

Pulp - Paper

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FOREST PRODUCTS LABORATORY

In cooperation with the University of Wisconsin

MADISON, WISCONSIN

CHEMISTRY OF THE SULPHITE PROCESS

VIII. Studies of the Acid Hydrolysis of Wood

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March 30, 1925

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The species of wood which serves most commonly as the raw material for the manufacture of sulphite wood pulp is white spruce. Balsam fir and hemlock are also used, and other species in smaller quantities.

The composition of spruce wood, as recorded in the literature, varies considerably with the methods employed in the analysis. Practical agreement is found as to the main constituents, but not as to their exact grouping. A typical analysis by Klason¹ gives: Cellulose free from pentosans, 53 per cent; hemicellulose, 15 per cent; lignin, 30 per cent; fat, resin, and proteins, 2 per cent. Johnson and Hovey² find cellulose, 50.33 per cent, lignin, 24.44 per cent as constants for balsam fir. The methods of Schorger³ at the Forest Products Laboratory show as a typical analysis of spruce wood: Cellulose, 55.4 per cent; lignin, 28.3 per cent; pentosans, 11.8 per cent; soluble in 7.14 per cent sodium hydroxide, 18.55 per cent; soluble in 1 per cent sodium hydroxide, 8.8 per cent; soluble in ether, 1.24 per cent. From these results it can be seen that while the distribution of constituents may vary, spruce wood may be taken to consist of a more resistant carbohydrate called cellulose, certain less resistant carbohydrates (called variously hemicelluloses, pentosans, etc.), lignin, and extractives, which

¹Svensk Pappers Tid., 26, 319-22 (1923).

²Paper, Vol. 21, 40 (1918).

³J. Ind. Eng. Chem., Vol. 9, 556 (1917).

latter class may be defined as materials consisting of resinous and fatty bodies soluble either in a mixture of benzene and alcohol or in ether.

The analytical methods employed in the present study were: (1) Schorger's modification of Cross and Bevan's chlorination method for cellulose; (2) lignin determination by means of 72 per cent sulphuric acid; and (3) Allihn's⁴ modification of Fehling's method for determination of reducing sugars. It is appropriate to note here that when the terms cellulose, lignin, etc., are used in connection with experimental results, they refer only to the material as defined by the analytical methods used.

Cross and Bevan⁵ and Cross and Engelstadt⁶ have advanced the idea that sulphurous acid is the active chemical in the sulphite process. More commonly the view is held, however, that the part of the cooking liquor known as "free," that is, all acid in excess of a monosulphite compound of the base, is the active constituent. The concept of the reactions of the sulphite pulping process that has at times seemed to the authors of paramount importance is that it is, from one point of view, essentially an acid hydrolysis of wood. The reaction from the standpoint of hydrolysis has therefore been made the subject of special study in the work reported here, and the results are interpreted from that point of view throughout.

The behavior of wood toward hydrolytic attack has been studied under a variety of conditions by Kressmann,⁷ Sherrard and Blanco,⁸ Haggland,⁹ Klason,¹⁰ and others. Generalizing from their results it may be stated that spruce wood when subjected to hydrolytic attack will yield a variety of reducing sugars with more or less marked reduction in the amount of stable cellulose, and with little or no change in the lignin content of the wood except in the presence of sulphurous acid and bisulphites.

⁴J. Assn. Off. Agr. Chem., pp. 107-108, (1916); see also Leach, Food inspection and analysis, 4th ed., p. 633.

⁵A Textbook of Papermaking, 5th ed., p. 73.

⁶J. Soc. Chem. Ind., 43, 253T-357T; also Paper, Vol. 34, No. 18, Aug., 1924.

⁷U. S. Dept. of Agric. Bul. 983.

⁸J. Ind. and Eng. Chem., Vol. 15, No. 6, p. 611, June, 1923.

⁹Svensk. Kem. Tids., Vol. 35, pp. 2-24 (1923).

¹⁰Paper, Vol. 35, No. 1, Oct. 23, 1924.

Hydrolysis of Wood with Hydrochloric Acid

It seemed rather desirable at the start of this study to establish a conception of the acid hydrolysis of wood in terms of the analytical methods to be employed and under a range of conditions, as regards destruction of cellulose, comparable with those obtaining in bisulphite cooking. To this end hydrochloric acid in a graduated series of weak concentrations was selected as the hydrolytic reagent, and white spruce, ground to pass an 80-mesh but to remain on a 100-mesh screen and extracted with a mixture of benzene and alcohol in proportions of 2 to 1, as the wood to be hydrolyzed.

The hydrochloric acid was prepared in a series of concentrations ranging from 0.05 to 3.00 per cent. Five-gram samples of the finely ground wood were heated with 100 cc. portions of the acid in a water bath at 96° C., under a reflux condenser, for 6 hours. The loss in weight suffered by the wood was determined and the residue was examined for cellulose.

The extract from the wood was divided into two parts. In one the reducing sugars were determined directly. The other part was rehydrolyzed by boiling again under a reflux condenser for 3 hours with 3 per cent hydrochloric acid,¹¹ and the reducing sugars were determined as before. The results obtained in both treatments are shown in Table 1.

