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The undersigned, acting as a Committee of the Graduate School, have read the accompanying thesis submitted by Samuel Isaac Aronovsky for the degree of Chemical Engineer. They approve it as a thesis meeting the requirements of the Graduate School of the University of Minnesota, and recommend that it be accepted in partial fulfillment of the requirements for the degree of Chemical Engineer.

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THE USE OF VACUUM in MAKING SULPHITE PULP

A THESIS

SUBMITTED to the GRADUATE SCHOOL

of the

UNIVERSITY OF MINNESOTA

by

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Samuel Isaac Aronovsky  
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In partial fulfillment of the requirements

for the

DEGREE of

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THE USE of VACUUM in MAKING  
SULPHITE PULP

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## INTRODUCTION

Sulphite pulp is manufactured by cooking wood chips with a solution of calcium bisulphite,  $\text{Ca}(\text{HSO}_3)_2$ , and sulphurous acid,  $\text{H}_2\text{SO}_3$ , in a digester under pressure. There are two methods used at present to make this pulp, namely, the "Mitscherlich" or "slow-cook" process and the "Ritter-Kellner" or "quick-cook" process. These two processes differ only in the method used to bring the pressure and temperature in the digester up to the desired points.

In the Mitscherlich process the pressure is brought up slowly by heating the contents of the digester by means of steam-heated lead coils. Live steam does not come in contact with the digester contents. This method requires 15 to 25 hours for a cook, with a maximum temperature of  $124^\circ$ - $130^\circ\text{C}$ . and a maximum pressure of 40 to 50 pounds, gauge. The "acid", or cooking liquor, used contains about 3.25 o/o total  $\text{SO}_2$ . This process is used to a large extent in Europe.

In the Ritter-Kellner process the live steam is forced directly into the digester contents, thereby raising the temperature and the pressure quickly, and shortening the time necessary for cooking. Wood pulped by this process is cooked for 8 to 10 hours at a temperature of  $150^\circ$ - $160^\circ\text{C}$ ., and a pressure of 80 to 100 pounds gauge. A higher content of  $\text{SO}_2$  is used in the acid for this cook than in the Mitscherlich process. The pulp made is not as strong as the Mitscherlich pulp, and the yield is less.

This quick-cook process is used in a majority of the sulphite pulp mills in this country.

The importance and use of sulphite pulp has recently increased to such a large extent in the paper and related industries, such as making woodboard, roofing, etc., that much work is being done now to improve the quality of the pulp and to shorten the time of cooking. This is more essentially true of the Ritter-Kellner process. Many methods have been proposed to reduce the time necessary for a sulphite cook. Some of these methods proposed the use of liquid  $\text{SO}_2$ , stronger bisulphite liquor (i.e., richer in  $\text{SO}_2$  gas), dry wood, superheated steam, <sup>(1)</sup> the preliminary extraction of the cementing of incrusting substance of the wood by means of organic solvents, <sup>(2)</sup> and others. These improvements are used more or less at present according to their economic and scientific merits.

The object of this paper is to introduce another method, as indicated by the title, namely, the use of vacuum in making sulphite pulp. In most of the improved methods for shortening the time of cooking the wood by the sulphite process the quality of the pulp is impaired and the yield is cut down due to the uneven impregnation of the wood with the liquor. The wood is therefore cooked on the outside and uncooked on the inside, because the liquor did not penetrate into the inside of the wood chips. In order to have completely cooked wood, the pressure in the digester would have to be kept low for two or three hours to allow the chips to become thoroughly saturated with cooking liquor. This would mean adding two or three hours to the time of cooking, which is the

undesirable feature of present operations.

If the pores of the wood could be exhausted of air and moisture, however, and the cooking liquor drawn into the digester under the vacuum formed, the chips would become impregnated with the "acid" in a very short time and full steam pressure could be applied right at the beginning of the cook. The chips would be thoroughly and uniformly saturated with the "acid" and the resulting pulp would then also be uniform. This method would mean, a saving in time and in steam consumption; it would increase the output and quality of the pulp; and it would also give more uniform cooks. It would do away with the acid pumps, as the liquor could now be run in under vacuum, assisted by gravity. The only additional cost would be the installation and the upkeep of the vacuum pumps. This cost would be more than offset by the savings made.

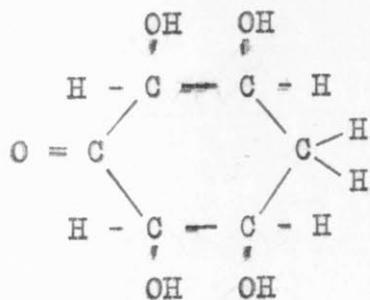
### THEORY OF THE PROCESS

The process of sulphite cooking is at present based more upon practical experience than upon scientific knowledge. This is due to the fact that very little is known of the chemical composition of the wood. Klason's investigations on the composition of one of the chief constituents of wood, lignin, has resulted in the theory that explains some of the most important reactions in the digester. According to Johnsen,<sup>(3)</sup> bone-dry spruce has the following composition:

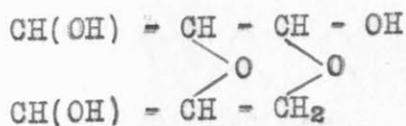
Cellulose	53 o/o
Other carbohydrates	14 o/o
Lignin	29 o/o
Protein	0.7 o/o
Resins, fats, etc.	3.3 o/o
	-----
	100 o/o

Twelve per cent of the weight of the wood is soluble in boiling water<sup>(4 d)</sup>

The cellulose part of the wood belongs to the class of organic substances known as carbohydrates. It has been given the empirical formula of  $(C_6H_{10}O_5)_n$ , n being unknown. Cellulose is known, however, to have a large molecular weight, about 6000. Cross and Bevan,<sup>(5)</sup> give it the following structural formula:



Green<sup>(5)</sup> also gave it a structural formula as shown below:



