

ETHANOL PULPING OF EUCALYPTUS VIMINALIS WOOD AND CHEMICAL
CHARACTERIZATION OF THE PULPING SPENT LIQUOR

by

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ABSTRACT

GOMIDE, JOSE LIVIO. Ethanol Pulping of Eucalyptus viminalis Wood and Chemical Characterization of the Pulping Spent Liquor. (Under the direction of JOSEF S. GRATZL.)

Several single and multi-stage cooks of Eucalyptus viminalis wood were carried out using aqueous mixtures containing 45 percent (by weight) ethanol as pulping agent. Kraft pulps were also prepared for reference. In order to obtain well delignified ethanol pulps (kappa number 22.8) it was necessary to use at least six cooking stages. The ethanol pulps obtained were less susceptible to beating, had lower yields, and were considerably weaker than reference kraft pulps. This could be explained as the result of excessive degradation and removal of hemicelluloses during cooking. The ethanol pulp yielded about the same alpha-cellulose content, based on original wood weight, than kraft pulp. Dissolution of lignin and carbohydrates during ethanol pulping was investigated. Delignification was found to proceed in two phases, i.e., an initial rapid bulk delignification followed by a slow removal of the remaining lignin. The dissolved solids in the spent liquors were recovered and separated into a carbohydrate and lignin fraction. Xylose was found to be the major component in the hydrolysis of the carbohydrate fractions with arabinose, rhamnose, mannose, galactose, and glucose present in small amounts only. The lignin fraction was analyzed for elemental composition, methoxyl content and solubility in chloroform. Ultraviolet, IR, and NMR spectroscopy were employed for further analysis. The chemical composition of the lignin fraction of the spent liquors did not change significantly in different cooking stages. Analyses indicated that guaiacyl units comprised about 60 percent of the lignin monomeric units.

BIOGRAPHY

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1. INTRODUCTION

1.1 Importance of Eucalypts as a Pulping Material

The Eucalypts are a large genus of tree with more than 700 species most indigeneous to Australia and the islands off its northern coast. Eucalypts are broad-leaved, evergreen trees belonging to the family Myrtaceae. They are known for their extremely fast growth rate. Eucalypts can grow year-round with favorable environmental conditions and one of their major advantages is that many species coppice well, enabling several rotations to be grown without the need for replanting.

They have been planted widely in many parts of the world in the last 100 years. Extensive plantations of suitable species are cultivated in several countries, mainly Angola, Argentina, Brazil, Chile, India, Italy, Portugal, Spain, and South Africa. Only in recent years, however, has attention been directed toward the growing of eucalypts specifically for the pulp and paper industry. In Brazil alone, during the ten-year period from 1966 to 1976, close to 1,300,000 hectares were planted with eucalypts for production of pulpwood and manufacture of charcoal for the local metalurgical industries (1).

The earliest information on the pulping of eucalypts relates to the 1906 production of sulphite pulps from Eucalyptus globulus grown in Portugal (2). Systematic studies were begun in western Australia in 1916 and by 1921 it had been demonstrated that a pulp and paper industry based on eucalypts was a feasible proposition. Since then, numerous investigations have shown that eucalypts compare quite favorably with other hardwoods. However, it should be noted that a very wide range of wood and fiber properties within the eucalypt genus

makes any general statement of this nature subject to qualification with respect to species, wood quality, tree age, etc.

For a long time, hardwoods in general, and eucalypts in particular, were regarded by some papermakers as a rather inferior material, and even the term "filler pulp" was sometimes used to describe them. The situation, however, has now changed so that the virtues of the eucalypt pulps are becoming more widely recognized. The pulping of eucalypts is today pursued commercially in several countries around the world using different pulping methods, including kraft, sulphite, soda, cold soda, neutral sulphite, groundwood, and chemi-groundwood processes (2, 3). Brazil was one of the first countries to utilize eucalypts in the production of paper pulp and its utilization has expanded the Brazilian pulping industry greatly in recent years. Today, Brazil is the major producer of eucalypt pulps producing 777,000 tons in 1974 (4).

The difficulties encountered with the short eucalypt fibers in papermaking have been overcome. Today, some mills use 100 percent eucalypt pulp for practically all paper grades, including bond, offset, envelope, book, cartons, and other specialty papers for writing, printing, and packing (5).

It is interesting to read the conclusion of a Swedish investigation to determine the ideal pulp, or pulp combinations, for fine papers, from the standpoint of quality and economy: "the pulp of the future for fine papers will be eucalypt kraft" (6, p. 226).

1.1.1 Eucalypts in the United States

In the United States, eucalypts can be found in the southern regions, basically in Florida, Gulf Coastal areas, Texas, and California, but they only represent a very small and insignificant percentage of the total forest plantations in this country.

In California, eucalypts were first planted around 1900 and by 1920 their planting was quite heavily intensified. Today, an excess of 50,000 acres of old and mature eucalypts can be found in this state (7). They have been used mostly as fuel and only recently are being commercially utilized for manufacture of particleboard and hardboard. Eucalyptus globulus is the major species and its wood is characterized by its severe interlocked grain.

In Texas, eucalypts have been planted as wind breaks to protect citrus crops and, therefore, do not presently have potential for industrial utilization.

Eucalypts were first planted in Florida before the turn of this century but on a very small scale to obtain shade and shelter quickly from the intense seasonal winds. In the early 1960's, efforts were made to introduce exotic hardwoods for timber production in southern Florida. Today, pulpwood is the primary goal of limited commercial planting of eucalypts in Florida which comprises roughly 10,000 acres (7). A recent study on the pulp of eucalypts grown in Florida (E. tereticornis, E. grandis, E. robusta, and E. camaldulensis) reported that the quality of the eucalypt pulps were found to be comparable with those from native hardwood species presently used (8).

In the early 1970's, research to develop commercial planting programs for eucalypt pulpwood production in the Gulf Coastal areas of

the United States was intensified and mostly concerned with selection of the best species for this particular area. Recent emphasis in genetic improvement has been on improved growth rates, survival, and cold hardiness. Cold hardiness is of particular importance because the subtropical Gulf Coastal areas have more severe frost than comparable areas of Australia. The eucalypt plantations in the Gulf Coastal areas today comprise an area of about 1,00 acres (7). These studies are still in progress but early results indicate that E. macarthuri, E. viminalis, E. camphora, E. nitens, E. rubida, and E. nova-anglica have the most potential. These possess good relative frost-hardiness and the ability to grow on pine sites as fast or faster than the best hardwoods (9, 10). Among those species E. viminalis was clearly the fastest growing species and seems to be the most promising for a combination of growth and cold hardiness.

Generally, studies involving the planting of eucalypts in the United States have been successful and reports from a cooperative of pulp and paper industries indicate that the results "have been more encouraging than we dared hope" (11, p. 19).

1.2 Organosolv Pulping

Nearly 100 years ago the rudiments of the kraft process were worked out. By the 1920's, present day practice of the kraft process were well established and since then the only major changes have been in equipment improvement, such as the development of continuous digesters.

Overall, the industry is satisfied with the advantages offered by the kraft process. It is based on well-proven technology, it gives

a higher quality product than other pulping methods, it generates much of its own steam, it recovers its chemicals with a high efficiency, it utilizes a variety of wood sources, and, with resinous softwoods, also yields valuable by-products such as turpentine and tall oil. Thus, it is not surprising that today kraft pulping is the dominant chemical pulping process.

However, kraft pulping presents some serious disadvantages which the pulping industry has been unable to overcome. The most significant of these are its pulp yield limitations, pollution of the atmosphere with volatile reduced sulphur compounds, the need to process its aqueous effluents, a high requirement of expensive bleaching stages and chemical to reach a given brightness, and an extremely high investment cost per ton of product. Those problems seem to lack a practical or economical solution and although the pulping industry has heavily invested in "add on" technologies the results have been only partially successful. For example, the air pollution problem in a kraft industry resulted in process modifications and utilization of very expensive pollution abatement equipment. These changes have not been completely successful. The problem of pollution abatement can be better understood when one considers that the kraft mill odors are not emitted from a single point at the mill, but are generated at a number of locations. Any single process modification can therefore curtail emissions from only a part of these sources. Also, although the amount of organic sulphur compounds usually formed during pulping is very small, being only a few pounds per ton of pulp, they create a pollution problem because they have a very low odor threshold (as low

as a few parts per billion). It will be a formidable, if not impossible, task to maintain the ambient air concentrations in kraft mill areas below such values at all times.

In recent years there has been a growing interest in seeking new pulping alternatives to the kraft process. Nearly every major research laboratory in the paper industry is engaged in evaluating some new aspect of pulping technology aimed at either modifying the present kraft process or completely replacing it with a new process. While the kraft process is still without a strong challenger, some potentially promising alternatives are beginning to emerge.

In view of the problems associated with kraft odor abatement, considerable research on non-sulphur chemical pulping methods have been conducted during the last few years. A large variety of non-sulphur alternatives have been proposed, such as soda-oxygen, nitric acid, chlorine dioxide, peracids, etc. but most of the methods did not lend themselves to viable commercial processes. At present, the soda-oxygen and a rapid-cycle nitric acid processes seem to have a good chance for introduction into large scale production (12, 13, 14). Soda-oxygen pulping is presently in pilot stage development. In both processes, however, it is necessary to somehow recover the inorganic chemicals. In the soda-oxygen process lignin is burned. The nitro-lignin from the nitric acid process may possibly find some use as a fertilizer, but it seems doubtful that large amounts can be marketed for this purpose (15).

In the early 1970's, efforts were begun to search for a sulphur-free pulping process in which recovery of inorganic chemicals was not

necessary, and which would give a lignin better suited for further utilization than are kraft lignin or lignosulfonic acids. Lignin can be expected to be in strong demand since non-renewable organic raw materials will become more expensive, while wood, in contrast, is one of the major renewable resources.

Worster suggested that the following criteria must be met for any future process that might challenge the dominance of kraft pulping (16):

- a) Be free of inorganic sulphides capable of forming reduced sulphur (odoriferous) compounds.
- b) Not require strong acids or alkalis which would degrade cellulose or hemicellulose and, consequently, provide low yields.
- c) Capable of solubilizing most of the lignin or chemically modifying the lignin so that it can contribute to the desired end-use properties with very little loss of cellulose and only a modest loss of hemicelluloses.
- d) Does not use multiple stage nor significantly higher pressures, temperatures, and times than current chemical processes.
- e) Uses an efficient and more simple chemical recovery than the kraft process without creating unsafe conditions.
- f) Not cause environmental problems.

Among several new pulping methods investigated in recent years with the potential to replace the kraft process, the organosolv processes have been seriously considered. In those processes an organic solvent is used as the pulping liquor and, therefore, the criteria suggested above by Worster are likely to be achieved. The

degraded lignin and carbohydrates in spent liquor would be expected to be recovered without major problems for further utilization. Several organosolv pulping methods have been investigated using the following solvents: dioxane, ammonia-ketone, phenol, dimethylsulfoxide, n-butanol, alkali methanol, and ethanol.

Delignification of wood with dioxane-water has been reported in the literature by either using a low temperature treatment of 100°C (17) or a higher temperature of 180°C (18). In those studies the hydrolysis of lignin by dioxane-water was analyzed and the degradation products identified but no pulping experiments were conducted.

DeHaas and Lang have reported the development of a non-oxidative pulping process for producing high yield pulps using ketones and ammonia mixtures in pulping (19). In their work, douglas-fir, lodgepole pine, and ponderosa pine were delignified using ketone in the presence of ammonia and water to produce pulps in the 55-68 percent yield range. The ketone-ammonia process produced pulps that were generally up to the level of high-yield unbleached kraft pulp (53 percent yield) except for tear strength. Typical ketones used in this process were methyl ethyl ketone, cyclohexanone, and acetone. The disadvantage of this process is it uses high temperatures (210°C), which means it cannot be adapted easily to present equipment. As with all the solvent chemical pulping processes, the pulping chemicals can be recovered for reuse and lignin can also be recovered from the spent liquors.

Schweers in 1974 proposed delignification of wood using phenol as a pulping agent (15). In this study using pine and beech, he

analyzed different pulping conditions including temperature (140-170°C), pressure (1-8 atm), time (2-3h), and acid catalysts (sulfuric, phosphoric, acetic, hydrochloric, oxalic, and methanesulfonic acids). He also verified the possibility of reusing the pulping liquor and a mixture of phenol, guaiacol and p-cresol, which are obtained in the pyrolysis of phenol lignin. He was able to produce a variety of pulps with kappa numbers ranging from 19 to 143. From the results obtained, he concluded that phenol pulping offers a new choice in unconventional pulping.

The use of dimethyl sulfoxide (DMSO) as a delignifying agent has been discussed by Fisher and Wienhaus (20). More recently, in 1977, a patent was granted to K. Uzo covering the use of DMSO as a pulping agent (21). According to that source, a high temperature (120±20°C) solvent cook (DMSO) is used to manufacture pulp from wood chips. It is claimed that the advantages of such solvent cooking are to decrease the damage to cellulose and hemicelluloses, and to allow extracting the organic soluble materials in a concentrated form which in turn minimizes the volume of waste materials.

Delignification of southern yellow pine meal with a 50:50 n-butanol-water solution for 4, 8, and 12 hours at 174° and 205°C in laboratory scale was recently reported (22). This mixture was found to be an effective delignification agent. The study concentrated on the mechanism of delignification. A mathematical model was proposed to represent the kinetics of aqueous n-butanol delignification of southern yellow pine. However, no experiment with commercial size wood chips was performed, but some comments were made concerning the kinetics of delignification of such larger size materials.

Japanese researchers have studied the use of alkali-methanol as a delignifying agent for a pollution-free pulping method (23, 24). The authors recommended cooking the wood chips for 30-60 minutes at 160°C in a liquor consisting of 40g NaOH and 400g methanol per liter of liquor. They claimed this pulping method results in more rapid delignification and 4-5 percent higher screened yield than the kraft method. The alkali-methanol pulp was reported to have the same sheet strength as a kraft pulp, except tear factor, when compared at the same lignin content. The process does have the disadvantage of using large amounts of NaOH (approximately 200 Kg/ton wood). This would require a recovery system, consequently making the isolation of lignin and carbohydrate by-products practically unfeasible. On the other hand, it has the advantage that it requires less energy to concentrate the spent liquor and that some methanol is generated from lignin and hemicelluloses during cooking.

Among the organosolv processes, pulping with ethanol has been studied most intensively. It seems to have the greatest potential of becoming economically feasible. Most of the ethanol studies have been conducted by Theodor N. Kleinert.

1.2.1 Ethanol Pulping

Alcohols, including ethanol, have been used as delignifying agents for more than 50 years. Their early studies were concerned with the isolation, structure, and properties of lignin. Phillips cites a large number of studies dealing with this subject (25).

