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Edward Dee Hansen (Name) for the M. S. (Degree) in Forest Products (Major)

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Title TWO-STAGE HIGH-YIELD SULFITE PULPING OF RED ALDER (ALNUS RUBRA BONG.)

Abstract approved Signature redacted for privacy.
(Major professor)

Two-stage sulfite pulping conditions were determined which produced a high-yield high-hemicellulose pulp from red alder (Alnus rubra Bong.). Those cooks with a bisulfite first-stage and an alkaline second-stage produced pulps with the highest hemicellulose content and the highest strength properties.

The major hemicellulose in red alder is 0-acetyl-(4-0-methylglucurono)xylan. Removal of the acetyl groups, oxidation of the reducing end group by bisulfite ion, and retaining the uronic acid groups are the reasons for the high hemicellulose content of the pulp.

The hydrolyzates from the pulp xylans contain the same lactonizable products as the xylan hydrolyzates from the chlorine-ethanol-amine and chlorous acid holocelluloses which had been extracted with dimethylsulfoxide (DMSO). Xylonolactone was indicated in the lactonizable fraction of the xylan hydrolyzates.

It has been shown that the end groups were protected to some extent by oxidation during the pulping reaction.

TWO-STAGE HIGH-YIELD SULFITE PULPING OF RED ALDER (*ALNUS RUBRA BONG.*)

by

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A THESIS

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TWO-STAGE HIGH-YIELD SULFITE PULPING OF RED ALDER (ALNUS RUBRA BONG.)

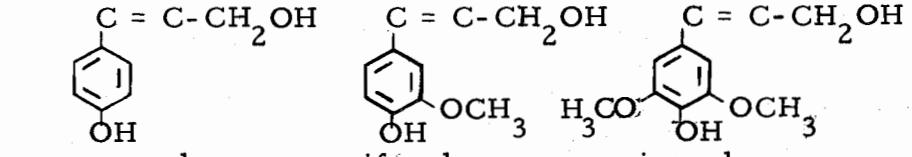
INTRODUCTION

Red alder (Alnus rubra Bong.) is the most important hardwood in the region west of the Cascade mountains in Oregon and Washington (92). There are approximately 11.75 billion board feet (91, 92) available for commercial exploitation. It is used in a limited amount for pulping, veneer, and lumber (9, 16, 35, 37, 38, 40, 45, 46, 64, 65, 80). The principal outlet for the lumber is the furniture industry. Even though it is attractive, its low density and strength restrict its use as lumber. Although it is used for pulping its use could be expanded since it has a high hemicellulose content, is easily delignified, and has short fibers which are desirable in the manufacture of corrigating medium.

Chemical Components of Coniferous and Deciduous Species

Chemically the major differences in structural components between coniferous (softwoods) and deciduous (hardwoods) species are the type and amount of lignin and hemicelluloses. The hardwoods contain 16-25% lignin while the amount varies between 23% and 33% in softwoods (39, 90). Of the three known monomeric units present in various lignins, two are present in hardwood lignin

while all three are present in softwood lignin. Hardwood lignin is a polymer containing monomeric units of coniferyl alcohol (54%) and sinapyl alcohol (46%). The monomeric units of softwood lignin are conferyl alcohol (80%), sinapyl alcohol (6%), and p-coumaryl alcohol (14%).



p-coumaryl coniferyl sinapyl

The lignin of softwoods has 108% of the 3- and 5-positions available on the aromatic nucleus while only 54% are available in the lignin of hardwoods (calculated as 100% for one vacant position). Therefore more carbon-carbon bonds of both the aryl-aryl and aryl-alkyl types, which in general are hard to break, could be formed in softwoods making this lignin polymer more highly cross linked and thereby making these species more difficult to delignify. The literature shows that this is actually the case (13, 68).

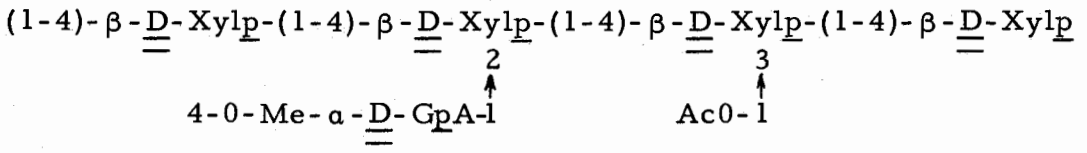
Hardwoods contain two hemicelluloses and softwoods contain four hemicelluloses. The major hemicellulose in hardwoods is 0-acetyl-(4-0-methylglucurono)xylan (20-30%) and the minor hemicellulose is glucomannan(3-5%) (89). In softwoods the major hemicellulose is 0-acetyl-glucomannan(15-18%) and the minor hemicelluloses are galactoglucomannan(2-3%), arabino-(4-0-methylglucurono)xylan(5-8%), and a trace of arabinogalactan (90).

There is one exception among the softwoods and that is with the genus Larix which contains approximately 25% arabinogalactan (90). This hemicellulose is unimportant in pulping since it is water soluble (see Figure 1 for formulas of the hemicelluloses).

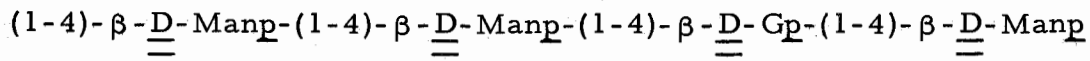
The major hemicellulose in hardwoods and softwoods is different, but it is this hemicellulose which contains the acetyl groups present in the wood (13, 34, 35, 89, 90). In hardwoods the major hemicellulose has a backbone of (1-4) linked β-D-xylopyranose units with 4-0-methylglucuronic acid (uronic acid) groups α- linked at carbon-2 (82, 89, 93, 94). This hemicellulose is also substituted at carbon-3 and to a lesser extent at carbon-2 with acetyl groups (12, 82, 89, 93). In general the acetyl groups are present on one of every three xylose units while the uronic acid groups occur on one of every ten xylose units (82, 89). The major hemicellulose in softwoods has a backbone of (1-4) linked β-D-glucopyranose and β-D-mannopyranose units in a ratio of 1:3 with random distribution of the individual sugar units (90). This ratio is 2:3 in hardwood glucomannan (34, 89). The acetyl groups occur on one of every three to four β-D-mannopyranose units at carbon-3 and to a lesser extent at carbon-2 (18, 34, 35, 90).

There are several differences worth emphasizing in the hemicelluloses of hardwoods and softwoods. Hardwoods contain only one hemicellulose that would be important in pulping whereas

HARDWOODS

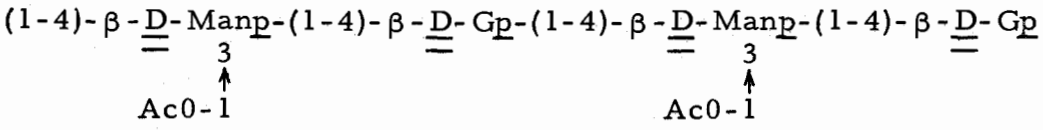


O-acetyl-(4-O-methylglucurono)xylan

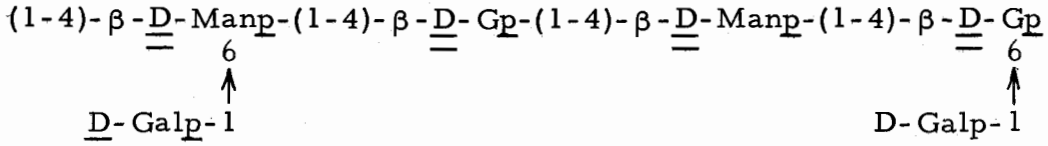


Glucomannan

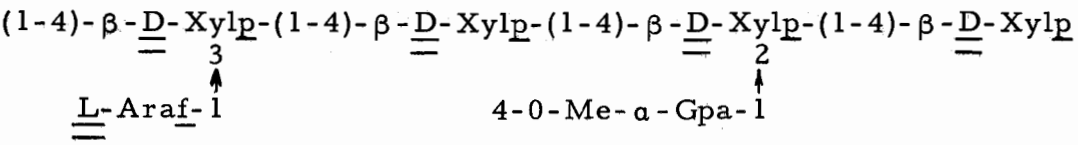
SOFTWOODS



O-acetyl-glucomannan



Galactoglucomannan



Arabino-(4-O-methylglucurono)xylan

Legend:		
	Xylp--Xylopyranose	Galp--Galactopyranose
	GpA--Glucopyranouronic acid	Araf--Arabinofuranose
	Me---Methyl	Manp-Mannopyranose
	AcO--Acetyl	Gp---Glucopyranose

Figure 1

softwoods contain two. The small percentage of glucomannan in hardwoods and galactoglucomannan in softwoods would probably be insignificant in its effect on the pulping process. The presence of one principle hemicellulose in hardwoods would make any subsequent pulp analysis easier and possibly more accurate. Of interest is the presence of the acetyl groups on the major hemicellulose in hardwoods and softwoods. The uronic acid groups appear only on the xylan fraction of both species and consequently are attached to the major hemicellulose in hardwoods and to the minor hemicellulose in softwoods.

