TOPOCHEMISTRY OF DELIGNIFICATION AND ITS EFFECT ON FIBER PROPERTIES OF

SPRUCE ORGANOSOLV PULP

by

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ABSTRACT

The catalysed organosolv process is a novel method of pulping that has many advantages over other chemical pulping processes. One of the most important advantages is its 6-12 percentage point higher yield of pulp in comparison to other chemical pulping processes. Short cooking time, low disintegration and refining energy requirements, ease of pulp washing and simplified method of by-product recovery are some of the other advantages. However, due to differences in the chemical nature of the cooking liquor, the basic properties of the fibers differ considerably.

In this thesis a detailed study has been carried out on some of the unique phenomena i.e., fiber liberation at a high yield, topochemical preference of delignification and their manifestation on morphology and strength properties of fibers.

Pulping results show that softwoods can be pulped easily to a high pulp yield (60%) with a high viscosity of cellulose of 50 mPas. The observed delignification pattern indicates two distinct stages both having first order kinetics. By this process, fast delignification occurs in the bulk delignification stage within which about 70% of the lignin is removed. Loss of residual lignin occurs at a slower rate in the residual delignification stage.

The ease of penetration of the cooking liquor and preferential removal of lignin from the middle lamella result in complete fiber liberation at a pulp yield of 57.3% and a Kappa number of 72 (7% residual lignin). The loss of lignin to carbohydrate ratio at 57.3% pulp yield is 1.21:1.

The topochemistry of delignification in organosolv pulping is limited to a preferential removal of lignin from the cell corner and middle lamella regions rather than from the secondary wall. In the initial stages of pulping, lignin removal is mostly from the cell corner and middle lamella region.

Secondary wall lignin was removed quite slowly and a substantial amount of lignin remained in the secondary wall even after extended delignification. This can be accounted for by the slow hemicellulose removal (loss) from the secondary wall.

The relatively high residual lignin retained in the cell corner in comparison to the complete delignification in the middle lamella raises questions about chemical differences and solubility characteristics of the cell corner lignin.

The fibers of high-yield pulps are found to be stiffer and form a low density paper with high tear, and average burst and tensile strength. These factors can be correlated with the higher amount of residual lignin material in the fiber secondary wall and the low bonding properties of the fibers. High residual lignin content decreases the internal fibrillation and ability of the fibers to conform with each other during sheet formation. On the other hand, the low-yield fibers (49.8%) were found to be quite flexible and showed higher strength than obtainable with high yield pulps. Organosolv handsheets contain 20 to 30% fewer fibers than kraft papers of the same basis weight. However, the apparent difference in strength properties between organosolv and kraft papers is not disproportionately large.

Organosolv lignins isolated from the spent liquor have low molecular weight (1400-2400) and low polydispersity (1.95) when recovered from extended pulping liquors. This indicates that most of the lignin is degraded to a fairly uniform low molecular weight polymer without substantially affecting the reactivity of the natural lignin as it occurs in the native fibers.

The simplicity of the pulping process together with the comparable strength properties of the fibers even at higher yields, reveals large potentials of this method as a new pulping process. With some refinements and closer optimization, pulp fully acceptable commercially could be produced by this process.

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1. INTRODUCTION

Long range forecast of paper consumption indicates a 2.8 to 3.0% annual growth requirement of the industry in the years ahead (3,19,62). Energy, raw material, environmental and economic considerations provide serious incentives for detailed investigation of alternate processes which could radically improve the world market position of chemical pulps (25,153,179). Large capital outlays required for environmentally acceptable new kraft mills seem to stifle further growth required of the industry (153,179,193) and hence production increases are temporarily provided by expansions and modernization of existing pulp mills. The desirability of finding new more efficient and less costly pulping methods has been suggested recently (32,153).

Several valid reasons were advanced in the past for the development of a new pulping process (19,25,32,153). The factors basically related to environmental concerns, materials and energy conservation, and high capital costs which seriously aggravate economic problems, affect markets and particularly affect the growth of the pulping industry (19).

Sulfurless pulping processes provide alternative means of reducing the heavy pollution loads created by pulping processes of today. The inability of the kraft industry to limit its sulfur emissions and to meet approved and acceptably low levels of air and water pollution (153), leads to serious questioning of the long term viability of the kraft process (25).

Demands on raw materials (75) and conservation pressures dictate new improved approaches to materials processing (126). In the near future, it will become imperative that low value by-products, hitherto unworthy of recovery be generated in a form which makes their recovery an integral and profitable part of chemical recovery efforts. Recent trends in increased energy and raw material demands have brought into focus more discriminate conversion of biomass into pulp and paper

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(19), base chemicals (55,64,104) and at least partial energy supplies (113,155,180). Thus, development and introduction of pulping technologies, characterized by improved wood substance recoveries in the form of higher pulp yield and · by-products (sugar and lignins), is imminent as more emphasis must be placed on co-generation of pulp and organic chemicals to improve the economics of pulp production.

Limits to high-yield chemical pulping are apparently set by ultrastructural and chemical complexities prevailing in lignocellulosic materials. Association of hemicelluloses and lignins are valid as are the preferred topochemical effects of the various pulping processes (136). Holopulping with sodium chlorite (32) was proposed earlier as a means of isolating low lignin content (less than 2%) fibers. Disadvantages of the process were high chemical and energy costs, corrosiveness of the chemicals, and lack of autoliberation of the fibers in spite of such a high degree of delignification. Alternate means to higher pulp yields by improved hemicellulose retention are hydrogen sulfide pretreatment of chips (189), polysulfide cooking (31,93) and anthraquinone addition to kraft pulping liquors (69). The improvements in carbohydrate retention and pulp yield by these processes are significant in their own right, yet they seem to be marginal when compared to theoretical yields demonstrated with holopulping. Only two stage soda pulping (107) is practised commercially; other processes are in various phases of development (32,179). However, because of the stricter and ever tightening environmental control guidelines and progressively declining economics of chemical pulping systems, these improvements become either environmentally restrictive or economically marginal.

Two of the most important advantages of the catalysed organosolv pulping process over kraft pulping are the process flexibility and substantial yield gains achievable with the organosolv process (128). Other advantages are: short cooking

time; elimination of steaming or preimpregnation and apparent ease of penetration of the liquor into the chips (irrespective of their size); the low cooking, refining and disintegration energy requirement; ease of pulp washing and the simplified method of recovery of cooking chemicals (distillation) and by-products recovery (precipitation) from the spent liquor. Chemical recovery from the spent liquor does not require combustion (burning) as is the case with kraft and sulfite spent liquors.

The ideal pulping process is expected to cause a high degree of delignification specifically concentrated in the region where the fibers are cemented together by lignin to allow facile separation of the individual fibers. Among the chemical pulping processes, the difficulties in separating wood fibers with a minimum mechanical treatment differ greatly. Fiber separation is achieved by preferential removal of lignin from strategically important locations in the wood, ie., middle lamella and cell corners for high yield pulps. All presently employed pulping processes show limitations in their ability to remove lignin from the middle lamella and/or the cell wall. Furthermore, pulp yield is often limited by the structural, chemical and ultrastructural features of the wood species. Among the various pulping processes, the specific mode of delignification results in significant differences in pulp yield, residual lignin content and hence the intrinsic fiber strength properties and fiber behaviour in beating and papermaking.

Catalysed organosolv pulping is one proposed new method of pulping. Only limited information is available so far. Though the fiber properties are comparable to kraft, fiber behaviour in PFI beating appears to be quite different (129). Therefore, it seems necessary to study the topochemistry of delignification by this process to fully understand the process and to devise the best method of treating the pulp for paper. Further attention is also needed to establish characteristics of the fibers in relation to potential maximum strength properties attainable with handsheets (papers) made of these fibers. Detailed systematic information is largely lacking in

these areas.

Catalysed organosolv pulping is a novel pulping process. In this regard the catalysed organosolv pulping process presents a unique opportunity to study a topochemical effect unobserved with any other pulping processes thus far. Basically, the process allows retention of the major fraction of hemicelluloses due to the fast initial delignification. Since initial delignification is largely limited to the middle lamella, complete fiber liberation at relatively high yield and at high Kappa number can be obtained. The phenomenon of initial topochemical preference in removing lignin from the middle lamella and cell corners needs particularly detailed study. Understanding the topochemistry of the various morphological regions during catalysed organosolv pulping should lead to further improvement in increasing the delignification and thereby production of low Kappa number pulps by this process.

Previous studies indicated that the various pulping processes have characteristic topochemical preferences of delignification, a process which leads to fiber furnishes having different papermaking properties. The initial removal of hemicellulose and lignin from the secondary wall in the kraft process is thought to be responsible for the less flexible and non-collapsible fiber. This may be one of the reasons for the relatively high tearing strength of paper produced from kraft fibers. Other features like the higher number of fibers per unit area and low hemicellulose content appear to be the factors that may also provide for better paper strength with kraft pulp fibers. While such effects are widely studied, few reports exist which correlate the topochemical effect and fiber strength characteristics of papermaking fibers.

Preferential initial removal of lignin from the middle lamella by the catalysed organosolv pulping process liberates fibers having high quantity of residual lignin concentrated in their secondary walls. Comparisons of strength properties of organosolv pulp with that of the kraft pulps of the same Kappa number reveal that

the organosolv pulp has comparable tensile but lower burst and tear strengths (128,129). The high fiber flexibility and hence low tearing strength of organosolv pulps in comparison to the kraft pulp of the same lignin content and viscosity indicates that not only the lignin content of the fiber is important for development of the strength properties, but also the relative distribution patterns of residual lignin and hemicellulose play significant roles for development of the sheet strength (129). The morphology and chemical properties of fibers provide further useful information regarding the basic behaviour of these fibers.

Based on this information the following hypotheses have been formulated:

1. That early fiber liberation is due to high delignification specificity of the solvent.

2. That removal of some of the hemicellulose is essential to remove secondary wall lignin.

3. That the topochemistry of catalysed organosolv delignification differs from other pulping processes in that there is a preferential removal of lignin from the middle lamella region.

4. That degradation of the lignin by the catalysed organosolv solvent leads to low molecular weight lignin fragments of low polydispersity.

5. That fiber properties are primarily governed by the state and composition of the cell wall. The higher carbohydrate and residual lignin retention in organosolv fibers might be affecting the strength parameters of the papers made therefrom.

To establish these hypotheses, a detailed study has been proposed as follows:

I. Trends of delignification: to study the pulping trends and chemical nature of pulp and lignin.

II.   Topochemistry of delignification: to study the specificity of solvent effect on the rate of delignification in the middle lamella and secondary wall by detailed microscopic topochemical investigation of organosolv fibers.

III.   Properties of fibers: to study the effect of fiber morphology and lignin and hemicellulose content of the fibers on development of strength properties of organosolv fibers.

2. LITERATURE REVIEW

2.1 TRENDS OF DELIGNIFICATION

2.1.1 BACKGROUND ON ORGANOSOLV PULPING

During the early thirties a process involving aqueous alcohol as the pulping liquor was reported (92). Subsequently a patent was issued to Kleinert and Tayenthal (91) on the process. It was found (91,92) that high-temperature (180-190 °C) extraction of wood chips in aqueous lower aliphatic alcohols (especially ethanol) resulted in preferential delignification of wood chips when the alcohol to water ratio was between 30 to 50% by weight. Catalytic amounts (<0.1%) of strong mineral acid and base were said to accelerate the delignification rate. Though original works by Kleinert and Tayenthal (91,92) and later by Kleinert (84-89) describe results with spruce, pine and poplars, experiments by Baumeister (12), Baumeister and Edel (13) and Lange *et al.* (100) indicate considerable resistance of softwoods to delignification and incomplete fiber liberation in 50% alcohol even on extended digestion.

Kleinert claimed that in the absence of added catalysts, pulping of wood chips with an aqueous alcohol (ethanol) occurred by a simple extraction process (90) via a high-temperature activated free-radical mechanism. On closer examination of his data, it is quite apparent that this free radical mechanism cannot be the only one operative in the system, as evidenced by the substantial carbohydrate losses before fiber liberation is obtained (83). For some reason the process worked reasonably well on aspen, straw and sugarcane rind, but not at all for the softwoods (88). To avoid the hydrolytic losses, Kleinert (90) goes on to suggest buffering or neutralizing with ammonia. However, it is found (131) that working around neutral or slightly alkaline pH

significantly reduces the delignification rate and makes softwood pulping totally impossible. Delignification is substantially slowed down and almost completely retarded as the ethanol content of the liquor approaches 70% and higher.

Dreyfus (42) and others (7,61) tried many combinations of lower aliphatic alcohol, ketone and nonpolar organic solvent mixture as pulping media in anticipation that successful and selective delignification was only a matter of solubility of the lignin in the organic solvent. Among the solvents most frequently used were the lower aliphatic alcohols (11,13,39,42,61,63,84,92,100,125,152), glycols, especially ethylene glycol, and glycerol (5,11,33,120), n-butyl and amyl alcohols (18,42,123,180) and other diverse solvents such as DMSO (71), dioxane (43,96,105,148) and various amines (72). Early summaries on organosolv pulping processes and solvent comparisons were provided by Aranovsky and Gortner (8) in 1936 and Brounstein (21) in 1952. In the intervening period until 1972, only sporadic mention of organosolv processing was made in the technical literature (137,157) and it was evident that due to various shortcomings, the process could not break the commercial barriers. Although organosolv pulping agents showed high specificity for delignification of wood, no entirely satisfactory organosolv system was found which would allow delignification of softwoods to low residual lignin content pulps without serious degradation of the cellulose. Thus as recently as 1980 McGovern (112) stated that "solvent pulping has made little progress ".

2.1.2 CATALYSED ORGANOSOLV PULPING PROCESSES

Acid catalysts, first suggested in the form of strong mineral and organic acids, were shown to cause severe attack on the cellulose (91,92).

Subsequently, Kleinert's patents (84,90) and papers (86,88,89) recommended a specific pH range between 4 to 8. In his German patent (90) Kleinert recommended neutralization with ammonia to avoid degradation of the cellulose. Lange *et al.* (100) observed that the delignification rate decreased drastically with ammonia-neutralized cooks (pH 9) and only 20 to 30% of the fibers were liberated by such cooks.

Results on catalysis with organic acids such as oxalic, maleic, salicylic, nicotinic, etc. were described by Paszner and Chang (130) and Nelson (120). These catalysts also gave improved results on softwoods and yielded medium viscosity (14-23 cps) and high lignin content pulps. Reject contents as low as 0.5% could be obtained even with softwoods in such cooks.

Hydrated aluminum chloride was first suggested by Orth and Orth (124) in anhydrous glycol and glycol ether solvents in an effort to produce well delignified aspen pulp for ruminant feed. Lately, Sarkanen and Hoo (150) have adopted these aluminium salts as catalysts in aqueous alcohol solutions (50% ethanol) aiming at production of fiber and chemicals from black cottonwood and red alder. Softwoods, particularly hemlock, remained refractory to aluminum chloride catalysed organosolv delignification. Delignification in an aluminum chloride catalysed aqueous ethanol solution gave quite acceptable pulping results with poplar (150).

Alkali-aqueous solvent pulping (35,36,74,111,117,118,119) provided more selective delignification and higher pulp yields at equal Kappa number than equivalent soda solutions (110). The difference was attributed to the prevention of condensation through the methylation of active benzyl alcohol groups in the lignin molecules (117). The required alkali concentration of 20 to 40 g/L is outside the true catalytic range, yet solvent losses and high energy demand for recovery of the solvent seemed to be the largest stumbling block

in commercialization of the process (94,118,119). Cooking with ammonium sulfide and a modified sulfite methanol process (24) face serious air pollution problems.

Alkali earth metal salt catalysts were found to improve the delignification rate and specificity of aqueous alcohol solutions in production of chemical pulps from both softwood and hardwood species (26,130,132). With catalysed solutions, the residual lignin content was found to be controllable within wide limits. The rate of delignification was found to respond well to kinetic factors, especially temperature and solvent composition, whereas, outside a narrow optimum concentration range, increased catalyst amounts had little beneficial effect. High-temperature (>200 °C) and high alcohol concentration (>80%) extractions result in rapid delignification and high carbohydrate retention in the pulps.

In comparing the relative efficiency of the uncatalysed Kleinert (84) process with that of calcium chloride catalysed cooks (27), Paszner and Chang (130) cooked chips under identical conditions except for the pulping liquors. It was found that with the Kleinert process aspen chips required roughly three times as long at temperature as with the catalysed cooks. Carbohydrate degradation during these cooks was evident from the lower screened yield, low viscosity and α-cellulose content of the pulps. On pulping aspen wood chips by the Kleinert process, high amounts of xylose were also removed. The strong hydrolytic conditions (pH 3.6 to 3.8) leading to heavy xylan losses was recently confirmed by Myerly *et al.* (116), who showed that 75% of the water-soluble substances lost could be accounted for by the glucose and xylose loss.

Solvent effect has long been a contentious and unexplained issue in organosolv pulping. Aranovsky and Gortner (8) observed that an increase in chain length in the alcohol used caused a rapid decrease in residual pulp yields.

This was interpreted to mean that n—butanol was a better delignifying solvent than ethanol. Better lignin solubility in butanol was recently confirmed by Hansen and April (65). From the extensive solvent effect studies in pulping and saccharification (26,27,130,132), it has been concluded that in the presence of a suitable catalyst (such as alkali earth metal salts) both carbohydrate loss and degradation can be suppressed by using methanol as the solvent. The use of methanol—water as solvent allows the delignification to occur at lower temperatures than in the corrosponding ethanol—water system. Increased carbon content in the straight chain portion of the solvent molecule resulted in only marginally better delignification selectivity, but caused faster degradation of the carbohydrates and hence resulted in lower pulp yield and lower viscosity (130,132).

It is also evident that in salt catalysed solvent pulping, the solvent concentration *per se* had a profound effect on the pulp yield and pulp viscosity regardless of the solvent type studied. Accordingly, increase in solvent concentrations normally resulted in higher residual lignin content, although delignification selectivity was improved at the higher solvent concentrations. This phenomenon was also observed by Kleinert (89), although the yield and viscosity losses were not considered serious until a water content greater than 50% was reached. Solvents containing high alcohol concentration (>50%) without a catalyst in the Kleinert process showed slow delignification (89).

The effects of different catalysts and varying concentrations were explored by Paszner and Chang (132). It is quite evident from the data that the chlorides appear to be somewhat more efficient delignifying agents than the nitrates and that the magnesium compounds are somewhat better than calcium. Higher concentrations of the catalysts (0.1 M), though quite efficient in delignification, cause excessive carbohydrate losses and degradation of

cellulose. The nitrates were found to be less degrading than the chlorides and allowed production of high viscosity pulps at very attractive yields. Magnesium sulfate showed poorer delignification power at comparable salt concentrations than either the chlorides or nitrates.

High temperatures up to 220 °C were found to be more advantageous at solvent to water ratios higher than 80:20, providing opportunities of producing high pulp yields at low Kappa numbers and relatively high viscosities. The cooking data clearly indicate the importance of temperature on cooking time, yield and viscosity of the pulp. Generally, with other pulping systems, high temperatures are considered to be detrimental to pulp yield and viscosity (89) due to the disproportionate increase in carbohydrate hydrolysis rates in uncatalysed solvent systems of equal or higher water content. In salt catalysed solvent systems (132), due to the catalytic and protective effects, there is acceleration of delignification as well as less depolymerization of the cellulose.

2.1.3 ORGANOSOLV DELIGNIFICATION

Kleinert (88) investigated organosolv pulping of spruce and poplar wood and found that delignification occurred in two distinct stages, viz. bulk and residual delignification. Both could be described by first order kinetics. It was determined (65) that delignification was considerably faster in the first portions of the cook and similar results have been widely reported in the literature (6,105,161). Bulk delignification was determined to be a composite phenomenon involving the breakdown of the lignin macromolecule as well as solubilization of the breakdown products. Previous work (63,65,161) has shown delignification to be a complex problem involving the breakdown of the lignin and carbohydrate molecules, followed by solubilization and repolymerization

of the breakdown products.

In brief, delignification with aqueous organic solvents is effective in separating wood into its three main components (18,85,88,123,154,161,186). Hemicelluloses are soluble in the aqueous phase whereas lignin is soluble in the organic phase. Cellulose is separated as a solid (5).

An important parameter for organosolv delignfication is the ability of the solvent to swell the wood structure (63,161). When a polar solvent initially comes in contact with wood, swelling takes place. One explanation of the swelling is that the molecules of the polar solvent are attracted to the dry solid matrix and held by hydrogen bonding forces. The repulsion of adjacent adsorbed polar groups causes a straightening of the cellulose chain and swelling of the matrix. Nonpolar ends of the adsorbed polar solvents would also result in repulsion of adjacent cellulose chains. Additional swelling of the cellulose matrix could be caused by diffusion of the organic solvent into bound water in the cellulose matrix or by repulsive forces between nonpolar ends of adsorbed solvents and the cellulose matrix. The swelling by the solvent can, therefore, be viewed as the driving force for opening of the wood structure and promoting early fiber liberation.

The changes in carbohydrate retention are strongly pH dependent (5,152) and loss of hemicelluloses can be ascribed to hydrolysis reactions (2,152). Few reports (55,151,186) indicate the relative importance of acidity on the rate and extent of hydrolysis. In an uncatalysed process the organic acids released probably act as catalysts (152).

Model compound experiments suggest strongly (152) that under mild hydrolytic conditions in aqueous alcohol solutions, the cleavage of ether bonds is exclusively restricted to those of the α-ether types. Although β-aryl ether (β-O-4) bonds predominate in the lignin structure, they are more resistant

towards hydrolysis than the α-aryl ether linkages.

Reports (44) on the nature of the chemical bonds anchoring lignin to the hemicelluloses are indicative of ether and 4-O-methyl-glucuronic acid ester bonds to the α-carbons of the lignin units. Although the hydrolysis rates of such linkages have not been characterized under acidic conditions, it can be surmised (152) that they are more readily hydrolysed than the β-O-4 bonds. These considerations lead to the proposition that the release of lignin in the organosolv process is essentially the consequence of the hydrolysis of α-aryl ether and lignin, and lignin-hemicellulose bonds (44). The high alcohol concentration in the catalysed organosolv pulping process (>75%) discourages carbohydrate dissolution.

The role of different catalysts for effective delignification is not very clear in the literature. At low catalyst concentration, the selectivity was found to be independent of the nature of the catalyst (152). The reaction system incorporates a combination of several physical and chemical steps such as adsorption, depolymerization, chemical reaction, dissolution, diffusion and condensation (186). The carbonium ions, which are electrophilic in nature, are postulated as intermediates in depolymerization reactions, especially in the breaking of α-aryl ether linkages (186). The stabilization of these ions by the use of aromatic compounds, such as β-naphthol, prevents lignin condensation and thus can lead to effective delignification at lower temperatures.

2.1.4 CHARACTERIZATION OF ORGANOSOLV LIGNIN

Organosolv cooking of wood in an aqueous organic solvent system with a proper catalyst at an elevated temperature provides an excellent procedure for simultaneous dissolution and quantitative recovery of lignin fractions of wood. The potential of recovering commercial quantities of

reactive lignins from the organosolv pulping liquor is very promising. Such lignins have many desirable properties including high chemical reactivity, low molecular weight and full solubility in many organic solvents.

Delignification of wood with mixtures of organic solvents is also gaining interest as an industrial option for preparing a carbohydrate-rich resource in which the cellulose is highly accessible to enzymatic depolymerization (53). Limited information indicates that organosolv delignification can apparently be performed under conditions by which useful lignin degradation products can be obtained. Tailoring the delignfication process therefore, to attain particular chemical and physical properties of the lignin residues by judicious choice of pretreatment and isolation conditions becomes important (52).

A variety of organosolv lignins prepared in different laboratories proved to constitute lignin preparations which were partially depolymerized hydrolytically. This structural variability underlines the flexibility of organosolv pulping process for isolating lignin coproducts with distinct structural properties (53,54). Nevertheless, organosolv delignification seems to be mild and produces lignins which resemble more or less the lignins in the native state.

One of the advantages of organosolv lignins is their high solubility in the usual lignin solvents, such as ethanol, methanol, pyridine, chloroform, tetrahydrofuran (THF) and acetone (28). Isolated organosolv lignins retain their good solubility in lignin solvents even after repeated precipitation and isolation from the spent liquor (28). Organosolv lignins are soluble in concentrations of 20% or higher in many solvents (51). Hydroxyalkylation raised the solubility of all lignins, and high molar substitution and higher methoxyl contents seemed to beneficially influence solubility (51).

Variation in total hydroxyl content is insignificant between various organosolv lignins (52). Methoxyl contents and syringyl to guaicyl ratios cover the range from 0.6 to 1.4 and 0.5 to 1.8 per C_9 unit, respectively (52). Moderately higher phenolic hydroxyl content, slight methoxyl losses and partially elevated carbon contents were found on preparation of organosolv lignins by Fengel *et al.* (45) and Meier *et al.* (115)

The molecular weight of lignin and its distribution is one of the most fundamental characteristics of lignin. The determination of the molecular weight of lignin macromolecules has been reviewed in detail by Brauns and Brauns (20) and Goring (58).

The methods developed by Brownell (22) and McNaughton *et al.* (114) are not much used due to many drawbacks. Currently, the most rapidly developing method is gel permeation chromatography (GPC). Depending on the size, the lignin macromolecules can diffuse in varying proportions into the porous volume of the column. The elution volume of any particular fraction is a function of the dimension of lignin macromolecules and the size of the pores in the gel (58).

Due to many limitations, dextran gels (Sephadex) or agarose gels (Sepharose) are not used frequently as the stationary phase for GPC to determine molecular weight of lignin and its distribution. Cross linked copolymers of styrene and divinyl benzene beads (styragel) are the most commonly used packing gels for high polymers.

Milled wood lignin preparations represent lignins with higher molecular masses than any other preparation, and these are in the range of 15,000 to 25,000. Kraft lignins have weight-average molecular masses of 4000 to 50,000; and organosolv and steam explosion lignins are in the range of 500 to 3000 with polydispersity factors of around 1.5 to 3.

The properties of solvent lignins from straw show that the molecular weight of the solvent lignin is significantly lower than that obtainable by the kraft process from the same species. Since small molecular weight particles are more desirable, due to their improved chemical and physical potentials, it can be pointed out that the quality of solvent lignin is definitely suitable for some commercial by-products.

The low polydispersity value of the solvent lignin indicates that it is available mostly in small molecular form, having relatively uniform molecular weight compared to polydispersed, condensed aggregate forms of the molecules of kraft lignin. The low polydispersity and small particle size of the solvent lignin suggest applications in reinforcing fillers and adhesives. Additionally, the smaller particle size of the solvent lignin enables replacement of phenol in increased amounts in phenolic resins over the present level of 20% possible with kraft lignin in binder applications (56).

2.2 TOPOCHEMISTRY OF DELIGNIFICATION

2.2.1 TOPOCHEMICAL PREFERENCES OF DIFFERENT PULPING PROCESSES

Some studies in topochemistry of delignification have been performed to establish the patterns of delignification preference of different pulping processes. Some contradictions and agreements can be observed on examining the available literature.

Bixler (16) observed that with kraft liquors, most of the lignin was removed from the middle lamella before any major dissolution of lignin from the secondary wall occurred. With sulfite liquors Bixler (16) found that the lignin was simultaneously removed from both the middle lamella and secondary wall regions. Lange (98), using UV microscopic techniques, observed

that in sulfite pulping of spruce the middle lamella was attacked at an early stage in the cook, and suggested that liquor penetration probably occurred via the pits. In the later stages of the cook, Lange (98) found that the fibers were held together by "spots" of lignin. However, location of the spots was not revealed. In the sulfite-bisulfite process, Marth (110) reported that in sulfite pulping of aspen, the lignin was removed from the cell wall near the lumen first.

Procter *et al.* (137) observed that in kraft and acid sulfite pulping of spruce, lignin was removed first from the secondary wall. Following about 50% delignification, the heavily lignified middle lamella and cell corner areas were attacked strongly and rapidly dissolved. Not much topochemical preference was found in the removal of lignin by neutral sulfite up to 50% delignification.

The reason for this trend was not known with certainity but the following quotation from Procter *et al.* (137) is quite pertinent:

> "The distinction of a neutral sulfite cook is that it allows delignification at a rather high yield. In both the kraft and acid sulfite cooks, considerable loss of hemicellulose (particularly glucomannan) occurs early in the cook. It may be that the initial selective removal of lignin from the secondary wall is associated with rapid early losses of hemicelluloses from this region. When the initial leaching of the hemicelluloses is restricted, as in the neutral sulfite cook, there is less topochemical preference for removal of lignin from the secondary wall."

Ahlgren and Goring (2) have shown that acidified sodium chlorite is a highly selective reagent for delignification, particularly up to 70% lignin removal. It has been observed that (191) there is an absence of topochemical effect in acid chlorite pulping in contrast to the behaviour during the kraft and sulfite process, in which the lignin in the secondary wall is removed preferentially. For kraft pulping, the topochemical preference for dissolution of lignin from the secondary wall is correlated with the quantity of hemicellulose removed early in the cook (59,76,77).

Wood *et al.* (191,192) and Goring (59) observed that the topochemical preference for the early lignin removal from the secondary wall was greatest for kraft and decreased for other delignification processes as follows:

Kraft > acid sulfite > neutral sulfite > acid chlorite.

This trend in topochemical effects was explained by the fact that lignin removal from the secondary wall is closely associated with the rate of hemicellulose removal during the initial stages of delignification (191), and seems to be related to the specific delignification site as defined by the pulping chemical used.

These effects may also be related to the difference between the chemical reactivity of the lignin in the compound middle lamella and in the secondary wall of the cell, respectively. Saka *et al.* (147) observed that in hardwoods more sinapyl (syringyl) lignin was present in the middle lamella than in the secondary wall (S_2). Another possibility might be that the effect may reflect differences in the porous structure of these two morphological regions, which in turn may be assumed to be governed by the presence of hemicelluloses (77). If the morphological concept of delignification as assumed is correct, it contains implications for development of an improved commercial pulping process.

Anthraquinone has been found to have a marked catalytic effect on delignification in both soda and kraft pulping (68,106). Enhancement of the delignification rate and stabilization of carbohydrates by oxidation of the reducing end groups (106) resulted in increased pulp yield. If topochemical effects are due to the pore size in the secondary wall, which is in turn governed by the rate of hemicellulose removal, there must exist some differences in the topochemical effects between soda and soda/AQ pulping systems.

Saka *et al*.(145), using a SEM-EDXA technique, showed that soda/AQ pulping was much more selective in removing lignin from the middle lamella regions than either soda or kraft pulping. However, a recent study on the topochemistry of delignification in soda and soda/AQ pulping by UV microscopy (23) revealed that although the addition of anthraquinone accelerated the delignification rate, no topochemical differences were detectable between the two pulping processes. In addition, it was observed that lignin removal occurred at the same relative rates from the secondary wall and middle lamella regions.

2.2.2 VARIABILITY OF LIGNIN IN DIFFERENT MORPHOLOGICAL REGIONS

Use of STEM/TEM-EDXA has provided better opportunity for studying lignin distribution in each individual layer of the cell wall. Earlier measurements (139,140) with the SEM-EDXA procedure revealed the possibility that the middle lamella in the cell corners had a higher lignin concentration than middle lamella regions adjacent to the radial or tangential trachied walls. As it was not possible at that time to measure the true middle lamella adjacent to the radial and tangential walls, this possibility could not be verified. However, the STEM/TEM-EDXA technique (142) has allowed measurements within the true middle lamella region and revealed a lower lignin concentration than in the cell corner region in Douglas-fir and loblolly pine.

It is becoming apparent that the chemistry of lignin is not uniform, but varies in different parts of the wood (59, 66). Most of the evidence for this has been microscopic (17,46,70,81,99,194). Only a few attempts have been made to characterize lignin from well defined morphological regions of wood (9,66).

There is an increasing awareness that the structure of lignin may depend on its location in and around lignified plant cells. Variations in, for example,

phenolic hydroxyl content, type and number of ether and carbon-carbon linkages between phenyl propane units, and variation in the syringyl/guaiacyl ratio may greatly affect such properties as the swelling and solubility of lignin and also its reactivity to pulping chemicals (66).

Phenolic hydroxyl analysis by pyrolytic gas chromatography (PGC) (59) confirmed the result of UV microscopy (194) in that the lignin in the secondary wall had twice the value of $PhOH/C_9$ as that found for the middle lamella lignin of black spruce. A similar trend was reported by Hardell et al. (66) in Norway spruce. It is seen (59) that the secondary wall lignin has an OCH_3/C_9 value of about unity while the methoxyl content of the middle lamella material is low.

The lignin in the secondary wall always reacts to a greater extent with sulfur and chlorine than the lignin in the middle lamella (59). During bromination a reaction similar to chlorination is expected. The ratio of bromine in the secondary wall lignin to bromine in the middle lamella lignin was found to be about 1.7 (146). This correction factor has been used in the determination of the distribution of lignin by bromination followed by STEM-EDXA (146). This suggests an inherent chemical difference between the secondary wall lignin and that found in the middle lamella.

In studying the different topochemical methods of determining the distribution of lignin across the cell wall, many assumptions have been made which are challenged by some recent studies (147).

Bromination of lignin model compounds showed that (147) for a non-condensed guaiacyl residue, only one bromine was incorporated into the C_6 position of the aromatic ring, while for a syringyl nucleus, two bromine atoms were introduced. For condensed guaiacyl residues, two bromine atoms were found to be incorporated per one aromatic ring of the condensed guaiacyl (β-5) residue. However, in the case of biphenyl structure, only one bromine was

incorporated into C_6 position of the aromatic ring.

Comparision of wood flour bromination with that of model compound studies is as follows (147). It is assumed that softwood lignin consists of an equal number of non-condensed and condensed guaiacyl nuclei (97). It is further assumed that (147) one bromine atom is introduced to a non-condensed guaiacyl nucleus, and one and a half bromine atoms, on average, to a condensed guaiacyl nucleus. Thus, 1.25 bromine atoms are incorporated into the pure guaiacyl moiety. Assuming the molecular weight to be 190 for the guaiacyl units, the bromine uptake will be 0.53 g/g for guaiacyl residues. It is likely that reactions similar to those observed with the model compounds take place during the bromination of wood lignin also.

Saka *et al.* (147) has indicated a caution for using their method as follows.

> "The lignin model compound study demonstrated that the reactivity of the non-condensed guaiacyl, condensed guaiacyl and syringyl nuclei towards bromination is different. Thus, the bromination EDXA technique has to be used with care as a tool for studying the distribution of lignin in wood. It is important to note that the validity of the analysis by bromination method depends upon the assumption of 1.2 for the ratio of the overall reactivity of the syringyl and guaiacyl residues. In fact, the proportion of the non-condensed and condensed guaiacyl moities of lignin may be different in different morphological regions and obscures the results. However, a minor change in the ratio is unlikely to affect the conclusion reached."

2.3 PROPERTIES OF FIBERS

2.3.1 BEHAVIOUR OF THE ORGANOSOLV PULP

The papermaking properties of organosolv pulps have been evaluated only by Kleinert (86) and Nelson (120). Their results suggest that, under favourable conditions, pulps can be obtained in higher yields than produced by the conventional kraft process, but with strength properties equivalent only to

those of bisulfite pulps.

One of the most important advantages of the catalysed organosolv pulping process over kraft pulping is the substantial yield gains achievable with the organosolv process (128). Furthermore, following standard fiber treatment procedures, organosolv pulps produced with catalysts were found to have comparable tensile strength and only somewhat lower burst and tear strengths in comparison to the kraft pulp of the same kappa number, made from the same chip furnish (27).

Some preliminary studies (15,129) were conducted to find an explanation for the differential fiber behaviour. Beating data and limited SEM studies indicated that organosolv fibers were more collapsible, fibrillated easily and yielded more extensive fiber to fiber bonding than possible with the kraft fibers. SEM photomicrographs also showed that organosolv fibers were susceptible to local cell wall damage in PFI mill beating. Sometimes, the severity of damage was so high that some of the fibers were destroyed.

The relationship between paper strength and fiber swelling has been demonstrated for many pulps (73,129). Thereby, it is known that paper properties can be enhanced by treating the pulp with selected alkali prior to sheet formation. For improving the strength of individual fibers, the modification of lumen diameter by alkaline treatment (swelling) has been suggested by Katz *et al.* (73). Levlin (102) on the other hand, proposed that depending on the pulp, improvement in the beating resistance can be obtained by varying the intensity of energy impulses to the pulp (102) during the beating process.

2.3.2 <u>THE EFFECT OF PULPING PROCESSES</u>

It was observed in earlier work in this laboratory (129,132) that organosolv pulping yielded up to 6-10 percentage points more pulp than the kraft process when the pulps were cooked to an equal Kappa number. Thus, organosolv pulps retain a higher amount of carbohydrates in the fibers than obtainable by kraft pulping.

The number of fibers per unit area (volume) of paper is an important factor determining the tear strength of the paper (50). Due to the higher pulp yield, individual organosolv fibers must weigh more and hence in making handsheets, fewer fibers (75-80% of the number of kraft fibers) are required to achieve papers of the same basis weight. The lower tear strength of organosolv pulp could then be explained on the basis of fewer number of fibers in the handsheets (129).

As regards to the expected behaviour of high yield pulps and relative strength properties of the pulp therefrom, Giertz (50) stated:

> " There is no type of pulp known that can be considered to be strong pulp and that can be easily beaten to a low freeness and good sheet formation. All means of increasing beatability involve a weakening attack on the fiber structure whether it is by over bleaching, by acid hydrolysis in sulfite cooking or by serious over cooking in kraft process; in all cases it results in a significantly lower D.P."

Organosolv pulps represent an unique case. It was observed (129) in organosolv pulping that pulps of high D.P. (>1500) and high yield (>60%) can be as easily beaten to a low freeness as those of lower DP and lesser yield kraft pulps. This would indicate that residual lignin and hemicellulose content, and their distributions play a significant role in beating and strength development of organosolv fibers.

The effect of pulping processes on ultrastructure of fibers and related strength properties is not well established. Only a few studies have been

published recently (59,70,136,139,191) on location and distribution of different chemical components in variously isolated fibers. Techniques of tagging (making lignin visible by fluorescence, UV and EDXA scanning) have been developed recently and attempts to quantify lignins in various morphological regions show much promise. Therefore, topochemistry has gained much attention in recent years as a tool for explaining the differential behaviour of fibers prepared by various means of isolation.

In chemical pulping operations, hemicelluloses are retained to a varying degree in the pulp. The nature and amount of the hemicelluloses depend upon the raw material and method of pulping (37). The interfibrillar hemicelluloses are supposed to play an important role in beating (30,37,50,122) as they imbibe water and act as an internal lubricant making the fibers more flexible. Furthermore, the swelling pressure facilitated by the presence of hemicelluloses contributes to the loosening of the fiber structure and thus promotes easy fibrillation (50). It is assumed that the hemicelluloses not only facilitate hydration and fibrillation (37), but, due to their gel-like nature, they contribute to the increased density of the paper on drying (50).

The presence of residual lignin in the fiber also has a significant role in defining the paper properties. In the plant, lignin acts as a cementing material and gives stiffness to the woody tissue. It is known that depending on the pulping process, different quantities of lignin are removed from the various morphological regions of the fibers. This process contributes significantly to the variability of fiber flexibility of different pulps. Thereby, fibers rich in lignin are expected to be more difficult to beat due to lignin's stiffening and water repelling effects in the fibers (50). High lignin content could further contribute significantly to fiber damage on beating.

2.3.3 FIBER MORPHOLOGY AND PAPER PROPERTIES

Numerous reviews are found in the literature on the relationship between fiber morphology and paper properties. Dinwoodie (40,41) and Barefoot *et al.* (10) have written fairly comprehensive reviews in which the variables influencing the principal paper properties are discussed.

Some of the parameters of fibers that affect papermaking are fiber length (14,30,47), lumen diameter (79), fiber flexibility and collapsibility (10,34,41,138). As most of the strength properties of papers are governed by a combination of fiber properties and the nature of the mechanical treatment applied to the fibers, it is difficult to isolate a single fiber parameter which could be adjusted to maximize a particular strength property of a pulp. Kibblewhite and Brooks (79) found that high yield bisulfite pulp fibers were more brittle and easily damaged by defibration and beating, than pulps of lower yield. No reasons have been proposed by them for this observation.

Wet fiber flexibility has long been known to be an important pulp property which can affect both the process of paper manufacture and the ultimate properties of paper products (163). Using a new Paprican fiber flexibility test (162), Tam Doo and Kerekes (163) showed that decreasing the pulp yield from 85 to 50% in acid sulfite pulping led to a four fold increase in the fiber flexibility. However, no inference has been drawn to correlate the chemical composition of the fiber to the fiber flexibility and its effect on strength properties.

The relationship between fiber flexibility and handsheet density has been discussed by Gallay (47). Gallay states that pulp fibers with a high degree of elasticity would have high "springback" at the time of beating and pressing in the papermaking press and thereby provide minimum potential contacts for bonding. Papers made of such fibers have low density. Robertson and Mason

(138) state that collapsibility of fiber is an important criterion for papermaking as it serves two functions: flattening of fibers which allows larger contact areas, and increased flexibility of fibers.

The commonly measured properties of tensile and bursting strength increase on pulp beating to a maximum point, then decrease (30,40). Specific surface area and fiber flexibility can also be developed and controlled by beating, since these are the fiber properties that promote interfiber bonding. When bonding increases, strength properties such as tensile and bursting strength increase (127). Fiber length also plays an important role in tensile and bursting strengths. For long-fibered fractions, both of these properties always surpass those of the short-fibered fraction especially on prolonged beating (14). Graham (60) and Van den Akker et al. (182) have given much emphasis to fiber strength as a limiting factor for tensile and bursting strength development. The reduction in the tensile and bursting strength after prolonged beating is usually attributed to a reduction in fiber length (30) and mechanical weakening of the fibers (41).