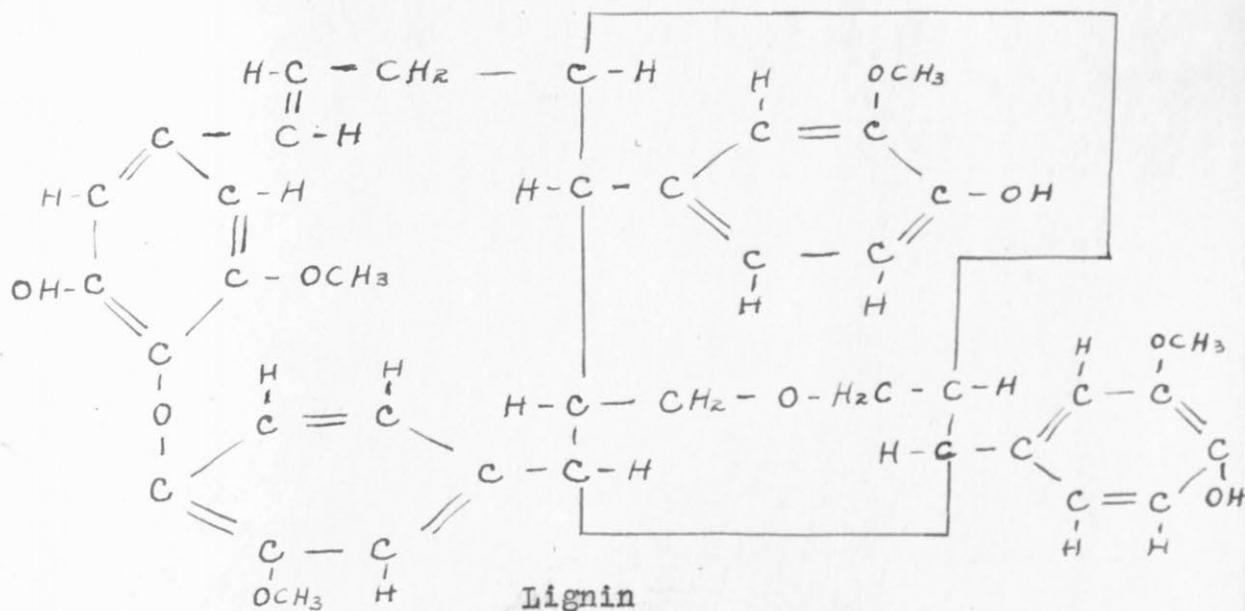
These formulae are not important because very little is known about the splitting and breaking up of the cellulose molecule.

Cellulose is very resistant to acids and chemicals in general. This property is the basis of all of the different processes of manufacturing wood pulp. Under certain conditions, however, cellulose may be hydrolyzed and oxidized,<sup>(3)</sup> and care must be taken to prevent these two reactions by controlling the cooking process. Otherwise the cellulose fibres will break down physically and chemically to form soluble products, thus giving a poor yield of pulp.

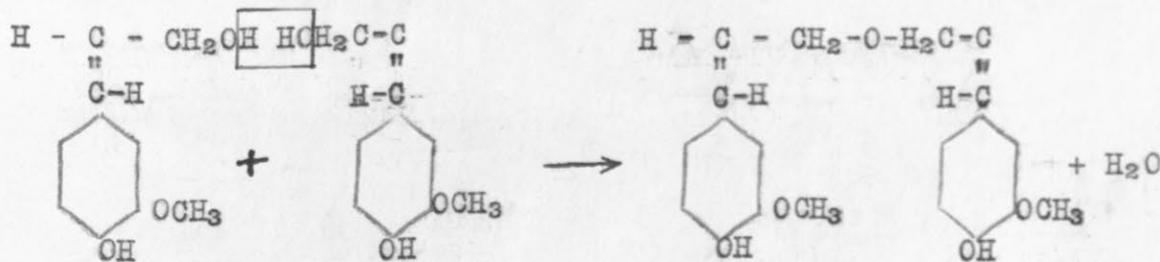
The other carbohydrates, which make up 14 o/o of the weight of the wood, constitute most of the soluble portion of the wood. These carbohydrates belong to the same general class as cellulose, but they have smaller molecular weights. They consist of sugars as both hexoses and pentoses. The higher sugars are broken down into hexoses and pentoses under the conditions in the digester. Galactose, dextrose, mannose, and xylose are among the

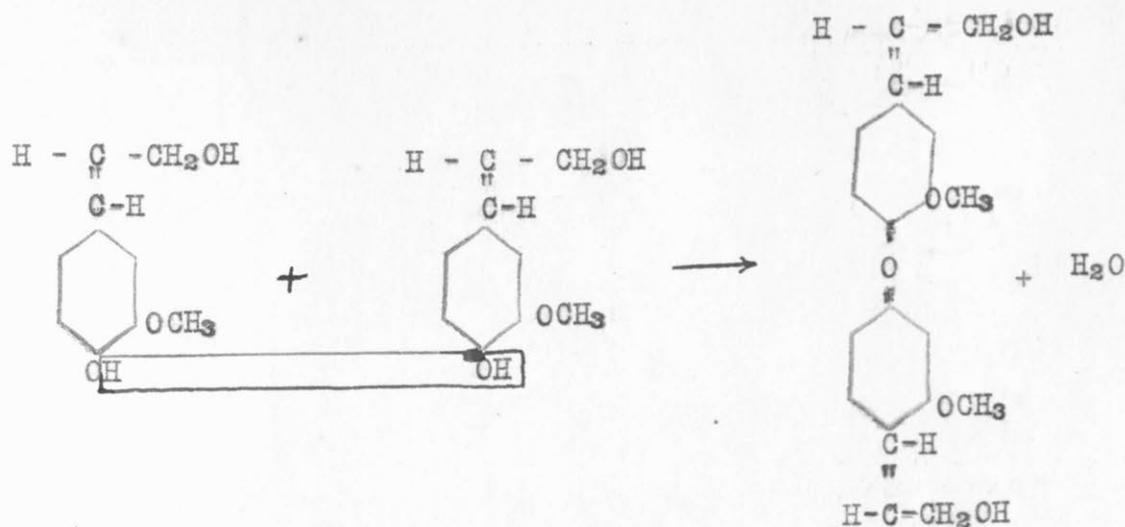


shown below, obtained from the condensation of 4 molecules of coniferyl alcohol with the elimination of 3 molecules of water;