Development of Sulfite Pulping Processes in the United States (49)

In the late 1890's the first calcium acid sulfite pulp mill was built in the United States. For approximately 40 years this process was the only one used to manufacture a chemical pulp. Then an acid sulfite process which used an ammonium base was introduced. The advantages of this process over the calcium process were the increased solubility of the ammonium salts and the higher rate of diffusion of the ammonium ion. However, when the spent liquor was burned in order to recover the ammonium salts, the ammonia was decomposed in the process. A similar attempt to recover the calcium base caused calcium sulfate to precipitate.

The inability to recover either the calcium or ammonium base led to the development of the magnesium acid sulfite process. With this new process the magnesium salts in the waste liquor could be burned to produce magnesium oxide and sulfur dioxide, the basic components of the cooking liquor. In 1950 the first acid sulfite mill with a complete recovery system was built in the United States. Even though the magnesium base could be recovered its use was limited to a small pH range (14). Next the Magnefite process was developed (14). This process utilized the wider solubility range of the magnesium salts and employed a bisulfite cooking liquor (pH=3.5). The lower hydrogen ion concentration of this liquor prevented the lignin from condensing with the phenolic substances in wood (13, 68) and consequently delignification could be effected in a shorter time.

There was still a need for a sulfite process that could be used over a still wider pH range and would allow the chemicals to be recovered. This need was responsible for the commercial development of the sodium base process which had been developed earlier in Scandinavia. Although a neutral sulfite semichemical process utilizing a sodium base had been used since the 1940's in the United States an acid or alkaline cook had never been attempted. The neutral sulfite semichemical process included the bisulfite region so its overall pH range was from 4.5 to 8.0. This rather mild

delignification process was used to produce a high-yield pulp from hardwoods since their lignin content and the cross linking within the lignin polymer is low. Due to the short fibered structure and high hemicellulose content, pulps from hardwoods could be used in the manufacture of corrigating medium and tissue. The bisulfite process is also adaptable to woods with a high resin content.

The next major change in sulfite pulping was the development of sodium base two-stage pulping by the Scandinavians in the late 1950's (3, 22, 23, 44, 47, 63, 66, 67, 76, 79, 87). In the early 1960's two Canadian companies started pulping by two-stage processes. One utilized a sodium base and the other a magnesium base (1, 7, 24, 79, 83). One American company in early 1961 developed a two-stage process utilizing a magnesium base (7, 10, 19, 77, 79). This interest in two-stage pulping did not last long in this country despite its wide range of applicability. Since pine is the principal species in the Scandinavian countries the two-stage process was effective in utilizing this species for chemical pulp.

The two, two-stage processes that have been developed in Scandinavia are the Stora and Sivola processes. The Stora process uses a pH of 5.5 to 8.0 in the first-stage and a pH of 1.0 to 2.0 in the second-stage. This process was developed specifically for the manufacture of a high-yield high-hemicellulose pulp from highly resinous species. The high pH in the first-stage promotes sulfonation of that portion of the lignin that condenses with phenolic

substances at the lower pH (13, 68). In the second-stage which is a typical acid sulfite cook sulfonation is completed and the lignin is removed.

The Sivola process utilizes two sets of conditions in the first-stage and one set of conditions in the second-stage. One variation is to use a pH of 1.0 to 2.0 in the first-stage followed by a pH of 8.0 to 9.0 in the second-stage. In the first-stage, hydrolysis of the hemicelluloses occurs and part of the lignin condenses with the phenolic substances. The alkaline second-stage removes the condensation products and any hemicelluloses that were left in the first-stage. The result is a chemical pulp (59-62). The other variation uses a pH of 3.0 to 5.0 (bisulfite region) in the first-stage and the second-stage is again alkaline. With this variation the hemicelluloses are stabilized in the first-stage, against alkaline "peeling" in the second-stage. This process retains the hemicelluloses and produces a pulp with strength properties similar to those of a kraft pulp (70).

Influence of Pulping Conditions on the Hemicelluloses

As was mentioned earlier the major hemicellulose in red alder, a hardwood, is 0-acetyl-(4-0-methylglucurono)xylan. By using a two-stage cook with the proper conditions a high-yield high-hemicellulose pulp should be produced from red alder. The

degree of removal of the acetyl and uronic acid side chains influences the degree of retention of this hemicellulose. Once the acetyl and uronic acid groups are hydrolyzed the xylan is easily absorbed onto the cellulose since the spatial configuration of the two polysaccharides is similar. The only difference in spatial configuration is that cellulose has a sixth carbon atom which is equatorial to the 6-membered ring. One other factor that influences the absorption of the xylan is its degree of polymerization (DP). The DP of a polysaccharide can be reduced to a point where the polysaccharide is no longer insoluble and once dissolved it will remain in solution.

Under acid conditions the acetyl groups are stable and the hemicellulose is hydrolyzed (4, 36). If bisulfite conditions (pH=4-7) are employed in the first-stage of a two-stage cook the acetyl groups are more easily hydrolyzed without damaging the hemicellulose (13, 18, 32, 36, 41, 93). The acetyl groups are more easily hydrolyzed as the solution becomes more alkaline (36, 41). Cleaving these groups would enhance the absorption of the hemicellulose onto the cellulose and thus it would be retained in the pulp. However the presence of the uronic acid group probably retards the absorption of the xylan onto the cellulose. Since the uronic acid occurs on only one of every ten xylose units its role in preventing absorption of the hemicellulose onto the cellulose may not be as important as expected. In fact this acid group under acidic condtions inductively stabilizes

the β(1-4) linkages between the xylose units (33, 85, 93). Therefore it may not be desirable to hydrolyze this acid group in the first-stage.

By employing mild alkaline conditions (pH=7.5-10.5) in the second-stage of a two-stage cook the uronic acid group could be hydrolyzed (36, 68, 89). In alkaline solutions the salt of the uronic acid is soluble in the liquor. Once dissolved the uronic acid group is cleaved from the xylan chain. Then as the cook progresses the alkalinity decreases which causes the xylan to precipitate onto the cellulose (54).

Under alkaline conditions all polysaccharides undergo an "alkaline peeling reaction" via the reducing end group (17, 25, 51, 68, 84). When a β(1-4) linked polysaccharide is treated with an alkaline solution the reducing end group is attacked and each unit of the polysaccharide is "peeled off" at this end of the polymer. Should one of the units be substituted at carbon-2 with a blocking group such as a uronic acid then the polymer would be stabilized when this unit is the end group. However at temperatures of 170°C and above, the uronic acid group no longer protects the polysaccharide against the "alkaline peeling reaction" because random cleavage of the β(1-4) linkages occurs (50, 81). The overall result of this alkaline reaction is the formation of metasaccharinic acid on the reducing end of the polysaccharide and isosaccharinic acid molecules

in solution (29). For every metasaccharinic acid end group formed approximately 40 isosaccharinic acid molecules are formed (15). Therefore, after alkaline treatment, a carboxyl group is present on the polysaccharide instead of the normal carbonyl group (27). The only way to avoid degradation by the "alkaline peeling reaction" is to either oxidize or reduce the reducing end group to a carboxylic acid or an alcohol respectively (13, 68). Since bisulfite ion is a good oxidizing agent (20, 21, 53) at elevated temperatures and is present in the first-stage liquor it will oxidize the reducing end group and prevent the "alkaline peeling reaction". Sodium borohydride and sodium polysulfide have been used in kraft liquor to eliminate the reducing end group by reduction and oxidation respectively (68). Neither of these compounds could be used in a sulfite cook which is not alkaline since they would decompose rapidly. Another disadvantage is that sodium borohyride is too expensive and sodium polysulfide has a very objectionable odor. Therefore, by stabilizing the hemicellulose in the first-stage against the "alkaline peeling reaction", alkaline conditions could be used in the second-stage without much degradation of the wood polysaccharide.

The lignin content of red alder is low and the polymer is less cross-linked than softwood lignin. Therefore red alder should be easy to delignify.

Research Proposal

In order to produce a high-yield high-hemicellulose pulp from red alder by a two-stage process the above factors must be kept in mind when setting the pulping conditions. A sodium base will be used because it is soluble over a wide pH range. The first-stage will be in the bisulfite-neutral region and the second-stage will be in the neutral-alkaline region. It is hoped that these conditions are mild enough to prevent degradation but strong enough to hydrolyze the acetyl and uronic acid groups. No attempt will be made to exhaustively find the best conditions of time, temperature, and liquor concentration. The time will be held constant at one hour in each stage and only the temperature and liquor pH value will be varied. The temperature range will be from 150°C to 165°C. A temperature of at least 150°C is needed to initiate the pulping reactions. Five liquors will be used varying the pH in 1.5 increments, from 4.5 to 10.5. Using the conditions given above, it is planned to produce pulps ranging in yield from 65% to 75%.