In 1931, Kleinert and Tayenthal (26) investigated the action of aqueous ethanol, with HCl as catalyst, on carbohydrates and lignin at

different temperatures (180-190°C), ethanol concentrations, and reaction times (2-6.5 hours). They obtained high yields of cellulose with a low lignin content. A strong delignifying effect was found when mixtures of water and the lower aliphatic alcohols were used (27).

These findings were substantiated by Aronovsky and Gortner in 1936 when they studied the delignifying action of different aqueous alcohols (28). The normal primary alcohols were found to be better pulping agents than the secondary and tertiary alcohols. The authors suggested that an alcohol must have apparently at least four carbon atoms, three of them in a straight chain, in order to produce a well-pulped residue by a treatment with 50:50 alcohol-water mixtures at 158-186°C for 1.5-5 hours. Aspen chips cooked with n-butanol alcohol yielded a pulp comparable to commercial aspen soda pulp with regard to strength characteristics. They also observed that coniferous woods were not pulped by buthyl alcohol as readily as aspen. The pulping effluent consisted of two layers. The top alcoholic layer contained the degraded lignin extracted from the wood (29).

In 1967 Kleinert investigated the kinetics of the delignification of beech wood (sawdust and chips) by ethanol-water (30). Two different delignification processes, both approximately first order reactions, were found: a relatively fast bulk delignification followed by a slow residual delignification, the latter resulting in considerable cellulose losses. He also noted that rates of bulk delignification in a flow-through autoclave were higher than in a stationary batch system. He explained these latter findings as a result of the higher ratio of

liquor to wood and of the continuous removal of reactive degradation products from wood during pulping.

In 1971, a patent was granted to T. N. Kleinert for a pulping process that utilizes volatile solvents, including lower aliphatic alcohols and ketones (31). The preferred pulping agents were specified as aqueous mixtures of ethanol in the range between 20 and 75 percent ethanol by weight. The subdivided fibrous plant material was cooked in a counter-current manner at temperatures preferably between 170° and 195°C. This patent disclosed some detail of the pulping operation, the continuous digester system, and the recovery cycle of ethanol including also recovery of lignin and sugars. The properties of washed and screened pulp obtained from aspen chips using aqueous ethanol (45.8 percent by weight) were comparable to pulps produced by conventional processes.

In 1974 Kleinert (32) conducted further studies on ethanol-water pulping, using sawdust of spruce and poplar. He observed that delignification of hardwoods was about twice as fast as that of the softwood. He also found that delignification was considerably faster in the very early stage of the cook where considerable losses of carbohydrates also occurred. Although ethoxyl groups were expected to be taken up by lignin, no ethoxyl was found in lignin preparation isolated from spent liquors. The explanation given was that the ethoxyl-lignin bonds formed at elevated temperatures are cleaved again under relatively mild conditions. Ethanol in the spent liquors was nearly quantitatively recovered and only about 0.5 to 0.7 percent, based on wood, were lost. Kleinert also conducted experiments with

commercial size hardwood and softwood chips using a vertical digester with a flow-through system to simulate a continuous operation. The cookings were carried out at 185°C for 30-60 minutes using an aqueous mixture of 45 percent (by weight) ethanol content. The screened yields ranged from 54 to 55.9 percent and the strength properties were comparable to bisulfite pulps produced from the same woods.

More recently, Kleinert (33) investigated the influence of wood moisture on the rate of delignification. It was observed that, in general, removal of wood moisture decreased the rate of delignification. It is interesting to note that even wood specimens air-dried to about 30 percent moisture content showed a lower rate than freshly cut wood (about 10 percent lower).

Summarizing the results available in the literature, the ethanol pulping process has the following characteristics (28, 33):

- a) Four to 4½ higher pulping yield than kraft, due to higher carbohydrate retention.
- b) Pulp strength is lower than kraft pulps but approximately in the same range as soda and bisulfite pulps.
- c) Relatively short cooking cycles.
- d) Ethanol does not seem to be consumed during pulping and can, therefore, be almost totally recovered.
- e) Reductions in investment costs up to 20 percent, when compared to those of conventional kraft mills of the same production capacity.
- f) Costs of stream pollution abatement are greatly reduced or completely eliminated.

4. RESULTS AND DISCUSSION

4.1 Chemical Analysis of Eucalyptus viminalis Wood

The chemical composition of the E. viminalis wood was studied using air-dried, screened, and benzene-ethanol extracted wood meal. All tests were carried out in duplicate. The results obtained are listed in Table 4.1 (page 18).

Holocellulose content was determined by delignifying wood meal with sodium chlorite. Alpha-cellulose content was determined by treating the holocellulose fraction with 17.5 percent NaOH (Tappi Standard T203 os-74). The alpha-cellulose content was 43 percent, indicating the potential for obtaining satisfactory bleached pulp yields.

Klason lignin content was determined by the 72 percent sulfuric acid method, according to Tappi Standard. The lignin content of 26.0 percent was within the normal range for hardwoods.

In the course of Klason lignin determination, some portion of the lignin is dissolved by the acid and, consequently, the observed lignin content is lower than the actual amount of lignin present in wood. The correction for acid-soluble lignin is very important, especially for hardwoods. In E. viminalis the acid-soluble lignin (3.9 percent) was found to be relatively high, comprising more than 13 percent of the total lignin. Details about determination of the acid-soluble lignin are given in the Experimental Section. A formula reported by Goldschmid (36) was used.

Although some eucalypt woods have a high extractive content, this species gave only 1.9 percent of solubles in alcohol-benzene (Tappi

Standard). One explanation for such low value might be the age of the trees which were only 3-4 years old and with little hardwood formed. This particular species is known to have a characteristic low extractive content. Eleven-year old E. viminalis, grown in Brazil, for instance, is reported to have 1.6 percent alcohol-benzene solubles (4).

The ash content was relatively low (0.6 percent). This is still within the normal range for hardwoods.

The acetyl content was determined using the method reported by Whistler and Jeanes as described by Timell (35) and presented in the experimental section. The acetyl groups play an important role during ethanol pulping. During cooking, they are hydrolyzed and the acetic acid generated acts as a catalyst for lignin and carbohydrate degradation. The amount of acetyl groups in E. viminalis wood was 2.2 percent, compared to 3 to 5 percent usually found in hardwoods.

4.2 Pulping Studies

Air-dried chips of E. viminalis wood were pulped using aqueous mixtures containing 45 percent (by weight) ethanol and methanol. Kraft cooks were carried out for reference.

4.2.1 Reference Kraft Pulping

Kraft cooks were performed using different active alkali charges. The cooking conditions are described in the experimental section. Kappa numbers and screened yields obtained are presented in Table 4.2 (page 20) and Figure 4.2 (page 38). The yield vs kappa number curve exhibited the typical pattern for a kraft cook with an abrupt decrease

in yield when the chips were cooked to kappa numbers below 20. A relatively high screened yield of 48.5 percent was obtained for pulps cooked with 13 percent active alkali to kappa number 22.5. This screened yield was about 6 percent higher than the total yield reported in the literature for water oak (Quercus nigra) pulped to the same kappa number by the kraft process (37).

In order to obtain sufficient pulp for handsheet testing and chemical analysis, eight additional kraft cooks were carried out using 13 percent active alkali. The cooked chips from the eight cooks were mixed together before defibration and screening. The mixed pulp gave a higher kappa number (25.5) and higher screened yield (51.2 percent). This may be due to the shorter cooking time and to the decrease in losses due to defiberizing and screening larger amounts of pulp.

The handsheet properties of the reference kraft pulp are presented in Appendix Table 10.1. In Figures 4.4-4.8 sheet properties were plotted against corresponding freeness values. In general, the strength properties of kraft pulp produced from young E. viminalis wood was found to be only slightly lower than those for water oak except for tear strength which was about 50 percent lower (37).

Since the E. viminalis wood used for this study came from 3-4-year-old trees, its morphological characteristics should be those of a juvenile wood. Better pulp qualities with higher strength properties will probably be obtained if older and mature trees are used.

4.2.2 Single-Stage Alcohol Pulping

A series of cooks with aqueous mixtures 45 percent (by weight) ethanol or methanol content was made using eucalypt chips. The cooks were carried out at a maximum temperature of 185°C using a liquor/wood ratio of 10/1. Yields and kappa numbers obtained, together with cooking times, are presented in Table 4.3 (page 23). Due to a malfunction of the heating system, the time required to reach 185°C was considerably longer (3.3 hours) for some cooks.

The pulps obtained had high lignin content and yields were very low. The lowest kappa number obtained was 53.4 with a corresponding yield of 41.4 percent after 5.7 hours of pulping. The results also showed that an increase in cooking time resulted in lower kappa numbers and yields for both ethanol and methanol pulps.

Comparing ethanol and methanol, at the same cooking conditions, ethanol was found to exhibit better delignifying properties. This observation is in accordance with Aronovsky and Gortner (28) who reported that a relationship exists between the straight-chain length of carbon atoms of alcohols and their pulping characteristics. They reported that an increase in the chain length results in better delignification and in lower yields.

In general, both ethanol and methanol did not give good results with a liquor/wood ratio of 10/1 in batch process at 185°C. Since somewhat better results were obtained with ethanol, further experiments were conducted with this alcohol.

To investigate the influence of the dilution factor upon ethanol pulping, a set of experiments was performed using different liquor/wood ratios (10/1, 20/1, 40/1, and 80/1). A higher dilution factor

would be expected to result in stronger delignification since it would lower the concentration of possible condensation prone structures and improve dissolution of degraded lignin fragments. The results are presented in Table 4.4 (page 25). It can be seen that higher dilutions resulted in better delignification. Although higher dilutions combined with long cooking times were used, the pulp yield was low (below 40 percent) and the pulps had relatively high kappa numbers. The lowest kappa number obtained was 32.8 and to achieve this rather moderate delignification, it was necessary to use a liquor/wood ratio of 80/1 and a total cooking time in excess of five hours. Even using more favorable pulping conditions, the ethanol-water mixture was not found to be an effective delignifying agent in batch type pulping.

In all previous experiments, the autoclaves were cooled with tap water at the end of the cook. The temperature drop was assumed to cause precipitation of dissolved lignin fragments. Consequently, one would expect to obtain pulps with higher lignin contents. In order to avoid such precipitation, a cook (referred to as B) was performed. In this case the spent liquor was removed immediately at the end of the cook. Pulping conditions, yields, and kappa numbers are listed in Table 4.5 (page 26). Cook B resulted in a pulp with lower kappa number and yield. The decrease in kappa number, however, was not substantial when compared with a cook carried out using similar conditions but without the immediate removal of spent liquor (cook A). Some precipitation of lignin on/in the fibers seems to occur during cooling when the spent liquor is in contact with the

chips. However, precipitation cannot be solely responsible for the high lignin content of ethanol pulps since ethanol-water has been demonstrated to be a good delignifying agent (32). A reasonable explanation seems to be condensation between lignin degradation products which are favored in batch type cooks.

Long cooking times seemed to be responsible, at least in part, for the low yields obtained in ethanol pulping. In order to verify that assumption, a cook was performed using an electrically heated autoclave. The heating-up period was decreased to 0.75 hour and time at maximum temperature was considerably shortened. The pulping conditions employed in this cook (referred to as C) and the results obtained are also shown in Table 4.5. Cook C showed that using relatively short heating-up periods and cooking times did not result in lower kappa number pulps or improved yields. The chips were incompletely delignified (kappa number 119) and difficult to defiberize. Yield was not determined because of the poor pulp characteristics.

Based on the results, it was concluded that batch-pulping using 45 percent aqueous ethanol at 185°C results in pulps with inferior strength properties. Ethanol-water mixtures, however, were reported to be effective delignifying agents in continuous digesters at 185°C (30, 31, 32, 33). In a continuous digester, it seems that the reactive lignin degradation products are removed as soon as they are formed, thus avoiding excessive condensation reactions. Since an apparatus allowing continuous pulping experiments was not available, it was decided to conduct experiments in a multi-stage fashion to simulate continuous pulping.

4.2.3 Multi-Stage Ethanol Pulping

Multi-stage ethanol pulping was studied up to six cooking stages using an aqueous mixture 45 percent (by weight) ethanol content at different temperatures. The objective was to produce bleachable grade pulps with kappa numbers around 25 with optimum yields.

4.2.3.1 Pulping Apparatus

A schematic diagram of the apparatus used for multi-stage ethanol pulping studies is shown in Figure 4.1 (page 29). Basically, the apparatus consisted of a nitrogen tank, three autoclaves (referred to as Transfer Vessel, Pre-Heater, and Digester), a condenser to recover the spent liquor, and a 500-ml Erlenmeyer flask to collect the spent liquor. The components of the system were connected by stainless steel pipes equipped with the appropriate valve system. For cooling the hot spent liquor, an efficient stainless steel water condenser was used.

The chips were charged in the digester which was then tightly closed. A pre-measured amount of ethanol-water mixture was drawn into the evacuated transfer vessel and then transferred to the pre-heater using pressurized nitrogen. In the pre-heater, the cooking liquor was heated to the desired pulping temperature before being transferred to the digester. During the treatment in the digester, fresh pulping liquor was introduced through the transfer vessel into the pre-heater and heated to the desired pulping temperature. At the end of the first stage the spent liquor was released through the condenser and collected in the 500-ml Erlenmeyer flask. This sequence of operation

was repeated as many times as was necessary to obtain multi-stage cooking.

After completion of the multi-stage treatment, the chips were washed. Washing consisted of transferring the hot cooking liquor from the pre-heater to the digester and fast removal of the liquor from the digester through the condenser. The spent liquors were stored at room temperature for future characterization.

Immediately after completion of the washing operation, the digester was removed from its heater, cooled with tap water and opened. Due to the small amount of chips used for cooking, defiberization was carried out in a laboratory disintegrator described in Tappi Standard (T205 os-71). Total yields and kappa numbers were determined.

Seventeen to 20 minutes were required to reach pulping temperature in the digester after transferring the hot cooking liquor from the pre-heater in the first stage. In subsequent stages, the heating-up period could be reduced to 7-15 minutes because the digester was already at temperature. The time required to heat the cooking liquor (560 ml) to temperature in the pre-heater was around 20 minutes. Thus, the shortest pulping time in a stage that could be achieved was also around 20 minutes.

