time. Stone cites three liquor samples at the beginning of the cook having S/V ratios of much less than 1.0, and extrapolatable to zero at zero cooking time; although the cooking schedules were not greatly different, the spent liquor obtained in this thesis yielded no ratios appreciably lower than unity. This was one of the justifications for the Series II cooks; the CI 7.2-30 and CI 9.0-30 liquors yielded almost identical amounts of syringaldehyde and vanillin on oxidation, and these cooks were repeated to determine if the original data were in error. The S/V ratios of the CII 30-minute liquors were also very close to 1.0, although the absolute yields of both aldehydes were lower. If the Series II cook data are correct, the percent vanillin was not constant over the whole time range of cooking, and if the Series I data are correct, the percent syringaldehyde did not decrease to zero at zero cooking time. The Series IV cooks confirmed the results of the Series I cooks at pH 9.0; the percent vanillin was fairly constant, and the percent syringaldehyde increased during the cook, but may not be extrapolated back to zero. This may also be seen in Figure 11A; the

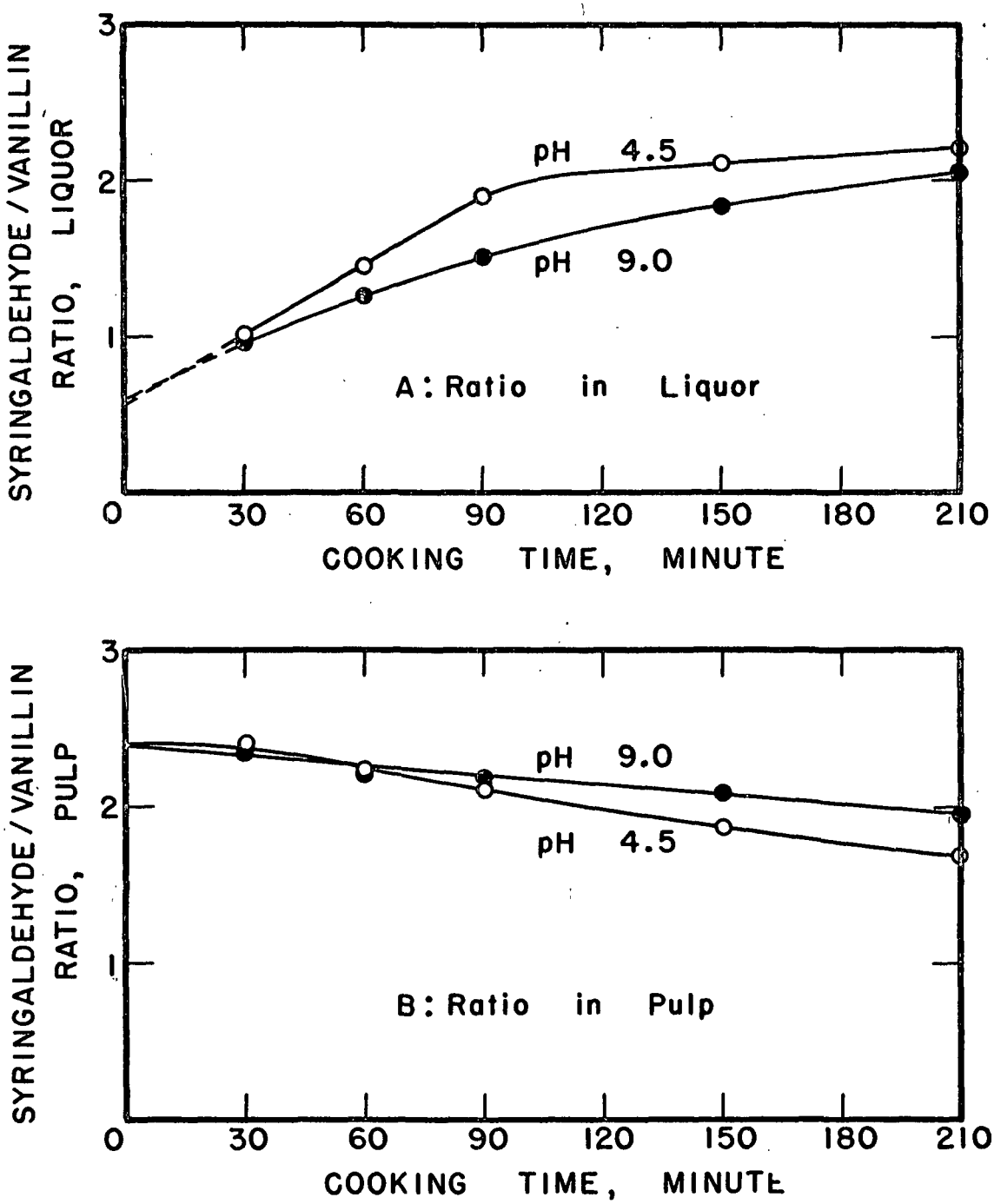


Figure 11. Syringaldehyde/Vanillin Ratio on Nitrobenzene Oxidation of Liquor and Pulp vs. Time of Pulping, Series IV Cooks

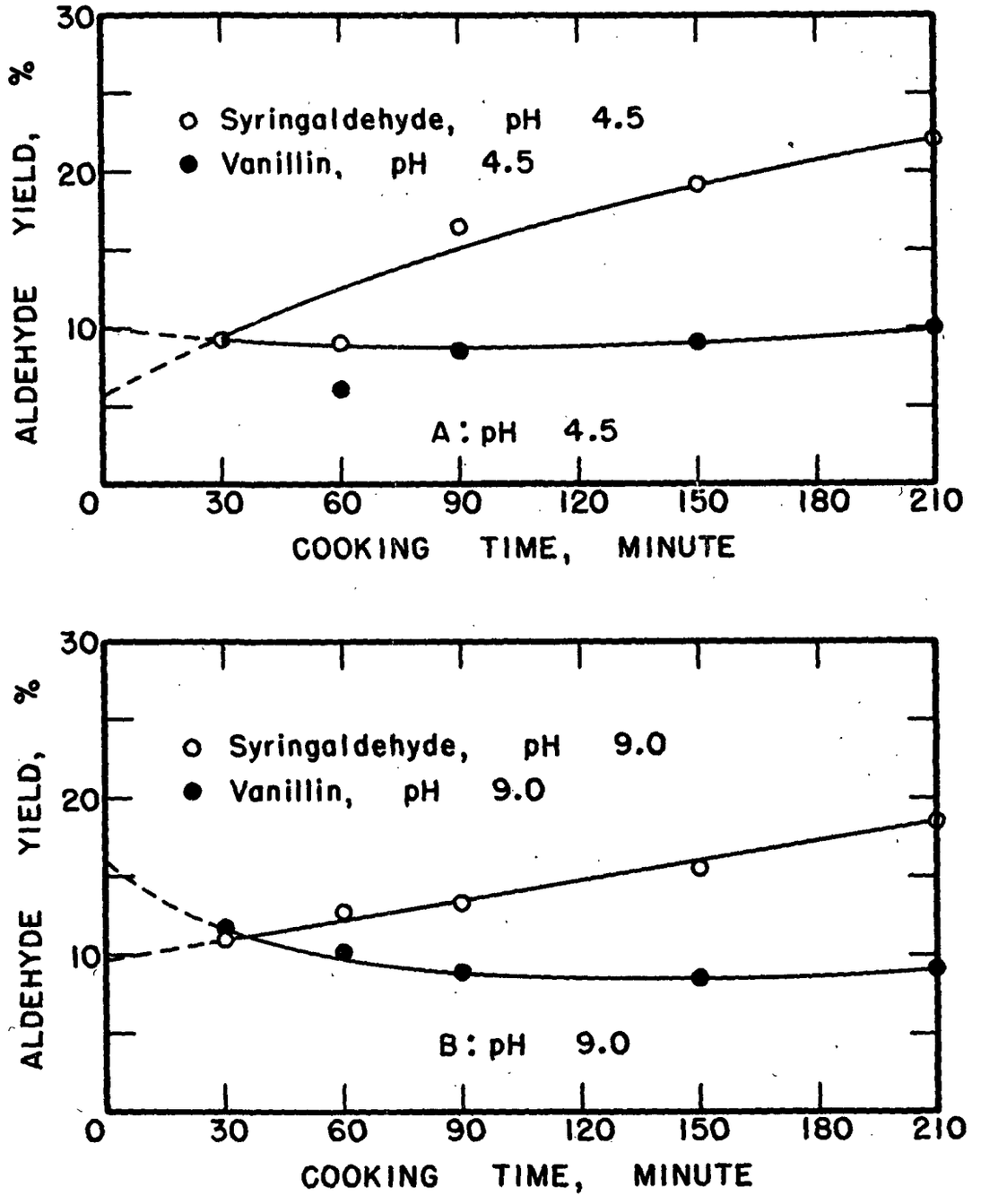


Figure 12. Aldehyde Yield on Nitrobenzene Oxidation of Spent Liquor Based on Total Lignin in Liquor vs. Time of Pulping, Series IV Cooks

extrapolated value of the S/V ratio at zero cooking time is about 0.6 for cooks at both pH levels. If the first lignin molecules to enter the liquor contained only guaiacyl (and no syringyl) groups, and the syringyl content of the liquor lignin rose regularly with increasing time, while the guaiacyl content remained fairly constant, it might be expected that the S/V ratio would approach zero if it were extrapolated back to zero cooking time.

In summary, the CIV 9.0 spent liquor lignins showed vanillin contents decreasing slightly from about 12% at 30 minutes cooking time to about 9% at the end of the cook, and syringaldehyde contents increasing from 11% to about 18%. At pH 4.5, the vanillin content remained fairly constant at about 9%, while the syringaldehyde content increased from 9 to 22%. The CI 7.2 cook oxidation data were very similar to those obtained from the CI 9.0 cooks. Under no conditions would the syringaldehyde content of the lignin in the liquor be extrapolated to zero at zero cooking time.

The nitrobenzene oxidation of pulps allows comparisons to be made not only of the lignin removed from the pulp, but also of that which remains at the end of each pulping interval. Figures 13A and 13B show calculated percent aldehyde in the total pulp lignin vs. cooking time for the Series IV cooks at pH 4.5 and 9.0, respectively. It may be seen that the percentage of both syringaldehyde and vanillin in the pulp lignin decreased markedly at pH 4.5, while at pH 9.0 the syringaldehyde content decreased and the vanillin content remained fairly constant. Since the syringyl fraction formed a greater and greater portion of the liquor lignin as the cook progressed (see Figures 11A, 12A and 12B), it might be expected that the syringyl content of the pulp lignin would decrease with increase in cooking

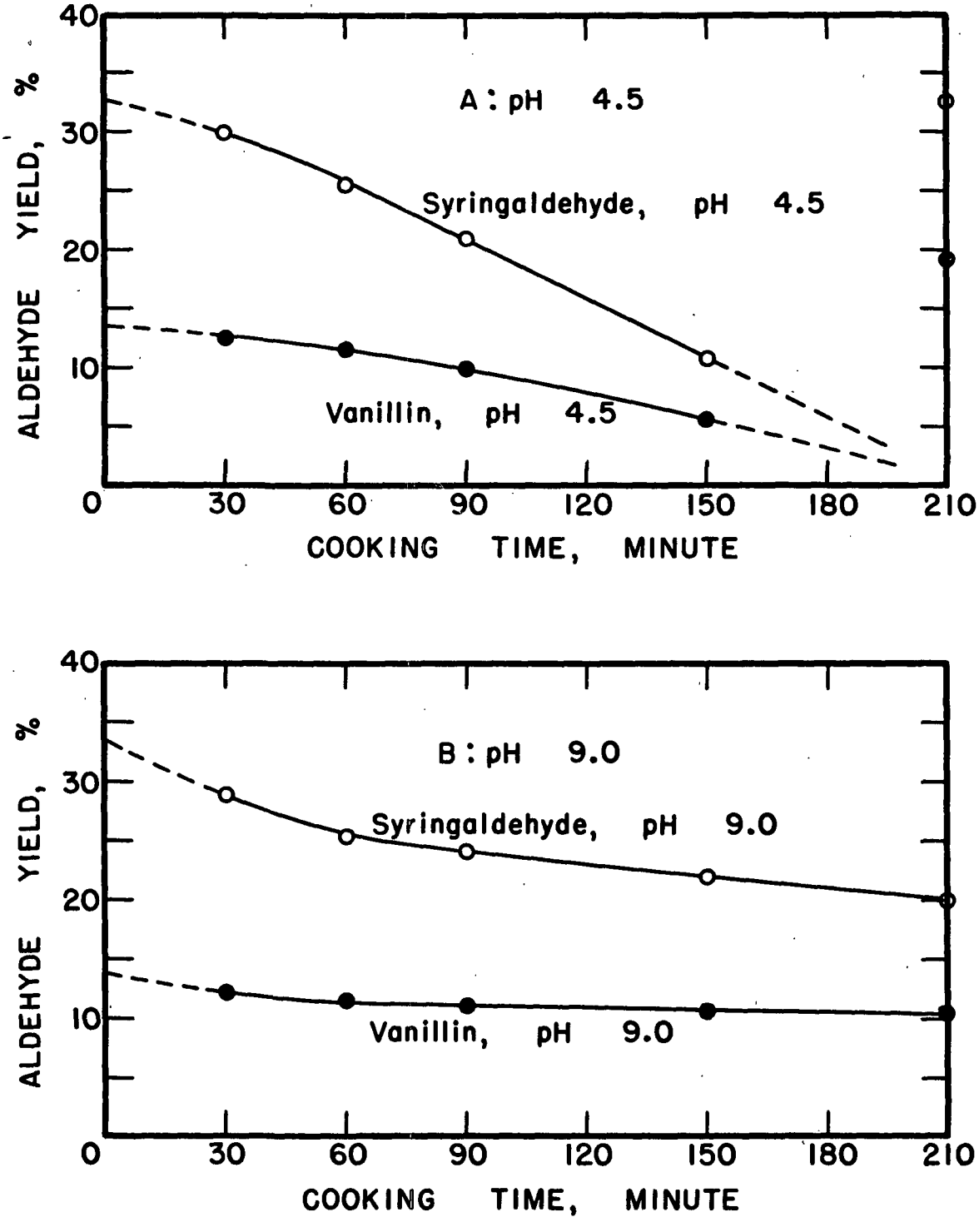


Figure 13. Aldehyde Yield on Nitrobenzene Oxidation of Pulp Based on Total Lignin in Pulp vs. Time of Pulping, Series IV Cooks

time. This is verified in Figures 11B, 13A and 13B. It might also be expected that the guaiacyl (vanillin) content of the pulp lignin would remain fairly constant during the cook, and this was the case for the CIV 9.0 cooks. The decrease in the vanillin content of the pulp lignin in the CIV 4.5 cooks indicated in Figure 13A may have been due to the greater severity of the pulping reaction at pH 4.5, resulting in condensation, which caused lower and lower proportions of both aldehydes to be liberated by oxidation as the reaction proceeded. This hypothesis is also supported by the vanillin data shown in Figure 13B; it might be expected that the vanillin content of the pulp lignin would increase very slightly, because of the slight decrease shown in Figure 12B. The fact that it decreased, however, indicates that even at pH 9.0 the reaction was drastic enough so that some condensation occurred, resulting in a decrease in aldehyde recovery with increase in cooking time.

If lignin reacted differently with liquors of different pH, differences in (1) sulfur content of lignin in pulp and liquor, and (2) amount and ratio of aldehyde in lignin in pulp and liquor, might be apparent with difference in pH, even when these parameters are compared at constant lignin content. The first case treats differences in liquor selectivity for the reactive groups in lignin; the second treats differences in selectivity for lignin structural groups. Sulfonation of the lignin in the liquor was not studied, but for any given degree of delignification, it was found that the percent sulfur in the pulp lignin was the same for cooks produced at any pH within the sulfite-bisulfite range. Rate of reaction was different, but the type of reaction appeared to be the same in cooks at all pH levels.

The relationship between aldehyde yield on nitrobenzene oxidation at constant degree of delignification for cooks at different pH level may be seen in Figures 14 and 15. Differences in rate of reaction at different pH levels may be eliminated by replacing time as the independent variable with lignin content. Then, the percent vanillin and the percent syringaldehyde in both the liquor lignin (Figure 14A) and the pulp lignin (Figure 14B), and the S/V ratio in the liquor and in the pulp (Figure 15), may be seen to be the same at any given degree of delignification for cooks at any pH level.