The loss in weight suffered by the wood under the primary hydrolytic treatment increases decidedly as the acid concentration is increased, until 0.75 per cent is reached. From that point on the loss in weight becomes nearly enough constant to suggest either a marked decrease in the rate of reaction or else a complete cessation. The latter is unlikely, as it has been shown that mineral acids may bring about complete resolution of the carbohydrate material of wood upon treatment at high concentrations. Rather, an acid concentration of 0.75 per cent seems the point of differentiation between two parts of the carbohydrate material with respect to their resistance to such hydrolytic conditions as are represented in the experiments.

¹¹The quantities marked with an asterisk (*) in Table 1 (fourth column) were obtained with 1.5 per cent and 2 per cent hydrochloric acid respectively and are therefore somewhat low.

Table 1.--Hydrolysis with hydrochloric acid

(All results are expressed as percentages of the weight of the original wood.)

Con- cen- tra- tion of HCl	Weight loss on hydro- lysis	Reduc- ing sugar formed during hydro- lysis	Reduc- ing sugar after rehydro- lysis	Cellu- lose in residue	Lignin in residue	Cellu- lose loss on hydro- lysis	Mate- rial unac- counted for
Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
	Original wood			58.88	28.55		12.57
0.05	9.88	2.31	6.59	51.18	28.55	7.70	13.68
.10	12.72	3.50	8.57	50.96	28.55	7.92	11.92
.15	14.67	4.54	12.07	50.08	28.55	8.80	9.30
.25	14.75	7.32	13.15	50.89	28.55	7.99	7.41
.50	18.33	12.52	16.28	49.06	28.55	9.82	66.11
.75	20.13	16.15	19.00	48.31	28.55	10.57	4.14
1.00	20.16	16.37	18.05	48.61	28.55	10.27	4.79
1.50	18.78	14.12	17.34*	48.74	28.55	10.14	5.37
2.00	19.28	15.24	17.48**	48.62	28.55	10.26	5.35
2.50	20.17	16.37	18.67	48.79	28.55	10.09	3.99
3.00	20.95	17.54	19.40	48.70	28.55	10.18	3.35

*Rehydrolyzed with 1.5 per cent HCl.

**Rehydrolyzed with 2 per cent HCl.

The determination of reducing sugars (column 3) shows a reduction in rate of their formation at about the same point as the reduction in rate of weight loss. The determination of reducing sugars after rehydrolysis of the extract with 3 per cent hydrochloric acid (column 4) shows an approach to constancy quite comparable to that shown by the loss in weight of wood; not only so, but the reducing sugars now fall but little short of accounting for the whole loss in weight. From these results it seems that the carbohydrate material of wood most subject to removal by the mild acid hydrolysis represented is, in part at least, removed as a nonreducing body and is further broken down by the rehydrolysis. This is in confirmation of earlier observations of Sherrard and Blanco.¹²

The values for cellulose in the residue (column 5) show a slow decrease in the earlier range of the hydrolysis. The highest of the figures after hydrolysis is, however, in marked reduction from the initial value, 58.88 per cent, obtained on the unhydrolyzed wood, and shows that part of the carbohydrate material included in the cellulose determination in wood, as performed at this Laboratory, is much more susceptible to hydrolytic attack than the rest. Similar effects are noted by Dore¹³ and also by Johnson and Hovey² in their work on the analysis of wood. The former includes, in his analytical summary, determinations of material soluble in 5 per cent caustic, besides mannans, galactans, and unaccounted for pentosans. The latter investigators provide a preliminary hydrolysis with acetic acid and glycerine as one step in the determination of cellulose in balsam fir.

From the foregoing analysis of the data, it is evident that the carbohydrates that are removed from wood by acid hydrolysis of varying intensity, within the range examined, come from at least two different sources or groups of bodies, and with different degrees of reluctance.

Again, if it is assumed, as is done throughout this paper, that the hydrolytic action does not alter the inertia of the cellulose toward the manipulations of the cellulose determination, it is interesting to observe that the reduction in cellulose in the experiment with the weakest acid is approximately equal to the reducing sugars formed, and that the reduction in cellulose does not increase greatly with the more drastic treatments. From Table 1 it can be

¹²J. Ind. and Eng. Chem., 15, 1166 (1923).

¹³J. Ind. and Eng. Chem., 12, pp. 264 and 476.

seen that the material unaccounted for, obtained by adding together the analytical results for lignin, cellulose, and reducing sugars after rehydrolysis, and subtracting from 100, decreases slowly as the strength of the acid increases. The loss in cellulose reaches a slow rate of change early in the series, whereas the reducing sugars in the rehydrolyzed extract increase at a rate comparable to the reduction in amount of material unaccounted for. It is, therefore, possible to conceive of the carbohydrate materials of wood as existing in three groups: (1) Those most resistant to hydrolytic attack and, (2) those least resistant, both of which are grouped as cellulose by the analytical method; and (3) a class of intermediate resistance, referred to by various writers as pentosans, carbohydrates other than cellulose, etc.

