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A Study of the Order and Nature of the
Aspenwood Hemicellulose Removed During a
Neutral Sulfite Semichemical Cook

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A STUDY OF THE ORDER AND NATURE OF THE ASPENWOOD
HEMICELLULOSE REMOVED DURING A NEUTRAL
SULFITE SEMICHEMICAL COOK

A thesis submitted by

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GLOSSARY

- A.H.P. - aniline hydrogen phthalate spray reagent for chromatograms.
- Alkali-Resistant Cellulose - the fibrous residue remaining after the holocellulose was extracted successively with 5 and 16% potassium hydroxide.
- C1P2 - the first neutral sulfite semichemical (NSSC) cook made with a sodium carbonate buffer.
- C1P3 - the first NSSC cook made with a sodium bicarbonate buffer. This cook is the model for all other cooks and is the terminal cook in the pulp-liquor study.
- C2P1 - the second NSSC cook. Liquor samples were removed from this cook at 30-minute intervals during the cook.
- C3P1 - the third NSSC cook. This cook was stopped after 30 minutes and was used in the pulp-liquor study.
- C4P1 - the fourth NSSC cook. This cook was stopped after 90 minutes. The pH of the spent liquor was high so this cook was rejected.
- C4P2 - a repeat of cook C4P1. The pH of the spent liquor was the same as cook C4P1 and this cook was used in the pulp-liquor study.
- C5P1 - the fifth NSSC cook. This cook was stopped after 150 minutes and was used in the pulp-liquor study.
- "Hemicellulose" - the material from the spent liquor which was precipitated by absolute ethanol.
- 5% Hemicellulose - the material which was dissolved from the holocellulose with 5% potassium hydroxide and precipitated by ethanol.
- 16% Hemicellulose - the material which was dissolved with 16% potassium hydroxide from the residue of the 5% hemicellulose extraction and precipitated by ethanol.
- Holocellulose - the material which remained after treatment with the Thompson and Wise (1) modified holocellulose procedure.
- IR-4B acetate form - the anion ion exchange resin Amberlite IR-4B which was in the hydroxyl form was reacted with acetic acid.
- Klason Lignin - the material from wood or pulp which was insoluble in cold 72% sulfuric acid and boiling 3% sulfuric acid.
- Polyuronide - a polymer containing only uronic acid units. The amount of this material was measured by the uronic acid determination and calculated as uronic anhydride.

Soluble Lignin - the material in the Klason lignin filtrate which has an ultraviolet absorption at 230 m μ .

Total Carbohydrate - the sum of the alkali-resistant cellulose plus 5% hemicellulose plus 16% hemicellulose.

9:2:2 - a chromatographic developer made up of 9 parts ethyl acetate, 2 parts acetic acid, and 2 parts distilled water.

10:3:3 - a chromatographic developer made up of 10 parts n-butyl alcohol, 3 parts pyridine, and 3 parts distilled water.

6:4:3 - a chromatographic developer made up of 6 parts n-butyl alcohol, 4 parts pyridine, and 3 parts distilled water.

INTRODUCTION

BACKGROUND OF THE PROBLEM

Neutral sulfite semichemical (NSSC) pulping is developing into one of the major commercial pulping processes. By its use a high yield pulp with good strength can be produced, and the operation is economically competitive with the other pulping processes. Furthermore, this method of pulping is especially suited to the production of pulp from hardwoods.

A better understanding of the effect of the process on the various wood constituents should lead to improvements in the NSSC method of pulping. A study of the order in which hemicellulosic material is removed during a NSSC cook could provide this type of information. For example, it would be interesting to know if the araban is removed before xylan, and if the low D.P. or high D.P. material is removed first. These questions are of interest because the hemicelluloses play an important role in strength development of paper. Both the chemical and the physical nature of the hemicelluloses removed from the pulp and remaining in the pulp should be studied, because some hemicellulosic fractions may be more important than others in strength development. In addition, an understanding of the chemical nature of the hemicellulosic material in the spent liquor must be known before an efficient recovery and utilization scheme can be worked out. If the chemical nature of the hemicellulose in the pulp during a NSSC cook is known, perhaps that part of the hemicellulose which has been shown to give the more desirable characteristics to the pulp could be retained by

modifying the cooking conditions. A logical development would be to design the cook so that the spent liquor contains useful hemicelluloses in a recoverable form, while at the same time retaining in the pulp those hemicelluloses which impart to it the desired physical characteristics.

Since it was developed in 1926 (2), the NSSC pulping process has been the subject of very little fundamental work. Recently, however, Lea (3) has studied the effect of a NSSC cook on the hemicellulose fraction of aspenwood. He compared the hemicellulose from the final pulp of a NSSC cook with the original wood hemicellulose, but he did not study the sequence of the removal of hemicellulose during the cook. Doriswamy (4) studied the kinetics of sodium sulfite pulping of aspenwood but the object of his study was to determine the cooking conditions for maximum lignin removal and minimum pentosan removal, and not to determine the chemical composition of the carbohydrate material removed during the cook. The studies which have been made in Finland on the chemical nature of the carbohydrate material removed by the cooking liquor during both the sulfite (5) and sulfate (6) processes have given an insight into the reasons for the differences in properties of pulps obtained by the two methods. However, the NSSC process, which in some ways may be considered to lie between the sulfite and sulfate processes, has not been studied insofar as the carbohydrate material removed during the cook is concerned. The purpose of the present work is an attempt to fill in this gap in our knowledge.

STATEMENT OF THE PROBLEM

The problem is to determine the chemical and physical characteristics of the hemicellulose removed at various stages during a NSSC cook of aspenwood.

HISTORICAL REVIEW

There are many literature surveys available on the general aspects of NSSC pulping as well as on hemicelluloses, so that only those references which are immediately pertinent to the present study will be included in this historical review.

The name hemicellulose was first proposed by Schulze (7) to describe the cell wall constituents which are readily soluble in hot dilute mineral acid, and which dissolve slowly in cold aqueous 5% sodium hydroxide. Many investigators have found fault with the name hemicellulose and have proposed such names as pentosans and hexosans, polyoses, cellosans and polyuronides, and the noncellulosic cell-wall polysaccharides (8). However, imperfect as it may be, the name hemicellulose still is used today.

O'Dwyer (9) was the first to develop a method for the isolation of hemicellulose from wood. The hemicellulose was extracted with 4% sodium hydroxide and precipitated in two stages, first by acidification and then by ethanol. More recently it has been found that less degraded hemicellulose can be prepared by extracting wood holocellulose rather than wood meal with alkali. Wethern (10) studied several

methods of preparing holocellulose, and found that the hemicelluloses extracted from holocellulose isolated by a modification of the Thomas (11) procedure were less degraded than those extracted from chlorine dioxide-pyridine (12) or chlorite (13) holocelluloses. In the present study the holocellulose was prepared by the Thompson and Wise (1) modification of the Thomas procedure.

In this more recent procedure for the preparation of hemicellulose potassium hydroxide has been used rather than sodium hydroxide because potassium salts are more easily removed from the hemicellulose than are the sodium salts. Wise, *et al.* (13) studied the effect of potassium hydroxide concentration on the removal of hemicellulose from holocellulose. In the range of 0 to 30% potassium hydroxide, it was found that successive extractions with 5 and 24% potassium hydroxide gave excellent yields of hemicellulose. Their data also indicated that good hemicellulose yields could be obtained by making successive extractions with 5 and 16% potassium hydroxide. The 16% extraction is preferable because it reduces the amount of inorganic salts remaining in the hemicellulose. Thus, in the present study, the holocellulose was extracted successively with 5 and 16% potassium hydroxide.

Physical studies of hemicelluloses indicate that they are quite heterogeneous. For example, Wethern (10) has shown that sprucewood hemicellulose has a D.P. range from 30 to 300. Other investigators (1, 3, 14, 15) have found number average D.P.'s of hardwood hemicelluloses to be approximately 150 ± 20 .

Chemical studies of the hemicellulose extracted from aspen (Populus tremuloides) have been made. Schoettler (16) found by qualitative chromatography glucose, galactose, arabinose, xylose, mannose, rhamnose, and a uronic acid in the hydrolyzate of aspenwood hemicellulose. Jones and Schoettler (17) chemically identified L-rhamnose from aspenwood (Populus tremuloides). Jones and Wise (18) separated and chemically identified D-xylose, D-galactose, L-arabinose, L-rhamnose, and a fully characterized aldobiuronic acid from the hydrolyzate of aspenwood (Populus tremuloides). Lea (3) chemically identified D-mannose from aspenwood, and found by both qualitative and quantitative chromatographic sugar analysis the presence of galactose, glucose, mannose, arabinose, xylose, and rhamnose in the hydrolyzates of his hemicellulose and NSSC spent liquor. Presumably the carbohydrates in the spent liquor were originally hemicellulosic in nature.

Until recently, the detection and determination of sugars has been extremely difficult and the procedures have been quite tedious. The development of paper chromatography and its application to the separation of reducing sugars (19, 20) has greatly simplified the detection and at the same time has increased the sensitivity of the sugar analysis. Inorganic salts have a deleterious effect on the chromatographic separations of sugars (20), but these salts can be removed by ion-exchange resins before applying the sugar solutions to the paper. Paper chromatography has been extended to the quantitative determination of reducing sugars present in a mixture of sugars (21, 22). The method of sugar analysis used in the present study was developed by Hirst and Jones (22). In

this method the sugars are separated on paper, eluted from the paper, oxidized with sodium meta periodate, and the resulting formic acid is titrated with about 0.0025 N sodium hydroxide. The method is reported to have an accuracy of $\pm 5\%$ for quantities of sugar ranging from 0.2 to 3 mg.

EXPERIMENTAL RESULTS

APPROACH TO THE PROBLEM

The following approach was used in studying the order and nature of the aspenwood hemicellulose removed during a NSSC cook: (a) Typical NSSC pulping conditions were selected and a complete cook was made (C1P3)*. All subsequent cooks were made according to the conditions established by this first cook. (b) The second cook, C2P1, was made and liquor samples were removed at 30-minute intervals during this cook. (c) On the basis of information gained from the liquor study, incomplete cooks were carried out in which both the pulp and liquor were studied. The experimental results are presented in the chronological order given above. The experimental procedures used are described in Appendix I, and an evaluation of the quantitative chromatographic method of sugar analysis can be found in Appendix II.

WOOD DATA

The tree (Populus tremuloides) used in this study was 22 years old. The tree had a growth rate of 5.6 rings per inch and the wood, which was sound, had a specific gravity of 0.46 (ovendry weight/ovendry volume).

COOKING CONDITIONS

The cooking schedules of Lea (3) and Boehm (23) were used in the first cook, C1P2 Table I. The initial and final pH of this cook were

* See glossary for an explanation of this term and all subsequent terms of this nature.

high. By replacing the sodium carbonate buffer with sodium bicarbonate (ClP3 Table I) the pH of the initial and final liquor could be reduced to pH 8.3 and pH 7.0, respectively. The cooking schedules for all the NSSC cooks made in this study are given in Table I.

SPENT LIQUOR STUDY DURING A NSSC COOK

COOK C2P1

This cook was made using the same schedule as that used for cook ClP3. The cooking data are shown in Table I. Cook C2P1 differed from cook ClP3 in that liquor samples were removed from the digester through the sample cook at 30-minute intervals. Samples were taken at cooking periods of 30, 60, 90, 120, 150, 180, and 210 minutes. Each unhydrolyzed sample was chromatographed about 20 minutes after the cook was completed. Chromatograms were run in both 9:2:2 and 6:4:3. The 9:2:2 developed chromatogram showed no spots before the first 60 minutes. Spots visible only under ultraviolet light appeared above galactose in the 90, 120, 150, 180, and 210-minute samples. Possible galactose spots, visible only under ultraviolet light, appeared in the 150, 180, and 210-minute samples. The 6:4:3 showed possible spots under ultraviolet light near the starting line on the 150, 180, and 210-minute samples. All of the liquors were rechecked. Chromatograms were run in both 9:2:2 and 10:3:3 developer for each of the seven spent liquor samples. After spraying with A.H.P., no simple sugars or disaccharides were detected in any of the seven spent liquors. Data on the liquors extracted from the digester are given in Table II. Similar data on cook ClP3 spent

TABLE I

COOKING SCHEDULES

	Cook Number						
	C1P2	C1P3	C2P1	C3P1	C4P1	C4P2	C5P1
Chemical ¹	11.9	11.8	12.0	12.0	11.9	12.0	11.9
Sodium sulfite as Na ₂ SO ₃	5.78	-	-	-	-	-	-
Sodium carbonate as Na ₂ CO ₃	-	5.67	5.77	5.72	5.78	5.83	5.65
Sodium bicarbonate as NaHCO ₃	11.30	8.30	8.30	8.25	8.30	8.25	8.25
Cooking liquor initial pH	4.00	3.96	3.99	4.01	4.01	4.00	4.01
Water ratio, ml./g.	170.5	170	171	64	135	136	171
Maximum temperature, °C.	120	120	120	30	90	90	120
Time to maximum temperature, min.	90	90	90	0	0	0	30
Time at maximum temperature, min.	128	129	137	6	45	45	131
Maximum pressure, p.s.i.	20	15	15	0.5	15	15	15
Relief time, min.	3664	3664	3664	3665	3665	3665	3665
Chip charge, g. ²	2689	2708	2797	3500	-	3241	2925
Pulp yield, g.	73.4	73.9	76.3	95.5	-	88.4	79.8
Pulp yield, %							
Spent liquor	5380	4840	4560	10,930	4430	5290	4820
Volume, ml.	9.60	7.30	7.05	8.20	8.90	8.90	7.01
pH	12.2	11.0	10.4	4.29	-	5.82	9.57
Solids, g./100 ml.	19,100	26,100	20,000	16,340	-	16,420	16,140
Wash liquor	3.3	2.5	2.8	0.73	-	1.25	2.70
Volume, ml.	1289	1199	1109	588	-	513	897
Solids, g./100 ml.	96.9	96.2	95.8	97.5	-	92.7	93.7
Total solids spent liquor, g.							
Organic material accounted for, % ³							

1 Based on percentage of oven-dry wood.

2 Oven-dry basis.

3 Percentage organic material = (yield of oven-dry ash-free pulp) + (oven-dry ash-free solids) / (oven-dry ash-free wood charged).

liquor are included for comparison.

Admittedly, the correction for sulfated ash is approximate because some carbon dioxide and sulfur dioxide may have been lost from the system during the cook. The assumed ratio of sodium sulfite to sodium bicarbonate may not be valid because it may vary as the cook proceeds. After analyzing the pulp and liquor study data a different factor was applied to the final spent liquor. From the last column in Table II, the inorganic material appears to be reasonably constant throughout the cook.

HYDROLYSIS OF C2P1 SPENT LIQUOR

All of the spent liquors were hydrolyzed and the hydrolyzates were analyzed for sugars by the quantitative chromatographic method. Results of these analyses are given in Table III, and the data are shown graphically in Figure 1. The curves show that glucan and mannan predominate early in the cook. After 90 minutes cooking until the end of the cook, xylan is the major polysaccharide in the spent liquor. Although part of the polysaccharides removed from the wood may have been destroyed, the data in Table III and Figure 1 indicate that the total amount of polysaccharides in the spent liquor increased with cooking time.

APPROXIMATE ORGANIC BALANCE ON C2P1 SPENT LIQUORS

An attempt was made to account for organic material in the spent liquor. The data on polysaccharides have been discussed. The lignin present in the spent liquor was estimated from ultraviolet absorption

TABLE II

SPENT LIQUOR DATA DURING COOK C2P1

Time Interval	Temp., °C.	Press., p.s.i.	Vol. Ext., ml.	pH	Solids, g./100	Sulfated Ash, %	Corr. ¹ Ash, %	Ash, g./100 ml.
30	64	9	270	8.21	3.97	109.5	86.1	3.42
60	100	25	230	7.80	4.21	103.7	81.6	3.43
90	133	42	210	7.86	4.77	90.8	71.4	3.41
120	164	103	220	7.40	5.60	76.1	59.9	3.35
150	171	130	215	7.12	6.83	60.8	47.8	3.27
180	171	135	215	7.00	7.92	51.6	40.6	3.21
210	170	137	4560	7.05	10.40	44.9	32.0	3.33
C1P3SL	170	129	4840	7.30	11.00	44.3	31.6	3.48

¹ Sulfated ash was multiplied by 112/142 except 210 and C1P3SL where the correction to unsulfated ash was used. Mol. wt. of Na₂SO₄ is 142. An average mol. wt. is 112, based on % Na₂SO₃ and % NaHCO₃ present at start of cook. $(.6588)(126) + (.3412)(28.66) = 111.7$.