EXPERIMENTAL

Preparation of Wood Chips and Wood Meal

A red alder (Alnus rubra Bong.) tree 14.5 inches in diameter, 65 feet in height, and approximately 60 years old was felled and bucked into two foot sections in MacDonald Forest, six miles north of Corvallis, Oregon. The two foot sections were manually debarked and chipped in an Appleton 24 inch, two blade chipper. The chips were screened and only those chips between one-quarter and three-quarters of an inch were used for the pulping experiments. The moisture content of the chips was 47.7%. Samples of green chips containing 900 grams of oven dry wood were weighed into polyethylene bags and stored air-tight in a cold room at 35°F until needed.

For the chemical determinations and hemicellulose extractions wood meal was used. Approximately ten pounds of unscreened chips were dried in a hot dry room (30% R. H. and 91°F) for one week, ground in a Wiley mill, screened, and the various mesh sizes collected separately.

Three 20 gram samples of wood meal were extracted in Soxhlet extracters for 48 hours using ethyl ether, 95% ethanol, and distilled water in this order.

Pulping

A two pound stationary digester with a heat exchanger and forced circulation was used for all cooks. Prior to injecting the cold liquor into the digester the chips were presteamed for 10 minutes at 50 psi. Immediately after presteaming, the cold liquor was injected and the temperature increased within 10 to 15 minutes to the desired cooking temperature. At the end of one hour the first-stage liquor was drained and the second-stage liquor injected. After 10 to 15 minutes the cooking temperature was again reached and held constant for one hour. The cooking was done at the following temperatures: 150, 155, 160, and 165°C (see Appendix Table 1).

The cooking liquor contained 5.25% by weight of sodium bisulfite or sodium sulfite (39). In order to obtain the desired pH the liquor was buffered with either sodium bicarbonate or sodium carbonate (11). The pH of the liquors used were 4.5, 6.0, 7.5, 9.0, and 10.5. All of these liquors were used in the second-stage and all, but the one of pH 10.5, were used in the first-stage. The liquor to wood ratio was 4:1 (42) (see Appendix Table 1).

Six experimental cooks were made using a kraft second-stage. The active alkali and sulfidity of the kraft liquor were 12.5% and 25% respectively. In those cooks having a kraft second-stage, all five sulfite solutions were used in the first-stage. The time required

for the kraft stage was reduced from one hour to as little as 15 minutes.

After the cook was completed the chips were removed from the digester, two 10 gram samples taken for a yield determination, and the remaining chips fed into a Bauer 24 inch double disc refiner with a 4 inch auger at a rate of 200 feet per minute. The plate clearance was 0.025 of an inch.

At the end of each stage a small sample of liquor was obtained and the pH and total SO_2 content (49) were determined.

Pulp Testing

The hand sheets were made and tested according to TAPPI standards T205m-47, T403ts-63, T404os-61, T410os-61, T411m-44, and T414ts-64. Mullen values, tear strength, breaking length, and density were determined on all hand sheets. Kappa numbers were determined in all pulps according to TAPPI standard T236m-60 and 1% sodium hydroxide solubilities were determined on the selected pulps according to TAPPI standard T212m-44 (see Appendix Table 1).

Hemicellulose Preparations

Direct Alkaline Extraction From Wood (86, 89)

Two hundred grams of 150 and finer mesh red alder wood meal were extracted with a 1:2 mixture of 95% ethanol and benzene

and then with 95% ethanol. The air dried extracted wood meal was then added to 3 liters of nitrogen purged 24% potassium hydroxide (by weight) solution in a 4 liter filter flask. The system was purged with nitrogen, stoppered tightly, and shaken overnight at -5°C. The liquid was separated from the wood meal by centrifuging. Each centrifuge tube was purged with nitrogen and stoppered before being placed in the centrifuge. Approximately 2 1/2 liters of caustic solution was reclaimed. This solution was added rapidly but dropwise to 12 liters of 95% ethanol, containing 25% acetic acid by volume, in order to precipitate the 4-0-methylglucuronoxylan. The hemicellulose was allowed to settle and then the supernatant liquid was decanted. The small amount of acidified ethanol remaining was removed by centrifuging. The hemicellulose was washed and solvent exchanged with following solvents; twice with 75% ethanol containing 5% acetic acid, three times with 95% ethanol containing 5% acetic acid, three times with 95% ethanol, and three times with ethyl ether in this order. The solvent exchanging was accomplished by adding the appropriate solvent to the centrifuge tubes containing the hemicellulose, thoroughly stirring the mixture with a mechanical stirrer, centrifuging, and decanting the solvent. This procedure was used for washing all the various hemicellulose samples. A vacuum dessicator attached to a water aspirater by means of a calcium chloride drying trap was used to dry the 4-0-methylglucuronoxylan. The

dessicant was removed from the dessicator in the event that bumping did occur. The yield of hemicellulose was 8.8%.

Chlorine-Ethanol-Amine Holocellulose (86, 89)

Three hundred ninety grams of 40 to 60 mesh red alder wood meal were extracted with a 1:2 mixture of 95% ethanol and benzene and then with 95% ethanol. After air drying, the extracted wood meal was chlorinated for 4 minutes at 1°C. Immediately after the chlorination, the wood meal was transferred to a Buchner funnel where it was washed with 3 liters of 95% ethanol, 6 liters of boiling 95% ethanol containing 3% monoethanolamine by volume, and water until the filtrate was clear. The entire chlorination and washing procedure was repeated four times for a total of five treatments. After washing with water the last time, the wood meal was washed with 3 liters of 95% ethanol containing 3% acetic acid by volume. A modification of the original procedure which proved to be very successful was to do all of the washing in the Buchner funnel. The yield of holocellulose was 75%.

DMSO Extraction from Holocellulose (12, 31, 57, 82, 86, 89)

The holocellulose was extracted by shaking with dimethylsulfoxide (DMSO) for five days at room temperature. Every 24 hours the solution was filtered and fresh DMSO added. The total

DMSO extract (4430 ml) was added rapidly but drop wise to 28 liters of 95% ethanol, containing 5% acetic acid by volume, to precipitate the 2-0-acetyl-4-0-methylglucuronoxylan. The hemicellulose was allowed to settle overnight and then the supernatant liquid was decanted. The washing and solvent exchanging procedure was the same as given above for the 24% potassium hydroxide extraction from the wood. The yield of hemicellulose was 18.3%.

DMSO Extraction from Selected Pulps (12, 31, 57, 82, 86, 89)

Pulps 1, 2, 3, and 4[1] were placed in separate 4 liter filter flasks. The flasks were filled with 3800 ml of 95% ethanol containing 3% monoethanolamine, purged with nitrogen, stoppered tightly, and allowed to stand overnight. The pulp slurry was filtered on a Buchner funnel with the aid of a rubber dam. After filtering, the pulp was spread out on aluminum foil and air dried. Then the pulp was placed back in the 4 liter filter flask and 3800 ml of DMSO added. This mixture was shaken overnight and then filtered on a Buchner funnel with the aid of a rubber dam. The individual DMSO extracts (3000 ml) were added rapidly but drop wise to approximately four times their volume of 95% ethanol containing 5% acetic acid by

[1] Pulp 1 from cooks 46 and 47
Pulp 2 from cooks 48 and 49
Pulp 3 from cooks 50 and 52
Pulp 4 from cooks 51 and 53

volume. After allowing the hemicellulose to settle and then decanting the supernatant liquid it was washed by the procedure given above for the 24% potassium hydroxide extraction of the wood.

Standard Chemical Analyses

Klason and UV Lignin

Klason lignin was determined on the extractive free wood, the selected pulp samples, and on all hemicellulose samples according to TAPPI standard T222m-54. Acid soluble lignin was determined by measuring the ultraviolet absorption of the hydrolyzates from pulps 1, 2, 3, and 4 at 280mμ (71, 75, 78). Before the absorption was measured the hydrolyzates were boiled down to approximately 350 ml. Then they were gel filtered on a column 1.6 x 25 cm packed with Sphadex G-10. After the filtration was completed the filtrates were diluted to 500 ml in volumetric flasks. Ten milliters of each of these solutions were diluted in separate 100 ml volumetric flasks before the UV absorption was measured. A standard solution containing 8 mg/l was made from a reference sample[2] which was 80.2% pure in calcium lignin sulfonate. This standard had an absorbance of 0.15 at 280 mμ.

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[2] Lignosite powder provided by Georgia-Pacific Corp., Bellingham, Washington.