The variation in percent aldehyde at low values of percent lignin removed in Figure 14A is probably due to the fact that at high pulp lignin contents the amount of lignin in the liquor is determined as the difference between two relatively large numbers; any slight inaccuracy in the lignin determination introduces a rather large error in both the amount of lignin in the liquor and the percent aldehyde in this lignin. If the amount of aldehyde present in pulp or liquor is plotted against lignin content, smooth curves increasing from the origin may be drawn for both syringaldehyde and vanillin; also, in Figure 14A, it may be seen that the S/V ratio of each of the deviating points at low values of lignin removed is relatively constant and close to unity, even for cooks at different pH level. This indicates that inconsistencies in these results are not due to nitrobenzene oxidation data, but to lignin data. It will be noted that, although only CIV cook data are plotted in Figure 14B and in one curve in Figure 15, Klason lignin values are still used as a basis for comparison. This was done so that the relationship between pulp and liquor could be observed; Figures 14A and part of 15 include data from all four series cooks, and

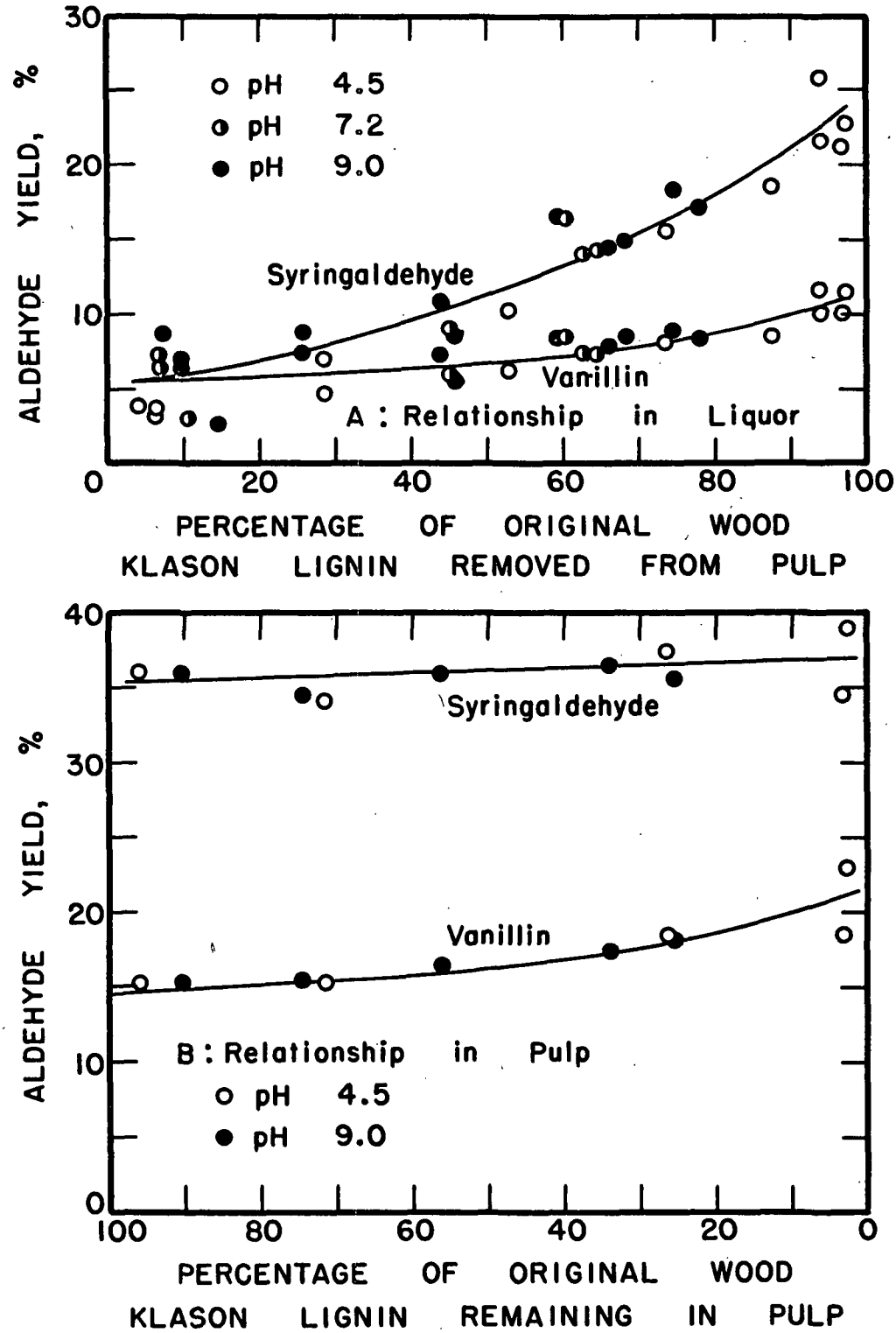


Figure 14. Relationship Between Aldehyde Yield on Nitrobenzene Oxidation Based on Lignin in (A) Liquor and (B) Pulp and Amount of Original Wood Lignin Present, Series I-IV Cooks

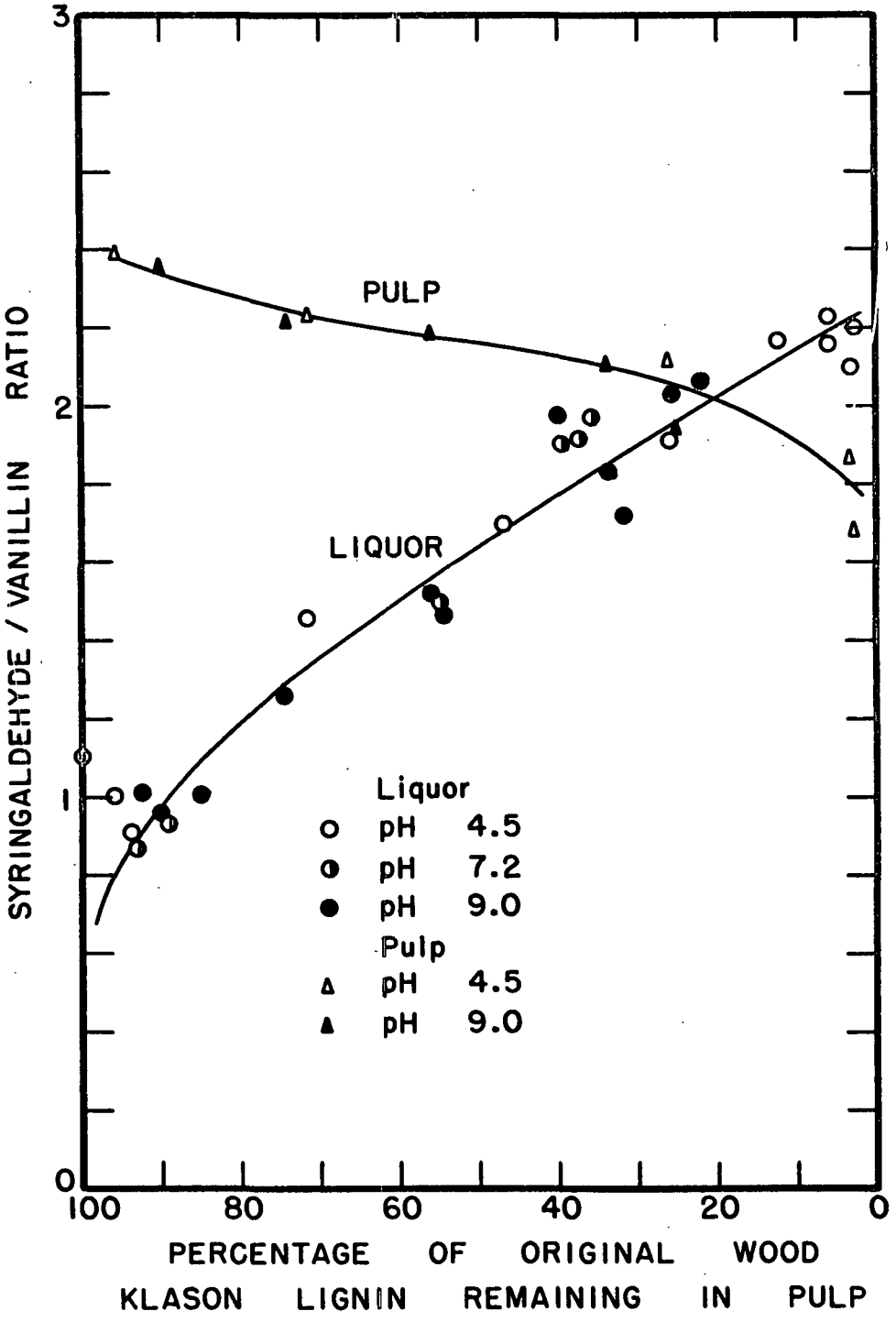


Figure 15. Relationship Between Syringaldehyde/Vanillin Ratio on Nitrobenzene Oxidation of Liquor and Pulp and Amount of Original Wood Lignin Present, Series I-IV Cooks

therefore may be compared only on the Klason lignin basis. These curves are still unique when plotted against total lignin, but their shapes are slightly different. The positive slope seen in the vanillin curve in Figure 14A becomes zero slope when Klason lignin is replaced with total lignin as the independent variable; the percent vanillin in the total liquor lignin was then constant throughout the cook, while the percent syringaldehyde increased in a straight-line relationship with total lignin removed. This indicates once more that the lignin which entered the liquor contained a relatively constant amount of guaiacyl nuclei, but increasing proportions of syringyl nuclei as the cook progressed. The slight increases shown in Figure 14B for percent of both aldehydes in pulp lignin become slight decreases when total lignin is used in the calculations; over the range of delignification found in the CIV 9.0 cooks, the vanillin content of the total pulp lignin decreased only slightly (due to recovery loss with increased time of reaction), while the syringaldehyde content decreased markedly (due to recovery loss and to the increasing syringaldehyde content of the lignin entering the liquor).

Therefore, just as the amount of sulfonation required to produce a given amount of delignification was the same for cooks at any pH level within the range of these experiments, the constitution of the lignin in both the pulp and the liquor as to guaiacyl and syringyl-type lignin groups was also the same for any given degree of delignification, for cooks at any pH level. This indicates that the same general reactions which govern the removal of lignin at pH 4.5 may apply as well at pH 7.2 and 9.0, not only in the sulfonation and removal of reactive groups, but also in the removal

of structural groups. If, as hypothesized previously, the differences in amount and ratio of structural groups in isolated lignin fractions are due to a heterogeneity of distribution across the cell wall, Figures 14 and 15 indicate that the path of liquor movement and reaction within aspenwood chips was similar (except for differences in rate) in sulfite liquors of any pH between 4.5 and 9.0. If these differences are due to differences in the actual selectivity of liquor at different pH levels for one of these groups, (and not to differences in liquor selectivity for a certain portion of the cell wall at given time during the cook), the variation in amount of structural groups in these fractions is related to the variation in amount of reactive groups. Then Figures 14 and 15 present evidence indicating that no difference was found in the lignin in liquors of different pH; that is, "B" groups were not cleaved by liquors at pH 4.5 unless they were also cleaved at pH 9.0.

MICROSCOPIC EXAMINATION

Wood chips, and whole pulp chip samples saved from the CIII and CIV cooks were sectioned on a freezing microtome, and stained according to the procedure outlined in the APPENDIX. The areas of total lignification are defined by the boundary of green coloration with malachite green (MG) (39), and the areas which contain sulfonated lignin are defined by the boundary of red coloration with p,p'-diazodimethylaniline (PP') (39,40). Color photographs of each of the sections were taken at 215X magnification, and are on file.

The wood sections stained rather uniformly green with MG, and did not

stain to any degree with PP'. The same general changes in areas of sulfonation and lignification are apparent for cooks at both pH 4.5 and pH 9.0, but these changes occurred more rapidly at pH 4.5. At 30 minutes cooking time, the middle lamella, vessel and ray cells were all quite dark green, while the cell wall appeared a uniform medium green at both pH levels. At 90 minutes time, the middle lamella, vessel and ray cells were still dark green but a gradation of green had appeared in the cell wall, with the outside of the cell almost as dark as the middle lamella, and the portion nearest the lumen quite a bit whiter. The pulp at pH 9.0 was whiter at the lumen, but the gradation from green to white was sharper for pulp at pH 4.5. At 150 minutes, the middle lamella at pH 4.5 was almost gone, due to the drastic reduction of over-all lignin content, and the cell structure was partially destroyed. However, what middle lamella remained was quite green, while the cell wall appeared very light green. At 210 minutes, the pulp produced at pH 4.5 contained very little middle lamella, and the cell wall was mottled green-white. At 210 minutes at pH 9.0, however, the cell structure was still intact; the middle lamella, vessel and ray cells were still quite dark green. The cell wall color gradation was still sharper than at 90 minutes, with the portion of the cell wall nearest the lumen almost pure white; the outer portion of the cell wall was lighter green than pulp CIV 9.0-90.

The pulps at 30 minutes stained red with PP' only in the middle lamella, with vessel and ray cells slightly red. The pulp produced at pH 4.5 seemed to show slightly more red color. At 90 minutes, the red in the middle lamella had become much more intense, and the outside of the cell wall started to show color, especially at pH 4.5. At 150 minutes, the cell wall at

pH 4.5 was a uniform light pink, and at 210 minutes it was almost white. At 210 minutes at pH 9.0, the middle lamella was almost as red as at 90 minutes, while the cell wall was much more red around the outside. The portion of the cell wall nearest the lumen never seemed to stain red, while the middle lamella stained slightly red at the beginning of the cook, more red toward the middle and less red again at the end of the cook. The vessel and ray cells were fairly uniform pink throughout the cook.

From these observations, it is possible to hypothesize the path of liquor movement within the cell structure in cooks at both pH 4.5 and 9.0; no differences in manner of penetration were observable for these two pH levels, but differences in rate coincided with the results of the analytical determinations on each pulp series. It appears that flow through vessel and ray cell pits to other vessel and ray cells was the main means of distribution of the liquor within the chip; these structures were among the first to become sulfonated, although they also retained total and sulfonated lignin for most of the cook. This retention was probably due to the higher concentration of lignin present, especially in the ray cells, and to the fact that liquor flow out of the vessels proceeded at least partially through pits, which did not allow as uniform a removal of lignin over the whole vessel or ray cell wall as did the diffusion through the cell wall which occurred in fibers. In any case, liquor flow within the fibers probably proceeded through the lumen and through the cell wall. It has been shown that the first portion of lignin to be removed was that nearest the lumen, but the first portion to be sulfonated was that in the middle lamella. Lignin removal appeared to proceed from the lumen outward, while sulfonation

proceeded from the middle lamella inward. It is unlikely that the apparent sulfonation of those areas of greatest lignification in the early portion of the cook was due only to the inability of the fiber wall to show color with PP' because of its low lignin content; the color intensity in the middle lamella was not greater for MG than PP' in the early stages of the cook, so it is expected that PP' indicated sulfonated lignin with approximately the same efficiency that MG indicated total lignin. Since the amount of pitting in aspenwood fibers is very slight, as a general rule only that liquor which has diffused through the cell wall may enter the lumen. This means that the middle lamella was first encountered by the liquor, and was sulfonated; the liquor then proceeded through the cell wall and into the lumen, carrying with it either soluble lignin from the portion of the cell wall around the lumen, or lignin solubilized by means of the sulfonation reaction in the middle lamella. From the lumen, the liquor again diffused through the cell wall to reach other middle lamellae and lumens. As the reaction proceeded, the area of delignification increased to encompass the whole cell, and finally the lignin in the middle lamella; when this occurred, defiberization freed the woody fibers from the incrusting lignin sheath. If this conception is correct, a certain portion of the lignin residue in the cell wall (that nearest the lumen) was removed without being sulfonated, or was removed instantaneously after its sulfonation, making observation of sulfonation in these areas very difficult. Some of the sections stained with PP' appeared slightly red in the area of higher lignin concentration very close to the lumen, but this may have been due to color inaccuracies in the lighting in conjunction with cell wall diffraction. If the middle lamella were removed preferentially in the early portion of the cook, followed by the

removal of the cell wall lignin, defiberization would probably occur at much higher residual lignin contents, and much earlier in the cook, than is generally thought to be the case.

Microscopic examination of stained chip cross sections indicates that fractionation of the cell structure proceeded along the lines of cell morphology during the cook. An attempt was made to relate this preferential isolation to the fractionation of guaiacyl and syringyl groups by the pulping liquors; if these selective processes are interdependent, the cell wall may be heterogeneous with respect to structural group distribution, and a hypothesis may be proposed concerning the location in the cell wall of the major portion of syringyl and guaiacyl nuclei. Plots of sulfur to syringyl and sulfur to guaiacyl ratio vs. cooking time in various fractions yielded no constant, straight-line relationships (which would have indicated that sulfur was most closely associated with one type of nucleus, leading to the hypothesis that this nucleus predominates in the middle lamella), but the ratio of both sulfur in pulp lignin to syringaldehyde in pulp lignin and sulfur in pulp lignin to syringaldehyde in liquor lignin remained much more constant during cooks at both pH levels than the corresponding sulfur to vanillin ratios. Also, the greater specificity of the Kullgren hydrolysis procedure for syringyl indicates a closer bond between sulfur and this group than between sulfur and guaiacyl, since presumably the main portion of the lignin isolated in a Kullgren hydrolysis is sulfonated.

The hypothesis that syringyl nuclei are present to a greater degree than guaiacyl nuclei in the middle lamella, and that guaiacyl nuclei predominate in the cell wall is not contradictory to the nitrobenzene oxidation and

microscopic examination data. Nitrobenzene oxidation data indicate that the relative proportions of syringyl and guaiacyl nuclei liberated during a cook varied with reaction time; the guaiacyl fraction was present in a much greater proportion than that in the wood in the lignin removed during the early stages of a cook. Microscopic examination has shown that this lignin fraction was not necessarily sulfonated, and that it originated from the cell wall near the lumen. It has been stated in the literature (31) that those lignins which are most soluble in neutral solvents, and therefore are removable without the aid of sulfonation, have been found to be low in methoxyl content. Thus, guaiacyl fractions may have been removed by virtue of solubility alone, while it was necessary to sulfonate syringyl groups before their removal. As the cook progressed, more and more syringyl nuclei were liberated; these fractions presumably originated in the more highly sulfonated areas in the middle lamella. It is possible that the guaiacyl group is homogeneously distributed across the cell wall and the middle lamella, and that only that portion near the cell lumen was removed during the early portion of the cook; the relationship between sulfur and syringyl groups indicates, however, that this fraction is probably not homogeneously distributed in the cell structure, but predominates in the middle lamella.

SUMMARY AND CONCLUSIONS

The following conclusions are based on experimental data obtained in the analysis of pulp and liquor samples from thirty-one cooks of aspenwood, at different cooking times, with sulfite-bisulfite liquors of initial pH varying from 4.5 to 9.0.

REACTION RATE AND SELECTIVITY

The rate of removal of both total woody material (yield loss) and lignin from aspenwood was found to be greater in bisulfite cooking liquors than in neutral sulfite cooking liquors. Liquors at neutrality removed less total material and lignin than liquors at either pH 4.5 or 9.0. At any given yield, however, the amount of lignin remaining in the pulp was greater for cooks at pH 4.5, and the nonlignin/lignin ratio in the pulp was greater for cooks at pH 7.2 and 9.0. Therefore, although the reaction rate was found to be greater at pH 4.5 than at pH 7.2 or 9.0, liquor at this pH level was found to be less selective for lignin removal than neutral or alkaline liquors. As the cook progressed, the selectivity of liquors at all experimental pH levels for lignin increased only slightly to about 70% yield, and then increased rapidly. It is hypothesized that this increase was due not to an increase in the rate of lignin removal, but to a decrease in the amount of carbohydrate material available for removal. The greatest amount of lignin was removed with the least amount of yield loss within the yield range 96 to 65% at all experimental pH levels of pulping.