TABLE III

QUANTITATIVE CHROMATOGRAPHIC ANALYSIS OF THE SPENT LIQUOR
TAKEN FROM COOK C2P1

Basis: mg./50 ml. of Spent Liquor

Polysaccharide ¹	30	60	90	120	150	180	210	C1P3SL
Galactan	1.2	2.0	4.1	9.6	16.9	21.6	28.2	30.0
Glucan	8.2	12.7	15.8	17.3	18.5	18.7	19.4	23.9
Mannan	2.5	4.6	5.1	5.7	8.1	11.3	11.6	10.7
Araban	0.8	1.2	2.9	5.6	10.9	15.1	24.7	28.2
Xylan	1.4	2.5	9.9	49.6	177.0	290.1	429.0	468.3
Rhamnan	0.9	1.4	3.4	4.8	11.1	12.0	13.3	16.3
Total	15.0	24.4	41.2	92.6	242.5	368.8	525.2	572.2

¹ Simple sugars calculated as the corresponding polysaccharides.

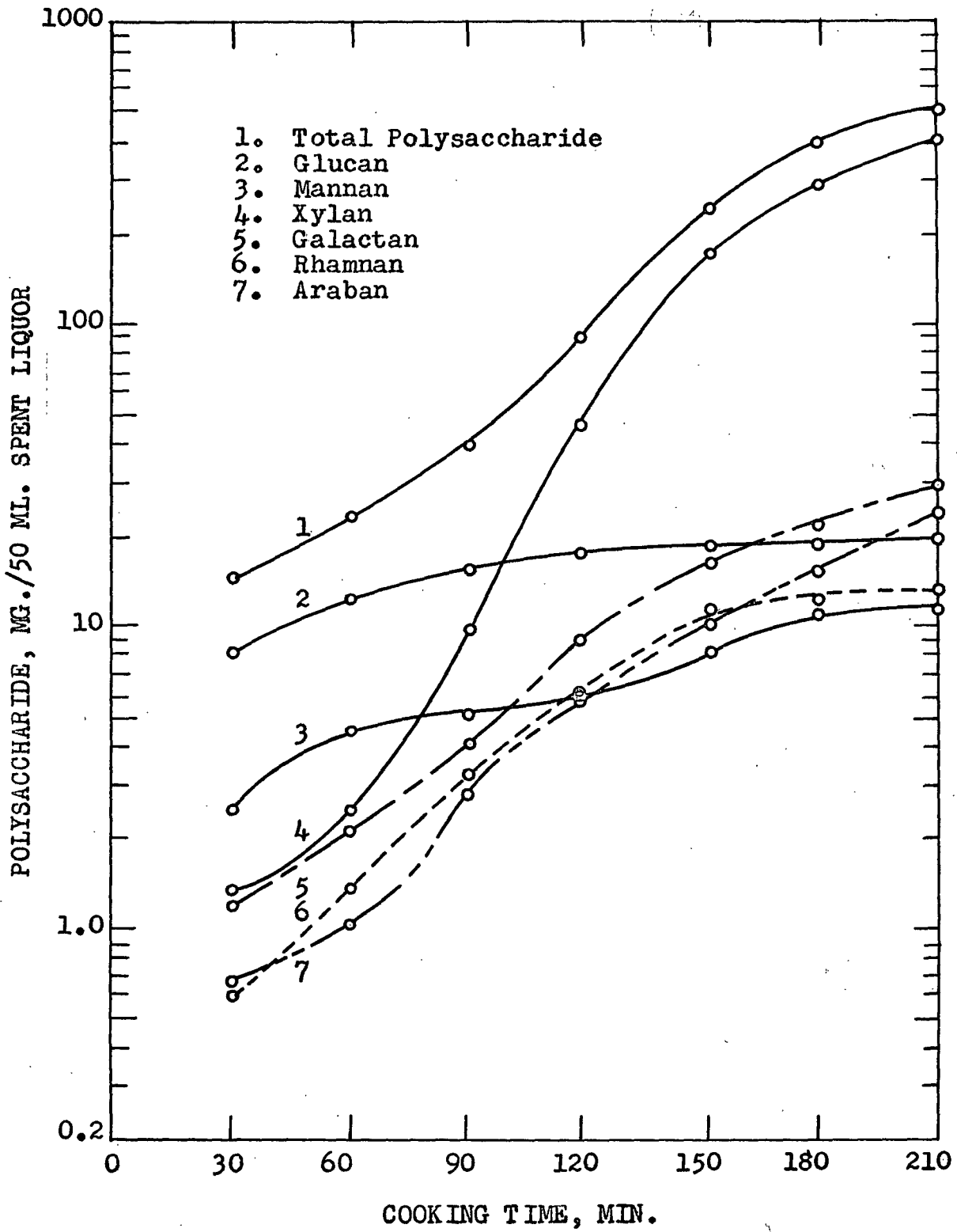


Fig. 1 Hydrolyzed Spent Liquor Removed During a NSSC Cook. Simple Sugars Calculated as the Corresponding Polysaccharides.

curves. Since the liquors were slightly alkaline, no furfural or hydroxymethylfurfural should have been present to interfere with the lignin determination. Thus, soluble lignin in the spent liquor could be determined at either 230 or 280 m μ . The wavelength of 280 m μ was selected instead of 230 m μ so that the carbohydrate degradation which occurs during hydrolysis (the products of which absorb at 280 m μ) could be measured by taking absorption data before and after hydrolysis.

Using the value Buchanan (24) determined for aspen native lignin for absorptivity, the soluble lignin determinations may be in error for three reasons: (a) The lignin in the spent liquor may be sulfonated or in the form of alkali lignin. (b) Buchanan used dioxane as a solvent for aspen native lignin whereas the spent liquor is an aqueous solution. (c) Salts present in the spent liquor probably affect the absorbance. However, these errors should not be too serious and the method should give a fair estimate of the lignin present. Ultraviolet curves are plotted in Figure 2 for the seven liquors from cook C2P1, C1P3 spent liquor; the cold water extract of aspenwood, and the white liquor. The curves are quite similar although the maxima at about 280 m μ are shifted slightly and the 30, 60, and 90-minute curves have a steeper slope at the lower wavelengths. This suggests that perhaps a different type of lignin was removed. The cold water extract curve is very similar to that of the spent liquor curves. The hydrolyzed spent liquor curves were plotted in Figure 3 and they are almost identical with the unhydrolyzed curves but are broader and have a higher absorption at 280 m μ , especially in the early stages of the cook.

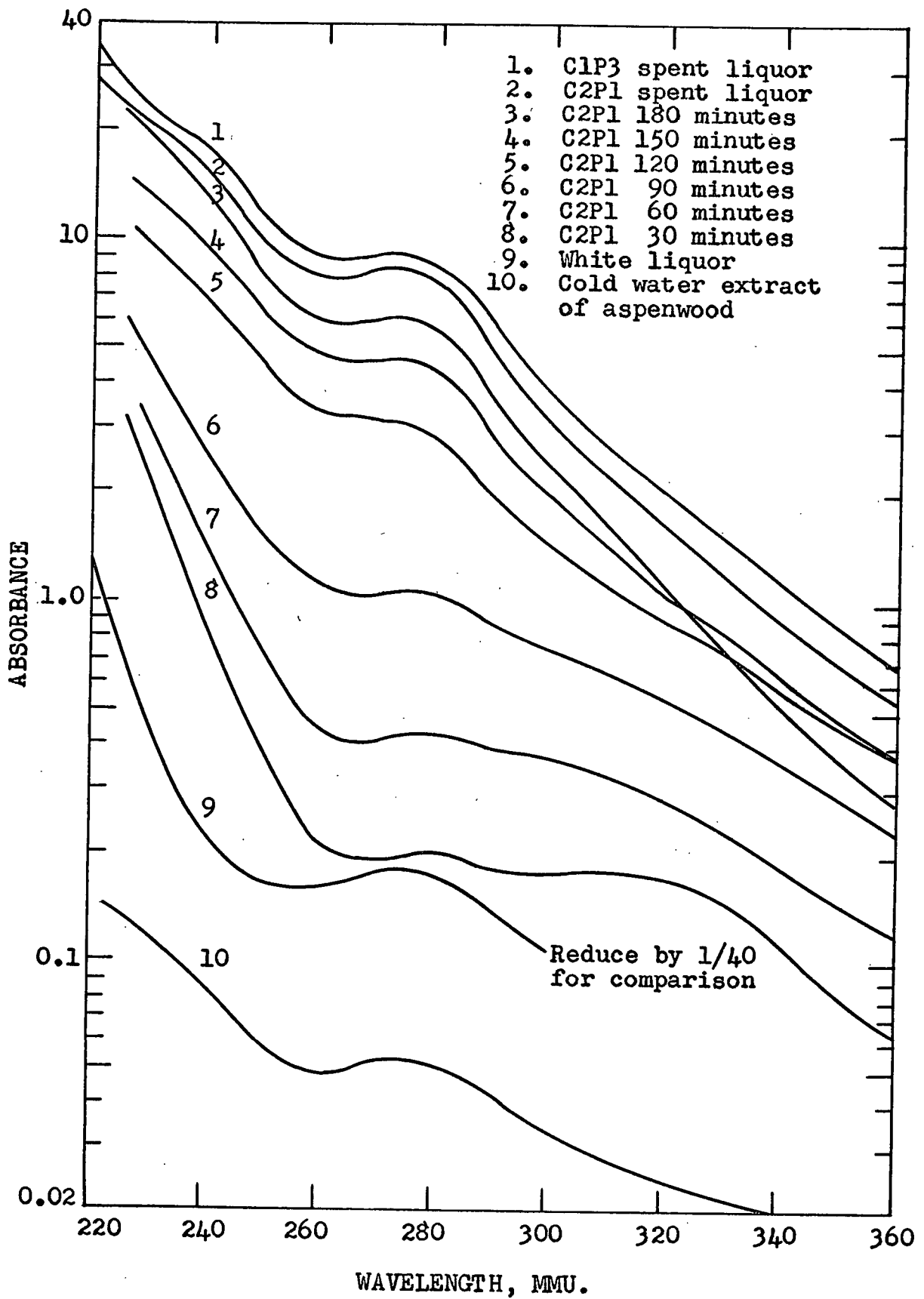


Fig. 2 Ultraviolet Absorption Curves of Unhydrolyzed Spent Liquor.

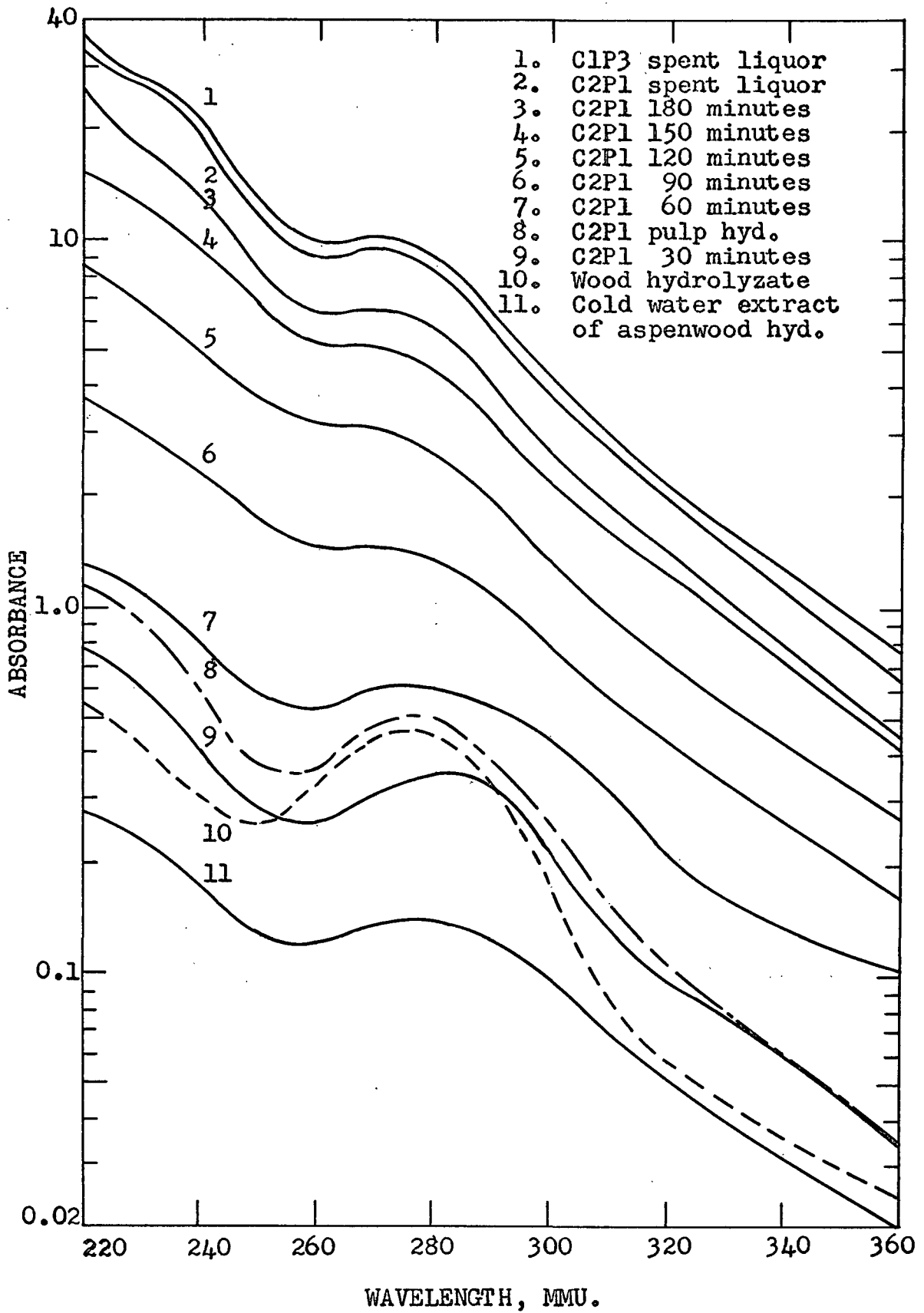


Fig. 3 Ultraviolet Absorption Curves of Hydrolyzed Spent Liquor.

After hydrolysis of the spent liquor, ultraviolet curves were made and an approximate value for degraded carbohydrates was obtained. This value was obtained by subtracting the ultraviolet lignin value for the unhydrolyzed spent liquor from the sum of the ultraviolet lignin after hydrolysis and the precipitate which separated during hydrolysis. This value for degraded carbohydrates is only approximate because not all degradation products absorb ultraviolet light. Some of the degraded carbohydrates may have precipitated with the acid-insoluble material. Therefore, the value calculated for degraded carbohydrates may include some of the degraded material but certainly not all of it. Curves are shown graphically in Figure 3 for the hydrolyzed spent liquor obtained in all seven of the intervals of cook C2P1, the C1P3 spent liquor, the cold water extract of aspenwood, the pulp hydrolyzate, and the wood hydrolyzate. These curves are similar to those of the unhydrolyzed spent liquors with the exception that the wood and pulp hydrolyzates show a higher absorbance at 280 m μ . The slope of the curves at the lower wavelengths is about the same for all spent liquors. However, after 150 minutes a "hump" appears at about 235 m μ and is quite pronounced in the 180 and 210-minute liquors.

The approximate material balances are shown in Table IV. The low percentage of accountable organic material is probably due to extractives, polyuronides, acetates and degraded materials which would not be detected by either the sugar analysis or the ultraviolet lignin determinations.

STUDY OF THE PULP AND LIQUOR

COOKS C3P1, C4P2, and C5P1

Cook C3P1 was made according to the schedule used for cook C1P3 except that the cook was ended after a 30-minute digestion period. Cook C4P2 was made by the established schedule except that the cook was ended after 90 minutes and cook C5P1 was stopped after 150 minutes. Schedules and cooking data are shown in Table I. Other than the time variable, the cooking schedule was held as constant as possible. Liquor removal from the digester, chip washing, and fiberizing were carried out according to the same procedure that was used for cook C1P3.

One of the reasons that a 90-minute time interval was selected was that a rise in pH from 7.80 to 7.86 was observed from the liquors removed during cook C2P1 (see Table II). At the end of the 90-minute interval (C4P1), it was found that the spent liquor had a pH of 8.9. This result appeared erroneous since the initial pH of the cooking liquor was only 8.3. The cook was repeated (C4P2) and again the spent liquor was 8.9. At this particular temperature, pressure, and cooking time, the system of sodium sulfite, sodium bicarbonate, water, and chips may be unstable as a result of the sudden release in pressure. When the digester is relieved after 90 minutes cooking time, carbon dioxide may be lost from the system causing a rise in pH.