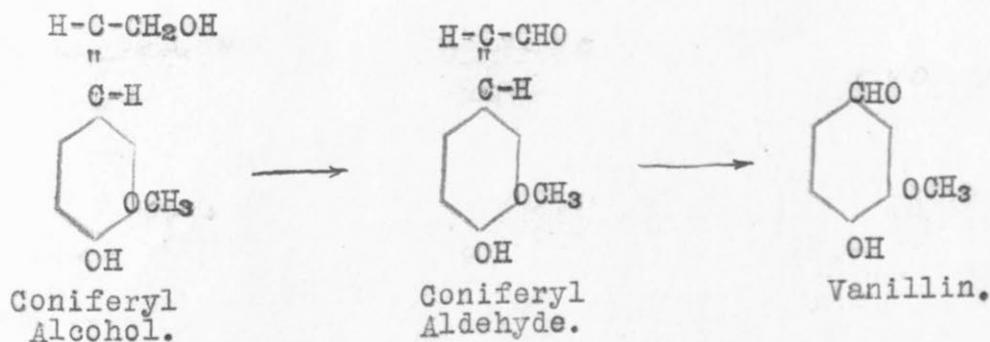


It may be noted that this formula contains 4 methoxy groups, 4 hydroxyl groups, and one ethylene group. Chambovet (4 c) claims that there is a carbonyl group also, but he does not show it in this formula. It may be assumed, however, that one of the hydroxyl groups can become a carbonyl group through keto-enolization. The above formula also shows that the elimination of the water molecules may occur at the alcoholic or at the phenolic hydroxyl groups as shown:





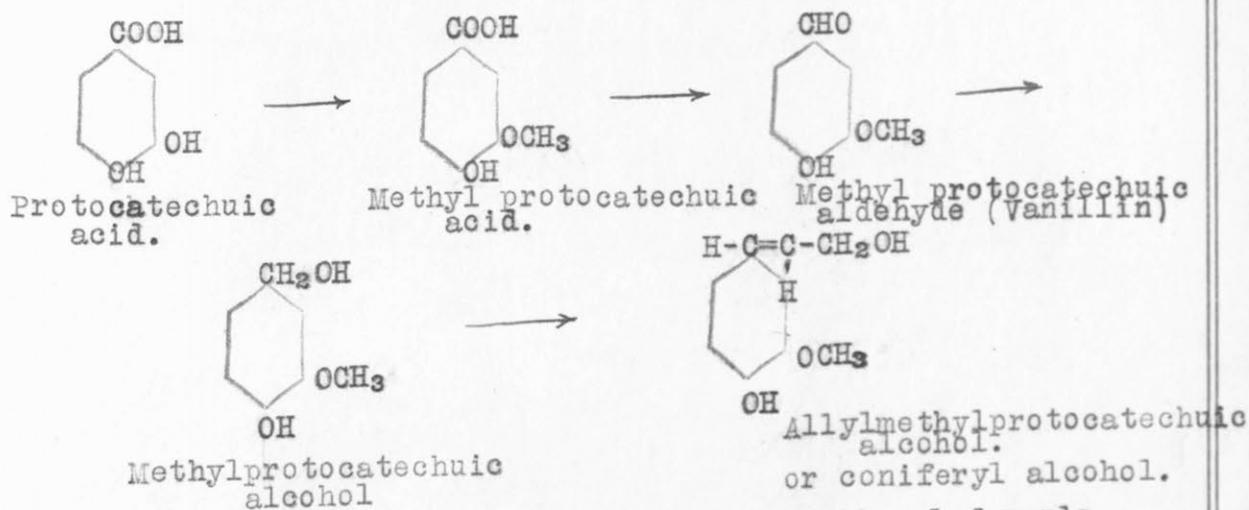
Considerable experimental work has been done concerning Klason's theory pertaining to the composition of lignin. Coniferyl alcohol being a primary alcohol may be oxidized to the corresponding aldehyde, which is closely related to vanillin, differing only in that it contains an ethylene group. By prolonged oxidation coniferyl alcohol finally yields vanillin:



Both vanillin and lignin give a light red color with phloroglucin, a violet color with hematoxylin, and a characteristic red color with indol and hydrochloric acid. Coniferyl alcohol and lignin are both slightly resinified by dilute mineral acids. Another positive proof of Klason's theory is the fact that the sulphonic derivative of coniferyl alcohol brought about by the action of calcium bi-

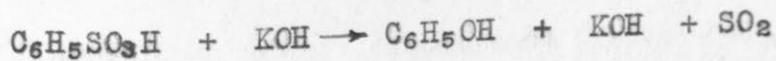
sulphite,  $\text{Ca}(\text{HSO}_3)_2$ , on this alcohol is very similar to calcium lignosulphonate which is the product of the main reactions in the digester.

The presence of cinnamic aldehyde and protocatechuic acid in the waste liquor also verifies Klason's theory. Cinnamic aldehyde can easily be made from coniferyl alcohol, and the latter can also readily be made from protocatechuic acid:



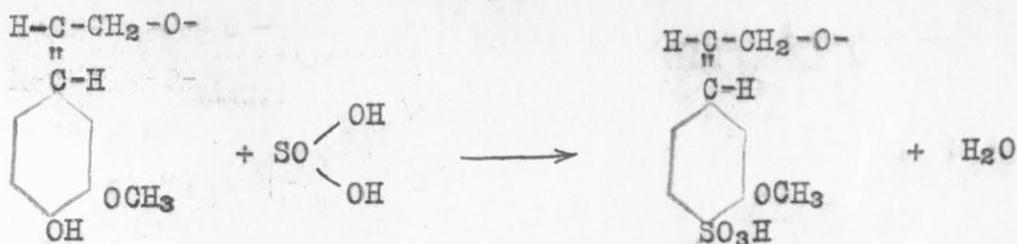
Lignin, as seen from its constitutional formula,

and from its reactions, possesses alcoholic or phenolic properties. The lignosulphonic acid (called an acid because the H atom in the sulphonic radical,  $(\text{SO}_3\text{H})$ , is replacable by a monovalent basic atom) formed by the combination of lignin with  $\text{SO}_2$  would then be a sulphurous acid ester of lignin. This has been proved by the fact that waste liquor freed from any remaining free  $\text{SO}_2$  gives off more  $\text{SO}_2$  on treatment with an alkali, in the same manner as in the case of benzenesulphonic acid:



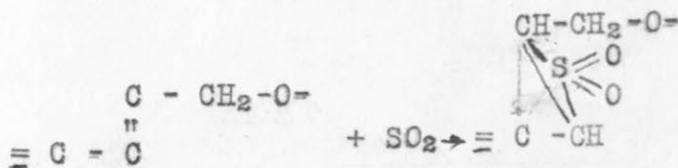
Benzenesulphonic acid.  $\rightarrow$  phenol.