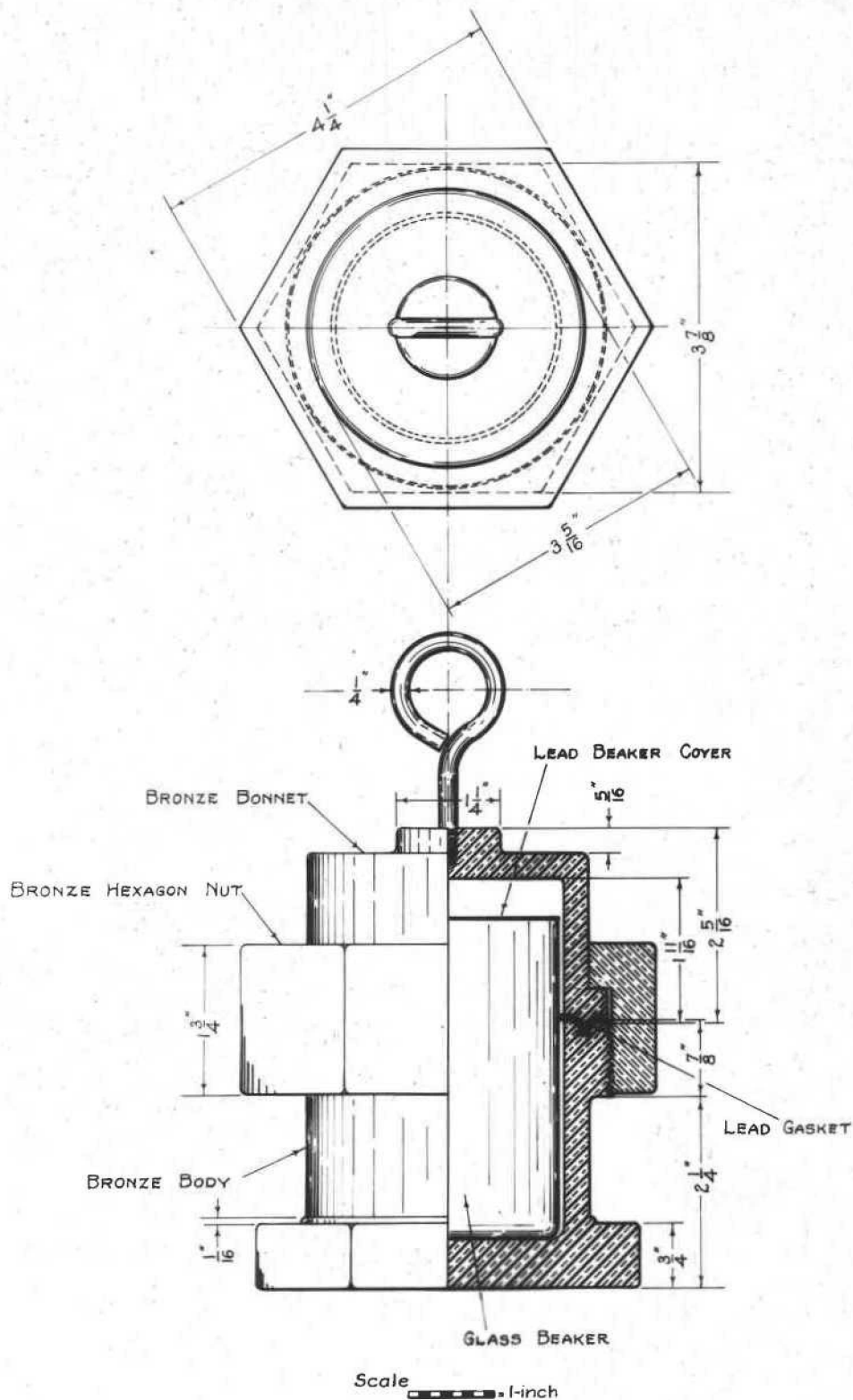
Hydrolysis with Sulphite Cooking Acid

Next, for the investigation of the acid hydrolysis of wood under conditions related to the foregoing but also favorable for the removal of lignin, that is, with sulphite cooking liquor, a special apparatus was contrived and a technique developed.

Apparatus

An autoclave of bronze, capable of withstanding high pressures and the solvent action of the cooking acid, was the digester used. Details of its construction are shown in the accompanying sketch (fig. 3). It was heated in a well-insulated bath of oil. Heat was supplied by two "Simplex" electric immersion heaters of 440 watts capacity, operating at 110 volts. One, the primary heater, was connected through a rheostat with the source of current. This heater was used constantly, and with proper adjustment of the rheostat would maintain the oil within 2° or 3° of the desired temperature. The secondary heater, furnishing the heat required to maintain the bath at the exact temperature, worked intermittently. It was connected to the source of current through a relay circuit breaker actuated by an adjustable mercury thermoregulator immersed in the oil. Temperatures up to 150° C. could thus be maintained within $\pm 0.5^\circ$ C. of that required.