Tear strength development takes a different course than the tensile and bursting strength. Sometimes the tear strength increases slightly in the initial stages of beating but the main effect is a regular fall in tear strength as the beating continues. Parsons (127) has stated that tear strength requires a certain minimum fiber bonding, after which an increase in fiber bonding reduces tear strength. Van den Akker (181) has proposed a theory for tear failure, and indicated the importance of fiber length, stiffness, relative bonded area and fiber strength for development of high tear resistance.

3. MATERIALS AND METHODS

3.1 TRENDS OF DELIGNIFICATION

3.1.1 PREPARATION OF CHIPS FOR PULPING

A mature wood sample of black spruce (*Picea mariana* (Mill.)B.S.P.) was taken from a tree growing in the interior forest of British Columbia. The sample was removed at breast height from the tree. The wood block was cut to discs 2.5 cm thick along the grain. The discs were air dried and stored in the controlled temperature and humidity (CTH) room at 23 ± 2 °C and $50 \pm 2\%$ relative humidity .

Chips were prepared by hand guillotine cutting the 30–100th growth increments of the 120 year old tree. The juvenile wood and part of the sapwood, along with the bark, were discarded. Standard size chips 2.5 cm x 1.5 cm x 0.2–0.5 cm were made from each disc and stored in the CTH room. The moisture content of the chips was determined before cooking and was found to be 9.4%.

3.1.2 CATALYSED ORGANOSOLV PULPING

The cooking liquor used for the pulping consisted of:

> Methanol: 78% (by volume)
>
> Water: 22% (by volume)
>
> Catalyst: $Mg(NO_3)_2$ – 0.035 M
>
> $CaCl_2$ – 0.015 M

Standard cooks were made in a 175 mL digester with 15g of OD equivalent charges of chips. Cooking liquor in the amount of 130 mL was added before sealing the reactor (wood liquor ratio was 1:8.7). Two digesters were

simultaneously placed in a preheated glycerol bath maintained at 200 °C. After the insertion of the digester, the temperature normally dropped to 194 °C and took about 7.5 min to come back to 200 °C. This heating recovery time was also considered as a part of the cooking time. Chips were cooked to different cooking times i.e., 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 min. For each cooking time at least three cooks were made to obtain statistically representative results.

The cooking liquor was decanted and the chips were stored in methanol overnight. Following this, the chips were soaked in acetone for fifteen minutes before disintegration in acetone in a Waring blender for three minutes at the slowest speed. The disintegrated pulp was then washed in a Buchner funnel with three consecutive changes of 300 mL acetone, water and acetone. The pulp was air dried and its moisture content determined. Per cent pulp yield (unscreened) was calculated based on the initial oven-dry weight of the sample.

The pulp was screened on a vibratory flat screen using an 8 cut plate. The screen rejects were dried in an oven and per cent rejects were calculated based on the initial oven-dry weight of the chips.

Kappa number of the pulp was determined by T236 os-76 (172).

Viscosity measurement was done according to T230 os-76 (171), using a 0.5% cellulose solution and 0.5 M cupriethylenediamine as a solvent. A Cannon-Fenske capillary viscometer #300 was used. Unbleached pulp samples were bleached by chloriting (108,190) before viscosity determination to ensure full solubility.

3.1.3 <u>CHEMICAL ANALYSIS OF PULP</u>

Air dried chips and pulps (unscreened) were ground in a Wiley mill to pass 40 mesh and retained on an 80 mesh screen. The ground materials were conditioned in a CTH room and the moisture content determined.

Alcohol-benzene extraction was carried out on these samples as per T12 os-75 (170).

3.1.3.1 Klason lignin

To determine acid-insoluble lignin (Klason lignin) content of the extractive-free saw dust, the procedure described in T13 os-54 (168) was followed. A modified secondary hydrolysis with 3% sulfuric acid was used by treating the reaction mixture in an autoclave under steam pressure of 20 psi and at 127.5 $^{\circ}$C for 1 h.

The insoluble residue (Klason lignin) was collected by vacuum filtration on a medium porosity glass crucible and dried at 105 $\pm$ 3 $^{\circ}$C. The filtrate from the filtration was saved for the determination of the acid-soluble lignin content.

3.1.3.2 Acid-soluble lignin

The acid-soluble lignin was determined according to TAPPI useful method 250 (175). The acid solution from the Klason lignin determination, which contained the acid-soluble lignin, was stored in a stoppered bottle in a refrigerator.

The maximum UV absorbance of the acid solution was measured at 205 nm and used for calculation of acid-soluble lignin content by using the following equation. Absorbance values were determined in an Unicam SP 800 Spectrophotometer.

$$\text{Lignin \%} = \frac{B \times V \times 100}{1000 \times W}$$

where   V = total volume of solution (mL)

W = ovendry weight of saw dust

B = lignin content (g/1000 mL) and

B can be calculated by

$$B = \frac{A \times D}{110}$$

where   A = UV absorbance at 205 nm

D = dilution factor.

110 = Absorptivity (extinction coefficient).

3.1.3.3 Holocellulose

A modified method (108) to the conventional method of Wise *et al.* (190) was used in this experiment.

An accurately weighed sample of wood meal (2g) was placed in a 100 mL Erlenmeyer flask. Acetate buffer solution (64 mL of 0.5 M, of pH 3.5) was added and the flask was then kept in a water bath at 70–75 °C. After 10 min, 0.2 mL acetic acid and 0.6 g of sodium chlorite were added successively and mixed by vigourous stiring. An inverted small glass beaker was placed on the neck of the reaction flask. The contents of the flasks were mixed by occasional swirling.

After one hour of heating, an additional 0.2 mL acetic acid, followed by 0.6 g of sodium chlorite, was added. Subsequent addition of the sodium chlorite and acetic acid was determined based on the degree of delignification in the different samples. This was determined by visual brightness (trial and error) of the wood meals so that the residual lignin content would be within the

range of 0.5-1% of the lignin content of the wood meal.

The mixture was then cooled in an ice bath and then filtered by suction on a medium glass crucible. The residue on the glass filter was washed with distilled water and twice with a mixture of ethanol and acetone (1:1,v/v), successively, then air dried in a CTH room. These samples were dried in an oven at 105±3 °C for 4h. After weighing, part of the samples were used for ash correction (176) and the other part of the samples for Klason lignin.

3.1.3.4 α-cellulose and hemicellulose

Three of the air dried samples from the holocellulose preparation were taken for α-cellulose determination by T203 os-74 (167). The procedure which was followed assumes that the holocellulose consists of two, arbitrarily defined, main carbohydrate fractions: first; the insoluble α-fraction of high molecular weight, which remains when a holocellulose pulp and 8.3% sodium hydroxide solution is filtered, after the fibers have been previously swollen in a 17.5% NaOH solution for a predetermined time and second; the hemicellulose fraction which dissolves as the short chain material and is contained in the filtrate. Corrections for ash and lignin were made for the α-cellulose estimations.

3.1.4 CHARACTERIZATION OF ORGANOSOLV LIGNIN

3.1.4.1 Isolation of the lignin

After cooking, the undissolved lignocellulosic residue was separated from the spent liquor by decanting and filtration under vaccum. The pulp residue was extracted with 200 mL methanol in a beaker for 24 h, then filtered off and extracted with acetone at room temperature. The methanol and acetone filtrates were collected and precipitated as descibed later.

The spent liquor, dark brown in colour, was stored in a covered beaker overnight at room temperature and the clear solution was decanted from the small amount of precipitate which formed. The decanted clear solution was evaporated on a flash evaporator at 45 °C, vacuum 25 psi, until the volume of liquor after evaporation was about 25 mL. The residual solution was cooled overnight in the round bottom flask at 3 °C. The clear, yellowish, aqueous solution was decanted. The precipitate was washed with 5 mL distilled water, and dried over P_2O_5 to constant weight. This part of the water insoluble organosolv lignin was designated as "LIGNIN A".

The yellowish, aqueous solution was stored at room temperature. No further precipitate formed on prolonged standing.

Further purification of the "LIGNIN A" was carried out by precipitation of the lignin after redissolving in acetone (5 mL of acetone per 1 g of crude lignin), into water–acetone solution of 1:10 by volume with constant stirring. The precipitated lignin was filtered through a millipore filter (pore size 0.2 nm), washed with warm water (40–50 °C) and dried over P_2O_5 at 30 °C.

The initial precipitate from the spent liquor was carefully washed twice with 5 mL portions of distilled water, dried (48 h) over P_2O_5 at room temperature to constant weight and weighed. This part of the lignin was designated as "LIGNIN B".

The soluble fractions collected by methanol and acetone extractions of the chips, as mentioned earlier, were evaporated on a flash evaporator, dried and purified. These parts of the lignin were designated as "LIGNIN M" and "LIGNIN Ac" respectively.

3.1.4.2 Preparation of acetylated lignin samples

Acetylation of the isolated lignin sample was done by the method used by DeStevens and Nord (38). The lignin sample (0.2 g) was dissolved in dry

pyridine (3 mL), and acetic anhydride (2.5 mL) was added to the solution with stirring. The mixture was then allowed to stand for 48 h at room temperature and centrifuged at a rotor speed of 6,500 rpm for 20 minutes. The clear solution portion was separated from the fine residual precipitate and poured into ice water (100 mL) to precipitate the acetylated lignin. The precipitates were collected by vacuum filtration through a millipore filter (pore size 0.2 nm) and washed with 0.1 N hydrochloric acid (50 mL) to neutralize any remaining pyridine. The acetylated lignin was then washed with distilled water several times until the filtrate became neutral and dried subsequently over P_2O_5.

3.1.4.3 Preparation of reduced lignin samples

Borohydride-reduced lignin samples were prepared by a modified Adler et al. method (1). The purified lignin samples (60 mg) were dissolved in a mixture of 95% ethanol (2 mL) and 0.1N NaOH (1 mL) in an argon atmosphere. $NaBH_4$ (20 mg) and water (2 mL) were added to the mixtures. After 2 days, the solutions were acidified to pH 4 with 0.1N HCl (2.1 mL). The precipitates formed were collected by centrifugation and washed with water five times. The reduced lignin samples were then dried over P_2O_5.

3.1.4.4 Total hydroxyl content

For determination of the total hydroxyl content after acetylation and precipitation of the acetylated lignin samples, 10 mL aliquot samples of the solution from the supernatant of acetylated preparations were titrated with 0.1 N NaOH in the presence of phenolphthalein as an indicator (38). The total hydroxyl content was calculated by the following equation.

$$OH\% = \frac{/bo - b/}{A} f.789$$

b   = volume of 0.1 N NaOH solution required

     for specimen (mL)

bo = volume of 0.1 N NaOH solution required

     for blank (mL)

f   = factor of 0.1 N NaOH

A   = moisture free weight of sample (mg)

The disadvantage of this method lies in its sensitivity to the variation in volume of acetylated sample mixture. An error of ±0.01 mL in the volume of the added mixture means an error of ±1.15 mL of 0.1N NaOH titrant. In order to remove this error the sample weight, instead of volume, was used for the calculations.

3.1.4.5 Ultraviolet spectra

The UV spectra for the isolated lignin were recorded with a Unicam SP 800 spectrophotometer. Determination of the phenolic hydroxyl groups was done by the $\Delta\epsilon$ method of Zakis *et al.* (195).

An isolated lignin sample (10 mg) was dissolved in p-dioxane (10 mL). A portion of this lignin solution (2 mL) was diluted to 50 mL with pH 12 buffer solution consisting of 6.2 g of boric acid in 1000 mL of 0.1 N NaOH. Another portion (2 mL) was diluted to 50 mL with pH 6 buffer solution and the third portion (2 mL) of dioxane solution of lignin was diluted to 50 mL with 0.2 N NaOH. The differential spectra were determined by measuring the absorbances at 300 and 360 nm with the pH 12 buffer and 0.2 N NaOH solution relative to that of the pH 6 solution, respectively.

Phenolic hydroxyl groups were estimated by using the following equations:

$$\text{OH [\%] total} = 0.425 \, \Delta\epsilon_{300} + 0.182 \, \Delta\epsilon_{360}$$

where $\quad \Delta\epsilon_{300} = D300/c.d$

$\Delta\epsilon_{360} = D360/c.d$

D = difference of absorptivity at λ

c = concentration of solution (g.L^{-1})

d = thickness of cell (cm).

3.1.4.6 Infrared spectra

IR spectra of the reduced lignin samples were obtained with a Perkin-Elmer Infrared 521 spectrophotometer. The frequency range was 4,000 – 600 cm^{-1}, with an accuracy of 0.5 cm^{-1} and reproducibility of 0.25 cm^{-1}. The KBr pellets were made by mixing the dry lignin (10 mg) with 500 mg of potassium bromide. A portion of the mixture (200 mg) was pressed at 20,000 psi into a 1 cm diameter pellet.

The relative intensities of the absorption bands in relation to the band at 1510 cm^{-1} were calculated by the base line method as proposed by Sarkanen *et al.* (149).

3.1.4.7 Proton nuclear magnetic resonance spectra

Acetylated lignin (10 mg) was dissolved in deuterochloroform (300 μL) and filtered through glass wool into a 5 mm thin-wall sample tube. Tetramethylsilane (TMS) was added as an internal reference standard. Sweep width was 10 ppm and sweep time was 2 minutes. Spectrum amplitude varied from 5000 to 6000. The integration of the spectrum was recorded to obtain the relative peak areas.

3.1.4.8 Macromolecular analysis of isolated lignins

Gel permeation chromatography results were obtained on a high-speed GPC, Water Associates Model HLC/GPC-201 instrument equipped with a differential refractive index detector. The acetylated lignin sample (10 mg) was

dissolved in tetrahydrofuran (2 mL) to make about 0.5% solution. The solution was filtered through two millipore filters (pore size 0.45 nm).

The injection of the sample (200 μL) was done with the aid of a Model U6K universal injector. A series of four columns packed with different sizes of highly porous gel (μ-styragel) in order of 10^4A$^\circ$, 10^3A$^\circ$, 500 A$^\circ$, and 100 A$^\circ$ for molecular weights of 10,000-200,000; 1,000-20,000; 50-10,000 and 0-700, were used respectively. The pressure of the flowing solvent (THF) system was 1000 psi and the flow rate was 1 mL per minute.

The differential refractometer detected a change in refractive index as small as 10^{-7} RI units, which corresponds to a concentration change of 1 ppm of the lignin sample. An X-Y recorder converted the differential refractometer signals to a continuous trace on the chart. The time required for a complete run was about 45 minutes.

A calibration curve was drawn with polystyrene of known molecular weights. Bisphenol A, oligomethylol phenol and phenol were used as molecular weight standards. The solution volume (Vo)[mL] was plotted on the x-axis against the corresponding value of a known molecular weight on the logarithmic Y-axis on semi-log paper.

A simple programme for the calculation of the weight average molecular weight ($\overline{M}$w), the number average molecular weight ($\overline{M}$n), z values ($\overline{M}$z) and the polydispersity $\overline{M}$w/ $\overline{M}$n was done based on the following equations (151):

$$\overline{M}w = \Sigma(H.M)/\Sigma(M)$$

$$\overline{M}n = \Sigma(H)/\Sigma(H/M)$$

$$\overline{M}z = \Sigma(H.M^2)/\Sigma(H.M)$$

where   H = height of peak of each count number

     M = molecular weight converted from the

count number (from the calibration curve).

3.2 TOPOCHEMISTRY OF DELIGNIFICATION

3.2.1 SPECIMEN PREPARATION

Handcut chips of spruce wood (2.5 cm x 1.5 cm x 0.2 cm) were obtained from the 80th annual increment of the same discs taken for the pulping experiments. These chips were marked with a few notches on the surface and delignified by the organosolv pulping process as described earlier. The labeled chips were carefully separated from the cooked chips and treated separately. These chips were washed with acetone, water, acetone and water. Small specimens (1 mm x 1 mm x 5 mm) were made by a sharp razor, and dehydrated gradually with increasing alcohol concentration up to 100% alcohol. These specimens were extracted with alcohol benzene (1:3), for 24 h and then with alcohol for 6 h. The samples were collected in the alcohol, which was gradually replaced with chloroform.

3.2.2 STEM-EDXA STUDIES

3.2.2.1 Bromination of fibers

Bromine (0.3 mL) in 20 mL chloroform was slowly added into a magnetically stirred solution of 70 mL chloroform containing 1 g samples of each specimen at room temperature. Stirring was continued for 3 h. Next, the reaction mixture was refluxed for an additional 3 h, and then filtered and washed with chloroform. The brominated specimens were then placed in the Soxhlet apparatus and extracted with chloroform until all unreacted bromine was removed (139,140).

3.2.2.2 Ultramicrotome sectioning of fibers

The extracted specimens were kept in ethyl alcohol overnight and then transferred to propylene oxide three times before embedding in the Spur medium-viscosity epoxy resin. The embedded samples were then sectioned with a diamond knife mounted on a Porter Blum MT2 ultramicrotome, to obtain transverse sections (0.5 μm).

Since the commercial specimen support grids were made of copper, a rather high amount of continuous white x-rays and intense x-rays characteristic of copper were produced. To reduce this effect, a thin collodion film was applied and subsequently coated with a thin film of carbon. After placing the section over the grid, another thin film of carbon was deposited over the sections.

3.2.2.3 Microscopy and energy dispersive x-ray analysis

The grids were mounted on the specimen holder in a Hitachi-800 Scanning Transmission Electron Microscope (STEM) equipped with a Ortec Energy Dispersive X-ray Analysis (EDXA) detector. Variables such as the distance of the x-ray detector from the specimen, tilt angle of the specimen holder ($0°$), specimen height and take off angle ($45°$) were held constant throughout the study. The accelerating voltage used was 200 kV. The objective aperture was kept at 1 and the condenser lens was at 45 throughout the study. Every other hour the electron beam was realigned. Under these conditions, point analysis and line-scan analysis of Br-L-x-rays (1.42-1.56 keV) were performed.

3.2.2.4 Analysis technique

The following three types of EDXA techniques were followed:

1. X-ray distribution mapping,

2. Line-scan analysis and

3. Point analysis.

The first two methods were found to be very convenient for visualizing lignin distribution across the cell wall in a qualitative manner, whereas the third technique (point analysis) was most appropriate for the semi-quantitative assay of lignin distribution because of greater precision. Therefore, only the point analysis was used in this study for semi-quantitative determination of lignin distribution. In this procedure, using the STEM image as a reference, the electron beam was kept stationary for a certain period in a particular morphological region and counts were accumulated to estimate the bromine concentration in that region, which in turn was taken as a reflection of lignin concentration of the region studied.

Preliminary work with brominated pulp fibers showed that with a condenser lens setting of 45 the electron beam spot was 0.01 μm in diameter. This diameter was found to be suitable to study the lignin in the middle lamella independent of the primary wall.

With the existing facility, preliminary studies were carried out to optimize the specimen thickness with respect to the accelerating voltage of the electron beam. Increasing specimen thickness, up to the depth of electron beam penetration, resulted in higher spectral emission, as the absolute amount of lignin (thus bromine) encountered by the beam was increased. Therefore, to avoid variation in bromine readings, close control of the specimen thickness was maintained. In the present study, specimens considerably thicker than the depth of electron beam penetration were used. The procedure which was followed assumes equal density across the cell wall and thus equal beam penetration in all morphological regions of the cell wall. Obviously, removal of lignin decreases the fiber wall density and should allow increased beam

penetration. The increased beam penetration could have resulted in an inappropriately high bromine peak. However, since all specimens were embedded in Spur medium-viscosity epoxy resin, resin diffused into the cell wall and presumably occupied the space from which the lignin was removed. It was assumed, therefore, that there was no significant change in the density of the sample. For the present study, 0.5 μm thick sections at an accelerating voltage of 200 kV were considered suitable for a comparative lignin distribution study.

In spite of all precautionary measures, it was difficult to get uniform 0.5 μm thick sections by the ultramicrotome. As specimen thickness was very important, the problem was overcome by selecting specimens of controlled thickness. The specimen selection was done by measuring the Cl-Kα x-ray counts (2.56-2.72 keV) for 60 s by point analysis in the embedding material found in the cell lumen. Specimens having essentially the same counts were chosen for subsequent analysis.

The process of delignification in earlywood tracheids for the organosolv process was followed by the x-ray mapping technique for bromine. In x-ray mapping, the number and location of the white dots (x-ray emitted spots) indicate the distribution of bromine. However, it did not really reflect the density of the lignin present. Hence, this procedure provided only observations of the relative trends of lignin removal. As KMnO$_4$ staining technique gives the same qualitative information, no further work was carried out with x-ray mapping.

For the line-scan analysis, the dwell time was optimized to be at 400 ms with all other microscopic conditions remaining the same. Sections close to the center of the grid were chosen for this study. The magnification of the area under observation was maintained uniformly to get line-scans across the cell

corner and in the middle lamella region from one lumen to the other lumen of two adjacent cells. The electron beam remained at a particular point for the specific dwell time. The x-ray count within the time was recorded and the beamed moved to the next point. The x-ray counts along the line were stored and presented in the form of a barchart. This chart shows comparative lignin concentrations across two cells, from lumen to cell walls, middle lamella/cell corner, cell walls and lumen. As the cell lumen was filled with epoxy, any signal observed in that area was considered as background noise. Sections from pulps at different cooking time were analysed in the same manner.

For optimization of the dwell time in a point analysis, the time duration was varied from 60 s to 500 s and bromine counts per second were calculated after the necessary background noise correction. It was seen that 200 s gave a suitable dwell time, after which there was no significant change in the bromine counts per second. Three readings were taken in the cell corner, middle lamella and secondary wall separately for each sample.

3.2.3 TEM STUDIES

3.2.3.1 KMnO$_4$ staining of fibers

Pulped and unpulped specimens as prepared before were hydrated back to water after alcohol-benzene extraction by sequentially increasing the water content in the aqueous alcohol solution. The specimen were stained with 1% KMnO$_4$ solution (133) for 4 hours. The stained samples were washed thoroughly in distilled water and dehydrated in solutions having increasing alcohol concentrations.

3.2.3.2 Ultramicrotome sectioning of fibers

The specimens were kept in ethyl alcohol for a few hours and then transferred three times to propylene oxide before embedding in the Spur medium epoxy resin. The embedded samples were sectioned with a diamond knife mounted on a Porter Blum MT2 ultramicrotome, to obtain thin sections of 0.1 μm. These sections were placed on a non-carbon coated grid and no coating was done subsequently.

3.2.3.3 Microscopy

The grid was mounted on the specimen holder in a Zeiss Transmission Electron Microscope (TEM). The tilt angle of the specimen holder was 0° and specimen height, take off angle (45°), the accelerating voltage (60 kV), the objective aperture set at 2 and the condenser lens at 3 were maintained. For photography purposes 22 mAmp and exposure for 2 seconds were kept constant throughout the study to facilitate comparisons for the intensity of lignin.

3.2.3.4 Analysis

Micrographs at different magnification were taken and observed very carefully for lignin removal and fiber separation and wall splitting.

3.3 PROPERTIES OF FIBERS

3.3.1 BEATING

All pulps were beaten in a PFI mill beater at 10% stock concentration at a half load and a relative housing speed of 6 m/s. The pulp charge used was 30g (oven-dry) and the pulp temperature during beating was 23 ± 2 $^{\circ}$C as per T248 pm-74 (169).

High-yield organosolv pulp (40 min cook) was beaten for 4000, 6000, 8000 and 10000 revolutions to obtain widely spaced freeness values at which strength properties could be studied. For comparison purposes, medium-yield pulp (60 min cook) needed 3000, 5000, 7000 and 9000 and the low-yield pulp (100 min cook) needed 1500, 3000, 4500 and 6000 revolutions to reach the same freeness levels. Canadian Standard Freeness (Csf) values of each beaten sample along with that of the unbeaten samples were recorded as per T227 os-58 (164).

3.3.2 PHYSICAL STRENGTH PROPERTIES

Handsheets were prepared in a British sheet machine from the unbeaten and beaten pulps according to T205 om-81 (177). The back water was not recirculated. The handsheets were pressed under a constant pressure of 345 kPa in a standard British sheet press.

The sheets so formed were conditioned according to T402 os-70 (166) at 23 ± 2 °C and $50 \pm 2\%$ RH before testing for grammage, caliper, bursting strength, tensile strength and tear resistance according to the appropriate TAPPI methods (165,173,174).

3.3.3 FIBER LENGTH FREQUENCY DISTRIBUTION

Fiber length distributions (population) of these pulps were determined on pulp before PFI beating with the Kajaani FS100 Fiber Analyser (129).

The procedure involves dilution of the pulp samples to 0.01% (approximately) and optical measurement of more than 1000 fibers for better accuracy. The instrument is calibrated with synthetic test fibers of known length. The length values are automatically fed into a computer and the distribution bar graphs as well as weighted average fiber length were printed

out.

3.3.4 FIBER FLEXIBILITY TEST

Fiber flexibility measurement was done on a new Paprican fiber flexibility tester (162). A single fiber is placed across the notched tip of a submerged capillary tube and water is drawn into the tube to deflect the fiber. The fiber is observed through a microscope and measurements are made for diameter and maximum deflection in the eye piece. The hydrodynamic loading that deflects the fiber is obtained by measuring the flow rate of water through the capillary tube with a suitable rotameter. Fiber stiffness was derived for eighty fibers using a simple equation (163). Flexibility of the fibers can be calculated from their stiffness, as flexibility is the inverse of stiffness.

4. RESULTS

4.1 TRENDS OF DELIGNIFICATION

4.1.1 CHARACTERISTICS OF PULP

Among the factors affecting the outcome of organosolv pulping, only time was chosen as a cooking variable in the present study. Other important conditions, such as temperature, cooking liquor composition and wood to liquor ratio were kept constant throughout the study. The effect of these parameters was described in some detail in previous studies (132).

Total pulp yield was measured after disintegration and drying. Pulp yield, rejects, kappa number and viscosity of the pulps are listed for the series in Table 1. It is observed (Fig. 1) that the pulp yield started to decline very fast in the initial stages of cooking (about 30 min) and subsequently slowed down in a specific pattern.

Disintegration of the pulps for the 10 min and 20 min cooks in the Waring blender was difficult due to the incomplete fiber liberation and high proportion of rejects in the pulp. The pattern for the percentage of rejects follows a different trend than observed for the yield and is shown in Fig. 2. There was a sharp drop in the reject fraction of the pulp following about 40 min of cooking. Subsequently, reject contents remained more or less the same at about 2% since the Waring blender does not give proper defibration. Most of the rejects from the later stages of cooking (50 min onwords) could be easily defibered by hand. Therefore, pulps with about 2% rejects were considered as "completely defibered pulp". Fiber breakage in the extended defibration was a concern and thus the defibration times were standardized throughout and kept as short as possible (3 min).

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Kappa numbers of the pulps at different cooking time are listed in Table 1, and the relationship between cooking time and Kappa number is shown in Fig. 3. The Kappa number of the 10 min cook was found to be relatively low as it was measured on the unscreened pulp. For this reason, to evaluate the degree of delignification, total lignin was determined by the Klason lignin and acid soluble lignin methods and these were considered in this study rather, than Kappa number, as most appropriate. It is remarkable to note that the intersection point of the two slopes of lignin content vs. cooking time curves has shifted to about 50 min in the Kappa number vs. cooking time plot (Fig. 3) from 30 min for total lignin content (Fig. 5). These results further question the suitability of the Kappa lignin method for estimating the lignin content in these pulps.

Viscosity of the pulp was determined after bleaching the pulp with a modified chloriting procedure. The results are listed in the Table 1. Viscosity of the 10 and 20 min pulps could not be determined accurately since the pulps did not dissolve properly in the 0.5% cupriethylenediamine. solution. A linear relationship between cooking time and viscosity (Fig. 4) was observed. As there was a steady decrease in the pulp viscosity observed on extended cooking, cooks longer than 100 min were not performed, although the lignin content of 100 min pulp was still 3.6%.

Lignin content and the percentage of delignification of the pulps at different cooking times are listed in Table 2. Total lignin content of the pulp was determined by adding acid-soluble lignin to the ash corrected Klason lignin. For comparative purposes, the lignin contents of the pulps were recalculated based on the wood, and the percentage of delignification was also determined on the original wood basis. The trend of delignification is shown in Fig. 5. Lignin content declined sharply in the initial stages of the pulping (about

30 min) and subsequently slowed down. The lignin content calculated on wood plotted against cooking time could be approximated by two straight lines. The steeper slope is related to the rapid solubilization of the bulk lignin (bulk delignification line) and the more gentle to the slow solubilization of the residual lignin (residual delignification line).

The yield changes vs. decreasing pulp lignin are shown in Fig. 6. The trend shows a linear relationship between delignification and pulp yield.

During bulk delignification (at pulp lignin values higher than about 14% calculated on the original wood basis), the ratio of the lignin to carbohydrate losses was about 0.83:1, whereas during residual delignification at 3.6% lignin content, this ratio was 1.08:1.

Holocellulose content was determined by a modified method (108). The loss of carbohydrates is expressed as the difference between the holocellulose content of the wood and the lignin free pulp-yield, calculated on a wood basis (Table 3). Holocellulose content decreased very sharply during the initial 20 min of cooking and gradually slowed down in longer cooking (Fig. 7). It showed a similar trend to that of the delignification. Carbohydrate losses were also higher in the initial 20 min and decreased considerably at later stages of delignification (Fig. 8). As the method of analysis is only approximate, minor differences in the holocellulose content were not considered significant.

In Table 4, α-cellulose content and the loss of α-cellulose of the pulps at different cooking time are listed. Loss of α-cellulose content was calculated from α-cellulose content of the wood. The decrease in the α-cellulose content was not regular and may be due to an inaccurate analysis method.

Hemicellulose content of pulps is reported in Table 5. The relationship between hemicellulose content and cooking time is shown in the Fig. 9. There

was a sharp decrease in the hemicellulose content during the initial 20 min of cooking. When hemicelluose removal was plotted against loss of lignin from the pulps (Fig. 10), the relation revealed substantial hemicellulose removal in the initial stages of pulping, followed by stabilization in the later stages, i.e., at about 48.8% delignification, hemicellulose removal was about 51%; however, at 87.1% delignification the loss of hemicellulose was only 66%.

4.1.2 CHARACTERISTICS OF ORGANOSOLV LIGNIN

Some characteristics of the lignin fractions separated after cooking from the spent liquor in consecutive washing are tabulated in Table 6. Changes in pH value of the spent liquor at different pulping times are also included in Table 6. The observed pH values ranged from mildly acidic (4.13) to more acidic (3.58) with increase in cooking time, and indicate the limited buffering capacity of the system chosen for this study.

Total-OH and PhOH contents of the selected acetylated lignin samples are given in Table 7. Comparative data of characteristics of "Lignin A", "Lignin B", "Lignin M" and "Lignin Ac" obtained from the 20 min cook are summarized in Table 8.

A series of lignin samples were analysed using a UV spectrophotometer to examine the effect of cooking time on the phenolic hydroxyl group content. The method used in the present study is based on differential absorbance which was obtained directly by scanning the alkaline vs. the neutral lignin solutions placed in the sample and reference cells of the spectrophotometer, respectively. It is observed that the phenolic hydroxyl content increased as cooking time increased in the initial stages and subsequently remained more or less at the same level.

The values of $\overline{Mw}$ and $\overline{Mn}$ as well as the polydispersity indices obtained from the GPC analysis are presented in Table 7.

Liberation of lignin from the wood by catalysed hydrolysis at high temperature yielded lignin with changed chemical structures, even when mild reaction conditions were used. NMR analysis is one of the best techniques to examine the chemical changes in the lignin molecules caused by the various cooking conditions.

Fig. 11 demonstrates a typical NMR spectrum of the acetylated organosolv lignin with description of each region of the spectrum. Assignments of the signal regions are listed in Table 9. Figures 11 to 15 reproduce the NMR spectra of the selected acetylated lignins. From each NMR spectrum the relative intensities of various proton types were obtained and the results were computed in Table 10.

Comparision of the integral spectra of NMR in these lignin samples revealed the following features:

1. There is decrease in integral signal at 4.55–4.00 ppm range which is contributed by γ-protons in the side–chain, mostly β–O–4– structures.

2. An increasing signal is observed at 4.00–3.45 ppm range. This is contributed by methoxyl protons in aromatic nuclei.

3. The sharp peak at 3.38 ppm (signal at 3.45–3.00) decreased rapidly during cooking due to the decrease in the aliphatic methoxyl protons.

4. A significant increase of the integral signal at 2.50–2.22 ppm range indicates an increase in free phenolic hydroxyl groups from 9.61 to 12.74.

5. The peak at 2.05 ppm increased in the early cooking time and subsequently declined. This reflects the changes in the aliphatic hydroxyl content.

6. The decreasing integral hydrocarbons in the range of 1.6-0 ppm is quite remarkable.

7. All signals were sharp and indicative of the lower molecular weight of the lignin polymers.

Assignments of the absorption bands in the IR spectra are reported in Table 11. Effects of cooking time on the IR spectra of the selected reduced organosolv lignin samples are compared in Fig.16 to 20 and Table 12.

4.2 TOPOCHEMISTRY OF DELIGNIFICATION

4.2.1 STEM-EDXA STUDIES

A preliminary analysis was made for the relationship between the bromine content in the brominated pulp fibers containing varying amounts of lignin. This provided the evidence required for ascertaining the specificity of the technique, and established a direct relationship between bromine content and the amount of residual lignin. The results corroborated the findings of Saka et al. (145) in that the lignin retained in various pulp fibers exhibited the same degree of reactivity towards bromination and this factor was independent of the pulping process used. Hence, no further work was done in this regard.

From the line-scan analysis the trend in lignin removal from different morphological regions was quite evident (Figs. 21-30). Preferential lignin removal in organosolv pulping from the middle lamella region has been established.

Scanning across the cell walls through the middle lamella region in the wood fiber (Fig. 21) revealed that the relative lignin content in the S_3 layer was quite low in comparison to the adjacent S_2 layer. Initially, there was a considerable quantity of lignin present in the S_2 layer and no concentration gradient was observed across that layer. The lignin concentration was quite low in the S_1 layer. The highest concentration of lignin was observed in the middle lamella region. It is interesting to note that within the middle lamella the distribution of the lignin is not very homogeneous as evidenced in Fig. 21.

During the early delignification stage, at 21.9% delignification, more lignin per volume was removed from the middle lamella than the secondary walls (Fig. 22). In subsequent delignification at 48.8% lignin loss, the cell wall was separated from the rest of the compound middle lamella due to complete removal of lignin in one portion of the middle lamella (Fig. 23). The line-scan also showed a sharp drop of the lignin content in that area. In subsequent delignification stages, lignin removal from the middle lamella was very distinct showing relatively higher concentrations of residual lignin across the secondary walls (Figs. 24-25). Although the reduction of lignin concentration in the secondary wall during pulping is quite gradual (Figs. 21-25), detectable amounts of lignin were found after 87.1% delignification.

Scanning across the cell wall through the cell corner revealed that the cell corner contains the highest concentration of lignin in comparison to the cell walls (Fig. 26). The lignin content of the cell corner during delignification declined quite steadily but remained always at higher concentration than in the secondary walls. Even at 87.1% delignification, the lignin content in the cell corner was quite high, though such relatively high lignin content did not affect the separation (liberation) of the fibers. Secondary walls in this region (across the cell corner) in Figs. 26-30 showed the same trend as observed earlier by

scanning through cell walls across the middle lamella (Figs. 21–25).

Table 13 shows average Br–L–x–ray counts obtained by 200 s point analysis for cell corner, middle lamella, and secondary wall regions of the earlywood fibers at various stages of delignification.

A few measurements were also made on the middle lamella and secondary wall regions on both the tangential and radial walls. As there was negligible difference in lignin content between the radial and tangential walls', further analyses were done only on the radial walls. As there was no significant concentration gradient of bromine observed across the secondary wall, and the S_2 layer is the major fraction of the cell layers, the middle portion of the S_2 layer was taken as representative for that region. Thereby, the secondary wall x–ray counts were used to characterize the S_2. By using the radial secondary wall counts from the uncooked wood tracheids as a base, the ratio of the counts was calculated for various pulps (shown in parentheses, Table 13).

Based on the count ratio obtained, delignification patterns were established for the different morphological areas. In the cell corner regions, the lignin was readily removed in the early stages of delignification (40 min cook), whereas during the latter stages of delignification the lignin distribution remained fairly constant showing a slight tendency to decrease.

In the middle lamella region, however, there was a sharp drop of lignin content in the early stages of pulping and this trend continued to the later stages. The separation of fibers was very distinct at 48.8% delignification in some preparations.

In the secondary wall region, there was a gradual reduction in the lignin content, but a considerable amount of lignin remained in the fiber wall even after 87.1% delignification.

The topochemical pattern of delignification in organosolv pulping observed in this study (Fig. 21-30,43) revealed that middle lamella lignin is removed preferentially in the initial stages of delignification, followed by a slow delignification from the secondary wall regions.

4.2.2 TEM STUDIES

$KMnO_4$ has been used widely for lignin detection. In order to secure a comparative study on lignin distribution in organosolv fibers delignified to different residual lignin contents, the $KMnO_4$ staining technique was also used to allow qualitative inferences on the process. In examination of ultrathin sections by transmission electron microscope, lignin-rich zones were revealed as dark areas due to the high electron-density of $KMnO_4$ when absorbed on lignin. Thus, various layers of the cell wall can be readily detected by contrast, which varies depending on the lignin content (Fig. 31,32). The most intensely stained areas were the cell corners and the middle lamella regions. The primary wall showed intense staining in comparison to the rest of the fibers, particularly when compared to the secondary wall. The intensity in the primary wall was closer to that found for the middle lamella, hence, the practice of considering primary wall and middle lamella together as compound middle lamella is quite acceptable.

The $KMnO_4$ studies revealed that the lignin in the cell corner was removed quite substantially in the initial stages of delignification. However, even at 87.1% delignification there was still some lignin left behind in the cell corner regions (Fig. 34,41).

Looking at the middle lamella, a gradual decline in the intensity of residual lignin was evident (Fig. 35-38), which eventually resulted in gradual depletion of lignin leaving behind empty spaces (Fig. 38).

In the initial stages of pulping, the primary wall was observed to remain attached to the middle lamella and secondary walls. A gradual change in the intensity of lignin (from dark to lighter) indicated the degree of delignification in these regions. At later stages however, a split in the primary wall area could be observed which mostly separated away from the secondary wall (Fig. 39).

The innermost margin close to the lumen showed a very intense dark colour. As the lignin was removed gradually by the pulping process, the intensity of the layer decreased (Fig. 35,36).

Cell corner lignin was observed to be resistant to removal and hence, careful observations were made in this study with regards to its relative behaviour. Representative transmission electron micrographs of ultrathin cross sections of cell corner areas are shown in Figs. 38 and 42. After cooking, the non-defibrated chip samples were carefully handled to avoid any physical separation of the fibers. Thus, the structural changes observed at different stages of delignification are considered to be due only to the effect of lignin removal during pulping.

For comparative purposes, samples were also carefully brominated prior to STEM study. During TEM examination of the ultrathin sections, lignin-rich areas were revealed as dark zones because of the high electron density of bromine, thus the absorption was specific for lignin. However, the contrast was not as good as with $KMnO_4$ stain, as noted in the foregoing section.

One unique observation made by electron microscopy with respect to patterns of lignin removal during organosolv pulping indicates that during the early stages of pulping this process removes a good amount of lignin from the cell corner. Residual lignin content in this area gradually decreased up to the point when 65% of lignin in that region was removed. Subsequently, the lignin

removal from that region was slow. It was interesting to note that there was a considerable amount of lignin left in the cell corner either in association with the cell wall or remaining in the center of the corner, even at very high degree of delignification (Fig. 42). It is not considered that this residual lignin delayed fiber liberation in a significant way. Middle lamella lignin was rapidly removed during all stages of delignification and generally led to early cell separation, mainly along the interface between the primary and secondary walls. While there was also some lignin removed from the secondary wall at the initial stages of delignification, lignin loss from this morphologically important region was slow and incomplete, even when the overall lignin removal was 87.1%.

4.3 PROPERTIES OF FIBERS

4.3.1 FIBER MORPHOLOGY

Results of the Kajaani Fiber Analyser showed that the weighted average fiber lengths of the three unbeaten pulps of different yields are quite different (Table 14). The weighted average fiber length value of 3.40 mm for the 40 min pulp was reduced to 2.99 mm for the 100 min pulp. An increasing amount of fines in the lower yield pulps is evident from the population distribution of the fibers for the three different pulps (Fig. 46). On the other hand, the diameters of the fibers in these three pulps were not found to be significantly different (Table 14).

Fiber flexibilty test showed that (Table 14) high-yield (40 min cook) pulps had almost two times higher fiber stiffness (21.1 10^{-12}N.m^2) than low-yield (100 min cook) pulps (12.7 10^{-12}N.m^2). Medium-yield (60 min cook) pulp showed a medium fiber stiffness of 15.9 10^{-12}N.m^2.

4.3.2 PHYSICAL PROPERTIES

Physical properties of the handsheets, beating revolutions and freeness of these pulps are reported in the Table 15. Changes in freeness with number of revolutions during PFI beating are plotted for the three organosolv pulps of different yields in Fig. 47. It is observed that the organosolv pulp with low lignin content developed lower freeness levels more rapidly with less beating time in comparison to the pulps with higher lignin content when beaten under identical conditions (Fig. 47). When the organosolv pulp having low yield was beaten in the PFI mill to 6000 revolution, there was a sharp drop in the freeness of the pulp from 720 mL Csf in the unbeaten pulp to 280 mL Csf in the beaten pulp. For the high-yield pulp on the other hand, the same number of revolutions decreased the freeness only to 550 mL Csf from 730 mL Csf. As expected the starting freeness was somewhat higher for the high-yield pulps.

Paper density (Table 15) of the unbeaten high-yield pulp was lower (0.441 g/cm³) than the density of the low-yield pulp (0.557 g/cm³), indicating higher bulk due to the stiffer fibers. However, it was interesting to note that after the initial beating (to about 650 mL Csf), there is a sudden increase in the sheet density with all the three pulps (Fig. 48). In subsequent beating the development of sheet density depends on the type of pulp.