For a given amount of sulfur dioxide consumed, the sulfur content of the pulp lignin and the amount of lignin removed in pulping were found to

be greater for liquors of initial pH 9.0 than for those at pH 4.5; therefore, not only was the selectivity for lignin greater in liquors at pH 9.0, but the efficiency of the sulfonation reaction was also greater at this pH level than at pH 4.5.

SULFONATION AND HYDROLYSIS

The calculated sulfur content of the lignin in the pulps produced at pH 9.0 rose to a maximum and then levelled off, while that of the pulps produced at pH 4.5 rose steadily throughout the cook. It might be expected that the sulfur content of the pulp lignin would rise to a given level (perhaps at different rates), then remain constant at that level in either bisulfite or neutral sulfite cooks, for according to Hägglund's theory, only the "A" lignin groups may be sulfonated in the solid state; the "B" lignin groups, sulfonatable only by acid sulfite liquors, must be cleaved before their sulfonation in solution. It is hypothesized that either (1) a second lignin group may be sulfonated in the solid state by liquors at pH 4.5 toward the end of the cook, or (2) only one reactive lignin group exists; it may be increasingly sulfonated in the solid state and completely removed by pulping liquor at pH 4.5.

Long cooks at pH 9.0 indicated that neutral sulfite liquors were also able to sulfonate and remove the bulk of the lignin present in aspenwood; the sulfur content of the lignin in the pulp rose in these long cooks much as in the pH 4.5 cooks at shorter cooking times. It appears that the additional lignin sulfonated in the solid state by liquors at pH 4.5 could also be sulfonated and removed by alkaline sulfite liquors. This hypothesis is

further supported by the discovery that, for any given amount of delignification, the sulfur content of the lignin remaining in the pulp was the same for cooks at any pH level within the experimental pH range. Therefore, the degree of sulfonation required to produce a given amount of delignification was not a function of liquor pH. Even the state of degradation of the lignin, as shown by the relative proportion of the total lignin of great enough solubility to enter the filtrate during a Klason lignin determination, was independent of pH; at any given Klason lignin content, the soluble lignin content was the same for pulps produced at either pH 4.5 or 9.0. The curve of sulfur content of the lignin vs. pulp lignin content rose linearly from zero sulfur at zero delignification to about 6% sulfur at over 90% yield, and then broke sharply, rising to over 30% sulfur over the last small increment of lignin loss. This curve is unique for both bisulfite and neutral sulfite cooking conditions, and may be drawn as the intersection of two straight lines, supporting the hypothesis that two sulfonation reactions occur in lignin in the pulp at both pH 4.5 and pH 9.0. If the rise indicates the sulfonation of "B" lignin groups, these groups were probably sulfonated in the solid state at pH 9.0 as well as at pH 4.5. If the rise does not indicate the sulfonation of "B" groups, and these groups actually exist, then they may be completely solubilized (and probably further sulfonated in solution) by liquors at both pH 4.5 and 9.0, since almost all of the lignin in the wood was removable by liquors at either experimental pH level. The data do not indicate that acid hydrolysis necessarily took place before sulfonation, unless hydrolysis occurred at pH levels of neutrality or greater as well as at acid pH levels. In conclusion, it is hypothesized that the same

sulfonation reaction or reactions occur at all pH levels of pulping within the sulfite-bisulfite system; only the rate of this reaction varies with change in liquor pH. It is possible that acid hydrolysis plays a minor role in delignification, and that differences in reaction rate at different pH levels may be explained on the basis of differences in bisulfite ion concentration alone.

GUAIACYL AND SYRINGYL GROUPS

The aldehyde yield on nitrobenzene oxidation of spent liquor samples increased at a faster rate in the cooks at pH 4.5 than in those at pH 7.2 or 9.0, in parallel with the differences in the rate of lignin removed at these pH levels. The aldehyde yield in the pH 4.5 pulps likewise decreased faster than in those at pH 7.2 or 9.0. The syringaldehyde/vanillin ratios in the liquors increased from about 0.6 to over 2 at both pH levels of pulping, but at a slightly faster rate in the pH 4.5 liquors; this ratio decreased more rapidly in the pH 4.5 pulps. The calculated syringaldehyde content of the lignin in the liquor increased during the cook for both pH levels of pulping, but the vanillin content remained fairly constant at pH 4.5 and decreased slightly at pH 9.0. The syringyl content could not be extrapolated back to zero at zero cooking time, in disagreement with experiments reported in the literature (31). The calculated syringaldehyde content of the pulp lignin decreased at both pH levels, while the vanillin content also decreased slightly, due to recovery loss with increased time and severity of reaction. It is apparent from the great variation found in ratio and amount of guaiacyl and syringyl groups in isolated pulping fractions that the pulping reaction served to fractionate these nuclei; the

lignins solubilized in the early stages of a cook at either pH 4.5 or 9.0 were deficient in syringyl content, while the guaiacyl content of lignins isolated at any time during a cook was seen to remain fairly constant.

The per cent vanillin and the per cent syringaldehyde in both liquor lignin and pulp lignin, and the syringaldehyde/vanillin ratio in the liquor and the pulp, were found to be the same at any given degree of delignification for cooks at any pH level within the range of these experiments. Therefore, just as the amount of sulfonation required to produce a given amount of delignification was the same in bisulfite or neutral sulfite pulping liquors, the constitution of the lignin in both the pulp and the liquor as to guaiacyl and syringyl type lignin groups was also the same for any given degree of delignification, for cooks at any experimental pH level. This indicates that the same general reactions which govern the removal of lignin at pH 4.5 may apply as well at pH 7.2 and 9.0, not only in the sulfonation and removal of reactive groups, but also in the removal of structural groups.

The fractionation of guaiacyl and syringyl groups by pulping liquors at different times during a bisulfite or neutral sulfite cook may be due either to (1) differences in the actual selectivity of the liquor for these structural groups, or to (2) differences in liquor selectivity at different times during the cook for the specific areas of the cell structure in which one of these groups predominates. If (1) is true, the variation in amount of structural groups in any sample would be related to the variation in amount of reactive groups; therefore no differences in reaction potential would be found in the lignin in liquors of different pH, and no lignin groups could be cleaved by liquors at pH 4.5 unless they were also cleaved at pH 9.0. If

(2) is true, these structural groups must be heterogeneously distributed across the cell wall; the path of liquor movement and reaction would therefore be similar (except for differences in rate) in sulfite liquors of pH 4.5 and 9.0.

MICROSCOPIC EXAMINATION

Microscopic examination of wood and pulp chip cross sections stained for total lignin (malachite green) and sulfonated lignin (p,p' azo dimethylaniline) showed that the position of attack of cooking liquor at both pH 4.5 and 9.0 was similar as to sulfonation and delignification at various times during the cook, except for differences in rate. Lignin removal proceeded from the lumen outwards towards the middle lamella, while sulfonation seemed to proceed from the areas of highest lignin concentration (the middle lamella) towards the lumen. This indicates that a portion of the lignin in the cell wall (nearest the lumen) may have been removed without first being sulfonated.

A hypothesis is advanced explaining the path of liquor movement within the cell structure in cooks at both pH 4.5 and 9.0. It appears that flow through vessel and ray cell pits to other vessel and ray cells was the main means of liquor distribution within the chip; liquor probably penetrated the fibers mainly through cell wall diffusion, due to the absence of fiber-fiber pitting in aspenwood. In this manner, the lignin in the middle lamella surrounding any fiber was encountered and sulfonated before the cell wall lignin; the liquor then proceeded through the cell wall to the lumen, carrying with it either soluble lignin from the portion of the cell wall nearest

the lumen, or lignin solubilized by means of the sulfonation reaction which occurred mainly in the middle lamella in the early portion of the cook. From the lumen, it was necessary for the liquor to diffuse through the cell wall a second time to reach other middle lamellae and lumens. As the reaction proceeded, the area of delignification increased to encompass the whole cell, and finally the middle lamella; when this occurred, the fibers were freed from their incrusting lignin sheath.

An attempt was made to relate the preferential removal of different portions of the cell structure by pulping liquors at various times during the cook to the fractionation of guaiacyl and syringyl groups observed in pulp and liquor fractions, so that the homogeneity of distribution of these nuclei across the cell wall might be characterized. Since nitrobenzene oxidation of the Kullgren hydrolysis extract (mainly sulfonated lignin) of a 90-minute pulp produced at pH 9.0 indicated greater concentrations of syringaldehyde than vanillin, and since less change was apparent with increased cooking time in the ratio of syringaldehyde/sulfur than that of vanillin/sulfur in the pulp, it is hypothesized that the bulk of the combined sulfur present in the cooking liquor had preferentially united with syringyl, rather than guaiacyl nuclei. Nitrobenzene oxidation indicated that guaiacyl nuclei predominated in the lignins removed during the early stages of the cook; these fractions originated mainly in the cell wall and were not necessarily sulfonated. In the latter portion of the cook, the more highly sulfonated middle lamella was removed; the nitrobenzene oxidation data showed that the proportion of syringyl groups available for oxidation in the lignin entering the liquor increased with increase in cooking time. It is

therefore further hypothesized that (1) guaiacyl nuclei form the bulk of the lignin present in the cell wall of aspenwood, and (2) the bulk of the syringyl nuclei present in aspenwood are located in the middle lamella, causing the syringaldehyde/vanillin ratio of the lignin in this area to be greater than that of the lignin in the cell wall.

These hypotheses are based upon the assumption that the nitrobenzene oxidation procedure yields an accurate ratio of syringyl to guaiacyl groups in a sample.

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APPENDIX

EXPERIMENTAL PROCEDURES AND ANALYTICAL METHODS

The reliability of the results and conclusions of a thesis are directly dependent upon the reliability of the analytical procedures used in gathering data. Each experimental procedure was investigated and evaluated so that its limitations might be known under the conditions of the experimental work, and modified, where necessary, to provide a more unbiased basis for comparison of analytical data. Methods for the determination of lignin and sulfur were investigated most fully, for although standard techniques are available, it was felt that the greatest amount of evaluation and modification might be required in these fields. The alkaline nitrobenzene procedure for the estimation of kind and ratio of ligninlike groups was examined for the presence of interfering reaction products. The Kullgren hydrolysis technique was investigated as an aid in the isolation and analysis of sulfonated lignin fractions in pulp. A method of staining and microscopic identification of the position of sulfonated and unsulfonated lignin residues in cooked chip cross sections was developed.

To provide raw material for these investigations, one relatively large scale cook was produced at conditions very similar to those used in the Series I through IV cooks. Cooking liquor was produced by the addition of sulfur dioxide gas to a 1.25N solution of sodium hydroxide until pH 9.0 was reached. This liquor was found by analysis to contain 49.8 g./l. sodium hydroxide and 39.5 g./l. sulfur dioxide. The equivalent of 400 g. ovendry aspenwood was cooked in 4000 ml. liquor in a 5 l. stationary stainless steel

digester with circulating pump. The temperature was raised from room temperature to 170°C. in 90 minutes, and the liquor was withdrawn. The pulp was removed, and the chips were placed in water; a portion of these chips was set aside for microscopic investigation, and the remainder was defibered in a laboratory Sprout-Waldron refiner, washed, dewatered, and bagged. The spent liquor pH was 7.1 and the pulp yield was 79.0%. This pulp and Wiley-milled aspenwood sawdust formed the raw material used in the investigations in analytical procedure which are treated on the following pages; the pulp may be identified by the symbol XC 9.0-90.

THE DETERMINATION OF KLASON LIGNIN

Brauns (41) has described lignin as "that incrusting material of the plant which is built up mainly, if not entirely, of phenyl propane building stones; it carries the major portion of the methoxyl content of the wood; it is unhydrolyzable by acids, readily oxidizable, soluble in hot alkali and bisulfite, and readily condensed with phenols and thio compounds". The term lignin is not the designation of a constitutionally defined compound, but is more a collective term for a group of similar high molecular, amorphous compounds which are present in woody fiber along with cellulose, hemicellulose, and extractives, and which exhibit different chemical characteristics in different woods and at different times under different reaction conditions.

Since lignin is not a chemical compound, the fractions produced in its attempted isolation are usually poorly defined, i.e., some lignin is generally present in the isolated nonlignin fraction and some nonlignin is present in the isolated lignin fraction. In the past, lignin has been isolated by hydrolysis, oxidation, condensation, and by the use of certain

solvents (41). Either carbohydrate or lignin may be selectively removed from wood or pulp by the use of fungi. The classic approach to the isolation of lignin is the hydrolysis of carbohydrate material by 72% sulfuric acid; this Klason procedure was chosen as the method of lignin determination in this thesis because (1) it is a simple, straightforward technique, (2) it is said to yield the most reliable results of any of the lignin procedures for NSSC pulps (42), (3) it yields data which are reproducible, and (4) it yields a solid, isolated lignin which lends itself well to chemical determinations.

Two difficulties are associated with the use of the Klason procedure; the first is the tendency of certain materials such as humic acids, furfurals, pectins, proteins, polyuronides, resins, tannins, and other extractives to become insoluble on treatment with acid (43), increasing the amount of "apparent" Klason lignin present. The second problem is the solubilization of some of the true lignin; it appears to enter the filtrate, and is not weighed as part of the solid residue. This solubilization tends to decrease the amount of "apparent" lignin in any woody sample. In the past, many attempts have been made to evaluate the amount of this loss by the use of UV absorption data at 280 mmu on the Klason filtrate (44, 37), but these results may have been clouded by the presence of interfering substances. Carbohydrate degradation products have been found to exhibit absorption in the UV range (4, 45); furfural has a maximum absorption at 280 mmu in its curve, but the absorption does not increase with decreasing wavelength, as does that of lignin.

It is recognized, therefore, that there is no method presently available

for the truly accurate determination of the amount of protolignin present in a woody sample. Whenever a lignin content is reported, the method of isolation must also be reported, because the kind and amount of lignin present in any sample is a function of, and therefore is defined by, its method of isolation. The rather large differences in lignin content which occur under such diversified cooking conditions as are prevalent in the pulping studies in this thesis may be indicated adequately by the Klason lignin value alone; however, in the interests of greater analytical sensitivity, expecially where the lignin content was used in the calculation of some other parameter, a method of determining the amount of "soluble" lignin in a Klason lignin filtrate was sought, so that the sum of solubles plus insolubles might characterize the total lignin content of pulp or wood samples. For the absolute value of each of the lignin determinations to be of future consequence, the cooks as pulped in this thesis, and their analytical determination, would have to be exactly duplicated; however, the trends which are shown are expected to be true for any sulfite cook on aspenwood within the range of experimental pH.

Certain major variations in the Klason lignin procedure were examined in an attempt to find out more about the determination of soluble and insoluble lignin residues. The program was planned to answer the following questions:

(1) Is the amount of insolubles obtained in an acid hydrolysis of wood changed

  (a) by refluxing instead of boiling the diluted reaction mixture?

  (b) by filtering the reaction mixture before the boil, and boiling or refluxing the precipitate in fresh acid?

(2) Are certain insolubles produced during the boil? Are they also produced under reflux or steam distillation?

(3) Can the furfural and other UV-interfering substances believed to be present in a Klason lignin filtrate be eliminated by steam distillation? Are they increased by reflux during the boil?

(4) Are UV-interfering substances produced before or during the boil?

In accordance with these aims, aspenwood sawdust was subjected to the following modified Klason lignin procedure: (1) a large sample was oven dried overnight at 105°C.; (2) the dried sawdust was weighed, extracted according to Institute Method 11, redried at 105°C., and reweighed; the extractive yield was 2.94%; (3) one-gram samples of this extracted wood were then treated with 72% sulfuric acid for 3.5 hours according to Institute Method 428; (4) each sample was diluted with 800 ml. water; and (5) the samples were boiled, refluxed, and/or filtered according to the reaction scheme given in Figure 16. All filtrations were performed through two previously tared filter papers (Whatman no. 40), and the weight of insolubles was calculated (after washing and drying) as the weight difference with the heavier paper containing the lignin minus the original weight difference of the papers.

The UV absorption curves of each of the filtrates obtained in the investigation may be seen in Figures 17 to 19. In all cases, dilute sulfuric acid of the same concentration as that of the sample (1 ml. 72% acid diluted to 150 ml.) was used as the standard of reference.

It may be seen that the average lignin content of the wood by the

"standard" method was 17.4%, and refluxing instead of boiling did not appear to cause significant differences in the amount of precipitate recovered. The unboiled lignin comprised 13.4% of the original material; the lignin boiled in fresh acid comprised 10.9% of the original. Another 5.9% average was precipitated and recovered from the unboiled filtrate by boiling, refluxing, or steam distillation. A portion (3.3%) of the lignin precipitate before boiling was soluble in hot water, but insoluble in 3% sulfuric acid. Another portion (2.0%) was recovered from the filtrate by boiling with 12% hydrochloric acid, and this total (5.3%) is very close to the amount removed in a straight four-hour boil. The total of the unboiled lignin and the lignin removed from the filtrate boiled alone (19.3%) was probably high because of the carbohydrate degradation products still attached to the lignin which might have been removed in the boil. The total of the lignin boiled or refluxed in fresh acid and the lignin recovered from the filtrate (16.8%) was probably low because of the solubility of the lignin in fresh acid; if it were boiled in its original liquor, the dissolved substances might have kept additional solubilization from taking place.