4.2.3.2 Total Yield and Delignification

To investigate the delignifying properties of the 45 percent ethanol-water mixture at different temperatures, a series of seven cooks was conducted using two or three stages for each cook. The results obtained are presented in Table 4.6 (page 31). Even when using a temperature of 195°C, the two-stage process gave a pulp with high lignin content (52.4 kappa number). In the series of three-stage

cooks, it was observed that an increase in temperature resulted in improved delignification yielding a pulp with kappa number 19.8 when pulping was carried out at 205°C. The yield, however, was low (39.6 percent) indicating severe degradations of carbohydrates. Employing the three-stage process at the recommended temperature of 185°C (32), a reasonably good yield was achieved (47.1 percent). However, the kappa number was rather high (53.1). By comparing the two cooks carried out at 195°C, it was observed that an increase from two to three stages resulted in a decrease from 52.4 to 32.4 in kappa numbers. To obtain well delignified pulps (kappa number below 30) in a three-stage treatment, it was necessary to use temperatures above 195°C.

The observed difficulties in delignification might be caused by certain types of extractives present in eucalypt wood. It is well known that in acid pulping some types of extractives may condense with themselves and/or with lignin, thus impairing the removal of lignin. To investigate this aspect, three cooks were carried out using three stages at 185°C. The first cook was performed in the usual manner. In the other two, the chips were submitted to a pre-extraction to remove the extractives before pulping. The pre-extraction was performed with the same cooking liquor and could be considered as a pre-cooking stage at a lower temperature and shorter time. The cooking conditions and the results are presented in Table 4.7 (page 33). Pre-extraction resulted in pulps with higher kappa numbers and yields. It appears that pre-extraction caused some changes in the lignin structure (presumably condensation) making it more difficult to be removed during the subsequent pulping stages. No further study was conducted to investigate this hypothesis.

Table 4.8 (page 35) shows the results obtained when chips were cooked with 45 percent ethanol-water using four-stage cooking at different temperatures. Again, an increase in temperature favored delignification. Kappa numbers obtained using the four-stage process were 7-15 units lower than those obtained by the three-stage process under otherwise the same conditions (see Table 4.6, page 31). In order to obtain a kappa number of 21, it was necessary to use a considerably higher temperature (200°C).

Since cooking temperatures above 185°C are expected to adversely affect strength properties, the following runs were carried out at that temperature using five and six cooking stages. Pulping conditions, yields, and kappa numbers are listed in Table 4.9 (page 36). The same table includes results from three- and four-stage processes for reference. Five-stage treatment resulted in pulps with lower yields and kappa numbers than those obtained from the three- or four-stage treatment. The kappa numbers were about five units higher than the target established (kappa number around 25) for handsheet preparation. The six-stage treatment gave the desired kappa number. Several such cooks were carried out to secure enough pulp for handsheet testing and chemical analysis. The reproducibility in terms of yield and kappa number was excellent as seen in Table 4.9 (page 36).

In the multi-stage ethanol cooks, the digester was charged with 80g (OD) of chips and for each stage 560 ml of cooking liquor was introduced into the transfer vessel. The initial dilution factor was 7:1. Due to the reactor configuration, it was not possible to transfer all the cooking liquor into the digester so a small portion would

Table 4.9 Yields and kappa number of *E. viminalis* ethanol pulps obtained by multi-stage processes at 185°C ^a

Time at Temperature [Min.]	Time to Temperature [Min.]	Total Yield [%]	Kappa Number
3 X 20	18, 8, 11	47.1	53.1
3 X 20	20, 9, 9	47.4	55.7
4 X 20	20, 8, 9, 9	45.4	38.0
4 X 20	19, 10, 8, 8	45.9	40.0
5 X 20	20, 8, 7, 10, 8	44.4	30.4
5 X 20	21, 9, 7, 7, 11	45.3	31.2
6 X 20	22, 8, 7, 9, 10, 11	43.5	24.1
6 X 20	18, 10, 7, 11, 10, 9	45.1	27.7
6 X 20	23, 11, 10, 10, 9, 9	44.8	25.5
6 X 20	20, 10, 11, 9, 10, 11	44.8	27.4
6 X 20	26, 10, 10, 8, 9, 11	44.8	25.3

^aCooking liquor: aqueous mixture 45 percent (by weight) ethanol content.

remain in the pre-heater vessel as vapor. Before introducing the next cooking liquor, the transfer vessel was vented and part of the previous cooking liquor was removed. By weighing the recovered spent liquors and determining their solids content, the actual liquor to wood ratio could be calculated. For a six-stage cook, the following ratios were computed:

1st stage - 3.8/1
2nd stage - 4.8/1
3rd stage - 5.3/1
4th stage - 5.2/1
5th stage - 5.1/1
6th stage - 5.3/1.

Yields and kappa numbers for the various multi-stage cooks are plotted in Figure 4.2 (page 38), together with data obtained from reference kraft cooks (Table 4.2, page 20). The yields of ethanol pulps were about 4 percent lower than those of kraft pulps at the same kappa number levels.

Figure 4.3 shows the temperature profile during a six-stage ethanol pulping process.

4.2.2.3 Removal of Wood Constituents during Ethanol Pulping

The spent liquors from each stage of the six-stage process were analyzed for lignin and carbohydrates. Details of the spent liquor analysis are presented in the section dealing with characterization of the spent liquor and in the experimental section. Carbohydrate analysis and the amount of lignin recovered from the various spent liquor fractions provided some information about the removal of cellulose,

hemicelluloses and lignin. The volatile wood degradation products were not considered in this analysis. The results obtained are presented in Table 4.10 (page 41) and are illustrated in Figure 4.4 (page 42) showing the general pattern of dissolution of wood constituents during the six-stage ethanol pulping at 185°C.

Figure 4.4 (page 42) shows that cellulose is quite stable during ethanol pulping. Only very small amounts were dissolved, obviously from easily accessible (amorphous) regions. Among the hemicelluloses, mannan was the most stable and only about 25 percent of its original amount present in wood was removed after six stages. A possible explanation for the mannan stability would be an alignment of glucomannan chains devoid of side branches onto cellulose crystallites. The glucosidic bonds connecting rhamnose and arabinose to the hemicellulose backbones were shown to be rapidly hydrolyzed during the ethanol-water treatment. About 60 percent of the amount of these monomers initially present in wood was removed. Xylan and galactan were also found to be very unstable. It was shown that 70 percent and 80 percent, respectively, of their initial content were dissolved. Lignin was rapidly removed during the initial three stages and the residual delignification in the last three stages was rather slow. In the first cooking stage, more than one-third of the lignin and hemicelluloses were dissolved and after the third stage, more than 80 percent of the lignin was dissolved.

In general the results obtained are in accordance with previous studies on wood saccharification with acidified aqueous organosolv mixtures (38, 39). According to Chang and Paszner (38) dissolution

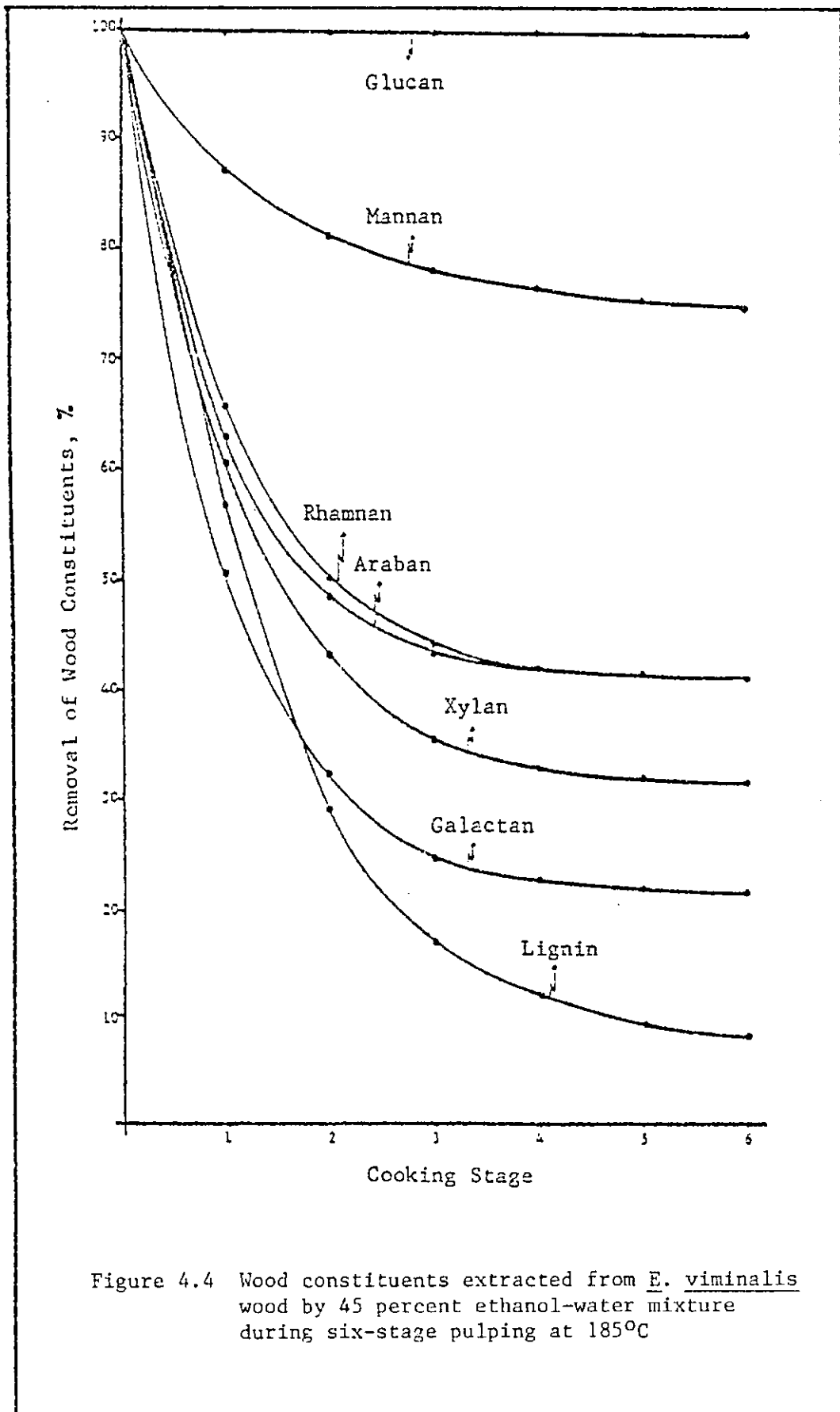


Figure 4.4 Wood constituents extracted from *E. viminalis* wood by 45 percent ethanol-water mixture during six-stage pulping at 185°C

of wood constituents consists not only of acidolysis and removal of lignin but also simultaneous degradation of wood carbohydrates.

4.2.3.4 Pulp Characterization

Pulps produced by the six-stage ethanol pulping process were used for handsheet testing. Pulps obtained from five cooks were combined by mixing with water to obtain a 2 percent pulp consistency. The total pulp mixture was screened and had a kappa number of 22.8.

The strength properties are presented in Appendix Table 10.2 (page 107).

4.2.3.4.1 Freeness. The freeness (Canadian Standard Freeness) - beating (PFI revolutions) relationships of kraft and ethanol pulps are shown in Appendix Table 10.1 (page 106) and Appendix Table 10.2 (page 107), respectively, and are plotted in Figure 4.5 (page 44). Kraft pulp is more sensitive to beating than ethanol pulp. This may be due to a higher hemicellulose content in the kraft pulp. Although the ethanol pulp was beaten up to 8000 revolutions, only a freeness level of about 320 ml could be achieved. The freeness of ethanol pulp almost leveled off when beating was carried out beyond 4000 revolutions, while the kraft pulp was still responding beyond that level.

4.2.3.4.2 Density. The sheet densities obtained from ethanol and kraft pulps at different beating levels indicated that sheets from ethanol pulps were about 10 percent denser (Figure 4.6, page 45). This could be taken as an indication that the ethanol pulp fibers were more flexible.

4.2.3.4.3 Burst Strength. Figure 4.7 (page 47) shows that the kraft pulp was much stronger than the ethanol pulp. Upon beating, the burst strength development was much more pronounced for the kraft pulp than for the ethanol pulp. Kraft pulp had a high burst factor, 95, while 35 was the maximum obtained from ethanol pulp. Although the ethanol pulp gave a denser sheet composed of possibly more flexible fibers, it seems that its intrinsic fiber strength is lower. This could perhaps be explained by excessive degradation of cellulose during ethanol cooking resulting in very low chain length (DP). Although only a small portion of cellulose was degraded to such an extent to be dissolved (Figure 4.4, page 42), it is still possible that its degree of polymerization had been substantially reduced. It should be considered that the solubility of carbohydrates on ethanol-water mixtures is limited to monomers and the lower oligosaccharides (perhaps up to about tetrasaccharides).

4.2.3.4.4 Tensile Strength. Tensile strength, expressed as breaking length, is shown as a function of freeness in Figure 4.8 (page 48). For both kraft and ethanol pulps, the curves followed the typical pattern. The breaking length data indicated that kraft pulp was much stronger than ethanol pulp. The maximum breaking length of kraft pulp was almost double of that of ethanol pulp. Even without any beating the tensile strength of kraft pulp was almost 1,000 meters higher than the highest strength obtained from ethanol pulp. Probably the same explanation for low burst strength of the ethanol pulp can account for the low tensile strength.

4.2.3.4.5 Tear Strength. Figure 4.9 (page 50) illustrates the relationship between tear factor and freeness of ethanol and kraft pulps. In general, the tear strength of kraft pulp is almost double of that of ethanol pulp. Although tear strength is expected to exhibit an inverse relationship to beating, the kraft pulp did not show a significant decrease in tear with beating. A similar behavior is reported in the literature for some kraft hardwood pulps (40, 41).

4.2.3.4.6 Holocellulose and Alpha-Cellulose Content. Kraft and ethanol pulps (3, 4, 5, and 6 cooking stages) were analyzed for holocellulose and alpha-cellulose content. The holocellulose determination was performed according to the procedure recommended by Cundy and Beck (42) and described in the experimental section. The results obtained are given in Table 4.11 (page 51).

Ethanol pulps had a higher holocellulose and alpha-cellulose content than kraft pulp. An increase in the number of ethanol-water treatments did not significantly affect the alpha-cellulose content. Based on original wood, the alpha-cellulose content of ethanol pulps was about the same as that of kraft pulp.

The six-stage ethanol-water treatment resulted in considerable dissolution of hemicelluloses. The pulp was well delignified (kappa number 22.8) and its alpha-cellulose yield, based on original wood, was about the same as in kraft. These results are of importance with respect to dissolving grade pulp production where pulp strength is not an important factor. On the other hand, the use of single-stage ethanol-water treatment at 185°C not only caused high

dissolution of hemicelluloses but also removed a considerable amount of lignin as well. Therefore, the use of ethanol-water in a pre-treatment stage in the manufacture of dissolving grade pulps seems to be an interesting proposition.