The initial tear strength of the high-yield pulp (tear index of 22.2 mN.m²g) was much higher than that of the medium and low-yield pulps (tear index of 15 mN.m²g, Table 15). However, when the tear index is plotted against density of the handsheets (Fig. 49), it can be observed that the tear strength is more or less the same for all three pulps when compared at the same density level.

The tensile index of the high-yield pulp is found to be much lower (43.7 N.m/kg) in comparison to the high tensile index of the low-yield pulp (76.4

N.m/kg) (Table 15). There was a drastic change of tensile index from 43.7 N.m/kg to 86 N.m/kg during the initial beating stage (630 mL Csf) of the high-yield pulps (Fig. 50). Subsequent strength development was found to increase steadily to 98.9 N.m/kg. However, the tensile index for low-yield pulp at 660 mL Csf(79.2 N.m/kg) remained quite low in comparison to its unbeaten tensile index (76.1 N.m/kg). For the low-yield pulp the tensile strength development in the subsequent beating stage was very fast. At higher beating levels (9000 revs) even medium-yield pulp developed comparable tensile strength to that of low-yield pulps.

Bursting strengths (Table 15) of high and medium-yield pulps showed almost the same trend as that observed for tensile strength. However, bursting strength of the low-yield pulp was observed to give an almost linear relationship with increase of sheet density (Fig. 51).

5. DISCUSSION

5.1 TRENDS OF DELIGNIFICATION

5.1.1 PULP PROPERTIES

The results show that cooking time is one of the important single parameters in regulating the pulping results of the catalysed organosolv pulping process. In general, longer cooking times resulted in lower fiber yield and higher recovery of precipitable lignin (Table 1,6).

In catalysed organosolv pulping, there seem to be two distinct trends observable with respect to the pulp yield and cooking time relationship (Fig. 1). In the initial stages of pulping, a sharp drop in the pulp yield was observed largely due to loss of lignin and some carbohydrates. In continued delignification (extended cooking), the yield loss was greatly moderated. Thus, the change can be directly correlated to the decrease in lignin (Fig. 5) and hemicellulose content (Fig. 9) of the pulps.

Table 16 gives comparative pulping conditions and pulp yields for kraft, soda, ethanol—soda and ethanol cooks on spruce wood chips as reported by Marton and Granzow (111). Results from cooks described herein are also included for comparison. From this table it is distinct that the Kleinert process with 50% EtOH as solvent is not suitable for softwood pulping, since the pulps retained about 90% of the lignin present in the original wood even after 150 min of cooking at 170 °C. The soda process yielded slightly more pulp in comparison to the kraft process, but delignification was slower since 50% of the original lignin was still retained at 52.5% pulp yield. Comparision of the soda and ethanol—soda pulping process showed that there was more lignin removed in the ethanol—soda process than in the soda process alone. Marton

and Granzow (111) assumed that the advantage of using the combination of alcohol and alkali acts in a distinct way on the wood lignin: The organic solvent reduces the surface tension of the cooking liquor at high temperature, thus increasing the diffusion of alkali into the chips. The same phenomenon, on the other hand increases the diffusion of the breakdown products of lignin and hemicelluloses from the wood into the cooking liquor, assuming a uniform distribution of the reagents within the wood. Simultaneously, recondensation of the lignin in the alcohol is prevented during the high temperature phase of the cook, thus resulting in a generally higher rate of delignification in the soda-ethanol cooks.

A comparison of ethanol-soda with kraft cooks shows that the soda-ethanol process is slightly slower in delignification (Table 16). However, the advantage of the ethanol-soda system is claimed to be less pollution, as it is sulfur free. Comparing pulps of kraft and catalysed organosolv processes (Table 16), it is clear that to get a pulp of about the same lignin content, kraft pulps need about 2.5 times more cooking time than the catalysed organosolv pulp. However, it is not to be ignored that organosolv pulping was done at 200 °C. At about the same lignin content, the pulp yield in the organosolv process is 6 percentage points higher than that for the kraft process. Comparing pulps at high yields, it is seen that at the same yield levels there are at least 3-5 percentage points more lignin removed in the organosolv process than in the kraft process. Therefore, it can be assumed that the higher pulp yield in organosolv process is due to the higher carbohydrate retention in the pulps.

From the results (Table 1), it is seen that the lower Kappa number for the high yield pulps might be an error, as numerous fiber bundles remain after disintegration. These could not be broken up properly before the addition of 0.1N $KMnO_4$ and hence the lower than expected Kappa number of the pulps.

Thereby, the 10 min duration of reaction might have been too short for completion of the reaction between the fiber and $KMnO_4$ and resulted in the lower consumption of 0.1N permangante.

It is interesting to note that there is no substantial drop in the Kappa number during the residual delignification stage in organosolv pulping (Fig. 3). No further attempt has been made to lower the Kappa number below 47, due to the already low viscosity of the pulps (Table 1). It was quite apparent that the buffering capacity of the solvent system was exhausted at about 30 min, and under the prevailing conditions further delignification (extension of cooking time) allowed the pH to sink to unacceptably low levels (pH 4). The high residual Kappa numbers might have been due to an imbalance of the relatively high organic solvent content and low buffering capacity of the cooking liquor. Another reason may have been the choice of the catalyst combination ($Mg(NO_3)_2$ and $CaCl_2$) used. From the previous studies (132), it is seen that $CaCl_2$ is more efficient in delignification, but leads to more excessive carbohydrate loss and degrading of cellulose, whereas $Mg(NO_3)_2$ was found to cause less degradation of cellulose, but was relatively slow in promoting delignification. For these reasons, it was assumed that through a compromise, the lignin content of the pulp could be reduced without much loss and degradation of carbohydrates. In this respect, the catalyst combination in the present study resulted in a reasonably good compromise between pulp yield, pulp viscosity and lignin content, even though the general rates of delignification observed in other systems (132) may have been higher. Generally, high temperature is considered to be detrimental to pulp yield and viscosity, due to the disproportionate increase in the carbohydate hydrolysis rates. In catalysed solvent systems (132) however, initial dissolution is restricted predominantly to lignin rather than to the degradation of the lignin-carbohydrate matrix, and

viscosity loss of the cellulose at high temperature is reduced. High temperature stability of cellulose might be due at least in part to the catalytic and protective effects afforded by the alkali earth metals buffering capacity in neutralizing, to a certain extent, both acetic and formic acids formed during the high temperature extraction process (132)

From the cooking results, it is seen that although there is a considerable protective effect to suppress carbohydrate degradation in the catalysed pulping process, extended pulping leads to a substantial decrease in the pulp quality (Table 1, Fig. 4), possibly due to exhaustion of the buffering capacity of the system.

Looking at the pH of the spent liquor (Table 6) and the relative viscosity values (Table 1), it is evident that the drop in pH of the spent liquor in the later stages of cooking is the most plausible explanation for the drop of cellulose viscosity and loss of hemicelluloses in the system used for this study. This carbohydrate degradation with the system used prevented exploration of lower lignin content pulps in this study.

5.1.2 DELIGNIFICATION

In general, softwoods are found to resist delignification more than the hardwoods by any pulping process, presumably because of differences in the structure of their respective lignins. Softwood lignin contains mainly guiaicyl units, together with minor amounts of p-hydroxy phenyl units. Linkages in softwood lignin are not as easily broken as those in hardwood lignins.

In organosolv pulping with different solvent solutions, many attempts were made to pulp softwoods (89,120,124,130,150). None of the attempts to cook softwoods were successful. Even some of the recent reports (13,105) show the difficulty and inabilty of the basic Kleinert (86) process to delignify

softwoods. However, in the present catalysed pulping process, most of the softwoods and hardwoods have been pulped properly with short cooking times (132).

Lignin content calculated on wood plotted against the cooking time (Fig. 5) in the catalysed organosolv process could be approximated with two linear trends. The initial steeper slope of the cooking time vs. lignin content of pulp is related to bulk delignification. The break in the curve is at about 34 min cooking time, at which point more than 60% of the lignin has been removed (Table 2, Fig. 5). The second slope of the curve in Fig. 5 is due to residual delignification and was found to be topochemically controlled.

The delignification of softwoods in the kraft pulping process is commonly divided into three kinetically distinguishable phases (159):

    a.   Initial delignification phase, during which approximately 23% of the original lignin is dissolved (188).

    b.   Slower bulk delignification phase, removing an additional 70% of the lignin from the wood matrix by a process which follows pseudo-first order kinetics (82,188).

    c.   Very slow residual delignification phase.

In some recent reports (95) further division in the initial delignification (ID) phases to ID_1 and ID_2 has been proposed.

As indicated above, delignification in catalysed organosolv pulping of sprucewood occured in two distinct phases, both of which could be described by first order kinetics. It is observed that delignification was considerably faster in the first phase during bulk delignification, which corroborates the previous results by Kleinert (88) and Hansen and April (65). Bulk delignification was determined to be a composite phenomenon involving the breakdown of lignin macromolecules as well as solubilization of the breakdown products

(65). The residual delignification is much slower and its mechanism may be penetration/ diffusion controlled. Matrix consideration and solvent affinity of cellulose may be far more important during delignification in the second stage. The solvent system was definitely geared for maximum lignin solubilization (high alcohol content) and minimal attack on the cellulose.

Studying the chemical nature of delignification, alcohol-water delignification is considered as a complex process involving degradation, solvation and solubilization (65). Some reaction of lignin degradation may be homolytic, as indicated by the free radical content of some lignin portions isolated from the spent liquor (65).

Assuming no major change in the composition of the solvent during cooking, degradation of lignin is primarily a function of temperature and residence time (5). Keeping the temperature constant, the change in the residence time solely regulates the lignin degradation process. However, solubilization of the degraded lignin depends upon the pore size distribution (5). Hence, factors which affect the pore size and pore distribution, such as hemicellulose removal, will also influence delignification from the cell wall. Ahlgren and Goring (2) have suggested that higher lignin removal resulted from a lower resistance to solvent penetration as the polysaccharides in the outer cell wall layers were degraded and removed in kraft pulping. This seems to hold good for the initial stages of delignification in kraft and sulfite pulping. However, in the case of residual delignification stages, where the relative pore size and pore distribution may have improved due to initial delignification and carbohydrate losses from the cell wall, the slower rate of delignification cannot be satisfactorily explained by the assumption of Ahlgren and Goring (2). It may be that the reactivity of the residual lignin in the pulp might be different, or has changed as a result of the action of the cooking liquor.

Resistance to degradation and solubilization of the lignin in the secondary wall of fibers may largely be due to differences in affinity of the cell wall to the cooking liquor and to the changes in the composition of the cooking liquor itself. New theories in extended delignification in kraft pulping by Sjoblom *et al.* (158) and by Diebold *et al.* (39) seem to recognize this problem. Thus, cooking is continued with fresh cooking liquor during the "extension" stages of the cooks. It appears however, that the problem has not been fully resolved since extended cooks are done with unoptimised liquors i.e., the same liquors as for Stage I. Changing the cooking liquor during the pulping process and studying the reactivity of the lignin toward these liquors in the residual pulp should throw some new light on the chemical limitations of residual delignification.

5.1.3 REMOVAL OF HEMICELLULOSES

In commercial chemical pulping processes, hemicellulose components are lost by reason of their solubility in delignifying agents (acids or alkali). This phenomenon assumes greater importance when it is realized that next to cellulose and lignin, the hemicelluloses constitute the third most important organic component of wood.

In earlier studies (26,27) it was found that about one third of the lignin and a large fraction (71%) of the hemicelluloses were dissolved in the first five minutes during the hydrolysis of Douglas fir sawdust by acidified organosolv cooking . In a similar organosolv pulping experiment on *Eucalyptus viminalis*, Gomide (57) also reported that about 60% of the hemicellulose and more than one third of the lignin were removed in the initial pulping stages. A similar observation is also reported for some hardwoods (116). Cho (28) found that within the first five minutes of acidified acetone cooking, about 30% of the

lignin and 21–22.5% (based on wood) of the hemicelluloses were removed. The weight loss was equivalent to about 83.5–89.5% of the total hemicellulose content of the wood. It is quite interesting to note that in the alkali earth metal salt catalysed organosolv (alcohol) pulping, a considerable amount of hemicellulose retention is found in the initial stages of pulping. At 25% and 50% delignification, the amount of hemicellulose removal was about 30% and 51% respectively (Table 2.5). It is seen from Fig. 10 that the removal of lignin and hemicellulose follow different trends, but hemicellulose removal stabilizes earlier than that of lignin.

At about 50% delignification in organosolv pulping, a maximum of 30% yield loss is observed, of which about 14% is lignin and 16% carbohydrate loss, based on the original wood (Table 2.5). For kraft pulp at 40% delignification, the yield loss was about 35%, of which 11% was lignin and 24% was carbohydrate losses (139). It has been seen that for kraft pulps, most of the carbohydrate losses are of the hemicelluloses type, during the initial stages. Dissolution of hemicelluloses takes place mainly from S_1 and neighbouring layers of P and S_2 (135).

It is believed that the substantial amounts of hemicelluloses removed from the wood in catalysed organosolv pulping are isolated in an unchanged state together with the lignin fraction from the spent liquor (28). The mild hydrolysis, which also aids the dissolution of lignin into the cooking liquor, occurs at aryl–glycosidic bonds of the lignin–saccharidic complex during the acid catalysed cooking (26).

Based on kinetic studies (5), it was observed that in an organosolv pulping process, glucomannan was the major component of hemicelluloses hydrolysed in the pulping media. Total weight loss during the initial stages of treatment is attributable to hydrolysis of hemicelluloses and loss of lignin.

During the later stages, the rate of hemicellulose hydrolysis diminishes and is thought to be controlled by loss of more resistant β-celluloses.

Kondo *et al.* (95) observed that the endwise degradation of hemicelluloses occurs in the initial delignification of kraft pulping and destroys more than 75% of the glucomannan.

It is quite likely that in the catalysed organosolv pulping, the same pattern of hemicellulose hydrolysis is followed as that observed in hydrolysis by acids, albeit at much reduced rates. The hydrolysis is observed to take place and a diminution in the degree of polymerization indicates that solubility of glucomannan results particularly from acid labile mannosidic linkages. The same specificity to mannan hydrolysis in Douglas-fir by acid catalysed hydrolysis in aqueous acetone solutions, noted by Chang and Paszner (26), seems to be supportive of this view. In kraft pulping the simpler saccharides formed further react rapidly by transformation into strong aldonic and saccharinic acids (67,121). Morever, the remaining xylan in the pulp loses its arabinofuranosidic units.

Marchessault and Ranby (109) have observed that the initial rate of carbohydrate hydrolysis was a function of the amount of modified groups, which represent "weak links" (carbonyl and carboxyl groups), which occur at random along the molecular chain of the wood cellulose. These electrophilic substituents exert an inductive effect on the glucosidic linkage A-B, as shown in next page.

As result of the inductive effect from these weak links, the 4-O-β linkage at the reducing end is activated so that it is more susceptible to hydrolysis, while the B-C linkage (reducing end) will be stabilized. The hydrolysis of xylan results in formation of aldobiuronic acid. The latter is formed (178) in accord with the stabilization effect of the

4-O-methylglucuronic acid residue on the B-C linkages.
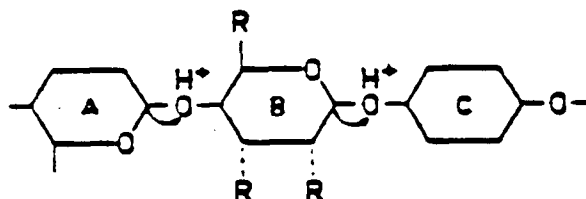
[Acidic hydrolysis of a polysaccharide initiated by functional groups (R). Linkage A-B is activated, and linkage B-C is stabilized. (61b)]

The mechanism of acid hydrolysis of an acetal bond is thought to be due to the addition of proton to the acetal oxygen. Heterolysis results in an intermediate carbonium ion, which finally reacts with water during reforming of the proton (109). This concept has since been confirmed by model compounds and tracer methods (156).

Acid hydrolysis of the glucosidic bond causes galactoglucomannan to undergo depolymerization, whereby the galactose side units are hydrolysed. The arabinose units in xylan are more easily removed than the glucuronic acid radicals.

5.1.4 FIBER LIBERATION

It has been claimed that (132) in the organosolv pulping process, fiber liberation occurs at a relatively higher lignin content and pulp yield than observable in any other chemical pulping process. This is an important advantage of the system, since it promises considerably fewer rejects in comparision to the kraft process if pulps of higher yield and Kappa number are to be prepared. The higher pulp yield is expected to contribute significantly to the better economics of the process.

In practice, mechanical agitation or defibration is required to complete separation of the individual fibers after cooking. The place of fiber separation, i.e., middle lamella, primary wall, S_1 or S_2 may vary, depending upon the degree of delignification and the pulping process used. However, fiber liberation has been seen to be affected widely by different processes and their topochemical preferences of delignification.

Fiber liberation of alkaline treated wood was found to be highly dependent on the amount of residual lignin present in the middle lamella region (80). Therefore, during the alkaline pulping a higher degree of delignification in the middle lamella region will lead to cleaner fiber separation between the double cell walls. Hence, direct measurement of the fiber separation in non-defibrated pulps was considered as an indication of the degree of delignification in the middle lamella region (143).

Considering the percentage of rejects as an indicator of fiber liberation, it was seen in this study that there was almost complete fiber separation at about 57.3% pulp yield. The Kappa number of this pulp was 72 (Table 1, Fig. 2), considerably higher than that at which fiber separation occurs in kraft pulping. The comparable kraft pulp yield at which fiber liberation occurs is about 45 to 48% (143).

Although the degree and completeness of fiber liberation increase as delignification proceeded, incomplete separation occurred at less than 25% delignification level. Fiber separation (decrease in rejects) was increased considerably at a higher degree of delignification, mostly due to removal of middle lamella lignin.

In the initial delignification stages, defibration of organosolv pulps caused fiber separation predominantly within the cell wall (Fig. 39). In most instances, both the S_1 and S_2 layers of the secondary wall became visible on

the fiber surfaces. In later delignification stages, although the S_2 layer was detected on some fibers, the majority of the exposed surfaces were the outer cell wall portions consisting of the S_1 layer or S_1 and primary (P) wall layer (Fig. 40,41), since hemicellulose dissolution is considered to be taking place mainly in these layers (135).

Therefore, it is quite likely that also in the organosolv process mechanical defibration caused fiber liberation within the cell wall regions, which were weakened by lignin and carbohydrate removal.

However, as there is a preferential removal of lignin from the middle lamella region in organosolv pulping (Fig. 43), the higher degree of delignification (70–75% lignin removal) facilitated complete separation of fibers. It has been noticed that even without mechanical agitation, cracks develop in the cell walls mostly in P and S_1 areas, due to the differential removal of hemicellulose and lignin materials.

5.1.5 CHARACTERIZATION OF ORGANOSOLV LIGNIN

It is evident that the organosolv lignin separation (recovery) from the spent liquor is very simple. The ease of getting relatively pure organosolv lignins is an added advantage for commercialization of the process.

The recovery of the small molecular weight fractions indicates that the recovered organosolv lignin undergoes a mild hydrolytic degradation or depolymerization during pulping. Hence, it seems quite unreasonable to describe these lignins as "original" lignin. However, these low molecular weight fractions underline the suitability of the organosolv pulping process for degradation of natural lignin units into low molecular weight products.

Organosolv lignin was found to be highly soluble in most of the lignin solvents. Although there was a slight increase in the methoxyl content of the

lignin with increase in cooking time (Table 10) its effect on solubility was not detectable. The concept that higher methoxyl content leads to better solubility (51) could not be verified as not much work was done in this area.

From the NMR studies, an increase in methoxyl content is observed with progress in pulping as seen from the increasing signal at 4.00–3.45 ppm range being contributed by methoxyl protons in the aromatic nuclei (Table 10). A contradictory trend has been reported by Cho (28) on lignins isolated by organosolv saccharification with acidified organosolv media. He proposed that in aqueous acetone solutions there was a decrease in methoxyl content (rather than an increase as expected) with the increase in cooking time. Especially at high acid content, the samples from acid catalysed saccharification cooks contained increasingly higher amounts of carbohydrate conversion products, due to secondary condensation between solubilized lignin and dehydrated carbohydrate fragments. This may not hold good in pulping in the presence of alkali earth metal salts, since repeated precipitation and isolation of the lignin preparation has removed all the carbohydrate fragments and no traces of carbohydrate or furfurals were noticed in the analysis of pulping lignins.

There is an alternate explanation for the variation of methoxyl content during pulping. Lignin in the wood is non–homogenous in terms of methoxyl content (134) and the lignin fractions having higher methoxyl contents may be more readily liberated (solubilized) from wood during organosolv cooking (51).

Higher content of aromatic hydroxyl groups in the present lignin sample (Table 7) can be explained by the release of phenolic hydroxyl groups, due to almost complete splitting of the alkyl–aryl ether bonds of lignin during cooking. Similar results have been reported by Cho (28).

Considering the UV results and NMR studies, it is likely that the active aromatic hydrogens rather than phenolic hydroxyl groups are involved in the

recondensation reaction of the lignins to form C-C linkages. It is significant that the increase in the hydroxyl content might be due to a cleavage of aryl-alkyl ether linkages as cooking time increases, even though some of the phenolic hydroxyl groups might have been consumed in the recondensation reaction.

Infrared spectra obtained from reduced lignin samples of different cooking times were also analysed (Table 11,12). The tests were designed to confirm the structural changes of lignin molecules which may have occurred as a result of various cooking conditions. Since a general similarity of IR spectra is evident for these samples, only the bands which varied markedly are discussed. As with many other polymers, the complexity of lignin molecules causes band overlapping and diffuse bands. Furthermore, cross linking may dampen vibrations. Nevertheless, structural changes in the lignin molecules due to differing cooking times can be observed.

There was a considerable increase of the peak in the range of 1710 cm^{-1}, which showed an increasing trend with longer cooking times (Table 12). Both unconjugated ketones and conjugated acids or esters absorb at 1715 cm^{-1}. Probably the most significant observation was that the intensities of the bands at 1270 and 1150 cm^{-1} for the uncondensed guaiacyl nucleus decreased substantially as the cooking time increased.

It was interesting to note that the weight-average molecular weight was less than 2000. A gradual decrease in the molecular weight was observed with increasing cooking time. The sharp peaks in NMR (Fig. 11 to 15) are also indicative of low molecular weight of the polymers. The polydispersity has also decreased from 3.62 to 2.31 with an increase in cooking time. This indicates a gradual cleavage of longer polymers to smaller fractions. The low polydispersity indicates that most of the lignin is available in a monodispersed

molecular form having fairly uniform molecular weight. The molecular weight and polydispersity values of the organosolv lignin, when compared to the highly polydispersed condensed aggregate molecules of kraft lignins, are very low. This low molecular weight lignin should have substantial advantage as a commercial lignin byproduct (55).

Based on the chemical nature of the isolated catalysed organosolv lignin, at least the following reaction steps can be hypothesized to take place during pulping:

a. Cleavage of β-O-4 bonds which is supported by increase in phenolic hydroxyl contents. These types of bonds are rapidly decreasing with an increase in cooking time as seen in the NMR signal at 4.55-4.00 ppm range (Table 10).

b. Protonation of α-carbon which may lead to subsequent alkoxylation due to the presence of methanol in the solvent.

According to Leary (101), benzylic hydrogen in methyl ether occurs at 5.2 ppm. He suggested that lignin p-hydroxy-benzyl alcohols may become etherified after they are laid down within the plant cell wall.

It is known from the literature (152) that under mildly acidic conditions cleavage of lignin ether bonds occurs predominantly. Such cleavage is assumed to be restricted exclusively to the α-ether bonds, but not the β-aryl-ether bonds. However, from the present study, it is assumed that along with the α-ether bonds, cleavage occurred also along the β-O-4 bonds. Hence, the previous assumption, that delignification in organosolv pulping is essentially the consequence of the hydrolysis of α-ether and lignin-hemicellulose bonds (44), may not be correct.

Ghose *et al.* (48) has proposed the following steps involved in delignification of lignocellulose with aqueous butanol.

Ionization of catalyst

$$AX \rightarrow A^+ + X^-$$

Adsorption of the catalyst on the lignin
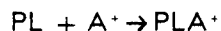
$$PL + A^+ \rightarrow PLA^+$$

Depolymerization of lignin

$$X^- + PLA^+ + ROH \rightleftharpoons DLOH + DLR + AX$$

Carbonium ion formation

$$PLA^+ \rightarrow DL^+ + DL$$

Lignin condensation

$$DL^+ \rightarrow CL$$
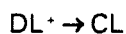
Carbonium ion stabilization

$$DL + \xrightarrow{AX} DLAX \rightarrow SL + AX$$

AX = catalyst

PL = polymer lignin

DL = degraded lignin

CL = condensed lignin

SL = stablized lignin

DL⁺ = carbonium ion

ROH = butanol

PLA⁺ = lignin catalyst complex

DLOH = degraded lignin hydroxide

DLR = acid moiety of lignin

The mechanistic concept proposed by Ghose et al. (48) for organosolv delignification does not seem to hold good as there is no or little adsorption of the catalyst to the lignin. Hence, depolymerization of lignin is not a consequence of the adsorption of the cation on lignin. In an unpublished work carried out earlier in this laboratory, no significant amounts of metal cations

were detected in the isolated lignin or pulp samples. The ash content of organosolv lignin was found to be very low (0.0004%). The subsequent steps of carbonium ion formation and stabilization through lignin condensation (48) seem also to be improbable under the prevailing pulping conditions, since little or no lignin condensation was observed even after extended cooking. From the present study, it is assumed that depolymerization of lignin in the presence of mild (neutral) alkali earth metal salts as catalysts occurs as a mild proton hydrolysis rather than through direct participation of the cation in the process. It is difficult to draw finite conclusions from this study regarding the mechanism of this process. Further study in this regard is recommended.

5.2 TOPOCHEMISTRY OF DELIGNIFICATION

5.2.1 TOPOCHEMICAL EFFECT

The principal objective of chemical pulping processes is to remove lignin from wood. Lignin removal from the middle lamella is important to facilitate separation of the fibers, whereas lignin loss from the secondary wall improves the flexibility of the fibers. Different pulping and bleaching processes show varying degrees of preferential attack of the lignin (delignification) found in the various morphological regions of the wood matrix. The topochemistry of delignification therefore, is of fundamental importance in pulping and bleaching research.

Residual lignin following delignification by organosolv pulping of the earlywood zones of spruce was made visible through the bromination and $KMnO_4$ staining. $KMnO_4$ staining and line-scan analysis were used to much advantage in this regard. The comparison of bromine distribution in the cell wall of variously delignified pulps reflects the relative concentration of

residual lignin present. Such observation gives visual evidence of patterns of lignin removal from the cell wall regions during the process of pulping.

From KMnO$_4$ staining experiments, it became evident that at 48.8% delignification, lignin was removed mostly from the cell corners and middle lamella rather than from the secondary wall. However, there was also a proportionally smaller quantity of lignin removed from the secondary wall at the same time. It is interesting to note that during the subsequent stages of pulping (77.7% delignification), middle lamella and secondary wall lignins were removed uniformly, whereas lignin concentration in the cell corners dropped slowly and remained relatively high even after prolonged cooking (87.1% delignification). This finding corroborates the results also noted for the kraft process, which showed that kraft pulp fibers contain significant quantities of lignin in the regions surrounding the cell corner along the primary wall even at the advanced stages of delignification (143). In the organosolv process, a good quantity of lignin is left behind in the central area of the cell corner. This lignin remains attached to one or the other primary wall of the neighbouring cells (Fig. 41).

Studying the line-scans (Figs. 21-30), a change in relative distribution of residual lignin in the different morphological regions of the fibers at different cooking time becomes quite evident. This technique confirmed the KMnO$_4$ staining studies. Thereby it can be qualitatively inferred that, although there was a gradual decrease in the lignin content from the secondary wall, most of the lignin was removed from the middle lamella and cell corners during initial stages of pulping. In other words, there was an apparent topochemical preference for the removal of lignin from the middle lamella and cell corners, a process which facilitates early fiber liberation by the organosolv process.

The low lignin content of the S_3 layer in comparison to S_2 was quite evident (Fig. 21) from the line-scan analysis and $KMnO_4$ staining (Figs. 31,35). Similar observations have been reported by Saka et al.(142) in Douglas-fir, but high residual lignin content was observed in the S_3 of loblolly pine (142).

The removal of lignin across the S_2 layer was found to be homogeneous, as there seems to be no concentration gradient across that layer. The low lignin content of S_1 in comparison to S_2 was also observed by Saka et al. (142). In the present study, the trend of lignin removal from the S_1 was indistinct in the later stages of pulping due to partial separation of the layer from S_2 or the compound middle lamella. The primary wall showed relatively high amounts of residual lignin.

The topochemical effect was further verified by the point scan analysis, a semi-quantitative method. Although the point analysis provides greater precision for quantitative measurement of bromine (lignin) concentration, the bromine peak to background ratio must be proportional to the unknown concentration of the bromine in the specimen for quantitative assay. The possibilty of absorption, fluoroscence and backscattering effects can disrupt this proportionality. However, it was demonstrated by Saka et al. (144) that these effects are so negligible that they can be ignored when relative comparisons are made using samples of the same thickness. Furthermore, the background radiation was essentially the same for the different morphological regions. Hence the relative ratio of bromine x-ray intensities provides background and sample concentration ratios of bromine, which is proportional to the lignin concentration in different morphological regions (139).

It has been seen in brominating cotton fibers that under the preferred condition for bromination, bromine does not react with the polysaccharides (143). An elemental analysis for bromine in brominated pulp fibers containing

varying amounts of lignin provided further evidence of its specificity and established a direct relationship between bromine content and the amount of residual lignin (143). Apparently, lignin retained in pulp fibers regardless of its position,exhibits the same reactivity towards bromination, and is independent of the pulping process used (143). Based on these observations and some preliminary work it was assumed that bromination of organosolv fibers will follow the same rules.

It was further confirmed by point analysis that a strong topochemical pattern of delignification in organosolv pulping was evident. The topochemical effect reveals the preferential removal of lignin in the middle lamella region particularly during the initial stages of pulping (at 21.9% lignin removal, Fig. 43). This effect is largely responsible for the early fiber liberation observed for this process. However, it is not to be ignored that the secondary wall is the largest morphological region, and even small differences observed in the lignin concentration in this region can mean very large differences in the total amount of lignin removed from the secondary wall.

Based on the observed count ratios it is found that at 21.9% delignification (10 min cook), the lignin removal from the cell corner, middle lamella and the secondary wall was 38%, 58% and 19%, respectively, based on the total (original) lignin content of these regions. At 48.8% delignification (20 min cook), the degree of lignin removal from the cell corners and secondary walls was about the same, however, the amount of lignin removed per volume is much higher in the cell corner than from the secondary wall. For comparison purposes, the relative bromine counts of middle lamella and the cell corners were multiplied by a factor of 1.7, due to the probable difference in reactivity of lignin between the middle lamella lignin and the secondary wall lignin (146). The relative proportion of lignin per volume for the cell corner, middle lamella

and the secondary wall was 3.69, 2.38 and 1.00 respectively. These values are in close agreement with those determined by UV microscopic methods for spruce by Fergus *et al.* (46), i.e., 3.769, 2.209 and 1.00 for the cell corner, middle lamella and secondary wall, respectively.

One interesting observation was that a portion of the cell corner lignin showed resistance to complete removal. In soda, kraft and soda/AQ pulping processes it is seen that up to 40% delignification, no qualitative changes could be observed and uniform darkening was apparent in the cell corner area. At about 50% delignification, the cell corner lignin in soda/AQ pulp was partly removed, whereas neither soda nor kraft pulp showed any visibile structural changes in the cell corner area (146). As delignification proceeded, soda/AQ pulps at 67% delignification revealed further removal of lignin from the center of the cell corner, whereas the kraft and soda processes showed no obvious changes in this region. In subsequent stages of delignification (close to fiber liberation), both kraft and soda processes removed lignin completely from the center of the cell corners although, residual lignin was still present along the primary wall in the vicinity of the cell corners. Even at a 92% delignification, as reported by Saka *et al.* (146), residual lignin in the cell corner region showed resistance to removal. On the other hand, in soda/AQ pulping no residual lignin was retained in the cell corner.

This particular aspect raises many questions. Why does residual lignin resist removal from the cell corner in kraft, soda and organosolv processes? Is there any difference in the chemical nature of the cell corner lignin to that of the middle lamella lignin? Is there a different type of bonding between the cell corner lignin and carbohydrates which makes the residual lignin difficult to remove from the cell corner? How is AQ able to release/liberate the residual cell corner lignin?

To answer these questions one has to isolate cell corner lignin from others and study the reactivity of the isolated lignin to different pulping chemicals. Reactivity and recondensation tendencies of cell corner lignins may prove to be substantially different from those of the middle lamella and secondary wall lignins.

The preferential removal of lignin from the middle lamella and cell corner in the initial stages in the organosolv process apparently contradicts the argument that the path of penetration of the solvent controls the topochemical pattern of removal of lignin, as proposed by Wardrop (185) and Wardrop and Davis (184). From these studies (184,185) on the path of penetration of the liquors into wood, they ascertained that the ray cells and vessels may govern the initial liquor flow and that the pits afforded a path of inter cell penetration. Moreover, liquor penetration into the cell wall was shown to take place by diffusion from the lumen side, whereby the direction of liquor contact was thought to be secondary wall, middle lamella and finally the cell corner areas. Wardrop and Davis (184) concluded that this scheme might also control the topochemical pattern of attack on the cell wall.

These findings were contradicted by Kerr et al. (78). When presteamed and refined coarse pulp was delignified by the kraft process and the fibers examined by ultraviolet microscopy, Kerr et al. (78) found that the middle lamella lignin on the surface of the fibers, although fully exposed to the liquor, was dissolved at the same rate as the middle lamella lignin from the interior of the fiber bundles. However, lignin was removed more rapidly from the secondary wall than from the middle lamella. Therefore, it seems that the middle lamella lignin is intrinsically more resistant to attack by kraft liquor than the cell wall lignin and its removal is controlled by location and possibly by chemical differences rather than by penetration of the liquor into the wood

chips.

Wood *et al.* (191) have also made observations with respect to the topochemical preferences of lignin removal in kraft, acid sulfite, neutral sulfite and acid clorite delignification. Their findings are presented along with organosolv delignification in Fig. 44.

Procter *et al.* (136) suggested that in kraft and acid sulfite processes, the initial selectivity of removal of lignin from the secondary wall is associated with rapid early losses of hemicelluloses, specifically glucomannan, from that region.

If the foregoing concept is valid, then the topochemical effect in pulping should be negligible for a delignification process in which all the hemicellulose is retained in the fiber wall.

Not much topochemical preference was observed (136) in the removal of lignin by the neutral sulfite process up to 50% delignification. In acid chlorite pulping there was an absence of a topochemical effect (191) and acidified sodium chlorite was found to be a highly selective reagent for delignification, particularly up to 70% lignin removal.

From the present findings on organosolv delignification in Fig. 44, it can be observed that organosolv delignification is very much different from the trends found in kraft, acid sulfite, neutral sulfite and acid chlorite pulping. There is a sequential change in the trends of delignification from the slow delignification in kraft process, acid sulfite and neutral sulfite; to no topochemical preference in the acid chlorite and finally to the rapid delignification from the middle lamella in the organosolv process. Thus, the topochemical preference for removal of lignin from the middle lamella by the different pulping processes can be arranged in the following order:

Catalysed organosolv > acid chlorite > neutral sulfite > acid sulfite >kraft

Wood *et al.* (191) and Goring (59) also observed the topochemical preference for early lignin removal from the secondary wall in different pulping processes. The decreasing order of delignification for these processes was found to be as follows:

Kraft > acid sulfite >neutral sulfite > acid chlorite

As seen in Fig. 44, the removal of secondary wall lignin in the organosolv pulp was the same or close to that found for the acid sulfite process in the early stages of delignification but slightly slower in the residual delignification stage. Hence, the order of preference for early delignification from secondary wall can be written as follows:

Kraft >acid sulfite, catalysed organosolv > neutral sulfite > acid chlorite

There is evidence, however, that in catalysed organosolv pulping, the rate of lignin removal from the secondary wall can be brought to the same level as observed in the middle lamella by simply manipulating the pulping parameters during organosolv cooking. Such manipulations will lead to very low residual lignin content pulps (132), thereby removing the topochemical preference observed for this process in the present study. Such a general delignification trend is certainly preferred and desirable in a commercial pulping process.

Comparing carbohydrate losses in kraft, acid sulfite and neutral sulfite processes, Wood *et al.* (191) observed that the topochemical preference for dissolution of lignin from the secondary wall is correlated with the quantity of hemicellulose removed early in the cook. They observed that the quantity of dissolved carbohydrates at the time when 33% of the lignin was removed by the kraft, acid sulfite and neutral sulfite processes was 16%, 13% and 6% respectively of the wood weight. Considering a carbohydrate loss of about 13% at 33% delignification for the organosolv process, this would indicate that the

pattern of lignin removal from the secondary wall in the organosolv process should follow that observed for the acid sulfite process. From Fig. 44, it is confirmed that lignin removal from the secondary wall by the organosolv process follows the same trend as that observed in acid sulfite pulping, at least in the initial delignification stages. However, lignin removal from the secondary wall is much slower by the organosolv process during the residual delignification stages in comparison to those maintained in the acid sulfite process. This latter phenomenon might be due to the effect of slower carbohydrate loss in the organosolv process during residual delignification.

Wood *et al.* (192) suggested that any hemicellulose protecting pulping process will tend to be slow because retention of hemicelluloses in the fiber makes it necessary to break down the lignin network into smaller fragments before the macromolecules can diffuse through the fiber wall. In order to speed up the delignification process and at the same time to retain more hemicellulose, it will be necessary to seek out new chemical reagents which are both protective of hemicellulose (31) and at the same time rapid in degrading the lignin into fragments small enough to filter through the pores in the cell wall. Organosolv delignification seems to meet most of these requirements.

In this regard, it could be expected that AQ addition to soda and kraft processes for greater stabilization of carbohydrates should have switched the topochemical preference of delignification completely from the secondary walls to the middle lamella lignin. As a result of such changes, no enhancement of the delignification rate should have occurred, if the lignin is not degraded into small molecular fractions. But that is not the case (Fig. 45).

Addition of AQ and Na$_2$S (kraft) to soda liquor results in an earlier transition from a slow initial to a rapid bulk delignification phase (particularly

in the middle lamella) and is responsible for the enhanced bulk delignification in the secondary wall. Anthraquinone was also found to promote residual delignification in the secondary wall where sodium sulphide was not effective. The great differences observed in the bulk delignification rates between the middle lamella and secondary wall in soda pulping as well as their response to additives, suggest structural differences or different chemical associations within the middle lamella and secondary wall lignins.

When organosolv delignification is compared to soda, kraft and soda-AQ pulping (Fig. 45), it is evident that much of the lignin is removed already from the cell corner and middle lamella regions in the organosolv process during the bulk delignification stage. However, the rate of lignin removal from the secondary wall was always higher in the other processes. This can be partly ascribed to the higher hemicellulose retention in the secondary wall of fibers pulped by the organosolv process. This indicates that maximum delignification potentials of the organosolv process were not realized under the conditions selected for this study.

On studying the relationship between hemicellulose removal and delignification by the organosolv process, it is apparent that delignification was also somewhat dependent and closely associated with removal of hemicelluloses. However, it is maintained that it is not the major mechanism which regulates the topochemical pattern in delignification by this process. The real controlling mechanism of delignification by organosolv may be closely tied to solvent-solute interactions in aqueous alcohols specific to lignin, while hemicellulose removal can be closely controlled by limiting the pH. It has been noted earlier that pH control was inadequate under the conditions chosen for this study. Hence, the confounding effect of hemicellulose hydrolysis (loss) was observed. Differences in chemical nature of the lignins in different

morphological regions is not thought to enter topochemical considerations at this time.

5.2.2 VARIABILITY OF LIGNIN IN DIFFERENT MORPHOLOGICAL REGIONS

Considerable differences assumed to exist in lignin structure and reactivity between different parts of wood cells would suggest that different forces control the assembly of the structure of lignins during the lignification process.

Most of the present evidence for the morphological variations in the structure of lignins in softwoods is open to question, since it is based on differences found in the properties of isolated lignins whose morphological origin could not be controlled or clearly defined. Isolated lignins are always a mixture of lignins from different morphological parts of cell walls. However, in a recent study, Yang and Goring (194), using direct UV microscopic analysis of thin wood sections, concluded that the secondary wall lignin of spruce fibers contains about twice the concentration of free phenolic hydroxyl groups as that of the middle lamella. This result presumes among other assumptions, that the observed differences are not the result of an uneven distribution of the conjugated carbonyl groups or other lignin chromophores (194) in the secondary wall lignin. Reasons for differences in reactivity are not definitely known but some speculations have been advanced (59).

It is seen (59) that the proportion of phenolic hydroxyl content is quite small, being about 0.12 PhOH/C_9 for the secondary wall and only 0.06 PhOH/C_9 for the middle lamella lignin. These units account for only 12% of the total aromatic groups in the lignin. Thus, they are quite unlikely to be the cause of the considerable difference in reactivity. In these studies, accessibility was not considered to be the problem either (59).

Perhaps the largest contributor to the reactivity difference could be the variation in methoxyl content of the middle lamella and the secondary wall lignin (59). It was found (146) that there are about 1.7 times as many methoxyl groups in the lignin of the secondary wall than in lignin originating from the middle lamella. The presence of a large proportion of the para-hydroxyphenyl groups (about 40%) in the middle lamella lignin thus could lead to a higher probability of formation of carbon-carbon bonds at the 3 and 5 positions of the aromatic ring. Such carbon-carbon bonds are resistant to chemical attack during the lignin degradation process and are expected to be responsible for the different physical properties observed in the middle lamella lignin. How such chemical variability should affect topochemical preferences by various pulping processes is not completely clear, though some speculations have been advanced on the experimental evidence to date (59).

