

Effect of pH on Sulphite Pulping of Holocellulose of *E. Tereticornis*

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INTRODUCTION

Today the sulphite and kraft processes are the main methods of producing chemical pulps. American chemist Benjamin Tilghman was the pioneer of the sulphite process. For many decades following 1890, the sulphite process was the most, important wood pulping process throughout the world because it yielded the brightest unbleached chemical pulps and could easily be bleached to high brightness.

Bisulphite process is of comparatively recent development. Haggland⁽¹⁾ and Hall and Stockman⁽²⁾ have described some earlier work on this process. First detailed study on bisulphite process was carried out by Husband⁽³⁻⁵⁾ Hart^(6,7) and Giertz⁽⁸⁾ simultaneously. Today bisulphite pulps are used in a number of products e.g. newsprint, board, fine papers tissue etc.

The action of sulphite process on the complex carbohydrate polymer system is widely varied and is dependent upon many factors⁽⁹⁾. The pH plays a most important role in chemical reactions and sulphite pulping is no exception. Chemically, the reactions of the sulphite cook can be subdivided⁽¹⁰⁾ into sulphonation, condensation, hydrolysis and redox reactions. Sulphonation mainly occurs with lignin but as a side reaction with carbohydrate also, condensation mainly concerns lignin and certain extractives, but is not completely excluded for some carbohydrates and their degradation products. Hydrolysis occurs in lignin as well as hemicelluloses and celluloses. Redox-reactions occur in the inorganic decomposition reactions, but also with carbohydrates and may also be the cause of some colour reaction of lignin. Thus there are numerous reactions taking place during sulphite cook, and that

they are influenced in different ways by the change of pH, a new type of pulps and improvements of different types can be expected.

EXPERIMENTAL

PREPARATION OF COOKING LIQUOR

For the sulphite pulping, cooking liquor was prepared by dissolving 10 g. of sodium meta-bisulphite in 150 ml of distilled water in well stoppered bottle. Generally, cooking liquor should be prepared freshly or 2-3 hours before pulping. pH of the cooking liquor was maintained either by adding dilute solution of ammonia or hydrochloric acid for alkaline or acidic range respectively.

TITRATION OF COOKING LIQUOR

Reagents :—10% KI, 0.2N H_2SO_4 , N/10 KIO_3 , starch. (N/10 KIO_3 was standardized by N/10 sodium thiosulphate by iodometric titration method).

Titration :—2 ml. of cooking liquor was pipetted out into 200ml. Erlenmeyer flask and diluted to about 100ml. with distilled water. Now 10ml. of 0.2 NH_2SO_4 and 10ml. of 10% KI were added alongwith 2/3 amount of N/10 KIO_3 solution for immediate reaction. After that starch was added as indication and whole solution was titrated against N/10 KIO_3 till a blue colour noted down. The amount of sulphurdioxide present in cooking liquor was calculated as follows :—

$$\text{gm. of free SO}_2/100 \text{ ml.} = \frac{\times \text{amount of N/10 KIO}_3 \times 0.16}{}$$

SULPHITE PULPING

Eucalyptus tereticornis holocellulose which was prepared by Wise and co-worker⁽¹¹⁾ was put to sulphite cooking by the following conditions :—

- A. Total percentage of sulphur di-oxide = 8%
- B. Bath ratio = 1 : 8

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- C. Initial pH = 4.5, 6.5 & 8.5
D. Maximum temperature = 153°C
E. Time of reaction
Room temp. to 110°C = $\frac{1}{2}$ hr.
at 110°C = 1 hr.
110°C—153°C = $\frac{1}{2}$ hr.
at 153°C = 0, 15, 30, 60 minutes

The principle variable in sulphite pulping for a given digester charge are temperature of cooking, free sulphur di-oxide present, total sulphur-di-oxide present, bath ratio and time of cooking. These variables are common for sulphite pulping carried out at pH 4.5, 6.5 and 8.5.

Twelve pulping experiments were carried out under above condition to see the effect of pH, cooking time on the degradation of holocellulose during pulping.

5 gm. of holocellulose (O.D. basis) was taken in each stainless steel bombs alongwith sulphite cooking liquor. Bomb was sealed and kept in stainless steel stationary digester containing water, under above conditions. After completing its maximum temperature and time, digester was blown to remove the inside pressure. Sealed bomb was taken out from digester, cooked and opened. Residual liquor was obtained by filtering it on fine muslin cloth. pH of residual liquor was determined and residual SO_2 was determined by N/10

KIO_3 titration method. Sulphite cooked holocellulose was washed with distilled water till the traces of acid were removed and kept for airdrying and weighed.