Immediately after completion of cooks C3P1, C4P2, and C5P1 the respective unhydrolyzed spent liquors were chromatographed. One such chromatogram was developed with 9:2:2 and the other with 10:3:3. The

TABLE IV

APPROXIMATE ORGANIC BALANCE DURING COOK C2P1

Basis: g./100 ml. of Spent Liquor

Time Inter.	Acid-Insol. ppt.	U.V. Lig. After Hydrol.	U.V. Lig. Before Hydrol.	Degraded Carbohy. ¹	Polysac. ²	Total Org. Acct. ³	Solids Less Ash ⁴	Acct. ⁵ %
30	0.0070	0.0805	0.052	0.0355	0.0296	0.117	0.55	21.3
60	0.0098	0.162	0.112	0.0598	0.0488	0.221	0.78	28.3
90	0.0390	0.364	0.284	0.119	0.080	0.483	1.36	35.6
120	0.0748	0.717	0.763	0.0288	0.185	0.977	2.25	43.4
150	0.1380	1.21	1.15	0.198	0.490	1.84	3.56	51.7
180	0.1764	1.90	1.47	0.61	0.738	2.82	4.71	59.8
210	0.1882	2.29	2.20	0.28	1.05	3.53	7.07	49.9
CLP3SI ⁶	0.1868	2.48	2.31	0.36	1.15	3.82	7.52	50.8

¹ Degraded carbohydrates = (ultraviolet lignin after hydrolysis + acid-insoluble precipitate) - (ultraviolet lignin before hydrolysis).

² Simple sugars calculated as the corresponding polysaccharides.

³ Total organic material accounted for = (ultraviolet lignin before hydrolysis + degraded carbohydrates + polysaccharide material).

⁴ Solids less ash = (spent liquor solids - ash in spent liquor solids).

⁵ Percentage of organic material which could be accounted for = (total organic material accounted for)/(solids less ash).

⁶ Spent liquor from cook CLP3.

resulting chromatograms were sprayed with A.H.P. and no simple sugars were detected in the spent liquor from any of the cooks. The spent liquor data from cooks C1P3, C3P1, C4P2, and C5P1 are shown in Table V,

The properties of the various fibrous residues taken after the several cooking intervals were very different. That from C3P1 resembled wet sawdust more than pulp, that from C4P2 while resembling pulp showed less felting properties and cohesiveness. Residue C5P1 had the same properties as residue C1P3 and could be regarded as a pulp.

HYDROLYSIS OF SPENT LIQUOR

The spent liquor from cooks C3P1, C4P2, and C5P1 were hydrolyzed by a procedure identical with that used for liquors from cooks C1P3 and C2P1. The sugars in the hydrolyzates were determined chromatographically and calculated as the corresponding polysaccharides. In order to put all these data on a comparative basis, the quantity of spent liquor on the oven-dry chips must be known. In cook C2P1 these data are available for only the over-all 210-minute interval. In the data shown in Table VI each polysaccharide has been calculated as a percentage of the total polysaccharides detected in each spent liquor so that adequate comparisons could be made.

In order to obtain information on the amount of carbohydrate material in the spent liquor detectable by the chromatographic method, the data in Table VII were calculated from the original data which were expressed in mg. of sugar anhydride per 50 ml. of spent liquor. The quantity of liquor and the oven-dry weight of the wood must be known to calculate the

TABLE V

SPENT LIQUOR DATA FOR COOKS NUMBER
ONE, THREE, FOUR, AND FIVE

	White Liquor	Cook Number			
		C3P1	C4P2	C5P1	C1P3
Cooking time, min.	0	30	90	150	210
Temperature, °C.	-	64	136	171	170
Pressure, p.s.i.	-	6	45	131	129
Volume of spent liquor, ml.	-	10,930	5290	4820	4840
pH	8.25	8.20	8.90	7.01	7.30
Solids, g./100 ml.	4.43	4.29	5.82	9.57	11.0
Sulfated ash, % ¹	110.9	111.9	87.5	54.1	44.3
Corrected ash, % ^{1,2}	100.0	88.0	68.8	42.6	31.6
Ash, g./100 ml.	4.43	3.78	4.00	4.08	3.48

¹ Ovendry, solids basis.

² Sulfated ash was multiplied by 112/142 except C1P3 where correction to unsulfated ash was used and white liquor which was corrected to 100%. Mol. wt. of Na₂SO₄ is 142. An average mol. wt. is 112, based on % Na₂SO₃ and % NaHCO₃ present at the start of the cook.
 $(.6588)(126) + (3412)(84) = 111.7$.

TABLE VI

A COMPARISON OF THE HYDROLYZED SPENT LIQUOR DATA FROM COOKS NUMBER ONE, THREE, FOUR, AND FIVE WITH COOK NUMBER TWO

Basis: Percentage of Total Polysaccharide Present

	Cook Number and Time in Minutes:								
	C2P1 30	C3P1 30	C2P1 90	C4P1 90	C4P2 90	C2P1 150	C5P1 150	C2P1 210	C1P3 210
Polysaccharide ¹									
Galactan, %	8.0	5.4	10.0	10.9	9.8	7.0	7.1	5.4	5.2
Glucan, %	54.7	51.7	38.3	38.9	37.8	7.6	7.0	3.7	4.1
Mannan, %	16.7	25.9	12.4	12.2	10.8	3.3	3.0	2.2	1.9
Araban, %	5.6	5.3	7.0	6.7	7.4	4.5	4.8	4.7	4.9
Xylan, %	9.3	5.2	24.0	23.3	25.7	73.0	73.3	81.5	81.1
Rhamnan, %	5.7	6.5	8.3	8.0	8.5	4.6	4.8	2.5	2.8
Total, %	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

¹ Simple sugars calculated as the corresponding polysaccharides.

TABLE VII

HYDROLYZED SPENT LIQUOR FROM NSSC COOKS

Basis: Owendry ash-free wood

	Cook Number and Time in Minutes			
	C3P1 30	C4P2 90	C5P1 150	C1P3 210
Polysaccharide ¹				
Galactan, %	0.0042	0.0251	0.17	0.18
Glucan, %	0.0405	0.0965	0.17	0.14
Mannan, %	0.0203	0.0275	0.07	0.06
Araban, %	0.0038	0.0188	0.12	0.17
Xylan, %	0.0041	0.0656	1.76	2.76
Rhamnan, %	0.0051	0.0217	0.11	0.10
Total, %	0.0780	0.2552	2.40	3.41

¹ Simple sugars calculated as the corresponding polysaccharides.

quantity of sugar on the basis of the oven-dry wood. The weight of wood is known accurately but the amount of liquor is only proximate. The volume of liquor from the digester and the volume of wash liquor were measured but the liquor remaining with the chips was lost during fiberizing and washing.

The data from Table VII, which are plotted in Figure 4, compare fairly well with the data plotted from cook C2P1 in Figure 1. Although it is impossible to plot these data on the same paper, it is evident that the curves show the same general characteristics.

WOOD AND PULP ANALYSES

The wood and pulp analyses are given in Table VIII. The holocellulose yield and analysis are given in Table IX. The data for the yield and analysis of the 5% hemicellulose, 16% hemicellulose, and the alkali-resistant cellulose are given in Tables X, XI, and XII, respectively.

From the analyses of the wood and pulps (see Tables VIII-XII) obtained during the early stages of cooking it was impossible to obtain satisfactory summations from only the chromatographic and polyuronide analyses. Table IX and X which refer to the holocellulose and 5% hemicellulose analyses, respectively, are extreme examples of this variability. The reason for these results is that there was lignin and extractives present in these materials which could not be accounted for. However, only the C5P1 and C1P3 16% hemicelluloses and alkali-resistant celluloses had no acid-insoluble precipitate. All other materials did give an acid-insoluble precipitate on hydrolysis and all these precipitates gave a positive Maule test.

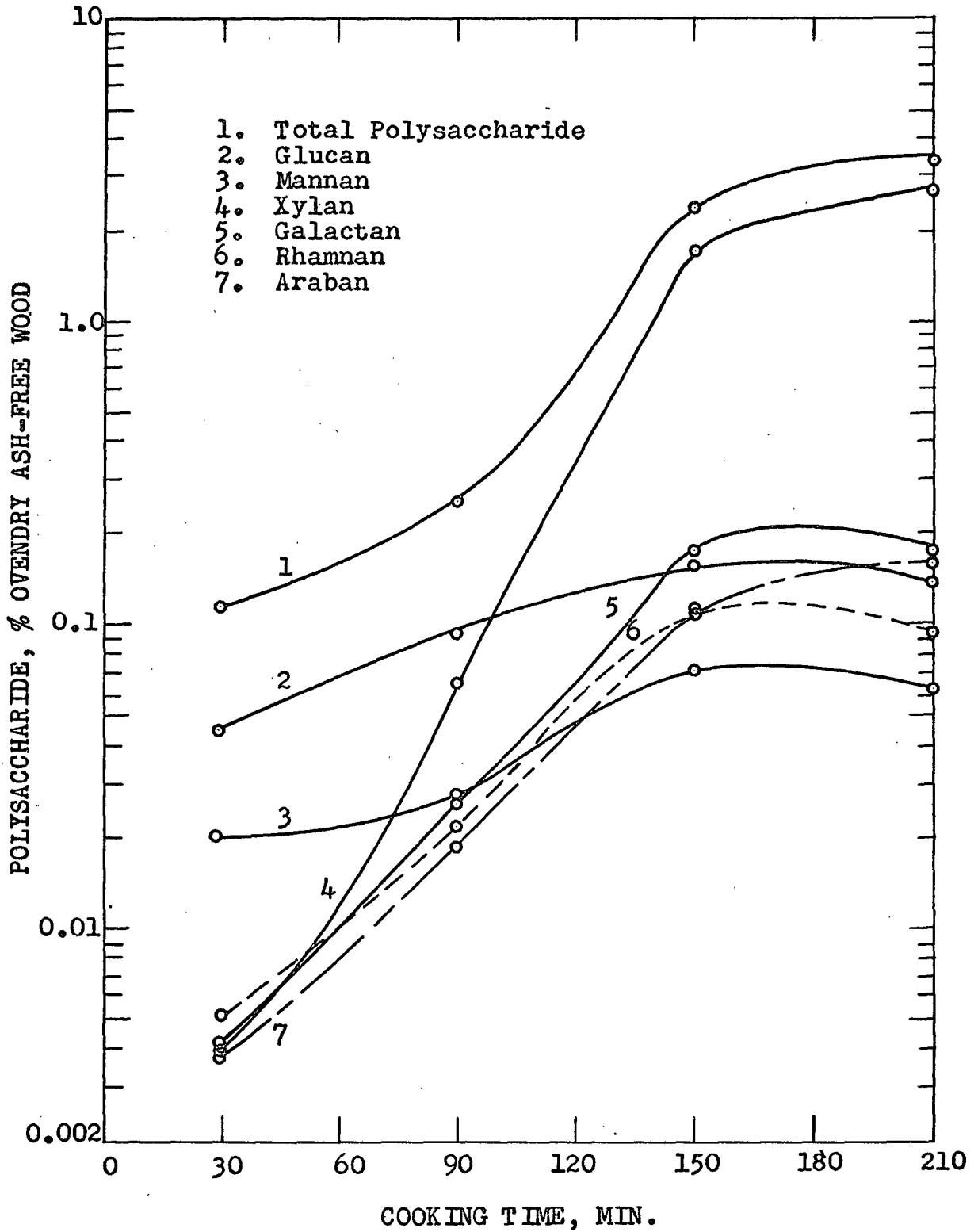


Fig. 4 Hydrolyzed Spent Liquor from the 30, 90, 150, & 210 Minute NSSC Cooks. Simple Sugars Calculated as the Corresponding Polysaccharides.

TABLE VIII

WOOD AND PULP YIELD AND ANALYSIS DATA

	Cook Number and Time in Minutes					
	Wood 0	C3P1 30	C4P2 90	C5P1 150	C1P3 210	C2P1 210
Yield, % ¹	100.0	95.5	88.4	79.8	73.9	76.3
Ash ²						
Sulfated ash, %	0.24	0.54	1.34	1.69	1.40	1.67
Sulfated ash as Na, %	--	0.17	0.42	0.52	0.43	0.52
Yield, % ³	99.8	95.6	88.2	79.6	73.8	76.1
Lignin ⁴						
Klason, %	18.4	18.5	18.0	13.9	12.2	13.2
Soluble, 230 mmu, %	2.8	3.6	3.9	4.9	4.2	6.4
Total lignin	21.2	22.1	21.9	18.8	16.4	19.6
Extractives ^{4,5}						
95% Ethanol-benzene, %	4.25	--	--	--	--	--
95% Ethanol, %	4.45	1.75	0.91	1.38	1.90	--
Cold water, %	2.74	--	--	--	--	--
Uronic anhydride, % ⁴	4.99	4.95	4.12	3.04	3.15	--
Pentosans, % ^{4,6}	18.7	--	--	--	18.1	--
Polysaccharide ^{4,7}						
Galactan, %	0.7	0.5	0.4	0.4	0.4	--
Glucan, %	41.9	42.0	43.9	48.9	52.4	--
Mannan, %	2.1	2.2	2.1	2.4	2.0	--
Araban, %	0.6	0.7	1.0	1.1	0.9	--
Xylan, %	16.5	16.9	17.1	17.6	16.8	--
Rhamnan, %	0.5	1.0	0.8	1.2	0.8	--
Total, %	62.3	62.3	65.3	71.6	73.3	--

¹ Ovendry, wood basis.

² Ovendry, wood or pulp basis. Wood ash was not sulfated.

³ Ovendry, ash-free, wood basis.

⁴ Ovendry, ash-free, wood or pulp basis.

⁵ Extractives were not determined by successive extractions.

⁶ Pentosan corrected for uronic anhydride.

⁷ Simple sugars calculated as the corresponding polysaccharides.

TABLE IX

HOLOCELLULOSE YIELDS AND ANALYSIS

	Cook Number and Time in Minutes				
	Wood 0	C3P1 30	C4P2 90	C5P1 150	C1P3 210
Yield, % ¹	95.6	95.4	87.7	83.7	83.9
Ash ²					
Sulfated ash, %	0.13	0.27	0.24	0.17	0.27
Sulfated ash as Na, %	0.036	0.082	0.073	0.053	0.085
Yield, % ³	95.8	91.3	77.7	66.9	62.1
Uronic anhydride, % ⁴	8.91	8.98	7.49	4.10	2.95
Polysaccharide ^{4,5}					
Galactan, %	0.4	0.5	0.2	0.3	0.4
Glucan, %	41.4	46.6	46.8	50.4	65.1
Mannan, %	2.1	2.3	2.5	2.3	2.0
Araban, %	0.8	0.8	1.0	1.1	0.7
Xylan, %	16.3	18.1	19.9	20.3	19.3
Rhamnan, %	0.6	0.7	0.9	0.6	0.5
Total, %	61.6	69.0	71.3	75.0	88.0

1 Ovendry, wood or pulp basis.

2 Ovendry, holocellulose basis.

3 Ovendry, ash-free wood basis.

4 Ovendry, ash-free holocellulose basis.

5 Simple sugars calculated as the corresponding polysaccharides.

TABLE X

5% HEMICELLULOSE YIELDS AND ANALYSIS

	Cook Number and Time in Minutes				
	Wood 0	C3P1 30	C4P2 90	C5P1 150	C1P3 210
Yield, % ¹	21.9	22.5	25.3	21.5	19.6
Ash ²					
Sulfated ash, % ³	9.22	9.94	10.62	8.14	7.60
Corrected ash, % ³	4.63	4.90	4.98	4.26	4.03
Yield, % ⁴	20.1	19.5	18.7	13.8	11.7
Uronic anhydride, % ⁵	16.7	16.6	13.7	12.1	11.6
Polysaccharide ^{5,6}					
Galactan, %	0.9	1.4	1.2	1.3	1.2
Glucan, %	0.5	0.5	0.3	0.3	0.2
Mannan, %	0.8	1.1	0.4	0.5	0.5
Araban, %	1.1	1.1	1.7	1.7	1.4
Xylan, %	62.7	63.6	63.7	73.3	89.3
Rhamnan, %	1.1	1.8	1.2	1.1	1.1
Total, %	67.1	69.5	68.5	78.2	93.7
Viscosity data ⁷					
Intrinsic viscosity, (η)	0.72	0.93	0.97	1.01	0.94
Degree of polymerization	164	211	220	230	214
Molecular weight	21,600	27,800	29,100	30,400	28,200

¹ Ovendry, holocellulose basis.

² Ovendry, hemicellulose basis.

³ Corrected ash: (a) sulfated ash dissolved in water, (b) % corrected ash = (water soluble ash)(76/174) + (water-insoluble ash) divided by sample weight of ovendry hemicellulose.

⁴ Ovendry, ash-free wood basis.

⁵ Ovendry, ash-free hemicellulose basis.

⁶ Simple sugars calculated as the corresponding polysaccharides.