There seem to be two factors involved in the dissolution of the lignin from the middle lamella and secondary wall of wood. First, as established above, there are inherent chemical differences in the lignin of the middle lamella and secondary wall. These differences might cause the middle lamella lignin to be less reactive in kraft pulping than the secondary wall lignin and more reactive to conditions of organosolv pulping. Second, dissolution of hemicelluloses from the secondary wall during pulping increases the size of the pores in the wall and thereby allows the secondary wall lignin to be removed more quickly (77). Thus, in a process such as kraft in which the hemicellulose is rapidly removed by the alkali solution, the reactive secondary wall lignin is dissolved more rapidly than the unreactive middle lamella lignin. However, when the hemicellulose is retained, as in the chlorite and organosolv pulping, the lignin is locked in the secondary wall and seems to dissolve slowly. Thus, there are both physical and chemical factors involved in

topochemical behaviour and the observed topochemistry is the result of an interplay of these factors.

Goring (59) has rightly suggested that eventually it might be possible to find ways of treating wood chemically so that the middle lamella dissolves more rapidly than the secondary wall lignin. Such behaviour could lead to methods of chemical defibration of wood as yet unexplored.

Whatever physical and chemical factors may be responsible for the topochemical preference observable in organosolv pulping, it follows the expectations of an ideal pulping process as proposed by Goring (59). The topochemistry which removes middle lamella lignin more rapidly than the secondary wall lignin is certainly responsible for early fiber liberation. This process results in more than 6-10 percentage points higher pulp yield than possible by the conventional kraft and soda processes. With some refinement and closer optimization, the process therefore, clearly qualifies as the pulping process of the future.

5.3 PROPERTIES OF FIBERS

5.3.1 PROPERTIES OF HIGH-YIELD PULPS

From an economic point of view, the yield of pulp is of great importance. As the number of fibers remains the same at different pulp yields from the same process and the same wood furnish, the yield gain merely indicates more lignin and hemicellulose retention in the fibers of high yield pulps. However, it is quite obvious that the structure of paper is influenced greatly by the number of fibers in a given basis weight paper. This characteristic is quite evident when organosolv pulps of different yields are compared for their tearing strength.

Comparison of pulps cooked to the same yield by two different pulping processes is difficult since the topochemistry of the process significantly affects the cell wall structure of the fibers. Generally, at lower pulp yield the middle lamella is completely dissolved in chemical pulping; thus the fiber surface consists of the primary wall and some exposed S_1 layer. At high yields however, the middle lamella is incompletely dissolved and therefore, lignin partly covers the fiber surface of semichemical pulps after defibration. It seems likely that such surface materials influence the bonding properties of the fibers. Because of the characteristic chemical reactions associated with the pulping process, swelling and bonding properties of fibers are greatly altered. This makes it difficult to predict the influence of such effects on the structure of paper.

For high-yield organosolv pulps, the most important consequence of the high yield is that considerable residual material is left in the fiber secondary wall and on the fiber surface. This condition leads to stiffer fibers giving hand sheets of lower density. Fiber stiffness is also considered to be affected by the solvent composition during delignification, since the solvent used in catalysed organosolv pulping is of at least partial dehydrating strength (78%).

An increase in pulp yield will not only produce fibers with more material on the surface, but it will also produce stiffer fibers with a lesser ability to form contacts with other fibers. This contrasts with the behaviour of low-yield pulps. Internal fibrillation, which is of utmost importance for the swelling and flexibility of the fibers, is also decreased by higher pulp yield. Lack of internal fibrillation in fibers also decreases their ability to conform (flatten) with each other during sheet consolidation. It can be assumed that the importance of the external fibrillation relative to the internal fibrillation is

increased as the yield of the pulp increases.

Andrew and Nicholls (4) observed that fibers in handsheets made from two pulps beaten for the same time are noticeably more fibrillated in the case of the lower Kappa number pulp. Easily fibrillated pulps would also be associated with faster fragmentation and generation of fines which would have a significant influence on the specific surface area for bonding. The number of fibers and the lignin content also affect the specific surface area of the paper.

5.3.2 BEATING BEHAVIOUR: NUMBER OF REVOLUTIONS AND CSF

In general, fibers of high-yield pulps were observed to be more brittle (79) and more easily damaged during defibration and beating than those of lower yield.

Sulfite pulps are more easily beaten, and have been found to be in many respects more sensitive to the beating conditions than kraft pulp fibers, as sulfite pulps are known to suffer from random hydrolysis damage during the acid cooks (137). Thus, the sensitivity of the organosolv pulps to mechanical degradation might be related to the dehydrating conditions with the alcohol solution (78%) or to similar structural modification of the cell walls, as observed with the sulfite pulps. In light of the high viscosity values in Table 1 hydrolysis damage may not be applicable to organosolv pulps in the initial stages of pulping.

The ability of the fibers to undergo changes as a result of high-frequency mechanical treatment (beating) depends partly upon the flexibility, i.e., ability to avoid hits. But the physical damage caused to the fibers during beating becomes more important to the further progress of beating than to the increase in flexibility of the fibers. It is reasonable to assume that in order to develop internal fibrillation of the organosolv fibers

with the least possible development of fines and fiber cutting, the beating energy has to be administered to the pulp in the form of a high number of low intensity energy impulses instead of lower frequency hard impacts (128,129) as also suggested by Levlin (102). Possibly a milder beating action, whereby fiber cutting could be avoided, may lead to better strength development of the fibers (129). Further, it was also found necessary to swell organosolv fibers in alkali (3%) before beating (129). This increases their resistance to fiber damage and breakage. However, no such treatment was included in this study in order to avoid the confounding effects of alkali swelling on the basic properties of the fibers. Hence, the fiber properties were not developed to their maximum potential in this study.

For these reasons, defibration conditions chosen for the present study in the beater were very mild. The number of impacts to fiber was minimized by lowering the stock consistency to 10 per cent and by lowering the beater arm load.

The changes in freeness with number of beating revolutions in the PFI beater for the three pulps of different yields can be observed in Table 15. It is seen that the high-yield pulp needed a higher number of revolutions to beat it to the same freeness level in comparison to the low-yield pulp. As high lignin containing pulps are stiff (Table 14), the higher energy requirements (larger number of revolution) for high-yield pulps can be explained by higher stiffness of the fibers of the high-yield pulp.

The beating behaviour of organosolv pulps as seen earlier (129) indicates that the number revolutions required in beating the organosolv pulp to a required level of freeness is much less than that of kraft pulps. High-yield organosolv pulps thus behave in the same way as observed for high-yield bisulfite pulps (79). This can occur by way of rapid fibrillation of the fibers, or

a sharp decrease in the fiber length of the pulp already during the initial stages of beating. It has been found earlier (15,129) that the sharp decrease in the freeness of the organosolv pulp in the early stages of beating was primarily due to the rapid decrease in fiber length, production of fines and collapse of the organosolv fibers. Assuming that the fiber wall and fiber diameter of the pulps of different yields were initially the same, a decrease in the fiber length will lead to a decrease in the bulk of the wet web. The fines will also generally impede the passage of water through the wet web, as observed by Dinwoodie (41). The higher collapsibilty of the fiber on beating, as seen for the organosolv pulps in comparison to kraft pulp (129), results in higher density of the organosolv paper sheet and restricts the passage of water through the wet web ie., decreases the pulp freeness.

5.3.3 DENSITY OF PAPER

In the present study, density of test sheets was used a basis for plotting the development of the strength properties (Figs. 49-51), instead of freeness, as per the suggestions of Clark (29). Such an approach appears to have many advantages. The basic reference in such a system is transferred from a drainage parameter (which is poorly understood, and influenced to a larger extent by a very small fraction of the total fiber furnish), to a paper property (which is primarily controlled by the most fundamental characteristics of the papermaking fibers, their conformability).

The change in the density of the paper at different pulp yields (Table 15, Fig. 48) is very pronounced in the unbeaten pulp. The changes in sheet density can be directly correlated to the pulp yield, fiber length (Fig. 46) and the extent of fiber collapse. Fiber collapse becomes more extensive with decrease in pulp yield. Fiber collapse in handsheets can be estimated quantitatively using

handsheet bulk values (79).

In beating of the three different organosolv pulps (Table 15, Fig. 48), it is observed that density is more gradually developed with low-yield pulps than the high-yield pulps. The rapid change in sheet density during initial stages of beating can be attributed to the rapid fibrillation of the fibers and to the sharp decrease in the fiber length of unswelled organosolv pulps as observed in the earlier studies in Fig. 52d (129). In comparing the pulps at the same freeness level following extensive beating, it was noticed that low-yield pulps invariably produced higher density papers than high-yield pulps. The stiffness of fibers although reduced during beating, persists throughout the beating process. With high-yield pulp, both stiffness and poor bonding contribute to a low density paper.

A high degree of fiber conformability was observed to give rise to sheets of higher density. On the other hand, a decrease in fiber length at constant diameter will also increase the density of the sheet by proportionally decreasing the number of fiber-crossings in the sheets. Fiber classification and results of electronmicrographs (Fig. 53) in an earlier study (129) clearly indicated that organosolv pulps were prone to breakage when beaten in a PFI mill under full load whereby, beating caused a considerable reduction in the average fiber length. Fibrillar connections between fibers outside of the projected area of fiber crossings were also observed earlier (Fig. 52d) to increase with beating (129). The contribution of fibrillation to the strength of paper was difficult to estimate from SEM pictures alone but it seemed reasonable to assume that its contribution was significant. This was true particularly for the highly beaten sheets. The effectiveness of a given amount of fibrillation is almost certainly dependent on the flexibility and collapsibility of the fibers in the sense that closeness of approach of fibers to one another

permits fibrils of shorter length to bridge gaps between fibers, thereby strengthening the bond.

It can be predicted that if pulping or other treatments influence those properties of the fibers which affect the density of the sheet, their effect can also be seen in many other important properties of the paper.

5.3.4 TEAR STRENGTH

The initial tear strength of the high-yield organosolv pulp was higher than that of the low-yield pulp as tear strength is especially dependent on the stiffness of the fibers. There is a drastic change in the tear strength in all the three pulps during the initial stages of beating (Table 15). By comparison at the same beating level, it is seen that high-yield pulps produced sheets which had invariably higher tear strength. This may be related to the fiber stiffness of the high-yield pulp fibers, as caused by the higher residual lignin and hemicellulose contents of the fibers. However, this statement is in direct contradiction to that of Giertz (50). According to him, tear is not directly influenced by the lignin content of the fibers, but is more, in a complex way, a result of the paper formation.

The tearing strength of organosolv pulps is generally found to be lower in comparison to that of kraft pulps (Table 16). One of the reasons for the low tear in the beaten and unbeaten pulps might be the rapid breakage (brittleness) of fibers at the tearing surfaces as observed earlier (129). This confirms the theory of tear failure proposed by Van den Akker in 1944 (181) in that any decrease in the number of fiber pullouts will result in a lowering of the tear strength, as the frictional drag per fiber is very much greater than the work to rupture the fiber. Conversely, tear resistance of papers reflects the number of fibers which are pulled out without breakage. The frictional drag of long fibers

is higher, and hence the higher tear strength.

Fiber bonding is also an important factor in controlling fiber pullout. Increase in rigidity of fibers will result in a decrease in fiber bonding and hence will affect the tear strength of paper. The higher fiber bonding observed with beaten organosolv fibers may be a further cause of the low tear strength.

It is reported (79) that as a result of internal swelling, lumen diameters of kraft fibers are relatively smaller than those of fibers from other processes. This is thought to increase the fiber strength. The apparent shrinkage (shortening the fiber length) caused by alkali in kraft pulping is explained by tightening of the fibrillar spiral in the fiber walls (73) which increases fiber rigidity. It has been observed earlier (129) that swelling in weak (3%) alkali decreased the lumen diameter (swelling) of the organosolv pulp. The tightening of the fibrillar spiral by alkali treatment had selectively improved the tear strength of the paper produced therefrom to almost that obtained for kraft papers made from the same chip furnish. The same treatment, however, had no measurable effect on the tensile strength of the paper.

5.3.5 TENSILE AND BURSTING STRENGTH

The initial tensile strength is always lower in the unbeaten high-yield pulps (Table 15). This can be ascribed to the higher fiber flexibilty and better bonding characteristics of the low-yield pulp.

During the initial stages of beating, a sudden change in the tensile strength is observed (Table 15) which can be directly related to the changes in the density of the sheet (Fig. 50). However, a steady increase in sheet density and tensile strength was observed with increase of beating in the low-yield pulp. At higher beating levels, the tensile strength did not significantly vary between the 60 min and 100 min pulps.

When the medium-yield organosolv pulp is compared at about 300 mL Csf with kraft, soda, soda-ethanol and ethanol pulping (Table 16), it is seen that the organosolv pulp shows better tensile properties than either the ethanol, soda-ethanol or soda pulps but had slightly lower strength values in comparison to the kraft pulp.

Under similar testing and sheet forming conditions, tensile strength of the unbeaten organosolv pulp was found to be somewhat higher than that observed for kraft pulp (129). This might be due to the better conformity of the unbeaten organosolv fibers in sheet formation (Fig. 52). However, the lower tensile strength development of the organosolv pulps on beating as compared to that of the kraft fibers might be due to a variety of factors, one of which might be the rapidly decreasing average fiber length of the unswollen organosolv fiber. Fiber length is an important parameter (30,39), since as a rule the breaking length of the long-fibered pulp surpasses that measured for short-fibered pulp even at higher beating levels (14). The effect of fiber length on breaking length has been described (47) as affecting the ability of the fibers to dissipate stress, whereby the longer the fiber (up to a certain critical level), the greater the area over which the stress can be distributed.

Graham (60) found that fiber strength was frequently the limiting factor, although interfiber bonding determines to a certain extent the tensile strength of strong paper. Even though there may be good fibrillation and apparently better bonding with organosolv pulps, it is obvious that the increase in degree of bonding did not compensate for the progressive weakening of the fiber wall during beating. Damage by the beater along the fiber surface increases the frequency of the weak areas at which stress concentration can lead to fiber failure on stressing. Thus the apparent fiber strength of organosolv pulps proves to be lower than that otherwise indicated by the high viscosity (>40

mPas) and zerospan tensile strength (129).

The lower bursting strength in the organosolv pulp can be explained in the same way as that of the tensile strength. Bursting strength is dependent on the same combination of factors, i.e., fiber length, fiber strength and bonding of fibers which affect both tensile and tear strength albeit, in a different manner.

5.3.6 LIGNIN CONTENT AND STRENGTH PROPERTIES

The purpose of pulping is to separate lignin from the fibers so that fiber can be used for papermaking. As discussed earlier, high lignin content organosolv pulps showed relatively higher stiffness (Table 14) in comparison to low lignin content pulp. Stiffness of the fiber plays quite a significant role in development of paper properties. Keeping in mind that lignin in the plant gives the woody tissue its stiffness, there is nothing remarkable in the fact that partially delignified fibers are still stiff and that lignin-rich fibers remain stiff even during beating. They are thus difficult to beat to high strength, as the lignin prevents the hemicellulose material from swelling and being plasticized.

Lignin may also affect the bonding properties of paper. Giertz (50) has mentioned that the presence of lignin will prevent mobility of the hemicellulose molecules and consequently will reduce the bonding capacity of hemicelluloses. Hemicellulose molecules on the surface of the fibers and fibrils function as an adhesive. The tensile index and burst index of unbeaten low-lignin organosolv pulp was always higher than that of the high lignin content pulp (Table 15). This can be explained by the topochemistry of the fibers in that the bonding of fibers was considerably higher for the low-yield pulp than the high-yield pulp, due to the absence of substantial amounts of lignin on the surface of the low-yield organosolv fibers, as seen earlier in Fig.

52b (129). This also justifies the low initial tensile strength values observed with the kraft pulp. This pulp shows considerable amount of residual lignin left on the fiber surface as seen in Fig. 52a (129)

However, the rapid change in the tensile and bursting strength of high-yield organosolv pulp on beating (Table 15) might be due to the effect of higher lignin retention in the secondary walls (Fig. 43). It is quite likely that due to the presence of higher residual lignin in the secondary wall of the fibers, the fibers are easily damaged (even by the milder conditions of beating as selected for this study) on defibration and beating. It is quite possible that due to the presence of the high lignin content in the secondary wall, the stiffer fibers of organosolv pulps might have been split to a number of larger fibrillar units rather than fine fibrils.

The sequential strength development in the low-yield pulp might be due to a gradual fibrillation of the fibers because of the lower lignin content in the secondary wall. However, strength development for these pulps was quite comparable to kraft pulps. With the kraft pulp, it was observed that during the process of beating, degradation of primary wall occurs whereby the stiff outer coating of lignin-rich primary wall is removed. Therefore, the fibers become more flexible in the subsequent stages of beating. Fibrillation and plasticization of the secondary wall of the organosolv pulp steadily increases as more lignin is selectively removed from the secondary wall (Fig. 43).

As mentioned above, comparing the initial tear values of the three organosolv pulps, it becomes evident that the high-yield pulp had much higher tear strength than the low-yield pulps. The initial tear value of organosolv pulp is quite comparable to that of the equivalent kraft pulp. Hence, it may be assumed that high lignin content of the secondary wall in organosolv pulps acts as reinforcement to the cellulose matrix and increases resistance to

rupture of the fibers. However, due to low plasticization by water and brittle behaviour of the non-swollen pulps during beating, the tear strength of organosolv pulps could not be retained as well as possible with the kraft pulp.

5.3.7 HEMICELLULOSE CONTENT AND STRENGTH PROPERTIES

There is no doubt today that hemicelluloses play an important role in paper making. The interfibrillar hemicellulose material is supposed to affect beating, as it imbibes water and acts as an internal lubricant making the fiber wall flexible. Furthermore, the swelling pressure contributes to the loosening of the structure and aids in fibrillation on beating. Here again, the amount of available hemicelluloses to carry out these functions must be of importance and generally, if delignified sufficiently, hemicellulose-rich high-yield pulps should be easily beaten. The important question, however, is to what extent is the amount of hemicelluloses responsible for the properties of paper.

Based on the theory that the hemicellulose materials act as the adhesive between the fibers in paper (50), it is tempting to postulate that the greater the amount, the stronger the paper. Against this, however, it can be argued that only a certain amount of surface adhesive is needed to form the bonds and that further amounts of hemicelluloses, particularly if located inside the fiber, are of less or no importance. It should be remembered, too, that, in all experiments in which the amount of hemicelluloses was varied, other properties of the fiber were also affected at the same time, making it very difficult or impossible to draw definite conclusions.

Another question also arises in that not all the hemicelluloses are retained in the pulp after beating. Reports on dissolution of carbohydrates during beating of kraft pulps (103) show that considerable amounts of carbohydrates go into solution at the time of beating. In most of the present

work, carbohydrate estimation for the organosolv pulps was done before beating. Hence it is difficult to assign any hemicellulose losses as result of beating.

Spiegelberg (160) has noted that removal of hemicelluloses reduced the breaking stress, modulus of elasticity, yield point stress and work-to-rupture of the fibers. It was observed that the effect of hemicellulose content on fiber strength is to allow more internal redistribution of stresses to occur when the fiber is subjected to an external load. Removal of hemicelluloses results in replacement of the relatively flexible cellulose-hemicellulose-cellulose bond by the more rigid cellulose-cellulose bond (hydrogen bond), thus inhibiting the stress redistribution. This resulted in lower strength properties. However, these observations were merely highlighting the expected result on further removal of hemicelluloses from already deficient in hemicellulose kraft pulps.

It is quite likely that although organosolv pulps contain higher amounts of hemicelluloses, the weakening of the fiber strength during beating could not be counterbalanced by the higher amounts of residual hemicelluloses. Their effect may have been particularly lost if their location was inside the fiber cell wall.

Unless further experimentation in selectively removing hemicelluloses from different pulps of varied yield is carried out, it will be difficult to determine the effect of hemicellulose content on the strength properties and to estimate the optimum hemicellulose requirement for better strength development of organosolv pulps. An equalization or removal of lignin can be done by selective bleaching, but it is more difficult to get pulps at three different yields with the same viscosity and hemicellulose content. Further work in this area is recommended.

6. CONCLUSIONS

The catalysed organosolv pulping process is different from the traditional chemical pulping processes in many respects. The present study explores some of the fundamental physical and chemical characteristics of the process in order to cast new light on some unique phenomena like fiber liberation at high pulp yield and topochemistry of delignification. These factors affect significantly the basic strength properties of papers made from these fibers. The following conclusions can be drawn from the present study:

1. In catalysed organosolv pulping, softwoods can be pulped with ease to a high pulp yield (60%). These pulps also have a remarkably high viscosity (51 mPas) of cellulose.

2. Two distinct trends in pulping are observed with respect to the cooking time and pulp yield. Thus, fiber liberation is due to a uniquely high delignification specificity of the solvent, whereby 75% of the lignin can be removed. Thereby, an initial sharp drop in pulp yield (to 60%) is observed largely due to loss of lignin and some carbohydrates. However, on extended delignification, the pulp viscosity and the ratio of lignin to carbohydrate removed decrease probably due to inadequate persistence of the buffering capacity of the system chosen for this study. Subsequently, on continued delignification (below 56% pulp yield), the yield loss was greatly moderated, as more lignin and less hemicellulose is removed.

3. In this process, complete fiber liberation occurs at a relatively high yield of 57.3% and at Kappa number of 72. This yield is about 10 to 12 percentage points higher than possible by the kraft process. The early fiber liberation can be accounted for by preferential removal of lignin from the middle lamella region and in part by the separation of the outer cell walls (primary wall-S_1). Wall separation is considered to be largely due to the weakening effect of removal

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of lignin and limited amount of carbohydrates.

4. In catalysed organosolv pulping, delignification takes place in two distinct stages. Both stages can be described by first order kinetics. Delignification is considerably faster in the bulk delignification stage (up to about 60% pulp yield and 90 Kappa number). This high rate may be due to rapid breakdown of lignin macromolecules and facile solubilization of the breakdown products in aqueous methanol. The residual delignification stage (less than 8.5% residual lignin in the fibers) is much slower. The mechanism of delignification in the second stage may be penetration/diffusion controlled in the particular system chosen for this study.

5. The pulping liquor used for this study is so designed as to represent a compromise in the rate of delignification and hydrolysis. The latter is effectively supressed by limiting the amount of water and acidity of the system used. Thus, by manipulation of the liquor composition, substantial quantities of hemicellulose can be retained in organosolv pulps following pulping. In this study, the ratio of lignin to hemicellulose loss was about 1.06:1 at 48.8% delignification. At 87.1% delignification, the ratio was increased to 1.47:1. This reveals some sort of hemicellulose stabilization in the later stages of pulping during catalysed organosolv pulping in spite of the fact that the pH of the cooking liquor dropped below the critical pH (4.0) considered to be safe for this process. On the other hand, slow hemicellulose removal may have been responsible for the slow residual delignification in the secondary wall region.

6. Through conventional $KMnO_4$ staining, line-scan and point analyses by the STEM-EDXA techniques, it became evident that in the initial stages of pulping, lignin removal was mostly from the cell corner and middle lamella rather than the secondary wall. Lignin from the cell corner was removed quite substantially in the initial stages of delignification. However, even at 87.1%

delignification, considerable amount of lignin still remained in the cell corner attached to one or the other cells. From the middle lamella region of adjacent cells, lignin was steadily removed, and at 87.1% delignification no or little residual lignin could be observed in this region.

7. In the secondary wall, lignin removal was relatively slow and substantial lignin remained in the pulp even after extended delignification. Thus, there is strong evidence for a topochemical effect on delignification within the middle lamella region which makes this process unique among all the chemical pulping processes, since preferential lignin loss from the middle lamella is considered to be one of the prerequisites of high yield chemical pulping.

8. The topochemical preference for removal of lignin from the middle lamella by the different chemical pulping processes can be arranged in the following order:

Catalysed organosolv > acid chlorite > neutral sulfite > acid sulfite > kraft

The order of preference for delignification from secondary wall on the other hand assumes the following order:

Kraft >acid sulfite, catalysed organosolv > neutral sulfite > acid chlorite

9. Lignin removal from the secondary wall was slower by the organosolv process in the residual delignification stage in comparison to that maintained in the acid sulfite and kraft proceses. This latter phenomenon might be due to such effects as limited pulping accessibility and slow carbohydrate loss during residual delignification in the organosolv system chosen for this study.

10. The high percentage of residual lignin present in the cell corner even after

87.1% delignification raises many questions about the chemical nature of cell corner lignin. These comparisons become particularly relevant when the soda-anthraquinone system is considered, where all the cell corner lignin is removed due to addition of anthraquinone in soda pulping.

11. With high-yield organosolv pulp, the considerable amount of residual lignin material retained in the fiber secondary wall and on fiber surfaces led to stiffer fibers. Unbeaten handsheets of high-yield organosolv pulps had low density, high tear and average burst and tensile strength properties. On beating in a PFI mill high-yield organosolv fibers showed a low tendency of internal fibrillation, and limited ability to conform with each other during sheet formation.

12. At low-yields (49.8%), however, organosolv fibers became highly flexible and resulted in high density papers having high tensile and burst strength but somewhat lower tear strength than found with the kraft pulps. Low-yield pulp fibers show extensive fibrillation and good bonding properties on beating.

13. In this study, the comparative physical strength properties of organosolv papers were lower than those obtained with kraft papers of the same basis weight. However, it is remarkable to note that the strength properties are comparable with kraft even at 20 to 30% fewer fibers in organosolv papers. When the strength of organosolv papers is compared on the basis of equal number of fibers per unit volume, strength values equal or better than those of kraft sheets are found. This observation illustrates well the tremendous potential of organosolv pulps for papermaking.

14. It is evident from this study that recovery of the organosolv lignin from pulping liquors is by simple solvent evaporation and precipitation. With increasing cooking time, an increase in the total hydroxyl, particularly phenolic hydroxyl content and a decrease in the weight average molecular weight ($\overline{M}w$)

of the isolated lignin was observed. The molecular weight of the lignin ranged from 2400 to 1400 for corresponding pulp yields of 86.4 and 49.8%. At the same time, the polydispersity decreased from 3.17 to 1.95 as the cooking time increased. This indicates an overall slow secondary reduction in molecular weight of dissolved lignin on extended cooking. Due to its purity and its non-condensed nature, the low molecular weight lignin from organosolv pulping is deemed to have substantial commercial potential as a chemical by-product in the future.

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Table 1.   Pulp characteristics of a catalysed organosolv pulping series.

Cooking time min	Pulp yield wood basis $\% \pm$ SD	Rejects wood basis $\% \pm$ SD	Kappa No. pulp basis $\% \pm$ SD	Viscosity m Pa s $\% \pm$ SD
10	86.4 ± 1.1	79.2 ± 0.64	116 ± 0.6	N.D.
20	70.4 ± 0.4	57.6 ± 0.12	110 ± 2.2	N.D.
30	63.9 ± 0.4	14.2 ± 0.11	95 ± 1.9	55.9 ± 0.6
40	59.8 ± 0.7	4.1 ± 0.07	84 ± 0.6	51.1 ± 0.5
50	57.3 ± 0.2	1.2 ± 0.08	72 ± 2.3	45.0 ± 0.2
60	55.7 ± 0.5	1.2 ± 0.07	64 ± 0.5	37.6 ± 0.3
70	53.5 ± 0.5	1.0 ± 0.03	60 ± 0.4	30.5 ± 0.4
80	52.5 ± 0.2	1.0 ± 0.01	58 ± 0.8	26.8 ± 0.2
90	51.0 ± 0.1	0.8 ± 0.01	50 ± 0.6	20.2 ± 0.3
100	49.8 ± 0.2	0.8 ± 0.01	47 ± 1.1	16.4 ± 0.2

Table 2.   Delignification in a catalysed organosolv pulping series.

Cooking time	Pulp yield	Lignin, pulp basis			Lignin, wood basis	
		Klason lignin	Acid soluble lignin	Total lignin	Total lignin	Deligni fication
min	%	% ± SD	%	%	%	%
0	100	27.9 ± 0.3	0.27	28.2	28.2	0
10	86.4	25.2 ± 0.3	0.24	25.4	21.9	21.9
20	70.4	20.2 ± 0.2	0.24	20.4	14.4	48.8
30	63.9	17.5 ± 0.5	0.23	17.7	11.3	59.9
40	59.8	13.9 ± 0.2	0.25	14.2	8.5	70.0
50	57.3	12.0 ± 0.4	0.24	12.2	7.0	75.2
60	55.7	11.1 ± 0.3	0.25	11.3	6.3	77.7
70	53.5	8.9 ± 0.1	0.25	9.1	4.9	82.6
80	52.5	8.3 ± 0.2	0.24	8.5	4.5	84.0
90	51.0	7.4 ± 0.3	0.25	7.7	3.9	86.1
100	49.8	7.1 ± 0.2	0.24	7.3	3.6	87.1

Table 3.   Holocellulose content and loss of carbohydrates of pulps as a result of different organosolv cooking time.

Cooking time min	Pulp yield %	Holocellulose pulp basis %±SD	Holocellulose wood basis %	Carbohydrate loss wood basis %
0	100	69.0±0.3	69.0	0
10	86.4	68.8±0.7	59.4	9.6
20	70.4	74.5±0.3	52.4	16.6
30	63.9	79.8±0.2	51.0	18.0
40	59.8	84.5±0.3	50.5	18.5
50	57.3	90.0±0.4	51.6	17.4
60	55.7	87.2±0.4	48.6	20.4
70	53.5	89.4±0.6	47.8	21.2
80	52.5	91.3±0.2	47.9	21.1
90	51.0	93.0±0.3	47.4	21.6
100	49.8	93.0±0.3	46.2	22.8

Table 4.   α–cellulose content and loss of α–cellulose of pulps of different organosolv cooking time.

Cooking time min	Pulp yield %	α–cellulose pulp basis % ± SD	α–cellulose wood basis %	α–cellulose loss wood basis %
0	100	43.7 ± 0.6	43.7	0
10	86.4	48.1 ± 0.6	41.6	2.1
20	70.4	56.9 ± 0.3	40.0	3.7
30	63.9	61.1 ± 0.8	39.0	4.7
40	59.8	67.2 ± 1.6	40.2	3.5
50	57.3	72.4 ± 1.2	41.5	2.2
60	55.7	70.3 ± 0.5	39.3	4.4
70	53.5	73.1 ± 1.1	39.1	4.6
80	52.5	72.9 ± 1.0	38.3	5.4
90	51.0	75.9 ± 0.6	38.7	5.0
100	49.8	75.7 ± 1.3	37.6	6.1

Table 5.   Hemicellulose content and loss of hemicelluloses of pulps of different organosolv cooking time.

Cooking time min	Pulp yield %	Hemicellulose pulp basis %	Hemicellulose wood basis %	Hemicellulose loss wood basis %
0	100	25.3	25.3	0
10	86.4	20.7	17.9	7.4
20	70.4	17.6	12.4	12.9
30	63.9	18.8	12.0	13.3
40	59.8	17.3	10.4	14.9
50	57.3	17.6	10.1	15.2
60	55.7	16.9	9.4	15.9
70	53.5	16.3	8.7	16.6
80	52.5	18.3	9.6	15.7
90	51.0	17.1	8.7	16.6
100	49.8	17.3	8.6	16.7

Table 6.   Percentage of lignin recovered from the cooking liquors after different period of cooking.

Cooking time min	pH of the spent liquor	Lignin A	Lignin B	Lignin M	Lignin Ac	Total lignin %
10	4.13	8.29	0.21	8.13	5.65	22.28
20	4.07	20.93	2.02	12.10	10.12	45.17
30	4.01	25.24	4.47	18.04	9.10	56.85
40	3.93	23.68	7.53	18.02	11.48	60.71
50	3.84	33.67	7.49	13.67	14.12	68.95
60	3.70	33.20	8.56	16.00	14.01	71.77
70	3.70	32.11	10.64	15.79	14.88	73.42
80	3.63	36.05	13.08	14.29	15.21	78.63
90	3.65	34.25	12.05	15.80	15.39	77.49
100	3.58	30.79	15.57	23.52	14.89	84.77

Table 7. . Characteristics of "Lignin A" recovered from cooking liquor after different periods of cooking.

Cooking time min	Total OH content %	Phenolic OH content %	$\overline{M}n$	$\overline{M}w$	$\overline{M}z$	$\overline{M}w/\overline{M}n$
10	8.16	0.72	694	2203	4721	3.17
20	9.30	1.36	755	2395	5240	3.17
30	9.90	1.76	900	2330	4578	2.59
40	10.80	1.72	720	1620	3002	2.25
50	7.90	1.83	909	1957	3357	2.15
60	9.30	1.87	808	1741	2992	2.15
70	9.00	1.79	628	1539	2673	2.43
80	10.30	1.65	704	1640	2600	2.33
90	10.30	1.94	728	1638	2693	2.25
100	12.90	1.81	787	1433	2366	1.95

Table 8. Comparative characteristics of different lignin fractions recovered after 20 min of pulping.

Lignin type	Lignin recovered[1] %	Total OH content %	Phenolic OH content %	$\overline{M}n$	$\overline{M}w$	$\overline{M}z$	$\overline{M}w/\overline{M}n$
A	20.93	9.3	1.36	755	2395	5240	3.17
B	2.02	19.5	0.42	1729	4996	8396	2.89
M	12.10	9.77	1.85	519	1304	2417	2.51
Ac	10.12	12.20	1.35	1282	4273	7186	2.12

[1] = based on orginal present in wood.

Table 9.   Assignment of signals in NMR spectrum of acetylated organosolv
             lignin samples.

Range symbol	Range δ-value (ppm)	Chemical shift δ-value (ppm)	Assignment (type of proton)
A	8.00–7.20	7.29	Solvent $CDCl_3$
B	7.20–6.15	6.96	Aromatic and α-vinylic
C	6.15–4.55	5.40	β-vinylic side chain protons
D	4.55–4.00	4.40	γ-protons in side chain (β–O–4 linkage and β–5 linkage)
E	4.00–3.45	3.83	Methoxyl protons in aromatic nuclei
F	3.45–3.00	3.40	α-protons and protons attached to aliphatic methoxyl group (β-protons β–β linkage)
G	3.00–2.50	2.60	do
H	2.50–2.22	2.32	protons in aromatic acetates
I	2.22–1.60	2.05	protons in aliphatic acetates
J	1.60–0.00	1.29	hydrocarbon protons

Table 10.   Relative intensity of various proton types in NMR spectra of acetylated lignin samples (%).

Symbol of range	δ−value (ppm)	20 min lignin	30 min lignin	50 min lignin	70 min lignin	90 min lignin
A	8.00−7.20	3.85	4.27	3.30	3.53	4.46
B	7.20−6.15	16.67	16.46	17.03	17.06	16.56
C	6.15−4.55	5.77	4.29	6.60	6.47	7.00
D	4.55−4.00	9.61	7.92	7.14	7.65	7.64
E	4.00−3.45	21.15	21.34	21.98	21.76	22.29
F	3.45−3.00	7.05	6.71	6.59	6.47	5.73
G	3.00−2.50	3.85	3.05	3.85	4.12	5.09
H	2.50−2.22	9.61	10.37	11.54	12.35	12.74
I	2.22−1.60	16.03	17.68	16.48	15.29	14.66
J	1.60−0.00	7.05	6.71	5.50	5.29	3.82

Table 11.   Assignments of infra red absorption bands of lignin samples.

Position cm^{-1}	Band origin
3450–3400	OH stretching
2940–2820	OH stretching in methyl and methylene groups
1715–1710	C=O stretching nonconjugated to the aromatic ring
1675–1660	C=O stretching in conjugation to the aromatic ring
1605–1600	Aromatic ring vibrations
1515–1505	Aromatic ring vibrations
1470–1460	C–H deformations (asymmetric)
1430–1425	Aromatic ring vibrations
1370–1365	C=H deformations (symmetric)
1330–1325	Condensed guaiacyl (?)
1275–1270	Guaiacyl ring breathing
1240–1170	C–O of acetyl group
1150–1100	Uncondensed guaiacyl
1090–1085	Aliphatic ethers, secondary alcohols, aldehyde groups
1085–1030	C–H, C–O deformations

Table 12.　　　Relative intensity of some infra red bands of lignin samples.

Wave number cm^{-1}	20 min lignin	30 min lignin	50 min lignin	70 min lignin	90 min lignin
1710	42	36	44	58	50
1660	42	36	42	46	42
1605	82	78	85	100	91
1510	100	100	100	100	100
1460	50	48	46	49	53
1420	32	34	38	32	36
1355	8	8	6	5	4
1330	4	4	4	5	
1270	50	48	43	42	38
1210	40	40	40	39	45
1150	34	30	29	30	32
1090	14	11	10	9	6
1030	48	40	52	60	60

Table 13. Effect of delignification on residual Br-L x-ray counts in different morphological regions of organosolv fibers.

Sample	Deligni-fication	Cell corner		Middle lamella		Secondary wall	
min	%	counts/s	%	counts/s	%	counts/s	%
0	0	44.5(2.18)	100	28.9(1.42)	100.0	20.4(1.00)	100.0
10	21.9	27.7(1.36)	62.3	12.2(0.60)	42.2	16.6(0.81)	81.4
20	48.8	23.7(1.16)	53.3	11.5(0.56)	39.8	10.2(0.50)	50.0
40	70.0	15.5(0.76)	34.8	8.8(0.43)	30.4	7.7(0.38)	37.4
60	77.7	14.7(0.72)	33.0	6.1(0.30)	21.1	7.3(0.36)	35.7
100	87.1	13.1(0.64)	29.4	2.5(0.12)	8.6	4.8(0.24)	23.5

Note: Relative values are indicated in parenthesis, using the radial secondary wall counts in uncooked wood as a base. Percentage is calculated based on the uncooked fiber.

Table 14. Weighted average fiber length, fiber diameter and fiber stiffness of organosolv pulps of three different yield levels and lignin content.

Pulp sample m	Pulp yield %	Lignin content %	Fibre length mm	Fiber diameter mm	Stiffness $10^{-12}N.m^2$
40	59.8	8.5	3.40	0.046	21.1
60	55.7	6.3	3.32	0.047	15.9
100	49.8	3.6	2.99	0.046	12.7

Table 15.   PFI beating behaviour and strength properties of paper prepared of 40, 60 and 100 min Organosolv pulps.

Sample	Revolu -tions	Csf mL	Density g/cm^3	Burst index kPa.m^2/g	Tear index mN.m^2/g	Tensile index N.m/kg
	0	730	0.441	2.45	22.2	43.7
40	4000	630	0.674	6.03	10.4	86.0
min	6000	550	0.691	6.39	10.2	94.4
pulp	8000	460	0.699	7.09	9.6	96.9
	10000	330	0.719	7.47	9.3	98.9
	0	720	0.510	3.02	14.9	63.3
60	3000	610	0.703	5.86	9.7	84.4
min	5000	520	0.704	6.38	9.6	91.3
pulp	7000	440	0.751	6.87	9.1	94.0
	.9000	270	0.773	7.59	8.2	107.7
	0	720	0.557	4.04	14.5	76.1
100	1500	660	0.683	5.44	10.3	79.2
min	3000	560	0.719	5.94	9.8	86.1
pulp	4500	440	0.754	6.50	9.4	94.9
	6000	280	0.836	7.57	7.8	105.2

Table 16. Comparision of strength properties of papers of kraft, soda, soda–ethanol, ethanol and medium–yield catalysed organosolv pulp of spruce beaten to about 300 mL Csf.