4.2.3.4.7 Intrinsic Viscosity, Molecular Weight, and DP of Alpha-Cellulose. Table 4.12 (page 53) shows that an increase in cooking stages results in a decrease in molecular weight and DP of alpha-cellulose. Kraft pulps had a higher DP than ethanol pulps. The DP of the alpha-cellulose isolated from a six-stage ethanol pulp was about 65 percent of that in kraft pulp. The degradation of cellulose indicated by the lower DP seems to be, at least in part, responsible for the low strength properties of ethanol pulps.

4.2.3.4.8 Carbohydrate Analysis. Carbohydrate analysis of the E. viminalis wood and of kraft and ethanol pulps were carried out following the procedure described in detail in the experimental section. The results obtained are presented in Table 4.13 (page 54). It shows that kraft pulps had higher hemicellulose contents than ethanol pulps. The higher hemicellulose content could be the reason for the better response of kraft pulps toward beating (Figure 4.5, page 44). In general, kraft pulps presented a higher content of all kinds of hemicelluloses, except mannan, than ethanol pulps. Xylan was heavily degraded and dissolved during ethanol cooking but was shown to be quite stable during kraft pulping.

Results listed in Table 4.13 (page 54) were plotted in Figure 4.10 (page 55) to illustrate the polysaccharides composition of ethanol pulps in the various stages.

Table 4.13 Carbohydrate analysis of different multi-stage ethanol pulps, kraft pulp, and E. viminalis wood

Sample	<u>Rhamnan, %</u>		<u>Araban, %</u>		<u>Xylan, %</u>		<u>Mannan, %</u>		<u>Galactan, %</u>		<u>Glucan, %</u>		<u>Total, %</u>		
	Pulp	Wood	Pulp	Wood	Pulp	Wood	Pulp	Wood	Pulp	Wood	Pulp	Wood	Pulp	Wood	
Ethanol Pulps	3 stages	0.04	0.02	0.2	0.09	7.1	3.3	1.9	0.9	0.3	0.1	82.9	39.2	92.5	43.7
	4 stages	0.1	0.04	0.3	0.1	6.8	3.1	1.9	0.7	0.4	0.2	81.2	37.1	90.6	41.4
	5 stages	0.2	0.09	0.4	0.2	7.2	3.2	2.0	0.9	0.5	0.2	81.0	36.3	91.2	40.9
	6 stages	0.1	0.04	0.1	0.04	6.5	2.9	1.3	0.6	0.03	0.01	85.4	38.1	93.6	41.7
Kraft Pulp	0.2	0.1	0.4	0.2	17.9	9.2	0.9	0.5	0.8	0.4	66.2	33.9	86.4	44.3	
Wood	—	0.4	—	0.6	—	16.6	—	1.4	—	0.9	—	41.9	—	61.8	

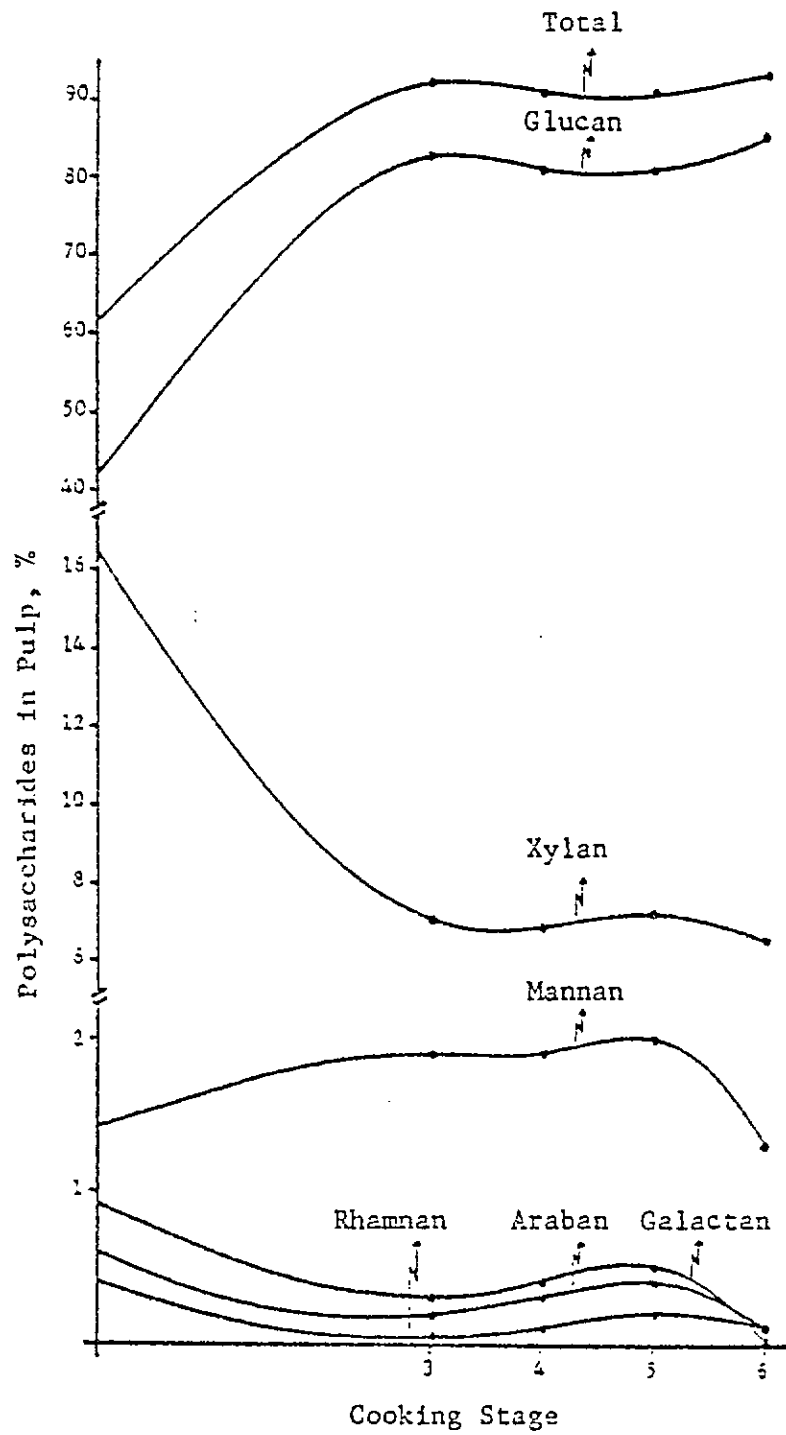


Figure 4.10 Carbohydrate content in ethanol pulps as a function of cooking stages

4.3 Characterization of the Spent Liquor from Ethanol Pulping

The carbohydrate and lignin fractions in the spent liquors should constitute an important source of by-products in the ethanol pulping process. To obtain some information about those fractions, the spent liquors obtained from a six-stage ethanol-water treatment were analyzed. A detailed description of the procedures is presented in the experimental section. Basically, it consisted of separating the spent liquors into three major fractions (volatiles, carbohydrate fraction, and lignin fraction).

Figure 4.11 (page 57) illustrates the scheme utilized to fractionate the spent liquors.

4.3.1 General Characteristics

Table 4.14 (page 58) shows the pH, carbohydrate and lignin content for each of the spent liquors from a six-stage ethanol-water treatment. The pH of the original cooking liquor was 7.3. A considerable drop is observed during ethanol-water treatment mainly caused by hydrolysis of the acetyl groups of the xylans and, to a minor extent, by other organic acids such as formic acid formed during ethanol pulping (46). The results presented in Table 4.14 also show that the composition of the dissolved solids in the spent liquors changed as the cook progressed. The spent liquor from the first stage contained almost equal amounts of lignin and carbohydrate degradation products. In subsequent stages the spent liquors became richer in lignin while the carbohydrate fraction decreased consistently. In the last stage, lignin comprised about two-thirds of the dissolved solids.

A material balance of six-stage pulping, based on the pulping yield and solids recovered from the spent liquors, is given in Table 4.15 (page 60). After the six-stage process, 44.8 percent of the original wood was recovered as pulp and 55.2 percent was degraded and dissolved. Although 55.2 percent of wood constituents were dissolved, only 49.7 percent was recovered as a solid residue (lignin and carbohydrates) after removing the solvent (ethanol-water) by distillation. This indicates that 5.5 percent of the original wood was degraded to low molecular weight volatile compounds which were removed by distillation. The volatile portion was not analyzed but according to the literature (38, 39, 46) it should comprise furfural, hydroxymethyl furfural, methanol, acetic acid, formic acid, and other low molecular weight volatile organic acids.

4.3.2 Removal of Carbohydrates and Lignin

Based on spent liquor analyses, the general pattern of the dissolution of wood constituents during a six-stage process could be established. Table 4.16 (page 61) and Figure 4.12 (page 62) clearly show that about one-half of the total material dissolved in the entire process is removed in the first stage. While in the first stage the rates of dissolution of lignin and carbohydrate were about the same; in subsequent stages the removal of lignin became more pronounced. The results also showed that about one-fourth of the wood material was removed in the first cooking stage. After the second stage, 40 percent of the wood had already been removed. The amount of material removed during the first cooking stage is close to 30 percent if the volatile degradation products, formed in the beginning of the cook, are taken into consideration.

4.3.3 Analysis of the Carbohydrate Fraction

The carbohydrate fractions recovered from the spent liquors of each of the six stages were analyzed (see Table 4.17, page 64). Due to the small amounts of carbohydrate recovered from the fifth and sixth stages, those two fractions were combined to obtain sufficient material for analysis. The results indicated that about 60-75 percent of the "carbohydrate fractions" is composed of different sugars. The remaining 25-40 percent consists of water soluble extractives, water soluble lignin degradation products, and of organic acids, such as 4-O-methylglucuronic acid. The molecular weight distribution of dissolved oligosaccharides was not determined but it is expected that the major part consists of monomers. Table 4.17 (page 64) also shows that xylose comprises the bulk of the carbohydrate fractions (46-65 percent) and that other sugars were present only in small amounts.

The data listed in Table 4.17 (page 64) were used to calculate the recovery of each sugar in the spent liquors. The results, expressed as percentage of the original amount present in wood, are shown in Figure 4.13 (page 65) and Appendix Table 10.5. More than 90 percent of the lignin initially present in wood was found in the spent liquors. Among the sugars from hemicelluloses, the percent recovery of galactose was the highest followed by xylose, rhamnose, arabinose and mannose, respectively. Only about 25 percent of the mannose originally present in wood was recovered from the spent liquors.

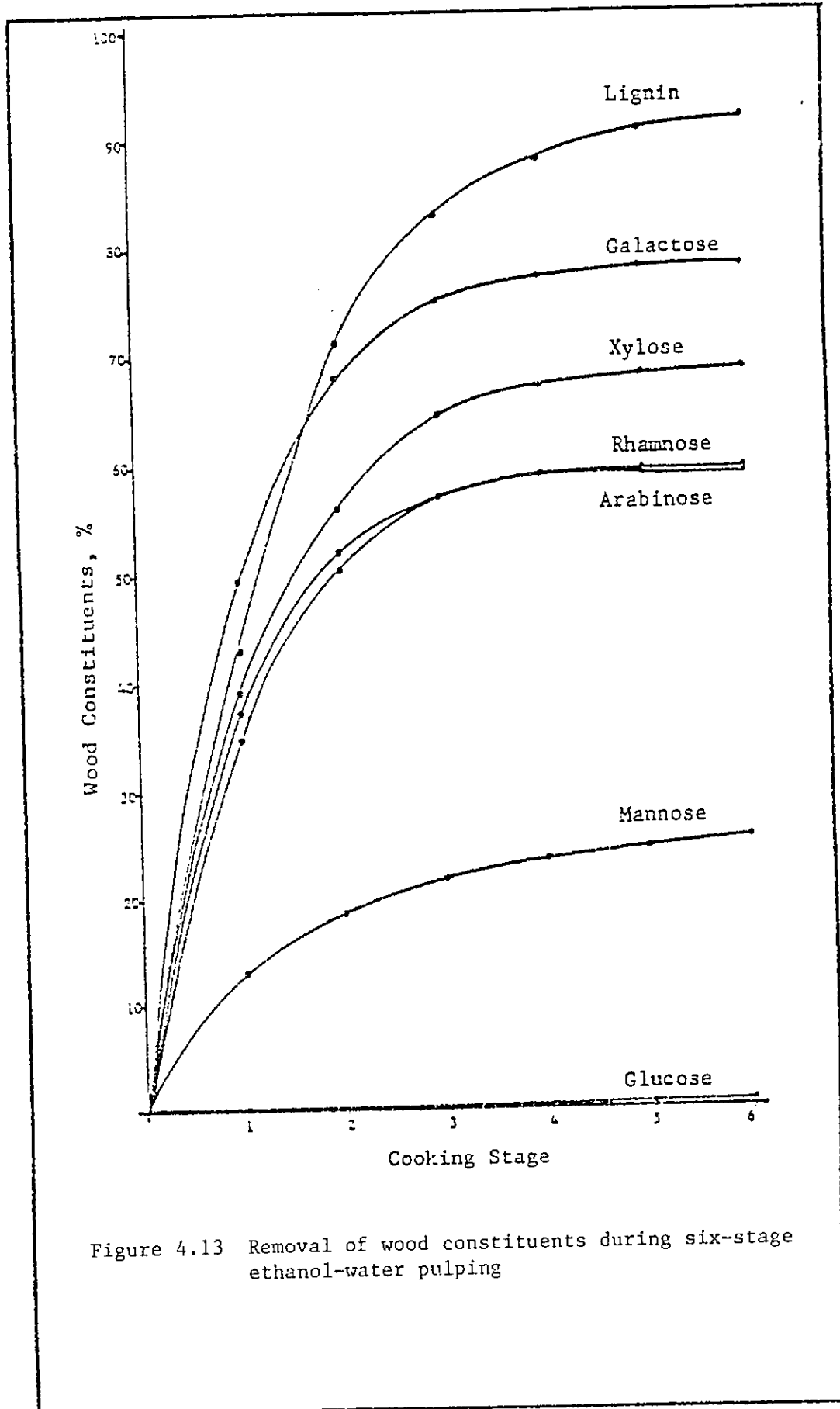


Figure 4.13 Removal of wood constituents during six-stage ethanol-water pulping

4.3.4 Characterization of the Lignin Fraction

The lignin fractions isolated from the spent liquors of the first, third, and fifth stages of a six-stage process were analyzed. Lignin was characterized by means of solubility in chloroform, ultraviolet spectroscopy, infrared spectroscopy, nuclear magnetic resonance spectroscopy of the acetylated material, and elemental and methoxyl analyses.