⁷ An Ostwald-Fenske viscometer and 10% KOH solvent was used. (η) = $K(DP)$, $K = (4.4)(10^{-3})$. Molecular weight calculated as pentosan.

TABLE XI

16% HEMICELLULOSE YIELDS AND ANALYSIS

	Cook Number and Time in Minutes				
	Wood	C3P1	C4P2	C5P1	C1P3
	0	30	90	150	210
Yield, % ¹	5.79	5.20	6.39	7.34	6.87
Ash ²					
Sulfated ash, %	8.72	6.42	6.75	4.86	5.23
Corrected ash, % ³	4.96	4.22	4.03	3.53	2.88
Yield, % ⁴	5.27	4.55	4.76	4.67	4.14
Uronic anhydride, % ⁵	12.1	10.6	9.93	8.83	8.26
Polysaccharide ^{5,6}					
Galactan, %	1.1	0.8	0.7	0.6	0.4
Glucan, %	2.5	2.0	1.7	1.6	1.9
Mannan, %	3.0	2.1	1.5	1.1	0.9
Araban, %	1.0	0.8	0.6	0.3	0.3
Xylan, %	69.1	75.9	73.0	77.2	81.6
Rhamnan, %	1.2	1.5	1.6	1.2	1.1
Total, %	77.9	83.1	79.1	82.0	86.2
Viscosity data ⁷					
Intrinsic viscosity, (η)	0.93	0.91	0.89	0.93	0.81
Degree of polymerization	211	207	202	211	184
Molecular weight	27,800	27,300	26,600	27,800	24,300

¹ Ovendry, holocellulose basis.

² Ovendry, hemicellulose basis.

³ See footnote 3, Table X.

⁴ Ovendry, ash-free wood basis.

⁵ Ovendry, ash-free hemicellulose basis.

⁶ Simple sugars calculated as the corresponding polysaccharides.

⁷ An Ostwald-Fenske viscometer and 10% KOH solvent was used. (η) = $K(DP)$, $K = (4.4)(10^{-3})$. Molecular weight calculated as pentosan.

TABLE XII

ALKALI-RESISTANT CELLULOSE YIELDS AND ANALYSIS

	Cook Number and Time in Minutes				
	Wood 0	C3P1 60	C4P2 90	C5P1 150	C1P3 210
Yield, % ¹	49.6	51.2	57.1	68.1	70.7
Ash ²					
Sulfated ash, %	0.89	0.96	0.62	0.63	0.66
Sulfated ash as K, %	0.39	0.42	0.27	0.27	0.38
Yield, % ³	47.3	46.5	44.3	45.5	43.8
Uronic anhydride, % ⁴	2.56	2.52	2.05	1.58	1.18
Polysaccharide ^{4,5}					
Galactan, %	0.3	0.3	0.6	—	—
Glucan, %	83.0	86.9	86.6	91.5	92.1
Mannan, %	3.4	3.8	4.0	3.3	3.4
Araban, %	0.8	0.6	0.7	0.1	—
Xylan, %	2.5	2.7	2.9	2.5	2.6
Rhamnan, %	0.2	0.2	0.2	—	—
Total, %	90.2	94.5	95.0	97.4	98.1
Viscosity data ⁶					
Intrinsic viscosity, (η)	7.2	—	—	—	11.3
Degree of polymerization	1220	—	—	—	1920
Molecular weight	198,000	—	—	—	311,000

¹ Ovendry, holocellulose basis.

² Ovendry, alkali-resistant cellulose.

³ Ovendry, ash-free wood basis.

⁴ Ovendry, ash-free alkali-resistant cellulose basis.

⁵ Simple sugars calculated as the corresponding polysaccharides.

⁶ An Ostwald-Fenske viscometer and cupriethylenediamine solvent was used. $DP = K(\eta)$, $K = 170$. Molecular weight calculated as hexosan.

When the material analyzed was practically free of lignin and extractives, satisfactory summations could be effected by the chromatographic and polyuronide analysis. For example, Table XII shows that the sum of the polyuronides and polysaccharides will account for only 92.8% of the wood alkali-resistant cellulose while the sum of the same two constituents will account for 99.3% of the C1P3 pulp alkali-resistant cellulose. These results from the purified material lend credibility to the method of hydrolysis and the subsequent analysis which were used.

The effect of the NSSC cook on the polyuronides is shown in Table XIII. A summation was made of the polyuronides from the 5% hemicellulose, 16% hemicellulose, and the alkali-resistant cellulose, and are in good agreement with the analysis of the wood or pulps. The polyuronides lost during the cook were calculated by difference and are compared with the polyuronides detected in the spent liquor "hemicellulose." The comparisons are good with the exception of the 90-minute cook, C4P2. The low recovery of polyuronides in the C4P2 "hemicellulose" may be correlated with the unusually high pH of this spent liquor.

Tables X and XI indicate that, in general, the number average D.P. of the 5% hemicellulose increases with cooking time and the D.P. of the 16% hemicellulose decreases with cooking time. An explanation of this phenomenon may be that as the cook proceeds, higher D.P. material is made susceptible to attack by the 5% potassium hydroxide extraction. Some of this material may have been removed only by the 16% potassium hydroxide extraction of the pulp holocellulose which came from the early stages of

TABLE XIII

POLYURONIDE DATA OBTAINED DURING NSSC COOKS

Basis: Percentage Owendry, Ash-free Wood

	Wood or Pulp	Summed Carb. ¹	Alkali-Resistant Cellulose	5% Hemi-Cellulose	16% Hemi-Cellulose	Poly-uronide Lost ²	Poly-uronide "Hemi." ³
Wood	4.99	5.20	1.21	3.35	0.64	0	0.10 ³
C3P1	4.73	4.89	1.17	3.24	0.48	0.26	0.40
C4P2	3.64	3.94	0.91	2.56	0.47	1.35	0.42
C5P1	2.42	2.80	0.72	1.67	0.41	2.57	2.01
C1P3	2.32	2.22	0.52	1.36	0.34	2.67	3.17

¹ Alkali-resistant cellulose plus the 5 and 16% hemicelluloses.

² Subtract pulps from wood.

³ Cold water extract of aspenwood.

the cook. When pulp obtained from the later stages of the cook was converted to holocellulose and this was extracted with 5% potassium hydroxide, the high D.P. material is removed leaving a lower D.P. material for the 16% potassium hydroxide to extract.

The D.P. of the alkali-resistant cellulose (see Table XII) increased with cooking time as might be expected since the lower D.P. material probably was removed during the cook.

SPENT LIQUOR "HEMICELLULOSE" ANALYSIS

The data on the spent liquor "hemicellulose" are given in Table XIV. Data on the cold water extract of aspenwood also are included. Table XV serves to compare the sugars obtained from the hydrolysis of: (a) the spent liquor, and (b) the "hemicellulose" precipitated from the spent liquor. The polysaccharide analyses are seen to be different in the two cases. This difference is probably due to the method of precipitating the "hemicellulose" and not to the method of sugar analysis. Total polysaccharide comparisons on an oven-dry ash-free wood basis are shown in Table XVI.

All six sugars found in the wood hydrolyzate were present in the hydrolyzate of the cold water extract; and in addition, fucose, a new sugar from aspenwood, was indicated. The hydrolyzed cold water extract does not have the same sugar composition as the hydrolyzed "hemicellulose." This suggests that different solvents remove different carbohydrate fractions from the wood. The unhydrolyzed cold water extract of aspenwood gave strong chromatographic spots for glucose and fructose, and a very

slight spot for sucrose. The same results were obtained from aspenwood meal which had the cambium zone and the first years growth of wood next to the cambium removed. The fucose which was reported, was indicated only by chromatographic methods. The material was eluted from a chromatogram and rechromatographed. The second chromatogram showed only one spot present opposite the known L-fucose spot, but no chemical identification was made.

When the spent liquor "hemicellulose" polysaccharide analysis is calculated on the oven-dry ash-free wood basis, the amount of material detected is very small (see Table XVI). It is not until after the 150-minute cooking period that the polysaccharide material in the spent liquor becomes appreciable. The total amounts of polysaccharide material detected in the spent liquor and in the spent liquor "hemicellulose" are fairly close considering the various treatments of the spent liquor.

TABLE XIV

SPENT LIQUOR "HEMICELLULOSE" DATA

	Cook Number and Time in Minutes				
	Cold H ₂ O Ext. ¹	C3P1 30	C4P2 90	C5P1 150	C1P3 210
Yield, % ² Ash ³	0.47	1.39	19.8	57.4	80.3
Sulfated ash, %	14.46	65.17	65.94	54.18	47.69
Sulfated ash as Ba, %	--	37.76	38.18	31.39	28.55
Yield, % ⁴	0.41	0.68	1.8	9.4	17.8
Uronic anhydride ⁵ Polysaccharide ^{5,6}	23.7	59.5	23.1	21.4	17.8
Galactan, %	5.2	1.3	1.0	1.6	1.4
Glucan, %	6.9	3.0	1.8	0.9	0.8
Mannan, %	8.6	1.8	1.4	1.2	1.1
Araban, %	3.3	1.4	0.8	1.4	1.6
Xylan, %	12.5	1.1	1.7	13.4	16.1
Fucan, %	0.8	--	--	--	--
Rhamnan, %	2.0	0.8	0.7	1.2	1.5
Total, %	39.3	9.4	7.4	19.7	22.5
Viscosity data ⁷					
Intrinsic viscosity	0.14	0.04	0.07	0.12	0.13

- 1 Wood meal extracted for 48 hours at about 22°C. with distilled water and the filtrate precipitated with absolute ethanol.
- 2 Owendry, solids basis. Cold water extract owendry, wood basis.
- 3 Owendry, "hemicellulose" basis.
- 4 Owendry, ash-free wood basis.
- 5 Owendry, ash-free "hemicellulose" basis.
- 6 Simple sugars calculated as the corresponding polysaccharides.
- 7 An Ostwald-Fenske viscometer and 10% KOH solvent were used.

TABLE XV

A COMPARISON OF THE POLYSACCHARIDES IN THE SPENT LIQUOR AND
IN THE SPENT LIQUOR "HEMICELLULOSE"
FROM THE NSSC COOKS

Basis: Percentage of Total Polysaccharide Present

Polysac.	C.W. Extr.	C3P1SL		C4P2SL		C5P1SL		C1P3SL	
		Hyd. ²	Hemi. ³	Hyd. ²	Hemi. ³	Hyd. ²	Hemi. ³	Hyd. ²	Hemi. ³
Galactan	13.3	5.4	13.5	9.8	13.8	7.1	8.0	5.2	6.4
Glucan	17.5	51.7	32.4	37.8	24.5	7.0	4.5	4.1	3.7
Mannan	21.8	25.9	18.9	10.8	18.1	3.0	6.1	1.9	4.8
Araban	8.5	5.3	14.9	7.4	11.7	4.8	7.1	4.9	6.9
Xylan	31.8	5.2	12.2	25.7	22.3	73.3	68.2	81.1	71.6
Fucan	2.1	--	--	--	--	--	--	--	--
Rhamnan	5.0	6.5	8.1	8.5	9.6	4.8	6.1	2.8	6.6
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

¹ Simple sugar calculated as the corresponding polysaccharides.

² Obtained by hydrolyzing the total spent liquor.

³ Obtained by hydrolyzing the "hemicellulose."

TABLE XVI

POLYSACCHARIDES IN THE COLD WATER EXTRACT OF ASPENWOOD AND
SPENT LIQUOR "HEMICELLULOSE" FROM NSSC COOKS

Basis: Percentage Oven-dry, Ash-free Wood

Polysac. ¹	C.W. Extr.	Cook Number and Time in Minutes				
		0	C3P1 30	C4P2 90	C5P1 150	C1P3 210
Galactan	0.0212	0.0084	0.0186	0.15	0.26	
Glucan	0.0280	0.0202	0.0329	0.08	0.15	
Mannan	0.0348	0.0118	0.0243	0.11	0.19	
Araban	0.0136	0.0093	0.0157	0.138	0.28	
Xylan	0.0509	0.0076	0.0301	1.25	2.87	
Fucan	0.0034	--	--	--	--	
Rhamnan	0.0081	0.0051	0.0129	0.11	0.27	
Total	0.1600	0.0624	0.1345	1.83	4.02	
Hyd. Total	--	0.0780	0.2552	2.40	3.41	

¹ Simple sugar calculated as the corresponding polysaccharides.

DISCUSSION OF RESULTS

LIQUOR STUDY

Chromatographic analysis of the final spent liquor from a NSSC cook showed that there were no simple sugars or disaccharides present. This is a confirmation of the work done by Lea (3). It was also found that liquors taken during a cook contained no free sugars or disaccharides. These same results were found when the final spent liquor was concentrated or deionized and chromatographed. This suggests that if any free sugars were formed they were immediately degraded or converted into compounds which were not detected by paper chromatography. The fact that none of the free sugars found in the cold water extract of the wood were detected in the spent liquor helps to support this theory. It has been shown that when simple sugars are added to a kraft cook (25) no sugars can be detected in the spent liquor by paper chromatography.

There is a difference in the order of the polysaccharide material removal during a NSSC cook and that of a sulfite or sulfate cook. Sundman (5) showed by qualitative paper chromatography that xylose and arabinose were the first sugars removed from aspenwood by a sulfite cook. He detected galactose about three-fourths of the way through the cook, and glucose and mannose at the end of the cook. Xylose predominated over the sugars present in the spent liquor and the total sugar present seemed to increase with cooking time. These results may be compared with those from a sulfate cook of birchwood which was carried out by Saarnio and Gustafsson (6). Their work suggests that the monosaccharides and

oligosaccharides are rapidly destroyed during a sulfate cook and only the more resistant polysaccharides remain. Using quantitative chromatography on the sulfate liquor hydrolyzate, they found that xylan was removed from birchwood prior to the other polysaccharides. Araban, galactan, and traces of mannan and glucan were detected in order during the cook. Halfway through the cook the xylan content of the cooking liquor began to decrease, and the amount of galactan and araban also decreased with cooking time. The predominant group of polysaccharides remaining in the liquor at the end of the cook was the pentosans. The above two studies suggest that the NSSC cook has some characteristics of both the sulfite and sulfate processes. The NSSC spent liquor contains no simple sugars or disaccharides, being similar in this respect to the sulfate cook. The polysaccharide material increases with cooking time thus resembling the sulfite cook. The NSSC pulping process removes polysaccharides which contain all six sugar units found in the wood hydrolyzate. This behavior is quite different from that of either the sulfite or sulfate pulping processes.

The source of glucose in the hydrolyzate of spent liquor removed during the early stages of the cook is unknown. It may come from some glycoside which was removed readily by the cooking liquor. Another possibility is based upon the physical nature of the chip. Since penetration of the chips was not complete after 30 minutes cooking, the glucose may have come from low D.P. cellulose which was removed from the ends and sides of the chips. Perhaps the chipping and drying made the glucose- and mannose-containing polysaccharide more available to attack

by the cooking liquor. Another possibility is that wood in a very finely divided or even colloidal form may have been present in the spent liquor. However, for this to be true, the hydrolysis of the spent liquor should have resulted in a high glucose, a high xylose, and a low mannose yield. The actual analysis showed a low xylose and a high mannose content, and therefore, this hypothesis can be rejected.

The slopes of the ultraviolet curves at the low wavelengths, 220 to 250 mmu, for the unhydrolyzed liquors were not the same. It is possible that the differences in slope in the early and later stages of the cook are due to the removal of a different type of lignin. This hypothesis has been somewhat supported by the nitrobenzene oxidations run on these same liquors by Stone (26). It was shown that in the early stages of the cook vanillin predominated, but was overtaken by syringaldehyde as the cook proceeded.

Quantitative sugar analyses accounted for about 36% of the hemicellulose removed from the wood during a NSSC cook. This value is lower than the value of 50% reported by Lea (3). This may be due to a difference in the species of populus used or in the cooking conditions.