If the lignin is considered as a dihydric phenol it can fix 2 molecules of  $\text{SO}_2$  according to the equation:

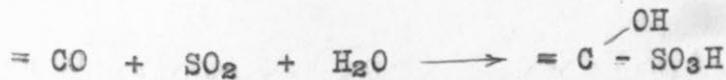


Although  $\text{H}_2\text{SO}_3$  is inert towards phenols, Bucherer's<sup>(4 c)</sup> researches on the sulphonic esters of aromatic compounds show that  $\text{SO}_2$  has a great affinity for polyhydric phenols. The phenolic ester thus formed is stable because aromatic sulphonic esters are quite stable and are not decomposed by water except as they follow the general laws of esterification and saponification. At equilibrium at a certain temperature, only about 67 o/o of the phenol is sulphonated, while the other 33 o/o is in the original form.

The ethylene group will add 1 molecule of  $\text{SO}_2$ , thereby saturating its double bond:



The carbonyl group will also combine with one molecule of  $\text{SO}_2$ ,



Hence the lignin molecule can fix 4 molecules of  $\text{SO}_2$ . This may be proved as follows:

Assuming a molecular weight of 698 for lignin, in

accordance with the formula  $\text{C}_{40}\text{H}_{42}\text{O}_{11}$ , it is seen that the lignin can combine with 256 grams of  $\text{SO}_2$ . Assuming 28-29 o/o of lignin in

spruce, 1 kilo of dry wood should theoretically require

$$\frac{256 \times 280}{698} = 102 \text{ grams SO}_2.$$

This amount is very near the quantities of SO<sub>2</sub> used in practice, where less SO<sub>2</sub> is needed, due probably to the unstability of addition compounds.

The lignosulphonic acid thus formed unites with the calcium of the calcium bisulphite to form calcium lignosulphonate. This salt is soluble and quite stable under the conditions attained in the cooking process in the digester. It is necessary to have enough calcium present to combine with all the lignosulphonic acid formed, because this acid is nearly as strong as sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) in its burning and charring properties. If there is not enough calcium present, a so-called "burnt" cook will result, the pulp from this cook being very dark and charred.

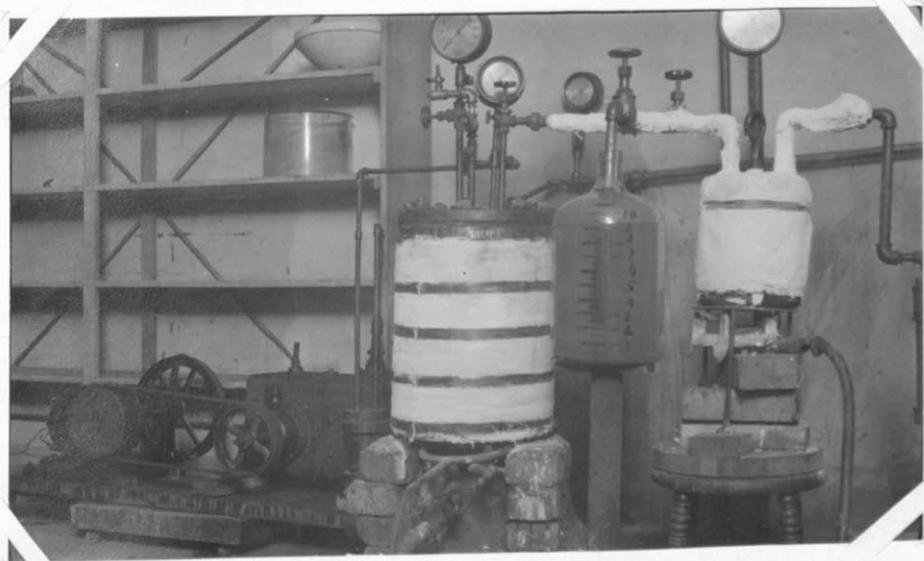
The resins, which with the fats make up 4 o/o of the weight of the wood, are considered to be mixtures of rosin and fat in about equal proportions according to Bjarne Johnsen<sup>(3)</sup>. It is thought that it is the fats which cause a lot of the so-called "pitch" troubles in sulphite pulp manufacture. These resins are not very soluble and a large part of them remains in the cooked wood. The parts of the resins that are soluble are usually the gums or sugars which add sulphur dioxide during the cooking process.

Sometimes the wood is "burnt" even if enough calcium has been added to neutralize all of the lignosulphonic acid. This is most likely due to the presence of fine sulphur brought in with the liquor, or to sulphur precipitated at the high temperatures

and pressures obtained in the digester according to the equation,



or to selenium. The finely divided sulphur has a catalytic effect on the formation of  $\text{H}_2\text{SO}_4$  from  $\text{SO}_2$ , and hastens it considerably, thereby precipitating the calcium as calcium sulphate. The effect of selenium is 300 times as great as that of sulphur, and it, together with sulphur, should be kept out of the cooking liquor as much as possible. <sup>(3)</sup> Chambovet <sup>(4 d)</sup> quotes Klason as saying that the precipitated sulphur has no effect on the formation of  $\text{CaSO}_4$ , or gypsum.