Modifications of procedure were made to correct for irregularities that appeared in the preliminary runs, and the experimental procedure as now used may be described in detail as follows:



M 226 F BRONZE AUTOCLAVE FOR SULPHITE COOKING

Preparation of Wood

Spruce ground to 40-60 or 60-80 mesh size was the material cooked. It was extracted with a 67 per cent benzene, 33 per cent alcohol mixture for 6 hours in a Soxhlet extractor in order to remove resins and waxes. Also, the wetting of the wood was thus enhanced. The sample for cooking was weighed approximately into a weighed aluminum can. Can and contents were then dried at 105° C. for 5 hours, cooled in a desiccator, and weighed to determine the oven-dry weight of the charge. About 15 grams of wood made a convenient portion. The wood was then transferred to a 250 cc. tall form pyrex beaker cut off just below the lip, making a size which fitted conveniently within the autoclave.

Liquor Preparation

The cooking liquor was made up in 250 cc. quantities, which amount was sufficient for one cook. Stock solutions of sulphurous acid and sodium bisulphite make a satisfactory source, respectively, for the acid and salt used in the liquor making. The two solutions were analyzed in the usual manner with N/16 iodine solution¹⁴ to determine the total sulphur dioxide. The Sander analysis¹⁴ was used to determine the bisulphite in the bisulphite solution. Five per cent total sulphur dioxide for the sulphurous acid and 7 per cent for the bisulphite solution were convenient strengths for the stock solutions. From the analysis the correct quantities of each solution necessary to produce the desired concentration of cooking acid when diluted with distilled water to 250 cc. were calculated. After the acid was made up, its composition was checked by analysis.

Two hundred cubic centimeters of the acid were siphoned into the beaker containing the wood, and 40 cc. more were poured into the autoclave around it. A lead disc was placed over the beaker, after which the autoclave cap was tightened on.

Cooking

The oil bath having been brought to a temperature 8° to 10° C. above that at which cooking was to be carried on, the autoclave was immersed, and when the temperature had dropped to the desired point, usually in about 5 minutes, the thermoregulator was adjusted to maintain it there. The time at which the desired temperature was reached was taken

¹⁴See Miller and Swanson, Paper Trade J., April 13, 1922.

as the starting point of the cook. When the autoclave had been in the oil for the intended length of time, it was withdrawn and cooled in a bucket of water. It was then opened, the beaker and contents were removed, and the pulp was separated from the liquor on a filter folded to fit a Buchner funnel. The paper had previously been dried at 105° C. and weighed in a covered aluminum dish.

After filtration and washing with hot water the pulp was air dried for 16 hours, oven dried for 5 hours at 105° C. in the aluminum weighing dish, cooled, accurately weighed, and the yield thus calculated. The pulp was then analyzed for lignin and cellulose in the manner noted earlier in this paper.

The results of the analyses are recorded in Table 2 and are shown graphically in Figures 1 and 2. The figures for yield, or residue after cooking, follow a descending curve with increasing time, but at a decreasing rate of change that becomes quite slow in the later stages. The curve showing the removal of so-called cellulose material (as defined by the application of the Cross and Bevan method) indicates a rapid onset followed by a slow continuation in the later stages of the reaction. The rate of removal of lignin is steady up to about the twelfth hour but decreases thereafter. The results confirm those previously obtained on a large scale.¹⁴

The reaction involving the removal of carbohydrate material from the wood shows certain similarities to that in the previous series in which hydrochloric acid was used. The reduction in amount of material determined by the application of Cross and Bevan's cellulose method to the residue after cooking is, as just stated, rapid at first and reaches a slowly changing value early in the series. The quantity of so-called cellulose showing a resistance to prolonged acid treatment at the higher temperature used is very close to that which in the previous series showed resistance to increased concentration of acid. That the resistance is not perfect is shown by the lower values appearing, especially, at the end of 15, 18, and 21 hours.

With further reference to the analysis of wood according to Dore, or the results of Klason, attention is again directed to the group of poorly defined materials of carbohydrate nature which are not included in the part often referred to as cellulose. In the first series of experiments

Table 2.---Action of sulphite cooking liquor at 120° C. for varying length of time

Cook No.	Weight of wood oven dry	Dura- tion of cook	Weight of oven- dry pulp	Yield of: oven-dry: pulp on: basis of: oven-dry: wood	Lignin: on: basis: of: oven- dry: pulp	Lignin: removed: on basis: of: original: lignin: present	Cellu- lose: on: basis: of: oven- dry: pulp	Cellu- lose: on: basis: of: oven- dry: wood	Cellu- lose: removed: on basis: of: original: cellulose: basis of present	Residue not accounted for as lignin, and cellulose on basis of oven-dry
	Grams	Hours	Grams	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
74	15.0913	1	14.0134	92.85	27.38	25.42	10.96	58.49	7.32	12.85
73	15.0743	3	12.1128	80.35	27.11	21.78	23.71	62.66	14.48	8.22
76	15.0734	6	10.5458	69.93	23.65	16.54	42.06	70.13	16.71	4.35
79	15.0670	9	9.4418	62.66	17.48	10.95	61.64	77.66	17.37	3.05
80	15.0874	12	8.4545	56.03	10.12	5.67	80.14	85.94	18.22	2.21
78	15.1848	15	8.0778	53.19	6.89	3.66	87.18	88.66	19.90	2.37
77	15.1081	18	7.8261	51.80	5.13	2.66	90.68	91.30	19.68	1.85
75	15.0766	21	7.6801	50.94	3.97	2.02	92.92	91.69	20.68	2.22

Wood used: White spruce, 40-60 mesh, benzene-alcohol extracted.