PULP AND LIQUOR STUDY

In order to make an appraisal of the chromatographic analyses of the wood, pulps, holocelluloses, 5% hemicelluloses, 16% hemicelluloses, and the alkali-resistant celluloses, Table XVII was constructed. Table XVII is actually a triple check of the polysaccharide analysis data from the wood and pulp. First, the wood or pulp was hydrolyzed and the quantity

TABLE XVII

SUMMARY OF THE WOOD AND PULP SUGAR ANALYSIS DATA

Basis: Ovendry, Ash-free Wood

Polysaccharide ¹	Wood or Pulp	Holo. ²	Summed Holo. ²	Alkali-Resistant Cellulose	5% Hemi-cellulose	16% Hemi-cellulose
				Wood		
Galactan, %	0.7	0.4	0.4	0.1	0.2	0.06
Glucan, %	41.9	39.6	39.5	39.3	0.1	0.13
Mannan, %	2.1	2.0	2.0	1.6	0.2	0.16
Araban, %	0.6	0.7	0.6	0.4	0.2	0.04
Xylan, %	16.5	15.7	17.4	1.2	12.6	3.64
Rhamnan, %	0.5	0.6	0.4	0.1	0.2	0.07
Total, %	62.3	59.0	60.3	42.7	13.5	4.10
				C3P1 Pulp (30 Minutes Cooking Time)		
Galactan, %	0.5	0.5	0.4	0.1	0.3	0.04
Glucan, %	40.2	42.5	40.7	40.5	0.1	0.09
Mannan, %	2.1	2.2	2.1	1.8	0.2	0.10
Araban, %	0.7	0.8	0.5	0.3	0.2	0.04
Xylan, %	16.2	17.2	17.2	1.3	12.4	3.46
Rhamnan, %	0.9	0.6	0.5	0.1	0.3	0.07
Total, %	60.6	63.8	61.4	44.1	13.5	3.80
				C4P2 Pulp (90 Minutes Cooking Time)		
Galactan, %	0.3	0.3	0.5	0.3	0.2	0.03
Glucan, %	38.8	39.1	38.4	38.3	Trace	0.08
Mannan, %	2.1	1.8	2.0	1.8	0.1	0.07
Araban, %	0.9	0.8	0.6	0.3	0.3	0.03
Xylan, %	15.1	15.8	16.7	1.3	11.9	3.48
Rhamnan, %	0.7	0.5	0.4	0.1	0.2	0.07
Total, %	57.9	58.3	58.6	42.1	12.7	3.76
				C5P1 Pulp (150 Minutes Cooking Time)		
Galactan, %	0.3	0.5	0.2	--	0.2	0.03
Glucan, %	38.9	38.4	41.8	41.7	Trace	0.07
Mannan, %	1.9	1.6	1.6	1.5	0.1	0.04
Araban, %	0.9	0.5	0.6	0.4	0.2	0.02
Xylan, %	14.0	13.8	14.8	1.1	10.1	3.61
Rhamnan, %	1.0	0.5	0.3	--	0.2	0.06
Total, %	57.0	55.3	59.3	44.7	10.8	3.83
				C1P3 Pulp (210 Minutes Cooking Time)		
Galactan, %	0.3	0.3	0.1	--	0.1	0.02
Glucan, %	38.7	40.4	40.4	40.3	Trace	0.08
Mannan, %	1.5	1.3	1.6	1.5	0.1	0.04
Araban, %	0.7	0.4	0.2	--	0.2	0.01
Xylan, %	12.4	12.0	15.0	1.2	10.4	3.38
Rhamnan, %	0.7	0.3	0.2	--	0.1	0.05
Total, %	54.3	54.7	57.5	43.0	10.9	3.58

¹ Simple sugars calculated as the corresponding polysaccharides.

² Holocellulose. Summed holocellulose = alkali-resistant cellulose + 5% hemicellulose + 16% hemicellulose.

of sugar was determined by the chromatographic method. Second, the holocellulose, which is reported to contain all the carbohydrate material, was hydrolyzed and analyzed. Third, the sum of the 5% hemicellulose, 16% hemicellulose, and the alkali-resistant cellulose analysis should be equal to the holocellulose analysis, and to the wood or pulp analysis. In order to evaluate the data in Table XVII, the data which showed the greatest change or difference were tested by the Student's t test (27). This test shows whether or not there is a significant difference in the means of sets of numbers. In using this test a hypothesis is set up that the sets of numbers come from the same population. If the results of the test are not significant, the hypothesis is accepted. However, if the results of the test are significant, the hypothesis is rejected and it is concluded that the sets of numbers probably came from different populations. When the glucan determinations of the wood and C1P3 pulp were tested in this way, the results indicated that there was no significant difference between the two means at the 5% level of significance. The same results were obtained in all of the following cases: when the glucan determinations of the C1P3 pulp and C1P3 holocellulose were tested; when the xylan determinations of the C3P1 pulp and C3P1 holocellulose were tested; when the glucan determinations of the wood and C1P3 alkali-resistant cellulose were tested; and when the glucan determinations of the wood and C4P2 alkali-resistant cellulose were tested. The xylan determinations of the wood and C1P3 pulp 5% hemicellulose and 16% hemicellulose were tested and found to be highly significant at the 5% level of significance. These statistical analyses suggest that the method of glucan analysis used was not capable of showing any differences in the

glucan in the wood or in the pulp when both are put on an oven-dry ash-free wood basis. This means that the glucan analysis of the wood and pulps had insufficient precision to predict the 0.14% glucan in the spent liquor by taking differences. This result could be expected because the precision of the chromatographic method was $\pm 5\%$ of the average. The statistical analysis suggests that there is a difference between the means of the xylan determinations. This result is further supported by the fact that of the 2.5% xylan removed from the wood by a NSSC cook, 2.8% of the xylan on a wood basis was detected in the spent liquor.

The polysaccharide analysis data for the alkali-resistant cellulose are shown in Table XVII and suggest a close association between mannan, xylan, and cellulose. It is possible that some of the xylan is also associated with lignin, but a small portion may be linked to cellulose. The data show that, as the alkali-resistant cellulose becomes free of lignin, the galactan, araban, and rhamnan are not detected in the C5P1 or ClP3 pulp alkali-resistant cellulose. Both of these alkali-resistant celluloses gave a negative Maule test and no precipitate formed on hydrolysis. This suggests that there may be a close association between galactan, araban, and rhamnan, and lignin. The data of Lea (2) and Boehm (23) also show that no galactose, arabinose, or rhamnose were detected in the hydrolyzate from the alkali-resistant cellulose obtained from the pulp. Other investigators (28) have found that galactose, arabinose, and xylose were present in lignin fractions from aspenwood after an extensive effort had been made to eliminate the carbohydrates.

Of the carbohydrate material which dissolved from the wood during a NSSC cook, 31% was detected in the spent liquor "hemicellulose" by chromatographic sugar analysis while 24% could be attributed to the polyuronides. This is about 55% of the carbohydrate material removed from the wood. These results suggest that some of the carbohydrates were converted or degraded to compounds which could not be detected by the analytical methods used. A plot of the carbohydrate material detected by the chromatographic sugar analysis and polyuronide analysis is shown in Figure 5. The curves are similar to the curve for the 5% hemicellulose. This is logical because the major part of the carbohydrate material removed was 5% hemicellulose.

A summary of the wood and pulp analyses is given in Table XVIII. All data reported are calculated on the oven-dry ash-free wood basis. Satisfactory balances of the constituents separated were obtained. This table provides the basis for Table XIX, which was constructed by subtracting the various pulp analyses from the wood analysis. The differences obtained are assumed to be the amounts of the material removed during the cook. A plot of the data is shown in Figure 6. The bar graphs in Figures 7 and 8 were constructed to show the amount of material remaining after the cook and the polysaccharides remaining after the cook, respectively.

These data show that it was possible to account for 95% or more of all the material removed during the NSSC cooks. At the end of the cook only 80% of the lignin plus carbohydrate could be accounted for in the spent liquor "hemicellulose." However, the slope of the total

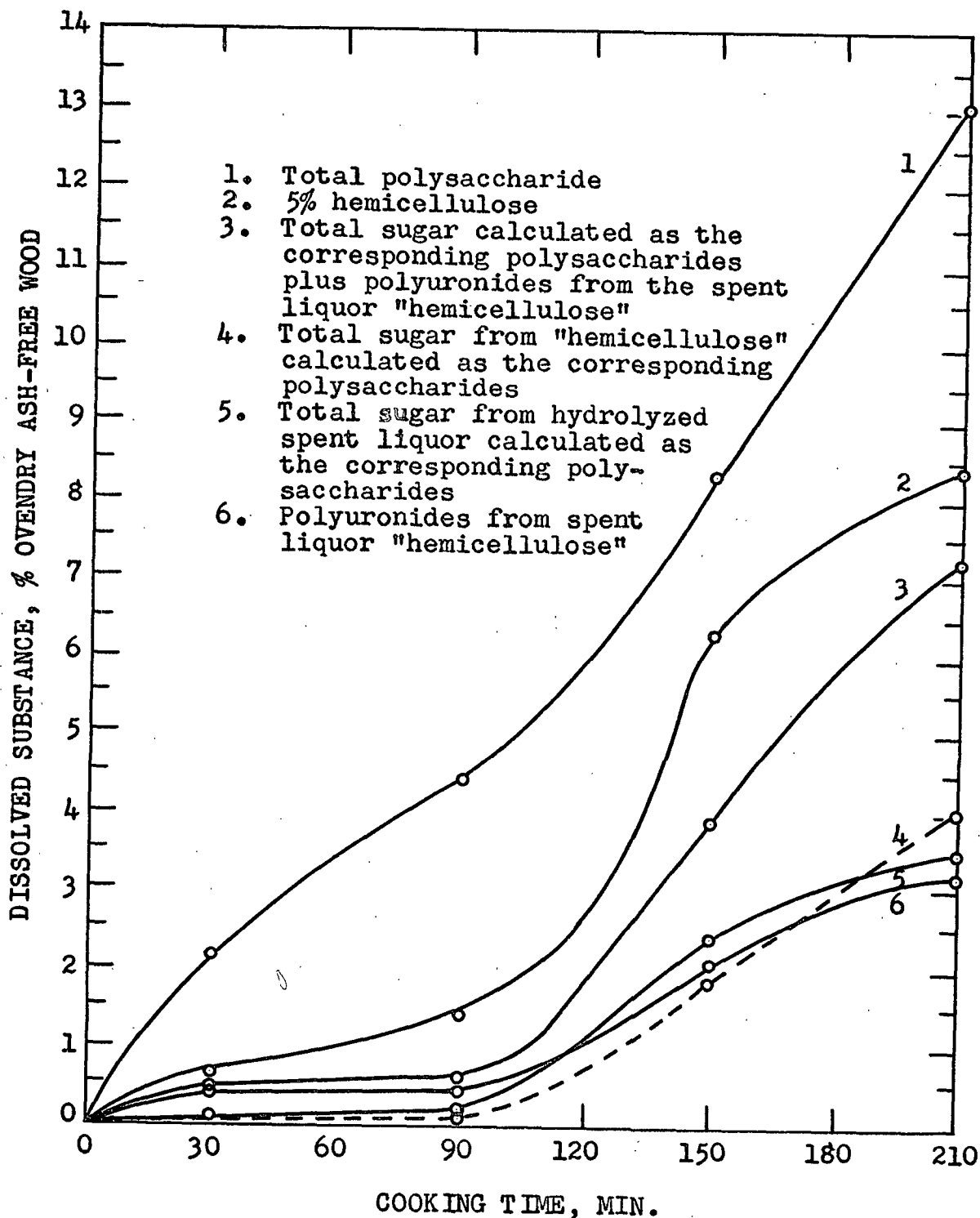


Fig. 5 A Comparison of the Carbohydrate Material Found in the Spent Liquor of a NSSC Cook by the Chromatographic Method & Polyuronide Analysis to the Total Carbohydrate & 5% Hemicellulose Removed from the Wood.

TABLE XVIII

SUMMARY OF WOOD AND PULP ANALYSIS

Basis: Percentage Owendry, Ash-free Wood

	Wood	Cook Number and Time in Minutes			
		C3P1 30	C4P2 90	C5P1 150	C1P3 210
5% Hemicellulose	20.1	19.5	18.7	13.8	11.7
16% Hemicellulose	5.3	4.6	4.8	4.7	4.1
Alkali-resistant cellulose	47.3	46.5	44.3	45.5	43.8
Lignin					
Klason	18.4	17.7	15.8	11.1	9.0
Soluble, 230 mmu	2.8	3.4	3.4	3.9	3.1
Extractives	4.3	1.8	0.8	1.1	1.4
Total found	98.2	93.5	87.8	80.1	73.1
Actually present	99.8	95.6	88.2	79.6	73.8

TABLE XIX

MATERIALS REMOVED FROM THE WOOD DURING A NSSC COOK

Basis: Percentage Owendry, Ash-free Wood

	Cook Number and Time in Minutes			
	C3P1 30	C4P2 90	C5P1 150	C1P3 210
5% Hemicellulose	0.6	1.4	6.3	8.4
16% Hemicellulose	0.7	0.5	0.6	1.2
Alkali-resistant cellulose	0.8	3.0	1.8	3.5
Total carbohydrate	2.1	4.9	8.7	13.1
Total lignin	0.1	2.0	6.2	9.1
Carbohydrate+lignin	2.2	6.9	14.9	22.2
Carbohydrate+lignin+extractives	4.9	10.6	18.3	25.3
Spent liquor "hemicellulose"	0.7	1.8	9.4	17.8
Total material ¹	4.2	11.6	20.2	26.0

¹ These data were obtained from differences in yield data.

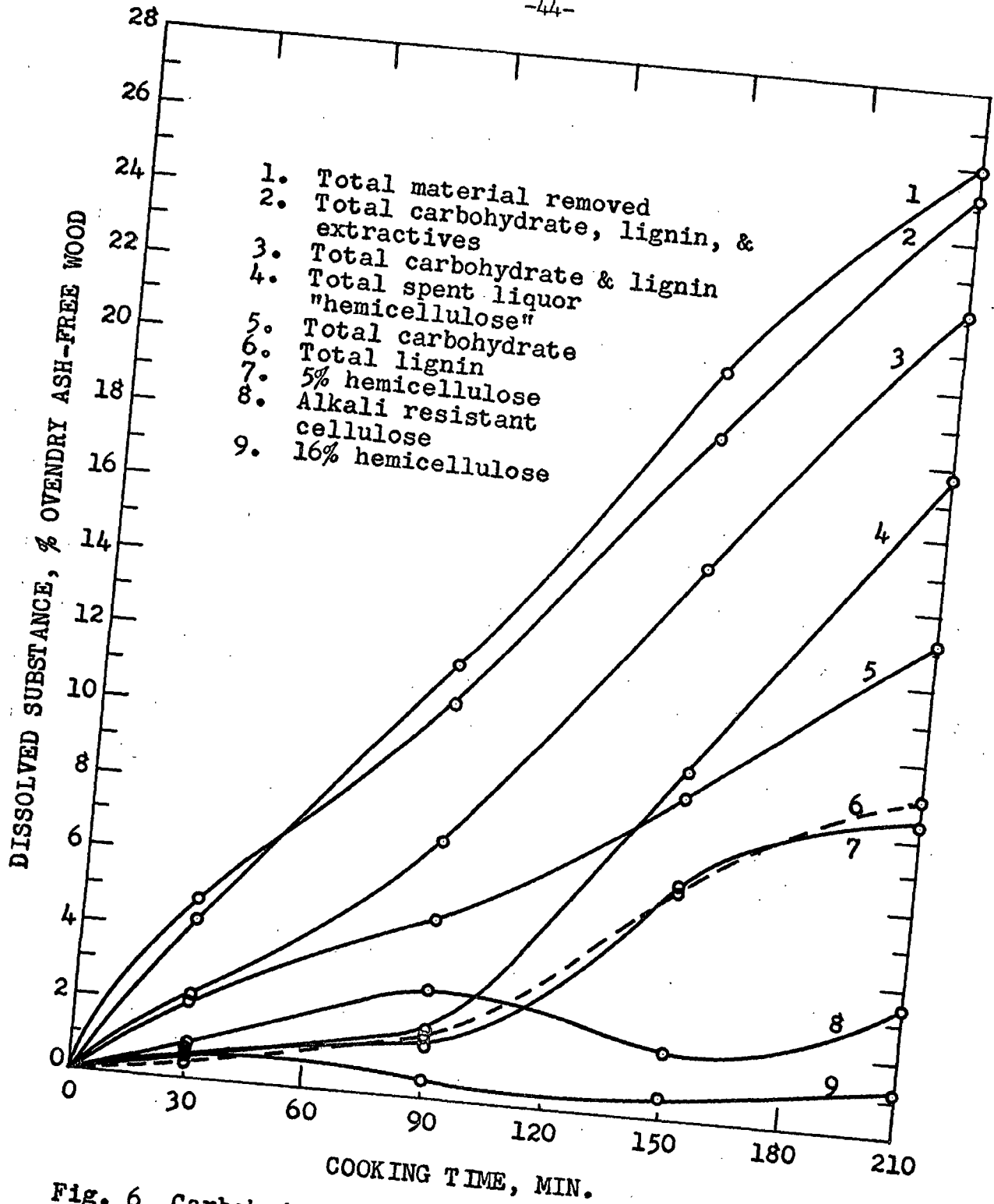


Fig. 6 Carbohydrate Material & Lignin Removed from the Wood by the NSSC Cooks.