4-0-Methylglucuronic Acid

The 4-0-methylglucuronic acid content was determined by decarboxylation in 12% hydrochloric acid with subsequent absorption of the CO_2 on Ascarite (86).

Total Sugars

Total sugar content was determined by the method of Seaman, et al.(74, 86) which involves hydrolyzing the sample in 72% sulfuric acid followed by quantitative paper chromatography of the neutralized hydrolyzate.

Acetyl Content

Saponification of all samples with p-toluenesulfonic acid in absolute ethanol, followed by transesterification with sodium hydroxide gave a good indication of the acetyl content (28, 88).

Isolation and Identification of Pulp Xylan Acidic End Groups

Paper Chromatographic Procedures

The neutral sugar fractions from the hydrolysis of the various xylan samples were evaporated to 50 ml and chromatogramed on Whatman no. 1 filter paper 17 1/2 inches long for 24 hours with an irrigating solvent of butanol, acetic acid, and water (70:7:23) (72).

The chromatogram was developed by spraying with a solution of ammoniacal silver nitrate and heating in an oven for 15 minutes at 100°C (86). Standard solutions of glucose, mannose, and xylose obtained from Eastman Organic Chemical Company were run at the same time. The neutral fractions were then acidified with 5 ml of glacial acetic acid and heated to 50-60°C on a water bath to lactonize any acids that might have been present. The acidified solutions were chromatogramed according to the procedure given below for the acid fractions.

The acid fractions were evaporated to 5 ml and Dowex 50W-X2 in the H^+ form was added and the solutions heated to 75°C on a water bath to lactonize the acids. After filtering off the Dowex the solutions were placed in 2.5 x 6.0 cm vials and evaporated, under water aspirator vacuum, to dryness in a vacuum dessicator containing sodium hydroxide as the dessicant. The vials were removed from the dessicator and 1.5 grams of water added. The acid solutions were chromatogramed on Whatman no. 1 filter paper 22 1/2 inches long for 8-10 hours using an irrigating solvent of ethyl acetate, acetic acid, and water (10:1.3:1) (55) (solvent A). Three other solvent systems used to identify the lactones present in the hydrolyzates are as follows; iso-amyl alcohol, ethyl acetate, formic acid, and water (4:2:1:3) (6) (solvent B); ethyl acetate, pyridine, and water (10:4:3) (6) (solvent C); and butanol, formic acid, and

water (500:115:385) (5) (solvent D). The chromatogram was first sprayed with a mixture containing equal amounts of 1.1M methanolic potassium hydroxide and 1M hydroxylamine hydrochloride, dried, and then sprayed with 1% hydrochloric acid containing 2% ferric chloride (2, 26). This spray will be referred to as the lactone spray throughout the remaining portion of this paper. Standard solutions of xylonolactone, xyloisosaccharinolactone, xylometasaccharinolactone, glucuronolactone, and 2-0-(4-0-methyl-α-D-glucopyranosyluronic acid)-D-xylopyranose(aldobiouronic acid) were used as references.

Xylonolactone was prepared from xylonic acid which was synthesized from xylose by bromine oxidation using a barium carbonate buffer (86). Xylometasaccharinic acid was prepared from 3-0-methylxylose which was synthesized from 3-0-methyl-1, 2-5, 6-Di-0-isopropylidene-D-glucofuranose (86). Lactonization of xylometasaccharinic acid gave xylometasaccharinolactone. The other standards were either bought or received as gifts.

Hydrolysis of Hemicelluloses with 72% Sulfuric Acid (86)

Four grams of each hemicellulose sample were hydrolyzed in 40 ml of 72% sulfuric acid. After standing for two hours with frequent stirring the samples were diluted with 1500 ml of distilled water and refluxed for 4 hours. The hydrolyzates were gel filtered

through a 1 cm layer of Sphadex G-10 in a 12 cm Buchner funnel. Solid barium hydroxide hydrate which had been crushed to a fine powder was used to neutralize the filtrates to pH 6.5. After allowing the barium sulfate to settle the supernatant liquid was decanted and the remaining liquid removed by centrifuging. The filtrates were evaporated to approximately 300 ml with an all glass rotary evaporator under water aspirator vacuum.

Column Separation of Hydrolyzates (74, 86)

A Dowex 1-X2 column 1.6 x 40 cm was used to separate the acids from the neutrals in the filtrates from the 72% sulfuric acid hydrolysis. First the column was washed with 2N acetic acid until it was free of chloride ion. The column was then washed with distilled water until a pH of 5 was reached. The sample was poured on the column and washed with water until a negative test was given with ammoniacal silver nitrate. This test consisted of placing a drop of filtrate on a piece of filter paper and developing by the procedure given under paper chromatography. If a brown spot failed to appear on the paper the washing was complete. It is necessary to run a blank when using this test. The acids were then eluated with 400 ml of 1N acetic acid. Further elution with 250 ml of 2.5N acetic acid was employed as a check. A drop of the second eluate was placed on a piece of filter paper and sprayed with the

lactone spray. A mauve colored spot did not appear which indicated that the second eluate did not contain any lactonizable acids.

The acid and neutral fractions obtained from the column were chromatogramed and developed as outlined above, under paper chromatographic procedures.

Determination of the Xylan End Units

A piece of Whatman no. 1 filter paper 22 1/2 inches long was streaked with approximately 1 1/2 cc of a solution containing equal quantities from five of the acid fractions. The five fractions used were from the selected pulps and the DMSO extracted holocellulose. The chromatogram was developed by the acid fraction procedure given above. Four strips 3/4 x 20 inches were cut at 5 inch intervals from the chromatogram, taped to a piece of Whatman no. 1 filter paper 22 1/2 inches long, and sprayed with the lactone spray. These developed strips were taped back in the undeveloped chromatogram to aid in cutting sections from the chromatogram which contained the desired compounds. The sections were cut into approximately 1/2 inch squares, placed in vials 2.5 x 6.0 cm, and soaked in water overnight. The water was decanted into some additional vials, these vials were placed in a vacuum dessicator with sodium hydroxide as the dessicant, and evaporated under water aspirator vacuum to approximately 2 ml. A small portion of these samples

were chromatogramed by the acid fraction procedure given above. The chromatogram was developed with the lactone spray. This procedure was employed to determine the purity of the isolated substances. The procedure outlined in the above paragraph was repeated four times.

Those samples which appeared to contain the same substance were combined, filtered to remove paper fibers, and evaporated to dryness. Optical rotations of these lactone samples were taken using a 1 decimeter tube containing 1.1 ml of a 2.0% solution.

RESULTS AND DISCUSSION

Chemical Wood Characterization

The extractive, lignin, individual sugars, and acetyl and uronic acid contents were quantitatively determined. The total extractive content of the red alder (Alnus rubra Bong.) used is 6.04%. The percent of extractives in each solvent is as follows; ethyl ether 4.32%, 95% ethanol 1.01%, and distilled water 0.71%. Acid insoluble lignin (Klason lignin) determined by hydrolysis of the wood meal in 72% sulfuric acid constituted 21.0% of the total wood substance. The results of the quantitative individual sugar determinations are given in Table 1. From these determinations the individual wood polysaccharides were calculated. In performing these calculations it was assumed that the information given earlier in the introduction on the structure of hardwood hemicelluloses is valid for the wood being used. Also the mannose and the xylose present in the wood could only have been derived from the hemicelluloses, glucomannan and 0-acetyl-(4-0-methylglucurono)xylan respectively. The wood contains 45.4% cellulose, 29.8% 0-acetyl-(4-0-methylglucurono)xylan, and 3.8% glucomannan. The acetyl groups and uronic acid content were 3.6% and 4.7% respectively. This information is also summarized in Table 6.

Table 1. Quantitative sugar analysis.

	Uronic Anhydride[1]	Glucose[2]	Mannose[3]	Xylose
Wood	4.36	66.35*	3.25*	30.40*
Pulp 1	2.92	73.66	1.96	24.38
Pulp 2	3.04	73.33	2.09	24.58
Pulp 3	2.36	78.93	1.91	19.16
Pulp 4	1.96	81.09	2.01	16.90
Xylan 1	11.68	0.67	0.51	98.82
Xylan 2	10.59	0.65	0.47	98.88
Xylan 3	10.84	0.66	0.44	98.90
Xylan 4	8.69	0.66	0.45	98.89
Xylan 5	9.92	6.42	0.78	92.80
Xylan 6	10.67	17.11	5.18	77.71

* Ratios

1 Percent calculated as four times weight of CO_2 collected.

2 Contains small amount of galactose.

3 Contains small amount of arabinose.

The amount of material extracted with DMSO from a 75% yield holocellulose was 18.3%. This material was not further purified and analysis showed it to be 93.2% xylan containing 10.8% acetyl groups and 10.7% uronic acid. Direct extraction of the wood with 24% potassium hydroxide at -5°C gave only 8.8% of material. This extract contained only 73.4% xylan based on individual sugar

analysis. A more complete chemical composition of these xylans is given later in the discussion. In neither preparation was any attempt made to obtain a complete hemicellulose extraction. Values reported in the literature for the xylan content of red alder vary between 14.5% and 24.3% (89). Although it is possible to extract as much as 80-95% of the total xylan lower values have been reported (89). It does not appear unreasonable to assume that the calculated value of 29.8% xylan is correct, although only 17.1% (93.2% xylan in 18.3% DMSO extract) was actually isolated as 0-acetyl-(4-0-methylglucurono)xylan.