The UV curves of the Klason lignin filtrates also produced interesting results; the peaks at 280 mmu for the filtrates refluxed with the insolubles (B) and alone (H) are probably high because the action of the reflux did not allow furfural and other interfering substances to escape. Curves A (filtrate boiled with insolubles) and G (filtrate boiled alone) are quite similar, and lower than B and H, but L and K (fresh acid filtrates boiled and refluxed with insolubles) are very low, indicating that little solid lignin becomes soluble during the boil, and that the absence of most of the

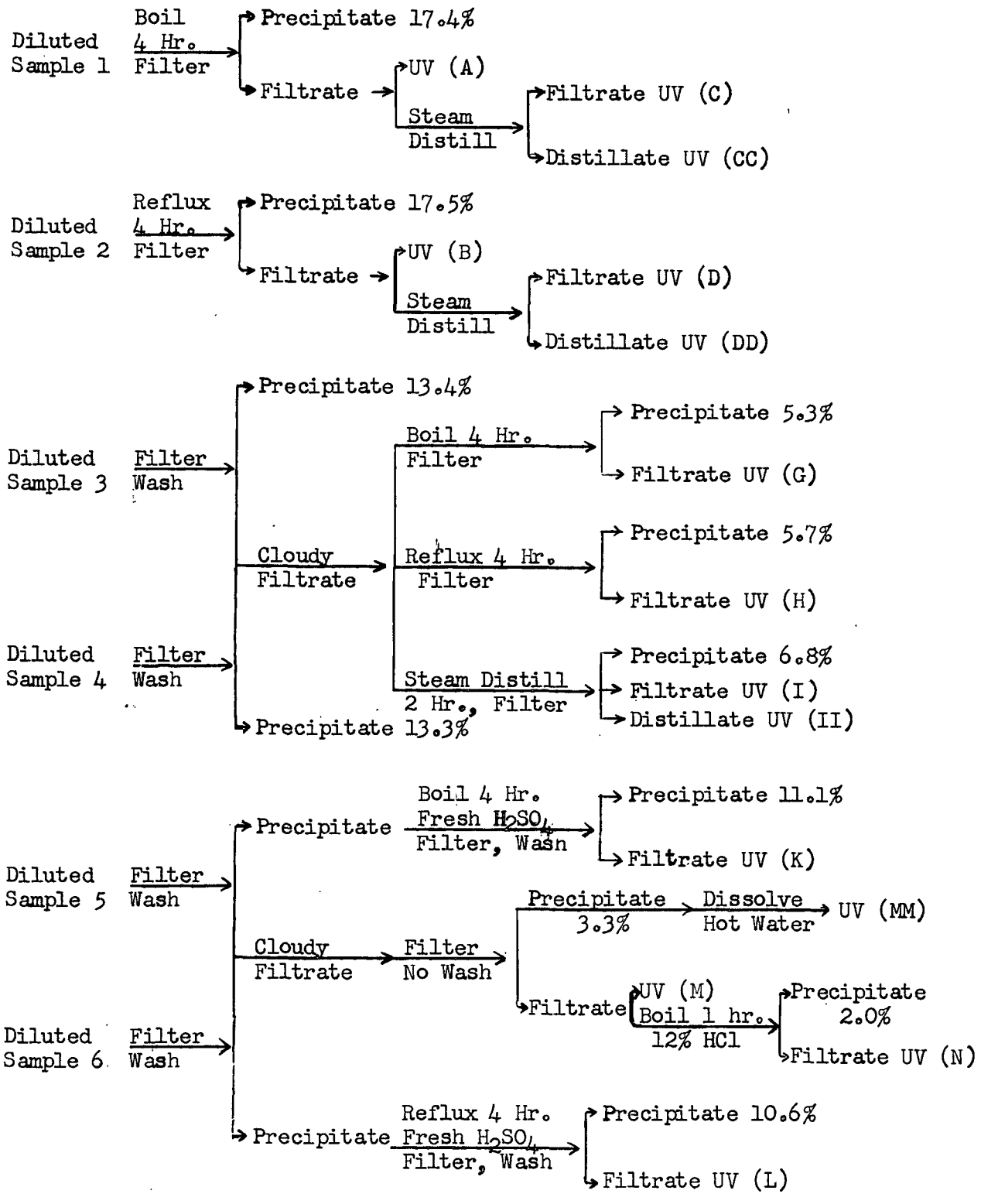

Figure 16. Analytical Scheme and Results: Variations in the Klason Lignin Procedure

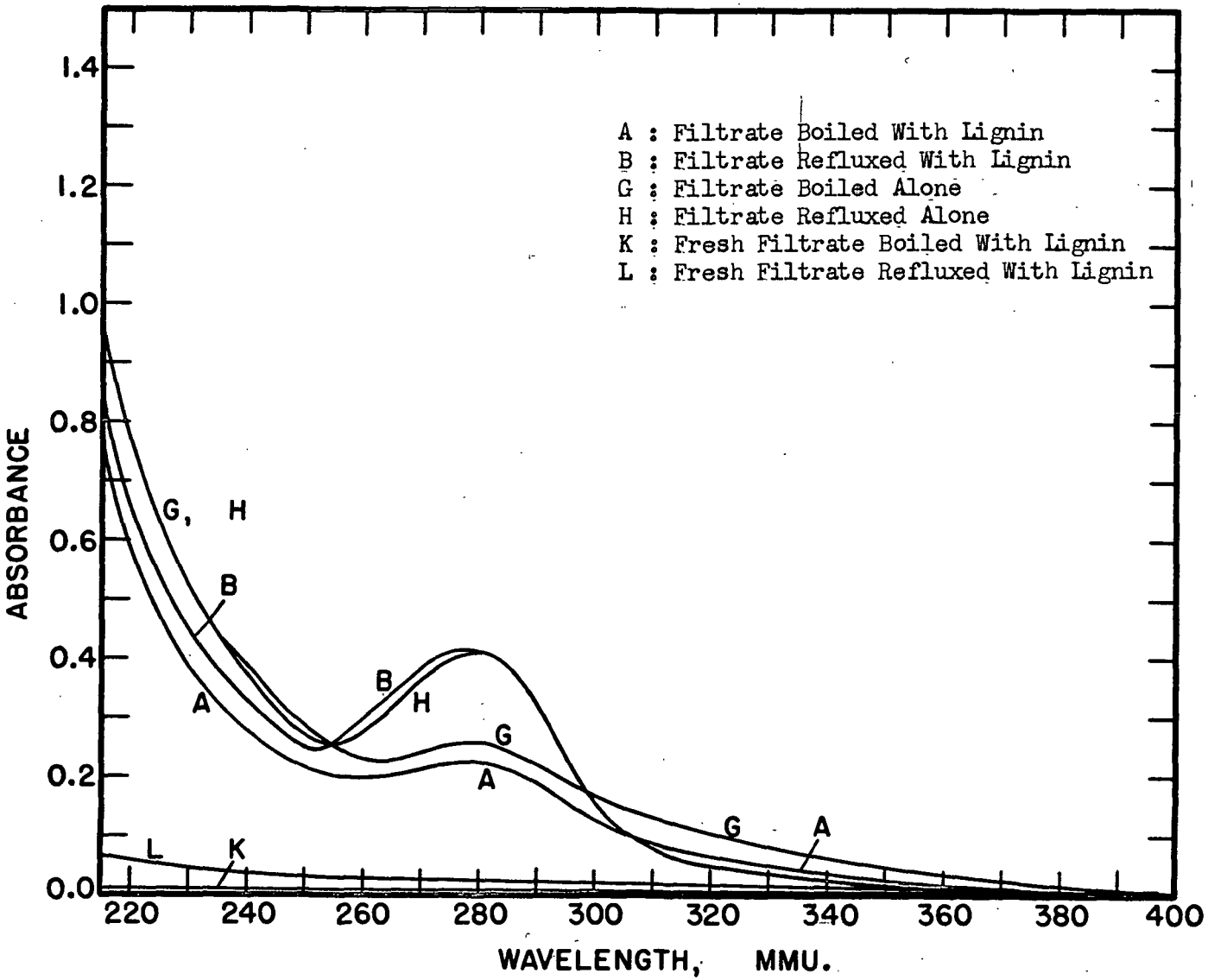

Figure 17. Absorption Spectra of Klason Lignin Filtrate, Pulp XC 9.0-90

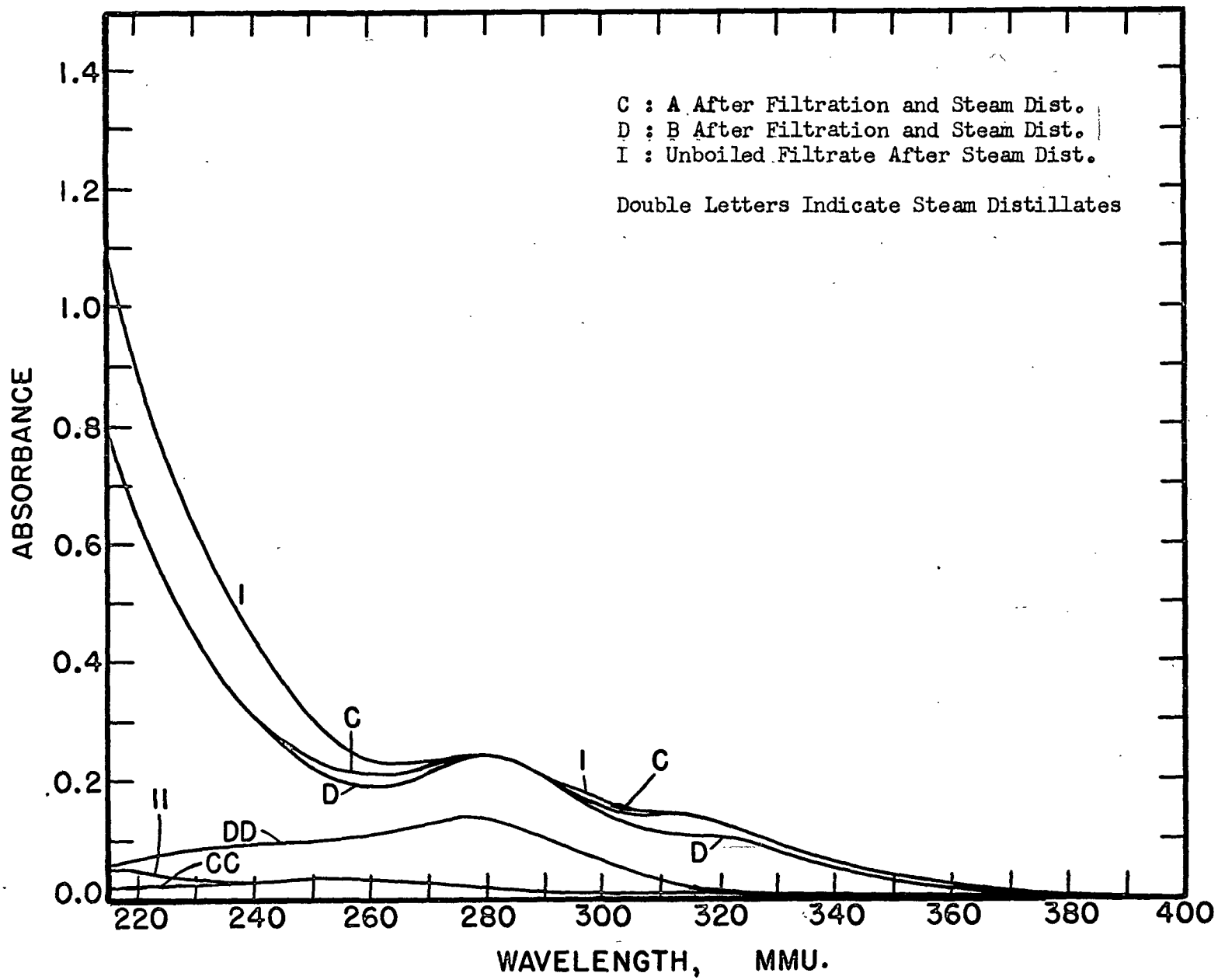

Figure 18. Absorption Spectra of Klason Lignin Filtrates, Pulp XC 9.0-90

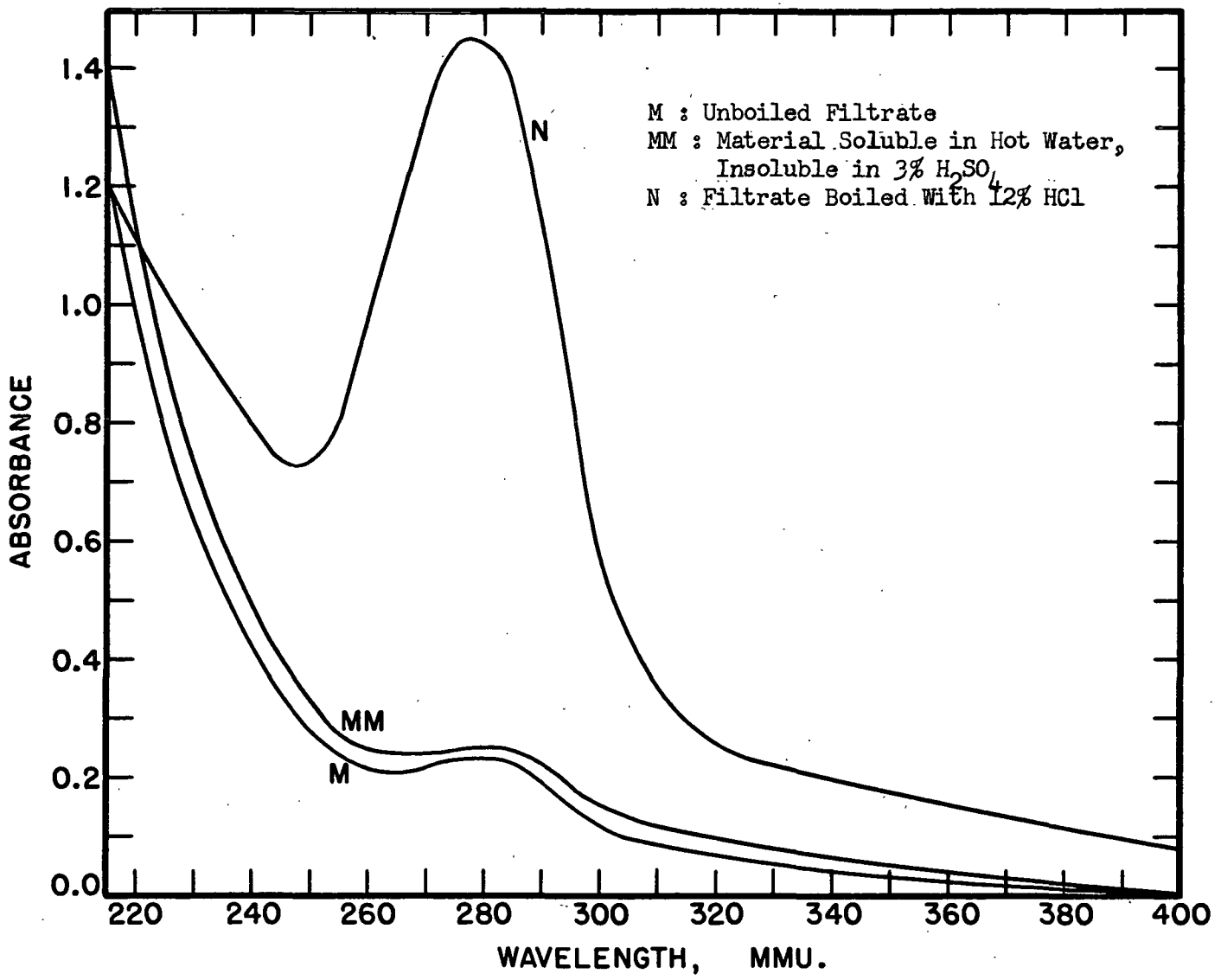

Figure 19. Absorption Spectra of Klason Lignin Filtrates, Pulp XC 9.0-90

carbohydrate material in a filtrate is conducive to low "soluble" lignin values. It is interesting to note that steam distillation was not more effective than boiling for the removal of furfural (the peaks of curves C, D, and I are approximately equal to that of curve A); it seems that the lowest UV curve, indicating the least amount of carbohydrate interference, may be obtained by the standard lignin procedure. The curves for the steam distillates are probably not very reliable, since the samples were allowed to stand several days before the curves were run, and furfural is rather unstable in solution. The close similarity between curves M and MM indicates that although the material comprising MM was insoluble in acid, and that comprising M was soluble, they are probably the same substance, and were separated by means of solubility only. Also, the peak of curve M is substantially the same as the peak of curve A, showing that no additional substances which absorb in the UV range were produced during the boil, or if they were produced, they have escaped. The dissimilarity between the peaks of curves B and M verify the fact that interfering substances were produced during the boil; however, if none of these substances were produced before the boil, none were present in boiled filtrates, unless some true lignin had been destroyed. Curve N shows the interference possible due to carbohydrate degradation products.

Other variations in the Klason lignin procedure were attempted, but the results of these investigations will be given in the next section, since they are more directly concerned with the determination of sulfur.

Another exploratory study of lignin concerned the use of an ion-exchange resin, Zeo-Karb 215, for the absorption of soluble lignin from Klason lignin

filtrates. This method was used by McKenzie, McPherson, and Stewart (38) on the Klason lignin filtrates of eucalyptus wood and its chlorite and chlorine holocelluloses; its effectiveness in the determination of soluble lignin in Klason lignin filtrates of aspenwood pulps has never been determined, so apparatus was assembled to compare its performance with that of the spectrophotometric method on the whole Klason lignin filtrate.

The resin was washed successively with 5% hydrochloric acid, water, and ethanol in bulk form; each solution was allowed to remain in contact with the resin overnight before it was removed by filtration. The alcohol eluates were evaporated to a small volume in a rotating evaporater, dried in a vacuum oven, and weighed. This bulk washing cycle was repeated five times, with the alcohol blank decreasing from about 2.8 g. to 0.11 g. Six columns were than prepared, 19 mm. in diameter and 60 cm. long; 70 g. wet resin was placed in each column, and the resin was washed according to the following cycle: one liter 5% hydrochloric acid, one liter water, one liter 95% ethanol, one liter 95% ethanol (a 24-hour waiting period is recommended between alcohol washes). The water and acid wash liquors were discarded, and the ethanol washes were evaporated to dryness and weighed. The combined weight of these two ethanol washes for each cycle may be seen in Table V for each of the six columns.