	Kraft[1]	Soda[1]	Soda–EtOH[1]	Ethanol[1]	COP
Chemicals	18% A.A. 25% S	20% NaOH	20% NaOH 50% EtOH	50% EtOH	78% MeOH Catalyst
Temperature °C	170	170	170	170	200
Cooking time h	2.5	2.5	2.5	2.5	1
Pulp yield %	47.7	52.5	47.4	77.61	55.7
Lignin content %	4.9	14.0	6.6	23.6	6.3
Density g/cm^3	0.730	0.680	0.709	0.549	0.626
Burst index kPa.m^2/g	9.70	6.68	8.20	2.60	7.60
Tensile index N.m/g	115.3	87.0	103.7	44.0	107.7
Tear index mN.m^2/g	11.3	10.9	9.6	8.7	8.2

Note: [1] From Marton and Granzow (111)
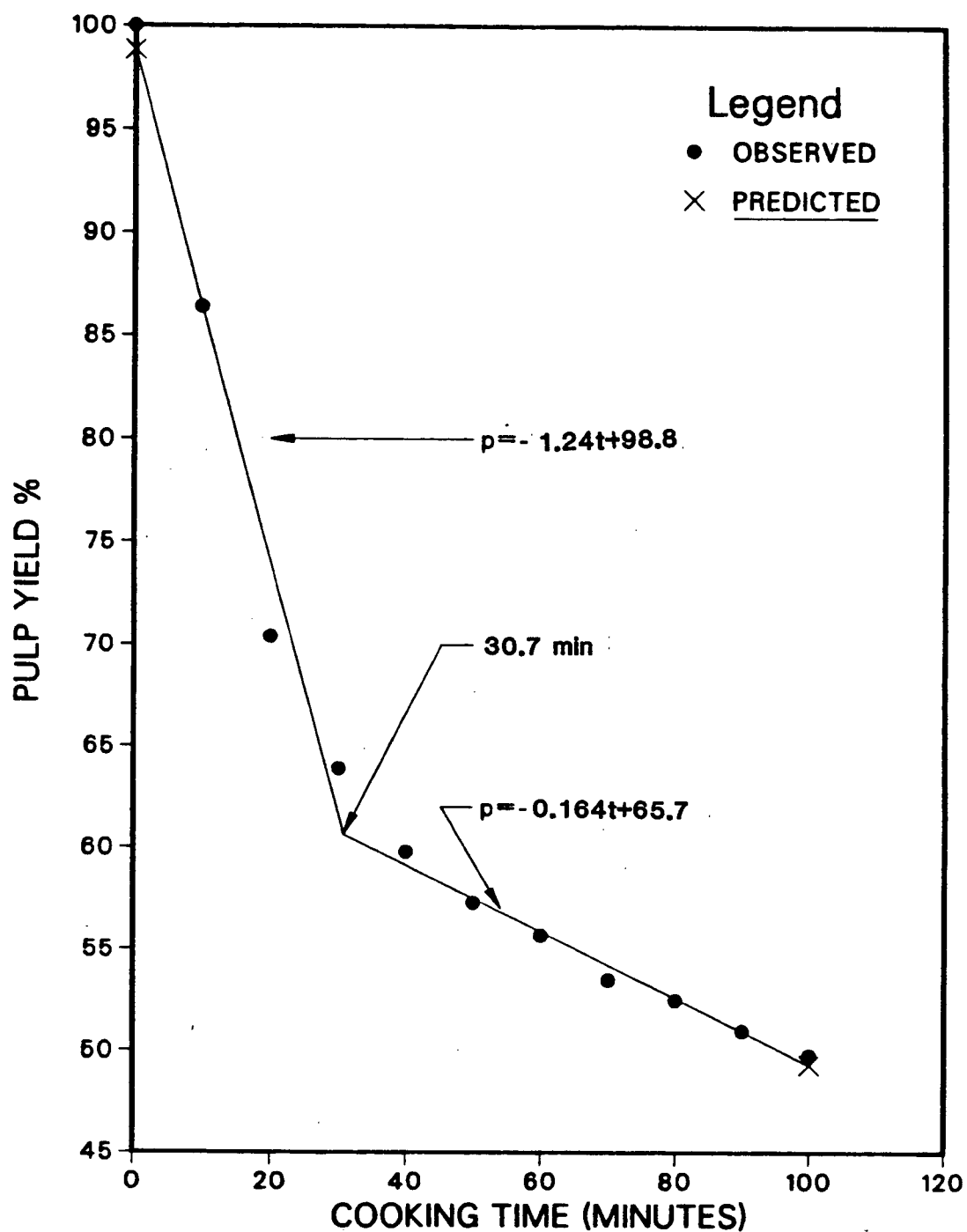
Fig. 1   The effect of cooking time on percentage of pulp yield.
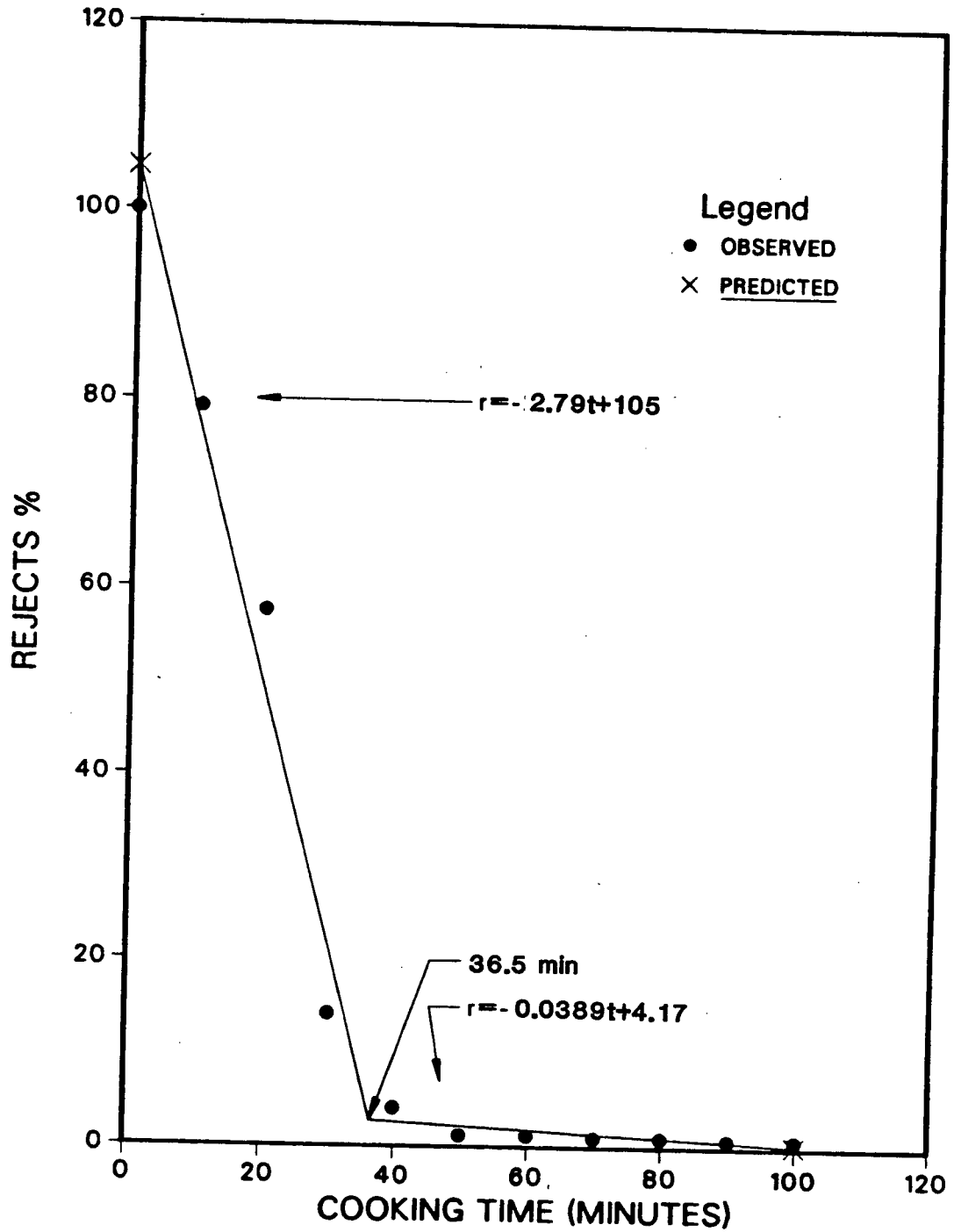
Fig. 2   The effect of cooking time on percentage of rejects in pulps.
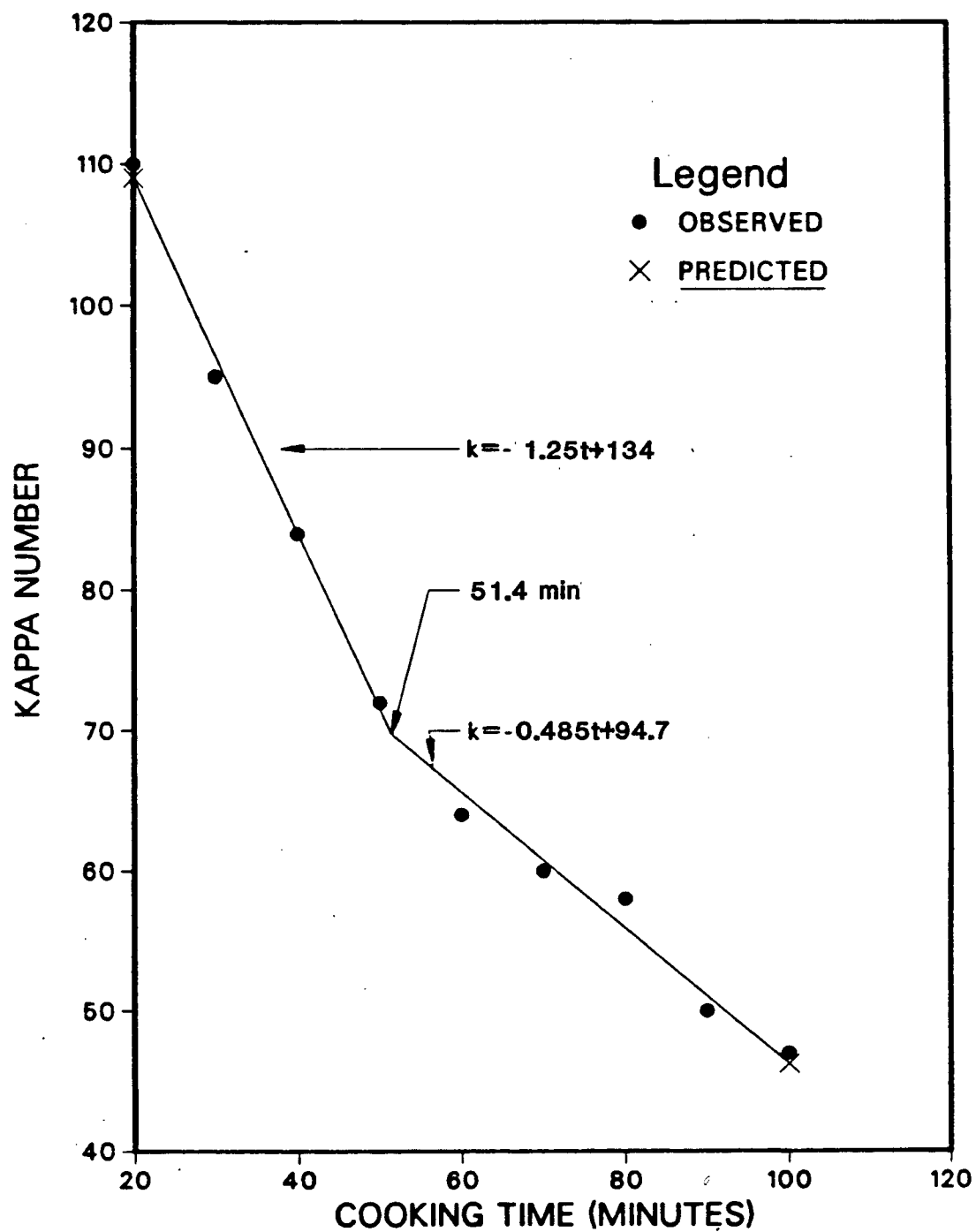
Fig. 3   The effect of cooking time on Kappa number of pulps.
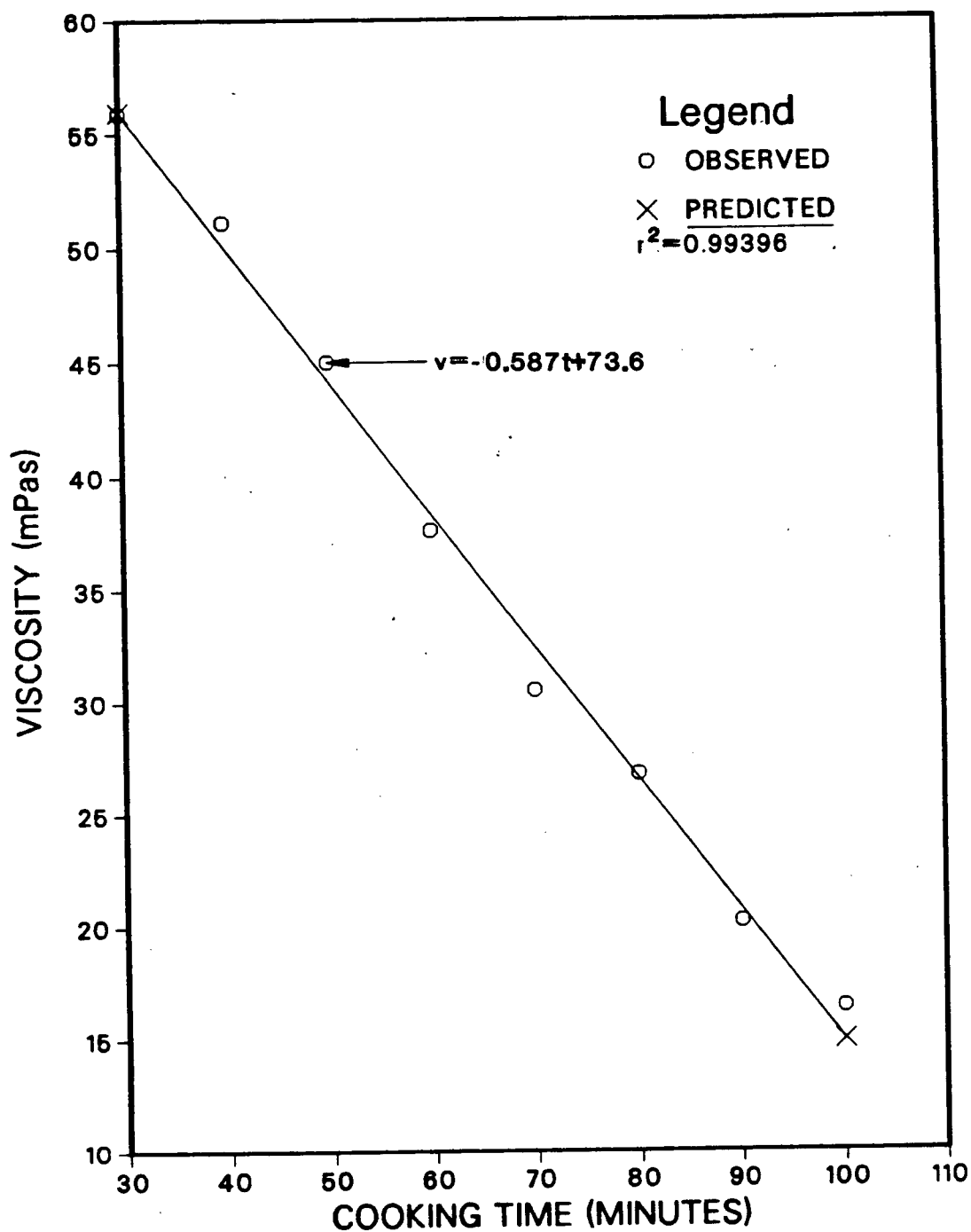
Fig. 4   The effect of cooking time on viscosity of pulps.
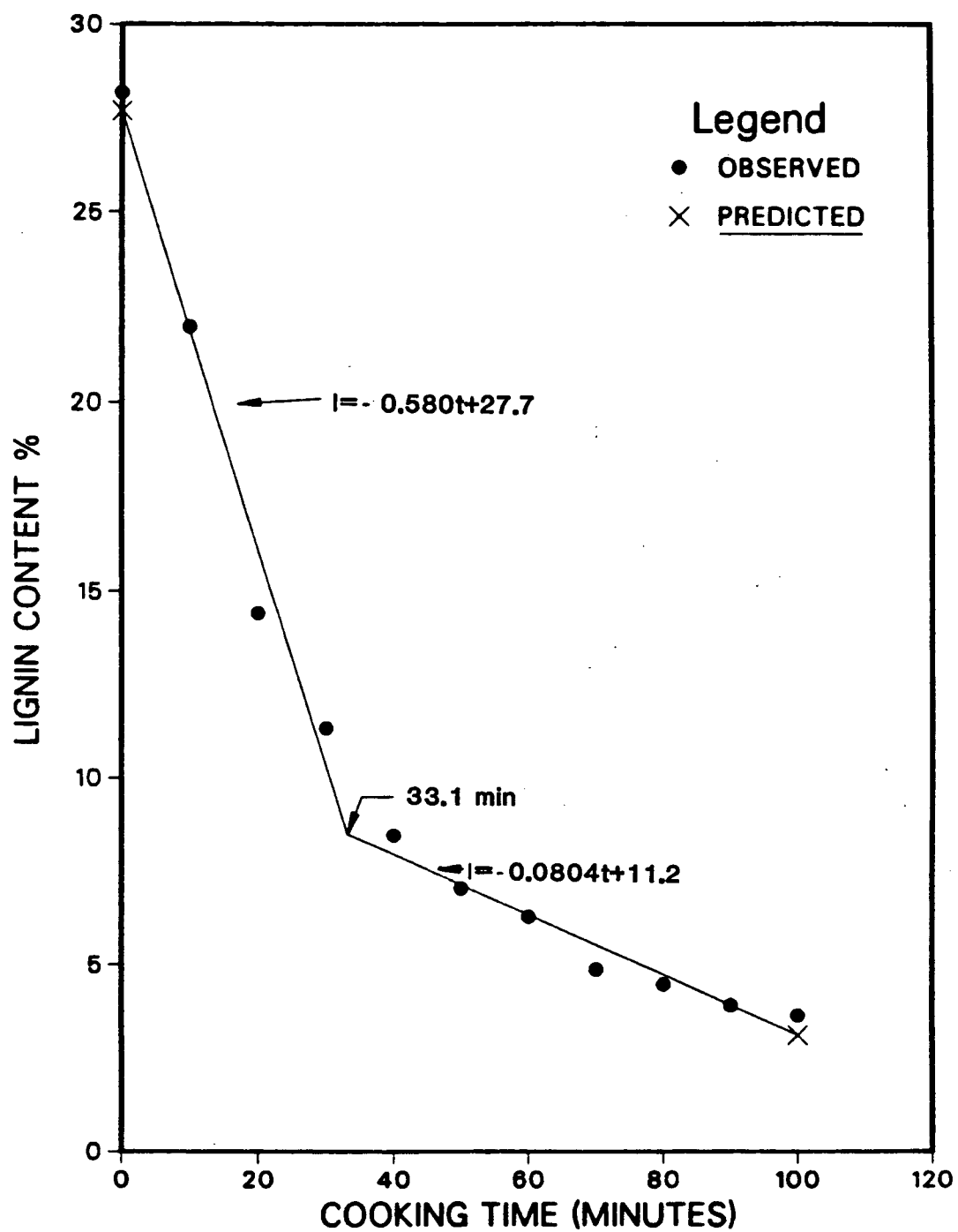
Fig. 5   The effect of cooking time on percentage lignin content of pulps (wood basis).
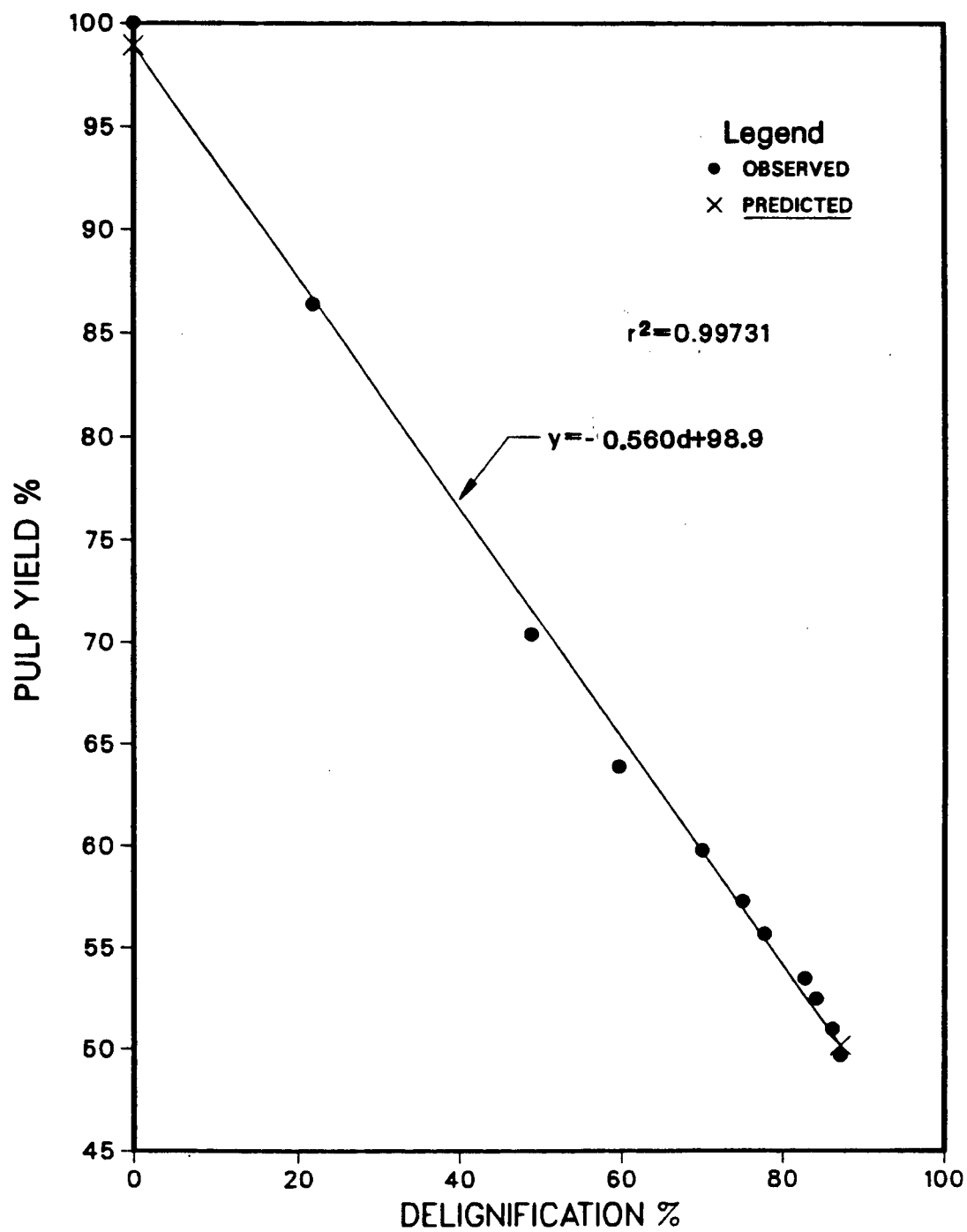
Fig. 6   Relationship of percentage of delignification vs. percentage of pulp yield.
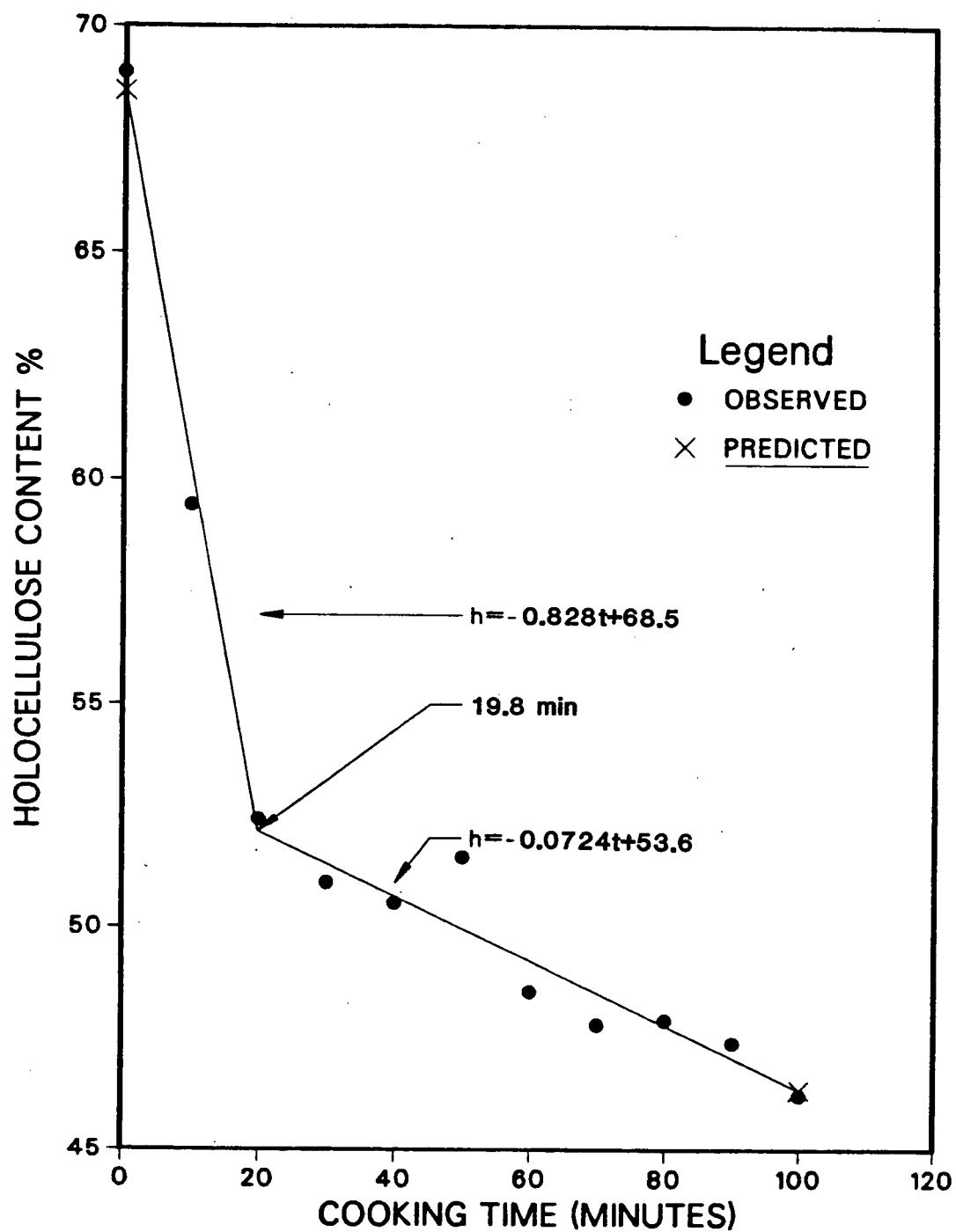