Analysis: Cellulose - 58.88 per cent, lignin - 28.55 per cent.

Acid analysis: Total SO₂ 3.00 per cent
Free SO₂ 2.00 per cent
Combined SO₂ 1.00 per cent
Excess SO₂ 1.00 per cent

FIG-1

YIELD GRAPHS OF PULP, CELLULOSE, AND LIGNIN
 AUTOCLAVE SERIES NO. 5
 ALL COOKS MADE AT 120°C.

A - O.D. Pulp, Basis O.D. Wood
 B - Cellulose " " "
 C - Lignin " " "

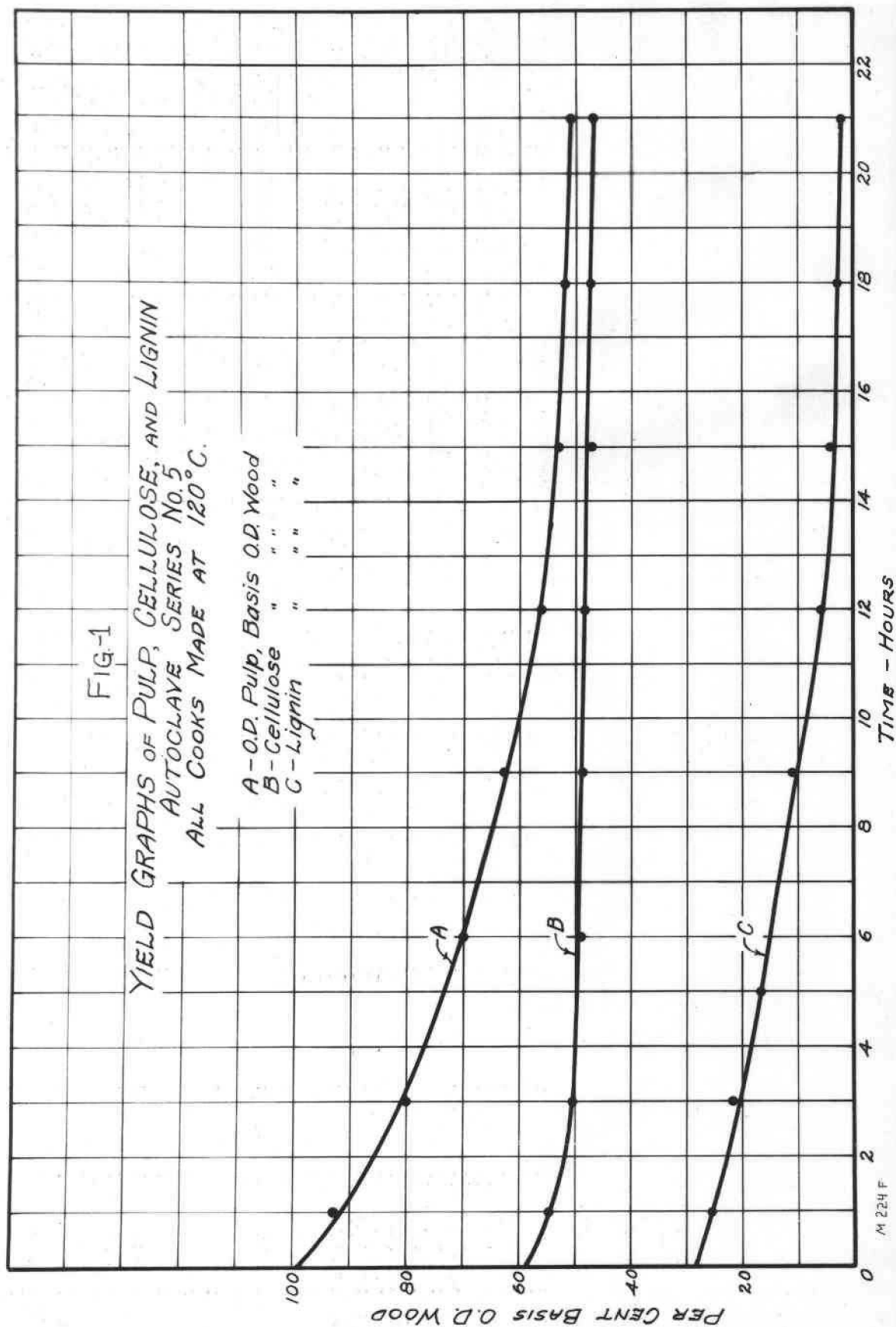
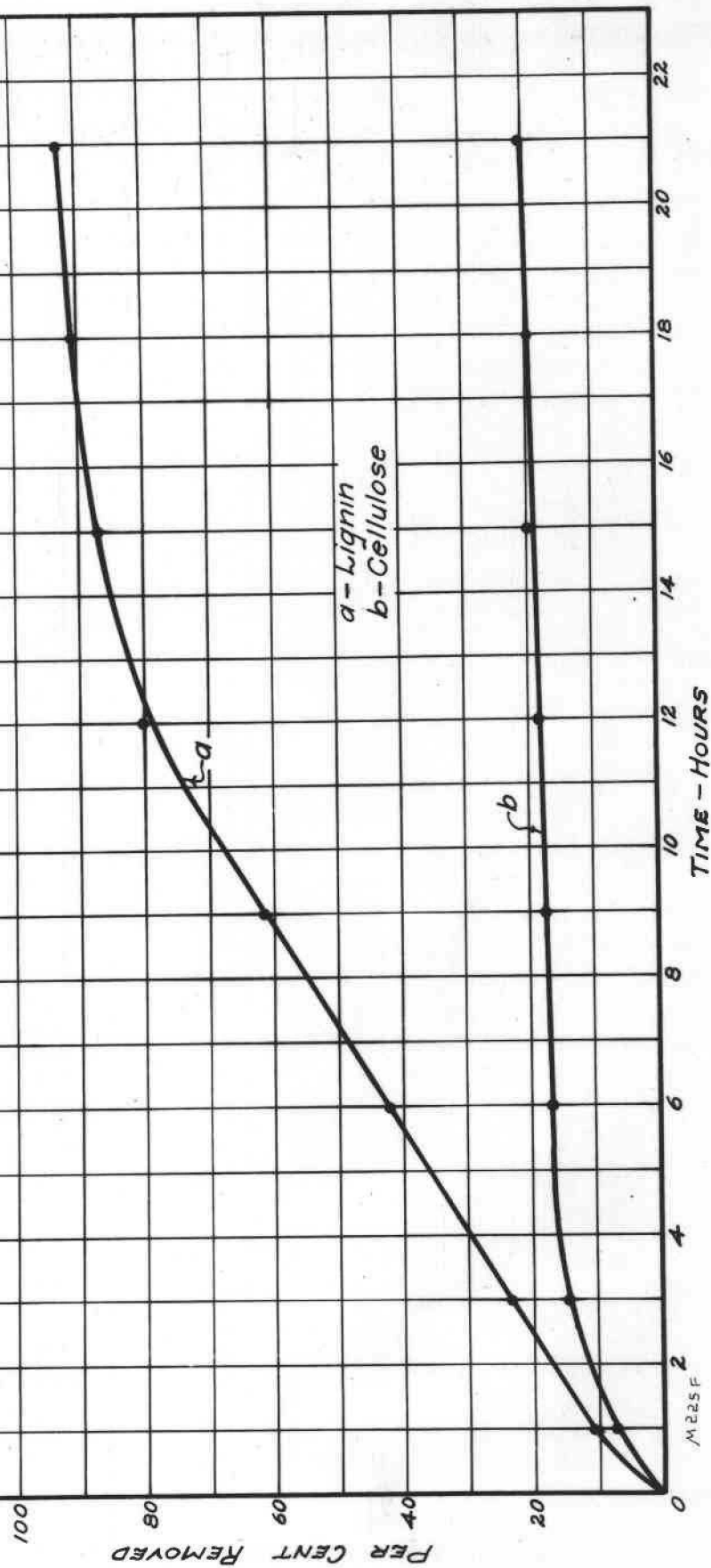