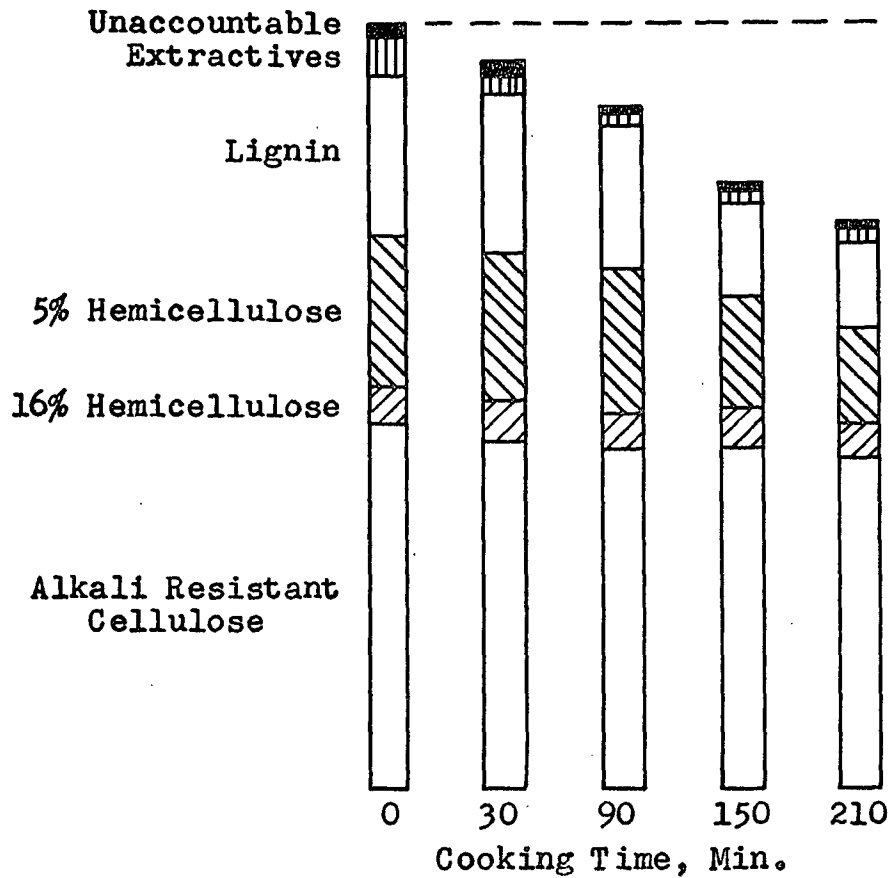


Fig. 7 Material Remaining in the Pulp Compared to Wood Based on Percentage Oven-dry Ash-free Wood.

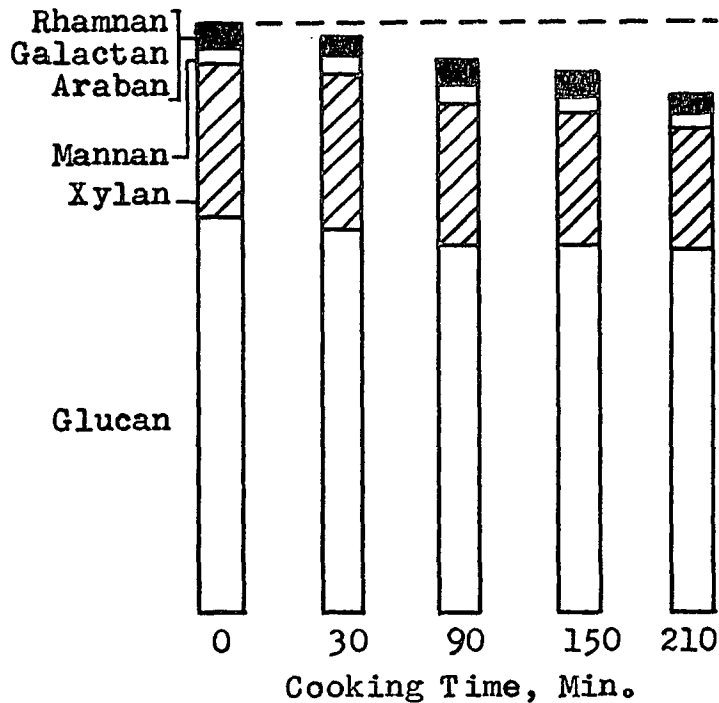


Fig. 8 Polysaccharides Remaining in the Pulp Compared to Wood Based on Percentage Oven-dry Ash-free Wood.

carbohydrate and "hemicellulose" curves is nearly the same which suggests a constant amount of unaccountable material. The actual amounts of 5% hemicellulose and of the lignin removed during the cook are about the same. This phenomenon has been noted by other investigators. Hagglund (29) has shown that there is a similarity in the lignin and sugar removal curves during a sulfite cook, while Aaltio and Roschier (30) have shown that the removal curves for lignin and pentosans from aspenwood meal were quite similar during a butanol-water cook. Since it is known that there are pentosans associated with lignin at least in the middle lamella (31), it is possible that these removal curves are an indication that lignin and hemicellulose may be located together in wood.

The removal curve (Figure 6) of the alkali-resistant cellulose increases slightly with cooking time with the exception of the 90-minute interval. At this point the removal is almost as high as at the 210-minute interval. This "hump" at 90 minutes, C4P2, may be due to the increased pH of the cooking liquor at this point and the subsequent attack on the alkali-resistant cellulose. This theory is made plausible by the decrease in the 16% hemicellulose removed at the 90-minute interval. The 16% hemicellulose removal during the cook is nearly constant with the exception of a slight dip at the 90-minute interval and a slight rise near the end of the cook.

From the data in Tables XVIII and XIX it can be shown that about 18% of the total carbohydrate material present in the wood and about 43% of the total lignin initially present in the wood were removed during the NSSC cook studied.

The present data may be compared with that of Boehm (23) to compare the effect of using a carbonate or bicarbonate buffer. The carbonate buffer apparently yields a pulp with a slightly lower lignin content and slightly higher uronic acid content than when the bicarbonate buffer is used. The yield of holocellulose was about the same in either case. These data suggest that the use of the carbonate or bicarbonate buffer has only a slight effect on the wood constituents removed by a NSSC cook. The variability within a species may account for the differences cited.

The D.P. of the alkali-resistant cellulose increased with cooking time while in a sulfite cook the D.P. decreases with cooking time (32). In the NSSC cook the conditions may be such that a minimum degradation of the cellulose and a selective removal of the smaller D.P. material occurs which would lead to a higher number average D.P. The polysaccharide analysis data show that the amount of glucan present in the pulp is not significantly different from the amount present in the wood, which adds support to this hypothesis.

From the polysaccharide analysis and polyuronide data of the "hemicellulose" it was possible to account for about 75% of the hemicellulose removed from the wood. Lea (3) could account for 25% of the hemicellulose removed from the wood by his spent liquor "hemicellulose." The methods of isolation of the "hemicellulose" differed and Lea may have lost considerable carbohydrate material when the lignin was precipitated and when the material was run through the anion column. This was avoided in the present study.

The data show that there was a large amount of polyuronides present in the "hemicellulose" isolated from the liquors at early stages of the cook. The weakly alkaline cooking liquor may have acted as a solvent for the pectic material in the wood. Since the pectic material is made up largely of galacturonic acid, it might account for the high uronic acid content of these early "hemicelluloses." Thomas (11) found a water-soluble fraction from aspen holocellulose which had a polyuronide content of between 30 and 40% and this material was assumed to be largely pectic in nature (33).

The intrinsic viscosities of the spent liquor "hemicellulose" are lower than those reported by Lea (3). The reason for this difference probably is that the methods of isolation of the "hemicellulose" from the spent liquor differed. Lea may have lost a good deal of low D.P. material on the anion column which would lead to a higher intrinsic viscosity. The use of the anion column was avoided in this study which resulted in a lower intrinsic viscosity of the "hemicellulose."

The structure of the polysaccharide material which is removed from the wood after 30 minutes cooking is unknown, but it was shown that all six sugars found in the wood hydrolyzate were found in the spent liquor hydrolyzate. The intrinsic viscosity of the "hemicellulose" isolated from the 30-minute cooking liquor is about 1/20 that of the 5% hemicellulose from the pulp of this cook. This suggests that the material removed from the wood is either removed by dissolving the chains at these lengths, by breaking the chains in the wood at these lengths, or by removing the polysaccharides in longer chains and further degrading them

by the cooking liquor after removal. The data do not indicate which of these mechanisms predominates. However, the data do show that the intrinsic viscosity of the spent liquor "hemicellulose" increases as the cook proceeds. This would indicate that as the cook proceeds, perhaps higher D.P. polysaccharide material is removed by the cooking liquor from the wood. This is somewhat different from a kraft cook where it has been shown that considerable destruction of the polysaccharide material occurs as the cook proceeds (6). Although the mechanism of attack may be similar, the NSSC cooking conditions probably are mild enough to reduce the destruction of polysaccharides below that of a kraft cook. This reasoning is substantiated by the data obtained during this study which showed that the total polysaccharide material detected in the spent liquor as well as the intrinsic viscosity of "hemicellulose" were continually increasing as the cook proceeded. It seems likely that the formation of saccharinic acids and other degradation products is much slower under the conditions of the NSSC cook than in the kraft cook.

It was shown that the cold water extract of aspenwood contains glucose, fructose, and traces of sucrose, and it is assumed that these free sugars are present in the wood as such. It is reasonable to expect that these sugars should be detected in the spent liquor; however, they were not detected by the methods employed in this study. It is possible that the sugars were not removed in the early stage of the cook because the cold water extract was prepared from wood meal instead of chips. The free sugars may not have been detected because of the time required for penetration and diffusion of the material from the chip. In the early

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stages of the cook, the volumes of liquor taken from the digester were quite large. Although some concentration of the spent liquor was effected, it may not have been enough to detect the very small quantities of sugar present. Perhaps the most logical explanation of this phenomenon is the conversion of these sugars to materials which would not be detected by the chromatographic method of analysis. This is almost certainly the case at the end of the cook where penetration is complete and diffusion from the wood should have taken place.

SUMMARY

The removal of hemicellulose from aspenwood during a NSSC cook has been studied. Cooking liquor was removed at 30-minute intervals during a NSSC cook, hydrolyzed, and the amount of each sugar component in the hydrolyzate was determined. On the basis of the preliminary investigation, four intervals during the NSSC cook were studied in detail. The liquor was reanalyzed and pulp analyses were made. Holocelluloses were prepared and extracted with 5 and 16% potassium hydroxide to give two hemicellulose fractions from each pulp. Sugar analyses were made by hydrolyzing all materials and quantitatively determining the sugars. Before any sugar analyses were made, however, a critical evaluation of the chromatographic sugar determinations was made after an orienting study.

The results obtained from the present work may be summarized as follows:

1. No simple sugars or disaccharides were found in any of the spent liquors by paper chromatographic analysis.
2. At the end of 30 minutes cooking time the sugars found in the spent liquor hydrolyzate were qualitatively the same as those found in the wood hydrolyzate. Surprisingly, over 50% of the total sugar in the hydrolyzate from this first spent liquor was glucose and over 25% was mannose. As the cook proceeded, the percentage of glucose and mannose decreased. By the end of the cook xylose represented about 80% of the total sugar in the hydrolyzate, whereas glucose and mannose constituted only about 4 and 2%, respectively. Analyses of the spent liquor hydroly-

zates during a NSSC cook showed that the total sugar in the spent liquor hydrolyzates was increasing continually with cooking time.

3. By using quantitative chromatography and ultraviolet lignin determinations it was possible to account for about 20% of the organic material present in the spent liquor in the early stages of a NSSC cook. Using these same methods, about 50% of the organic material was accounted for at the end of the cook.

4. Using the cooking schedule selected for this study, it was found that when a cook is blown after a 90-minute cooking period there is a rise in pH of the spent liquor from 8.3 for the white liquor to 8.9 for the 90-minute spent liquor.

5. Pulp yields for the 30, 90, 150, and 210-minute cooks were 95.6, 88.2, 79.6, and 73.8%, respectively, on the oven-dry ash-free wood basis. About 9.6% hemicellulose and 9.1% lignin based on the oven-dry ash-free wood were removed by the end of the cook.

6. In the early stages of cooking, the "hemicellulose" precipitated from the spent liquor represents about 32% of the total carbohydrate plus lignin removed from the wood, while at the end of the cook the "hemicellulose" represents about 80% of the carbohydrate plus lignin removed.

7. About 33% of the hemicellulose removed in the early stages of the NSSC cook could be accounted for by chromatographic sugar data and the polyuronide analysis of the spent liquor "hemicellulose," while about 75% of the hemicellulose removed at the end of the cook could be accounted for analytically.

8. In the early stages of the cook about 60% of the spent liquor "hemicellulose" was of the polyuronide type, while only 18% polyuronide was found in the "hemicellulose" at the end of the NSSC cook.

9. Chromatograms of the unhydrolyzed cold water extract of aspen-wood showed the presence of glucose, fructose, and traces of sucrose. The hydrolyzate derived from the isolated cold water extract showed the presence of all six sugars which are found in the hydrolyzate of aspen-wood. In addition a new sugar, presumably fucose, was detected by paper chromatography.

10. About 42% of the 5% hemicellulose, 23% of the 16% hemicellulose, and 7% of the alkali-resistant cellulose present in aspenwood are removed during a NSSC cook. This amounts to a removal of about 18% of the total carbohydrate material in the wood. About 43% of the total lignin present in aspenwood was removed by the NSSC cook. The greater part of the lignin and 5% hemicellulose lost in the cook was removed between the 90 and 180 minute cooking intervals. The curves for the 5% hemicellulose and lignin removed during a NSSC cook were very similar.

11. The number average D.P. of the 5% hemicellulose increases slightly with cooking time, while the number average D.P. of the 16% hemicellulose decreases slightly with cooking time. The number average D.P. of the alkali-resistant cellulose increases markedly with cooking time. The intrinsic viscosity of the "hemicellulose" precipitated from the spent liquor increases with cooking time.

12. The alkali-resistant cellulose from the final NSSC pulp can be hydrolyzed and almost accounted for quantitatively in terms of simple sugars using the methods of chromatographic analysis.

CONCLUSIONS

Quantitative sugar analysis data indicate that in the early stages of the cook the sugar composition of the cooking liquor hydrolyzate was not the same as that of the 5 and 16% hemicellulose hydrolyzates. However, as the cook proceeded the sugar composition of the cooking liquor hydrolyzates gradually approached the sugar composition of the total wood hemicellulose hydrolyzate. This difference in sugar composition might be due to the location of the various hemicelluloses in the cell wall and/or middle lamella, the more easily accessible hemicellulose being removed during the early stages of the cook and the more inaccessible hemicellulose being removed later in the cook.

When the alkali-resistant cellulose from the various pulps was hydrolyzed and analyzed for sugars, it was found that as the cook proceeded less galactose, arabinose, and rhamnose was found. By the end of the cook these three sugars could not be detected in the alkali-resistant cellulose. However, the amount of anhydromannose and anhydroxylose present in the alkali-resistant cellulose remained nearly constant throughout the cook. These results suggest that possibly the polysaccharides containing galactose, arabinose, and rhamnose are closely associated with lignin; whereas, the polysaccharides containing mannose and at least part of the xylose are more closely associated with the alkali-resistant cellulose.

The fact that the lignin and 5% hemicellulose removal curves are almost identical suggests that there may be a close physical association

of these two substances in wood. Since the 5% hemicellulose is largely xylan, the similarity in the removal curves suggests that it is xylan and lignin which are closely associated.

Apparently the polysaccharide material removed from the wood at the beginning of the cook has a number average D.P. of from 10 to 20 and as the cook proceeds these chains increase in length. Some of the shorter chains may be destroyed. However, the xylan data from the 5 and 16% hemicelluloses suggest that this destruction has not occurred. Thus, the increase in the D.P. of "hemicellulose" during the cook probably is due to the removal of longer chains from the wood rather than a destruction of the low D.P. "hemicellulose." The fact that the total amount of hydrolyzable polysaccharide material in the spent liquor increases throughout the cook shows that if destruction actually has occurred, the rate of destruction cannot be greater than the rate of removal from the wood.

It seems probable that any free sugars which may have existed in the wood were destroyed by the conditions of the NSSC cook. The destruction of monosaccharides in a kraft cook has been demonstrated, and this destruction seems to be equally true for the NSSC cook.

APPENDIX I

EXPERIMENTAL PROCEDURES

PREPARATION OF CHIPS

An aspen tree (Populus tremuloides) was cut May 13, 1954 near Eagle River, Wisconsin. The tree was cut into six foot lengths, and brought to Appleton, Wisconsin where it was peeled. Sample disks for wood analysis were taken according to Institute Method 2. The logs were chipped in the Institute two knife 36-inch chipper which was set for three-fourths inch chips. The chips were screened and those passing a one by two-inch screen and retained by a one-fourth inch screen were collected. Since wet aspen chips spoil readily (34) when stored for long periods of time, the accepted chips were air dried for one week at an average temperature of 29°C. The moisture content of the chips was reduced from 52.6 to 7.5%. The chips were mixed thoroughly and stored in glassine-lined kraft paper bags in digester charges of 3600 grams of oven-dry chips. The wood used for analysis was dried under the same conditions as the chips.