Fig. 7   The effect of cooking time on percentage of holocellulose
           content of pulps (wood basis).
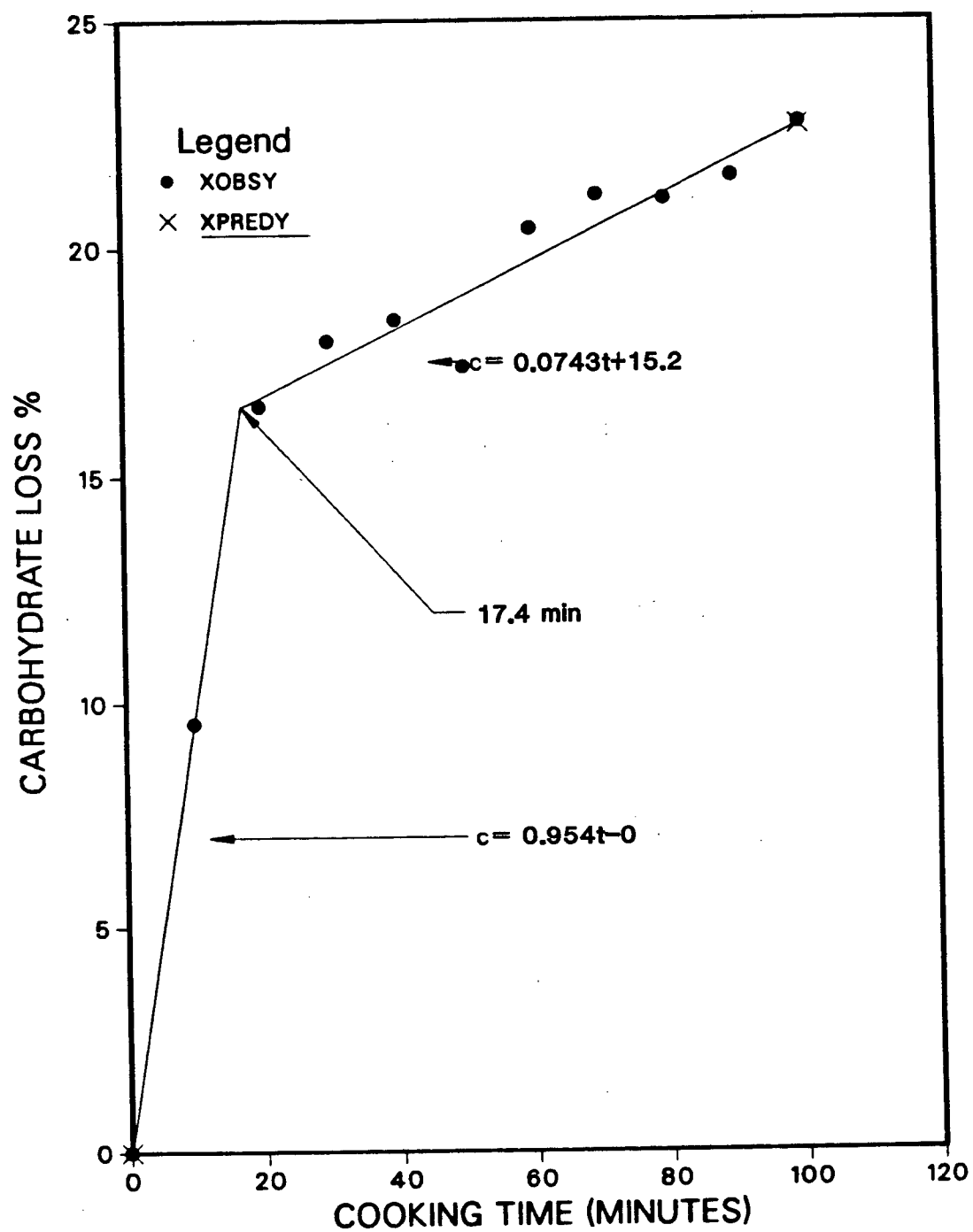
Fig. 8   The effect of cooking time on percent carbohydrate loss of pulps (wood basis).
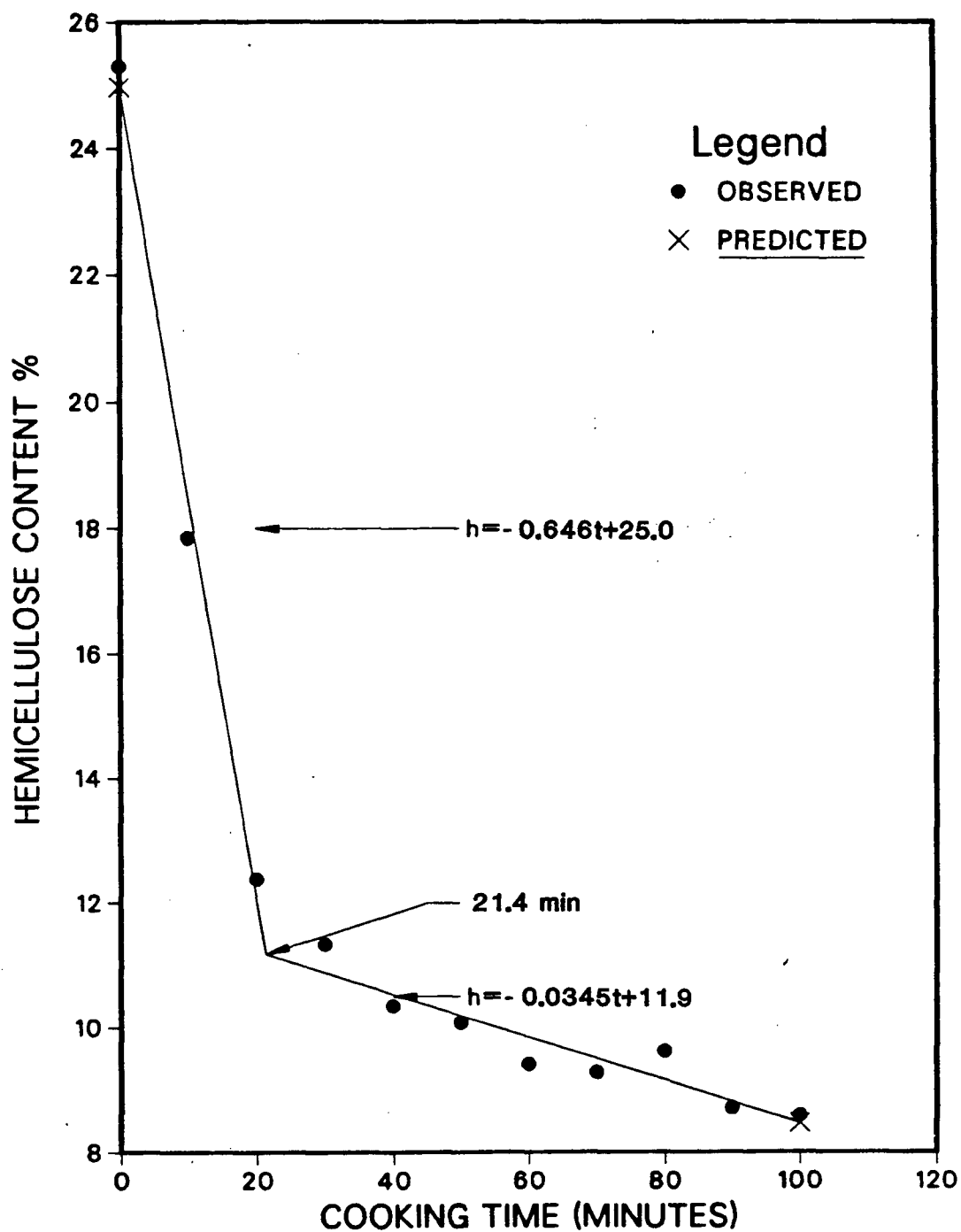
Fig. 9   The effect of cooking time on percentage of hemicellulose content of pulps (wood basis).
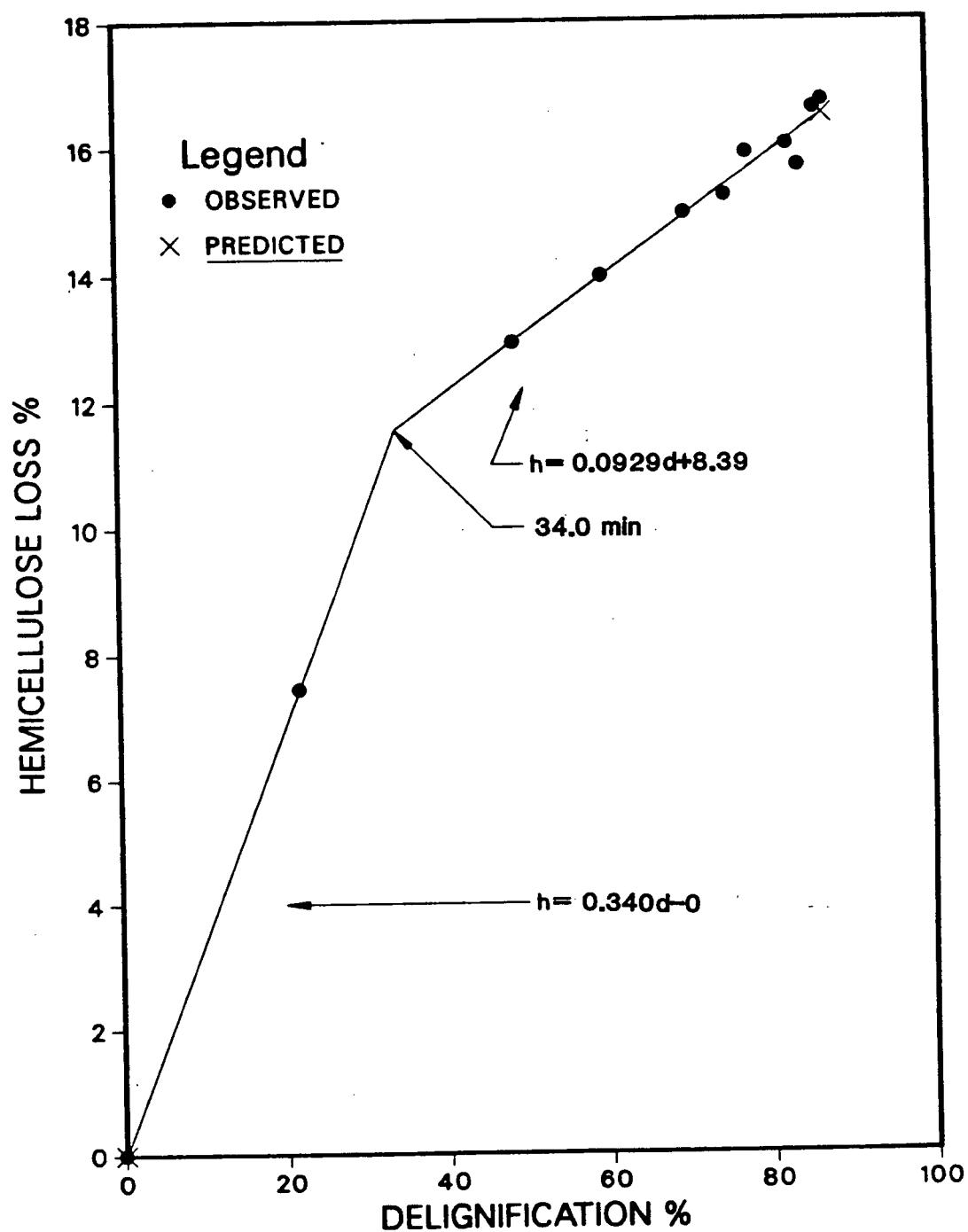
Fig. 10   Relationship of percentage delignification vs. percentage of
          hemicelluloses loss of pulps.
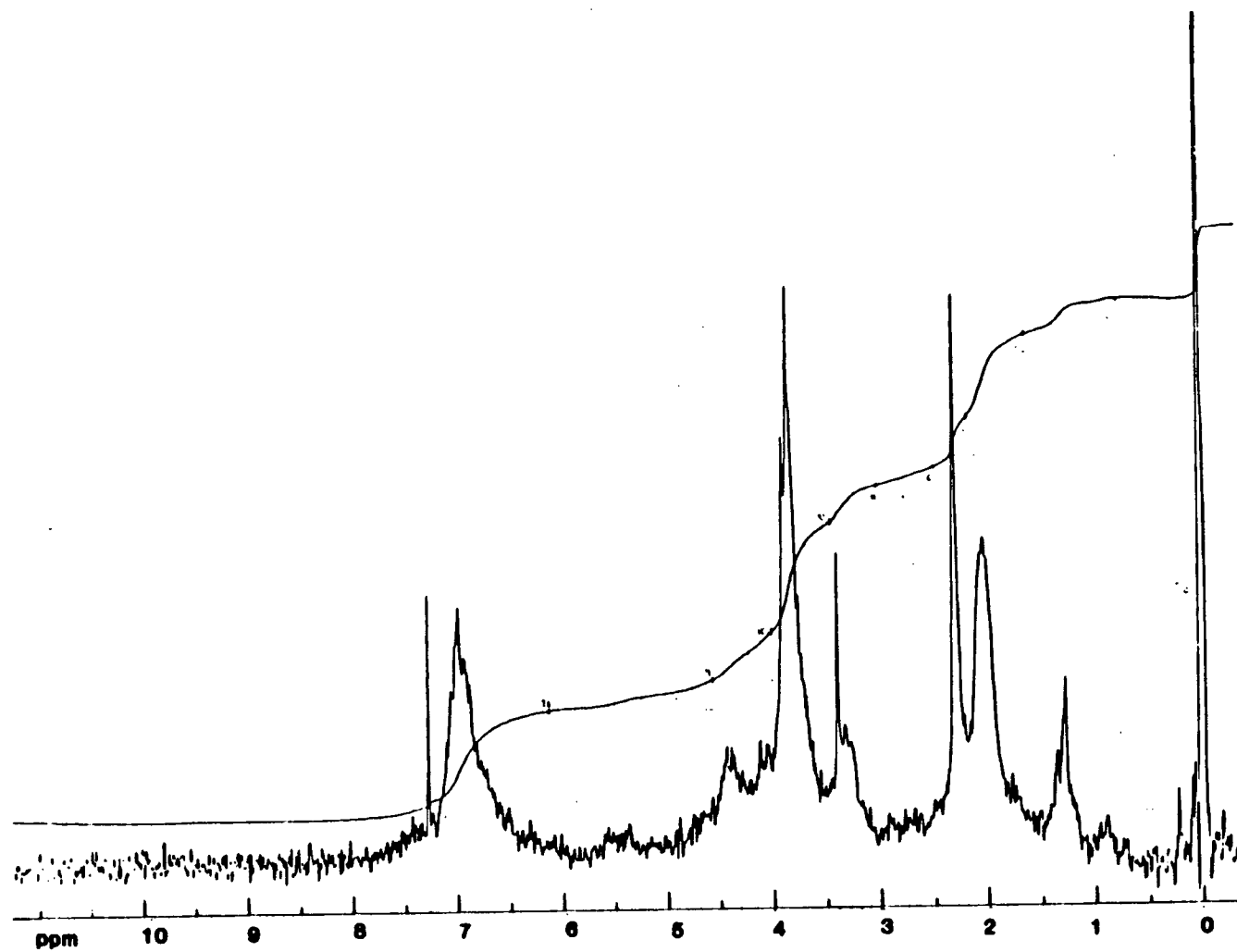
Fig. 11   NMR spectrum of lignin from 20 min cook.
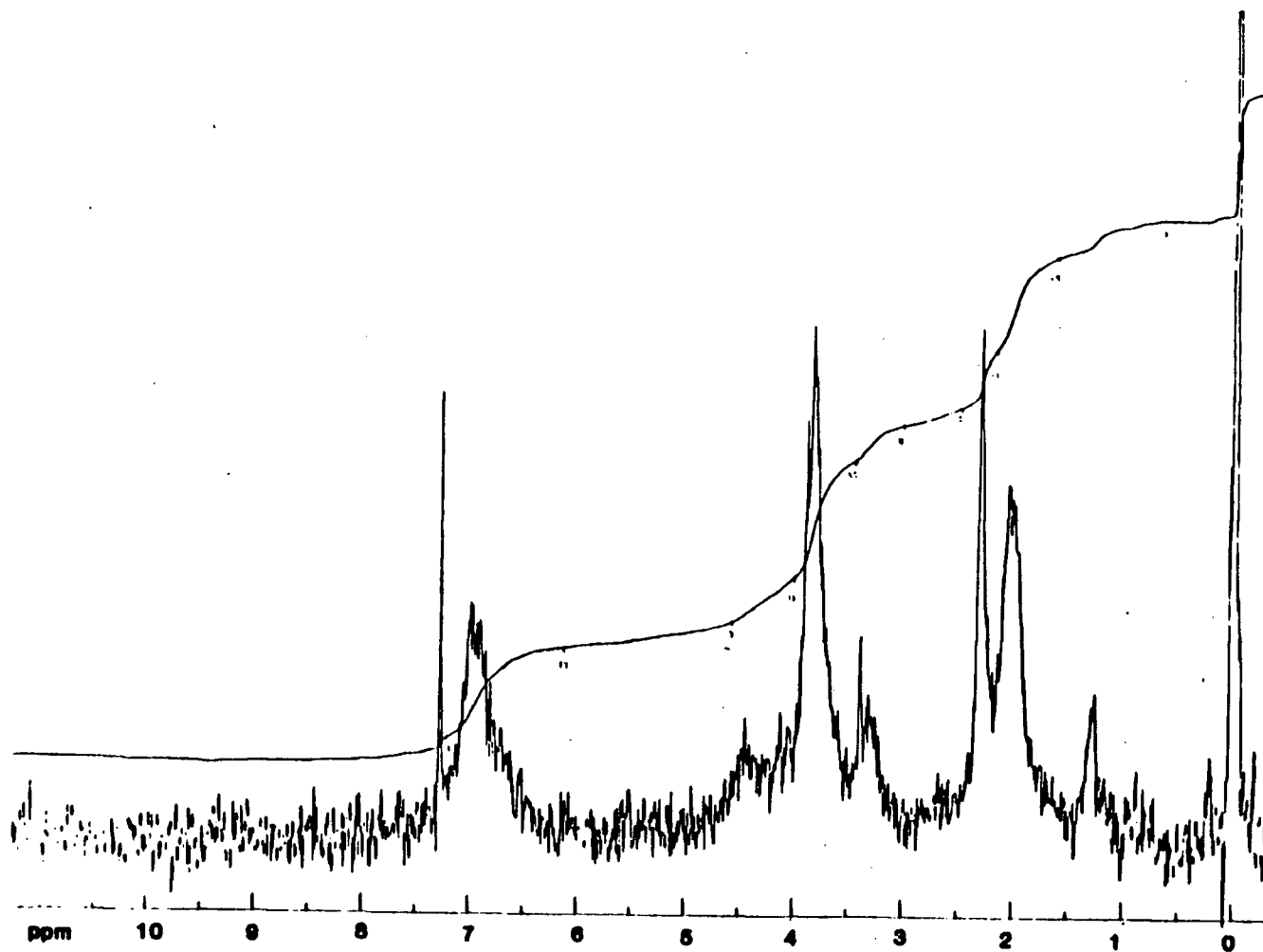
Fig. 12   NMR spectrum of lignin from 30 min cook.
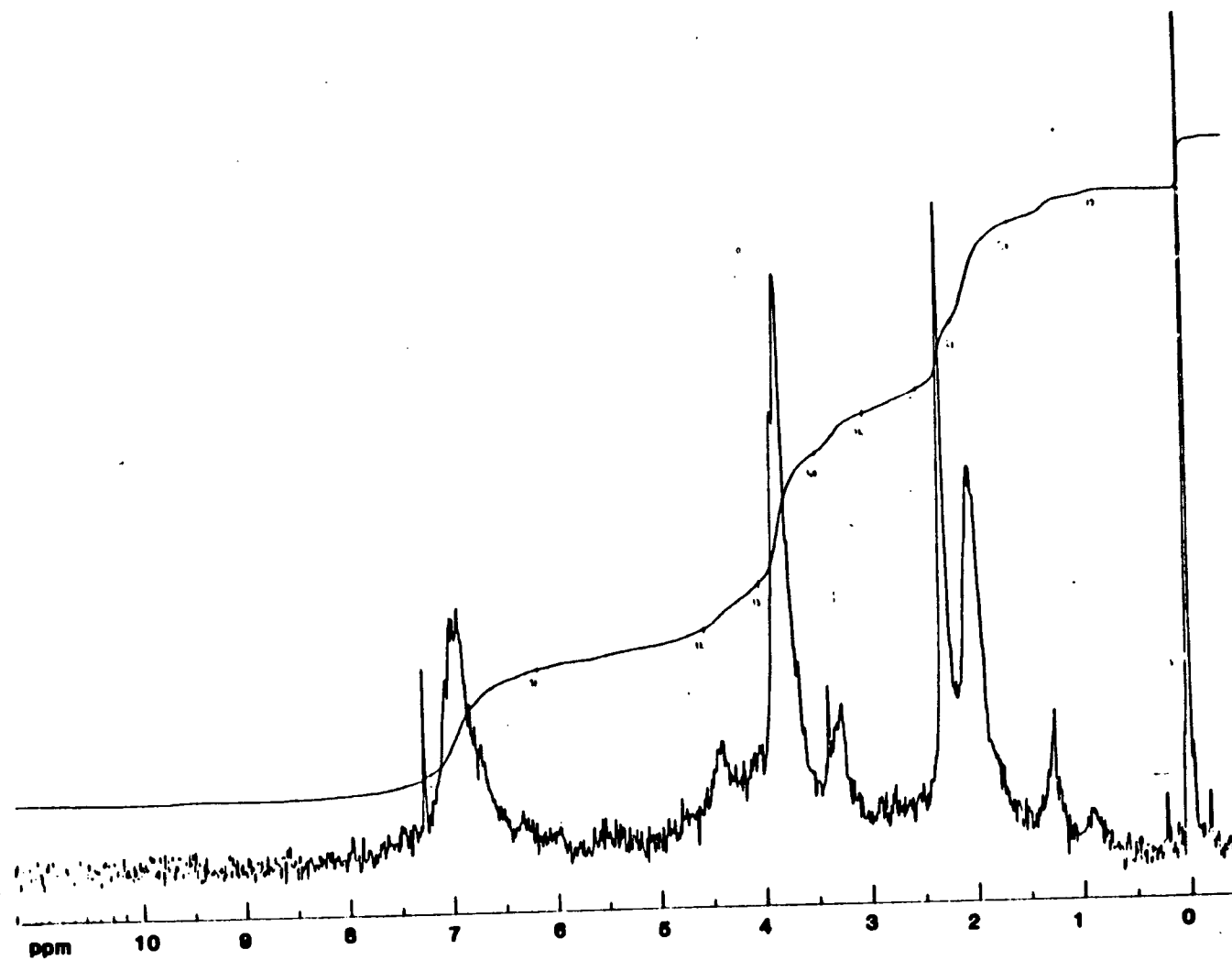
Fig. 13   NMR spectrum of lignin from 50 min cook.
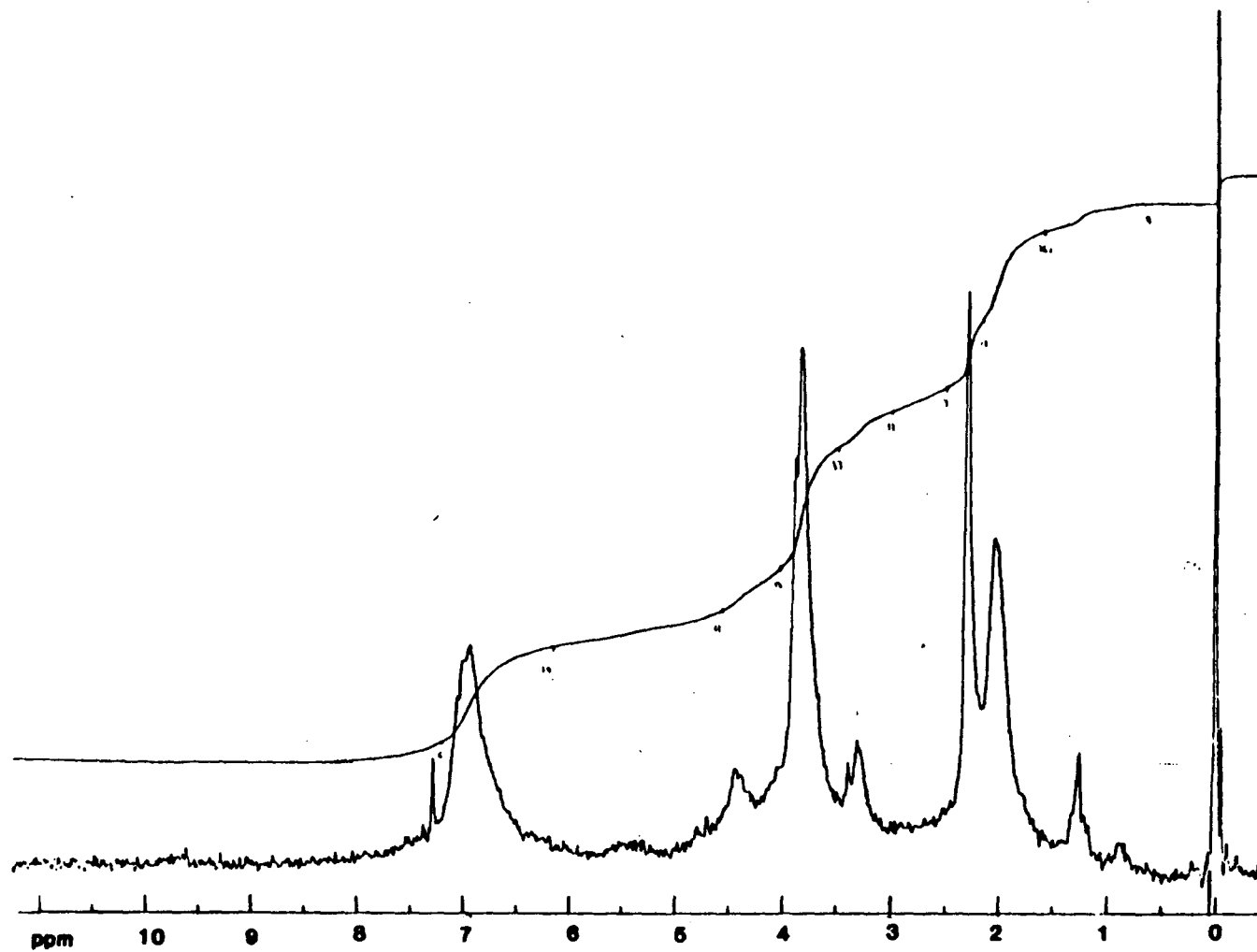
Fig. 14   NMR spectrum of lignin from 70 min cook.
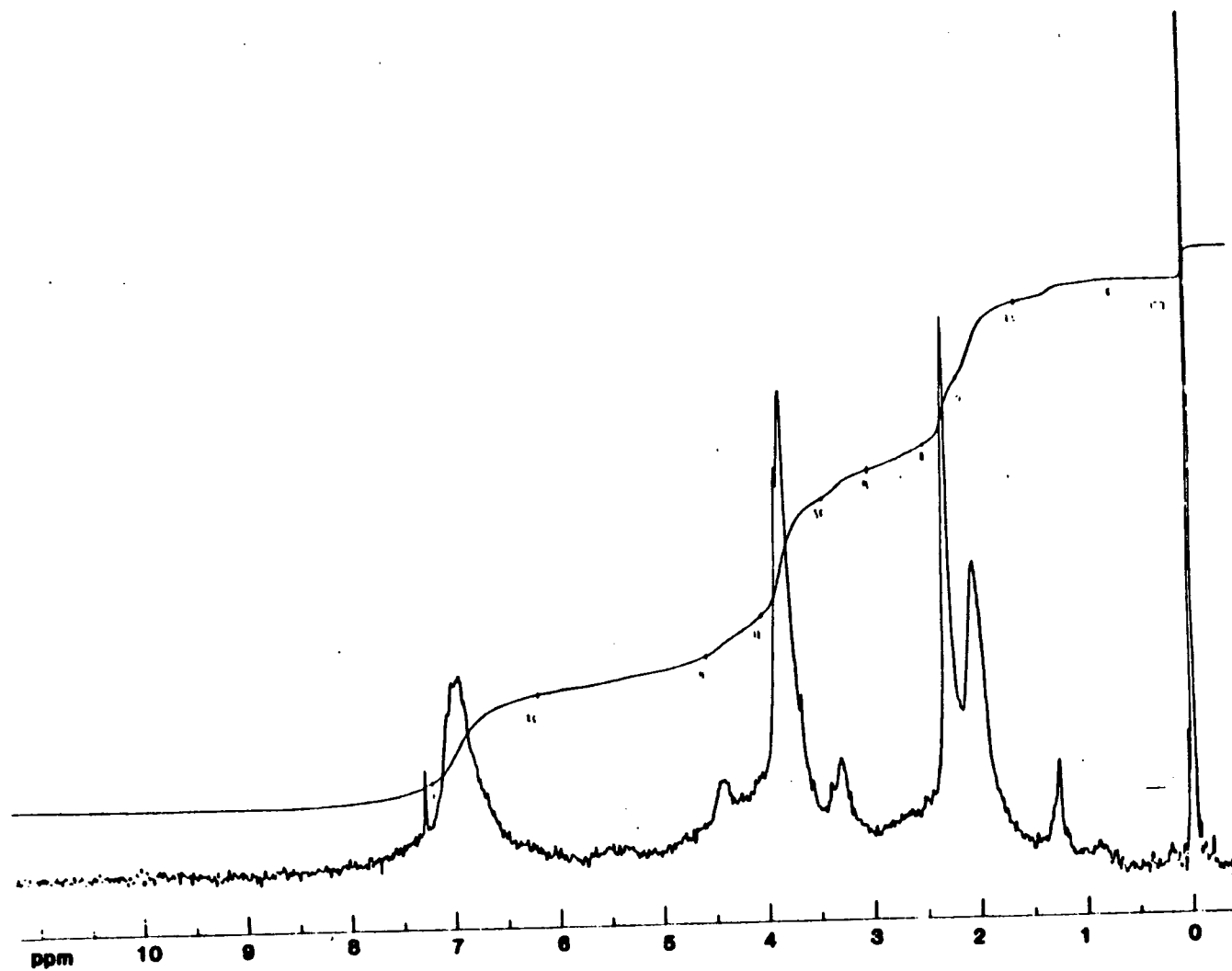
Fig. 15   NMR spectrum of lignin from 90 min cook.
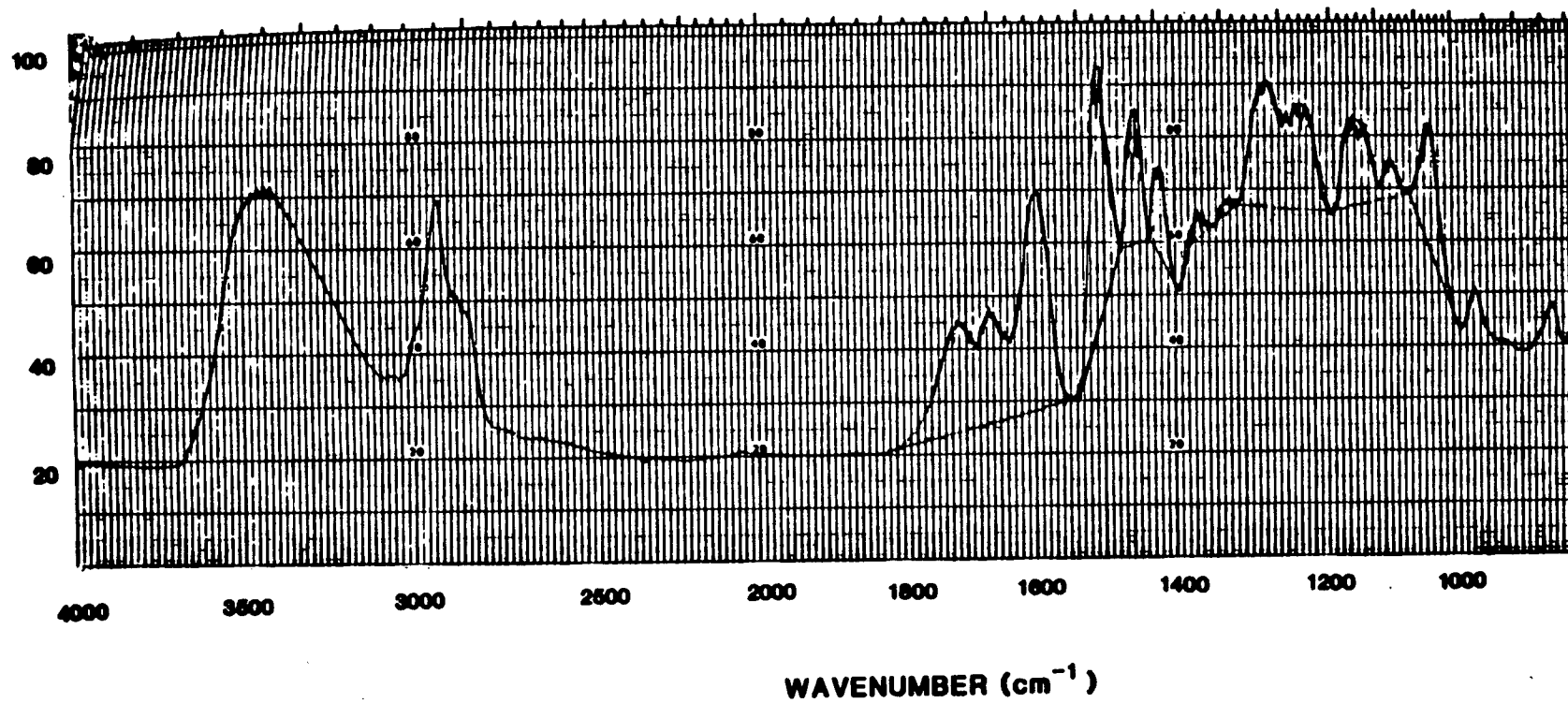
Fig. 16   IR spectrum of lignin from 20 min cook.
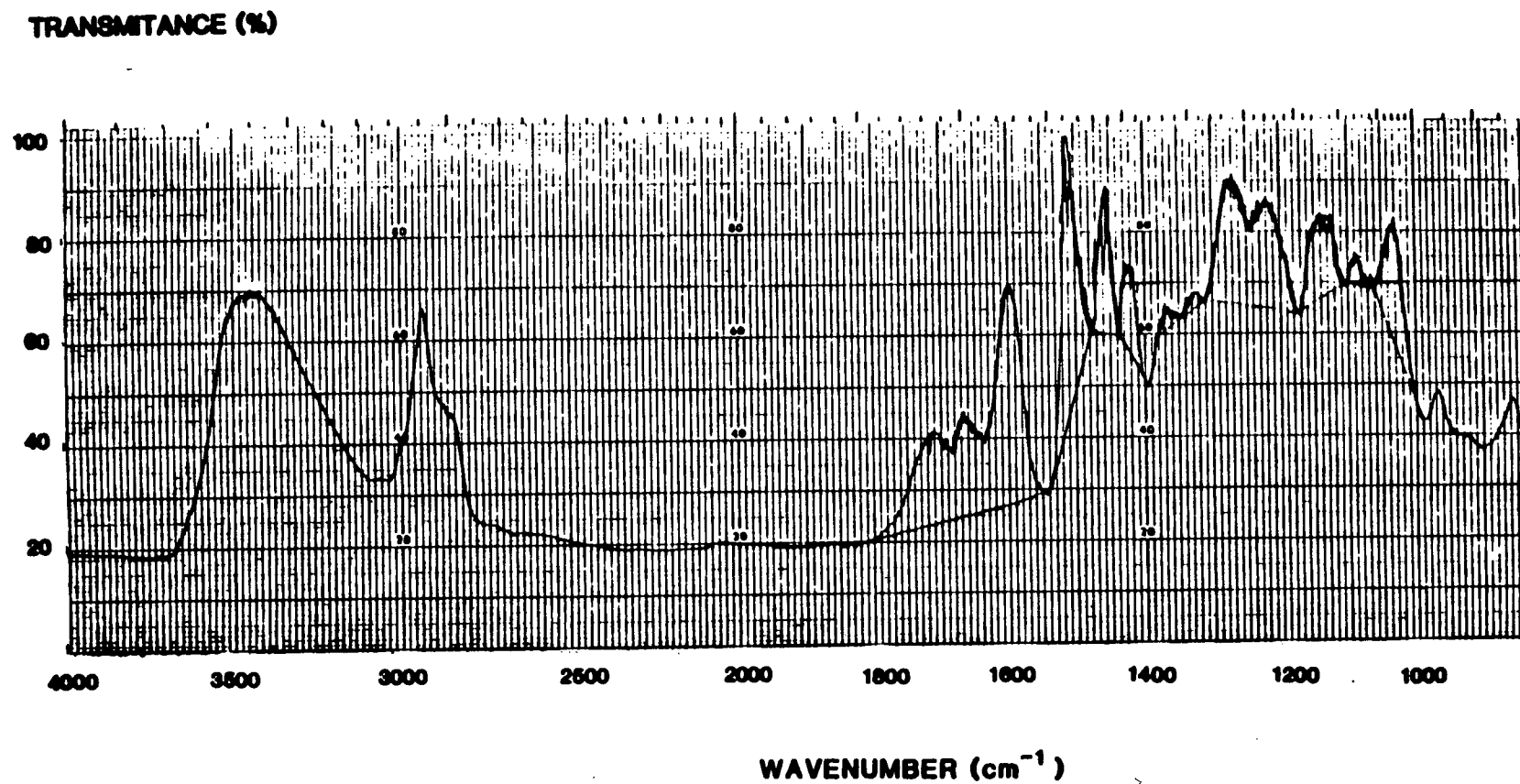
Fig. 17   IR spectrum of lignin from 30 min cook.
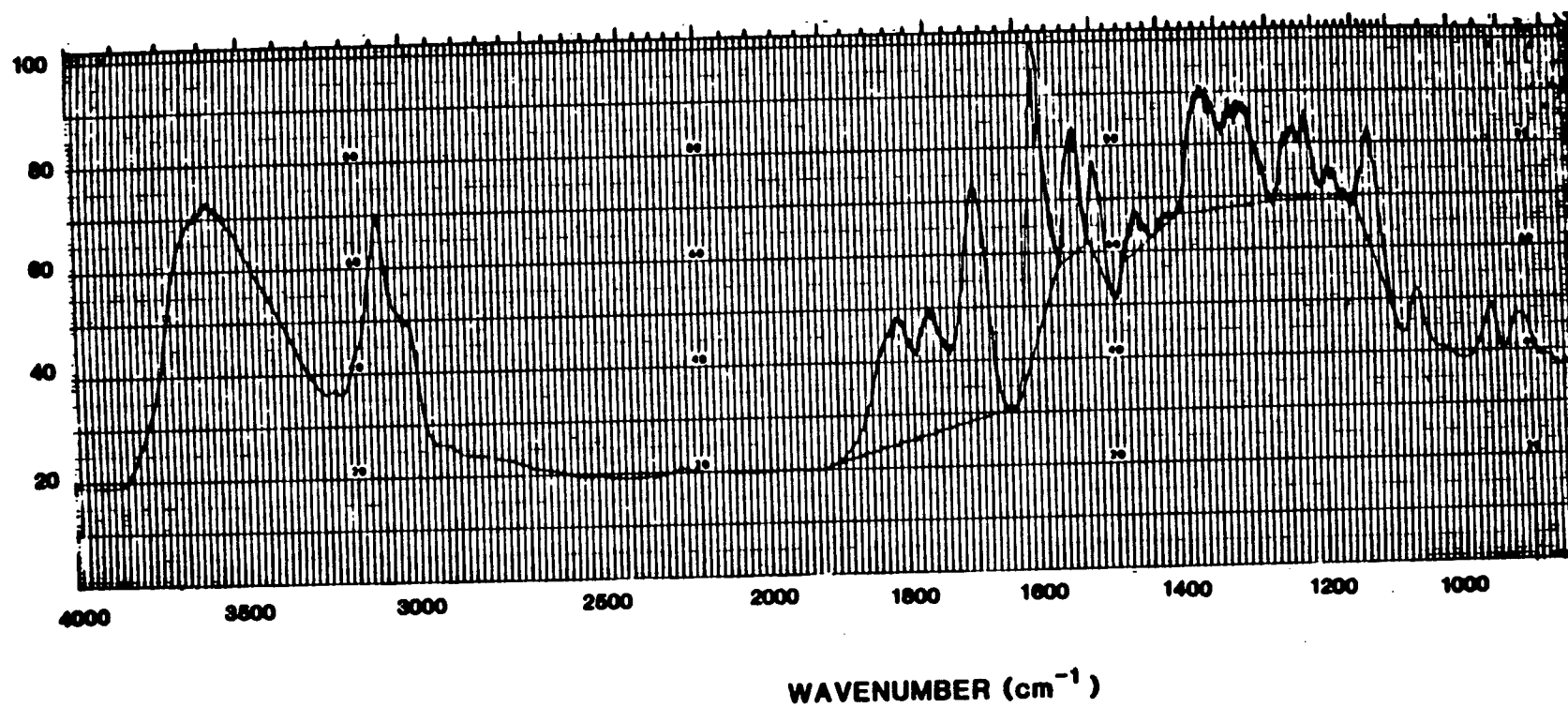
Fig. 18 IR spectrum of lignin from 50 min cook.