FIG-2

RATES OF REMOVAL OF LIGNIN AND CELLULOSE,
BASIS ORIGINAL LIGNIN AND CELLULOSE CONTENT OF WOOD=100 %



(Table 1) considerable proportions of these ordinarily unaccounted for substances were left in the wood residues after hydrolysis. In the second series the more complete degradation of the wood has been accompanied by their more nearly complete removal. (See Table 2, last column.)

In the first series it was shown that a part of the carbohydrate material defined as cellulose by the analytical treatment was very susceptible to mild hydrolytic attack, and that the materials unaccounted for in the analytical methods used, and frequently defined as pentosans, are more resistant. The same conditions can be seen to exist in the second series. The values for cellulose based on weight of original wood show an immediate initial drop, while the portion of the residue unaccounted for in the analytical methods used shows a continuous decrease, but without reaching zero. The latter fact should occasion no surprise, as it has been shown by Sieber¹⁵ and others that sulphite pulps always contain a portion of furfural-yielding bodies.

Of especial interest is the fact that the part of the cellulose most susceptible to hydrolytic attack is removed so easily, with or without accompanying lignin removal. Nor does there seem to be any interdependence whatever between the removal of lignin and that of the carbohydrates other than cellulose, the latter having been reduced practically to the minimum before the lignin had been removed even to the extent of one-half.

The general similarity of the results obtained in the two series of experiments indicates that the reaction upon the carbohydrate materials of the wood remains unaltered by the presence or absence of lignin.

Relative Effects of Acid Concentration and of Temperature upon Cooking Time

The idea of a differentiation between more and less stable carbohydrate material in the wood having been fortified by the results of the study thus far, it seemed desirable to examine the reactions under different but comparable conditions of temperature, acid concentration, and time of cooking. To this end the series of cooks, results for which are tabulated in Table 3, was performed. The aim in all instances was to reduce the lignin to between 1 and 2 per cent of the weight of the wood.