The procedure for the isolation of soluble lignin is much the same as that of the blank, except that the Klason lignin filtrate is passed through the column just prior to the first alcohol wash; the material sorbed on the resin from the filtrate may be removed by alcohol elution. McKenzie, et. al., state that after repeated washing, a constant blank value of about 15 mg. per

column was attained; it may be seen from Table V, however, that blank values did not decrease regularly for any one column, and that the average blank in these experiments was somewhere in the neighborhood of 50 mg. per column.

TABLE V

BLANK DETERMINATIONS ON ZEO-KARB 215 RESIN

	Column Number					
	1	2	3	4	5	6
First blank, g.	0.3136	0.2817	0.2834	0.3151	0.3716	0.3929
Second blank, g.	0.0861	0.1023	0.1169	0.1416	0.1201	0.1109
Third blank, g.	0.1777	0.0913	0.1368	0.1708	0.1696	0.1708
Fourth blank, g.	0.0578	0.0401	0.0779	0.0594	0.0653	0.0608
Fifth blank, g.	0.0687	0.0473	0.0868	0.0384	0.0667	0.0530
Sixth blank, g.	0.0659	0.0692	0.0568	0.0746	0.0512	0.0311
Seventh blank, g.	0.0481	0.0665	0.0740	0.0536	0.0601	0.0498
Eighth blank, g.	0.1116	0.0760	0.1055	0.0941	0.0826	0.0725
Ninth blank, g.	0.0494	0.0388	0.0441	0.0460	0.0553	0.0490
Tenth blank, g.	0.1109	0.1128	0.0618	0.1015	0.1073	0.0681
Eleventh blank, g.	0.0531	0.0427	0.0372	0.0395	0.0366	0.0400

The magnitude and variation in blank was too great to expect a precise evaluation of the amount of soluble lignin in a sample to be made by ion exchange, but since all lignin methods are at best estimates, this method is compared both by weight of residue and by calculation from spectrophotometric data with the "standard" UV method for the Series IV cooks; these results have been shown in Table IV.

The ion-exchange method is recommended for use on wood Klason lignin filtrates, although it appears to work equally well for soluble lignin determinations on hardwood pulp filtrates. A balance on the ion-exchange method may be seen in Table VI. It was reasoned that the optical density of the soluble lignin present in the alcohol eluate (eluate minus blank) should

equal the optical density of the original Klason lignin filtrate minus the optical density of the filtrate after passage through the column (filtrate after column minus water blank) minus the optical density of the wash water (water wash minus water blank). These calculated values are in fairly good agreement for both pulp and wood lignin determinations. It may be noted that a greater proportion of the UV-absorbing material was removed from the wood filtrate than from the pulp filtrate by the resin, perhaps due to the fact that during pulping, small fragments which may not properly be called lignin, and which are not sorbed on the resin, were produced from the wood lignin. The UV curves for each of the components cited in Table VI may be seen in Figure 20.

THE DETERMINATION OF SULFUR

It is possible to follow the sulfonation of lignin at various cooking times and pH levels only if reasonably accurate estimates may be made of the sulfur content of lignin and pulp residues. The great difficulty in this analysis lies not in the method itself; the total sulfur content of any sample may be accurately determined by the Carius method (46), or, more easily by the Leco procedure. This method consists of igniting a sample completely to carbon dioxide, water, and sulfur dioxide in a specially designed, oxygen-fed furnace, and routing the gases to a bubbler tube containing dilute hydrochloric acid, starch, potassium iodide, and enough potassium iodate to form a slightly blue color, according to the reaction:

$$KIO_3 + 5KI + 6HCl \longrightarrow 3I_2 + 6KCl + 3H_2O.$$

As the sulfur dioxide produced in the furnace decolorizes the starch-iodine

TABLE VI

BALANCE ON THE ION-EXCHANGE METHOD OF SOLUBLE LIGNIN DETERMINATION

Sample	Optical Density 230 mmu, per liter dilution					
	Pulp[1]	Pulp[1]	Wood	Wood	Wood	Wood
A Alcohol eluate of Klason lignin filtrate	2.28	2.50	2.00	2.10	1.82	1.84
B Klason lignin filtrate before passage through column	2.35	2.58	1.37	1.45	1.30	1.40
C Klason lignin filtrate after passage through column	0.72	0.70	0.25	0.16	0.24	0.30
D Water wash after passage through column	0.56	0.46	0.28	0.20	0.28	0.20
E Water blank	0.17	0.14	0.16	0.10	0.11	0.16
F Alcohol blank	0.72	0.79	0.88	0.72	0.63	0.54
G Soluble lignin in alcohol eluate (= A-F)	1.56	1.71	1.12	1.38	1.19	1.30
H Material remaining in Klason lignin filtrate (= C-E)	0.55	0.56	0.09	0.06	0.13	0.14
I Material in wash water (= D-E)	0.39	0.32	0.12	0.10	0.17	0.04
J Material in Klason lignin filtrate not sorbed on column (= H+I)	0.94	0.88	0.21	0.16	0.30	0.18
K Soluble lignin in alcohol eluate, calculated (= B-J)	1.41	1.70	1.16	1.29	1.00	1.22
% Difference between K (= B-C-D+2E) and G (= A-F)	9.6	0.6	3.5	6.5	15.9	6.1

[1] Pulp sample is CIV 9.0-90

complex according to the reaction

$$2H_2O + SO_2 + I_2 \longrightarrow H_2SO_4 + 2HI,$$

more iodate is added, so that the initial color is present when the combustion reaction has gone to completion. The percent sulfur of any given weight sample may be calculated from the amount and normality of potassium iodate consumed. This method greatly reduces the time of one determination, and is reported to be extremely accurate.

If a study of sulfonation is to be made, however, the only sulfur which is important to the investigation is that which has become chemically combined with the lignin of the wood during the cook; this lignin becomes sulfonated by the active sulfur in the cooking liquor. The possibility of performing a sulfur balance on each cook was considered, in order to fix the amount of sulfur bound to the lignin residue in each sample. The total amount of sulfur added to the cooking liquor (A) must be the sum of the sulfur present in the pulp (B) plus that present in the spent liquor (C); the sulfur in (C) must be the sum of the sulfur not consumed during the cook, and still present as inorganic sulfite, bisulfite, or thiosulfate (D), and that which has become combined with that lignin which later split off from the solid lignin in the pulp to enter the liquor (E). The sulfur in the pulp must be the sum of the sulfur which remains sorbed on the fibers from the cooking liquor (F) and that which has combined with the carbohydrate fraction of the pulp (G), plus that which has combined with the lignin in the pulp (H). Due to the proposed method of isolation, the sulfur content of the lignin may again be divided into the amount combined with the solid Klason lignin precipitate (I), and the amount present in the filtrate

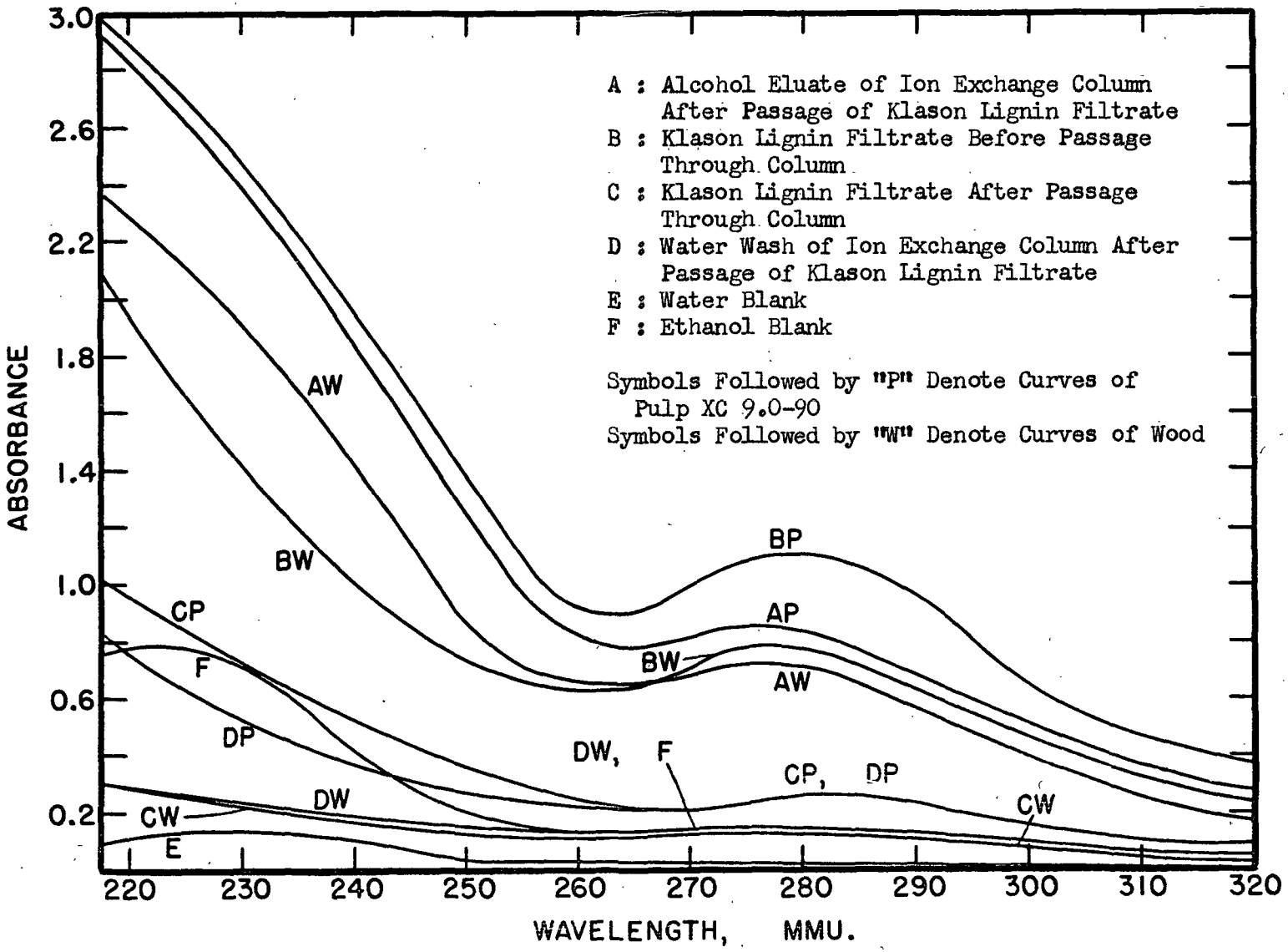

Figure 20. Average Absorption Spectra of Klason Lignin Filtrates, Ion Exchange Fractions

lignin (J). The fraction (G) would also be present in the Klason lignin filtrate. Interference may be expected in all of the isolated Klason lignin fractions from the sulfur present in the great mass of sulfuric acid used in the separation.

It is apparent that a great many problems must be solved before a reliable sulfur balance may be made. Sulfur content (A) may be accurately determined by iodimetric titration methods, and (B) may be analyzed by the Leco procedure. (C), however, is probably most accurately determined by difference. No method for the complete separation of fractions (D) and (E) is known at present. Fraction (F) may also not be analyzed directly, but may be made inconsequential by exhaustive washing. Although sulfonation of carbohydrate residues, especially those of low molecular weight, is known to exist under certain conditions, no evidence has been found to indicate that this sulfonation is great enough under the conditions of a sulfite-bisulfite cook to make fraction (G) significant in a sulfur balance. Fraction (H) cannot be analyzed directly; lignin may not be isolated in the same form and composition as it exists in the pulp. Sulfur content (I) may be measured directly by the Leco technique, but might be expected to vary with change in the degree of washing of the Klason lignin precipitate; sulfur content (J) is completely masked by the great quantity of sulfuric acid used in the separation, and cannot be measured directly unless the inorganic sulfur present in the filtrate may be removed by chemical or physical means.

Such a sulfur balance as tentatively proposed above is not feasible with the present state of knowledge of wood chemistry. It was found to be

possible, however, to make a valid estimate of the sulfur content of the lignin present in the pulp; the investigations leading to the development of this method are outlined below.

A number of Klason lignin determinations were run on aspenwood sawdust to provide samples for sulfur determinations. The sulfur content of the wood was found to be 0.002%, so if any substantial amount of sulfur were found in the Klason lignin precipitate, either (1) sulfuric acid reacts with lignin during the hydrolysis of wood, or (2) sulfuric acid becomes sorbed on the lignin, and is not removed in the subsequent washing step. The sulfur content of a Klason lignin precipitate produced according to the general procedures cited in the section on lignin was extremely variable over the range 0.20 to 0.64%, even though the precipitate had been washed free of acid as shown by the litmus paper test. This was attributed in the main to sorption of sulfuric acid, so another determination was made, and the precipitate was washed exhaustively on the filter paper. This precipitate yielded lower, more precise values of sulfur content averaging 0.16%. A third experiment was run in which the procedure was altered slightly, as follows, to allow the sulfuric acid to diffuse out of the precipitate: after washing, the precipitate was resuspended in one liter of distilled water, allowed to remain overnight, refiltered and dried. The sulfur content averaged 0.10%, with fairly good agreement between duplicate determinations. This "well-washed" Klason lignin procedure was found to be inapplicable for the determination of insolubles because of the high values obtained (20.8% vs. 17.6% in the normal procedure), but it might be useful for obtaining a better estimate of the amount of sulfur bound within

a Klason lignin precipitate. It may be noted that a substantial amount of sulfur was present in the precipitate even after extensive washing; it is not known whether its origin was reacted or strongly sorbed sulfuric acid, but it did not originate in the wood.

Two duplicate sets of Klason lignin determinations were run on pulp XC 9.0-90; both yielded 12.7% insolubles, with sulfur contents of 0.853%. A Klason lignin precipitate resuspended in water after filtration ("well-washed" lignin) yielded 18.8% insolubles with a sulfur content of 0.645%. The sulfur content of the pulp itself was 0.363%, and that of a pulp washed exhaustively with distilled water was 0.316%. It appears that cooking liquor ions also became strongly adsorbed on the pulp, and were not removed by ordinary washing methods; this will be discussed fully later in this section.

If all the sulfur present in the pulp is assumed to be associated with the lignin, it is possible to calculate the theoretical sulfur content of the lignin by dividing the sulfur content by the lignin content. This calculated value (2.5%) would be decreased slightly by the inclusion of soluble lignin data, but the experimental value of the sulfur content of the Klason lignin precipitate was only a fraction of this total lignin sulfur content. It appears that the sulfur content of the lignin fractions produced in the Klason determination were dissimilar, and that the bulk of the highly sulfonated lignin entered solution under the reaction conditions of this determination. This is not unreasonable, since from theory the highly sulfonated lignin molecules are split off during the cook, entering the liquor before further sulfonation may occur. The addition of a sulfonate

group greatly increases the solubility of a molecule; a sulfonated lignin molecule, which has not entered the spent liquor, might be expected to preferentially enter the liquid phase during a Klason determination. It is also hypothesized that under the conditions of a mild auto-hydrolysis, such as in a Kullgren hydrolysis, the more highly sulfonated portion of the lignin becomes soluble and may be recovered from the extract; this may be the same lignin which becomes soluble in a Klason determination. The Kullgren hydrolysis of pulp XC 9.0-90 was investigated, and will be discussed in a later section of the APPENDIX, but it was found that although the sulfur content of the extract was in the range of theoretical sulfur content of the total pulp lignin, the extract was composed in part of carbohydrate residues, making analysis of separate fractions extremely difficult. It is no easier to separate carbohydrate from lignin in a Kullgren extract than it is in a pulp sample or a Klason lignin filtrate. Therefore, the Kullgren procedure is not applicable for the separation of uncontaminated sulfonated lignin residues.

It might still be possible to calculate the over-all sulfur content of all of the lignin in the pulp by the weight proportion

$$\frac{\text{weight}_A \times \%\ \text{sulfur}_A + \text{weight}_B \times \%\ \text{sulfur}_B}{\text{weight}_A + \text{weight}_B} \qquad \text{where } A = \text{Klason lignin},\ B = \text{soluble lignin}$$

if the sulfur content and the weight of both the insoluble and soluble portions of the Klason lignin were known. The required data may be obtained for the insolubles only if a constant blank value of sulfur, equal to the amount of sulfuric acid reacted with or sorbed on the precipitate, be subtracted from each experimental sulfur content. The soluble lignin fraction might be isolated and weighed by ion-exchange methods, as already outlined, but the resin is a sulfonated coal type, and its blanks would introduce

still more sulfur interference. Since these blanks were found to be quite large and variable, this tentative method is not considered reliable.

Another method of separating the organically bound sulfur in soluble lignin from inorganic sulfate in a Klason lignin filtrate was attempted as follows (47): a portion of the Klason lignin filtrate was treated with solid barium hydroxide until the pH of the solution rose to about five; solid barium carbonate was then added in excess (final pH about eleven). The samples were then centrifuged, and the clear filtrate was decanted; a sample was set aside for UV investigation. The precipitate was washed with fresh water and centrifuged four more times; after the final wash, the filtrates were filtered and UV curves were run. The UV curves of the filtrate before precipitation were very much greater in optical density than those of the filtrate after precipitation; even extended washing did not bring the values at equal dilution up to those of the original filtrate. When the pH of the original filtrate was raised to that of the washed precipitated filtrate, the difference in optical density was even greater, but when the pH of this precipitated filtrate was lowered to the original filtrate pH, the difference was smaller than the original differences at different pH, even though the curves were still not identical. It appears that much of the material responsible for the UV curve of a Klason lignin filtrate remained sorbed on the sulfate precipitate, even when fairly exhaustive washing was performed. Therefore, this method is not applicable for the complete separation of organically bound sulfur and inorganic sulfate in a Klason lignin filtrate.