Evaluation of Pulping Conditions

All cooks were presteamed before the liquor was added. This removed a large portion of the red coloring matter present in red alder and saturated the chips so the liquor would penetrate faster. By presteaming and then waiting for a few minutes after the steam was turned off, a partial vacuum was created in the digester which helped to give immediate penetration of the liquor into the chips.

All the cooks that were made are listed in Appendix Table 1. The first 6 two-stage cooks were made to become familiar with the heat control on the digester.

Cooks 7 through 17 are single-stage cooks. All five liquors were used twice with the temperature being raised 5°C from 150°C

to 155°C for the second cook at each of the specified pH values. The information obtained from these cooks was invaluable in helping to determine the cooking conditions for the two-stage cooks. One fact was obvious. As the pH increased the temperature also had to be increased if a pulp of a given yield were to be obtained (68, 93).

Next the two-stage cooks are listed. Only the liquors of pH 4.5, 6.0, 7.5, and 9.0 were used in the first-stage while all five liquors were used in the second-stage. The fact that the temperature must be increased as the pH increases (68, 93) if a pulp of the desired yield is to be obtained is substantiated by the data from these cooks. As the pH of the first-stage increases the pulp strength decreases. However as the second-stage pH increases the strength of the pulp increases. If the first-stage liquor has a lower pH than the second-stage liquor the pulp is stronger than a pulp from a cook with a high first-stage pH and a low second-stage pH.

Although it was not the objective of this research six two-stage cooks were made with a kraft (pH=14) second-stage. As indicated in Appendix Table 1 cooks 38, 39, 40, 42, 43, and 44 exhibit very high strengths. The kraft conditions in the second-stage probably caused some of the dissolved xylan to be reabsorbed (54) onto the cellulose which accounts for the high strengths of these pulps.

After examining the data in Appendix Table 1 it was decided

that cooks 23 and 24 had the best combination of yield, kappa number, and strength. The yields are approximately in the middle of the desired range (65-75%). The kappa numbers, although high are relatively low when compared with the other kappa numbers of this project. The outstanding feature of these two cooks is their high strengths. Since the properties of both these cooks are similar it was decided to combine the cooking conditions so as to make one select pulp. The cooking conditions chosen were as follows; first-stage pH and temperature of 4.5 and 150°C, and second-stage pH and temperature of 8.0 and 160°C for pulp 1.

Cooking conditions different than those of the first selected pulp were wanted for the second selected pulp. After a cursory examination keeping the above restriction in mind four cooks (28, 29, 32, and 33) were selected. However a closer examination revealed that the strength properties of cooks 28 and 29 were superior to those of cooks 32 and 33. The yield of cooks 28 and 29 was lower and the kappa numbers were very similar. Therefore the cooking conditions of cooks 28 and 29 were combined into the following cooking conditions; first-stage pH and temperature of 6.0 and 155°C, and second-stage pH and temperature of 10.0 and 165°C for pulp 2.

After making two cooks of approximately 75% yield at each of the cooking conditions given above it was decided to raise the

temperature in order to obtain two more pulps of approximately 65% yield. The cooking conditions for the two pulps of lower yield are as follows; first-stage pH and temperature of 4.5 and 155°C, and second-stage pH and temperature of 8.0 and 165°C for pulp 3; and first-stage pH and temperature of 6.0 and 165°C, and second-stage pH and temperature of 10.0 and 165°C for pulp 4. In all there were two cooks made at each of the given conditions; however after making handsheets the pulps which had been cooked by the same conditions were combined in order to have enough pulp for the chemical analyses.

Physical Properties of Selected Pulps

The strengths, yields, and kappa numbers of the four select pulps are given in Table 2. Since pulps 1 and 3 are complimentary to one another they will be discussed together and then pulps 2 and 4 will be discussed. At a freeness of 600 ml pulp 1 has a higher mullen value than pulp 3 which indicates more fiber to fiber bonding (68) in the handsheets from pulp 1. However pulp 3 has a higher tear value and a higher breaking length which are indicative of the strength of the individual fibers. At a freeness of 400 ml pulp 3 has higher values than pulp 1 for all three strengths. The mullen and breaking length values are higher at freeness 400 than at freeness 600 for both pulps while the tear value has decreased for

Table 2. Strengths of red alder two-stage pulps.

Cooking Method: Two-stage sulfite 1st stage pH	2nd stage pH	Pulp #	Freeness CSml.	Mullen factor	Tear factor	Breaking length meters	Yield	Kappa no.
				pts./lb.	g./lb.			
4.5	8.0	1	600	28.0 (0.56)	59.6 (0.84)	4890	75.9	139
4.5	8.0	3	600	25.6 (0.51)	73.1 (1.02)	4940	66.1	121
6.0	10.0	2	600	23.4 (0.47)	62.9 (0.89)	4520	76.5	139
6.0	10.0	4	600	25.4 (0.51)	71.4 (1.00)	4840	66.0	125
4.5	8.0	1	400	39.9 (0.80)	59.8 (0.84)	6450	75.9	139
4.5	8.0	3	400	41.5 (0.83)	66.4 (0.93)	7310	66.1	121
6.0	10.0	2	400	36.9 (0.74)	57.9 (0.81)	5950	76.5	139
6.0	10.0	4	400	39.4 (0.79)	67.6 (0.95)	7420	66.0	125

pulp 3 and remained unchanged for pulp 1. Since the tear test is more localized than either the mullen or breaking length tests the lower value at freeness 400 indicates some localized fiber damage (68). The localized fiber damage is probably due to an unraveling of the fiber. As this unraveling progresses the area for fiber to fiber bonding increases while the fiber strength decreases.

At both freeness values pulp 4 is stronger than pulp 2 for all three test values. The trend within each pulp at the different values is similar to the trend for pulps 1 and 3. The mullen and breaking length values increase for both pulps when proceeding from freeness 600 to freeness 400 while the tear value decreases. The same reason as given above can be given here. As the length of beating increases the fiber is unraveled which increases the surface area of the fiber and gives rise to more fiber to fiber bonds but decreases the strength of the individual fiber.

Pulps 3 and 4 have lower yields than pulps 1 and 2, and consequently the kappa numbers of pulps 3 and 4 are lower since the kappa number indicates the degree of delignification.

In general the lower yield pulps are stronger than their corresponding higher yield pulps. Pulp 3 appears to be slightly stronger than pulp 4 except for tear and breaking length strength at the lower freeness. However pulp 1 is stronger at both freeness values than pulp 2 which indicates that the pulps cooked with a first-stage pH of

4.5 and a second-stage pH of 8.0 are superior to the pulps cooked with a first-stage pH of 6.0 and a second-stage pH of 10.0.

Table 3 lists strengths of red alder pulps produced by other methods. A comparison of these pulps with those in Table 2 indicates that the two-stage pulping of red alder produces pulps of slightly higher strength. Only the values in Table 2 will be used to compare with values in Table 3. The two-stage pulps are vastly superior to the groundwood and sulfate semi-chem pulps. A comparison of the mullen values from the chemi-groundwood and neutral sulfite semi-chemical indicates the two-stage pulps are stronger with respect to mullen strength. However the tear value of the chemi-groundwood is higher than the tear value for the two-stage pulps, but the two-stage and neutral sulfite semichemical pulps have very similar values for tear. The breaking length of the two-stage pulps is longer than the breaking length for the groundwood and chemi-groundwood pulps except for pulp 2.

Table 3. Strengths of typical red alder pulps.

Cooking method	Freeness CSml	Mullen pts./lb	Tear g/lb	Breaking length meters	Yield
Groundwood (8)	55	0.11	0.32	1640	----
Chemigroundwood (8)	405	0.63	1.09	6200	----
Neutral sulfite semi-chem (43)	450	0.60	0.85	----	76.8
Neutral sulfite semi-chem (43)	450	0.72	0.95	----	69.8
Sulfate semi-chem (43)	450	0.40	0.75	----	----

Table 4 lists several hardwoods that have been pulped by several different methods. The birch wood gives higher mullen and breaking length values for all three pulping methods than pulps 1, 2, 3, and 4 at either freeness 600 or 400. The birch calcium bisulfite pulp has a tear value comparable to pulps 1 and 2 at both freeness values, while the neutral sulfite semichemical tear value is comparable to pulps 3 and 4. The birch kraft pulp is superior to all four of the red alder two-stage pulps.

