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FOREST PRODUCTS LABORATORY

In cooperation with the University of Wisconsin

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CHEMISTRY OF THE SULPHITE PROCESS

V. Effect of Various Compositions of Acid Upon Yield and Quality of Pulp

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V. Effect of Various Compositions of Acid Upon Yield and Quality of Pulp

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By

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The results of the tests herein described show that under the conditions of cooking used the presence of calcium base above a certain minimum is without appreciable effect upon the yield of pulp obtained by the sulphite cooking process, and in the acid it is that part of the so-called "tree" that is present as excess sulphurous acid which has the greatest effect upon the yield of pulp.

In the industry manufacturing sulphite wood pulp a considerable diversity of opinion exists as to the most desirable strength and composition of acid to use. The advocates of a high free sulphur dioxide content and a low combined sulphur dioxide content are probably in the majority, but there are advocates of low free and high combined.

The diversity of opinion is founded upon individual experience in different mills and is difficult to reconcile because the different conditions under which the opinion have been developed. The series of cooks considered here was made in an endeavor to determine, in a carefully controlled system, the influence of variations in the acid composition upon the yield and quality of the pulp produced.

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Equipment and Manipulation

The cooks upon which this study is based were made in the experimental digester at the Forest Products Laboratory. In that digester because of the greater ratio of surface to contents than exists in a commercial digester it has been found impractical to make a cook under strictly Ritter-Kellner or direct steam conditions. Some heat must be maintained on the coils to prevent excessive condensation.

The rate of steam flow into the digester and consequent dilution was approximated by determining the rate of condensation when cooking a digester filled with water over a temperature rise similar to that of a sulphite cook. The rate of condensation obtained with various openings of a needle valve was noted and in actual cooks the steam valve was set at the point that would give a rate of condensation comparable to that in a commercial cook. In the later cooks of the series the remaining uncertainty as to the volume of liquor present was eliminated by cooking entirely with the coil and forcing in measured quantities of water in the right amount to produce the dilution effect present in commercial cooking by direct steam.

The relief was handled as was necessary to keep the maximum cooking pressure at 75 pounds per square inch over a cooking temperature curve that has given the best results to date with jack pine. This curve is shown in Fig. 1 and was followed in all cooks.

Materials

The wood was well seasoned jack pine from northern Wisconsin. The acid used was made up to give a uniform free sulphur dioxide content in the first three cooks. In these the combined sulphur dioxide was 2.00 per cent, 1.60 per cent, and 1.20 per cent.

In the second three cooks the excess sulphur dioxide was kept nearer to a constant value than in the first three and the combined varied as in the first three cooks. The base used was high grade calcium lime.

Table 1 gives the concentration of chemical as total, free and combined sulphur dioxide and also the concentration of excess sulphurous acid in the acid after dilution by the water in the wood.

Table 1. -- Composition of cooking acid yield and chemical analysis of pulp.

Cook No.	Sulphur dioxide				Screened pulp	Cellulose on basis of wood	In pulp		Bleach
	Total	Free	Combined	Excess			Lignin	Cellulose	
	Per cent				Per cent		Per cent		
664-I	6.40	4.48	1.92	2.56	44.5	42.2	2.4	94.7	24
665-I	6.07	4.50	1.57	2.93	43.8	42.2	2.4	96.3	15
666-I	5.62	4.42	1.20	3.22	42.4	41.0	2.8	96.7	18
668-I	7.18	5.17	2.02	3.15	44.8	42.8	1.8	95.5	15
669-I	6.67	5.06	1.61	3.45	44.7	42.8	2.6	95.9	18
671-I	5.53	4.26	1.26	3.00	44.3	41.8	3.0	94.3	15

Results and Discussion

Table 1 also gives the yield from the wood[3]. The uniformity of yield is noteworthy and if one has preconceived ideas as to the effect of acid composition upon yield it is rather disconcerting. Quite obviously one cannot show any variation in yield attributable to any of the factors in acid composition commonly considered. Total, free and combined as ordinarily understood in commercial practice do not appear to have any direct influence upon the yield from the wood when comparison is made on cooks carried on over the same temperature rise.

Table 2. -- Excess sulphur dioxide.