TRANSMITANCE (%)

WAVENUMBER (cm^{-1})
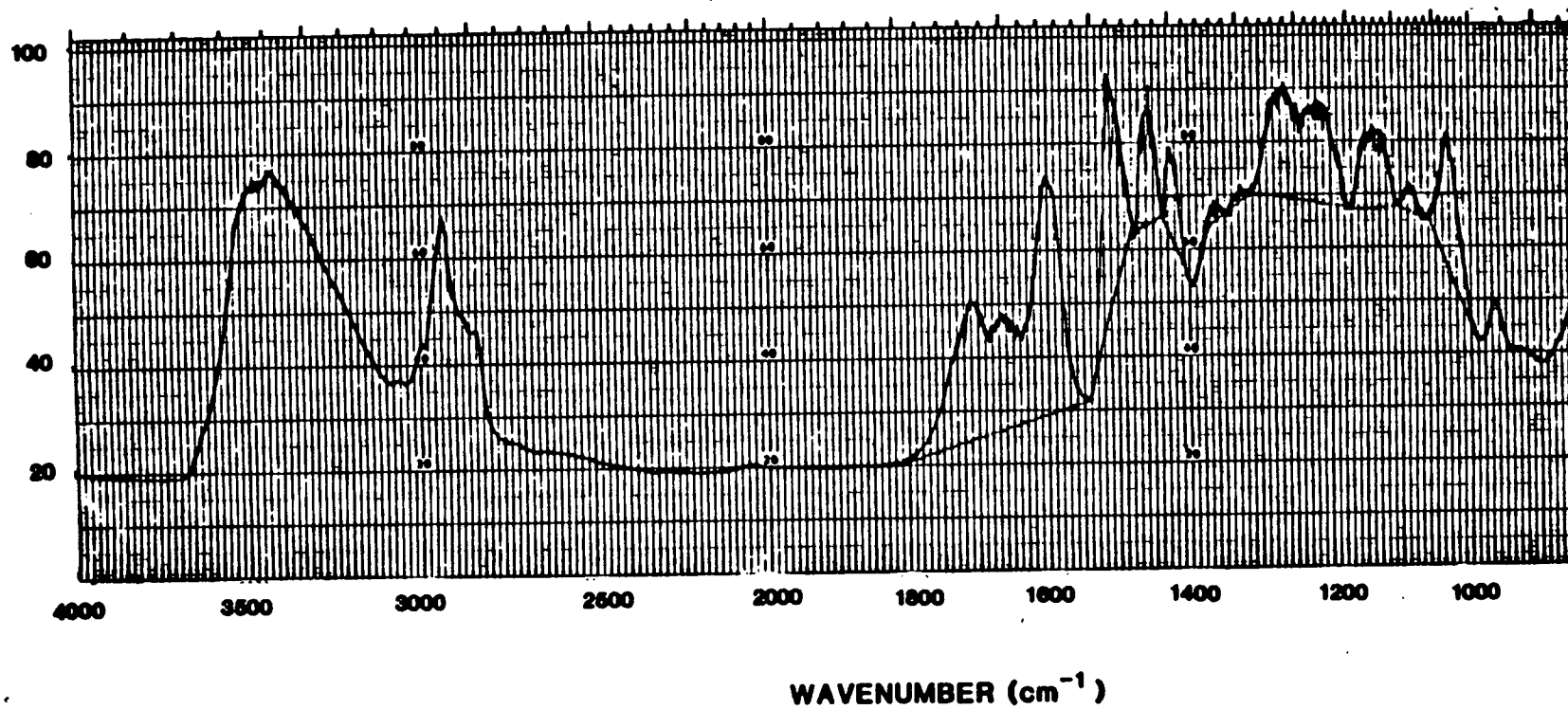
Fig. 19   IR spectrum of lignin from 70 min cook.
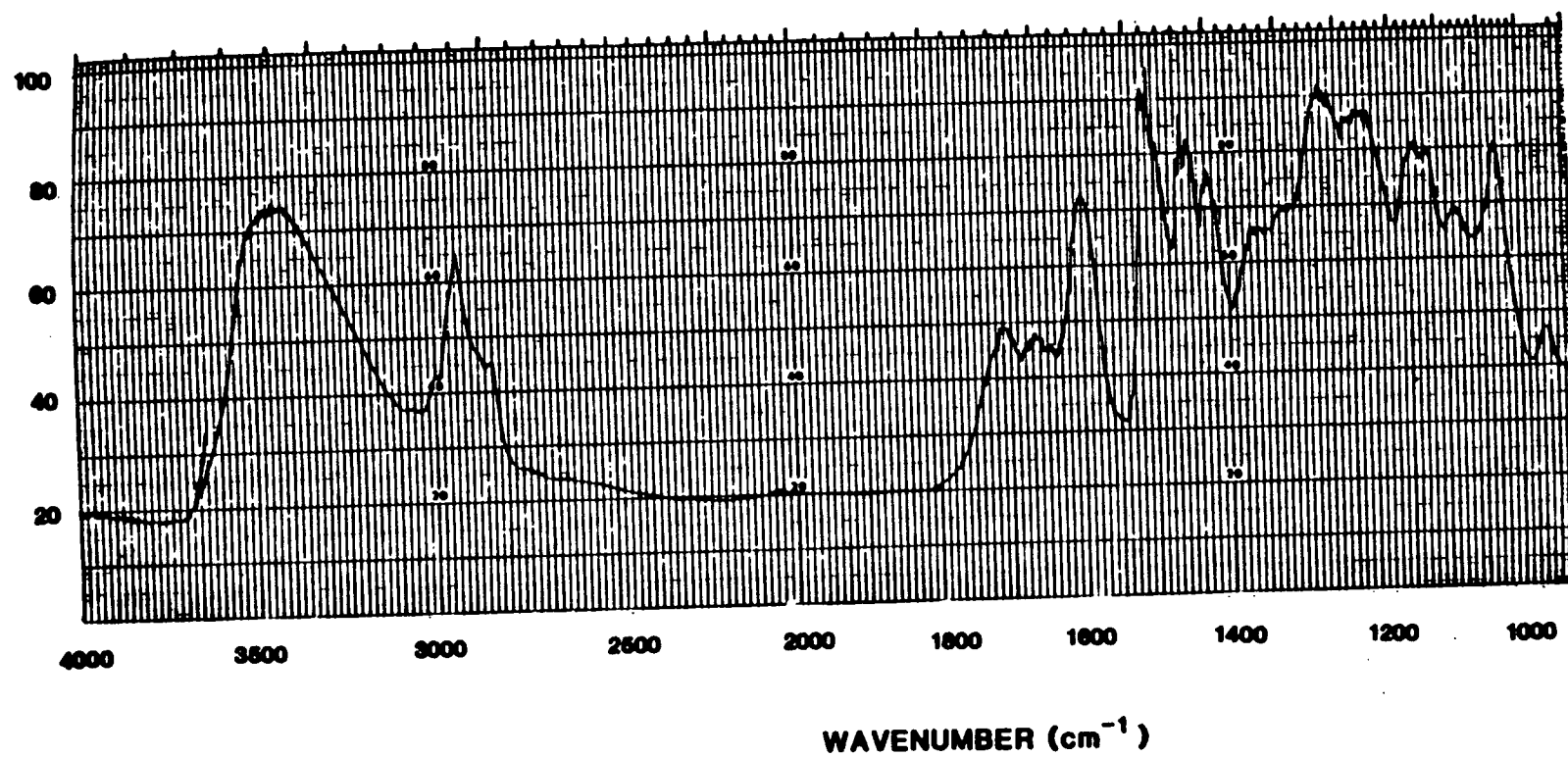
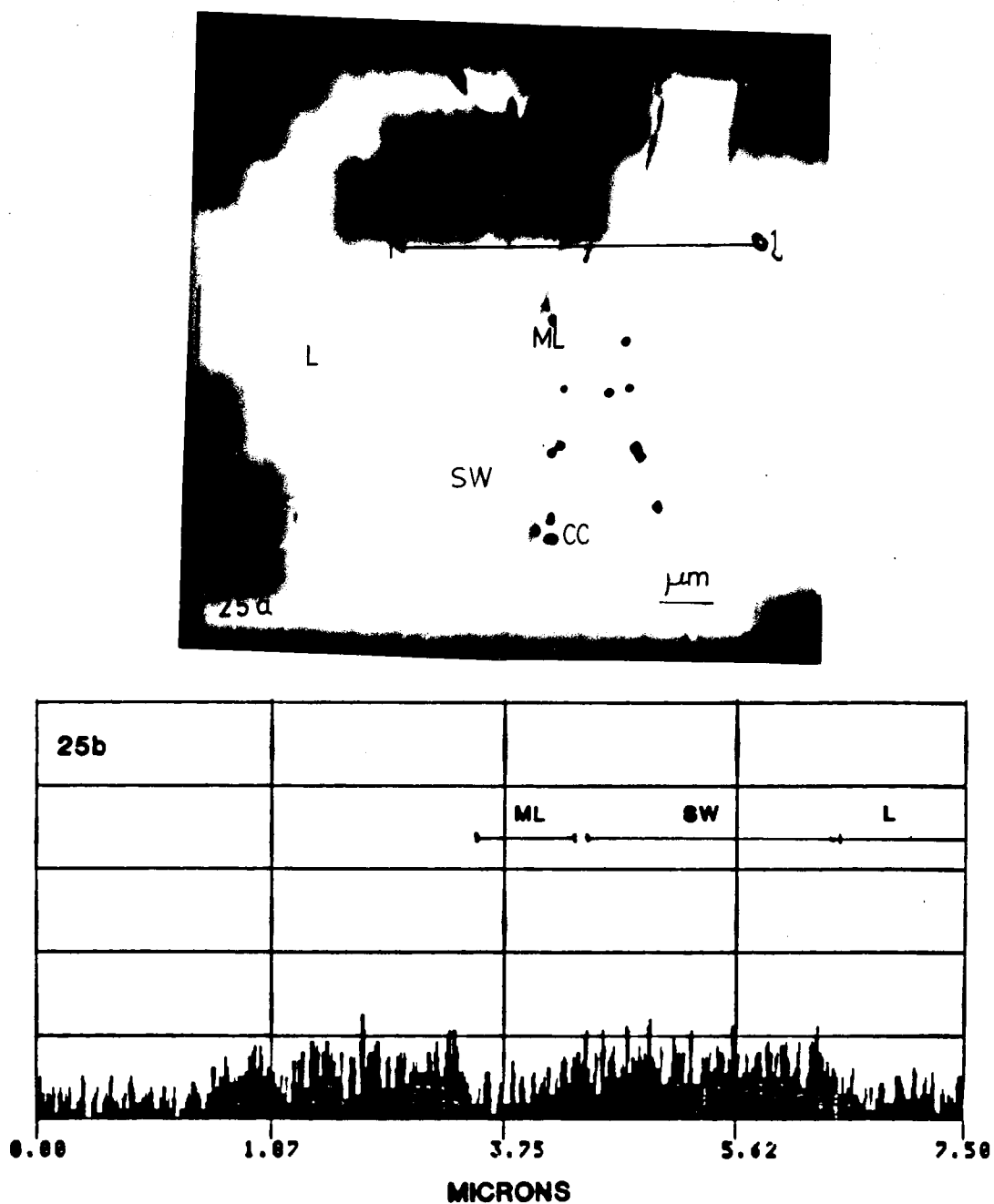Fig. 20   IR spectrum of lignin from 90 min cook.
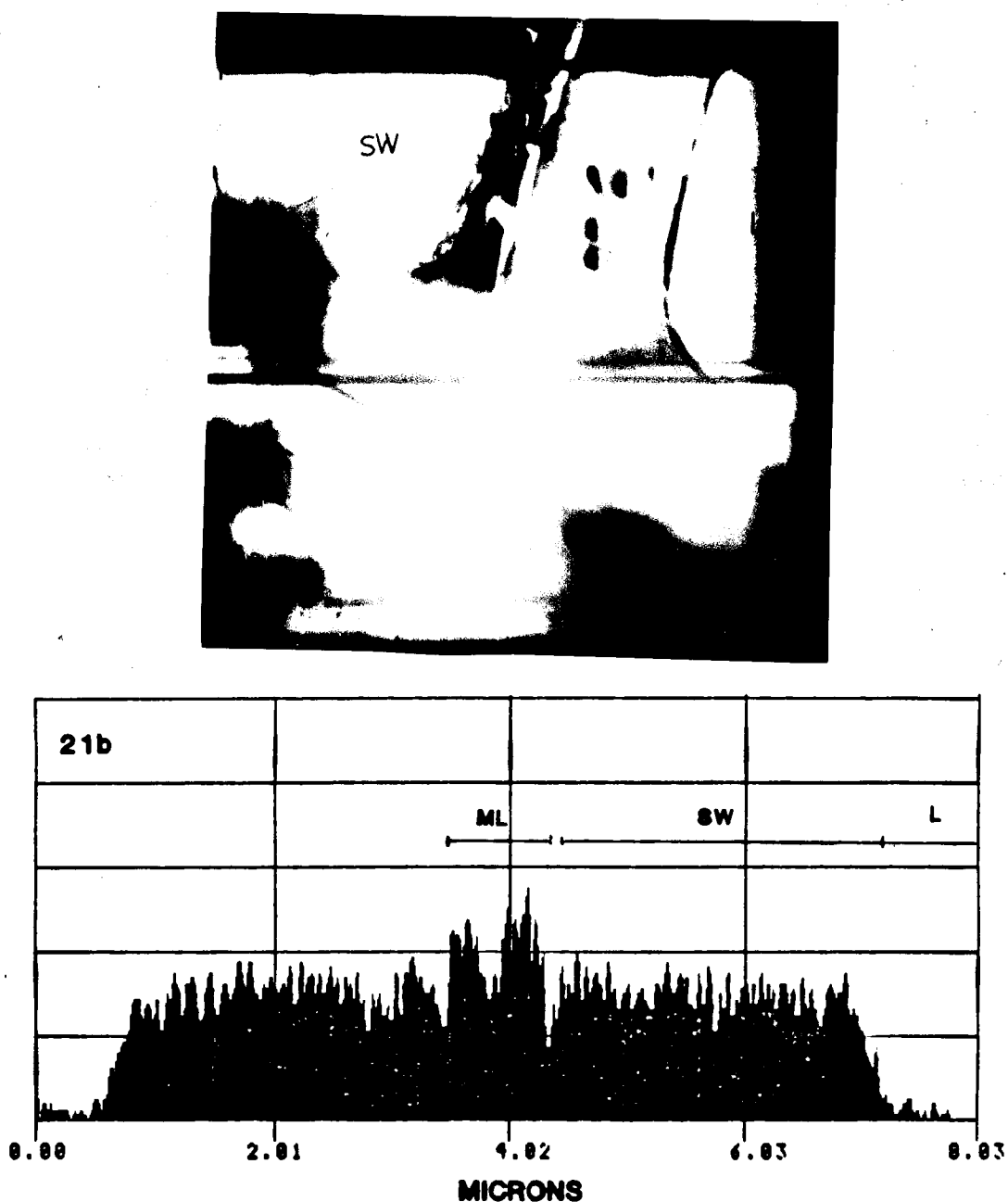
Fig. 21   STEM photomicrograph and Br-L-x-ray scan across
untreated earlywood fiber walls. (CC - cell corner, ML -
middle lamella, SW - secondary wall and L - lumen. Dark
spots are point scan areas.) a. STEM photomicrograph of 0.5
μm cross section of brominated earlywood fibers, 1-1 is the
line-scan. b. Br-L-x-ray distribution profile across the
middle lamella along the line-scan.
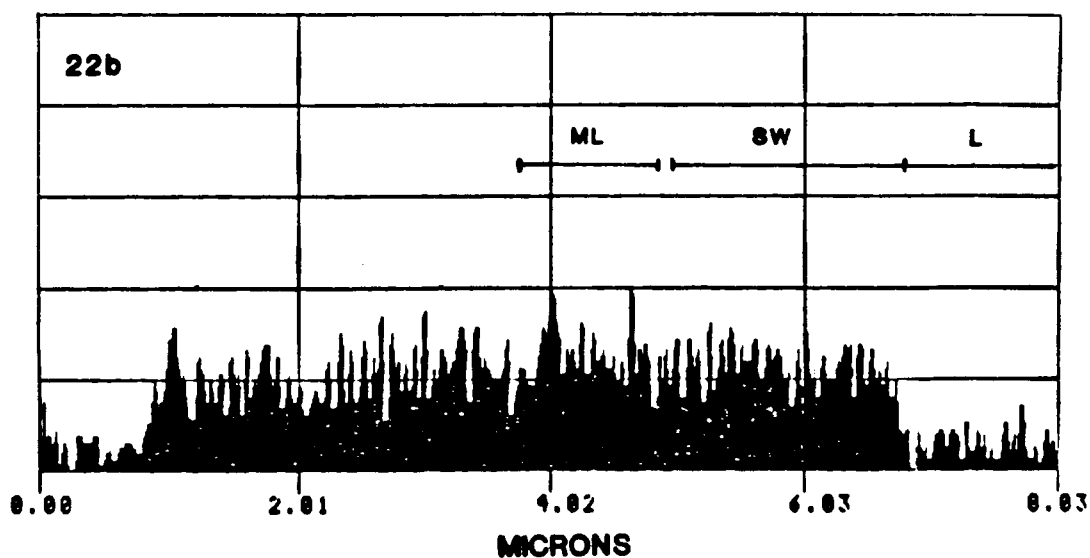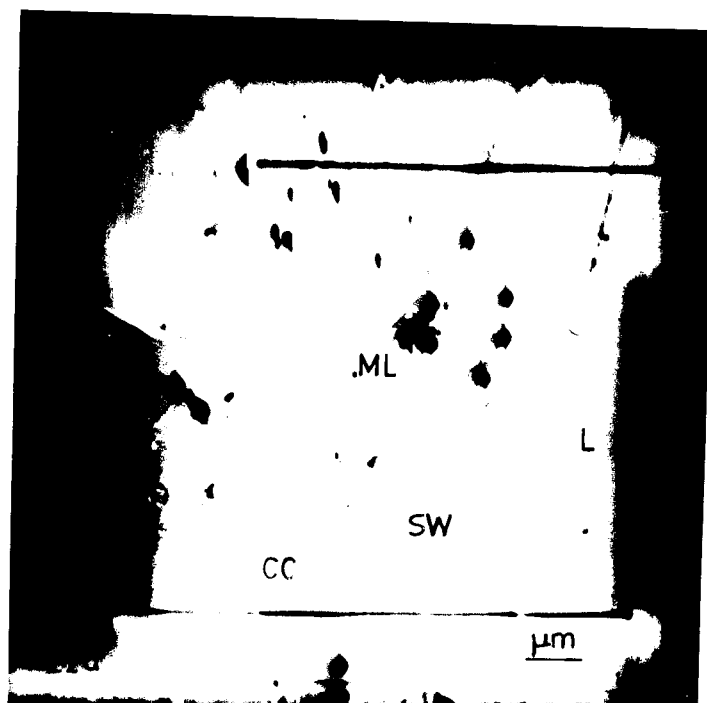
Fig. 22   STEM photomicrograph and Br-L-x-ray scan across treated earlywood fiber walls. (CC - cell corner, ML - middle lamella, SW - secondary wall and L - lumen. Dark spots are point scan areas.) a. STEM photomicrograph of 0.5 μm cross section of 21.9% delignified brominated earlywood fibers, 1-1 is the line-scan. b. Br-L-x-ray distribution profile across the middle lamella along the line-scan.
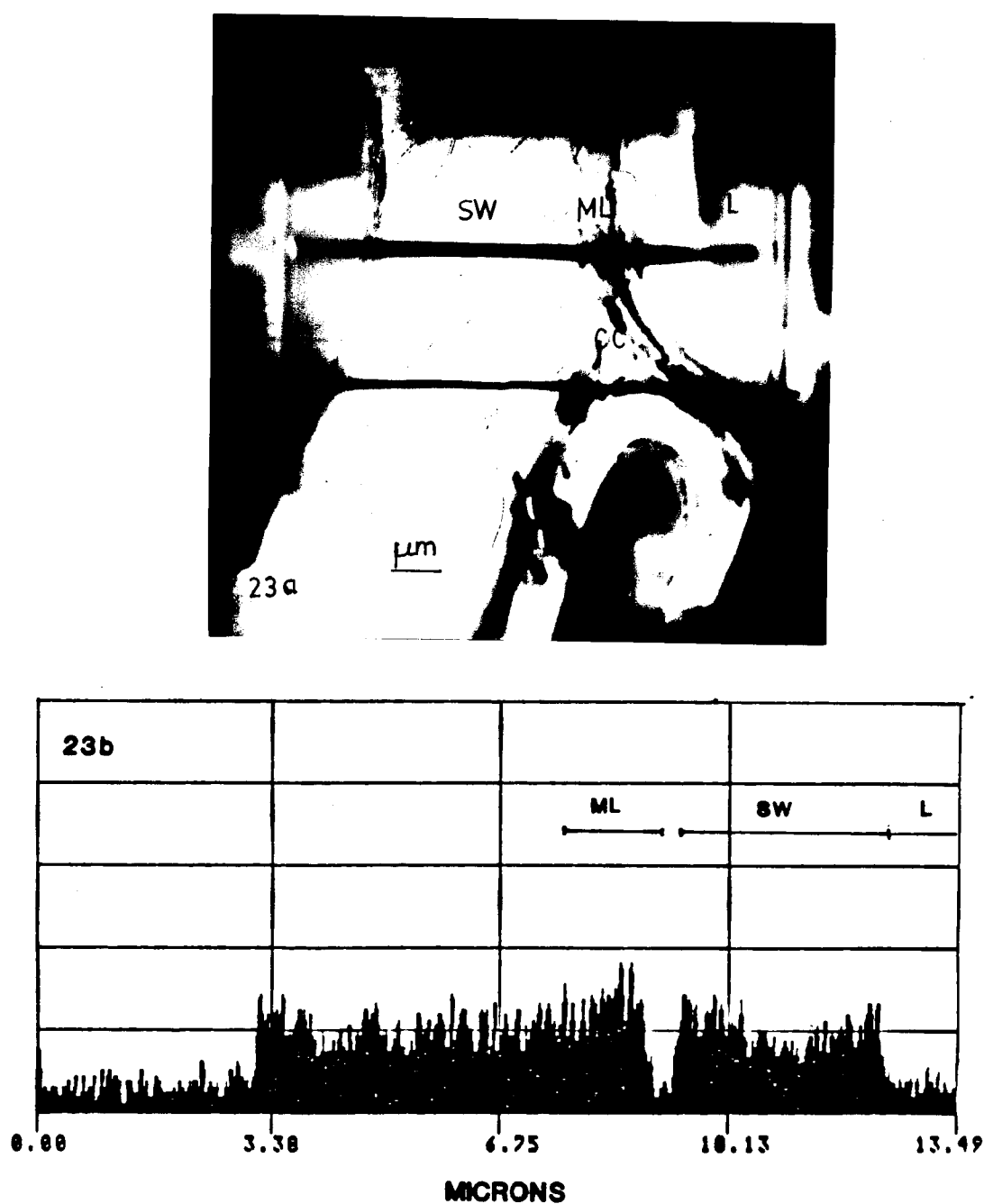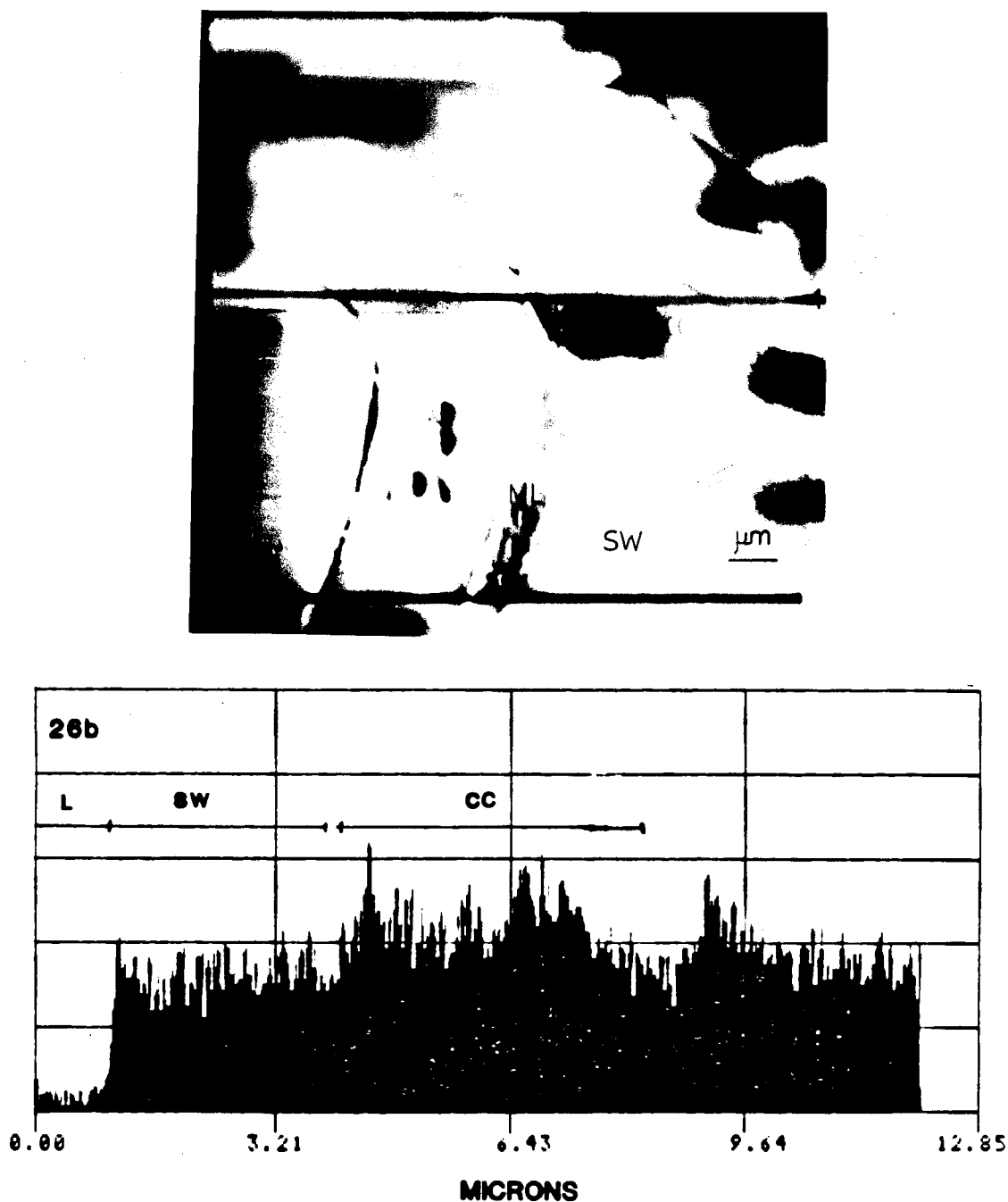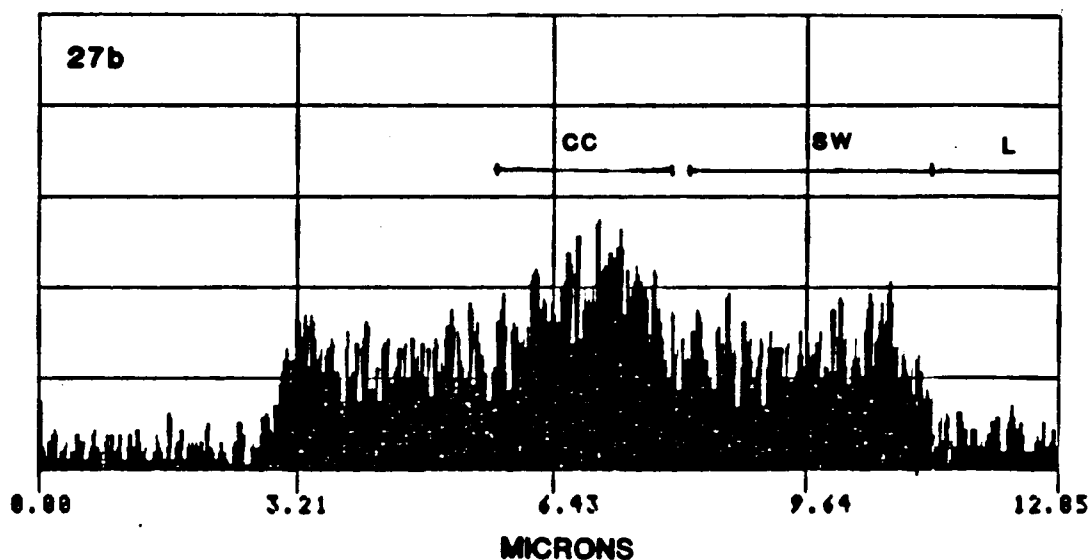
Fig. 23   STEM photomicrograph and Br–L–x–ray scan across treated earlywood fiber walls. (CC – cell corner, ML – middle lamella, SW – secondary wall and L– lumen). a. STEM photomicrograph of 0.5 μm cross section of 48.8% delignified brominated earlywood fibers, 1–1 is the line–scan. b. Br–L–x–ray distribution profile across the middle lamella along the line–scan.
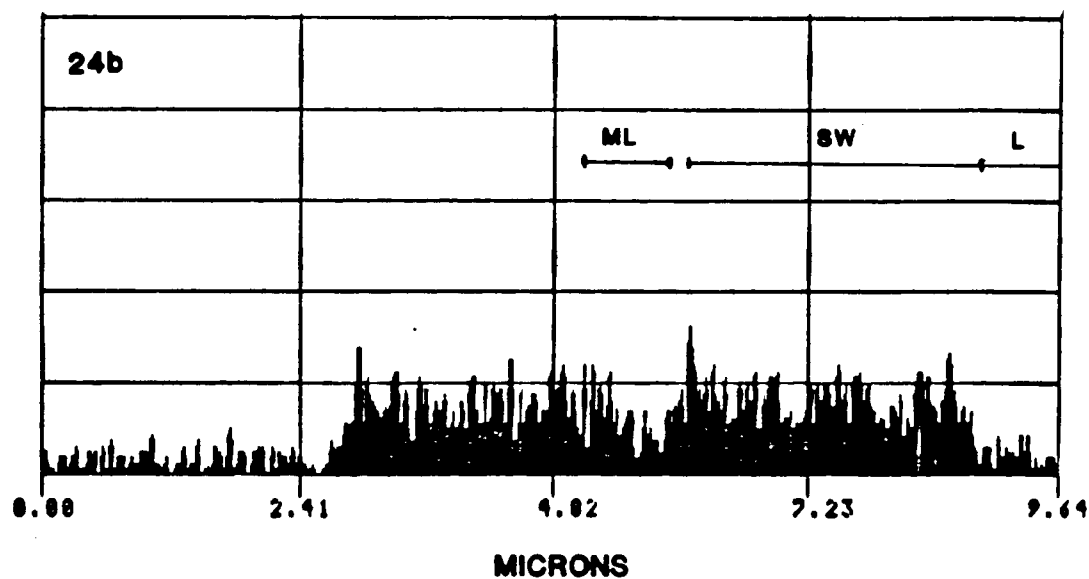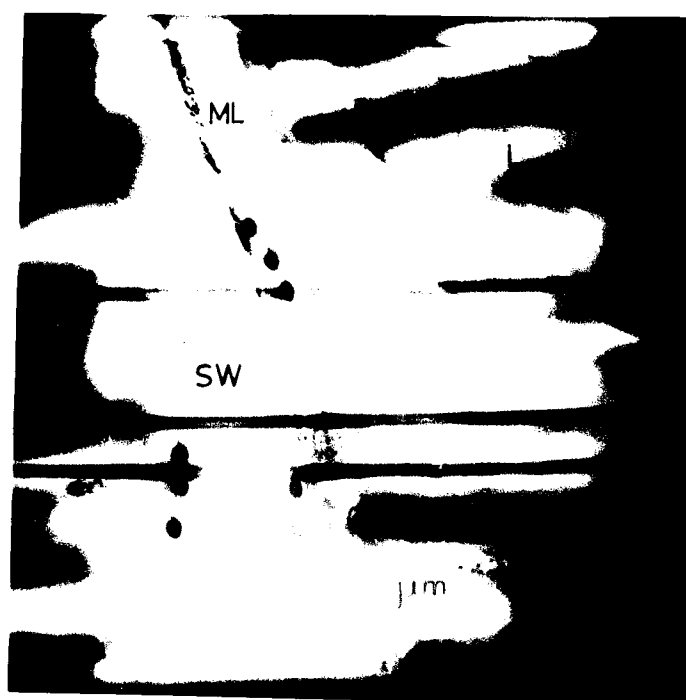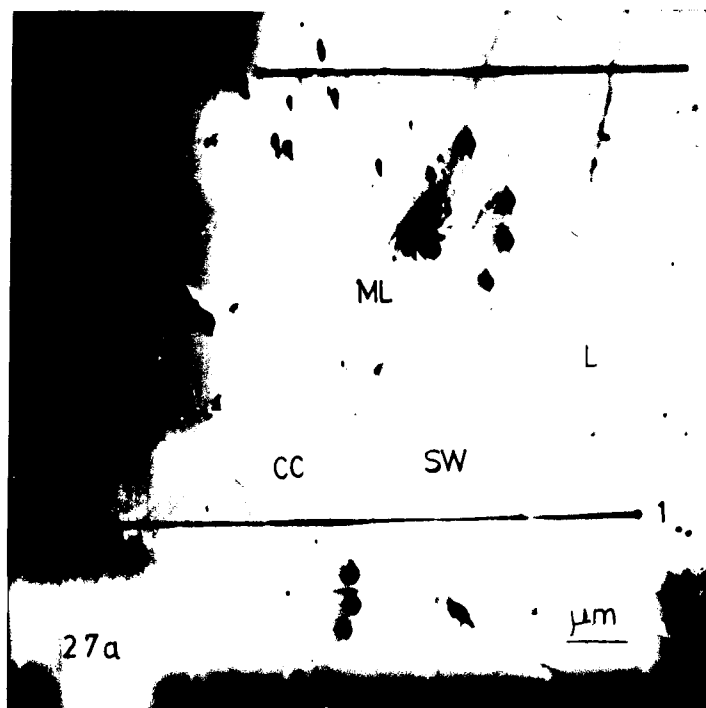
Fig. 24   STEM photomicrograph and Br-L-x-ray scan across treated
earlywood fiber walls. (CC - cell corner, ML - middle
lamella, SW - secondary wall and L - lumen. Dark spots are
point scan areas.) a. STEM photomicrograph of 0.5 μm cross
section of 77.7% delignified brominated earlywood fibers,
1-1 is the line-scan. b. Br-L-x-ray distribution profile
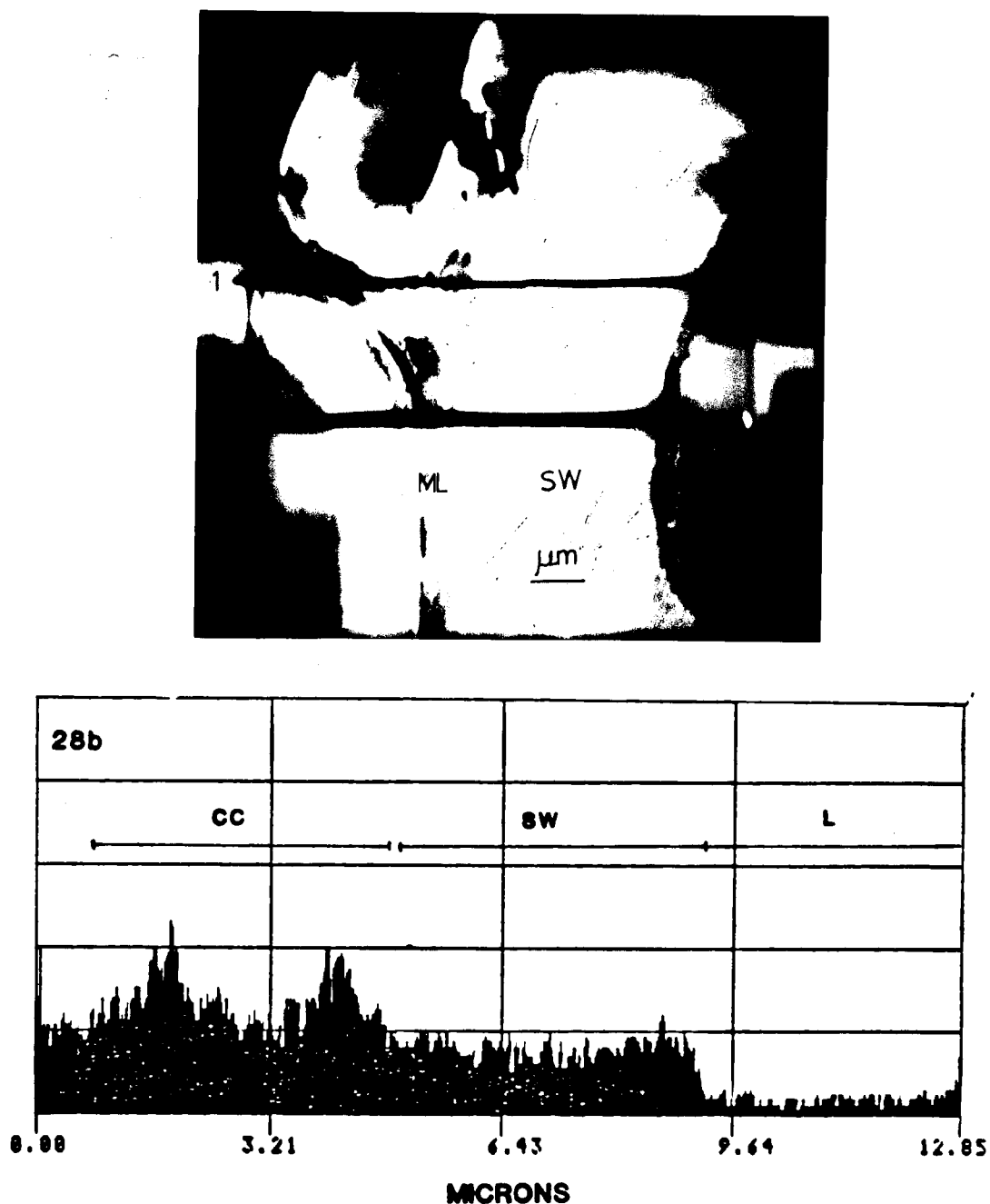across the middle lamella along the line-scan.

Fig. 25   STEM photomicrograph and Br-L-x-ray scan across treated
earlywood fiber walls. (CC - cell corner, ML - middle
lamella, SW - secondary wall and L - lumen. Dark spots are
point scan areas.) a. STEM photomicrograph of 0.5 µm cross
section of 87.1% delignified brominated earlywood fibers,
1-1 is the line-scan. b. Br-L-x-ray distribution profile
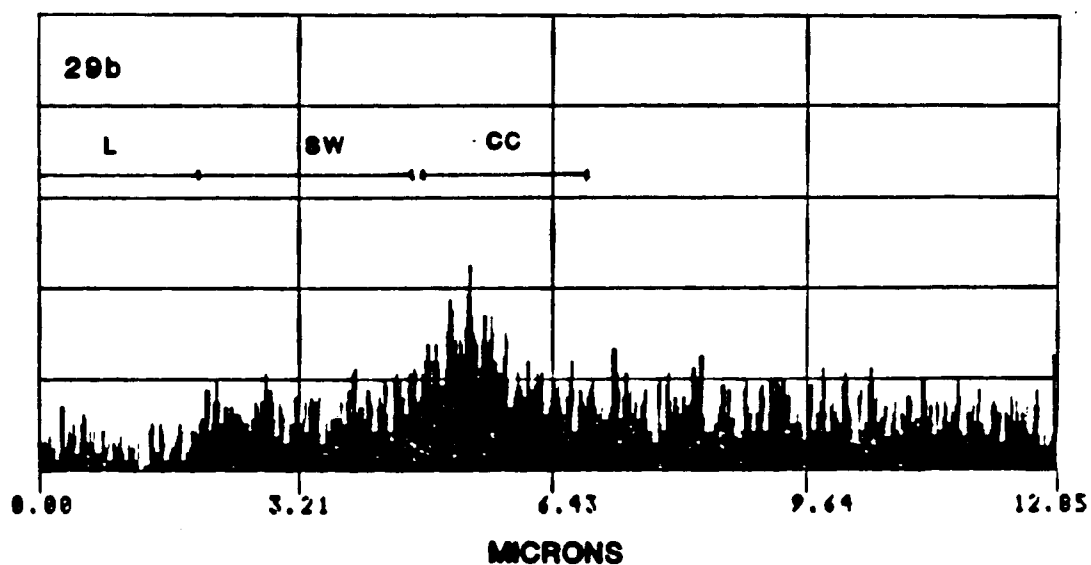across the middle lamella along the line-scan.

Fig. 26   STEM photomicrograph and Br-L-x-ray scan across untreated earlywood fiber walls. (CC - cell corner, ML - middle lamella, SW - secondary wall and L - lumen. Dark spots are point scan areas.) a. STEM photomicrograph of 0.5 μm cross section of brominated earlywood fibers, 1-1 is the line-scan. b. Br-L-x-ray distribution profile across the cell corner along the line-scan.
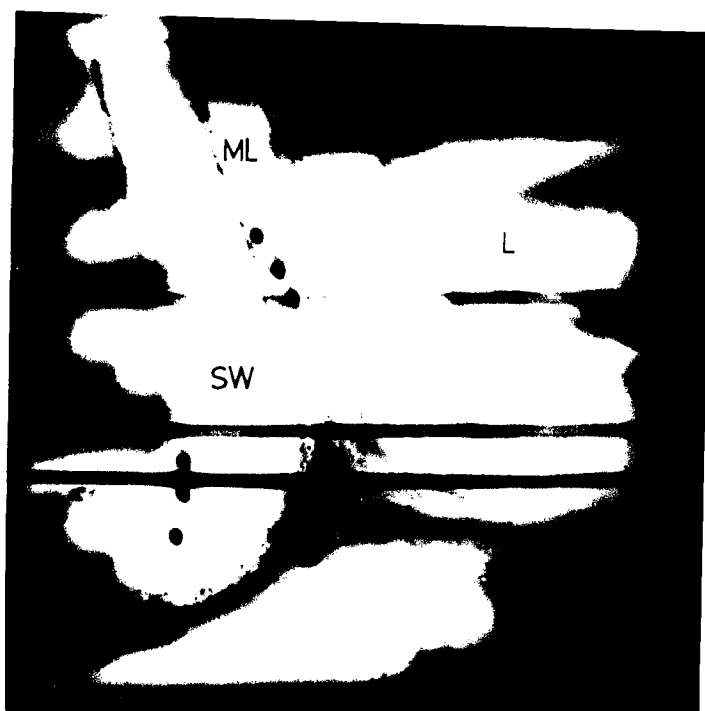
Fig. 27   STEM photomicrograph and Br-L-x-ray scan across treated
earlywood fiber walls. (CC - cell corner, ML - middle
lamella, SW - secondary wall and L - lumen. Dark spots are
point scan areas.) a. STEM photomicrograph of 0.5 μm cross
section of 21.9% delignified brominated earlywood fibers,
1-1 is the line-scan. b. Br-L-x-ray distribution profile
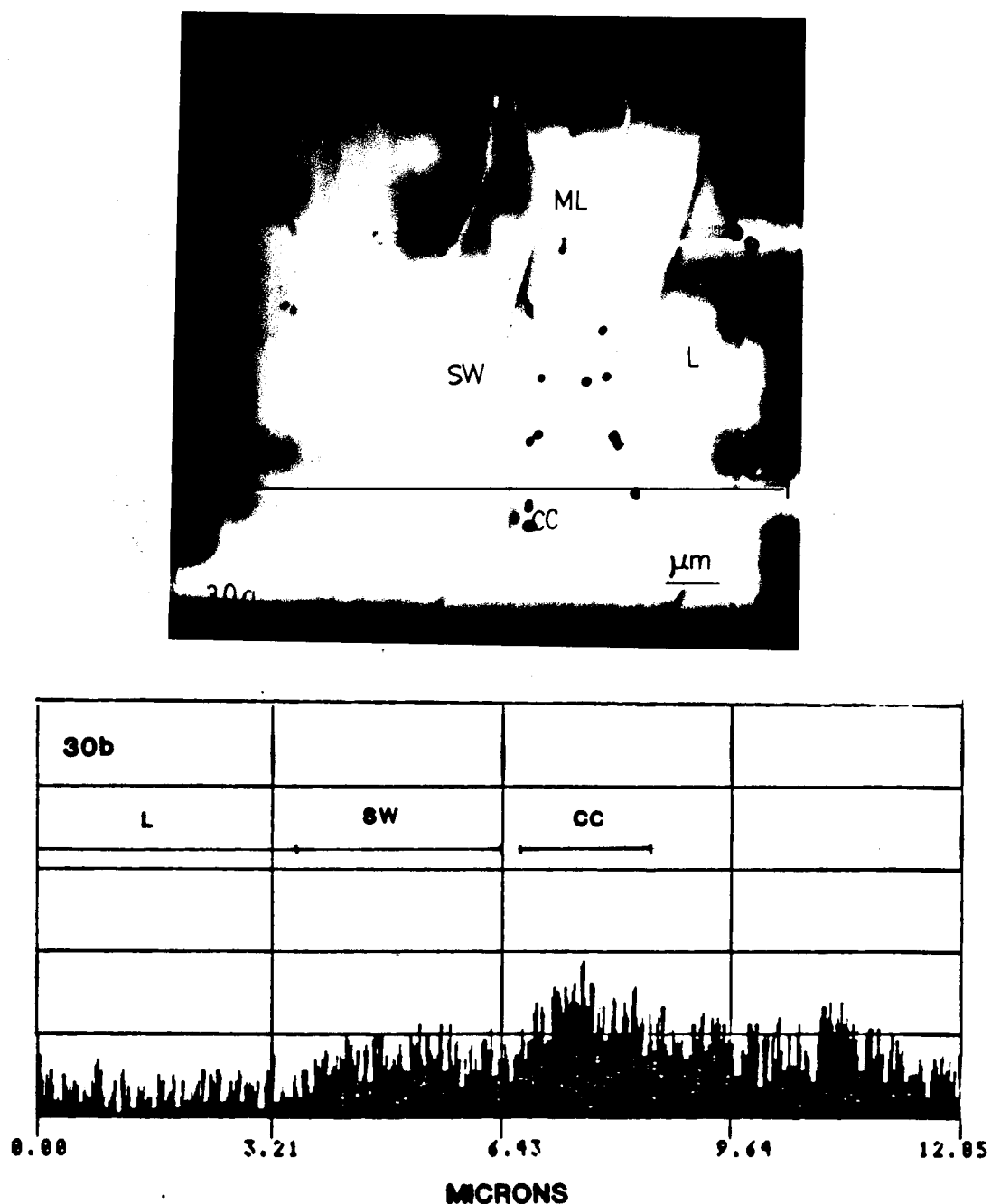across the cell corner along the line-scan.

Fig. 28   STEM photomicrograph and Br-L-x-ray scan across treated
earlywood fiber walls. (CC - cell corner, ML - middle
lamella, SW - secondary wall and L - lumen.) a. STEM
photomicrograph of 0.5 μm cross section of 48.8%
delignified brominated earlywood fibers, 1-1 is the
line-scan. b. Br-L-x-ray distribution profile across the cell
corner along the line-scan.

Fig. 29   STEM photomicrograph and Br-L-x-ray scan across treated
earlywood fiber walls. (CC - cell corner, ML - middle
lamella, SW - secondary wall and L - lumen. Dark spots are
point scan areas.) a. STEM photomicrograph of 0.5 μm cross
section of 77.7% delignified brominated earlywood fibers,
1-1 is the line-scan. b. Br-L-x-ray distribution profile
across the cell corner along the line-scan.

Fig. 30   STEM photomicrograph and Br-L-x-ray scan across treated
earlywood fiber walls. (CC - cell corner, ML - middle
lamella, SW - secondary wall and L - lumen. Dark spots are
point scan areas.) a. STEM photomicrograph of 0.5 μm cross
section of 87.1% delignified brominated earlywood fibers,
1-1 is the line-scan. b. Br-L-x-ray distribution profile
across the cell corner along the line-scan.
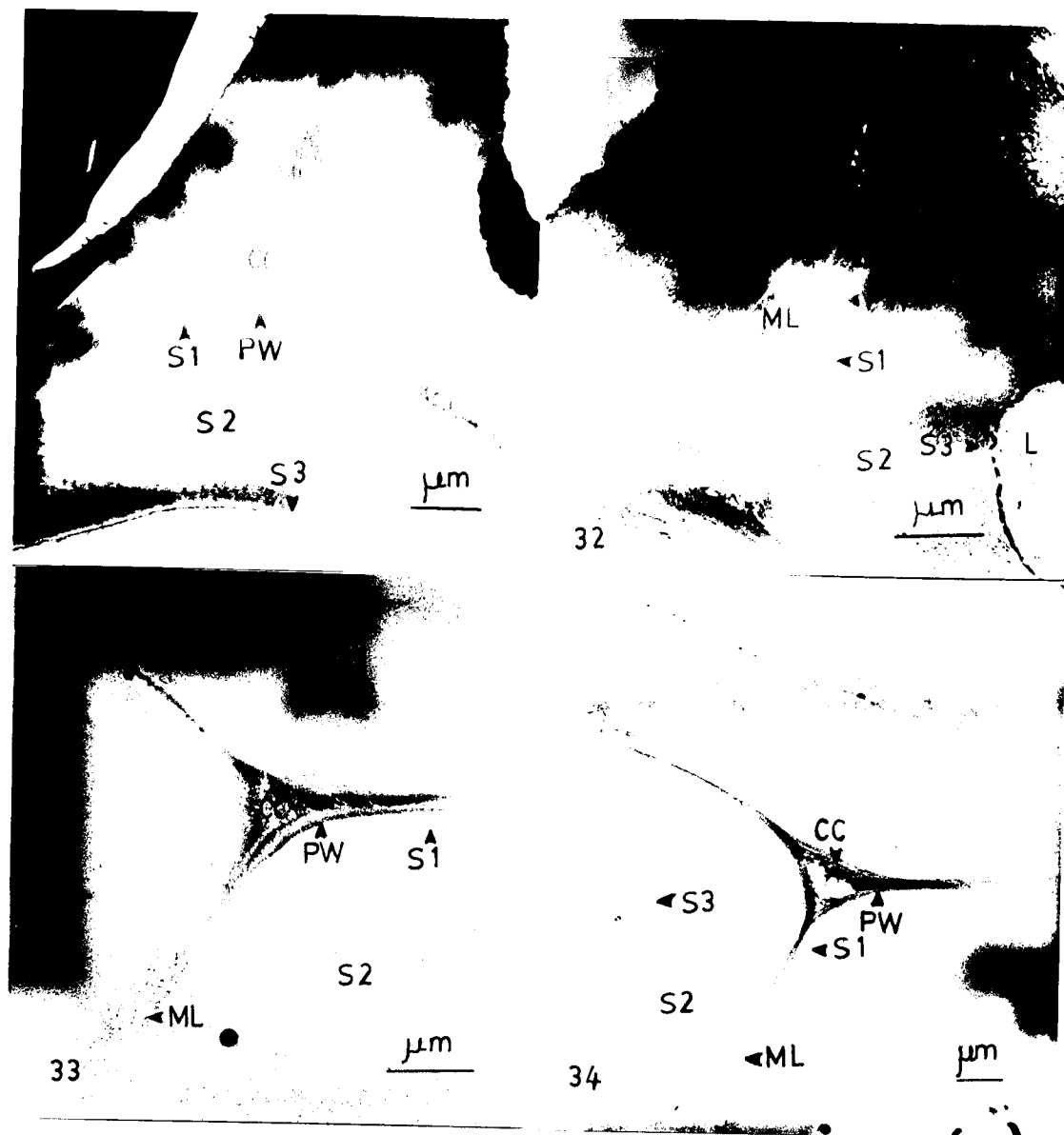
Fig. 31   TEM photomicrograph of permanganate stained spruce wood.

Fig. 32   TEM photomicrograph of permanganate stained spruce wood, 48.8% delignified pulp.

Fig. 33   TEM photomicrograph of permanganate stained spruce wood, 77.7% delignified pulp.

Fig. 34   TEM photomicrograph of permanganate stained spruce wood, 87.1% delignified pulp.

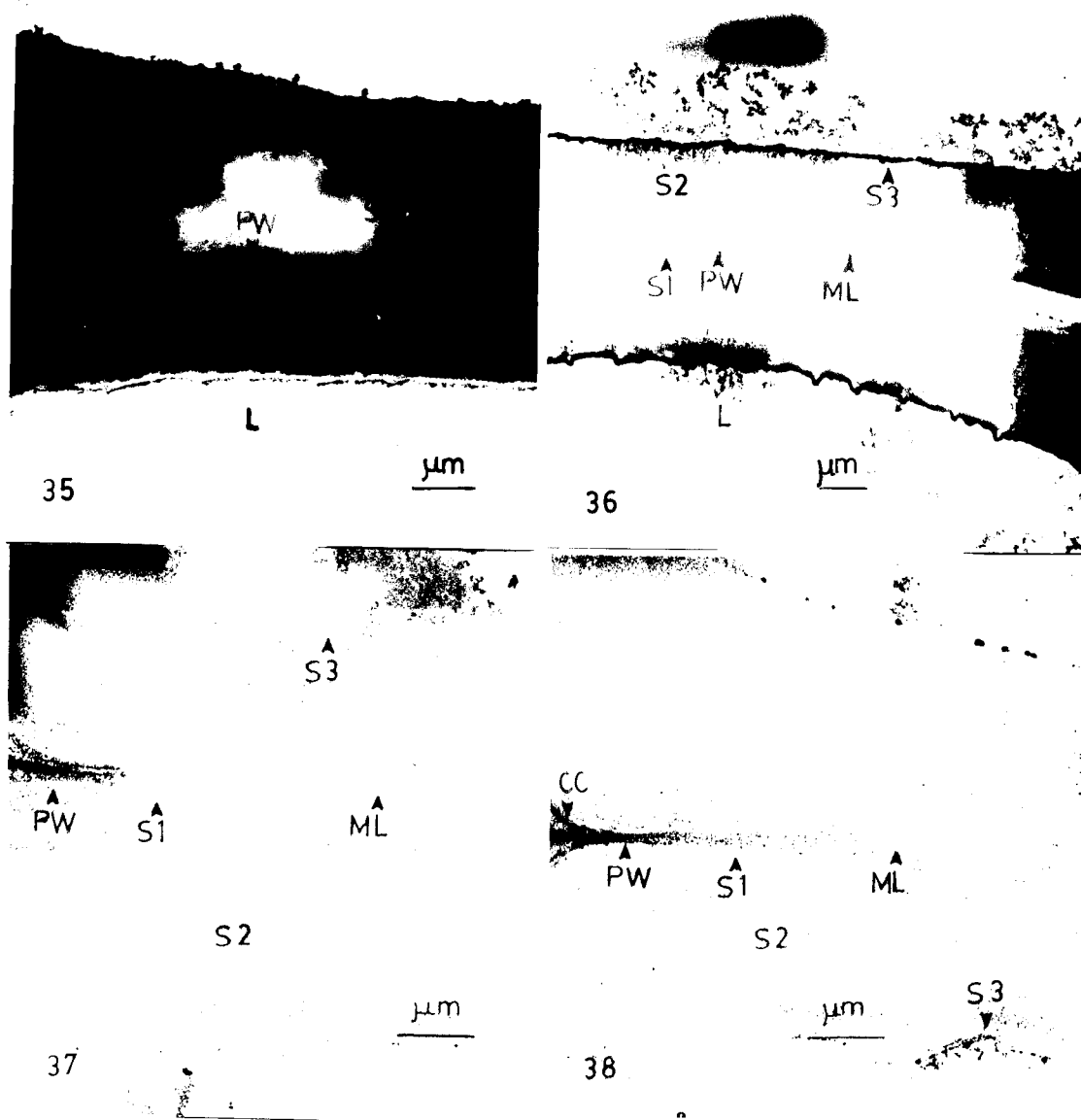(Note: CC – cell corner; ML – middle lamella; PW – primary wall; S1, S2 and S3 – secondary walls and   L – lumen.)

35

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Fig. 35   TEM photomicrograph of permanganate stained spruce wood along the radial wall.

Fig. 36   TEM photomicrograph of permanganate stained spruce wood, 48.8% delignified fiber, along the radial wall.

Fig. 37   TEM photomicrograph of permanganate stained spruce wood, 77.7% delignified fiber, along the radial wall.

Fig. 38   TEM photomicrograph of permanganate stained spruce wood, 87.1% delignified fiber, along the radial wall.

(Note: CC – cell corner; ML – middle lamella; PW – primary wall; S1, S2 and S3 – secondary walls and   L – lumen.)
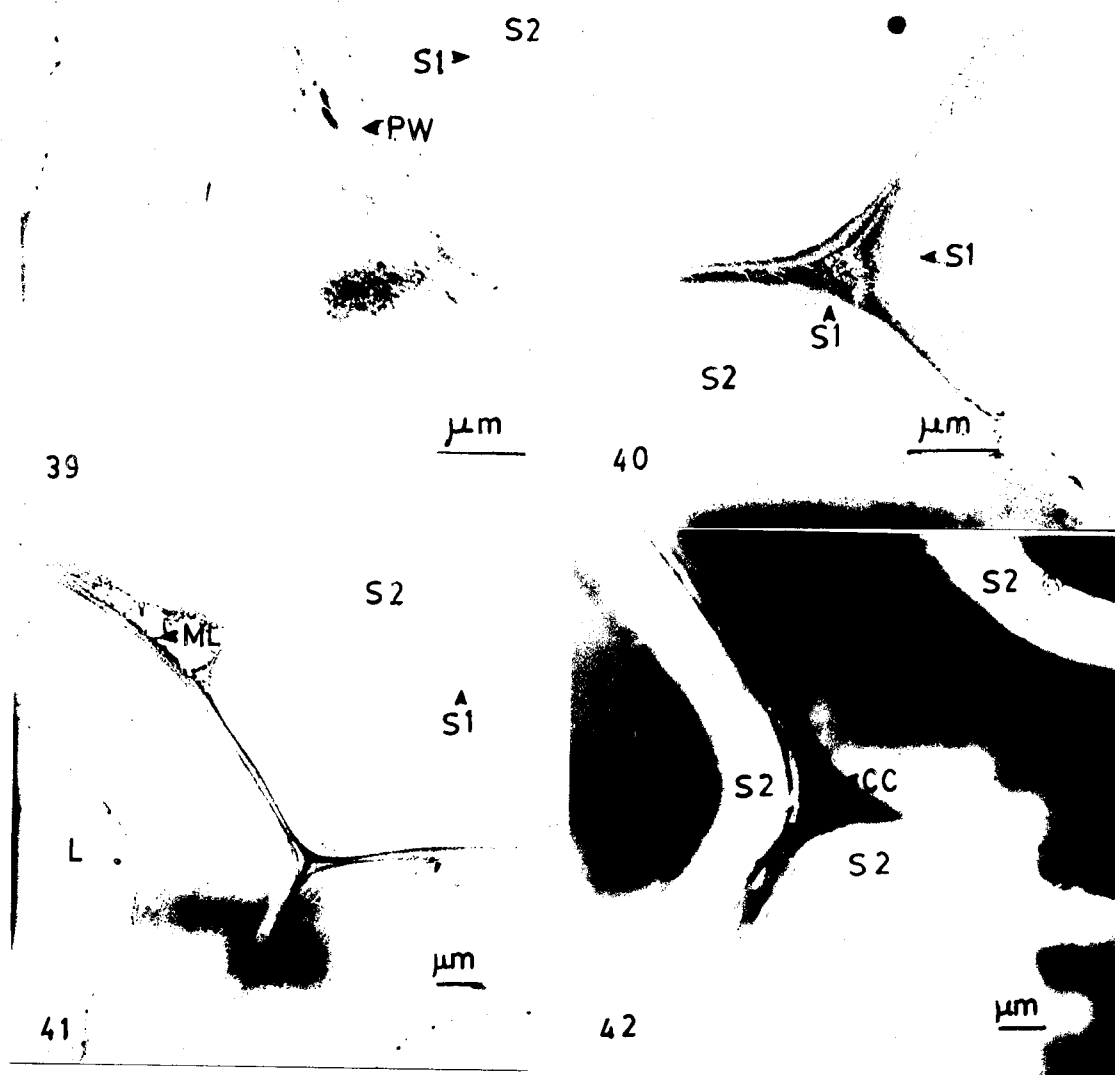
Fig. 39   TEM photomicrograph of permanganate stained spruce wood, 48.8% delignified fiber. Separation of primary wall from the rest of the secondary wall.