4.3.4.1 Solubility in Chloroform

The carbohydrate and lignin fractions recovered in the spent liquor from the first stage ethanol pulping were extracted with chloroform using the following procedure:

Three grams of the lignin and carbohydrate fractions were extracted with chloroform for 24 hours using cellulose thimbles and a Soxhlet extractor. The chloroform was then evaporated under vacuum and the weight of the residue was determined. The results showed that only a small amount of the carbohydrate fraction (4.3 percent) was soluble in chloroform while a considerable larger portion of the lignin fraction (68.3 percent) was soluble. The large solubility in chloroform indicates that the lignin in the spent liquor is obviously degraded to low molecular weight fractions.

Some preliminary examination of the portion of the carbohydrate fraction extracted with chloroform were performed. A thin layer chromatogram of this fraction was sprayed with Folin-Denis reagent and it gave a positive blue color indicating its phenolic nature. High pressure liquid chromatography indicated the presence of two major

compounds. Ultraviolet spectra showed the presence of phenolic alpha-carbonyl structures.

The chloroform extracted lignin was analyzed by thin-layer chromatography using a mixture of ethyl acetate and methanol (5:1) as the developer. The thin-layer chromatogram showed the presence of a compound with a R_f value of 0.57, the same as for vanillin. This compound gave a positive blue color reaction with Folin-Denis Reagent (Phenol Reagent), indicating its phenolic nature. It also gave a positive orange color reaction with 2,4-dinitrophenyl hydrazine which indicated the presence of a carbonyl group.

4.3.4.2 Ultraviolet Spectroscopy

The lignin fractions in the spent liquors from the first, third, and fifth stages were analyzed using ultraviolet spectroscopy. The method reported by Goldschmid (47) was used.

All three lignin fractions had quite similar UV spectra in neutral and alkaline media (Figures 4.14 and 4.15, pages 68 and 69). This suggests that the chemical composition of degraded lignin in ethanol-water pulping does not seem to change significantly as the cook progresses. The $\Delta\epsilon$ curves of all three lignin fractions in the 360-370 nm region indicate the presence of phenolic alpha-carbonyl and/or stilbene structures. The presence of alpha-carbonyl or double bonds conjugated to aromatic group could be responsible for the less pronounced maximum in the 300 nm region due to overlapping with absorption bands of phenolic structure.

To check the presence of alpha-carbonyl groups, lignin samples were treated with NaBH_4 in alkali. Reducing the carbonyl functions to

alcohols would prevent overlapping and thus allow better estimation of phenolic groups.

The $\Delta\epsilon$ spectra of the reduced lignin samples clearly indicate a decrease in absorption in the 360-370 nm region, as shown in Figure 4.16 (page 71). This suggests the presence of phenolic alpha-carbonyl groups in the lignin structure. After reduction, there was still some absorption in the 360-370 nm region suggesting the presence of conjugated double bonds (stilbene structure).

The ultraviolet data for phenolic hydroxyl and phenolic alpha-carbonyl groups in the three lignin fractions are listed in Table 4.18 (page 72). Phenolic hydroxyl contents of the lignin fractions were estimated according to Goldschmid (47) and the results are listed in Table 4.19 (page 73) together with the percentages of phenolic units with and without alpha-carbonyl groups, calculated according to Alder and Marton (48). The unit weight of 203 (Table 4.20, page 74) was used to calculate the phenolic alpha-carbonyl content. As seen in Table 4.19 (page 73), only a small amount (less than 2 percent) of the total weight of the lignin fraction is phenolic hydroxyl. It was observed that the total phenolic hydroxyl content of lignin in spent liquors increased slightly from first to third stage and then decreased in the latter stages. The same trend was also indicated for the phenolic hydroxyl with and without alpha-carbonyl functions in the side chains.

4.3.4.3 Infrared Spectroscopy

The lignin fractions in the spent liquors from the first, third, and fifth stages of ethanol pulping were analyzed by infrared

Table 4.20 Analytical composition and C₉-formulae of the lignin fraction isolated from the spent liquor after the first stage of a six-stage ethanol pulping

Lignins	C%	H%	O%	OCH ₃ %	COCH ₃ %	C ₉ Formula				
						C	H	O	OCH ₃	COCH ₃
Original	61.58	5.70	32.72	21.58	—	9	7.34	2.74	1.40	—
Reduced	61.34	5.72	32.94	21.68	—	9	7.39	2.77	1.42	—
Reduced & Acetylated	61.26	5.57	33.17	17.20	24.44	9	5.81	2.50	1.46	1.50

Hydroxyl groups in lignin (estimated from UV and Elemental Analysis data):

$$\begin{array}{l}
 \text{HO in Lignin: } 1.50/C_9 \\
 \left| \begin{array}{l}
 \text{Phenolic: } 0.3/C_9 \\
 \text{Non-Phenolic: } 1.2/C_9
 \end{array} \right| \begin{array}{l}
 \text{With alpha-carbonyl: } 0.05/C_9 \\
 \text{Without alpha-carbonyl: } 0.25/C_9
 \end{array}
 \end{array}$$

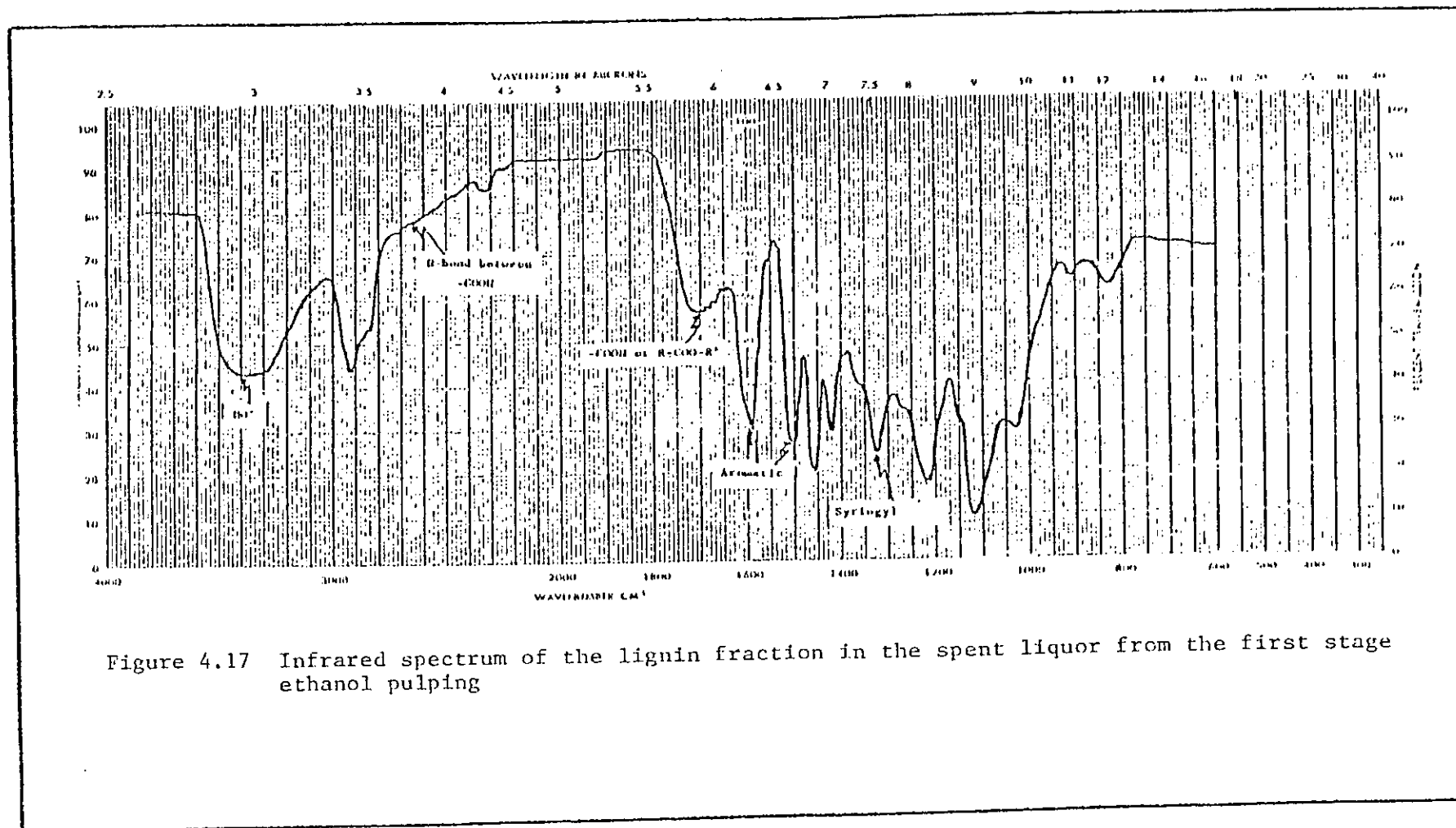
spectroscopy. Their infrared absorption spectra are presented in Figures 4.17, 4.18, and 4.19 (pages 76, 77, and 78), respectively. All three lignin fractions exhibited infrared spectra characteristic for hardwoods. The similarity of the IR spectra indicates that the degraded lignin in the spent liquors from different stages of ethanol pulping are similar in nature.

In order to obtain more information about the nature of the functional groups responsible for the absorption in the 1700 cm^{-1} band, lignin isolated from the first stage was reduced with NaBH_4 and its IR spectrum was recorded. Reduction did not affect absorption in that region (Figure 4.20, page 79) indicating the presence of carboxylic acid or ester groups. Closer inspection of the spectra revealed that the carboxylic acid and/or ester group content of the lignin seems to decrease slightly in the spent liquors from the latter stages.

Infrared spectral data of reduced lignin were also utilized to estimate the methoxyl content per C_9 lignin unit and the relative amounts of guaiacyl and syringyl units. The procedure described by Sarkanen, Chang, and Allan (49) was utilized. A MeO/C_9 ratio of 1.45 was computed indicating that approximately 55 percent of the C_9 units were of the guaiacyl and 45 percent of the syringyl type.

4.3.4.4 Nuclear Magnetic Resonance Spectroscopy

The lignin products isolated from the spent liquors of the first, third, and fifth ethanol cooking stages were acetylated by pyridine-acetanhydride. The NMR spectra of the acetylated lignin preparations



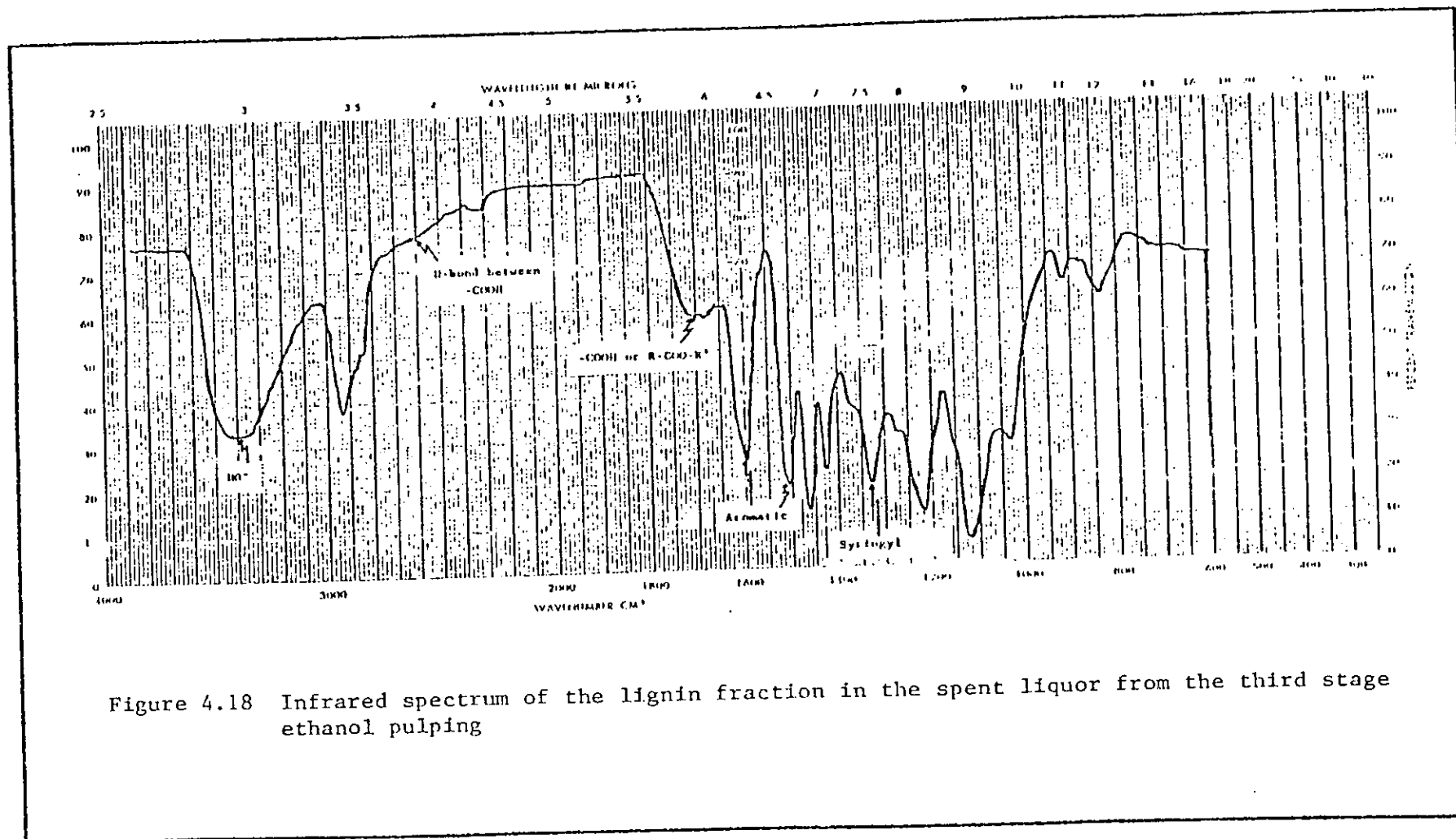


Figure 4.18 Infrared spectrum of the lignin fraction in the spent liquor from the third stage ethanol pulping