The beech calcium bisulfite mullen value is comparable, the tear value is slightly lower, and the breaking length is higher than the corresponding values for pulps 1, 2, 3, and 4 at freeness 600. At freeness 400 the red alder pulps have higher values. The kraft pulp from beech is comparable in mullen and breaking length values, and is superior in tear to pulps 1, 2, 3, and 4 at freeness 400. At freeness 600 pulps 1, 2, 3, and 4 are inferior in mullen and breaking length, and similar in tear to the beech kraft pulp. The beech neutral sulfite semichemical pulp is comparable to pulps 3 and 4 and slightly better than pulps 1 and 2 at freeness 400. At freeness 600 the beech neutral sulfite semichemical is better than pulps 1, 2, 3, and 4 except for tear which is comparable.

The mixed Japanese beech and oak pulps given in Table 4 appear to be weaker than pulps 1, 2, 3, and 4. The 75% yield Japanese pulp is 50-60% lower in mullen, 35-45% lower in tear,

Table 4. Strengths of other hardwood pulps; single- and two-stage.

Wood	Cooking method	Freeness CSml	Mullen factor	Tear factor	Breaking length meters	Yield %	Kappa
Birch (30)	Calcium bisulfite	550	54.0	60	9800		
	Kraft	550	56.3	78	9100		
	NSSC	550	60.0	68	10500		
Beech (30)	Calcium bisulfite	550	27.9	58	6000		
	Kraft	550	38.0	70	6500		
	NSSC	550	40.0	64	7200		
Japanese Beech and Oak mixed Two-stage (93)							
1st stage pH	2nd stage pH						
4.0	6.0	500	12.3	39.4	2690	76.0	105.3
4.0	6.0	500	28.1	55.5	4650	61.4	81.0
4.0	6.0	500	30.8	49.4	5290	57.4	70.3
4.0	8.0	500	20.0	49.4	3590	72.8	105.8
4.0	8.0	500	36.7	57.0	5480	57.3	67.9

and 40-50% lower in breaking length than pulps 1, 2, 3, and 4 at either freeness. The 61.4% yield pulp is comparable in mullen to pulps 1, 2, 3, and 4, is 10% lower in tear than pulps 1 and 3 and 20-25% lower than pulps 2 and 4, and is comparable in breaking length to pulps 1, 2, 3, and 4 at freeness 600. At freeness 400 pulps 1, 2, 3, and 4 are comparable in mullen, 5-20% higher in tear, and 20-35% higher in breaking length than the 61.4% yield pulp. The 57.4% yield pulp is higher in mullen, lower in tear, and higher in breaking length than pulps 1, 2, 3, and 4 at freeness 600. At freeness 400 pulps 1, 2, 3, and 4 are 15-25% higher in mullen and tear, and 10-30% higher in breaking length than the 57.4% yield pulp.

The 72.8% yield pulp was cooked under the same conditions as pulps 1 and 3 and has a yield about half way between the yields of pulps 1 and 3. At freeness 600 pulps 1 and 3 were 20-30% higher in mullen, 15-30% higher in tear, and 25% higher in breaking length than the 72.8% yield pulp. The differences at freeness 400 are 50% higher mullen, 15-25% higher tear, and 45-50% higher breaking length for pulps 1 and 3. The 57.3% yield pulp has a lower strength for most of the tests but usually low yield pulps exhibit stronger properties. However it is 25-30% higher in mullen, 5-20% lower in tear, and 10% higher in breaking length than pulps 1 and 3 at freeness 600. At freeness 400 pulps 1 and 3 are 10% higher in mullen, 5-15%

higher in tear and 15-25% higher in breaking length than the 57.3% yield pulp.

Pulps 2 and 4 have the same strength advantages as pulps 1 and 3 do over the Japanese pulps of yields 72.8% and 57.3%.

Although differences in methods of digestion and refining are probably some of the reasons for the differences in strength properties, the differences in pulping conditions and, of course, use of different hardwoods must also be considered. Pulps 1, 2, 3, and 4 were cooked in a closed digester with a direct heating system and refined in a Bauer 24 inch double disc refiner. The Japanese made their cooks in autoclaves with indirect heating and used a Sprout-Waldron refiner to refine their pulps.

The strength values given in Table 5 for Douglas-fir are much higher than any of the values for red alder. This difference is due to the long fibered anatomy of softwoods (13, 90).

Table 5. Douglas-fir two-stage pulps (69).

Cooking method	Freeness CSml	Mullen factor	Tear factor	Breaking length meters	Yield %	Kappa No.
Bisulfite-alkaline	500	67	90	9800	62.7	117
Bisulfite-neutral	500	62	79	10500	65.4	124

In Table 6 the amount of 0-acetyl-(4-0-methylglucurono)xylan (xylan), cellulose, glucomannan, and lignin present in the wood, pulps, and xylans is given. Since the purpose of this project was to produce a high-yield pulp from red alder by retaining the hemicelluloses an examination of Table 6 indicates that pulps 1 and 2 have retained approximately 80% of the xylan present in the wood. The difference in the degree of delignification between these two pulps is quite large with pulp 1 having a lower lignin content than pulp 2. Pulp 1 also has more cellulose which indicates that the cooking conditions used to produce pulp 1 are more selective for delignification than the cooking conditions of pulp 2. Both pulps retained a majority of the glucomannan. Although the percent glucomannan indicated in the table is small it may in reality be too large since the glucose and mannose were analyzed together with galactose and arabinose respectively. The amount of galactose and arabinose is less than 0.5%. Therefore its influence if any on the percent glucomannan will be relatively small. It is very possible that the galactose and arabinose were lost in pulping so they would only influence the percent glucomannan in the wood and in xylans 5 and 6.

All samples were analyzed for glucose, mannose, and xylose. Since the ratio of mannose to glucose is 1.5 in hardwood hemicellulose

Table 6. Chemical composition of wood, pulps, and xylans (percentages).

	Xylan[1]	Acetyl groups	Uronic acid	Cellulose	Glucomannan	Lignin	Yield
Wood	29.8	3.6	4.7	45.4	3.8	21.0	
Pulp #1	24.1	0.7	3.2	60.0	2.7	13.2[2]	75.9
Pulp #2	23.5	0.6	3.3	57.3	2.8	16.5[2]	76.5
Pulp #3	20.3	1.1	2.5	67.8	2.8	9.1[2]	66.1
Pulp #4	17.5	0.9	2.1	68.5	2.8	11.2[2]	66.0
Xylan #1	95.9	2.9	12.6	0.2[3]	0.7	3.1	4.4
Xylan #2	95.0	3.0	11.4	0.2[3]	0.7	3.0	5.0
Xylan #3	95.8	3.4	11.7	0.2[3]	0.7	3.3	5.4
Xylan #4	95.2	2.0	9.4	0.3[3]	0.7	3.8	4.6
Xylan #5	93.2	10.8	10.7	4.6[3]	1.0	1.2	18.3
Xylan #6	73.4	2.2	11.5	10.3[3]	7.0	8.8	8.8

[1] Contains acetyl and uronic acid groups -0-acetyl-(4-0-methylglucuronon)xylan

[2] Acid insoluble plus UV at 280mμ

[3] Low molecular glucan (cellulose)

(34, 89) this value was used to calculate the percent of glucose in glucomannan. Addition of this percent to the percent mannose gave the percent of glucomannan. The remaining percent of glucose assumed to be due to the cellulose or low molecular weight glucan in the samples.

The lower yield pulps give results similar to their respective higher yield pulps. Pulps 1 and 3 were cooked using the same liquor concentration but the temperature was raised 5°C in the first- and second-stages of cook 3. With pulps 2 and 4 the liquor concentrations were the same but the temperature was raised 10°C only in the first-stage of cook 4. Pulp 3 retained 10% more of its xylan and was delignified more than pulp 4. The difference in cellulose content of the two pulps is only 0.7% with pulp 4 having a larger amount. This small a difference is probably within the limits of experimental error. The percent glucomannan has remained the same as it was in pulps 1 and 2.

Therefore pulping with a first-stage pH of 4.5 and a second-stage pH of 8.0 produces a pulp higher in hemicellulose content and lower in lignin than pulping with a first-stage pH of 6.0 and second-stage pH of 10.0. The physical properties given earlier in the discussion are further proof that the pulps produced with a first-stage pH of 4.5 and a second-stage pH of 8.0 are superior to the pulps produced with a first-stage pH of 6.0 and a second-stage pH of 10.0.