Fig. 40   TEM photomicrograph of permanganate stained spruce wood, 77.7% delignified fiber. Degradation of S_1 layer and separation of secondary wall from S_1, primary wall and middle lamella .

Fig. 41   TEM photomicrograph of permanganate stained delignified spruce wood fibers. Separation of secondary wall from the compound middle lamella at 87.1% delignification.

Fig. 42   TEM photomicrograph of 87.1% delignified fibers. Separation of fibers at cell corner and residual cell corner lignin.

(Note: CC – cell corner; ML – middle lamella; PW – primary wall; S1, S2 and S3 – secondary walls and   L – lumen.)
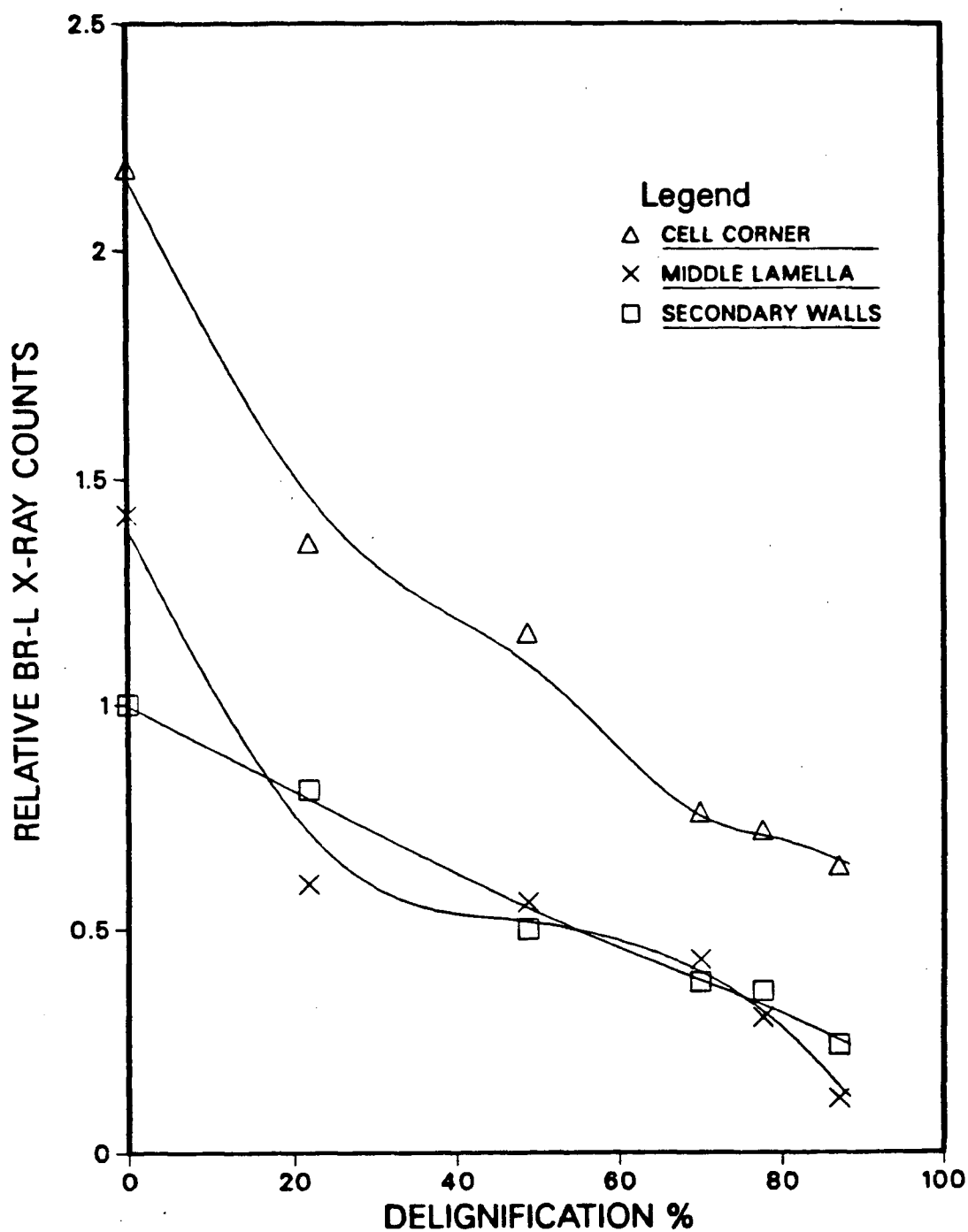
Fig. 43   Comparision of topochemical effect in different morphological regions of organosolv pulp fibers.

KRAFT **ACID SULFITE** **NEUTRAL SULFITE** **ACID CHLORITE** **ORGANOSOLV**
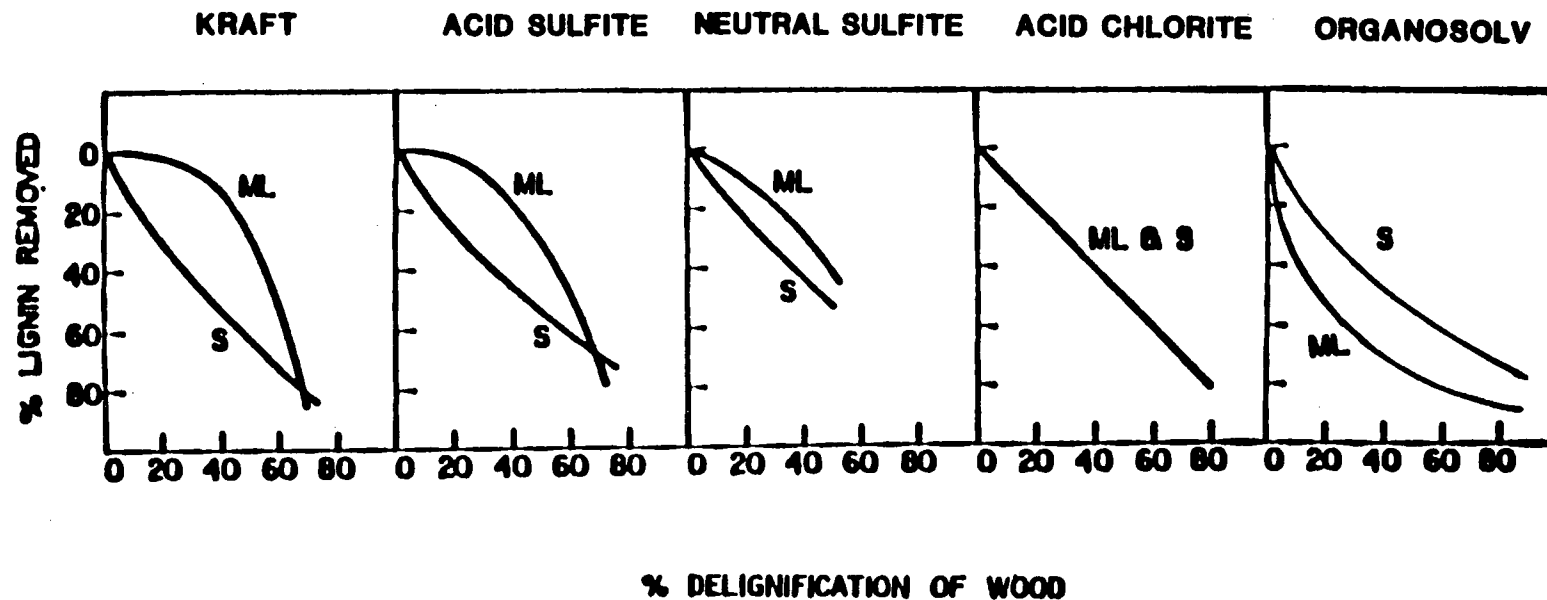
% LIGNIN REMOVED

% DELIGNIFICATION OF WOOD

Fig. 44   The percentage removal of lignin from the middle lamella
(ML) and secondary wall (S) as a function of percentage
delignification from kraft[1], acid sulfite[1], neutral sulfite[1], acid
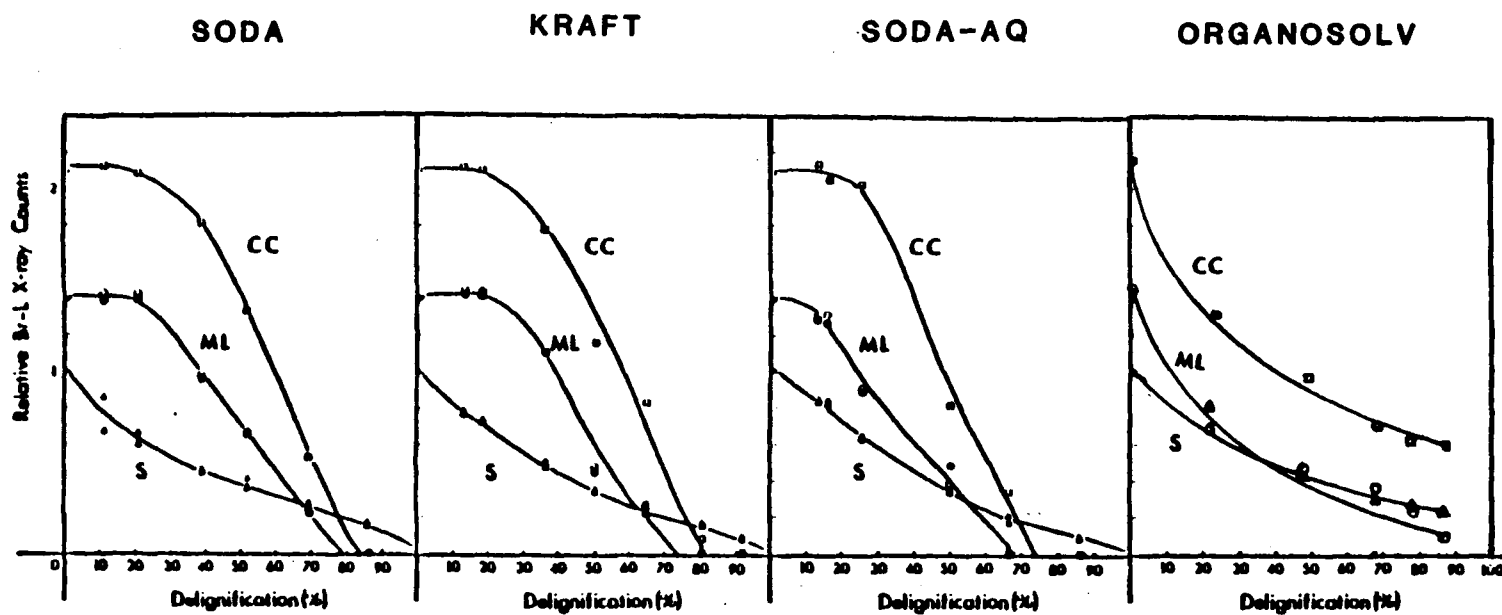chlorite[1] and organosolv pulping processes ([1] Wood *et al*. (110)).

Fig. 45   The topochemical effect of delignification in different morphological regions by soda[1], kraft[1], soda/AQ[1] and organosolv pulping process ([1] Saka *et al.* (86)). CC, ML and S respectively represent cell corners (◦), Middle lamella (◦ radial, ● tangential) and secondary wall (△ radial, ▲ tangential) regions.

Fig. 46   Change in fiber length distribution of organosolv pulps at three different yields.

100 min pulp

POPULATION DISTRIBUTION

mm	%	
0.00	4.42	----
0.20	8.86	--------
0.41	13.68	--------------
0.61	5.44	-----
0.82	4.03	----
1.02	3.21	---
1.23	3.03	---
1.44	3.08	---
1.64	3.19	---
1.85	3.60	---
2.05	3.58	---
2.26	3.89	---
2.47	3.98	---
2.67	4.17	----
2.88	4.07	----
3.08	3.87	---
3.29	3.77	---
3.50	3.60	---
3.70	3.52	---
3.91	3.20	---
4.11	2.95	--
4.32	2.27	--
4.52	1.83	-
4.73	1.06	-
4.94	0.72	
5.14	0.29	

80 min pulp

POPULATION DISTRIBUTION

mm	%	
0.00	11.44	------------
0.20	1.88	-
0.41	2.18	--
0.61	1.20	-
0.82	1.13	-
1.02	1.51	-
1.23	1.98	-
1.44	2.58	--
1.64	3.18	---
1.85	3.92	---
2.05	4.69	----
2.26	5.11	-----
2.47	5.37	-----
2.67	5.59	-----
2.88	5.77	-----
3.08	5.60	-----
3.29	5.25	-----
3.50	4.91	----
3.70	4.92	----
3.91	4.81	----
4.11	4.71	----
4.32	3.92	---
4.52	3.24	---
4.73	1.91	-
4.94	1.25	-
5.14	0.44	

40 min pulp

POPULATION DISTRIBUTION

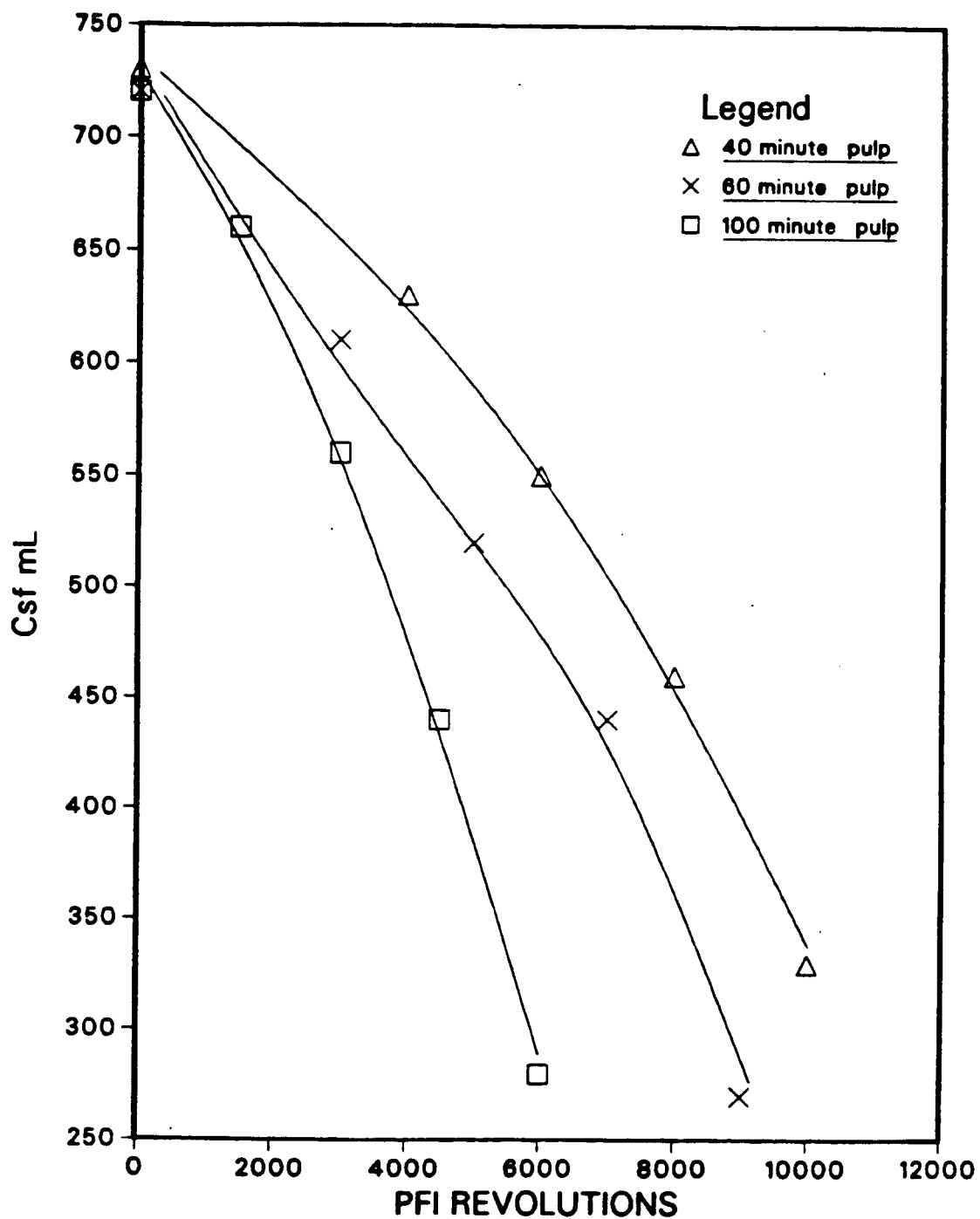| mm	%	
0.00	2.50	--
0.20	2.89	--
0.41	6.69	------
0.61	3.56	---
0.82	3.02	---
1.02	2.91	--
1.23	3.24	---
1.44	3.34	---
1.64	3.36	---
1.85	3.70	---
2.05	3.71	---
2.26	4.12	----
2.47	4.26	----
2.67	4.58	----
2.88	4.60	----
3.08	4.69	----
3.29	4.76	----
3.50	4.83	----
3.70	4.83	----
3.91	4.75	----
4.11	4.66	----
4.32	4.03	----
4.52	3.49	---
4.73	2.36	--
4.94	1.77	-
5.14	0.86	

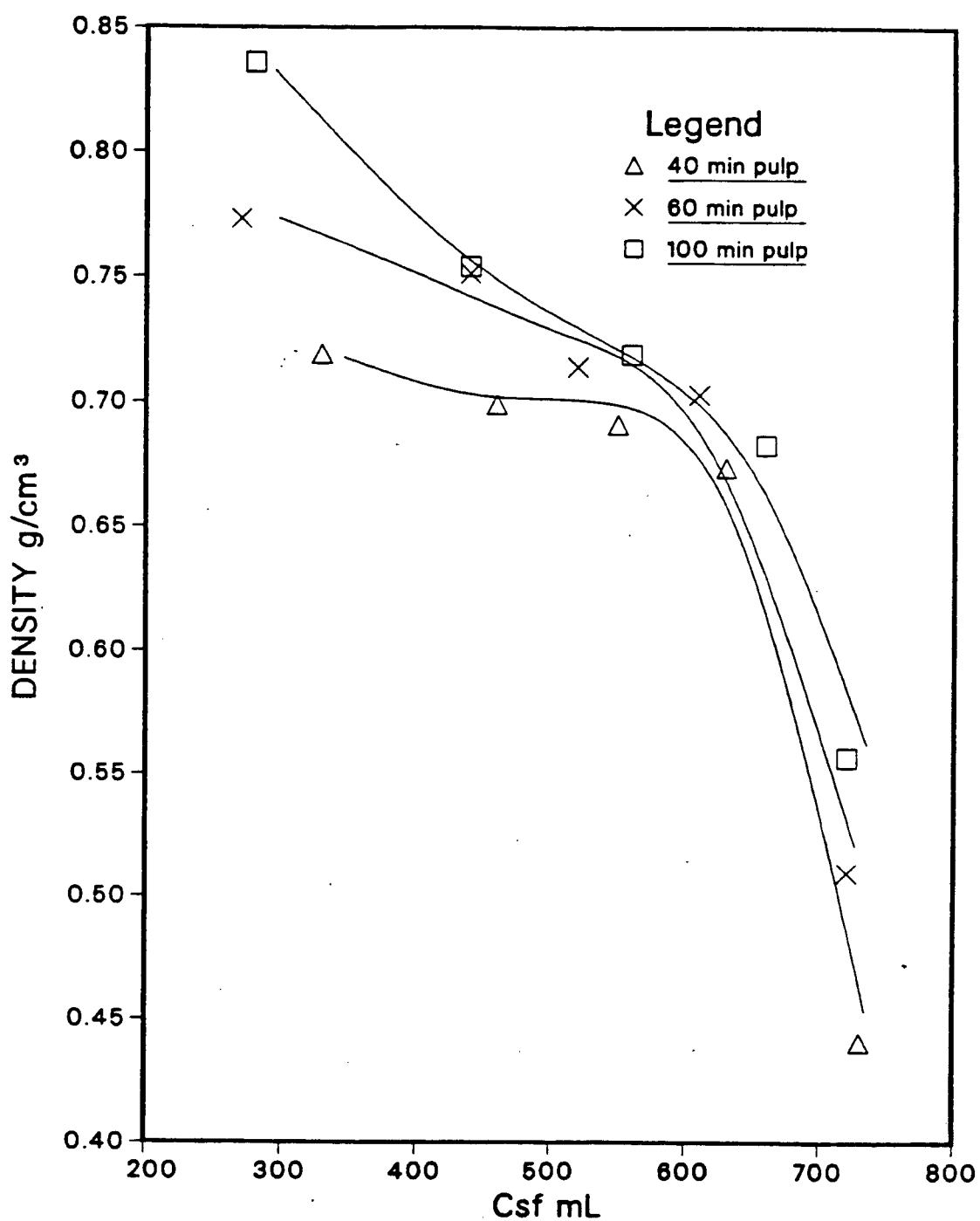Fig. 47   Freeness development of organosolv pulps of three different yields during PFI beating.

Fig. 48   Comparision of sheet density development of organosolv
pulps of three different pulp yields with decrease in freeness.
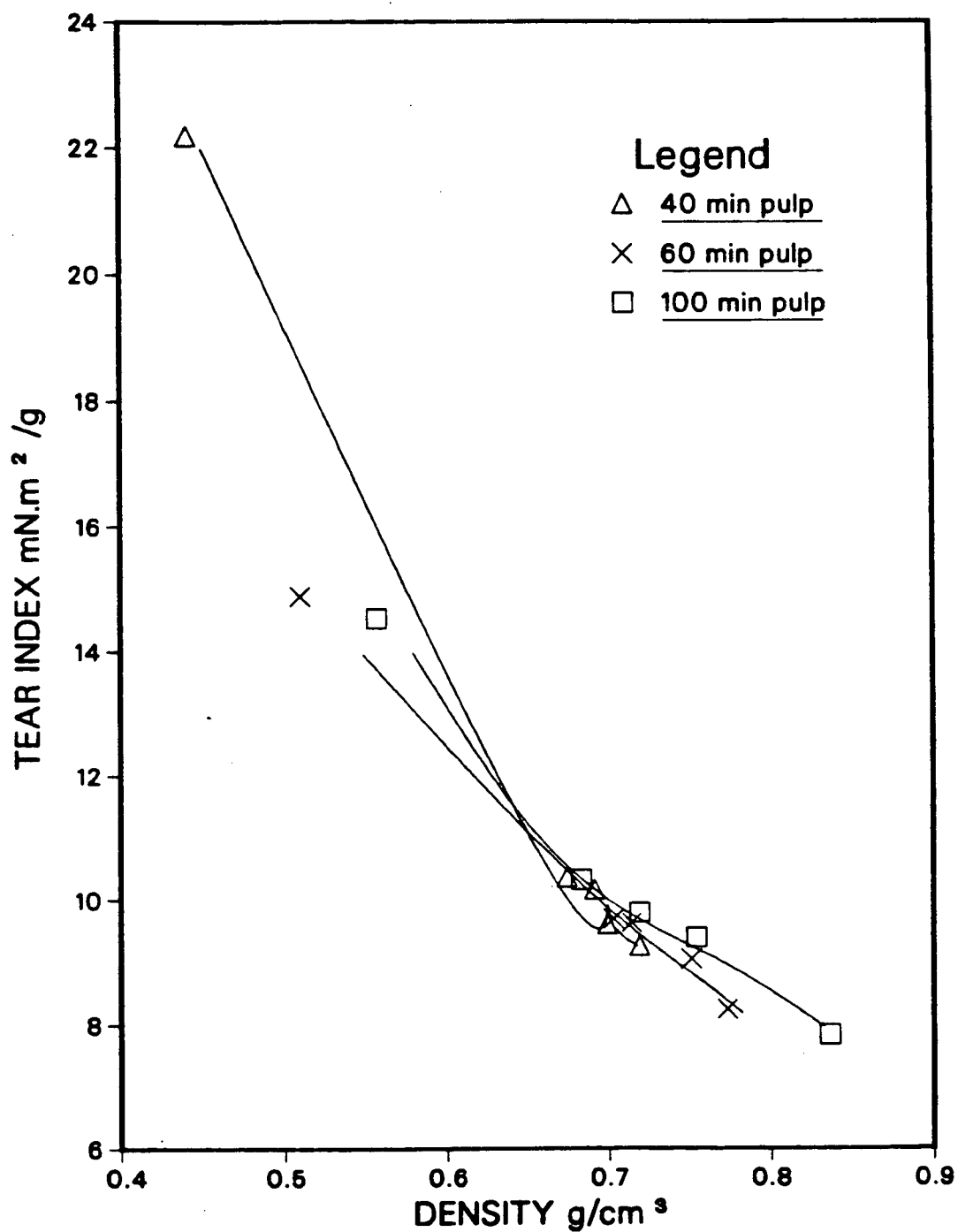
Fig 49   Effect of sheet density on tear strength of PFI mill beaten
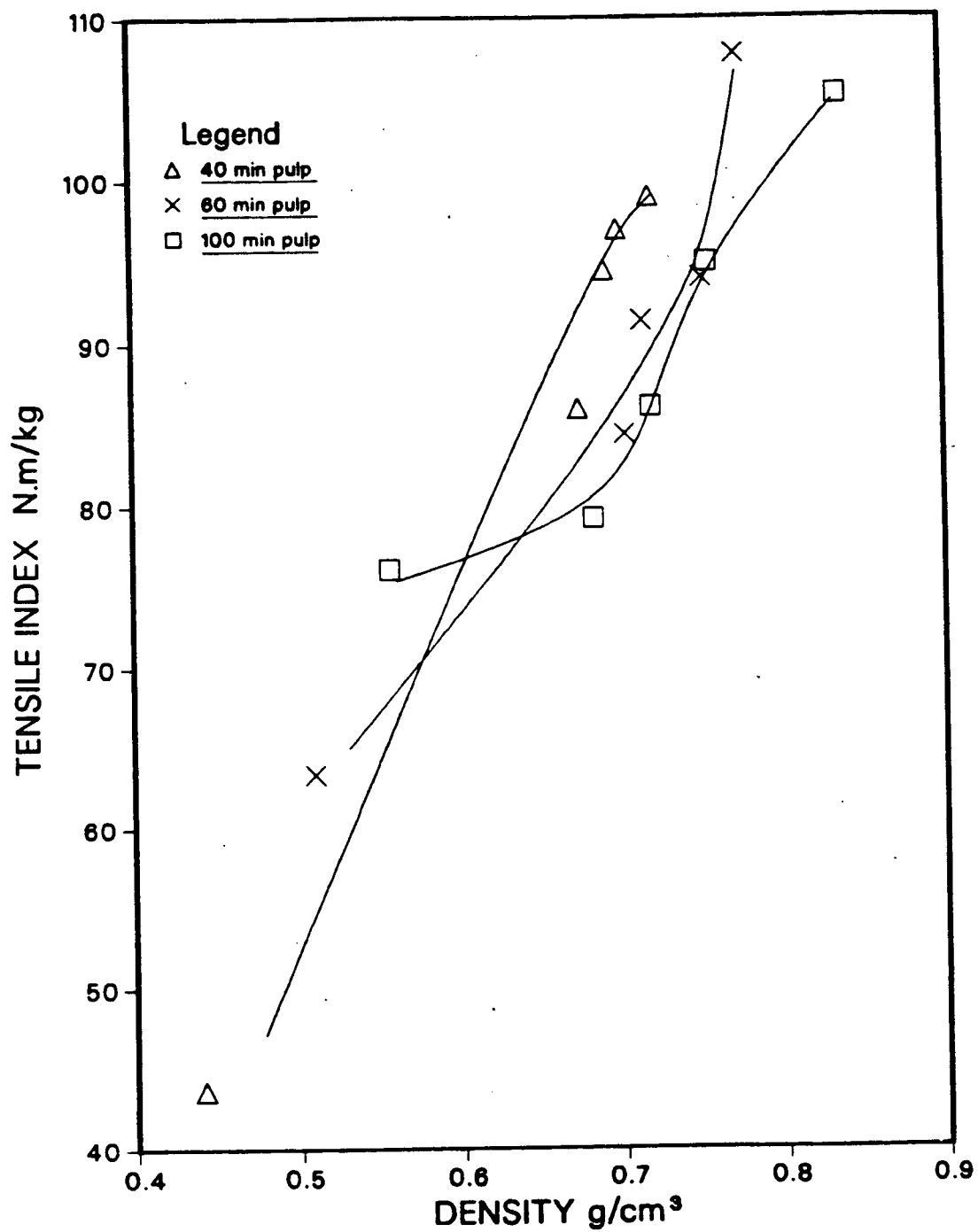organosolv pulps of three different yields.

Fig. 50   Effect of sheet density on tensile strength of PFI mill beaten organosolv pulps of three different yields.
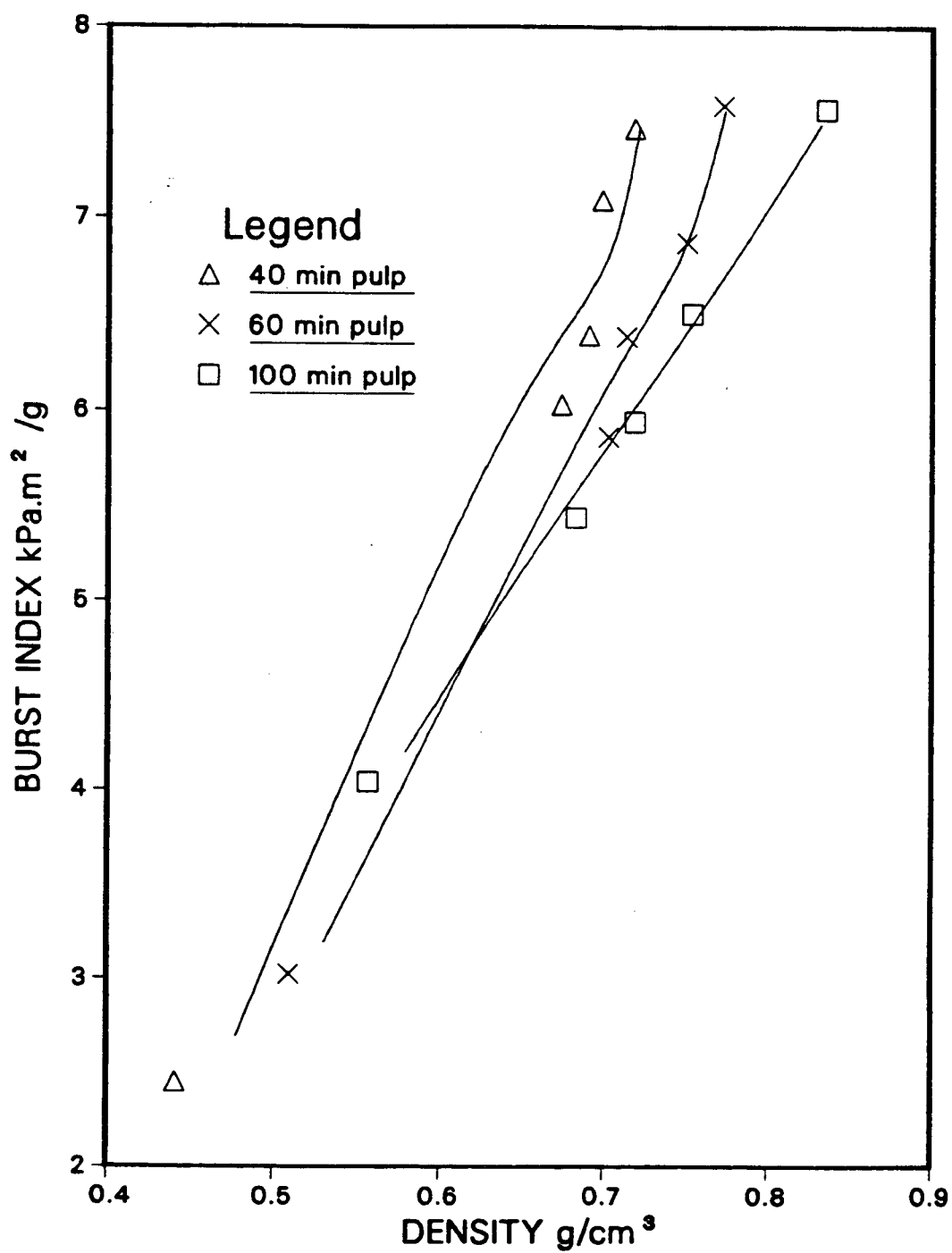
Fig. 51   Effect of sheet density on bursting strength of PFI mill
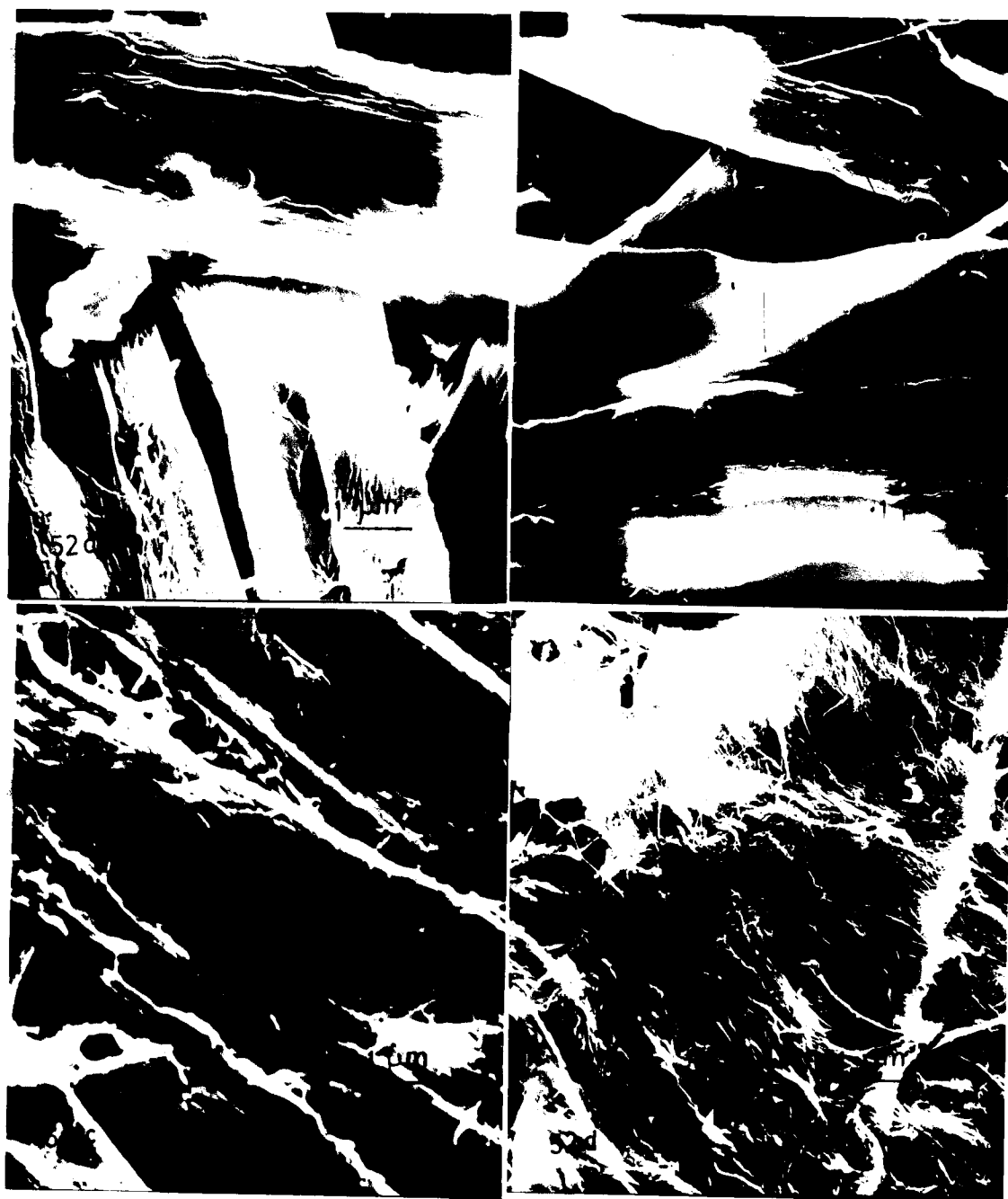beaten organosolv pulps of three different yields.

Fig. 52   SEM photomicrographs of unbeaten and beaten radiata pine kraft and organosolv pulps, 1000x. a. Unbeaten kraft pulp. b. Unbeaten organosolv pulp. c. Highly beaten kraft pulp. d. Highly beaten organosolv pulp (75c).
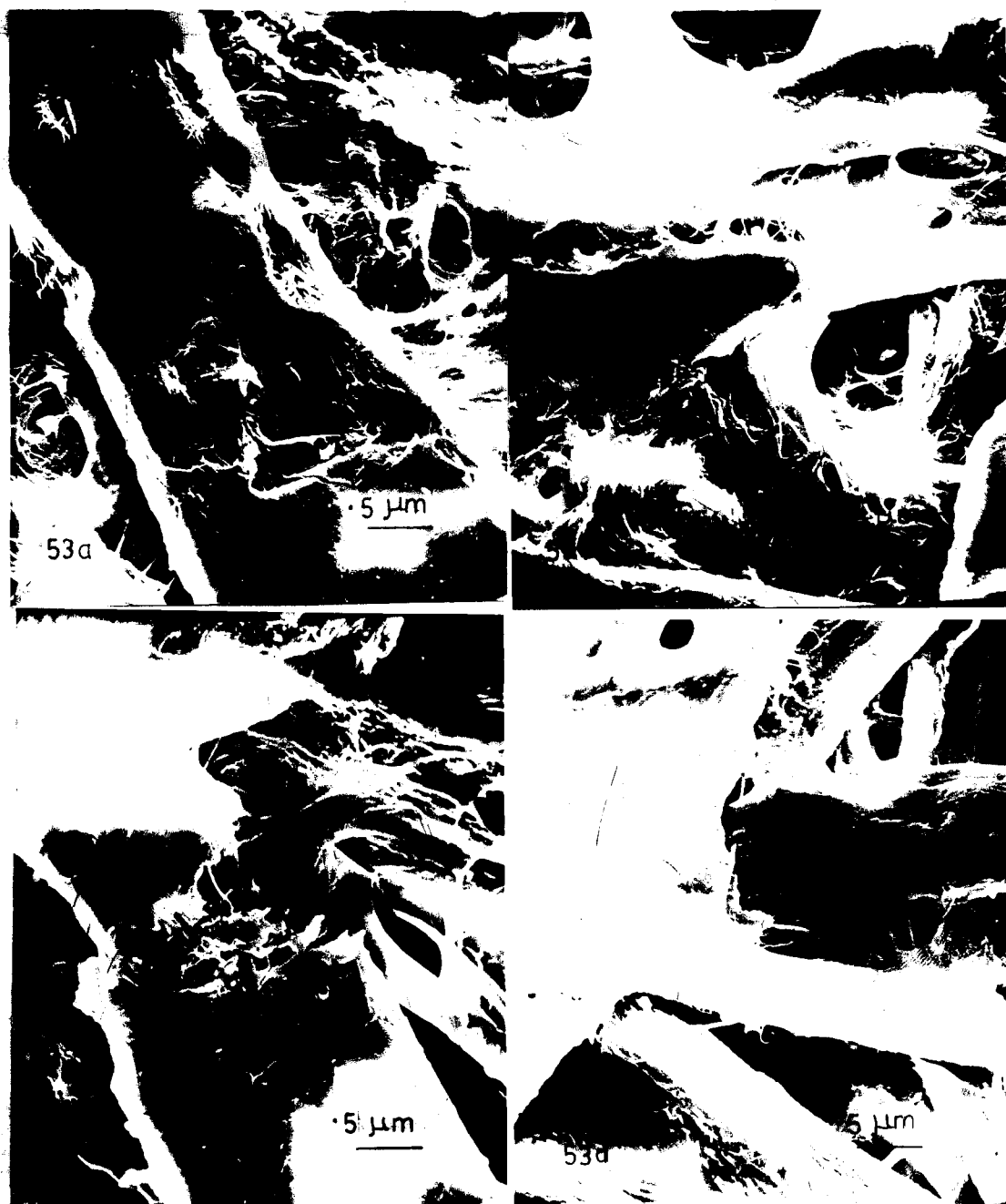
Fig. 53   Evidence of severe mechanical damage during beating on the
highly beaten radiata pine organosolv pulp fibers, 1800x (75c).

PUBLICATIONS

Paszner, L. and Behera, N.C. 1985. Beating behaviour and sheet strength development of coniferous organosolv fibers. Holzforschung 39(1): 51-61.

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In addition to the above publications, the following papers were presented in

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Antal, M., Paszner, L., Behera, N.C. and Micko. M. 1984. Influence of quarternary ammonium groups on mechanical properties of softwood organosolv pulps. TAPPI R&D Conf., Appleton, Wisconsin. Proc. 223-227 (Sept 30 Oct. 3,1984).

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Behera, N.C. and Basu, S. 1980. Studies on improvement of pulp strength by fiber fractionation and blending technique. APPITA Annual Conf.,1980, Melborne, Australia.