Cook No.	Raw acid	Six hours	Nine hours	Ten hours	Ten and one-half hours
664-I	2.56	1.85	1.03	0.77	0.54
665-I	2.93	2.04	1.00	.51	.22
666-I	3.22	1.96	1.08	.41	.24
668-I	3.15	1.96	1.18	.51	.45
669-I	3.45	2.38	1.10	.65	.13
671-I	3.00	1.96	1.25	.57	.27

Table 3. -- Total sulphur dioxide

664-I	6.40	3.93	2.45	1.59	0.54
665-I	6.07	4.00	2.24	1.15	.34
666-I	5.62	3.36	1.80	0.85	.30
668-I	7.18	4.36	2.66	0.87	.65
669-I	6.67	4.22	2.34	0.85	.29
671-I	5.53	3.28	2.03	0.77	.27

[3]Chemical analysis by M. W. Bray and T. M. Andrews, Forest Products Laboratory, Madison, Wisconsin.

Table 4. -- Free sulphur dioxide.

Cook No.	Raw acid	Six hours	Nine hours	Ten hours	Ten and one-half hours
664-I	4.48	2.89	1.74	1.18	0.54
665-I	4.50	3.02	1.62	0.83	.28
666-I	4.42	2.66	1.44	.63	.27
668-I	5.17	3.16	1.92	.69	.55
669-I	5.06	3.30	1.72	.75	.21
671-I	4.26	2.62	1.64	.67	.27

Table 5. -- Combined sulphur dioxide.

664-I	1.92	1.04	0.71	0.41	0.00
665-I	1.57	0.98	.62	.32	.06
666-I	1.20	.70	.36	.22	.03
668-I	2.02	1.20	.74	.13	.10
669-I	1.61	0.92	.62	.10	.08
671-I	1.26	0.66	.39	.10	.00

Further attention is directed toward the values for excess SO_2, that is the excess over that necessary to combine with the base as bisulphite. This should be thought of as sulphurous acid. In Table 2 this value is seen to vary markedly in the raw acid but upon further examination of the table it is seen that at and after the sixth hour this constituent of the cooking liquor is nearly constant in all cooks. In view of the remarkable uniformity of yield of screened pulp and cellulose the attention is centered at once upon this the only factor in acid strength and composition that shows a corresponding uniformity as is seen upon examining tables 3, 4 and 5. The reason for this uniformity is not far to seek if one considers the cooking acid to be composed of sulphurous acid and a bisulphite, in this case calcium bisulphite.

Upon heating a solution of a gas in water as is the case when sulphurous acid is considered, the elementary physics lead one to expect a driving out of the gas, and if the heating be carried on in a closed vessel, a generation of pressure. Further, the more gas is dissolved, the greater will be the pressure at any temperature. The numerical value for the pressure generated depends upon the conditions of the experiment and will not be taken up here except to reproduce the curves obtained when heating sulphurous acid in a closed receptacle in which the volume of the solution was 90 per cent of the total enclosed volume. (Fig. 2.) To determine roughly the effect of combined SO_2 or bisulphite SO_2 upon the system a further experiment was made by heating a cooking acid of 1.10 per cent combined. The variation in the pressure from that of a solution of sulphurous acid containing the same concentration of sulphurous acid as the excess sulphurous acid in the cooking acid was not within the range of sensitiveness of an ordinary pressure gauge, so for the purpose of this discussion it will be considered that the gas pressure generated during cooking results entirely from the excess sulphurous acid.

The explanation of the uniformity in concentration of excess sulphurous acid follows simply enough from the before-mentioned points. In the cooking of sulphite pulp the pressure is usually held at a certain maximum. This pressure is made up of steam pressure, gas pressure and at some stages hydrostatic pressure. In a system in which the volume of liquor and pressure are fixed as they are in commercial cooking, there can be only one concentration of excess sulphurous acid at every temperature. In other words, when a digester has reached 120° or any other temperature along the rise the concentration of excess sulphurous acid will be the same at the maximum pressure regardless of the concentration of excess sulphurous acid in the raw acid. This statement is strictly true when certain factors such as quantity of liquid in the digester are constant and equilibrium is maintained and in commercial practice it is only possible to say that the concentration of excess sulphurous acid is approximately the same at the same temperature and pressure maximum. The closeness of approximation to be expected is seen in Table 2, that of the concentration of excess sulphurous acid at different stages of the cook.

The addition of quantities of calcium base above that required does not appear to increase the yield from the wood and when a certain maximum is exceeded is detrimental because of precipitation of base in the digester. This maximum was exceeded in the cooks made with 1.60 per cent combined or more and in all these the base precipitated between the ninth and tenth hour. This is further corroboration of the view held by the majority of those connected with the industry and expressed

in the publications of this laboratory by S. E. Lunak[4] that additional calcium base above a certain minimum is unnecessary or undesirable. The numerical value for that minimum in commercial practice is variable and ranges between 0.9 per cent and 1.40 per cent combined sulphur dioxide.