¹⁵Paper, Vol. 34, No. 17, Aug. 14, 1924.

Table 3.---Sulphite cooks with varying temperature and acid concentration

Cook: No.	Weight of wood oven dry	Acid				Cook- ing tem- pera- ture	Dura- tion of cook-	Weight:		Yield of:		Lignin:		Lignin:		Cellu- lose on:		Cellu- lose on:		Cellulose					
		Analysis		Quan- tity				oven- dry	pulp	oven- dry	wood	oven- dry	basis of	oven- dry	wood	oven- dry	basis of	oven- dry	wood	oven- dry	basis of	oven- dry	wood	basis of	oven- dry
		Total:	Free:	SO ₂	SO ₂	SO ₂																			
		Per cent	Per cent	Per cent	Per cent	Per cent			Grams	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
		Grams	Grams	Grams	Grams	Grams	O C.	Hours	Grams	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
47	14.301	3.00	2.00	1.00	1.00	(120	20.00	7.3589	51.46	3.02	1.55	94.89	94.93	48.27	16.48									
32	14.301	4.00	3.00	1.00	2.00	(120	14.00	7.0286	49.14	2.95	1.45	95.22	94.55	46.46	19.61									
31	14.301	5.00	4.00	1.00	3.00	(120	10.50	7.0018	48.96	2.82	1.38	95.45	95.67	46.84	18.96									
37	14.301	3.00	2.00	1.00	1.00	(130	10.50	7.0409	49.23	2.88	1.42	95.32	95.07	46.80	19.01									
35	14.301	4.00	3.00	1.00	2.00	(130	7.00	6.8909	48.18	2.37	1.14	96.24	96.13	46.31	19.87									
25	14.301	5.00	4.00	1.00	3.00	(130	4.75	6.9755	48.77	2.44	1.19	96.08	93.87	45.78	20.79									
39	13.875	3.00	2.00	1.00	1.00	(140	5.25	6.8601	49.44	2.56	1.26	95.85	96.18	47.55	17.73									
50	14.301	4.00	3.00	1.00	2.00	(140	3.25	7.1083	49.70	3.27	1.62	94.66	95.08	47.27	18.22									
51	14.301	5.00	4.00	1.00	3.00	(140	2.75	6.9672	48.72	2.11	1.02	96.69	95.27	48.41	16.24									
40	14.300	3.00	2.00	1.00	1.00	(150	2.75	6.8788	48.10	2.02	0.97	96.80	96.45	46.39	19.76									
54	14.300	4.00	3.00	1.00	2.00	(150	2.00	6.8868	48.15	2.37	1.14	96.24	96.20	46.33	19.88									
34	14.300	5.00	4.00	1.00	3.00	(150	1.33	6.9789	48.79	5.89	2.87	90.54	92.33	45.04	22.07									

Wood used: White spruce, 60-80 mesh, not extracted.

Analysis: Cellulose - 57.80 per cent, lignin - 30.36 per cent.

It may be remarked that the effect upon the rate of cooking shown by both temperature and acid concentration change is in the direction which earlier experiments on a larger scale, already reported, had indicated.¹⁶ The greater refinement of the later experiments, however, makes possible a more exact estimate of the relative magnitude of the effects of temperature and acid concentration on the rate of cooking.

It has been shown, in this report, and also in earlier publications,¹⁶ that the removal of carbohydrate material from wood by sulphite cooking proceeds much more rapidly than the removal of lignin. The factor controlling the rate of pulping, then, must be the rate at which lignin is removed. In the cooks here reported it is seen that at any particular acid concentration within the experimental range (between 1 and 3 per cent excess sulphur dioxide) the rate of cooking is doubled by each successive 10° increase in temperature between 120° and 150° C.,¹⁷ with but slight tendency toward greater loss of cellulose at the higher acid concentrations. Also, at a particular temperature, a change in acid concentration from 1 to 3 per cent is necessary to make an equivalent change in rate. As pointed out in a previous paper, such a change in acid concentration is not possible in present commercial practice.

It is quite a fortuitous circumstance that the resistance of the desired fibrous carbohydrate material of wood to sulphurous acid hydrolysis should be such as to permit the removal of the lignin by the same reagent, and further remarkable that such a wide variation in cooking conditions should produce approximately the same amount of pulp of approximately the same composition. The picture of the course of the sulphite pulping reactions that can be drawn from the foregoing results is not that of a successive breaking down of the wood in various parts, but rather that of a set of simultaneous reactions proceeding at different rates.¹⁸

Effect of Acids and Salts on Cooking Action

With reference to the changes that might be manifest in the qualities of the residual fibrous material as a result of adding reagents to alter the rate of lignin removal, much

¹⁶See Miller and Swanson, Paper Trade J., Apr. 10, 1924.

¹⁷Cf. R. Manisawa, Eng. Chem. Jour. (Japan), 1, 194-206 (1921).

¹⁸See Sieber, loc. cit.

speculation has prevailed, and some experiments are on record. The following cooks, the results of which are given in Table 4, were performed to show the effects producible by the addition of a few simple chemicals to the cooking liquor.