Extraction and Properties of Xylans from Wood and Pulps

Since DMSO is relatively inert and selective for the xylan hemicellulose it was used as the extracting solvent for obtaining most of the xylan from the pulps as indicated in Table 6. Xylans 1, 2, 3, and 4 were extracted from pulps 1, 2, 3, and 4 respectively. The small percent of cellulose present in xylans 1, 2, 3, and 4 is probably a low molecular weight glucan produced by hydrolysis of the cellulose during pulping. Only a small amount of glucomannan was extracted with the DMSO.

Xylan 5 was extracted with DMSO from a chlorine-ethanolamine holocellulose. A high percent of xylan was obtained with a small amount of cellulose which is probably low molecular weight glucan produced by oxidation of cellulose by chlorus acid.

Xylan 6 was extracted directly from red alder wood meal with cold 24% potassium hydroxide. This procedure is probably the least selective method of obtaining a hemicellulose since a large amount of contaminants are present. The cellulose in this sample is assumed to be low molecular weight glucan. The amount of this material is surprisingly high since under the conditions of extraction it should not be produced by alkaline degradation of the cellulose. The amount of glucomannan in this extract is high, indicating little selectivity under the conditions of extraction between

the hemicelluloses present in the wood.

After the initial isolation of the xylan samples no attempt to further purify them was made. The reason for not purifying the xylan was to avoid alteration of the end groups and side chains of the hemicellulose. By not purifying the xylan samples they all are slightly contaminated with other substances such as glucomannan and lignin.

Pulps 1 and 2 have retained approximately 20% of the acetyl groups present in the wood as indicated in Table 7. Although all of

Table 7. Acetyl and uronic acid groups per xylose residue.

	Acetyl/xylose	Uronic acid/ xylose
Wood	0.51	0.15
Pulp #1	0.11	0.11
Pulp #2	0.09	0.12
Pulp #3	0.20	0.10
Pulp #4	0.19	0.10
Xylan #1	0.11	0.11
Xylan #2	0.12	0.10
Xylan #3	0.13	0.10
Xylan #4	0.10	0.10
Xylan #5	0.46	0.10
Xylan #6	0.11	0.13

the acetyl groups have not been removed the number has been greatly reduced. Probably enough have been removed to allow the xylan to be absorbed more closely onto the cellulose. No reasonable explanation exists for why pulps 3 and 4, the lower yield pulps, have more acetyl groups per xylose residue than do pulps 1 and 2. To complicate matters more is the fact that the xylans from the pulps all have approximately the same acetyl content. The mild ethanol-amine treatment prior to the DMSO extraction might be responsible for the xylans from pulps 3 and 4 having a lower acetyl content but this seems unlikely. If this were true then it would be expected to occur with the xylans from pulps 1 and 2.

Xylan 5 when compared with the wood appears to have retained most of its acetyl groups during the chlorine-ethanol-amine treatment and the subsequent DMSO extraction. This indicates the stability of the acetyl groups to oxidation (86).

Xylan 6 from the cold 24% potassium hydroxide extraction gives a value for acetyl groups contrary to the fact that acetyl groups are easily hydrolyzed in alkaline solutions. A possible explanation for this observation is that lignin is degraded in alkali and some of the products of this degradation could subsequently form acetic and formic acids, which would give positive values with the procedure used for determining acetyl groups. Xylan 6 contained 8.8% Klason lignin.

A cursory examination of Table 7 indicates that the uronic acid goups are quite stable under the pulping conditions used (58). It is known that in strong alkaline solutions (pH=14) at 165-170°C the uronic acid groups are easily hydrolyzed (36, 52, 68, 89). It was hoped that the uronic acid groups could be cleaved in mild alkaline solution but from the data given in Table 7 this is not the case. A possible advantage of retaining the uronic acid groups is that the acid function tends to inductively stabilize the β(1-4) links between the xylose residues of the xylan in acid solution (33, 85). This is evidently what has happened in the first-stage since a large amount of xylan was retained in the pulps and the xylan retained enough uronic acid side chains to prevent it from being closely absorbed to the cellulose. Therefore the xylan must be relatively stable in mild alkaline solutions because if it were readily attacked the xylan content of the pulps would be much lower.

Hydrogen bonding between the hydrogen of the carboxylic acid and the oxygen of the β(1-4) link could account for the stability of the β(1-4) linkages. Although direct experimental proof is lacking the use of Dreiding-Stereomodels indicates that hydrogen bonding could occur.

In Table 8 the acid insoluble lignin as determined by hydrolysis in 72% sulfuric acid and the acid soluble lignin as determined by the ultraviolet absorption at 280 mμ are given. The amount of acid

soluble lignin varies from 1.4% for the lower yield pulps to 2.2% for the higher yield pulps. These values are slightly lower than what has been reported for bisulfite pulps; however, the reported values were for spruce (71).

Table 8. Acid insoluble and UV* lignin.

	Acid insoluble	UV	Total
Pulp #1	11.4	1.8	13.2
Pulp #2	14.3	2.2	16.5
Pulp #3	7.6	1.5	9.1
Pulp #4	9.8	1.4	11.2

* Measured at 280 mμ.

When the 1% sodium hydroxide solubilities in Table 9 are compared with total xylan content of the pulps in Table 6 the results appear to be contradictory. A probable explanation would be as follows: Pulps 2 and 4 contained less xylan than pulps 1 and 3. Therefore the xylans of pulps 2 and 4 had been attacked more readily during the pulping process and the degree of polymerization (DP) has probably been shortened leaving several xylan fragments of short DP in the pulp which are readily soluble in 1% sodium hydroxide. The xylans of pulps 1 and 3 have not been attacked as severely therefore fewer xylan fragments are present in the pulps. Consequently the 1% sodium hydroxide solubility for pulps 1 and 3 is

lower than it is for pulps 2 and 4.

Table 9. 1% sodium hydroxide solubility of pulps.

Pulp #1	8.0
Pulp #2	9.5
Pulp #3	8.75
Pulp #4	10.25

Determination of Xylan End Units

The $R_{glucuronolactone(g-1)}$ values for the lactones in the four solvent systems are given in Table 10. Unknown substance 5 appears to be xylonolactone. Definite proof of this lactone is provided only with solvent A since the xylonolactone and the trailing portion of the xylometasaccharinolactones have the same R_{g-1} values in the other three solvents. Unknowns 3 and 4 appear to be the α and β xylometasaccharinolactones. Irrigating solvent D does not produce a separation of the substances of interest, but it does show that xyloisosaccharinic acid is not an end-group unit of the xylan. Unknown substance 2 seems to be closely associated with unknown 5 or xylonolactone and could possibly be the unknown lactone reported by Nord (56). Unknown 1 had a much higher R_{g-1} value than any of the standards.

Table 10. Solvent systems.

Unknowns	A	B	C	D
1	2.88	----	----	----
2	1.09	----	----	----
3	2.13	2.17	1.38	1.18
4	1.89	1.54	1.16 1.11	
5	1.35	1.54	1.11	1.18
Xylometa-Saccharinolactone	2.13 1.89	2.14 1.54	1.36 1.16 1.14	1.19
Xylonolactone	1.34	1.54	1.14	1.19
Xyloisosaccharino-lactone	2.78	3.16	1.49	1.74

The presence of xylonolactone in the pulp hydrolyzates indicates that the reducing end of the xylan was oxidized by bisulfite ion (20, 21, 53) during the first-stage of the pulping process. The mild alkaline solution in the second-stage degraded the xylan polymers which retained a reducing end group, and eventually xylometasaccharinic acid was formed thus stopping the "peeling reaction" at the end group (25, 29, 50, 51, 84). The reason for xylometasaccharinolactone being present in the pulp xylan hydrolyzates is probably due to incomplete oxidation of the end group in the first-stage by bisulfite ion. That not all xylan reducing end groups were oxidized

in the first-stage is to be expected. When alkaline polysulfide or sodium borohydride solutions are employed in order to eliminate the reducing end groups during pulping similar results are obtained (50, 84).

The absence of the xyloisosaccharinolactone in the pulp hydrolyzates indicates that the xyloisosaccharinic acid, formed during the pulping reaction, went into solution. This is expected when a β(1-4) linked polysaccharide is treated with alkali (29).

The aldobiouronic acid was present and appeared as a concentration spot with the lactone spray. The presence of the 4-0-methylglucuronic acid on carbon-2 of xylose appears to prevent the lactone from being formed.

Lactones present in the pulp xylan hydrolyzates were also present in the hydrolyzates from xylan isolated from the chlorine-ethanolamine and chlorus acid holocelluloses (73). These lactones were not present in the hydrolyzates from xylan extracted directly from the wood with cold 24% potassium hydroxide. Both of the holocellulose preparations are oxidizing reactions (35, 68). The above results verify that a bisulfite pulping solution is an oxidizing system (53). That the wood polysaccharides can be protected from alkaline degradation through use of a prior bisulfite-neutral sulfite stage has been indicated.