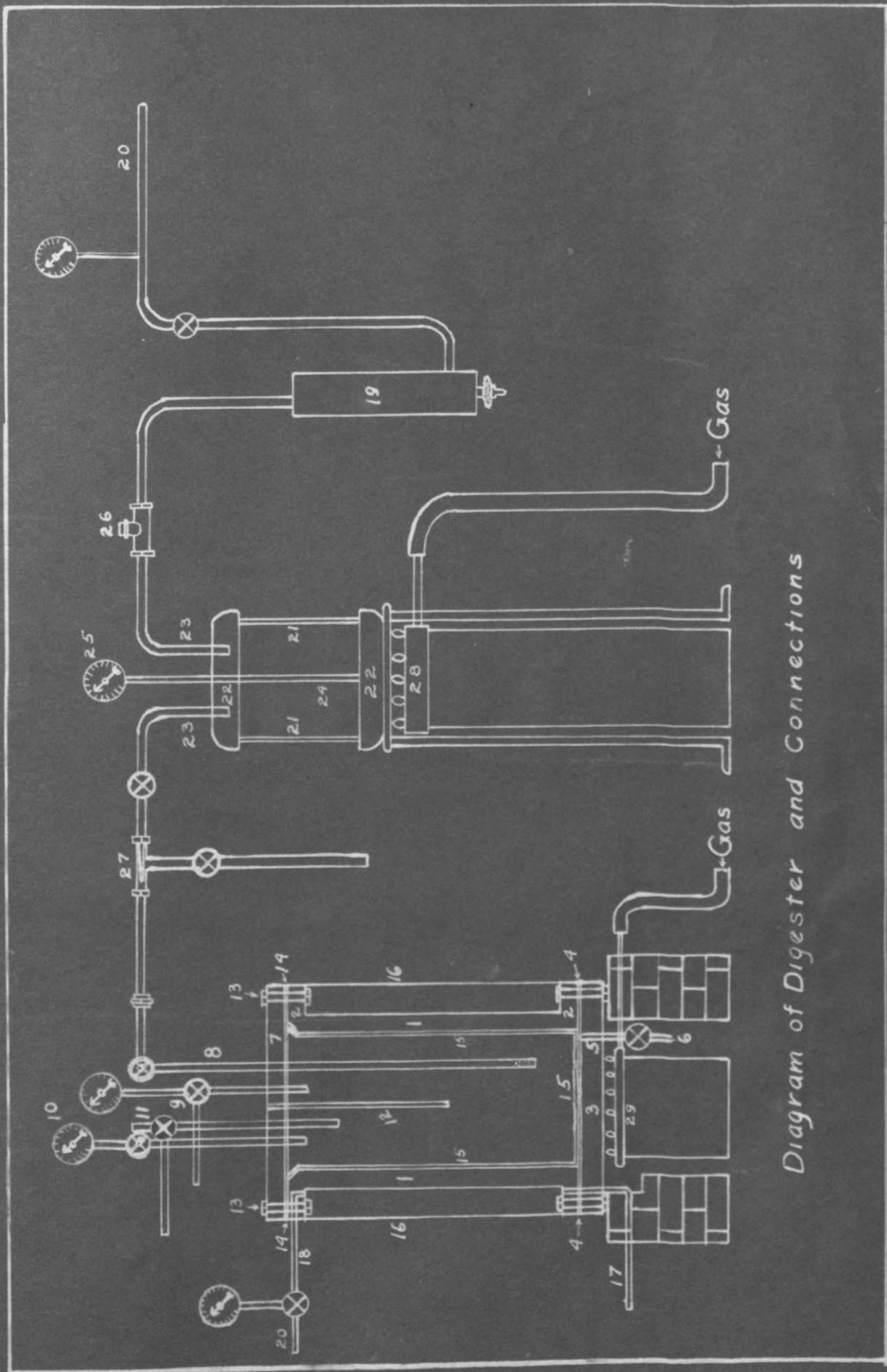


Diagram of Digester and Connections

## EXPERIMENTAL

### Apparatus

The digester as shown in the accompanying drawing consisted of an 8" wrought-iron pipe (1) about 17" long and threaded on both ends. Cast-iron flanges (2) were then screwed on these threaded ends. A cast-iron cover (3) was bolted on the bottom with a lead gasket (4) for packing. This bottom was tapped for a 1/2" pipe (5) and connected with a valve (6) for draining the digester and drawing off liquor for tests. The top plate (7) was drilled and tapped for steam inlet (8), suction pump connection (9), steam gauge (10), acid intake (11), which also acted as a gas release opening, and thermometer well (12). All of these connections were for standard 3/8" brass-pipe except the connections for the suction pump and the thermometer well which were for 1/4" pipe. The top was fastened to the digester by means of bolts (13).

The under side of the top or cover plate was covered with sheet lead (14), 1/8" thick, to protect the iron pipe from the action of the cooking liquor and also to serve as a gasket between the cover and the flange. The inside of the digester was also lined with 1/8" sheet lead (15). A galvanized-iron jacket (16), was then soldered to the edges of the top and bottom plates, thus forming an enclosed space between them for a steam jacket. A hole was drilled thru the bottom flange and plate and tapped for a 3/8" pipe (17), for steam and water outlet from the jacket. Another hole was drilled in the top flange for steam inlet to the jacket (18). The outside of

the jacketed digester was covered with a  $3/4$ " layer of asbestos. A trap (19) was then placed between the steam main (20) and the digester to remove as much water from the steam as possible.

#### Materials.

The acid used in this work was furnished by the Northwest Paper Company at Cloquet, Minnesota. Their analysis was 4.52 o/o total  $\text{SO}_2$ , 3.32 o/o free  $\text{SO}_2$ , and 1.20 o/o combined  $\text{SO}_2$ . The total  $\text{SO}_2$  content of the acid was determined by titrating a 1 cc. sample of the acid with 0.0906 N. iodine solution, using freshly made starch as an indicator. Each cc. iodine solution was then equivalent to 0.29 o/o total  $\text{SO}_2$ . The free  $\text{SO}_2$  concentration was determined by titrating 1 cc. of the liquor with 0.1478 N. sodium hydroxide solution, using phenolphthalein as the indicator. Each cc. NaOH solution used was equivalent to 0.45 o/o free  $\text{SO}_2$ . The combined  $\text{SO}_2$  is the difference between the total  $\text{SO}_2$  and the free  $\text{SO}_2$ . The acid concentration decreased gradually on standing, due to the fact that the room temperature was high and that  $\text{SO}_2$  is not very soluble in water at moderately high temperatures.

The wood chips used were also furnished by the Northwest Paper Company. They were commercial chips, probably a mixture of spruce and balsam, and had been in the furnace room of the Chemistry Building of the University of Minnesota for about a year and a half. The moisture content was 5.58 o/o. These chips were used in cooks no. 1 to 7 inclusive. For cooks no. 8 and 9, aspen chips were used, while for cook no. 10 spruce chips fresh from the paper mill were used.

Method of Procedure.

In making a run, 500-1000 grams of chips were weighed out and put into the digester and the cover bolted on. Steam was let into the steam jacket, and the vacuum started by means of a rotary vacuum pump which could maintain 25"-28.5" vacuum. The vacuum was maintained for 1-1 1/2 hours. Then the vacuum connection was shut tight and liquor drawn into the digester by means of this vacuum. The amount of liquor used was 7 to 10 liters for every kilogram of bone-dry chips. When the required amount of acid had been drawn into the digester, the acid intake valve was shut off and the steam valve opened. This steam was dry, after passing a trap and through a pipe heated by four Bunsen burners. Glycerine was put into the thermometer well and the thermometer inserted.