PULPING

All cooks were made in the Institute Pulp Laboratory digester number 4. This is a stainless steel vertical digester with a 44-liter capacity. The liquor is circulated by a pump and heated by an external heat exchanger. The cooking temperature is controlled by varying the steam input to the liquor heater. A stainless steel liner was used in the digester to hold the chips to facilitate the removal of the softened chips.

The first cook, ClP2, was made according to the cooking schedule outlined by Boehm (23). Cooking liquors were analyzed for sodium sulfite and sodium carbonate by Institute Method 107. The pH of the cooking liquor was 11.3 and the final pH was 9.6. Because this range of pH's seemed high for a NSSC cook, it was decided that sodium bicarbonate should be used instead of sodium carbonate. McGovern (35) found in a study of commercial pulping practices that sodium bicarbonate is used more commonly than sodium carbonate. The average amount of chemical used was about 4% sodium bicarbonate and 12% sodium sulfite.

The second cook, ClP3, and all subsequent cooks were made using 12% sodium sulfite and 5.75% sodium bicarbonate on the oven-dry wood basis. Using sodium bicarbonate, the initial pH was reduced from 11.3 to 8.3 and the final pH from 9.6 to 7.3.

At the end of the cook the softened chips were removed from the digester and stored under 20 liters of distilled water for at least 42 hours. The wash liquor was decanted and the chips were centrifuged and passed through the Institute Bauer refiner. The Bauer plates were set for a clearance of 0.007 inch. The pulp was washed thoroughly, dewatered, put into pliofilm bags, and stored in the cold room at about 10°C. The volume of all spent liquors was determined. The spent liquors were stored in the cold room in glass containers over chloroform and under toluene.

PREPARATION OF HOLOCELLULOSE

The method suggested by Thompson and Wise (1) was used to prepare holocelluloses from wood, partially cooked wood, and pulp. This method

was reported to produce a good holocellulose from wood with minimum degradation of the hemicelluloses. The method is outlined below.

A 100-gram (ovendry basis) sample of wood or pulp was placed in a 4-liter beaker and cooled to about 0°C. The beaker was put into an ice-alcohol-salt bath (temperature about -17°C.) and chlorinated 10 minutes with 1 liter of chlorinating solution which was prepared by saturating 3 liters of carbon tetrachloride with chlorine gas. The mixture was cooled below 0°C. before chlorination and the temperature during chlorination was kept below 5°C. After chlorination, the mixture was filtered immediately, washed twice with 3% ethanolamine in absolute ethanol at room temperature, soaked for 5 minutes in 3% alcoholic ethanolamine at room temperature, washed once with absolute ethanol at room temperature, washed once with cold absolute ethanol below 5°C., and washed once with cold 50% ethanol. This procedure was repeated twice.

After the final chlorination and wash with cold absolute ethanol, the wood meal or pulp was washed again with cold absolute ethanol instead of the cold 50% ethanol. These washes were followed by two acetone washes at room temperature. The holocellulose was air dried; then, moisture and sulfated ash determinations were made so that yield data could be computed.

The wood meal fraction passing the 30-mesh screen and retained on the 80-mesh screen was used for the holocellulose determination. The wood meal was mixed with 225 ml. of distilled water before the first chlorination. It was not necessary to add water to the pulp because it had been stored in the cold room in the wet state.

All holocelluloses were determined singly. With the exception of the well-cooked pulps, the material obtained from this procedure was not a true holocellulose because it contained considerable lignin.

EXTRACTION OF HEMICELLULOSE FROM HOLOCELLULOSE

A 30-gram (ovendry basis) sample of holocellulose was placed in a 1-liter filter flask, which was placed in a water bath and controlled at $20 \pm 0.1^\circ\text{C}$. Two inlets were provided in the top of the flask so that the system could be filled with nitrogen and charged with potassium hydroxide while the system was under nitrogen.

The system was flushed three times with gaseous nitrogen (99.5% pure), evacuated, and filled again with nitrogen; then, 600 ml. of 5% potassium hydroxide were added. The system was evacuated again, flushed with nitrogen three times, and finally filled with nitrogen. The mixture was swirled at 0, 30, 60, and 90 minutes. At the end of the 120 minutes the mixture was filtered immediately into 80 ml. of glacial acetic acid. The filtration was carried out in the cold water bath to prevent excessive heating during neutralization. The residue was washed with 150 ml. of 5% potassium hydroxide and 150 ml. of distilled water. It was washed twice with 2% acetic acid, twice with distilled water, and twice with acetone. The residue was air dried. The acidity of the filtrate and of the first 300 ml. of washings was checked, and then these solutions were added to 4 liters of 95% ethanol. The precipitate which formed was allowed to stand for at least 48 hours, the supernatant liquid was decanted, and finally a more complete separation was effected by centrifuging. The precipitate was washed three times with hot 95%

ethanol at 75 to 80°C., three times with absolute ethanol at room temperature, and three times with ethyl ether at room temperature. The washed precipitate was dried in vacuo at room temperature for at least 24 hours. This material has been termed 5% hemicellulose. Duplicate extractions of the 5% hemicellulose were made and the precision was $\pm 0.9\%$ of the average.

The air dry residue from the first extraction was returned to the 1-liter filter flask, which was placed in the water bath. The system was flushed with nitrogen as described for the 5% extraction. The addition of 600 ml. of 16% potassium hydroxide was made and the system was flushed again with nitrogen. The mixture was swirled as described for the 5% extraction, and after 120 minutes it was filtered into 240 ml. of glacial acetic acid. The residue was washed with 75 ml. of 16% potassium hydroxide, 75 ml. of 5% potassium hydroxide, and 150 ml. of distilled water. This was followed by two 2% acetic acid washes, three distilled water washes, and two acetone washes. The residue was air dried, and moisture and sulfated ash determinations were made to obtain yield data. This residue has been termed alkali-resistant cellulose. Duplicate determinations of this material had a precision of $\pm 0.3\%$ of the average. The filtrate was precipitated into 4 liters of 95% ethanol. The precipitate was allowed to stand at least 48 hours, the supernatant liquid was siphoned off, and the precipitate was washed by the same procedure as in the preparation of the 5% hemicellulose. The 16% potassium hydroxide soluble material has been termed 16% hemicellulose. Duplicate extractions of the 16% hemicellulose were made and the precision was $\pm 1\%$ of the average.

Both the 5 and the 16% hemicelluloses were ground to a powder for future analysis. Moisture and sulfated ash determinations were run on all hemicelluloses. The sulfated ash was corrected according to the method used by Wise (36). The sulfated ash was dissolved in water, filtered, and the crucible plus the filter paper was reignited. The weight lost was assumed to be potassium sulfate which is water soluble. The ash was corrected by multiplying the water-soluble ash by the factor 76/174 and adding the water-insoluble ash to this value. The sum of these two weights was divided by the oven-dry weight of the sample to obtain the percentage of corrected ash. It was assumed that the potassium is held by carboxyl groups in the hemicellulose. This was the reason for using the value of 76 instead of 78 in computing the weight of potassium in potassium sulfate.

RECOVERY OF "HEMICELLULOSE" FROM THE SPENT LIQUOR

In order to account for the uronic acids present in the spent liquor, material was isolated from the spent liquor so that uronic acid determinations could be made. The method used for recovery of "hemicellulose" was as follows: (a) The sodium ions were removed with a cation ion exchange column (IR-120) from liquor samples which contained about 12 grams of organic material. (b) The effluent from the cation column was treated with barium hydroxide solution to a pH of 4.5. (c) The insoluble barium salts were centrifuged from the solution. (d) The filtrate was concentrated in vacuo at 50°C. to less than 100 ml. (e) Any barium salts which separated during concentration were centrifuged out. (f) The concentrate was precipitated into 1500 ml. of

absolute ethanol. (g) The precipitate was separated from the ethanol after 48 hours, and washed three times with absolute ethanol, and three times with ethyl ether. (h) The precipitate was dried in vacuo at room temperature. Duplicate determinations were made for each liquor studied and the precision was within $\pm 4\%$ of the average.

The cation column was used to remove sodium because sodium salts are insoluble in ethanol. The effluent from the cation column had a pH of 1.7. This pH was too low to prevent degradation or reversion; thus, a neutralization was necessary. Barium hydroxide was selected because barium sulfite, barium carbonate, and barium sulfate are very slightly soluble in water. This method does not produce a lignin free "hemicellulose," but the lignin should not interfere with the sugar analysis or uronic acid determinations.

ISOLATION OF THE COLD WATER EXTRACT OF ASPENWOOD

About 60 grams of air-dry wood meal were mixed with 4 liters of distilled water and stirred occasionally during the 48-hour reaction period at 22°C. This was followed by: (a) filtration through two sheets of Whatman Number 40 and two sheets of Whatman Number 50 filter paper. (b) concentration in vacuo at about 50°C. to less than 60 ml. (c) precipitation by pouring into 1500 ml. of absolute ethanol. (d) removal of the precipitate after 48 hours and separation by centrifuging, followed by three washings with absolute ethanol and three washings with ethyl ether. The precipitate was dried in vacuo at room temperature. Duplicate determinations indicate a precision of $\pm 3\%$ of the average.

DETERMINATION OF THE DEGREE OF POLYMERIZATION

Hemicellulose

Thompson and Wise (1) suggest that a rapid and accurate method of determining D.P.'s of hemicellulose is to use the viscosity method. This method is not absolute and must be calibrated by osmotic pressure, light scattering or sedimentation equilibrium methods. Viscosity measurements are related by the equation $[\eta] = KM^a$; where $[\eta]$ is the intrinsic viscosity and is defined by $\lim_{c \rightarrow 0} \eta_{sp}/c$, K and a are constants which must be determined by one of the absolute methods, and M is the molecular weight of the polymer. When the molecular weight range is narrowed to 15,000 to 30,000, which is also the range of hemicellulose, the "a" constant is combined with a new constant K' and the equation becomes $[\eta] = K'M$. The intrinsic viscosity, $[\eta]$, is obtained experimentally by plotting η_{sp}/c versus c and extrapolating the curve to c=0. The specific viscosity, η_{sp} , is equal to $(\eta \text{ solution} - \eta \text{ solvent}) / (\eta \text{ solvent})$. The concentration of the polymer in grams per 100 ml. of solution is represented by c. K' was obtained by osmotic pressure measurements and was found to be $(4.4)(10^{-3})$ (1) for aspen hemicellulose, where $K' = [\eta]/D.P.$ In the present study the Ostwald-Fenske viscometer was used and the fractions tested were dissolved in 10% aqueous potassium hydroxide. Duplicate determinations were made and the precision for the 5% hemicelluloses and 16% hemicelluloses was within $\pm 3\%$ of the average. The precision for the spent liquor "hemicelluloses" was within $\pm 7\%$ of the average.

Alkali-Resistant Cellulose

The D.P. of the alkali-resistant cellulose was determined by the viscosity method. The material was dissolved in cupriethylenediamine and kept under nitrogen until the solution was transferred to the Ostwald-Fenske viscometer. One intrinsic viscosity was determined for each alkali-resistant cellulose tested. The number average D.P. was calculated from the relationship $D.P. = K[\eta]$. The value for K was taken as 170 (37).

HYDROLYSIS PROCEDURES

In all the hydrolysis procedures, D-ribose was added after the hydrolysis but before the neutralization. The sugar to be added was accurately weighed and the amount was at least one-half of the weight of the major sugar present in the hydrolyzate.

Wood and Pulp Hydrolysis

The materials showing a high D.P. cellulose; namely, wood pulp, holocellulose, and the alkali-resistant cellulose, were hydrolyzed according to the procedure of Seaman, *et al.* (38). The addition was made of 5 ml. of 72% sulfuric acid to about 350 mg. of the material to be hydrolyzed. The mixture was allowed to react for 60 minutes in an oil bath controlled at $30 \pm 1/2^\circ\text{C}$. After this primary hydrolysis, the mixture was diluted with 140 ml. of distilled water and boiled under reflux for 4-1/2 hours, cooled, and a known quantity of D-ribose was added. The acid-insoluble material which formed was removed by filtering and weighed. The remaining solution was taken to a pH of 4.5 with a

solution of barium hydroxide, centrifuged, and the filtrate put through the cation (IR-120) and anion (IR-4B acetate form) ion exchange columns. The solution from the anion column was concentrated in vacuo at about 50°C. to about 3 to 4 ml.

Hemicellulose Hydrolysis

All hemicelluloses including the spent liquor "hemicellulose" were hydrolyzed according to the following procedure developed by Boehm (23). About 200 mg. of air dry hemicellulose were conditioned in a water bath controlled at 20° ±0.1°C. Addition was made of 2 ml. of 72% sulfuric acid and the mixture was allowed to react for 20 minutes. The mixture was diluted with 116 ml. of distilled water to give a 2% acid solution. The dilute solution was refluxed for three hours, cooled, and a known weight of D-ribose was added. If an acid insoluble material separated, it was filtered from the solution and the weight determined. The filtrate was taken to a pH of 4.5 with barium hydroxide solution and centrifuged. The precipitate was discarded, but the solution was put through the cation (IR-120) and anion (IR-4B acetate form) ion exchange columns. The solution from the anion column was concentrated in vacuo at 50°C. to about 3 to 4 ml.

Spent Liquor Hydrolysis

A 50-ml. aliquot of spent liquor was diluted to 200 ml., 3.5 ml. of concentrated sulfuric acid were added, and it was refluxed for four hours and cooled. The reference sugar, D-ribose, was then added, and the resulting brown curdy precipitate was filtered, dried and weighed, and all such precipitates gave positive Maule tests. The filtrate from

each precipitate was treated with aqueous barium hydroxide to a pH of 4.5, centrifuged, the filtrate was passed through the appropriate cation and anion ion exchange columns, and the resultant solution was concentrated in vacuo at 50°C. to about 2 to 3 ml.

SUGAR ANALYSIS

Paper partition chromatography was used in both qualitative and quantitative analyses. The charcoal-celite column technique was explored as a possible means of separating oligosaccharides, but proved unsuccessful when applied to NSSC spent liquor due to the loss of carbon from the column.

Qualitative Analysis

The material to be chromatographed was spotted on Whatman Number 1 filter paper together with known reference sugars and developed with either 10:3:3 or 9:2:2. The former requires 48 to 72 hours for sugar separations whereas the latter requires 36 to 48 hours. By using the two solvent mixtures on the same chromatogram, it is possible to obtain sharper separations of mannose and arabinose which do not separate well in the pyridine system. The 9:2:2 system separates mannose and arabinose but not glucose and galactose which are easily separated by the 10:3:3 system.

After developing, the chromatograms were air dried and sprayed with a A.H.P. or p-anisidine hydrochloride. These reagents generally develop a color with sugars when heated for 5 minutes in an oven at 100 to 105°C. Both reagents give a pink color with pentose sugars, brown with hexoses and yellow-brown with methyl pentoses. However, the A.H.P.

color is less fugitive than is that obtained with the p-anisidine hydrochloride. A.H.P. was used almost exclusively in this study.

Quantitative Analysis

The quantitative method developed by Hirst and Jones (22) was used. A narrow band of the sugar mixture 6-1/2 inches in length instead of a spot was placed on the paper. Alternate developing and drying during the migration of the sugars resulted in more compressed sugar bands and sharper sugar separations. Hence, the chromatograms were developed as follows: 12 hours with 9:2:2, dried, 24 hour with 9:2:2, 12 hours with 10:3:3, dried, 24 hours with 10:3:3, and dried. The final drying requires at least 24 hours or spurious results will be obtained. After the paper was developed, longitudinal strips were cut off each side and sprayed with A.H.P. The strips were attached to the chromatogram so that the location and identification of the sugar bands could be effected. The bands were cut from the chromatogram and the sugars eluted from the paper with water. The eluted sugar solution and washings were treated with one ml. of 1/4 M sodium metaperiodate solution, heated in a boiling water bath for 20 minutes, placed in a container of cold water for 5 minutes, and 1/2 ml. of ethylene glycol was added to the mixture to consume the excess periodate. The mixture was shaken vigorously and allowed to stand 5 minutes so that the ethylene glycol periodate reaction would be complete. The formic acid formed was titrated with about 0.0025 N sodium hydroxide. Methyl red was used as an indicator and the titration was carried to a greenish-yellow end point. These titrations were corrected for blank determinations and

then the ratios of the weight of the various sugars to the weight of the reference sugar could be calculated from the titration data.