Summary

In the previous publications in this series it has been pointed out that a high free acid was necessary to produce a well cooked easy-bleaching pulp under the cooking conditions outlined, that is, a relatively fast cook, and that the reactions involving the combination of sulphur and base with the wood material were of secondary importance from the standpoint of yield and quality of pulp. The results obtained in this series make it possible to make a still more definite statement, namely, that as regards acid composition that part of the so-called "free" which is present as excess sulphur dioxide is the factor having the greatest influence on the character and yield of pulp and that under the conditions studied, the amount or concentration of calcium base is without great influence if above a certain minimum.

The opinion has been long held by well-informed sulphite chemists that an important reaction in the pulping of wood by the sulphite process was a hydrolytic reaction. This is often lost sight of in commercial cooking in the perplexity caused by the influence of variables of a physical nature. The data in this and previous papers of this series strengthens the opinion as to the importance of considering the sulphite pulping process, from one point of view, as an acid hydrolysis of wood.

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[4] U. S. Department of Agriculture Bulletin No. 620.

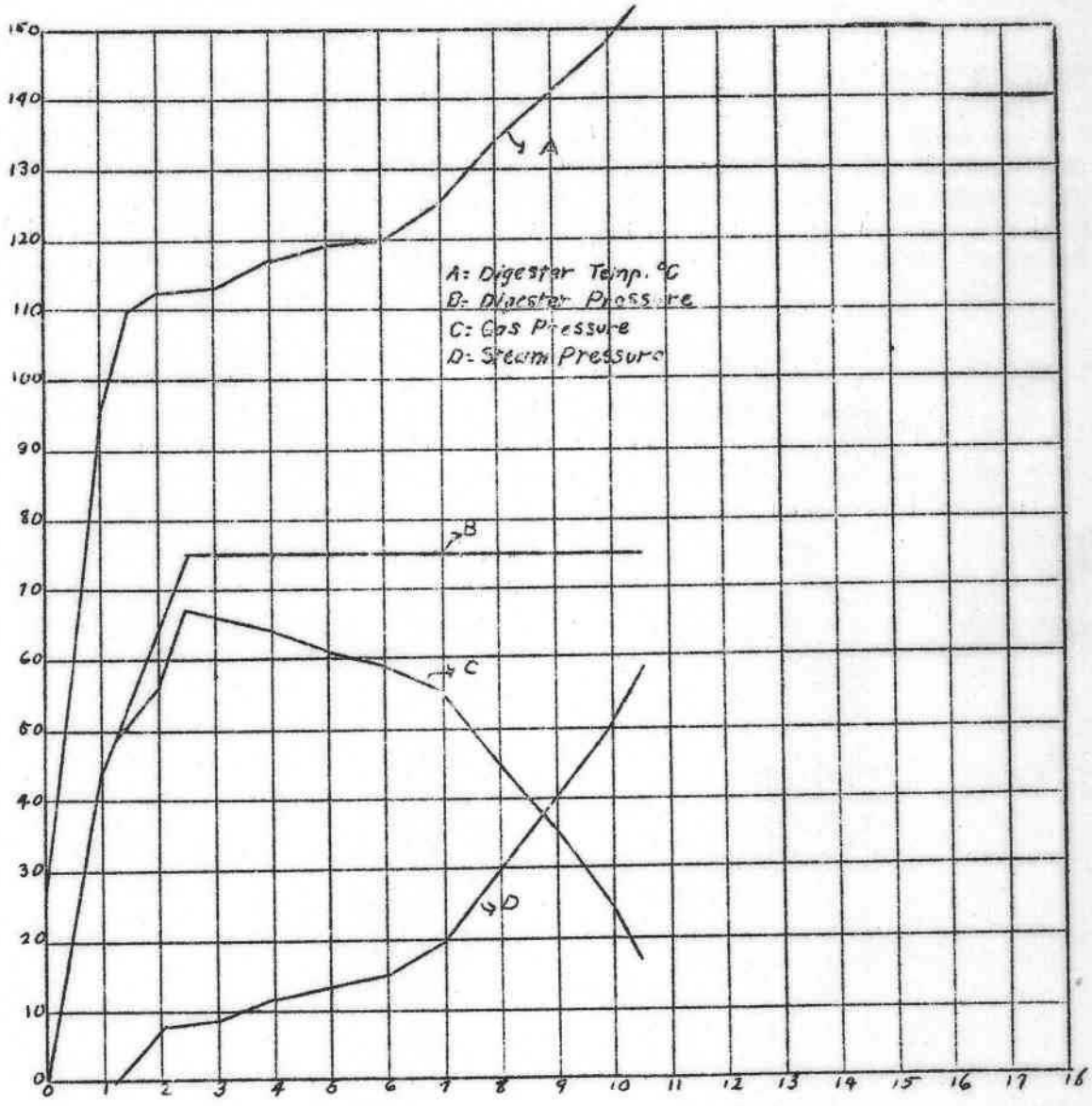
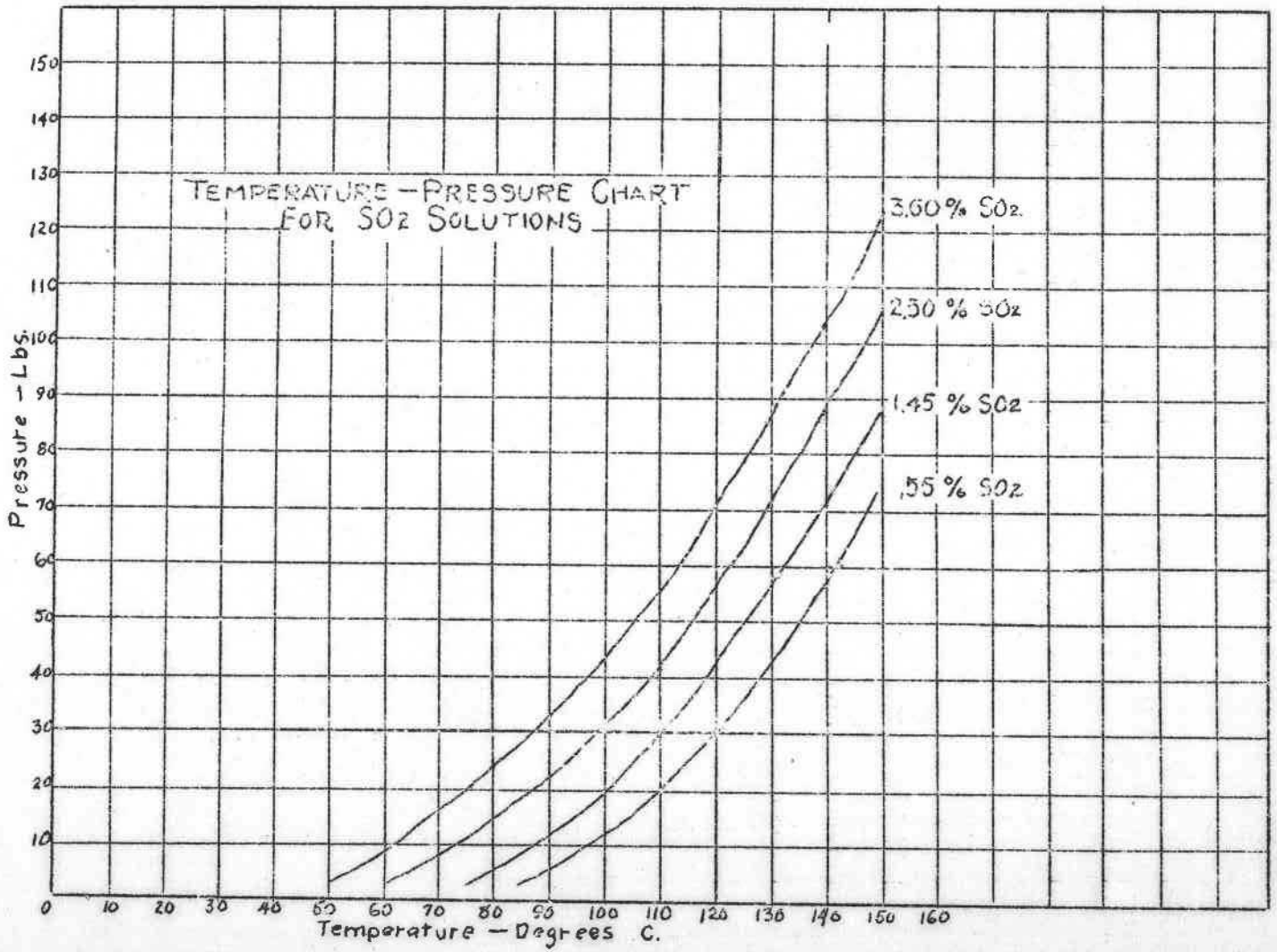

A: Digester Temp. °C
B: Digester Pressure
C: Gas Pressure
D: Steam Pressure
A
B
C
D
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18

FIGURE 1

R9


TEMPERATURE – PRESSURE CHART
FOR SO2 SOLUTIONS
3.60% SO2
2.50 % SO2
1.45 % SO2
.55 % SO2
Pressure – Lbs.
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
Temperature – Degrees C.