During the run, the line pressure, digester pressure, temperature, and acid concentration were taken at intervals. The acid was drawn off through the bottom and titrated with  $I_2$  solution and NaOH solution. When the run was considered complete, the steam was let out gradually, and when all out, the digester was flushed first with warm and then with cold water. Then the chips were taken out and some were ground in the ball mill with much water for 2 to 3 hours. The pulp was then taken out from the mill and separated from the unpulped wood. A sample of this pulp was then bleached, in order to find the comparative ease of the bleaching. The bleaching medium was ordinary bleaching powder. A quantity of

this powder was shaken up with warm water and let stand till the insoluble material had settled. The clear liquor was decanted off and mixed with the pulp that was to bleach, and shaken well.

Data.

Cook No.1.

Feb. 21, 1922.

Chips = 1000 g.

Acid = 7 liters.

Vacuum started

9:30 A.M.

Vacuum ended

11:00 A.M.

Vacuum = 27" for

1 1/2 hours.

Pressure (Gauge)

SO<sub>2</sub> Concentration

Time.	Temp. °C.	Digester lbs.	Line. lbs.	I <sub>2</sub> sol. used cc.	Total SO <sub>2</sub> o/o	NaOH sol. used cc.	Free SO <sub>2</sub> o/o
11:10	150°	77	84	14.50	4.21	6.56	2.94
11:30	146°	74	79	4.20	1.22	2.20	0.98
12:00	147°	68	74	3.65	1.06	2.02	0.90
12:30	147°	77	82				
1:00	143°	68	74				
1:30	136°	77	79.5				
2:00	136°	78	83	2.20	0.68	1.04	0.47
2:30	137°	71	78				
3:00	140°	78	81				
3:30	140°	79	83				
4:15	135°	68	73	2.20	0.68	0.80	0.36
4:30	132°	64	69				

The product was dark and approximately 50 o/o of the wood pulped after being in the ball mill for about 2 hours. The exact amount pulped could not be ascertained because there was no screen to screen the wood pulp. Although quite dark, the pulp from this run bleached with some difficulty.

Much of the  $SO_2$  from the digester was lost in the first 10 minutes of the run, due to some leak in the top flange and bolts. An asbestos fibre gasket was now added between the top flange and the upper cover, and fibre asbestos washers were put beneath the steel cut washers.

The pulping was done by rotating a small quantity of cooked wood, a number of "balls" or stones, and a large quantity of water in a porcelain mill, which is a stout-walled porcelain jar, for about two hours. The speed of the mill was approximately one revolution per second, or 60 R.P.M. The contents of the ball mill were then taken out, and separated from the "balls". The wood and pulp mixture was then washed with much water in a large porcelain sieve. The unpulped wood was left in the sieve, while the pulp was in the wash water. This wash water was then filtered through a cheese-cloth and the pulp remaining on the cloth was washed.

Cook No. 2.

March 2, 1922.

Chips = 500 g.

Acid = 4.5 liters.

Vacuum started

11:00 A.M.

Vacuum ended

12:05 A.M.

Vacuum = 28"

for 1 hour - 5 minutes.

Steam let in at 12:05 M. reduced the vacuum to 22". The the 4.5 liters acid were drawn in by the remaining vacuum. Full steam pressure was put on at 12:10 M.

Pressure (Gauge).

SO<sub>2</sub> Concentration.

Time.	Temp. °C.	Digester lbs.	Line lbs.	I <sub>2</sub> sol. used cc.	Total. SO <sub>2</sub> o/o	NaOH sol. used cc.	Free SO <sub>2</sub> o/o
12:10	130°	80	84	15.17	4.40	6.49	2.92
12:30	145°	80	84.5	4.38	1.27	2.10	.95
1:00	152°	80	84	3.22	.93	1.18	.53
1:30	153°	77	80				
2:00	155°	81	86	2.66	.77	1.14	.51
2:30	145°	81	86				
3:00	130°	78	82.5				
3:30	120°	70	73				
4:00	110°	72	76	1.54	.42	.85	.38
4:10	110°	71	74.5				

The SO<sub>2</sub> liquor was enriched by bubbling SO<sub>2</sub> into it from a liquid SO<sub>2</sub> tank. The yield was approximately 65 o/o pulp, and was easily bleached. The cooked wood was dark. This was probably due to a quick loss of SO<sub>2</sub> since lack of sufficient SO<sub>2</sub> will cause "burnt" cooks as well as lack of calcium. The pressure was fairly constant all through this cook, but the temperature went down quite fast, due to an excess of liquid having formed in the digester from con-

densed steam. Soaking the wood in steam before the acid was drawn in did not seem to help keep the SO<sub>2</sub> in the wood when pressure was applied. It seems probable, though, that the impregnation of the wood was fairly uniform.

Cook No. 3.

March 16, 1922

Chips = 500 grams.      Acid = 4.0 liters.  
 Vacuum started      11:15 A.M.  
 Vacuum ended      12:30 A.M.  
 Vacuum = 24" for 1 hour - fifteen min.

Time.	Temp. °C.	Digester lbs.	Line. lbs.	SO <sub>2</sub> Concentration.			
				I <sub>2</sub> sol. used cc.	Total SO <sub>2</sub> o/o	NaOH sol. used cc.	Free SO <sub>2</sub> o/o
12:30	75°	20	76	16.50	4.79	7.34	3.29
12:40	144°	61	85	5.26	1.52	2.25	1.01
12:50	157°	86	89				
1:00	160°	85	88	3.20	.93	1.67	.75
1:30	157°	73	76	2.68	.78	1.42	.64
2:00	163°	88	90				
2:30	162°	85	88	2.08	.60	1.30	.58
3:00	153°	77	80				
3:30	143°	86	89				
4:00	135°	86	89				
4:30	129°	85	87	.60	.17	.34	.45

The liquor was enriched as in cook no. 2. The yield of pulp was approximately 50 o/o and it was fairly easily bleached. Most of the SO<sub>2</sub> was kept in the digester by opening the steam pressure valve slowly and letting the pressure in the digester come up gradually.

The pulp was somewhat lighter in color than that of the other cooks but it was still a light brown. A large part of the wood remained hard and it was not very thoroughly cooked on the inside. This is probably due to too much air being admitted with the acid and steam into the digester, as a considerable amount of  $\text{CaSO}_4$  was found in the bottom of the digester.

The free  $\text{SO}_2$  at the end was greater than the total  $\text{SO}_2$  because of the presence of organic acids formed by the decomposition of some of the products of the reactions in the digester.

Cook No. 4. April 6, 1922.  
 Chips = 500 grams. Acid = 2.5 liters.  
 Vacuum started 9:00 A.M.  
 Vacuum ended 10:00 A.M.  
 Vacuum = 22.5" for 1 hour.