If a hexose, pentose, or methyl pentose is oxidized, it is theoretically possible to get 5 moles, 4 moles, and 4 moles of formic acid respectively from each of the sugars. Thus, one mole of formic acid is equivalent to 36.03 grams of hexose sugar, 37.53 grams of pentose sugar, and 41.03 grams of methyl pentose sugar. In order to facilitate calculations, the volume of solution used to titrate the formic acid from the hexose is taken arbitrarily as unity while the volumes used for the pentose and methyl pentose titrations were multiplied by 1.0416 and 1.1388, respectively. After the titration volumes were adjusted, each volume was multiplied by a factor obtained by dividing the weight of ribose added by the adjusted titration volume of ribose, which gives the weight of the sugar. In order to calculate the weight of the polysaccharide from the weight of the simple sugar, the latter was multiplied by the ratio of the molecular weight of the sugar anhydride to the molecular weight of the simple sugar. These ratios are 0.90 for hexoses, 0.88 for pentoses, and 0.89 for methyl pentoses. A sample calculation is included in Appendix III. Each analysis was run in quadruplicate and the average reported. Details on the accuracy and precision of this method are given in Appendix II.

OTHER ANALYSES

Ash

Ash determinations on the aspenwood were run according to Institute Method 4 (1952). All other ash determinations were sulfated according

to Institute Method 109 (1951). It was assumed that the cation had been held by a carboxyl group in the organic material, and on this basis, the percentage of ash was calculated as a function of the cation present. All ash determinations were run in duplicate and the precision was $\pm 1\%$ of the average.

Cooking Liquor Analysis

All cooking liquors were analyzed according to Institute Method 107 (1951) for total alkali and total reducing material. From these data the amounts of sodium sulfite and sodium bicarbonate were calculated. All analyses were run in duplicate and the precision was within $\pm 1\%$ of the average.

Extractives

In duplicate determinations the wood meal was extracted with alcohol-benzene according to Institute Method 13 (1951). The precision was within $\pm 2\%$ of the average.

The wood and pulp was extracted with 95% ethanol according to Institute Method 428 (1951). The extractions were done in duplicate and the precision was within $\pm 4\%$ of the average.

The cold water extractives of the wood were determined in duplicate according to TAPPI Method T 207 m-47. The initial pH of the extracting water was 6.5 and the pH after the 48-hour extraction was 5.6. The wood meal and water was filtered through two sheets of Whatman Number 50 filter paper and the filtrate was filtered again through two sheets of this same filter paper. The precision was within $\pm 0.5\%$ of the average. The extractives determinations were not done successively.

Lignin

Lignin in the wood and pulp was determined in duplicate by Institute Method 13 (1951) and Institute Method 428 (1951), respectively. The precision was within $\pm 0.5\%$ of the average.

The soluble lignin was calculated using Equation (1) and the ultraviolet absorption data at 230 m μ . Lignin in the spent liquor was calculated from Equation (1) and ultraviolet absorption data at 280 m μ . The value of "a" at 230 m μ is 42 and at 280 m μ is 15 according to

$$\underline{C}_L = \underline{A}/\underline{b}a \quad (1)$$

\underline{C}_L = concentration of lignin in grams/liter
 \underline{b} = cell width in cm.
a = absorptivity
 \underline{A} = absorbance

Buchanan's (24) ultraviolet absorption data on aspen native lignin. All determinations on Klason lignin filtrates were run in duplicate and the precision was within $\pm 4\%$ of the average.

Ovendry Content

All ovendry determinations were made in duplicate according to Institute Method 423 (1951). The precision was within $\pm 0.1\%$ of the average.

Pentosans

All pentosan determinations were run according to Institute Method 424 (1951). The pentosan determinations were corrected for polyuronides by the following factor:

$$\frac{\text{M.W. furfural}}{\text{M.W. carbon dioxide}} \times \frac{\text{M.W. pentosans}}{\text{M.W. furfural}} \times \frac{0.42}{4} = 0.315$$

All determinations were run in duplicate and the precision was within $\pm 0.4\%$ of the average.

Uronic Anhydride

All uronic anhydride determinations were run in duplicate according to Institute Method 25 (1951). The apparatus and method were checked with pure glucuronolactone before unknown samples were run. The precision was within $\pm 2\%$ of the average.

APPENDIX II

EVALUATION OF THE QUANTITATIVE SUGAR ANALYSIS PROCEDURE

STUDY OF KNOWN SIMPLE SUGARS

A study of the periodate oxidation of known simple sugars was undertaken for two reasons: (a) to become familiar with the technique involved, and (b) to determine the accuracy with which D-galactose, D-glucose, D-mannose, L-arabinose, D-xylose, D-ribose and L-rhamnose could be determined.

The procedure was the same as that used by Hirst and Jones (22). To determine the precision as well as accuracy, a weighed sugar sample was transferred quantitatively into a 10-ml. volumetric flask and diluted with carbon dioxide-free distilled water. The pipet to be used in this study was checked by weighing the delivery of distilled water at a known temperature.

A 1-ml. aliquot of the sugar solution was delivered to the reaction flask and 2 ml. of carbon dioxide-free distilled water and 1 ml. of $1/4$ M sodium metaperiodate were added to the solution. The reaction tube (38 X 200 mm test tube) was stoppered with a 25 ml. Erlenmeyer flask and kept in a boiling water bath for 20 minutes. Subsequently the reaction tube was cooled under tap water and 0.2 ml. of technical grade ethylene glycol was added. The mixture was allowed to stand 5 minutes and then was titrated with about 0.004 N sodium hydroxide.

The type of indicator used for indicating the end point of the titration was found to be very important. In the initial studies the 0.004 N sodium hydroxide was standardized with potassium acid phthalate using phenolphthalein as the indicator. When the formic acid from the oxidized sugars was titrated methyl red was used as the indicator. The results were very poor and recoveries of 80 to 90% were obtained. In any individual case, however, the precision was satisfactory. The sodium hydroxide was standardized with one indicator and the sugar titration was made with another indicator, an obvious error. Thus, two different normalities of sodium hydroxide are involved which can make a sharp difference in the quantity of sugar determined.

The use of phenolphthalein for both standardization and sugar determinations is preferred because the indicator changes as the equivalence point is reached. The methyl red indicator changes before the equivalence point, making determinations more difficult to obtain on account of the changing slope of the titration curve. Methyl red has the advantage of having an end point which is little affected by carbon dioxide. When phenolphthalein is used, carbon dioxide must be excluded from the system.

Both indicators were studied. Carbon dioxide-free distilled water was used to make up the 0.004 N sodium hydroxide, ascarite guards were used on the buret, and carbon dioxide-free distilled water was used. Sugar recoveries of 90 to 96% were obtained with good precision using phenolphthalein as the sole indicator. Using methyl red as the indicator, sugar determinations were made with accuracies of 95 to 102% with good precision. These data are shown in Table XX. There is no apparent

reason for the relatively poor recovery of galactose since all sugars used in this study were high quality c.p. chemicals.

TABLE XX

QUANTITATIVE SIMPLE SUGAR STUDY

Sugar	Recovered, mg.	Known, mg.	Recovered, %	δ^1
Galactose	2.65	2.76	96.0	0.01
Glucose	3.18	3.20	99.4	0.02
Mannose	2.96	2.96	100.0	0.00
Arabinose	3.02	3.07	98.5	0.01
Xylose	11.32	11.36	99.6	0.01
Rhamnose	3.24	3.17	102.2	0.00
Ribose	3.11	3.13	99.4	0.01

¹ Standard deviation

DETERMINATION OF KNOWN SUGARS TAKEN FROM PAPER CHROMATOGRAMS

The quantitative determination of sugars from paper chromatograms is more difficult than the oxidation of the simple sugars from a known solution. The problem is complicated by the oxidation and titration errors as well as the separation and elution errors. It is very easy to separate galactose from mannose, xylose, and ribose; but it is difficult to separate galactose from glucose and mannose from arabinose on the same chromatogram. A method for separating and determining the sugars on one chromatogram seemed most appropriate for studying the spent liquor hydrolyzates at various intervals during a NSSC cook. Fairly satisfactory separations of all sugars were effected by using the following procedure with solvents in parentheses; 12 hours (9:2:2), dry, 24 hours (9:2:2), dry, 12 hours (10:3:3), dry, 24 hours (10:3:3), and dry. Solvent 9:2:2 separates arabinose from mannose and 10:3:3 separates glucose from galactose. A longer time in either system will aid separations but will cause the loss of the rapidly migrating rhamnose from the paper. The intermediate drying seemed to give sharper separations of the sugar bands. The final drying should be at least 24 hours so that as much solvent as possible can be removed from the paper to avoid spurious results.

Another dilemma was encountered when known sugar solutions were made in proportion to the sugars present in the hydrolyzed spent liquor. At the end of a cook, the xylose present in the hydrolyzed spent liquor represents about 32% of all the sugars present. Thus, it is difficult to keep the xylose titrations in the optimum range of 20 to 30 ml. of

sodium hydroxide. The problem was alleviated but not solved by using 0.0025 N sodium hydroxide instead of 0.005 N and by increasing the amount of sugar as much as possible without hindering the sugar separations. In addition, the blank titration was reduced by eluting the sugar from the paper strips directly into the reaction flask with water. The elutions were carried out using the microscope slides and Petri dish method used by Lea (3), who used the cut off method, in which the sugar was eluted to the bottom of the paper strip and then that portion of the strip containing the sugar was cut off and placed in the reaction flask. However, this method gave rise to blanks which were high due to the oxidation of some of the cellulose in the paper. Even when the blanks were corrected for the area of paper transferred to the reaction flask, the serious errors persisted. The error becomes especially great when only small quantities of sugar are determined. A comparison of the standard deviation (δ) of the sugars eluted by the cut and drip methods is given in Table XXI. Evidently the drip method yields a lower and more constant standard deviation. All the quantitative chromatographic sugar analyses reported in this study were eluted by the drip method.

The sharpness of sugar separations and the detection of the sugar by the described method was checked by spraying a previously marked chromatogram. The results were good unless there was a serious "dip" or "doming" in the sugar band. The dipping was minimized by intermittent drying but irregularities may occur due to the variability of the paper. It was found that an eluting time of 2-1/2 hours was sufficient to remove all the sugar from the paper strip. The eluted paper strip was checked

TABLE XXI

COMPARISON OF CUT AND DRIP METHODS OF DETERMINING
THE AMOUNT OF SUGAR FROM A PAPER CHROMATOGRAM

Basis: mg. of Sugar/50 ml. of Spent Liquor

Polysaccharide ²	C2P1SL 30 ¹			C2P1SL 60 ¹			C2P1SL 120 ¹		
	mg.	δ Cut	δ Drip	mg.	δ Cut	δ Drip	mg.	δ Cut	δ Drip
Galactan	1.2	0.42	0.03	2.0	1.44	0.21	9.6	3.2	0.66
Glucan	8.2	0.10	0.34	12.7	0.15	0.13	17.3	1.9	0.53
Mannan	2.5	0.29	0.34	4.6	0.32	0.24	5.7	1.6	0.38
Araban	0.8	0.20	0.23	1.2	0.46	0.18	5.6	2.7	0.16
Xylan	1.4	0.34	0.14	2.5	0.93	0.17	49.6	0.6	0.13
Rhamnan	0.9	0.51	0.11	1.4	1.48	0.06	4.8	0.5	0.22
Total	15.0	1.16	0.21	24.4	0.97	0.30	92.6	8.8	1.14

¹ The data presented are from cook C2P1. The spent liquor was extracted at 30, 60, and 120-minute intervals, hydrolyzed, and chromatographed.

² Simple sugars calculated as the corresponding polysaccharide.

by spraying with A.H.P. and observing under ultraviolet light. The eluted sugar solution was allowed to react with periodate according to the method previously described for simple sugar solutions. The only differences in the method are that 0.5 ml. of ethylene glycol was added instead of 0.2 ml. and that the reaction tubes were cooled in water for 5 minutes prior to its addition. Results of the known sugar chromatographic study are shown in Table XXII. These data show that it was impossible to separate and detect sugars with the accuracy or precision that was obtained with known unchromatographed sugar solutions (Table XX). However, considering all the variables involved, the results are quite satisfactory.

DETECTION OF GALACTOSE IN THE PRESENCE OF LARGE AMOUNTS OF GLUCOSE

When wood or pulp is hydrolyzed completely the major constituent in the hydrolyzate is always glucose. Small quantities of galactose are also present. This study was carried out to determine whether small quantities of galactose could be measured quantitatively in the presence of a large quantity of glucose. From the sugar analysis data of the wood hydrolyzate the ratio of galactose to glucose was estimated at about 1 to 100. The results of this study are shown in Table XXIII. Developer I was 10:3:3 while developer II was a combination of 9:2:2 and 10:3:3. When developer I was used, the paper was put into 10:3:3 for 48 hours, dried, 24 hours in 10:3:3, dried, 24 hours in 10:3:3, and finally dried for 24 hours. When developer II was used, the paper was put into 9:2:2 for 12 hours, dried, 9:2:2 for 24 hours, dried, 10:3:3 for 12 hours, dried, 10:3:3 for 24 hours, dried, 10:3:3 for 12 hours, and finally dried

for 24 hours. Although the results from developer I were slightly better than from developer II, the latter was used in all cases in this study when small quantities of galactose were to be detected in the presence of large amounts of glucose. The reason for this selection was that five other sugars were separated on each chromatogram and some of the effectiveness of the 10:3:3 for separating galactose from glucose had to be sacrificed in order that the other sugars could be separated satisfactorily.

TABLE XXII

QUANTITATIVE CHROMATOGRAPHIC SUGAR STUDY

STRIPS ELUTED BY THE DRIP METHOD

Sugar	Known, mg.	Recovered, mg.	Recovered, %	δ^1
Galactose	26.7	24.2	90.6	1.5
Glucose	20.3	19.7	97.0	1.2
Mannose	12.8	13.7	107.0	1.2
Arabinose	25.1	23.5	93.6	0.7
Xylose	430.4	414.1	96.2	17.1
Rhamnan	10.3	9.5	92.2	0.2
Total	525.6	504.7	95.8	15.9

¹ Standard deviation

TABLE XXIII

QUANTITATIVE DETECTION OF SMALL AMOUNTS OF GALACTOSE
IN THE PRESENCE OF LARGE AMOUNTS OF GLUCOSE

Sugar	Developer I				Developer II			
	Known, mg.	Recovered, mg.	Rec., %	¹	Known, mg.	Recovered, mg.	Rec., %	¹
Galactose	10.7	14.1	132	2.2	10.7	6.6	61.7	1.4
Glucose	995.4	963.7	96.8	27.9	995.4	922.7	92.7	19.2
Total	1006.1	977.8	97.2	27.9	1006.1	923.3	92.4	18.3

¹ Standard deviation

APPENDIX III

SAMPLE CALCULATIONS OF SUGAR DATA

SIMPLE SUGARS

Data: 0.00516 N sodium hydroxide
 Glucose titration 17.08 ml. sodium hydroxide
 Ribose titration 16.04 ml. sodium hydroxide
 Rhamnose titration 13.46 ml. sodium hydroxide

Weight of glucose¹ = (17.08)(0.00516)(36.03) = 3.18 mg.

Weight of ribose¹ = (16.04)(0.00516)(37.53) = 3.11 mg.

Weight of rhamnose¹ = (13.46)(0.00516)(45.54) = 3.16 mg.

¹ Weight of sugar = (ml. of NaOH)(N of NaOH) $\left(\frac{\text{M.W. of sugar}}{\text{theoretical moles of formic acid}} \right)$

QUANTITATIVE CHROMATOGRAM SUGARS

Data: Weight of material hydrolyzed 0.3439 g. oven-dry ash-free
 Weight of D-ribose added 0.1216 g.
 Titration made with about 0.0025 N sodium hydroxide

<u>Sugar</u>	<u>NaOH, ml.</u>	<u>Corr. Bl., ml.</u> ¹	<u>Adj. Titr., ml.</u> ²	<u>Wt., g.</u> ³	<u>Anhyd. Wt., g.</u> ⁴
Glucose	35.25	34.85	34.85	0.1731	0.1558
Xylose	14.00	13.60	14.17	0.0704	0.0619
Rhamnose	0.90	0.50	0.57	0.0028	0.0025
Ribose	23.90	23.50	24.48		
Blank	0.40				

¹ Corrected for blank = (ml. NaOH sugar - ml. NaOH blank)

² Adjusted titration to hexose: (hexose sugar)(1.0000)
 (pentose sugar)(1.0416)
 (methyl pentose sugar)(1.1388)

3 Weight of sugar = (adjusted titration) $\left(\frac{\text{g. of ribose added}}{\text{adjusted titration of ribose}} \right)$

4 Weight of sugar anhydride: (hexose weight)(0.90)
(pentose weight)(0.88)
(methyl pentose weight)(0.89)

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