Due to the difficulties outlined above in the separation and sulfur content determination of various pulping reaction products, a new approach was considered and developed. This method entailed the use of radioactive sulfur^{35} in the cooking liquor, making the reaction products radioactive in proportion to their degree of sulfonation. Although the spent liquors were extremely radioactive, making separation and analysis of the lignin in the liquor no more feasible than before, the method did allow the evaluation of pulp washing techniques, and promised to free the determination of sulfur in Klason lignin fractions from interference by sulfuric acid and resin sulfur, which are not radioactive; only that which persisted in each fraction from the original cooking liquor could be counted by radioactive means.

The first radioactive cook (designation XRCI 9.0-90) was made in a 200-ml. bomb in an electrically heated rocking jacket according to the general cooking schedule of XC 9.0-90. To achieve a counting rate of 500 per minute at 5% efficiency at the Klason lignin filtrate level, it was calculated that approximately nine millicuries of radioactive sulfur^{35} as sodium sulfite would have to be added to the original cooking liquor. A theoretical amount of 9.85 mc. (according to the decay curve based on 87.1 days half-life) was added to 1.25N sodium hydroxide; this alkali was then sulfited to pH 9.0 with gaseous sulfur dioxide, and placed in a small-scale digester with 20 g. wood. The charge, cooking schedule, and liquor and pulp analyses of this cook and the other radioactive cooks may be seen in Table VII.

TABLE VII

PULPING DATA AND ANALYSES, RADIOACTIVE COOKS

Cook Designation	XRCI 9.0-90	XRCII 9.0-90	XRCII 4.5-90
White Liquor			
Total sodium as NaOH, g./l.	50.0	50.6	50.6
Total sulfur as SO_2, g./l.	32.8	35.9	73.3
Initial pH	9.0	8.9	4.5
Charge, ml.	152.5	148.0	148.0
Wood			
O.D. charge, g.	15.0	20.0	20.0
A.D. charge, g.	16.0	20.9	20.9
Schedule			
Time to 170°C., min.	90	90	90
Time at 170°C., min.	0	0	0
Total pulping time, min.	90	90	90
Spent Liquor			
pH	7.1	7.2	4.0
Yield			
% of wood, o.d. basis	77.4	87.3	66.2
Lignin			
Klason, % of pulp	13.0	10.3	9.4
Klason, % of wood	10.0	8.6	6.2
Sulfur			
% in pulp, pulp basis	0.342	0.345	0.360
% in pulp Klason lignin, calc.	2.63	3.34	3.81

The possibility that inorganic sulfur compounds from the liquor, such as sulfate, sulfite, and thiosulfate, may become adsorbed on, and tenaciously held by pulp fibers has already been mentioned; it has been shown that exhaustive washing resulted in a lower pulp sulfur content. The problem is aggravated by the fact that partially sulfonated lignin may be sparingly soluble in water, and would be removable on prolonged washing even though it should properly be considered as belonging to the insoluble portion of the lignin. The radioactive cooks allowed an evaluation of the completeness of washing, since the residual inorganic sulfur^{35} in each wash liquor could be accurately measured by radioactive counting.

After the cook, the pulp was washed as follows: the chips were allowed to stand in water in the cold room overnight; the water was then decanted off, one liter fresh water added, and the chips were disintegrated in a Waring Blendor and filtered on a Büchner funnel. This procedure was repeated ten more times; after each filtration, a 2-ml. aliquot of the filtrate was placed in an aluminum dish containing sodium sulfate (inactive) as carrier. The dishes were then placed in a vacuum oven and dried, and the radioactive contents were counted. The results of these counts may be seen in Table VIII.

TABLE VIII

RADIOACTIVITY IN PRC 9.0-90 WASH LIQUOR

Wash	1	2	3	4	5	6	7	8	9	10
CPM - B	421	116	20	3	4	6	3	7	7	5

The standard washing technique for pulps produced in the experimental portion of this thesis follows: each pulp was washed ten times with one liter of distilled water, followed by suction filtering in each case, and drying after the washing cycle is complete. This virtually eliminates the sulfur present in the pulp as sorbed inorganics from consideration in any pulp sulfur balance, and assures that the washing is no more prolonged than necessary for the complete removal of these sorbed inorganics. The radioactive determination of sulfur is not complex; all the sulfur present in the sample is oxidized to sulfate and precipitated as barium sulfate, filtered to form a pad and counted. The final eight-step procedure, which evolved

throughout the experimentation, follows directly below.

(1) Combustion: a 0.1-g. pulp or Klason lignin sample is placed in a porous ceramic boat and burned in the Leco furnace;

(2) Absorption: the gas stream is routed to two gas bubbler tubes, each containing about 40 ml. 1.25N sodium hydroxide, for absorption of sulfur dioxide;

(3) Oxidation: nonradioactive sulfur as sulfate to make the final pad weight up to infinite thickness, and an excess of hydrogen peroxide are added to the slightly sulfited sodium hydroxide, and the mixture is allowed to stand stoppered overnight at room temperature;

(4) Removal of excess peroxide: the next day, the flask is unstoppered and heated in a 105°C. oven until effervescence stops;

(5) Removal of carbon dioxide: the sample is then brought to a boil, methyl orange is added, and concentrated hydrochloric acid is added to the color change of the methyl orange (pH 3 to 4); the sample is then boiled for one additional hour;

(6) Precipitation: excess barium chloride solution is added dropwise while boiling, and the mixture is boiled one more hour, and allowed to settle one hour in a 105°C. oven;

(7) Pad formation: the clear filtrate is decanted off into a beaker; the precipitate is washed into the suction filter pad former previously charged with three sheets Whatman no. 42 filter paper, and allowed to settle; suction is applied and the filtrate is filtered through the pad, which is then washed with water and ethanol, removed from the funnel, and dried overnight at 105°C.;

(8) Counting: the pad is removed from the oven, weighed, and counted.

The first 22 samples were not burned in the Leco furnace; they were composed for the most part of white liquor samples with sulfur already present as sulfate or sulfite. Steps (3) through (7) were investigated and developed; it was found that oxidation was quantitative, removal of peroxide and carbon dioxide was complete, and that precipitate size was sufficiently large to permit uniform pad formation without loss if the procedures as given were followed.

White liquor samples burned in the Leco furnace gave results consistently lower than those obtained with an identical sample simply oxidized with peroxide and carried through the same procedure. Ground glass joints were inserted in the flow line between the furnace and the absorption tubes to prevent gas losses, but the flow rate of oxygen before entering the furnace was still seen to be greater than that of the gases entering the absorption tubes. It appears that these gas losses (which are not present in a normal sulfur determination using the Leco gas absorption tube) were due to an increase in hydrostatic pressure created within the system by the special absorption tubes used in the radioactive determination, causing leakage at the rubber stopper holding the oxygen flow line in the furnace tube.

The general method as outlined above has been used successfully for carbon^{14} (48), and more recently for sulfur^{35}, in a study of sulfur exchange and solubilization of sulfonated lignin (49), although chemical oxidation was used in place of combustion. The use of the Leco furnace was proposed in the experimental procedure outlined above because it produces "clean" reaction products, which are likely to present the least amount of chemical

interference in the subsequent reactions. Besides the possibility of gas leakage in the Leco furnace, one other probable source of error may be indicated; in normal quantitative sulfur determinations (50), the sulfate precipitate is washed thoroughly with a jet of water and ignited in a muffle furnace to remove all impurities and water. Both these steps were omitted in the proposed procedure, since pad formation would be disrupted, and the intensive washing might cause a loss of precipitate into the filtrate. The sample might be ignited only if a "pill" of barium sulfate of constant geometry and density were later formed and counted, or if the ignited sample were reslurried with water in a cup to form pads of constant dimensions, dried, and counted (49).

The value of counts per minute for any sample may be easily transposed into grams of sulfur by calculation, if the counting pad is of "infinite thickness". If increasing amounts of a constant proportion mixture of radioactive and nonradioactive sulfur are converted to barium sulfate, a plot of counts per minute (c.p.m.) vs. pad weight increases from zero to a constant level, and then remains constant for all greater pad weights. The lowest pad weight at which the value of c.p.m. is a constant for all greater pad weights is called the infinite thickness pad weight. Then, if known increasing amounts of radioactive sulfur are added to a constant amount of inactive sulfur great enough to produce a pad of infinite thickness, the amount of radioactive sulfur is found to be directly proportional to the c.p.m., for any given pad weight, and to the product of the c.p.m. and the pad weight for varying pad weights. The infinite thickness pad weight was found to be under 16 mg./cm.^{2} pad area for radioactive sulfur^{35} as barium

sulfate; a plot of c.p.m. vs. mg. sulfur from the original liquor was drawn for one-gram pads, and the experimental points were found to fall very well on the average line of slope 12835. The mg. sulfur in any pad weight might be calculated by multiplying the experimental c.p.m. by the pad weight, and dividing by 12835.

With this analytical tool, it was then possible to find the sulfur content of the pulp and lignin fractions of XRCI 9.0-90. Neither lignin nor pulp samples gave more than a few counts per minute over background. Finally both pulp and lignin samples were counted as such, i.e., without conversion of the sulfur to barium sulfate; these counts were also very low. It appears that none of the lignin had become sulfonated by radioactive sulfur; nevertheless, radioactivity was known to be present in the liquor. It was hypothesized that the radioactivity was due to sulfur as sulfate, which would not pulp wood, but which would show up in liquor determinations as radioactive sulfur.

To test this hypothesis, a liquor sample was acidified and swept with nitrogen gas; the output gases were routed to additional gas bubbler tubes filled with sodium hydroxide solution. After the stripping reaction had gone to completion, it might be expected that all the sulfur present as sulfate in the liquors would remain in the first tube, and all that present as sulfite might be found absorbed in the sodium hydroxide. The count of the sulfate portion was 53 and 78.7 times that of the sulfite portion for the white liquor and spent liquor, respectively. It was concluded that the sulfur^{35} either arrived at the Institute as sodium sulfate, or was converted to sodium sulfate by air oxidation in the interval between its arrival and

use. In any case, cook XRCI 9.0-90 was useless as a vehicle for the estimation of radioactive sulfur content in pulp and lignin fractions.

Therefore, white and spent liquor samples were oxidized and precipitated to recover all or most of the radioactivity as sulfate. This sulfate was then burned in the Leco furnace and absorbed in sodium hydroxide in an attempt to recover radioactive sulfite to be used in the preparation of more cooks. Since cooking liquor at pH 4.5 contains twice as much sulfur as that at pH 9.0, two-thirds of the slightly sulfited sodium hydroxide was further sulfited to pH 4.5, and used in the production of XRCII 4.5-90; one-third was sulfited to pH 9.0, and used in the production of XRCII 9.0-90. The liquor-to-wood ratio was changed from 10/1 to 7.5/1 to provide more pulp for analysis in these cooks. The cooking schedules, liquor and pulp analyses for these cooks may be seen in Table VII B and C. A small aliquot of diluted white liquor from each cook was treated with barium chloride, and the voluminous precipitate formed showed that although the Leco furnace may convert any sulfur compound quantitatively to sulfur dioxide, the passage of oxygen gas through slightly sulfited solutions of sodium hydroxide resulted in at least partial oxidation of the sulfite to sulfate. The c.p.m. of precipitated and nonprecipitated white liquor from XRCII 9.0-90 showed that almost 85% of the sulfur was still present as sulfate.

Each of the pulps was washed ten times as in the procedure given for XRCI 9.0-90. Ten milliliter aliquots from each last wash were dried on sodium sulfate in an aluminum dish and counted, yielding 16 and 6 c.p.m. over background for the XRCII 4.5-90 and XRCII 9.0-90 cooks, respectively. Extremely poor agreement between duplicate values of sulfur content was obtained on both pulp and liquor samples from the XRCII series radioactive

cooks. None of the values were close to background, as in the XRCI cooks, however, so it is assumed that the small amount of radioactive sulfur present in the liquor reacted with the lignin in the wood during the cook. The Klason lignin samples counted without conversion to sulfate were all quite high in radioactivity; therefore, some sulfonated lignin remained in the insoluble fraction during the Klason lignin determination.

The inadequacy of the method as outlined for the determination of sulfur content by radioactive means rendered further use in its present form inadvisable. Gas losses plagued the investigations whenever the Leco apparatus was used, and impurities may be present in the counting pad whenever the precipitated barium sulfate is not ignited. The Leco method was not found to be applicable for the conversion of sulfate to sulfite in recovered cooking liquors; duplicate sulfur contents were not obtained on duplicate samples even though the method as proposed has been refined to its probable maximum efficiency. The radioactive sulfur investigations have been important in that they produced a tool for the evaluation of the completeness of pulp washing, but their importance in the determination of the sulfur content of lignin fractions is diminished by the fact that even if the amount of sulfur from the original cooking liquor in the Klason insoluble and soluble fractions may be found, the soluble lignin must be isolated and weighed to calculate the over-all sulfur content of all of the lignin as it exists in the pulp. No method is presently available for the accurate isolation and determination of soluble lignin; since this thesis is not concerned with the fate of combined sulfur as lignosulfonate in the process of lignin isolation, it was decided that the simplest approach would

be the most realistic, and very probably the most accurate. Therefore, the sulfur content of the lignin in each experimental cook was calculated as the quotient of the sulfur content of the pulp, divided by the lignin content of the pulp. This quotient is submitted as an estimate of the sulfur content of all of the lignin as it exists in the pulp, and is not dependent upon the chemical and physical changes manifested in lignin isolation. It is most improbable that a grossly inaccurate estimate would yield checks and correlations as may be seen in the discussion of results on sulfonation.

THE DETERMINATION OF LIGNINLIKE GROUPS BY NITROBENZENE OXIDATION

Alkaline nitrobenzene oxidations were performed in this thesis according to the method of Stone and Blundell (36). The procedure may be summarized as follows: 40 mg. of wood or pulp, or 1 ml. liquor is placed in a 3-5 ml. stainless steel bomb, along with 1.5 ml. 2N sodium hydroxide (wood or pulp) or 0.5 ml. 6N sodium hydroxide (liquor) and 0.16 ml. nitrobenzene. The alkalinity is adjusted to 2N for any sample. This bomb is then sealed, placed in a 200-ml. bomb, covered with water, and heated at 170°C. for two hours, after the fastest possible rise to temperature. The bomb is then cooled in running water; its contents are centrifuged, and 0.1 ml. of the clear liquor is spotted across the top of a chromatogram together with a small spot for location of aldehydes. The spots are then acidified over boiling acetic acid, and the sheets are placed in a chromatographic tank with the solvent system n-butyl ether saturated with water. After three or four hours, the chromatogram is removed and allowed to dry; the test strip is cut off, sprayed with 2,4-dinitrophenylhydrazine, and the sections of the

paper corresponding to the spots on the test strip are cut out, labelled, and eluted with ethanol in micro-soxhlets for one hour. The eluates are then transferred to 50-ml. volumetric flasks containing 4 ml. of 0.2% alcoholic potassium hydroxide, diluted to the mark with ethanol and read on a spectrophotometer against standard 95% ethanol. The optical densities at 352 mmu for vanillin and 368 mmu for syringaldehyde were converted to mg./l. extract and then to mg./g. pulp or mg./ml. liquor. The nitrobenzene oxidation of pulp XC 9.0-90 yielded the following results: syringaldehyde, 52.9 mg./g. pulp; vanillin, 20.3 mg./g. pulp; S/V ratio, 2.60.

A fluorescent material with an R_f slightly greater than that of vanillin was noted on some of the nitrobenzene oxidation chromatograms, so a cursory examination of the oxidation products of the liquor was conducted. A chromatogram run in butanol-2% ammonia yielded six spots, all dark under UV and yellow under visible light. A summary of their color reactions with various spray reagents may be seen in Table IX, following a list of the abbreviations of the reagents used in these experiments.

24D	2,4 dinitrophenylhydrazine
DB	diazotized benzidene
M	Mäule reagent
VL	visible light
UV	ultraviolet light
DPN	diazotized p-nitroaniline
DPNC	sodium carbonate on DPN
P	phloroglucinol

Another similar chromatogram was run in butanol saturated with formic acid, and the aldehydes (greater R_f than the corresponding acid) were allowed to run off the sheet, presumably leaving the acids remaining on the sheet. The five spots and their color reactions are given in Table X.

TABLE IX

COLOR REACTIONS OF NITROBENZENE OXIDATION CHROMATOGRAM; ALDEHYDES

R_f	24D	DE	M	Probable Identity
0.10				
0.28	*	*		
0.39	*	*	*	Syringaldehyde
0.48	*	*		Vanillin
0.56				
0.89	*	*		p-Hydroxy azobenzene, Nitrobenzene

TABLE X

COLOR REACTIONS OF NITROBENZENE OXIDATION CHROMATOGRAM: ACIDS

Increasing R_f	VL	UV	DB	DPN	M	Probable Identity
	-	-	pink	-	-	
	yellow	-	-	-	-	
	-	fluor.	blue	-	-	
	-	-	pink	orange	pink	Syringic Acid
	-	-	purple	pink	-	Vanillic Acid

These materials were all present at very low concentrations, since the solutions had to be repeatedly applied to the chromatogram for the spots to become visible. The fluorescent material, which was not apparent on the aldehyde chromatogram run in butanol-2% ammonia, was partially separated from vanillin by eluting sections cut from a butanol-water chromatogram. The UV absorption spectrum of this substance may be seen in Figure 21. Although the curve is ligninlike in character, its optical density is seen to be quite low at 352 mmu. Little interference with vanillin is expected; even if only half of the fluorescent material was separated and eluted, its total absorbance at 352 mmu comprised less than 3% of the total vanillin absorbance.