NEUTRAL SULPHITE PULPING

PREPARATION OF COOKING LIQUOR :

The cooking liquor was prepared by dissolving 4 gm. sodium sulphite and 1 gm. sodium bicarbonate (3:1) in 250 ml. distilled water in well stoppered bottle. pH of cooking liquor was taken by pH meter at room temperature. Amount of free SO_2 present per 100 ml. of water was done by usual N/10 KIO_3 titration method.

Four samples of holocellulose were cooked under the condition mentioned earlier. Digestion was carried out in a similar manner as described earlier.

CHEMICAL ANALYSIS OF SULPHITE AND NEUTRAL SULPHITE COOKED HOLOCELLULOSE

The yield, amount of SO_2 consumed, ash content, lignin content, alpha cellulose, pentosans, were carried out by Tappi Standards and Acetyl Value, and uronic anhydride by Dore method & Diskson method, respectively. Results are calculated and recorded in Table I, II, III and IV.

TABLE—I CHEMICAL ANALYSIS OF SULPHITE COOKED HOLOCELLULOSE AT pH 4.5
(% based on oven-dry weight of Holocellulose)

Sl. No.	Component	0 Mint.	15 mint.	30 mint.	60 mint.
1.	Total % of sulphur dioxide	8%	8%	8%	8%
2.	Bath ratio	1:8	1:8	1:8	1:8
3.	Initial pH of cooking liquor	4.5	4.5	4.5	4.5
4.	Maximum time (hour)	2.0	2.15	2.30	3.0
5.	Maximum temperature (°C)	153	153	153	153
6.	Final pH	3.9	3.6	3.5	3.3
7.	Percentage of SO_2 consumed/100ml	5.6	6.0	6.3	6.5
8.	Yield %	94	82	74	64.6
9.	Ash content %	0.38	0.6	1.0	1.0
10.	Klason lignin content, %	1.0	0.6	0.4	0.4
11.	Alpha-cellulose, %	60.5	67	70	78.4
12.	Acetyl value	—	—	—	—
13.	Pentosans	16.15	11.7	10.1	5.8
14.	Methoxyl value	1.7	0.91	0.71	0.64
15.	Uronic anhydride	3.62	3.5	3.42	3.35

TABLE—II CHEMICAL ANALYSIS OF SULPHITE COOKED HOLOCELLULOSE AT pH 6.5
(% based on oven-dry weight of Holocellulose)

Sl. No.	Component	0 mint.	15 mint.	30 mint.	60 mint.
1.	Total % of sulphur dioxide (%)	8	8	8	8
2.	Bath ratio	1.8	1.8	1.8	1.8
3.	Initial pH of cooking liquor	6.5	6.5	6.5	6.5
4.	Maximum time (hr.)	2.0	2.15	2.30	3.0
5.	Maximum temperature (°C)	153	153	153	153
6.	Final pH	5.1	4.8	4.5	4.4
7.	Percentage of SO ₂ consumed/100ml	5.6	5.9	6.3	6.4
8.	Yield %	82.1	74.1	69.7	64.5
9.	Ash Content (%)	0.2	0.3	0.3	0.3
10.	Klason lignin content (%)	0.62	0.54	0.3	0.3
11.	Alpha-cellulose (%)	66.0	69	73.4	80
12.	Acetyl value	—	—	—	—
13.	Pentosans	16.32	11.15	9.2	5.5
14.	Methoxyl value	0.96	0.71	0.68	0.50
15.	Uronic anhydride	3.6	2.95	2.8	2.55

TABLE—III CHEMICAL ANALYSIS OF SULPHITE COOKED HOLOCELLULOSE AT pH 8.5
(% based on oven-dry weight of Holocellulose)