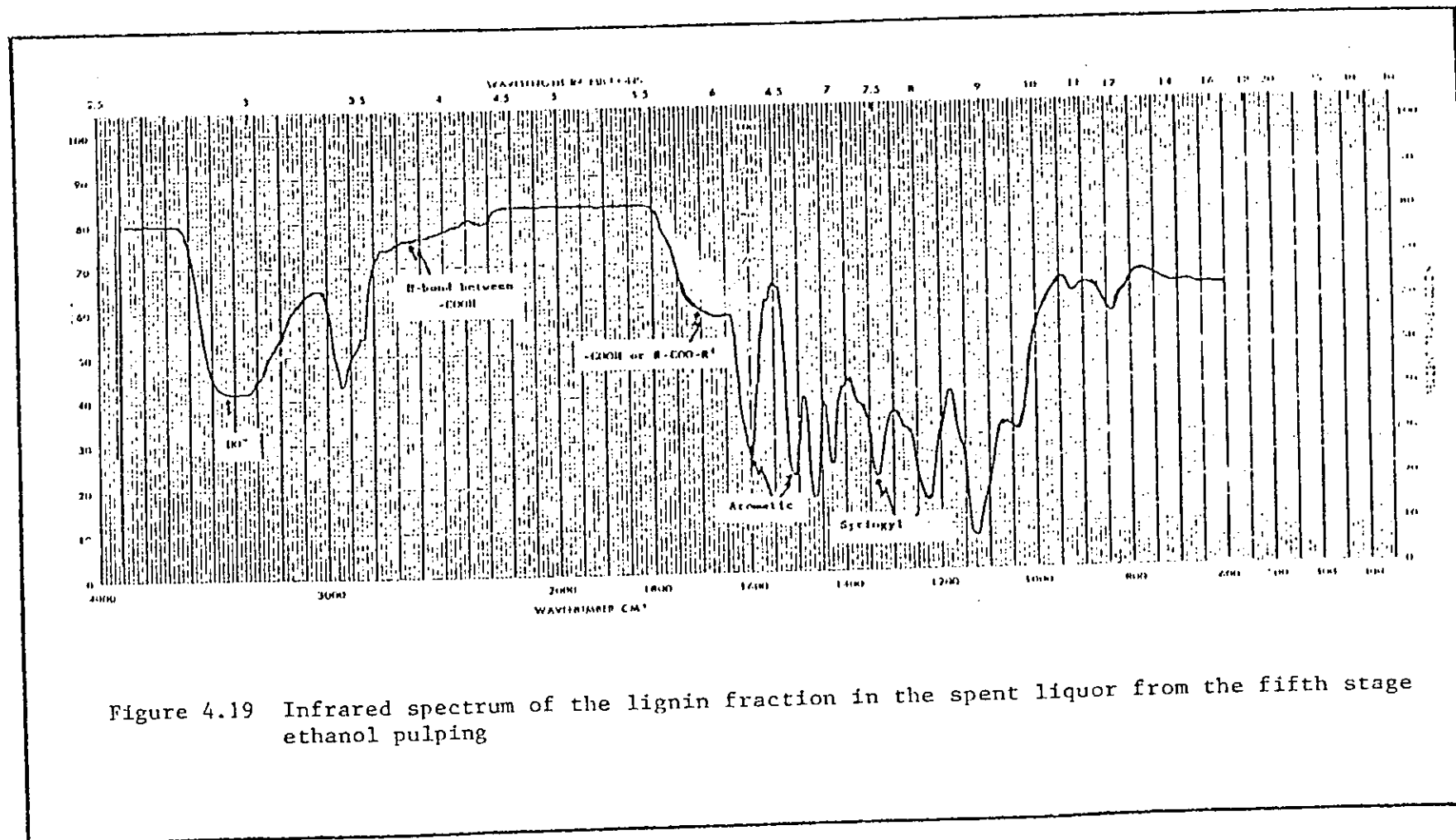


Figure 4.19 Infrared spectrum of the lignin fraction in the spent liquor from the fifth stage ethanol pulping

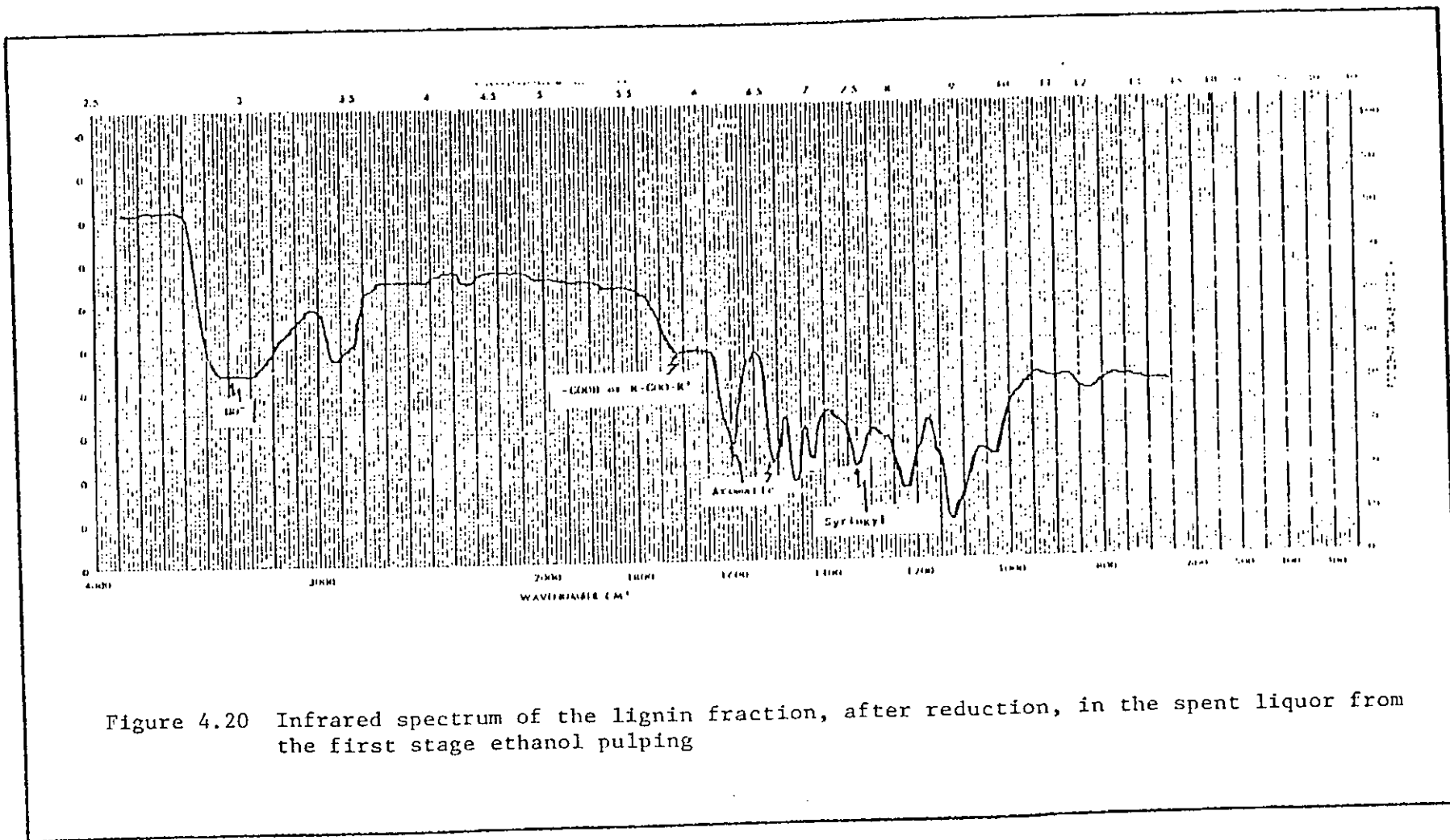


Figure 4.20 Infrared spectrum of the lignin fraction, after reduction, in the spent liquor from the first stage ethanol pulping

were recorded (Figures 4.21, 4.22, and 4.23 (pages 81, 82, and 83)). It can be seen that lignins from different cooking stages had very similar NMR spectra. Integration for methoxyl and acetyl protons allowed computation of ratios of methoxyl H/acetyl H for each lignin. The ratio ranged from 1.01 to 1.16. That supports the UV and IR data suggesting that lignin degradation products in spent liquors from different stages are chemically very similar.

4.3.4.5 Elemental and Methoxyl Analyses

Since a rather close similarity of the lignin fractions was repeatedly demonstrated by UV, IR, and NMR spectroscopy, only the lignin fraction in the spent liquor from the first stage was analyzed. The elemental and methoxyl analyses were made for the original lignin sample, for the reduced lignin, and for the reduced-acetylated lignin. All analyses were performed in duplicate. The elemental analyses were presented as a percent of carbon and hydrogen content in the moisture free lignin samples. Oxygen content was assumed to be the difference. The results are presented in Table 4.20 (page 74).

C_9 -formulae of the non-reduced lignin products reveal that both preparations contained almost the same amount of hydrogen atoms. The presence of carbonyl groups in the original lignin would cause, after reduction with $NaBH_4$, an increase in H content of the reduced lignin. However, such an increase could not be detected. This indicates that either carbonyl groups were absent or, what seems more likely, were present in concentrations too low to be detected by this method.

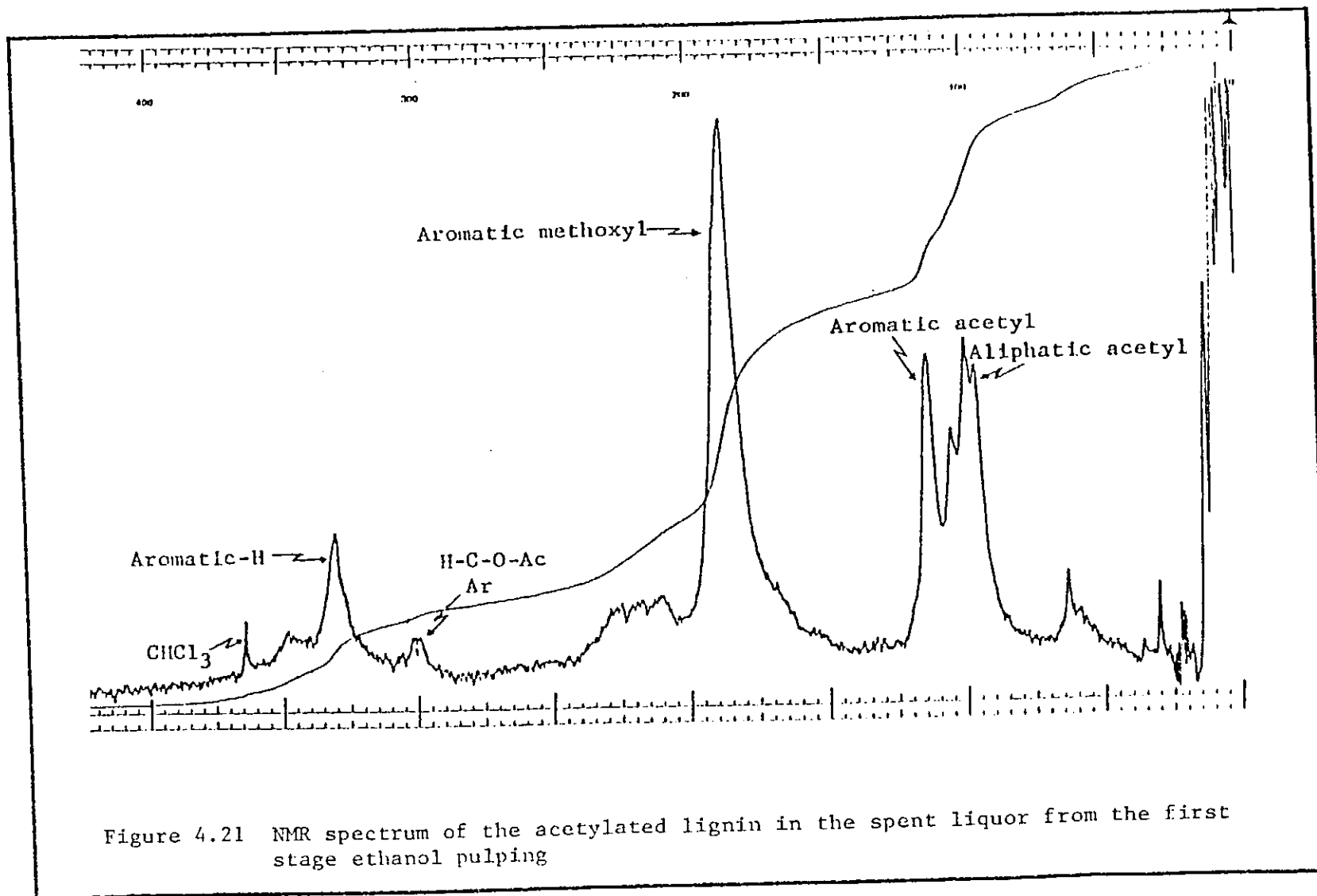


Figure 4.21 NMR spectrum of the acetylated lignin in the spent liquor from the first stage ethanol pulping

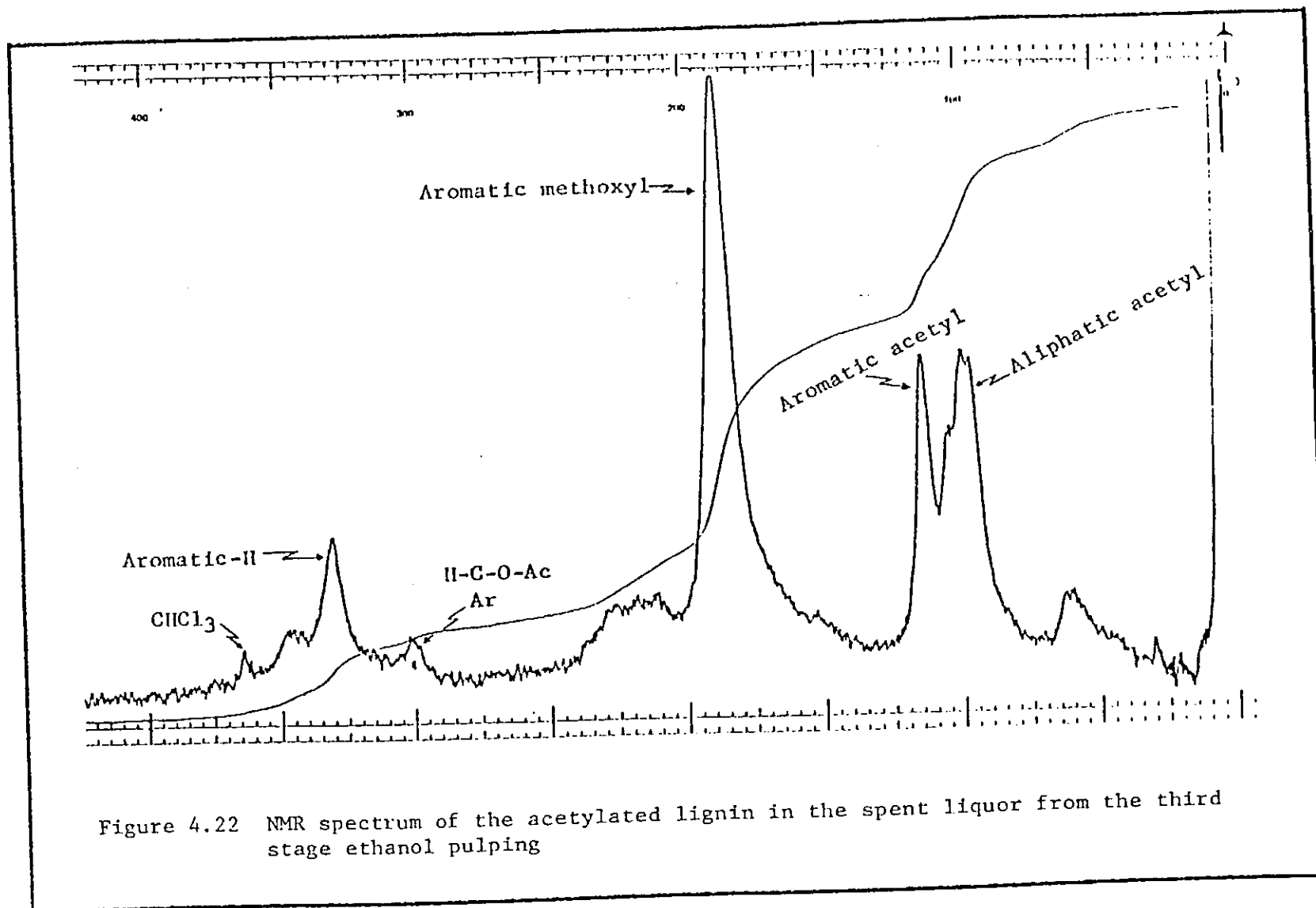


Figure 4.22 NMR spectrum of the acetylated lignin in the spent liquor from the third stage ethanol pulping