It was suggested that the lead gaskets ordinarily used in sealing nitrobenzene oxidation bombs were in some way detrimental to the formation of syringaldehyde, producing lower apparent S/V ratios than actually present in isolated lignin fractions. For this reason, similar oxidations were made on wood using lead and teflon gaskets; the syringaldehyde yield was no lower for the lead gasket oxidations than in those using teflon. No definite trends in either amount or ratio of aldehydes could be observed for either type of gasket material; this may be due to the almost negligible amount of gasket material which comes in contact with the reaction mixture.

KULLGREN HYDROLYSIS

The Kullgren hydrolysis reaction involves the replacement of the cation present in a lignosulfonate radical in pulp lignin with a hydrogen ion, followed by the heating of the pulp in water at temperatures to about 90°C. A reaction occurs which some have called "auto-hydrolysis"; the strongly acidic lignosulfonate catalyzes its own breakdown, with the theoretical completion of the second stage of delignification, i.e., the removal of the sulfonated lignin from the solid pulp structure. The Kullgren extract, then, is presumably composed of that lignin fraction which would be solubilized by the cooking liquor during the next pulping interval; the position of this fraction in the cell structure may be seen in the stained microscopic cross sections.

Kullgren hydrolysis products were examined in the hope that isolated sulfonated lignin might be characterized by nitrobenzene oxidation and sulfur content. These data would be used to show differences in kind and amount of

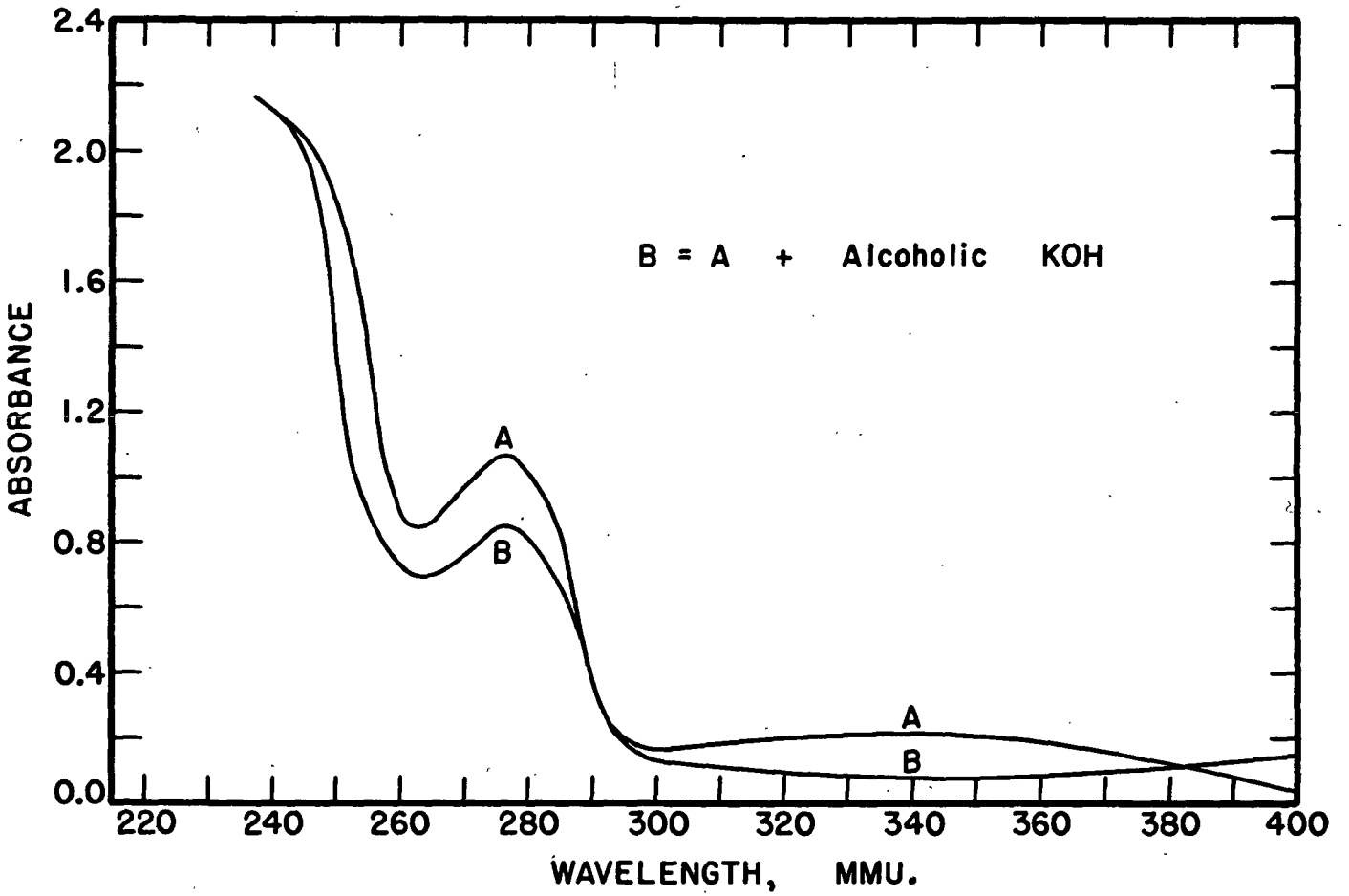

Figure 21. Absorption Spectra of Concentrated Alcohol Eluate of Fluorescent Spot Isolated From Nitrobenzene Oxidation Chromatogram, Spent Liquor From Series I Cooks

ligninlike groups and their amount of sulfonation (1) for different stages of pulping, and (2) in different portions of the cell structure. In preparation for the Kullgren hydrolysis, it was necessary to estimate the ion-exchange capacity of the pulp. Therefore, a known weight of pulp XC 9.0-90 was allowed to stand in a 0.3% solution of hydrochloric acid for one hour; the pulp was then washed thoroughly with water, until the filtrate gave no precipitate with silver nitrate solution. Theoretically, at this point all of the sodium ions within the pulp had been replaced with hydrogen ions, but no free hydrogen ions were present in solution. The pulp was then allowed to stand overnight in a 1% sodium chloride solution; the pulp was separated from the aqueous phase, and the hydrogen ions which had exchanged with sodium ions in solution were titrated with 0.004N sodium hydroxide. After subtraction of the blank, the ion-exchange capacity of the pulp was found to be 0.7 meq./g. pulp. Although this is not in the range of capacity of a good resin, it is a substantial value of pulp exchange capacity.

The Kullgren hydrolyses were begun in much the same manner as the ion-exchange capacity determinations; pulp XC 9.0-90 was soaked in dilute hydrochloric acid, filtered and washed until no precipitate formed with silver ion. Four pulp samples (Kullgren hydrolysis no. 1 through 4) were heated with distilled water in a water bath at 90°C.; the mixture was then filtered, more water was added, and the cycle was repeated until a number of extracts had been consecutively removed from each pulp sample. The extracts were evaporated to a small volume in rotating evaporators, and were finally dried in a vacuum oven at 50°C.

"Hydrolyses" in buffer of pH 8.29 were also run under the general conditions of a Kullgren hydrolysis; since this thesis is concerned with the removal of lignin, and since hydrolysis is presumably the main mechanism by which lignin is solubilized in pulping, an investigation of the amount of lignin isolated under nonhydrolyzing conditions is of great interest. The effect of buffer and water solutions on wood under Kullgren hydrolysis conditions was also studied. Hydrolyses no. 5, 6, and 7 were run under much the same conditions as Kullgren hydrolyses 1 through 4 on pulp samples, but no. 6 and 7 were performed on wood instead of pulp, and no. 5 and 7 were run with buffer solution instead of distilled water. Kullgren hydrolysis no. 8 differed from the first four only in the time of heating in a single volume of water.

Larsson (51) reports that solution of low-sulfonated aspen lignosulfonic acid after cation exchange may be hindered by polymerization and precipitation even in neutral solution, and at temperatures as low as 50°C. Lignin-like materials were isolated in this thesis at temperatures of 85 to 88°C.; no precipitation was observed until the extracts had been evaporated down almost to dryness.

The amount of material removed, percent sulfur, and nitrobenzene oxidation data may be seen for all of the hydrolyses in Table XI. Plots of cumulative percent woody material removed, and mg. aldehyde/mg. Kullgren extract, vs. hours of hydrolysis may be seen in Figures 22 and 23, respectively. These curves show that decreases in both the amount of material removed and the aldehyde content of this material contributed to a decreasing aldehyde yield from the original pulp with increased time of heating. There

is a rather sharp break in each of these curves at or before the 20-hour mark, but some ligninlike material seems to have been removed in Kullgren hydrolyses carried out to 141 hours. The extremely low rate of lignin removal at these longer times may be seen in Table XI, under the headings % removed per hour and mg. total aldehyde/g.-hr. extract. It appears that a certain portion of the lignin (probably that which is highly sulfonated) was removed with ease by the Kullgren procedure, and that the remainder was only very gradually removable over long periods of time. Kullgren hydrolysis no. 8 was run to determine if as much material may be removed in one long hydrolysis (one volume of water) as in many consecutive, shorter hydrolyses (many changes of water); Figure 22 shows that more ligninlike material was removed when the pulp was heated in many changes of water for shorter time increments.

It may also be noted in the hydrolysis plots that the rate of removal of ligninlike material from wood under the conditions of a Kullgren hydrolysis was very different from that of pulp. These low rates may be attributed to the absence of lignosulfonic acid in the wood, inhibiting the "autohydrolysis" reaction. The removal of the wood material was probably due to a combination of extraction (solubilization) and hydrolysis by wood acids; note the final pH of 3.8 for the wood Kullgren extract solution.

Table XI is incomplete in per cent material removed for the buffered "hydrolyses"; this is due to the interference manifested by the great amount of crystallized buffer present in the dried extract. In many cases, the total amount of extract plus buffer was less than the theoretical amount of buffer alone (2.52 g. in "hydrolysis" no. 5, 1.26 g. in "hydrolysis" no. 7).

TABLE XI

ANALYSIS OF KULLGREN HYDROLYSIS PRODUCTS

Kullgren No. & Reactants	Sample	pH After Hydrolysis	Sample Weight	Pulp Removed, %	Pulp Removed Per Hr., %	Sulfur, % of Extr.	Mg. Syr./ G. Extr.	Mg. Van./ G. Extr.	S/V Ratio	Mg. Syr./ G. Pulp	Mg. Van./ G. Pulp	Mg. Total Aldehyde/ G.-Hr. Extr.
	Residue		4.4861			0.21	29.8	12.7	2.35	--	--	--
1	Ext. 0-1	--	0.1213	2.52	2.52	2.64	--	--	--	--	--	--
Pulp	Ext. 1-3	--	0.0885	1.84	0.92	1.34	--	--	--	--	--	--
Water	Ext. 3-6	--	0.0759	1.58	0.53	1.36	--	--	--	--	--	--
	Ext. 6-10	--	0.0487	1.01	0.25	1.87	--	--	--	--	--	--
	Total Ext.	--	0.3344	6.95	0.70	--	--	--	--	--	--	--
	Residue		25.0980			0.22	29.6	12.5	2.36			
2	Ext. 0-1/3	--	0.2175	0.79	2.37	2.05	242.0	72.6	3.34	1.91	0.57	943.8
Pulp	Ext. 1/3-1 1/3	--	0.6086	2.22	2.22	1.72	211.0	65.3	3.23	4.67	1.45	276.3
Water	Ext. 1 1/3-3 1/3	--	0.5088	1.85	0.92	1.73	175.5	55.3	3.17	3.25	1.02	115.3
	Ext. 3 1/3-7 1/3	--	0.5119	1.86	0.46	1.38	137.6	44.2	3.11	2.56	0.82	45.4
	Ext. 7 1/3-15 1/3	--	0.5799	2.11	0.26	1.15	101.9	35.9	2.84	2.14	0.76	16.7
	Total Ext.	--	2.4267	8.83	0.58	--	--	--	--	--	--	--
	Residue		23.4486			--	--	--	--			
	Ext. 0-3	--	1.5026	5.46	1.82	--	180.7	61.4	2.94	9.87	3.35	80.7
3	Ext. 3-9	--	0.8785	3.20	0.53	--	124.4	41.1	3.03	3.97	1.31	27.7
Pulp	Ext. 9-21	--	0.6186	2.25	0.19	--	102.4	35.9	2.87	2.30	0.81	11.5
Water	Ext. 21-45	--	--	--	--	--	--	--	--	--	--	--
	Ext. 45-69	--	--	--	--	--	--	--	--	--	--	--
	Ext. 69-93	--	0.1915	0.70	0.03	--	86.8	28.1	3.06	0.60	0.20	4.8
	Ext. 93-117	--	0.1293	0.47	0.02	--	89.1	30.3	2.94	0.42	0.14	5.0
	Ext. 117-141	--	0.1263	0.46	0.02	--	--	--	--	--	--	--
	Total Ext.	--	4.0868	14.87	0.11	--	--	--	--	--	--	--

TABLE XI (Continued)

ANALYSIS OF KULLGREN HYDROLYSIS PRODUCTS

Kullgren No. & Reactants	Sample	pH After Hydrolysis	Sample Weight	Pulp Removed, %	Pulp Removed Per Hr., %	Sulfur, % of Extr.	Mg. Syr./ G. Extr.	Mg. Van./ G. Extr.	S/V Ratio	Mg. Syr./ G. Pulp	Mg. Van./ G. Pulp	Mg. Total Aldehyde/ G.-Hr. Extr.
	Residue		17.1740			--	—	--	—			
	Ext. 0-1	3.24	0.5616	2.91	2.91	--	218.4	71.2	3.07	6.35	2.07	289.6
	Ext. 1-4	3.10	0.5682	2.94	0.98	--	174.6	60.5	2.89	5.13	1.78	78.3
4 Pulp Water	Ext. 4-9	3.23	0.3503	1.81	0.36	--	131.1	38.8	3.38	2.38	0.70	34.0
	Ext. 9-19	3.32	0.3336	1.73	0.17	--	103.7	34.3	3.02	1.79	0.59	13.8
	Ext. 19-39	3.36	0.3492	1.81	0.18	--	114.7	36.1	3.18	2.07	0.65	6.9
	Total Ext.	--	2.1629	11.20	0.29	--	—	—	—	—	—	—
	Residue		19.1800			—	—	—	—			
	Ext. 0-1	6.62	1.8804	—	—	—	—	—	—	—	—	—
5	Ext. 1-4	8.03	2.3026	—	—	—	—	—	—	—	—	—
Pulp	Ext. 4-9	8.20	2.2152	—	—	—	—	—	—	—	—	—
Buffer	Ext. 9-19	8.20	2.1653	—	—	—	—	—	—	—	—	—
	Ext. 19-39	8.20	2.7468	—	—	—	—	—	—	—	—	—
	Total Ext.	—	-- *	—*	— *	—	11.4*	7.2*	1.58*	—	—	—
	Residue		9.7079			—	—	—	—			
	Ext. 0-1	3.83	0.0699	0.71	0.71	—	29.9	35.8	0.83	0.21	0.25	65.7
6	Ext. 1-4	3.88	0.0519	0.52	0.17	—	63.5	60.7	1.04	0.33	0.32	41.4
Wood	Ext. 4-9	3.78	0.0384	0.39	0.08	—	60.1	48.1	1.25	0.23	0.18	21.6
Water	Ext. 9-19	3.95	0.0444	0.45	0.04	—	79.9	48.7	1.64	0.36	0.22	12.9
	Ext. 19-39	3.63	0.0789	0.80	0.04	—	71.4	33.1	2.16	0.56	0.26	5.2
	Total Ext.	--	0.2835	2.86	0.07	--	—	—	—	—	—	—
	Residue		9.8603			--	—	--	—			
	Ext. 0-1	7.81	0.6999	--	--	--	—	--	—	--	--	—
7	Ext. 1-4	7.59	1.0358	--	--	--	—	--	—	--	--	--
Wood	Ext. 4-9	7.30	1.0189	--	--	--	—	--	--	--	--	--
Buffer	Ext. 9-19	7.10	1.2919	--	--	--	—	--	--	--	--	--
	Ext. 19-39	7.43	1.1960	--	--	--	—	--	--	--	--	--
	Total Ext.	--	-- *	— *	—*	—	14.8*	11.1*	1.34*	—	—	—
8	Residue		17.7300			—	—	—	—			
Pulp-H_2O	Ext. 0-24	2.99	1.54	8.08	0.33	--	135.7	57.8	2.34	10.84	4.62	0.6