Time.	Temp. °C.	Pressure (Gauge).		SO <sub>2</sub> Concentration.			
		Digester lbs.	Line. lbs.	I <sub>2</sub> sol. used cc.	Total SO <sub>2</sub> o/o	NaOH sol. used cc.	Free SO <sub>2</sub> o/o
10:10	88°	79	82	15.75	4.63	7.20	3.23
10:25	156°	82	85	It was not possible to take			
10:40	160°	83	85	off samples of the liquor			
11:10	161°	83	85	from the digester for tests,			
11:40	161°	84	86	because the sampling pipe was			
12:10	161°	82	84	clogged.			
12:40	155°	70	73				
1:10	147°	64	68				
1:40	147°	63	67				
2:10	133°	78	81				
2:40	130°	78	81				

The liquor was enriched as in cook no. 2. The vacuum in the digester drew in only 2.5 liters of acid, and as there was no way of forcing the remaining acid in, the run was completed with an insufficient quantity of acid. The wood was not cooked thoroughly and pulping was not attempted. It was comparatively light in color.

In order to get more pressure in the digester during the cook, a superheater was now inserted between the digester and the high pressure steam line. This superheater consisted of a 7" wrought-iron pipe, about 10" high. Two cast-iron caps (22) were screwed on the two ends of the pipe. Two holes were drilled in the top cap and threaded for 1/2" pipe (23) for inlet and out-let steam. Another hole was drilled and tapped for a 1/4" pipe (24). The pipe screwed into this latter hole reached nearly to the bottom of the superheater, and was used to empty the apparatus of water after each run. During the run, a steam gauge (25) was screwed into this hole.

A check valve (24) was then placed between the superheater and the steam main so that the steam generated in this superheater under a higher pressure than that of the steam in the main could not go into the latter. An injector (27) was then connected between the superheater and the digester to facilitate the drawing in of acid if the vacuum created by the pump is not enough, or if the liquor has too much free  $\text{SO}_2$  in solution. The whole apparatus and connections were then covered with an inch layer of asbestos. It was heated from the bottom by a gas burner (28).

Cook No. 5.

April 20, 1922.

Chips = 500 grams.

Liquor = 500 cc.

Vacuum started

10:00 A.M.

Vacuum ended

10:45 A.M.

Vacuum = 24" for 45 minutes.

Pressure (Gauge).

SO<sub>2</sub> Concentration.

Time.	Temp. °C.	Digester lbs.	Line. lbs.	I <sub>2</sub> sol. used cc.	Total. SO <sub>2</sub> o/o	NaOH sol. used cc.	Free SO <sub>2</sub> o/o
10:50	155	80	84	24.4	7.08	11.8	5.29
11:00	156	79	82				
11:30	149	80	82				
12:00	137	86	72				
12:30	127	89	76				
1:00	117	91	61				
1:30	114	85	73				
2:00	113	58	60.5				
2:30	110	54	57				
3:00	106	56	59				

Data not taken.

The liquor was enriched by adding to it a little solid CaSO<sub>3</sub> and bubbling in SO<sub>2</sub> gas from a liquid SO<sub>2</sub> tank. The pressure was high enough at first but, it decreased in the last hour probably because there was no more water in the superheater, and the steam heated in it was not enough to keep the pressure up above that of the main. The temperature went down very fast due, most likely, to too much water let in with the steam at the beginning.

The wood from this run was lighter than that from any of the other runs. About 50 o/o of it was pulped in the ball mill after two hours. It was more easily bleached than the pulp

from the other runs. The light color of the wood and the ease with which it was bleached, seems to indicate that in the former runs the color was largely due to the rust in the mains being carried over with the steam and deposited on the wood.

Cook No. 6.

April 25, 1922.

Chips = 500 grams.

Liquor = 500 cc.

Vacuum started

10:10 A.M.

Vacuum ended

10:55 A.M.

Vacuum = 24.5" for 45 minutes.

Pressure (Gauge)

SO<sub>2</sub> Concentration.

Time.	Temp. °C.	Digester lbs.	Line lbs.	I <sub>2</sub> sol. used cc.	Total. SO <sub>2</sub> o/o	NaOH sol. used cc.	Free SO <sub>2</sub> o/o
11:00	35	0	74	19:30	5.60	8.90	3.99
11:15	146	69	75	5.69	1.65	2.24	1.01
11:30	157	80	83	3.45	1.00	1.35	.61
11:45	158	79	81				
12:00	150	62	65	1.55	.45	.70	.31
12:30	148	68	71				
1:00	132	64	67	1.14	.33	.70	.31
1:30	121	75	77				
2:00	115	65	68				
2:30	106	61	64				
3:00	105	75	78	1.14	.33	1.15	.52

A little CaSO<sub>3</sub> was added to the liquor and SO<sub>2</sub> bubbled in. The temperature went down due to too much water being brought in with the steam. The superheater did not increase the pressure because there was not enough water in it. The wood from this run was light in color, but too hard and pulping was not attempted. The temperature in the digester decreased quite fast, due probably, to the

fast condensation of the steam there and the accompanying increase in the quantity of liquid.

Cook No. 7.

April 27, 1922.

Chips = 380 grams.

Liquor = 400 cc.

Vacuum started

10:25 A.M.

Vacuum ended

11:25 A.M.

Vacuum 25" for 1 hour.

Time.	Temp. °C.	Pressure (Gauge).		SO <sub>2</sub> Concentration.			
		Digester lbs.	Line. lbs.	I <sub>2</sub> Sol. used cc.	Total. SO <sub>2</sub> o/o	NaOH sol. used cc.	Free SO <sub>2</sub> o/o
11:25	40	0	82	16.85	4.89	8.09	3.62
11:30	144	72	82				
11:45	159	81.5	84	2.20	.64	1.10	.49
12:00	158	76	78	2.14	.62	1.10	.49
12:30	159	82	84				
1:00	149	85	83	1.04	.30	.55	.25
1:30	133	85	87				
2:00	117	88	90	1.00	.29	.66	.30
2:30	117	86	88				
3:00	112	81	84				
3:25	106	82	85	.90	.26	.84	.38

Much of the SO<sub>2</sub> was lost due to leaks in the top flange during the first 10 minutes. The superheater did not work this time either but the line pressure was fairly high and it kept the digester pressure up pretty well. The temperature again went down fast, showing an excess of liquor in the digester. The wood was comparatively light in color. It was pulped to about 50 o/o in the ball mill and bleached fairly easily.