As standards of comparison, the two cooks, Nos. 67 and 68, were made with 1.05 and 0.55 per cent excess sulphur dioxide, respectively. A 6-hour cooking period was allowed in all cases, and conditions were identical in all respects except for the addition or substitution of some reagent.

In cooks Nos. 63, 64, and 65 enough hydrochloric acid, sodium chloride, and acetic acid, respectively, were added to produce $1/2$ per cent concentration of each in a cooking acid containing the usual 1 per cent combined sulphur dioxide and $1/2$ per cent excess sulphur dioxide. The results in all three cases show a tendency toward the removal of more lignin and cellulose than in cook No. 68. The difference is most decided in the case where hydrochloric acid was added. Cook No. 71, in which sodium bisulphate was added, also shows a tendency toward rapid removal of lignin and cellulose, while in cook No. 82 with sodium acetate, the same cellulose destruction is seen with less lignin removal. Cook No. 70, with an extra $1/2$ per cent of sodium bisulphite, is little different from the control in cook No. 68. In cooks Nos. 72 and 81 the only base present was that added as sodium chloride and sodium acetate in amounts equivalent to the quantity of sodium bisulphite necessary to give 1 per cent combined sulphur dioxide. In the case of cook No. 72 containing sodium chloride, a decided increase in the destruction of cellulose is seen without accompanying acceleration in lignin removal; the pulp was decidedly burned. Cook No. 81, with sodium acetate, shows a decided and general slowing up of the reaction.

It is unprofitable to generalize too widely on results with so small positive differences, but it may be observed that there is a tendency for strong acids and salts of strong acids to "speed up" the reaction; while weak acids or salts of the same have a contrary effect, if any. Such a generalization points directly to the theory of the pulping process as an acid hydrolysis of wood, and to a consideration of the influence of the concentration of the hydrogen ion on the pulping process. Results of experiments to establish the possible relation of hydrogen-ion concentration to the sulphite pulping process will be included in a future paper of this series.

Table 4.---Sulphite cooks with added reagents. (All cooks at 120° C. for 6 hours.)

Cook No.	Weight of wood oven dry	Acid				Reagent added	Concentration of reagent	Weight of oven-dry pulp	Yield			Lignin			Cellulose		
		Analysis		Excess SO ₂	Per cent				Grams	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	
		Total SO ₂	Free SO ₂														Per cent
68	14.3559	2.55	1.55	1.00	0.55	None	--	11.0526	77.00	25.13	19.35	67.67	52.10				
63	14.9863	2.50	1.50	1.00	.50	HCl	0.50	9.8402	65.66	21.73	14.27	75.27	49.42				
64	14.9408	2.50	1.50	1.00	.50	NaCl	.50	11.3767	76.16	24.24	18.56	66.68	50.78				
65	14.9346	2.50	1.50	1.00	.50	CH ₃ COOH	.50	11.3529	75.68	24.48	18.53	67.69	51.23				
82	14.8461	2.50	1.50	1.00	.50	CH ₃ COONa	.50	12.1442	81.80	26.48	21.66	63.74	52.13				
70	14.8833	3.00	1.76	1.24	.52	NaHSO ₃	1.48	11.6430	78.23	24.61	19.25	67.00	52.41				
71	14.7515	2.50	1.50	1.00	.50	NaHSO ₄	.50	10.8072	73.26	24.60	18.02	69.40	50.84				
67	14.8070	2.93	1.99	0.94	1.05	None	--	10.2875	69.47	21.49	14.93	72.01	50.52				
72	14.8789	1.00	1.00	0.00	1.00	NaCl	21.82	9.9232	66.69	32.98	21.99	64.64	43.11				
81	15.5012	1.00	1.00	0.00	1.00	CH ₃ COONa	22.56	13.6356	87.96	27.02	23.76	61.05	53.70				

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Wood used: White spruce, 60-80 mesh, benzene-alcohol extracted.

Analysis: Cellulose - 60.82 per cent, lignin - 27.90 per cent.

1 0.48 per cent SO₂ as NaHSO₃.

2 1.82 per cent NaCl = 2.00 per cent NaHSO₃ (NaCl substituted for NaHSO₃ in acid).

3 2.56 per cent CH₃COONa = 2.00 per cent NaHSO₃ (CH₃COONa substituted for NaHSO₃ in acid).

Summary

The results recorded in this paper show:

1. That the same amount of carbohydrate materials are removed from wood by mild hydrolysis with hydrochloric acid as are removed by sulphite digestion which reduces the lignin content of the residue below 2 per cent.
2. That the carbohydrate materials removed by hydrolysis are, in part at least, removed as complex bodies that can be further hydrolyzed to reducing sugars.
3. That the time of lignin removal by the sulphite reaction is reduced approximately one-half by each 10° increase in temperature between 120° and 150° C.
4. That a change in acid concentration from 1 to 3 per cent is necessary to reduce the time of lignin removal by one-half.
5. That the tendency of salts of strong acids added to the cooking liquor is to increase the rate of reaction, and for those of weak acids to decrease the rate of reaction, suggesting a process dependent upon hydrogen-ion concentration.