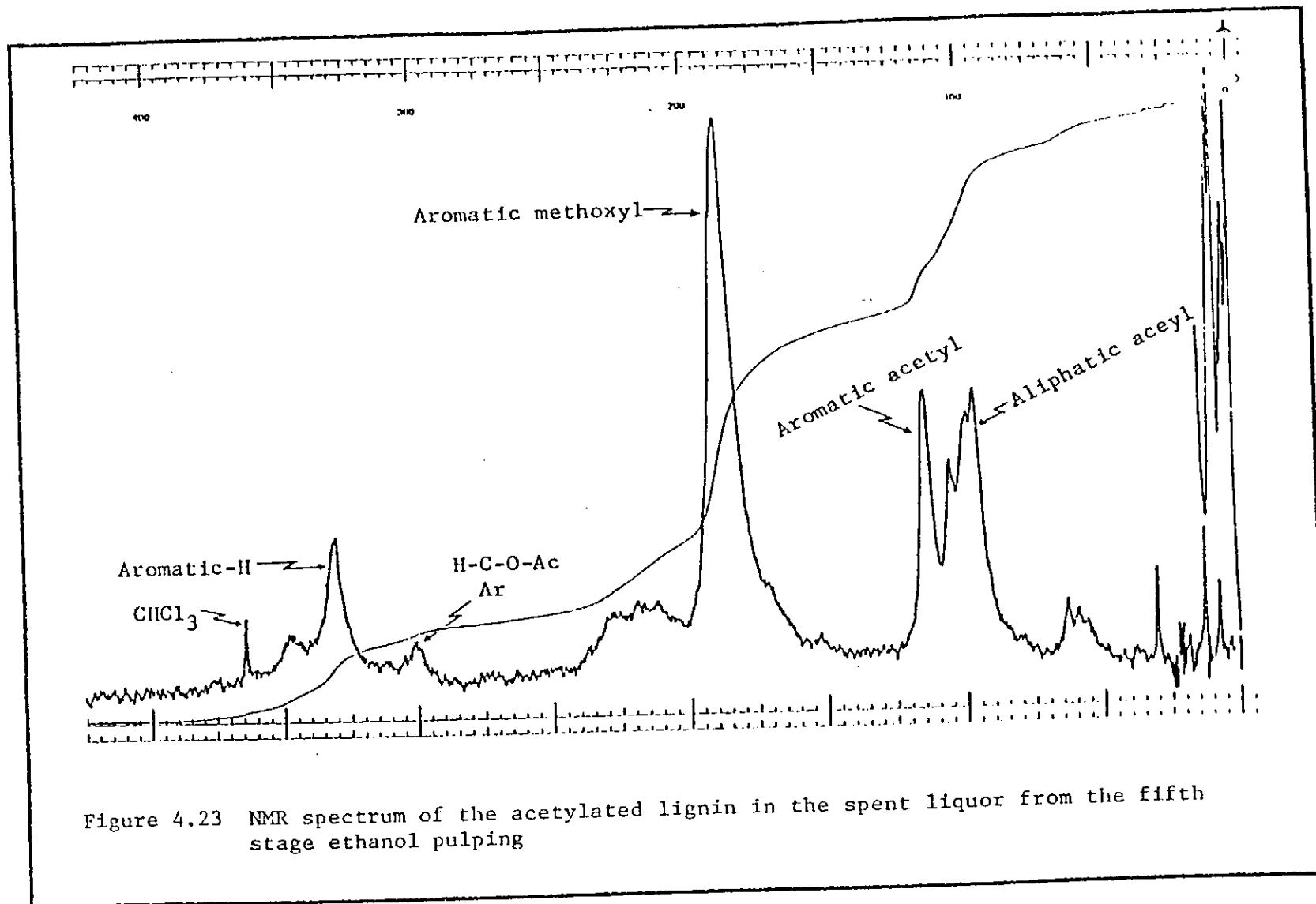


Figure 4.23 NMR spectrum of the acetylated lignin in the spent liquor from the fifth stage ethanol pulping

5. SUMMARY

Pulps produced by single-stage methanol- or ethanol-water treatments at 185°C had high residual lignin contents and relatively low yields. Aqueous mixture containing 45 percent (by weight) ethanol at 185°C had better delignifying properties than a comparable methanol-water mixture. Increases in cooking times, dilution factors, cooking stages, and temperatures were found to favor delignification. Pulping yields from two to six ethanol-water treatments at 185°C were about 4 percent lower than kraft pulping at a same kappa number. In order to produce a well delignified ethanol pulp with a kappa number of 22.8, it was found necessary to use at least a six-stage process (20 min. each) at 185°C.

Compared with kraft pulps, six-stage ethanol pulps had a lower heating response, considerably lower strength, a similar alpha-cellulose content, a lower alpha-cellulose DP (800 vs 1240), and a lower hemicellulose content (8.2 vs 20.2 percent).

During the six-stage ethanol-water treatment, the pH dropped from 7.3 to approximately 4. Analysis of the spent liquors from such treatment indicated that about one-quarter of the wood constituents was removed in the first stage. After the second stage, 40 percent had already been removed. The DP of alpha-cellulose dropped drastically during ethanol pulping, indicating excessive splitting of glucosidic bonds along the cellulose chains.

Fractionation and analysis of the spent liquors from six-stage process indicated that degraded lignin comprised 28 percent and carbohydrates 22 percent of the dissolved solids. The xylan

degradation products constitute the bulk of the carbohydrate fractions (46-65 percent) in spent liquors.

Analysis of the degraded lignin dissolved in spent liquors indicated its relatively high solubility in chloroform. Presence of vanillin was detected in the lignin fraction. Ultraviolet, infrared, and nuclear magnetic resonance spectra of the lignin degradation products isolated from different stages were practically identical suggesting that lignin fragments dissolved in various phases of the treatment exhibit the same or very similar structural features. Ultraviolet analysis indicated that phenolic units comprise about one-fifth of the total C_9 lignin units. The C_9 -formula for lignin of $C_9H_{7.34}O_{2.74}(OCH_3)_{1.40}$ was established. Methoxyl analysis and IR spectroscopy indicated a guaiacyl to syringyl ratio of 1.5.

6. CONCLUSIONS

Kraft pulping experiments indicated that bleachable grade pulps with good strength properties and yields can be produced from immature (3-4 years old) Eucalyptus viminalis wood. It is anticipated that by using mature wood, pulps with better strength properties could be obtained.

Aqueous mixture containing 45 percent (by weight) ethanol seems to be a better pulping agent at 185°C than a comparable methanol mixture. Ethanol-water did not bring about sufficient delignification in batch digesters at 185°C.

To produce well delignified ethanol pulps in batch digesters requires a multi-stage process. At least six stages (20 min. each) at 185°C are required to obtain pulps with a kappa number value of 22.8 and 44.6 percent yield. Such pulps exhibit poorer beating characteristics and considerably lower strength properties than kraft pulps. For production of high quality pulps, it seems that a multi-stage ethanol-water treatment cannot substitute a continuous process.

Multi-stage ethanol pulping results in severe degradation and dissolution of hemicelluloses and in a significant decrease of the cellulose DP. Lignin removal during ethanol pulping is accomplished by an initial rapid bulk delignification followed by a slow removal of the residual lignin.

The chemical composition of the degraded lignin in ethanol spent liquors does not seem to significantly alter as the cook progresses.

7. RECOMMENDATIONS FOR FURTHER STUDIES

On the basis of this study the following recommendations are proposed for further investigation of ethanol pulping processes:

1. The possibility of making dissolving grade pulp by ethanol treatment should be investigated in more detail by either using the ethanol-water as the only pulping agent or as a pre-treatment to conventional kraft pulping.
2. Studies to investigate the possibilities of retarding lignin condensation reactions taking place in batch digestions. Further, the use of catalyst to improve lignin degradation should be evaluated.
3. An important advantage of ethanol pulping is the rather simple recovery of ethanol and of carbohydrate and lignin degradation products from the spent liquor. Therefore, detailed investigations should be conducted to evaluate the by-product potential of those products.

8. EXPERIMENTAL

8.1 Preparation of Wood for Chemical Composition and Pulping Studies

The pulping experiments and chemical analysis were performed with selected chips. Bark, knots, and defective chips were removed. Chips used for single-stage alcohol pulping had a moisture content of 40.9 percent; those used for kraft and multi-stage ethanol pulping had a moisture of only 19.7 percent.

To determine the chemical composition the chips were cut into matchsize pieces and ground in a Wiley Mill. The wood meal after air drying was screened and the fraction that passed 40 mesh and was retained by 60 mesh screens was stored in air-tight bottles.

8.2 Holocellulose Content in Wood

In a 500 ml Erlenmeyer flask, 5.0 grams of air-dried wood meal were treated with 200 ml of water, 2.5 ml acetic acid, and 7.5 g of sodium chlorite. A water-bath was used to keep the reaction temperature at $70 \pm 5^{\circ}\text{C}$ and a small, inverted Erlenmeyer flask was used to keep the reaction flask closed. After one hour, an additional 2.5 ml of acetic acid and 7.5 g of sodium chlorite were added. The same amounts of reagents were added each hour for four hours. The holocellulose suspension was filtered through a filtering crucible and washed with distilled water until the washings were colorless. Finally, it was washed three times with small portions of methanol and air-dried. A separate sample was used for moisture content determination.

8.3 Acid Soluble Lignin in Wood

The filtrate from the Klason lignin determination was diluted to 1000 ml. One volume of this filtrate was diluted with two volumes of distilled water for UV analysis. A blank solution was prepared by diluting 10 ml of 72 percent H_2SO_4 to 100 ml and then diluting one volume of this solution with two volumes of distilled water.

Using the absorbance values of the diluted lignin filtrate, the acid soluble lignin was calculated using the following equation (36):

$$C_L = \frac{4.53A_{215} - A_{280}}{300}$$

where A_{215} and A_{280} are the absorbance values of the diluted lignin filtrate and C_L is the concentration in g/l of soluble lignin in the filtrate.

8.4 Acetyl Content of Wood

Oven-dried wood meal (1 g) and a few boiling chips were introduced into a 300 ml round-bottom flask. The flask was attached to an adapter equipped with a condenser and a dropping funnel. Fifty ml of 0.2N solution of methanol was introduced followed by 100 ml anhydrous methanol. The flask was placed in a water-bath at 75-80°C. The distillate was collected in a 500 ml flask completely immersed in ice-water.

When most of the liquid in the flask had been removed, an additional 100 ml of methanol was added and distillation was continued. This was repeated once more. The distillate, 300-325 ml, was boiled under reflux for exactly 20 min. with 40 ml of 0.1N aqueous NaOH.

After cooling to room temperature, excess alkali was determined by titration with 0.1N HCl. A blank determination was carried out with 300 ml anhydrous methanol and same amount of alkali as was used in the analysis. The amount of acetyl groups was calculated by employing the formula:

$$\% \text{ Acetyl} = \frac{43 N (V_2 - V_1) 0.1}{W}$$

where 43 is the molecular weight of the acetyl group, N is the normality of alkali, V_2 the volume (ml) of alkali remaining after boiling blank titration, V_1 the volume (ml) of alkali remaining after saponification of methyl acetate, and W the oven-dry weight (g) of the wood meal sample.

8.5 Conditions for Kraft and Single-Stage Alcohol Pulping

The kraft and single-stage alcohol cooks were carried out in 2.8 liter stainless steel autoclaves which were heated and rotated in a hot air heater system controlled within $\pm 2^\circ\text{C}$. The temperature inside the autoclaves was monitored by thermocouples.

a) Kraft Pulping:

Active alkali = 9-22 percent

Sulfidity = 25 percent

Chips = 200 g (OD)

Liquor/Wood = 3.5/1

Temperature = 170°C

Time to Temperature = 1.5 h.

Time at Temperature = 1 h.

b) Methanol- and Ethanol-Water Pulping:

The conditions for single-stage alcohol treatments are given in Tables 4.4 and 4.5 (pages 25 and 26). After the treatment, the chips were refluxed for about 30 minutes with fresh alcohol-water mixture using a liquor/wood ratio of approximately 7/1.

Fiber separation of both kraft and alcohol pulps were achieved by passing the cooked chips through a 12-inch single disk laboratory refiner using 0.01 inch plate separation. When the chips were not sufficiently soft, the defibration was done in two steps using first a plate separation of 0.04 inch and in the second pass at a plate separation of 0.01 inch.

8.6 Pulp Characterization

A PFI mill was used for beating kraft and six-stage ethanol pulps. Kappa number determination, handsheet preparation, and strength properties were performed according to Tappi Standard Methods. The brightness was measured using a Photovoltmeter.