*see text

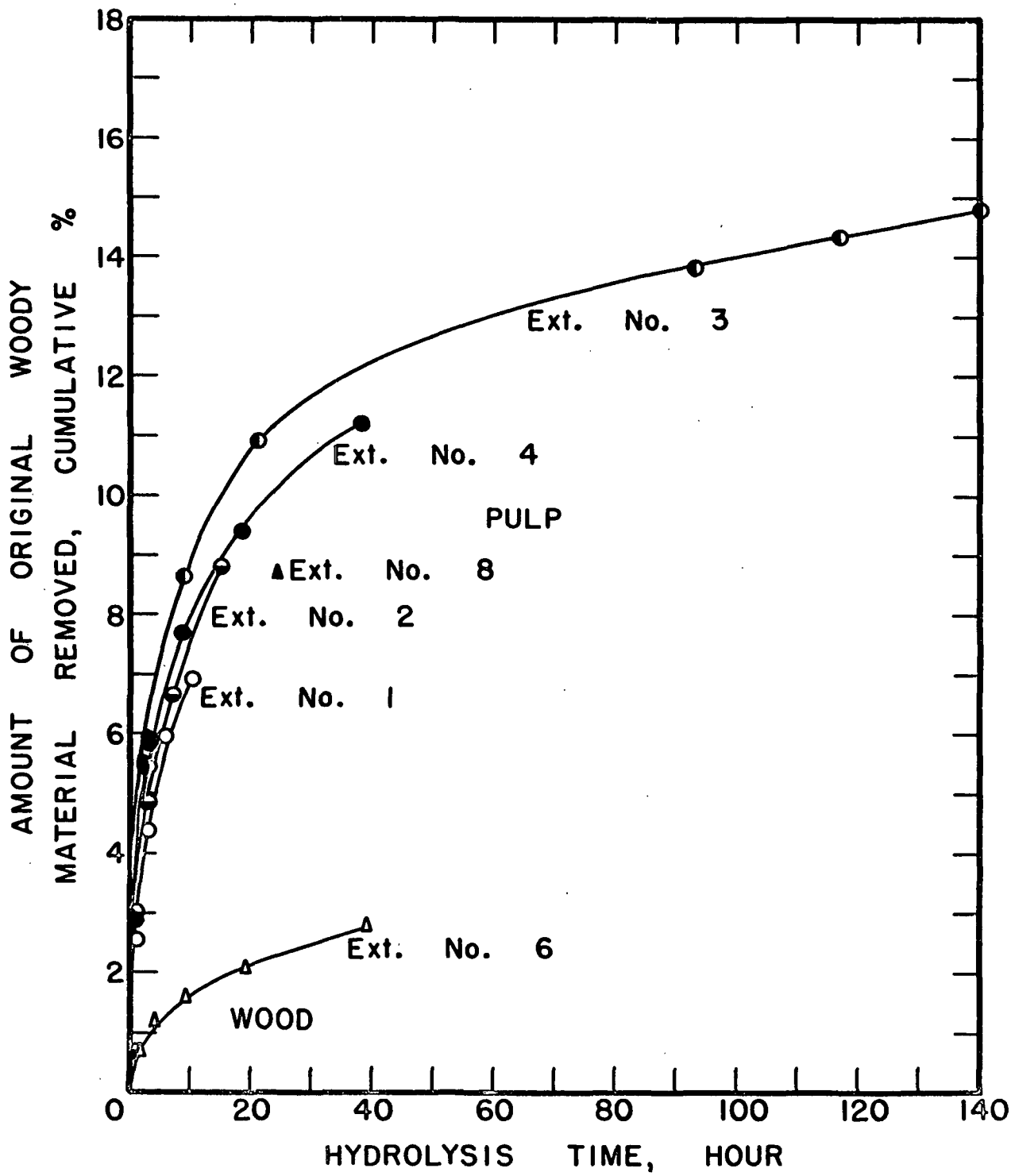

Figure 22. Yield of Kullgren Hydrolysis Extract vs. Time of Hydrolysis, Pulp XC 9.0-90 and Wood

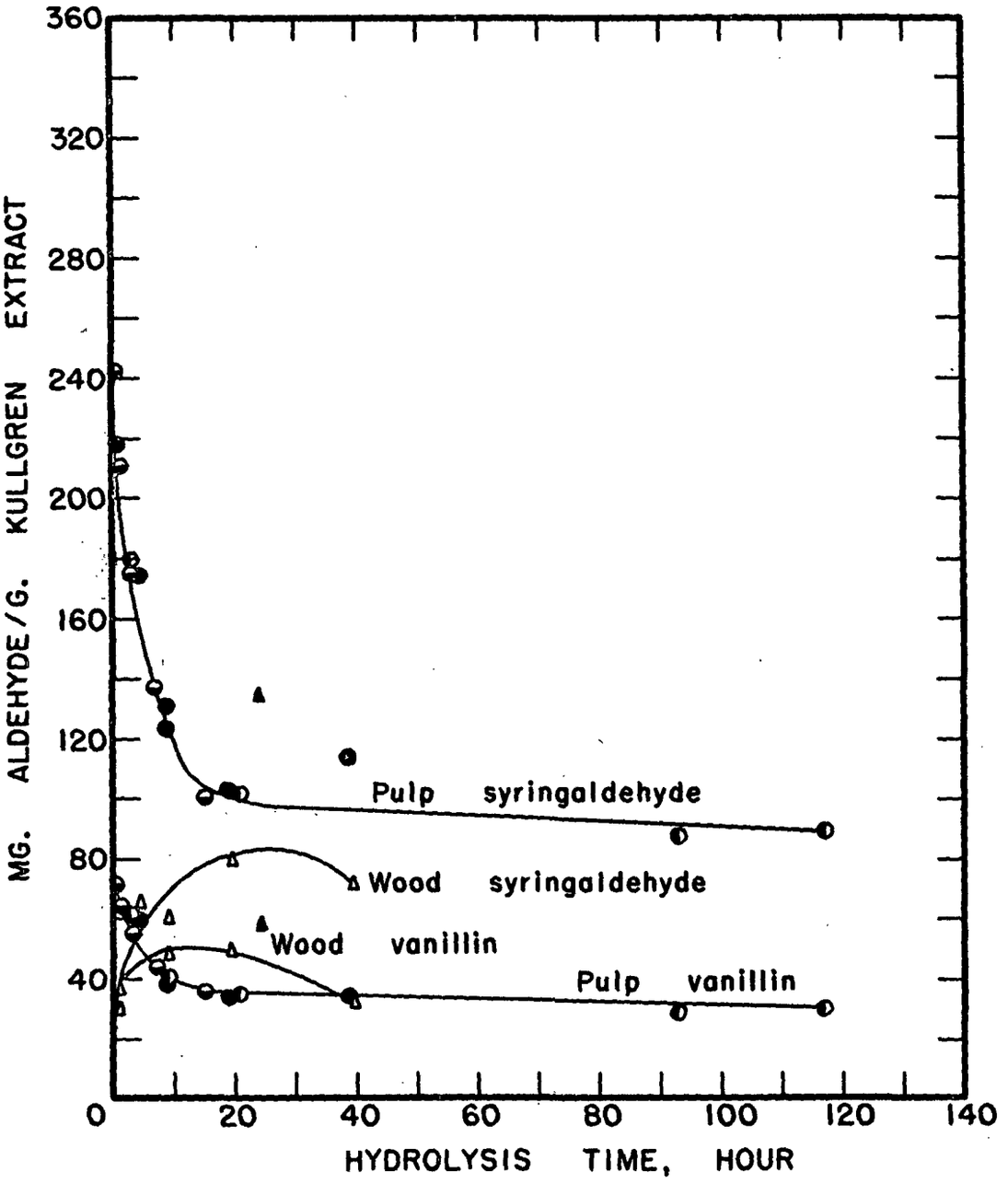

Figure 23. Aldehyde Yield on Nitrobenzene Oxidation of Kullgren Extract vs. Time of Hydrolysis, Pulp XC 9.0-90 and Wood

The buffer in these extracts also produced streaked nitrobenzene oxidation chromatograms. To prove that ligninlike material was removed from the pulp under alkaline buffer conditions, the five extracts in each hydrolysis were combined, ground together, and approximately half was extracted with cold ethanol-ether. The dried extract (about 100 mg.) yielded small amounts of syringaldehyde and vanillin on oxidation, with low S/V ratios of 1.58 (pulp-buffer) and 1.34 (wood-buffer). This indicates that although some lignin-like materials were solubilized under alkaline buffer conditions, the amount removed was not nearly so great as in unbuffered water hydrolyses.

Contrast these low S/V ratios with the high ratio of 4.77 (144 mg. syringaldehyde/g. extract, 30.2 mg. vanillin/g. extract) obtained in the nitrobenzene oxidation of a 0.78% dried ten-minute cold ethanol two-cycle extract of pulp XC 9.0-90, and with average ratios of pulp XC 9.0-90 (2.6), liquor (1.7), wood alcohol-benzene extractives (1.02), Kullgren hydrolysis residue (2.4), pulp-water Kullgren extract (3.1), and wood-water Kullgren extract (1.6). Relatively more syringyl groups were isolated in the Kullgren hydrolyses than in the cooks themselves; since the Kullgren procedure is said to be preferentially selective for sulfonated lignin, the high S/V ratio in the Kullgren extract may indicate that the syringyl nuclei were more closely associated with the sulfur present in pulp lignin, and that more of these groups had been sulfonated than guaiacyl groups in 90 minutes cooking time at pH 9.0. The high S/V ratios found in pulp extractives may indicate that ligninlike materials which might be counted as soluble or insoluble lignin (especially syringyl groups, which may have become sulfonated and therefore increasingly soluble) were removed from the pulp by alcohol extraction before

the Klason lignin determination. While lignin may be solubilized by hydrolysis at low pH, as in a water Kullgren hydrolysis or an acid sulfite cook, it was also solubilized under nonhydrolyzing conditions, such as in alkaline buffered "hydrolyses", NSSC cooks in the alkaline pH range, and by neutral solvents.

Aldehyde balances from the nitrobenzene oxidation of pulping and Kullgren hydrolysis products (Table XII) are very interesting, because they show the decrease in aldehyde yield with increased handling or reaction of ligninlike materials. In both cases, the per cent recovery of syringaldehyde appeared to be slightly lower than that of vanillin; the guaiacyl group may have been more stable to degradation by pulping or hydrolysis than the syringyl group.

TABLE XII

ALDEHYDE BALANCE: PULPING AND KULLGREN HYDROLYSIS PRODUCTS

	Pulp Balance	mg. S/g. Wood	mg. V/g. Wood	Total
A	Wood	58.5	24.0	82.5
B	Pulp LPC 9.0-90	41.8	16.0	57.8
C	Liquor PC 9.0-90	6.9	4.7	11.6
B+C	Pulp + Liquor	48.7	20.7	69.4
(B+C)x100/A	% Recovery	82.3	85.5	84.2
	Kullgren Bal.	mg. S/g. Pulp	mg. V/g. Pulp	Total
A	Pulp	52.9	20.3	73.2
B	Residue No. 2	26.9	11.4	38.3
C	Extract No. 2	14.5	4.7	19.2
B+C	Residue + Extract	41.4	16.1	57.5
(B+C)x100/A	% Recovery	78.4	79.4	78.6

Klason lignin determinations run on Kullgren residues no. 1, 2 and 3 yielded results of 10.3, 10.0 and 9.6%, respectively. The sulfur content of the Klason precipitate from residue no. 1 was 0.58%, and that of a "well-washed" precipitate from the same residue was 0.76%. This is the only case in the thesis work where the sulfur content of a "well-washed" lignin was higher than that of a regularly prepared precipitate. The sulfur contents of the Kullgren extracts approached the calculated value of 2.5% sulfur for the whole pulp lignin fraction much closer than did the experimental sulfur contents of the Klason lignin precipitates. The low sulfur contents of the Kullgren residues show that although sulfur-bearing materials were removed in the hydrolyses, the calculated sulfur content of the lignin remaining in the residue (about 2%) is still much greater than the sulfur content of the insoluble Klason lignin precipitate; therefore, the Kullgren hydrolyses did not remove all of the sulfur-bearing materials which enter the filtrate during a Klason lignin determination.

If the ratio of aldehyde (obtained by nitrobenzene oxidation) to sulfur in the Kullgren extract is plotted against time of hydrolysis, the vanillin ratio remains fairly constant, while the syringaldehyde ratio decreases slightly with increased time of heating; the relationship between both aldehydes and sulfur is fairly linear. The decrease observed for syringaldehyde is probably due to the decreased stability of this group with increased severity of reaction. If one of the nuclei types were not sulfonated, the linear relationship cited between sulfur and aldehyde would not be expected to hold over the entire time range of Kullgren hydrolysis; it appears, therefore, that when the cook had progressed 90 minutes at pH 9.0,

some guaiacyl groups had become sulfonated as well as syringyl groups. Since the hydrolyses were performed on fibrous pulp rather than chips, it is probable that this reaction was not selective for a particular portion of the cell wall, as was the pulping reaction; rather, the Kullgren reaction seemed to be selective for sulfonated lignin, and both guaiacyl and syringyl nuclei were removed in proportion to their degree of sulfonation.

It is obvious from the Klason lignin contents of the Kullgren residues that some of the 12.7% insolubles present in the pulp were removed in hydrolysis, but this value is much lower than the per cent total material removed. This may be due to the fact that a Kullgren hydrolysis tends to remove that lignin which would enter the filtrate in a Klason lignin determination, or that the Kullgren procedure removes carbohydrate from the pulp structure as well as lignin. To test these hypotheses, an attempt was made by qualitative paper chromatography to find out more about the composition of the Kullgren extracts. A portion of Kullgren extract no. 8 was refluxed for eight hours in 1N sodium hydroxide to break up the large lignin molecules into simpler phenols. Concentrated ether extracts of the Kullgren extract and of its neutralized alkaline hydrolyzate, along with the original Kullgren extract, were spotted on chromatograms and developed in butanol-2% ammonia. Six spots were seen with various spray reagents; their reactions are given in Table XIII.

The Kullgren extracts were also analyzed for sugars by chromatographic techniques; the developer in each case was 10-3-3 butanol-pyridine-water, and the spray p-anisidine hydrochloride.

TABLE XIII

COLOR REACTIONS OF KULLGREN EXTRACT CHROMATOGRAMS: PHENOLS

R_f	UV	24D	M	DPN	DPNC	P	Probable Identity
0.000	--	yellow	violet	--	--	--	
0.059	--	--	--	yellow	--	--	Vanillic Acid
0.082	flour.	--	--	--	red	--	p-Hydroxy benzoic acid
0.305	--	yellow	violet	orange	blue	--	Syringaldehyde
0.453	flour.	--	--	--	--	purple	Coniferyl or sinapyl aldehyde
0.883	flour.	yellow	--	brown	brown	--	

Kullgren extract no. 8 showed the following sugars, in approximate decreasing order of amount present: xylose, arabinose, galactose, and traces of glucose and acidic substances. A portion of this extract was hydrolyzed for three hours in 2% hydrochloric acid, and yielded greater amounts of galactose, arabinose, and xylose, some mannose, and traces of glucose and acids.

Extracts of different total hydrolysis time were spotted for Kullgren extracts no. 4 through 7. Kullgren extracts no. 5 and 7 (buffer with pulp and wood) showed no sugars on the chromatogram, but Kullgren extract no. 4 showed galactose and xylose present after one-hour hydrolysis time, and increasing thereafter, glucose present in traces after one hour, and arabinose present until 19 hours and continually decreasing. Kullgren extract no. 6 (wood and water) showed increasing amounts of galactose and arabinose after one hour, but no glucose, mannose, or xylose.

The chromatographic analysis of the Kullgren extracts indicates that only a small portion of the lignin removed in a Kullgren hydrolysis was broken down into small molecules; the remainder was presumably partly

degraded large molecules originally present as sulfonated residues within the pulp. These analyses also show that Kullgren hydrolysis removed sugars and polysaccharides from the pulp; under the experimental conditions of the hydrolysis, arabinose was removed first, followed by galactose and glucose. It appears that hemicellulosic polysaccharides, and not cellulose fragments, were removed along with the lignin; nevertheless, the Kullgren hydrolysis was more selective for the removal of sulfonated lignin than NSSC cooking liquor.

When the buffer solution was used in place of water in the Kullgren procedure, no sugars were liberated from wood or pulp. This may indicate that no acid hydrolysis occurred, but yet small amounts of ligninlike materials were freed by the reaction. This may be due to the solubility of highly sulfonated pulp lignin residues in water at any pH, or to the solubility of small wood or pulp lignin residues by virtue of size alone.

MICROSCOPIC EXAMINATION

A method of staining wood and partially pulped chip cross sections to show areas of lignification and sulfonation was developed according to the general techniques proposed by Jayme (39) in his work on isolated pulp fibers. Green and Yorston (40) first proposed the use of p, p' azo dimethylaniline (PP') as a precipitant and stain for lignosulfonic acid; they cite its use in fiber identification, and state that it is specific for unbleached coniferous sulfite fibers, and does not stain groundwood, unbleached or bleached kraft, bleached sulfite, or (as a rule) unbleached hardwood sulfite. The amount of stain taken up by the fiber varies with the chlorine number of

the pulp. Jayme (39) reports the use of PP' for the location of the areas of sulfonation within sulfite pulp fibers, and malachite green (MG) (which reacts with lignin in any form, whether protolignin, thiolignin, or lignosulfonic acid) for the location of areas of total lignification in a study of the path of liquor movement and delignification within the fiber. Green and Yorston state that PP' may also react with acidic groups such as carboxyl in oxycellulose, but Jayme maintains that neither resins, hemicelluloses, or carboxyl groups are stained.

Wood and pulp chips were cut in half, and sections were taken from a point near the center on a freezing microtome; it was found that wood sections of ten micron thickness could be cut without injury to the cell structure, but that the increased fiber flexibility in pulped chips demanded greater thicknesses of twelve to twenty microns. The sections were placed on microscope slides, unrolled and straightened with dissecting needles under a low power binocular microscope, and stained with PP' or MG. The staining solutions were prepared as follows: (1) MG: 1 ml. of stock solution (1.5 g. dye per 70 ml. ethanol plus 30 ml. water) was diluted to 200 ml.; (2) PP': a saturated solution of dye in 30 parts acetic acid and 70 parts water was used full strength. The stain was allowed to stand on each section 30 seconds; the slides were then drained, washed with water, and covered.

Solutions of PP' did not stain wood cross sections, indicating the absence of sulfonated lignin; MG stained both the middle lamella and the cell wall heavily. Pulp XC 9.0-90 sections showed areas of red within the middle lamella with PP', contrary to the work of Yorston and Green, who state that

hardwood lignosulfonic acids are not stained. MG stained the pulp sections slightly less than the original wood. This showed that the cell structure was not sulfonated uniformly, and that preferential areas of sulfonation may be expected during the cook. Each Series IV pulp was sectioned and stained with both PP' and MG, so that the position of the total lignin, and that of the sulfonated fraction might be observed at each time and pH level. By difference, the position of the unsulfonated lignin, and those areas of lignification and sulfonation which change during each pulping interval, may be characterized. Basic information may be obtained on differences in liquor penetration, diffusion, and movement within the chip for cooks of different initial pH; correlations between chemical changes in reaction products and physical changes in areas of sulfonation and lignification at corresponding pulping intervals may yield information on the differences in chemical composition of lignin residues present in various portions of the cell structure.