Suggestions for Further Research

The lactonizable end groups of the xylan isolated from the pulps should be more thoroughly characterized. If possible the five unknown substances should be isolated and identified by means other than paper chromatography. It was not possible in this research to obtain pure crystalline compounds for more positive identification. Preparative paper chromatography was attempted but this did not yield pure crystalline substances. Optical rotations of the isolated samples were inconclusive.

A more complete study of the variables effecting optimum pulping conditions would be desirable. It should be possible to produce even better pulps than were obtained by the two procedures finally selected and used in this research project.

The six pulps prepared by first-stage sulfite and second-stage kraft appear to have good strength properties for their yield ranges. The kraft second-stage was mild and of short duration, and the pulps produced were in the range of chemical pulps having a high-yield. Further studies of this two-stage pulping process are strongly indicated.

CONCLUSION

Two-stage sulfite pulping of a hardwood using a first-stage pH of 4.5 and a second-stage pH of 8.0 produces a pulp with the highest hemicellulose content and strength.

These two-stage pulps have strength properties comparable to, and usually higher than, other hardwood pulps produced in the yield range of 65-75%.

The high strength properties of these pulps are due to their high hemicellulose content. As much as 80% of the xylan present in the wood can be retained. Retention of the xylan is due to the following factors: removal of the acetyl groups by hydrolysis, retention of the uronic acid groups, and oxidation of the end groups. Removing the acetyl groups would allow the xylan to be more closely absorbed to the cellulose. Retaining the uronic acid groups would protect the $\beta(1-4)$ linkages between the xylose units. Oxidation of the reducing end group would protect the wood polysaccharides against the "alkaline peeling reaction".

It has been shown in this research project that some of the end groups of the xylan have been oxidized during the pulping reaction by the bisulfite ion. Xylonolactone was indicated in the lactonizable fraction of the xylan hydrolyzate.

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APPENDIX TABLE 1

Cook	Yield	Kappa No.	First-Stage pH	First-Stage Temperature	First-Stage Time*	Second-Stage pH	Second-Stage Temperature	Second-Stage Time	750 Freeness Mullen	750 Freeness Tear	750 Freeness Breaking length	750 Freeness Density	600 Freeness Mullen	600 Freeness Tear	600 Freeness Breaking length	600 Freeness Density	400 Freeness Mullen	400 Freeness Tear	400 Freeness Breaking length	400 Freeness Density
7	88.7	129	4.5	150	1 hr.								9.3	28.7	1440	0.601	12.9	31.2	2190	0.651
9	88.3	150	6.0	150													10.5	28.6	1860	0.600
10	84.3	136	7.5	150					4.9	49.3	2660	0.454	14.2	45.2	2620	0.676	22.0	42.4	3550	0.678
11	85.5	143	9.0	150					6.1	47.6	1250	0.519	14.0	46.8	2470	0.669	22.0	42.4	3990	0.749
12	86.9	135	10.5	150					4.2	39.2	796	0.492	11.2	39.9	2100	0.679	20.8	42.2	3580	0.729
13	88.5	130	4.5	155					2.2	26.3	236	0.403	9.8	31.7	1700	0.629	13.8	32.6	2530	0.696
14	86.7	136	6.0	155									8.0	27.6	1810	0.562	13.3	34.1	2860	0.666
15	81.9	145	7.5	155					6.8	49.4	1480	0.589	14.4	43.6	2670	0.645	24.4	46.8	3770	0.777
16	82.8	145	9.0	155					6.6	44.0	1410	0.501	13.6	37.0	2560	0.672	21.8	42.7	4060	0.755
17	83.6	144	10.5	155					5.4	43.5	1130	0.564	11.2	39.3	2560	0.613	21.8	38.4	3600	0.754
19	77.2	124	4.5	155		6.0	155	1 hr.	7.9	43.6	1130	0.502	20.9	50.5	4000	0.652	31.8	47.9	5720	0.725
20	73.8	111	4.5	155		7.5	155		17.2	62.9	3250	0.634	27.8	63.2	4940	0.727	38.0	58.3	6730	0.812
22	75.4	140	4.5	155		6.0	160						16.0	62.4	3350	0.608	32.4	63.2	5480	0.756
23	71.2	108	4.5	155		7.5	160		17.0	72.8	3380	0.582	30.8	66.7	5680	0.691	39.5	63.1	6790	0.806
24	69.9	110	4.5	155		9.0	165		16.9	64.3	3350	0.620	27.3	66.4	5200	0.718	41.6	64.3	6730	0.811
25	72.3	119	4.5	155		10.5	165		15.4	68.7	3140	0.592	24.4	63.0	4520	0.684	39.9	61.9	6300	0.828
26	72.2	128	6.0	165		4.5	155		10.3	49.8	2730	0.542	21.2	56.0	4300	0.686	30.3	58.4	5520	0.779
27	72.8	122	6.0	160		7.5	160		14.0	66.7	3010	0.596	24.4	60.5	4280	0.714	36.9	61.3	6240	0.745
28	68.6	108	6.0	165		9.0	165		14.9	60.4	3160	0.553	27.1	56.5	5440	0.720	40.8	50.7	6170	0.743
29	69.1	109	6.0	165		10.5	165		13.5	63.1	2880	0.549	30.4	57.6	4990	0.676	39.5	52.5	6750	0.770
30	80.0	131	7.5	160		4.5	160		7.3	50.7	1760	0.472	22.9	45.7	4340	0.666	33.4	45.6	5740	0.779
31	78.5	135	7.5	165		6.0	160		9.6	54.0	2390	0.537	24.1	50.8	4170	0.693	33.7	46.0	6280	0.763
32	72.9	109	7.5	165		9.0	165		9.3	63.7	2280	0.517	24.9	53.5	4970	0.696	36.7	47.2	6730	0.768
33	70.9	116	7.5	165		10.5	165		10.7	54.1	2280	0.539	26.3	57.2	4580	0.734	38.4	48.5	6900	0.795
34	78.3	141	9.0	165		4.5	155		8.2	57.3	1780	0.529	20.0	46.8	4300	0.664	31.5	47.0	6060	0.771
35	78.0	123	9.0	165		6.0	165		6.6	60.5	1200	0.494	27.2	50.1	4470	0.668	36.5	43.6	5830	0.764
36	72.6	128	9.0	165		7.5	165		9.4	58.9	1530	0.528	26.7	55.0	5010	0.561	39.4	51.7	6990	0.751
37	72.1	118	9.0	165		10.5	165		8.8	62.1	2130	0.510	27.9	57.2	4920	0.625	38.9	51.3	6400	0.779
38	53.8	97.8	4.5	155		14.0	165	30 min.	18.9	56.0	3910	0.510	32.6	57.7	6060	0.638	47.3	63.5	7350	0.714
39	52.5	57.5	4.5	155		14.0	165	25 min.					28.2	78.1	5220	0.707	53.8	94.0	8340	0.790
40	54.0	59.5	6.0	160		14.0	165	25 min.					34.5	93.9	5760	0.687	61.7	88.9	8710	0.888
42	59.4	118	7.5	160		14.0	165	15 min.	20.0	75.4	3680	0.626	37.6	84.5	6150	0.742	56.3	74.6	7420	0.839
43	53.0	76.2	9.0	165		14.0	165	15 min.	25.1	69.7	4560	0.659	37.4	79.1	5870	0.733	58.8	82.3	8210	0.869
44	56.6	78.3	10.5	165		14.0	165	15 min.					26.4	88.3	4580	0.636	55.1	82.2	7570	0.837
46	77.5	144	4.5	150		8.0	160	1 hr.	9.2	63.6	2260	0.569	29.2	61.0	5420	0.687	39.3	60.4	6450	0.727
47	74.4	134	4.5	150		8.0	160		8.0	72.7	1910	0.500	26.8	58.2	4360	0.667	40.5	59.1	6450	0.773
48	75.8	132	6.0	155		10.0	165		7.4	66.1	1910	0.528	25.7	65.3	5140	0.645	36.7	61.4	5950	0.759
49	77.3	146	6.0	155		10.0	165		7.9	62.1	2410	0.501	21.2	60.5	3910	0.618	37.2	54.4	5950	0.760
50	68.1	117	4.5	155		8.0	165		15.0	71.4	3160	0.561	27.2	68.4	5270	0.642	42.4	63.3	7140	0.740
51	67.4	127	6.0	165		10.0	165		14.4	74.8	3680	0.539	28.0	69.7	5780	0.689	35.9	67.4	6730	0.743
52	64.2	126	4.5	155		8.0	165						24.0	77.8	4620	0.621	40.7	69.2	7480	0.795
53	64.6	122	6.0	165		10.0	165						22.8	73.1	3890	0.629	43.0	67.8	8100	0.790

* All times are one hour unless otherwise stated.