8.7 Determination of Holocellulose in Pulps

The procedure used was one recommended by Cundy and Beck (42). The air-dried equivalent of 3 grams of moisture-free unbleached pulp was placed in a 400-ml beaker containing 100 ml of water and 0.5 ml of glacial acetic acid. After the pulp suspension had been thoroughly stirred, the pH of the mixture was checked. When necessary acetic acid was added to bring the pH to 4-5. One gram of sodium chlorite was added to the pulp suspension and the mixture was heated in a water-bath for 30 minutes at 70° to 80°C. The beaker containing the

pulp suspension was covered with a watch glass. During heating, the mixture was frequently agitated. Then the mixture was filtered through a sintered glass crucible (coarse) and the holocellulose was washed thoroughly with water. Finally, holocellulose was washed with acetone and air-dried. Moisture content was determined and the holocellulose content in the pulp was calculated.

8.8 Intrinsic Viscosity, Molecular Weight, and Degree of Polymerization of Alpha-Cellulose

Alpha-cellulose samples (0.05g) were stirred with 10.0 ml of water until completely dispersed (4-6 hours) using a stirrer prescribed by Tappi Standard T230 su-66. After complete dispersion of the alpha-cellulose, 10.0 ml of 1M Cuene (Cupriethylenediamine) were added and the mixture stirred for an additional 30 minutes. The 0.5M cuene solution containing the dissolved alpha-cellulose was diluted with pure 0.5M cuene to four different concentrations which were used for viscosity measurements. Suitable Fenske-Ostwald viscosity pipettes were used at 25°C. The relationship between viscosity number and concentration was established by linear regression analysis and the intrinsic viscosity was obtained as the intercept. The molecular weights were calculated using the following equation:

$$[\eta] = K \cdot M^a$$

where $[\eta]$ is the intrinsic viscosity, K and a are constants, and M is the molecular weight. The following values for K and a were used (43):

$$K = 1.33 \times 10^{-4}$$

$$a = 0.905.$$

The DP was calculated by dividing the molecular weight by 162, the molecular weight of anhydrous glucose.

8.9 Fractionation of Ethanol Spent Liquor

The fractionation scheme used is illustrated in Figure 4.11 (page 57). The spent liquor samples were transferred to a 1000-ml round-bottom distillation flask. A small amount of distilled water (50 ml) was used to transfer a remaining residue formed during storage. The spent liquor was evaporated under vacuum (rotatory evaporator) at 70°C. The residue was freeze-dried and weighed. The sample was then transferred to a centrifuge bottle and water was added to make a 10 percent mixture. Upon centrifugation the water insoluble lignin was separated and the water solubles, mainly sugars, were decanted. The lignin washing step was repeated twice using about one-fourth of the amount of water employed for the first step. The aqueous phase containing the dissolved wood carbohydrates and the two washings were combined, concentrated in a rotatory evaporator, freeze-dried and weighed. This residue was designated as the "Carbohydrate Fraction". The dark residue from the centrifugation steps was freeze-dried and weighed. This water-insoluble residue was designated as the "Lignin Fraction". Both fractions were stored over phosphorous pentoxide in a vacuum desiccator.

8.10 Carbohydrate Analysis

The carbohydrate analysis was conducted following the procedure outlined by Borchardt and Piper (44). The powdered oven-dry sample (300 mg) was hydrolyzed in 3 ml of 72 percent sulfuric acid for one hour in a water bath maintained at $30 \pm 0.1^\circ\text{C}$. The hydrolyzate was diluted with 84 ml of water and then poured into a serum bottle. The bottle was sealed with a septum and aluminum cap and heated to 120°C in a pressure cooker for one hour. After cooling, precisely 0.1000 g of the internal standard, myo-inositol, was added to the hydrolyzate. The solution was then neutralized to pH 5.5 with barium hydroxide. After centrifuging this neutralized solution, exactly 50 ml of the supernatant was transferred to a round-bottom flask which contained 0.14-0.16 g of sodium borohydride. This mixture was allowed to react for 2 hours at room temperature; then acetic acid was slowly added until gas evolution ceased. This reduced hydrolyzate was concentrated by a rotatory evaporator to a syrup. Then methanol (10 ml) was added and the solution was evaporated to dryness. This step was repeated. Complete dryness was accomplished by heating in a oven at 105°C for 15 minutes. Acetylation was accomplished by addition of acetic anhydride (15 ml) and concentrated sulfuric acid (1 ml). The mixture was allowed to react for 1 hour in a water bath at 55°C . The flask was then cooled, and the contents added to a stirred ice-water mixture (1000 ml). The mixture was then transferred to a separatory funnel and extracted four times with methylene chloride. The extracts were combined for a given sample and concentrated to near dryness with a rotatory evaporator (75°C). Water (1 ml) was added to

the residue and evaporated to dryness. This end-product, a mixture of alditol acetates, was dissolved in 4 ml of chloroform and an aliquot (1 μ l) was injected into the gas chromatograph for qualitative and quantitative analysis.

The gas chromatograph used was a dual-column Perkin-Elmer Model 990 equipped with a flame ionization detector. Operating temperatures were as follows: 265°C for the injection port, 195°C for the column oven, and 255°C for the manifold. The flow rate of helium, the carrier gas, was maintained at 60 ml/min. through the stainless steel column (6 ft x 1/4 in.). The column packing was ECNSS-M (liquid phase) applied (3 percent by weight) to 100/120 mesh Gas Chrom Q (solid support).

Retention times were determined with known samples. The hydrolysis survival factor (H) for each carbohydrate was obtained from the literature (45) and is shown in Table 8.1 (page 97) together with the corresponding k value (slope of the calibration curve) which had been previously determined.

8.11 Ultraviolet Spectroscopy of the Lignin Fraction

The ultraviolet spectra were recorded with a Cary 15 spectrophotometer. One cm quartz cells were used. The procedure used was one recommended by Goldschmid (47) using pH 12 and pH 6 buffers. A mixture containing 100 mg per 50 ml of lignin in pH 12 buffer solution was prepared. This mixture was heated to 50-60°C and stirred for about 90 minutes to completely dissolve lignin. A portion of this solution (1.0 ml) was diluted to 50 ml with pH 12 buffer solution

(alkaline solution). Another 1.0 ml portion was neutralized with 1.0 N sulfuric acid solution (1.0 ml) and diluted to 50 ml with the pH 6 buffer solution (neutral solution). Both neutral (pH 6) and alkaline (pH 12) spectra were recorded. Each sample spectrum was determined against a suitable reference solution. The difference spectra were calculated by subtracting the neutral from the alkaline spectra. Phenolic hydroxyl groups were estimated using the equation reported by Goldschmid (47).

The ultraviolet spectra were also recorded from lignin samples reduced with NaBH_4 . The alpha-carbonyl content was estimated by the procedure reported by Adler and Marton (48) based on the difference in extinction at 305 nm before and after reduction with NaBH_4 . An average extinction of 9500 lit./mole-cm for relevant model compounds was assumed.

8.12 Reduction of Lignin with NaBH_4

Two hundred milligrams of lignin were mixed with 30 mg of NaBH_4 and 5 ml of 0.1 N sodium hydroxide solution in a centrifuge tube. This mixture was stirred and allowed to stand overnight. The mixture was acidified with 0.1 N sulfuric acid to pH 1-3 and then centrifuged. The reduced lignin residue was washed 3-4 times with small amounts of distilled water and, finally, was freeze-dried.

8.13 Infrared Spectroscopy

The infrared spectra were obtained from potassium bromide wafers using 1 mg of lignin and 400 mg of KBr. The spectra were recorded in a Beckman spectrometer, Model IR 20A.X.

8.14 Acetylation of Lignin

The lignin sample (200 mg) was dissolved in pyridine (3 ml) at room temperature. Acetic anhydride (2.4 ml) was added and the solution was allowed to stand for 24 hours. This mixture was centrifuged and the soluble fraction was poured into about 100 ml of crushed ice to precipitate the acetylated lignin. The acetylated lignin was recovered by centrifugation. Dilute HCl was added to neutralize excess pyridine (litmus paper). The acetylated lignin was washed four times with water, then dispersed in water and freeze-dried.

8.15 Nuclear Magnetic Resonance Spectroscopy

The nuclear magnetic resonance spectra (NMR) were recorded with a Varian HA-100 NMR spectrometer. The NMR spectra were obtained using acetylated lignin preparations. To record NMR spectra, lignin samples were dissolved in deuteriochloroform containing tetramethylsilane (TMS) as an internal standard. The NMR analysis was carried out at room temperature.

8.16 Determination of Methoxyl/C₉ Lignin Unit by IR Spectroscopy

The procedure described by Sarkanen, Chang and Allan (49) was followed. Base lines were arbitrarily drawn through the minima on each side of the absorption bands, as shown by the dotted lines in Figure 8.1 (page 100). The absorbance values were computed as shown below:

$$A_i = \log \frac{I_o}{I}$$

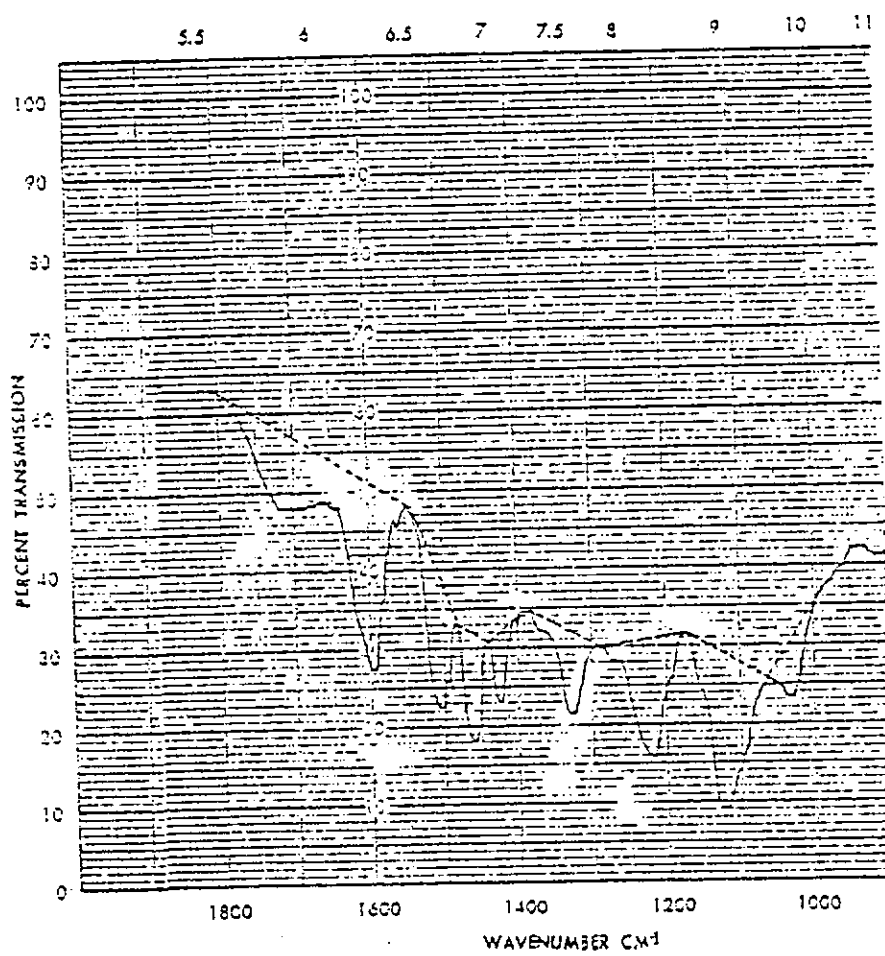


Figure 8.1 Determination of MeO/C₉ lignin units by IR spectroscopy

where i = Absorption band,

A_i = Absorbance of \underline{i} ,

I = Transmission value of maxima \underline{i} ,

I_0 = Corresponding transmission value of \underline{i} on the base line.

The absorbance of individual maxima was divided by the absorbance value of the 1500 cm^{-1} maximum ($A_i/A_{1500\text{ cm}^{-1}}$). This ratio value was then used to obtain the corresponding MeO/C₉ value by using appropriate graphs where relative absorptivities were plotted against MeO/C₉ (49).

Appendix Table 10.6 illustrates the calculations performed.

8.17 Elemental and Methoxyl Group Analyses

The elemental and methoxyl group analyses were made at the Microanalytical Laboratory of the Institute of Physical Chemistry of the University of Vienna, Vienna, Austria.

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Appendix Table 10.1 Handsheet properties of *E. viminalis* kraft pulp

Pulp Characteristics	Beating, PFI (revolutions)						
	0	1000	2000	3000	4000	5000	6000
C.S. Freeness, ml	475	358	295	271	231	187	180
Basis weight, g/m ²	60.29	59.18	59.18	59.52	58.99	61.31	61.62
Bulk, cc/g	1.58	1.35	1.26	1.24	1.20	1.13	1.13
Density, g/cc	0.63	0.74	0.79	0.81	0.83	0.88	0.88
Tear factor	75.4	74.1	75.2	75.8	76.5	76.7	74.3
Breaking length, m	7770	10470	11650	11990	12350	11940	12420
Burst factor	40.0	75.6	84.3	89.2	93.9	93.6	95.6
Brightness ^a	29.7	26.2	24.3	23.2	21.7	19.7	19.2

^aBrightness in photovolt units.

Appendix Table 10.3 Viscosity measurements and corresponding regression equation values of alpha-cellulose from ethanol and kraft pulps

Pulps	Dilution 1		Dilution 2		Dilution 3		Dilution 4		Slope	Intercept	Correlation Coefficient	
	A	B	A	B	A	B	A	B	"m"	"b"	"r"	
Ethanol Pulps	3 stages	8.66	0.126	7.87	0.084	7.46	0.063	7.04	0.051	20.54	6.09	0.99
	4 stages	8.30	0.126	7.46	0.084	7.13	0.063	6.75	0.050	17.72	6.03	1.00
	5 stages	8.04	0.128	7.35	0.085	6.98	0.064	6.75	0.051	16.79	5.90	1.00
	6 stages	7.33	0.128	6.76	0.086	6.44	0.064	6.31	0.051	13.36	5.61	1.00
Kraft Pulp	13.29	0.127	11.60	0.085	10.81	0.064	10.38	0.051	38.31	8.39	1.00	

A = Viscosity Number

$$\text{Viscosity Number} = \frac{\text{Specific Viscosity}}{\text{Concentration, g/dl}}$$

$$\text{Relative Viscosity} = \frac{\eta}{\eta_0} = \frac{\tau_s}{\tau_0}$$

Linear Regression Equation: $Y = mX + b$

B = Concentration of alpha-cellulose in Cuene, g/dl

$$\text{Specific Viscosity} = \eta_{sp} = \frac{\eta}{\eta_0} - 1$$

τ_s = Efflux time of a given volume of polymer solution

τ_0 = Efflux time of the solvent under the same conditions

Intercept "b" = Intrinsic Viscosity = $[\eta]$