Cook No. 8.

May 4th, 1922.

Aspen Chips = 500 grams.  
 Vacuum started  
 Vacuum ended  
 Vacuum 25" for 30 minutes.

Liquor = 400 cc.  
 10:20 A.M.  
 10:50 A.M.

The acid was left to soak the wood for 10 minutes before steam was let into the digester.

Time.	Temp. °C.	Pressure (Gauge).		I <sub>2</sub> sol. used cc.	SO <sub>2</sub> Concentration.		
		Digester lbs.	Line. lbs.		Total. SO <sub>2</sub> o/o	NaOH sol. used cc.	Free SO <sub>2</sub> o/o
11:00	45	0	80	14:00	4.06	6.00	2.86
11:15	146	64	70				
11:30	143	55	62	6.70	1.94	2.77	1.25
11:45	141	53	72				
12:00	152	80	82	3.52	1.02	1.74	.78
12:15	155	85	87				
12:30	158	87	89				
1:00	154	87	89	1.60	.46	.94	.42
1:30	148	87.5	89				
2:00	114	60	62				
3:00	107	74	76	1.38	1.40	1.30	.58

The liquor used in this run was from a new batch just received from the Northwest Paper Company. Aspen chips were used in this run because the spruce was all used up. The aspen contained 5.48 o/o moisture. Much of the acid was lost at first as in the previous runs. About 60 o/o of the wood was pulped in the ball mill in two hours. It was light in color and bleached easily. Pats were then made of both the bleached and unbleached pulp, and they compared

favorably with samples of pulp from commercial mills.

In order to reduce the amount of water condensed in the digester and at the same time to bring the pressure up to 90-95 pounds gauge, a ring burner (29) was now placed underneath the digester.

Cook No. 9.	May 11, 1922.
Aspen Chips = 500 grams.	Acid = 500 cc.
Vacuum started	10:50 A.M.
Vacuum ended	11:35 A.M.
Vacuum 25" for 45 minutes.	

The acid was sucked in by the vacuum, and then steam was sent through the jacket, and the burner underneath the digester was lighted. After 15 minutes, the pressure in the digester having come up to 5 pounds gauge, steam was admitted under full pressure.

Time.	Pressure (Gauge).			SO <sub>2</sub> Concentration.			
	Temp. °C.	Digester lbs.	Line lbs.	I <sub>2</sub> sol. used cc.	Total. SO <sub>2</sub> o/o	NaOH sol. used cc.	Free SO <sub>2</sub> o/o
11:50	75	0	85	15.10	4.38	7.02	3.14
12:00	140	83	85	9.55	2.77	3.58	1.61
12:15	154	81	83				
12:30	154	82	84	4.69	1.36	2.60	1.07
1:00	155	85	87				
1:30	157	83	85	2.20	.64	1.26	.87
2:00	157	80	82				
2:30	153	79	81				
3:00	147	81	83				
3:30	133	85	87				
4:00	130	84	86	1.24	.36	1.00	.45

The chips were light in color and thoroughly cooked. About 95 o/o of the wood was pulped in the ball mill in two hours. It bleached very easily. The pressure in the digester did not come up above that of the main because the steam in the digester condensed too fast, and the ring burner was not able to give heat enough to prevent this condensation. It was up above 80 pounds constantly however, due to too high pressure in the main. The temperature went down again, although the pressure remained the same, because of the large quantity of water in the digester.

## Cook No. 10.

Chips = 500 grams.

Acid = 5 liters.

Vacuum started

12:15 M.

Vacuum ended

1:00 P.M.

Vacuum = 23" for 45 minutes.

The acid was let into the digester at 1:00 P.M. and steam was turned on in the jacket, and the burner underneath the digester was lighted. At 1:15 P.M. steam under the full pressure of the main was let into the digester.

Time.	Temp. °C.	Pressure (Gauge)		I <sub>2</sub> sol. used cc.	SO <sub>2</sub> Concentration.		
		Digester lbs.	Line lbs.		Total SO <sub>2</sub> o/o	NaOH sol. used cc.	Free SO <sub>2</sub> o/o.
1:15	78	8	78	16.20	4.70	7.34	3.30
1:30	151	82	85	6.20	1.80	2.72	1.22
1:45	155	80	83				
2:00	154	78	81	3.00	.87	1.58	.71
2:15	156	79.1	81				
2:30	156	79.5	81				
3:00	159	88.5	87	1.48	.43	.76	.34
3:30	164	98	82				
4:00	159	82	83				
4:30	155	84	83				
5:00	145	95	84				
5:15	156	81	78	.70	.20	1.00	.45

Fresh spruce from the Northwest Paper Company was used in this run. This wood had a moisture content of 16.92 %. The combined heat of the burners underneath the superheater and digester forced the pressure in the latter up above that in the main, although the main pressure was above 80 pounds gauge all

through the cook. The high pressure and consequent high temperature obtained was detrimental to the cooking, however, since the wood was slightly burned. This was most likely caused by the precipitation of sulphur, and consequent formation of gypsum, as a considerable quantity of the latter was found in the digester. Some  $\text{SO}_2$  escaped from the digester at the beginning of this run. This loss of  $\text{SO}_2$  also helped to "burn" the wood. The wood, though somewhat burned was fairly well cooked, yielding approximately 75 percent pulp, after being rotated in the ball mill for two hours. The high moisture content was probably one reason why this spruce was not cooked as thoroughly as the aspen, since the vacuum formed in the pores of the wood would not be enough to draw the liquor into them. The pulp was colored a reddish brown, while the solid chips remaining were somewhat darker. Considerable bleach was required to remove the reddish brown color of the pulped wood.

## CONCLUSION

The preceding data shows clearly that by the use of vacuum the cooking period of the sulphite process can be lowered to practically half of what it is at the present time in commercial practice. No doubt the size and type of equipment used will also have its effect on the time of cooking. The pulp made by this modified method is uniform, but the cooking conditions must be carefully controlled. Aspen cooks much quicker than does a mixture of spruce and balsam or spruce alone. The best conditions for cutting down the cooking period are: (a) a cooking liquor of 5.00 percent total  $\text{SO}_2$ , (b) a pressure of 90 pounds, gauge, (c) a temperature of  $155^\circ\text{C}$ , (d) dry steam, and (e) a low moisture content of the wood.

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