S'. No.	Component	0 mint.	15 mint.	30 mint.	60 mint.
1.	Total % of Sulphur dioxide (%)	8	8	8	8
2.	Bath ratio	1:8	1:8	1:8	1:8
3.	Initial pH of cooking liquor	8.5	8.5	8.5	8.5
4.	Maximum time (hr.)	2.0	2.15	2.30	3.0
5.	Maximum temperature (°C)	153	153	153	153
6.	Final pH	6.4	6.0	5.4	5.3
7.	Percentage of SO ₂ consumed/100ml.	5.7	5.9	6.2	6.35
8.	Yield	80	70.6	67	60.8
9.	Ash Content (%)	0.2	0.3	0.4	0.4
10.	Klason lignin content (%)	0.6	0.4	0.2	0.2
11.	Alpha-cellulose (%)	65	70	75	85
12.	Acetyl value	—	—	—	—
13.	Pentosans	14.2	10.3	8.4	5.01
14.	Methoxyl value	0.94	0.78	0.53	0.40
15.	Uronic anhydride	1.04	0.520	0.414	0.21

TABLE—IV CHEMICAL ANALYSIS OF NEUTRAL SULPHITE COOKED HOLOCELLULOSE
(% based on oven-dry weight of Holocellulose)

Sl. No.	Component	0 mint.	15 mint.	30 mint.	60 mint.
1.	Total % of Sulphur dioxide (%)	8	8	8	8
2.	Bath ratio	1:8	1:8	1:8	1:8
3.	Initial pH of cooking liquor	9	9	9	9
4.	Maximum time (Hr.)	2.0	2.15	2.30	3.0
5.	Maximum temperature (°C)	153	153	153	153
6.	Final pH	7	6.9	6.8	6.7
7.	Percentage of SO ₂ consumed/100ml.	5.9	6.02	6.1	6.25
8.	Yield	73.9	72.1	70.1	68.2
9.	Ash Content %	2	1.4	0.96	0.36
10.	Klason lignin content %	1.01	1.15	2.1	2.6
11.	Alph-cellulose %	74.6	75.7	76.6	78.6
12.	Acetyl value	—	—	—	—
13.	Pentosans	11.27	11.01	10.1	9.47
14.	Methoxyl value	1.0	0.56	0.41	0.24
15.	Uronic anhydride	3.61	2.99	2.84	2.72

RESULTS AND DISCUSSION EFFECT OF pH AND COOKING TIME ON YIELD

It is observed from tables I, II, III, IV that when the cooking of holocellulose was carried out at different pH levels of 4.5, 6.5 and 8.5, the loss in carbohydrate material was 6 to 35%, 18 to 36%, and 20 to 36% respectively. The cooking required approximately 6.5 to 5.6 percent sulphur dioxide based on oven dry holocellulose. Consumption of sulphur dioxide may be an indication of degree of sulphonation of the lignin in holocellulose since original holocellulose has only about 1.25% lignin, the consumption of SO_2 /100 ml. is very low, whereas in the case of sulphonation of original wood which has 25.46% lignin, the percentage of SO_2 consumption is very high (9.52%) at pH 4.5. Fig. 1, 2 show that residual pH and increase in cooking time has no effect on sulphur-dioxide consumption during sulphite pulping. Consumption of sulphur-dioxide in case of neutral sulphite cooking was much higher (i.e. from 5.9 to 6.3%) than that of sulphite cooked holocellulose.

It is evident from the results and Fig. 3,4 that there is a gradual decrease in yield with increase in cooking time and residual pH. Yield decreases more at pH 8.5 while less at pH 4.5 but

yield at pH 6.5 is approximately the same as it was pH 8.5 but in case of N.S.S.C. pulping gradual decrease in yield is not so prominent which is due to the selective delignification with as much of the hemicellulose preserved as possible.

EFFECT OF pH AND COOKING TIME ON KLASON LIGNIN

Acid insoluble lignin or klason lignin content considerably decreases from 1 to 0.4%, 0.6 to 0.3% and 0.6 to 0.2% when cooking was carried out at pH 4.5, 6.5 and 8.5 respectively due to the formation of lignosulphonates. From Table I, II & III, it is observed that a minimum of 0.2% lignin always remained in the cooked holocellulose. By making the cooking conditions more severe i.e. by varying the pH of the cooking liquor and time of cooking the lignin content of the resultant holocellulose could not be lowered below 0.2%. This may be due to the fact that this small amount of lignin is present as lignin carbohydrate complex which could not be removed under the normal pulping conditions. Fig. 5 and 6 shows that delignification is maximum at pH 8.5 followed by at pH 6.5 and 4.5. At all pH conditions, acid insoluble lignin decrease as the cooking time increases from 0 to 60 minutes. With yield klason

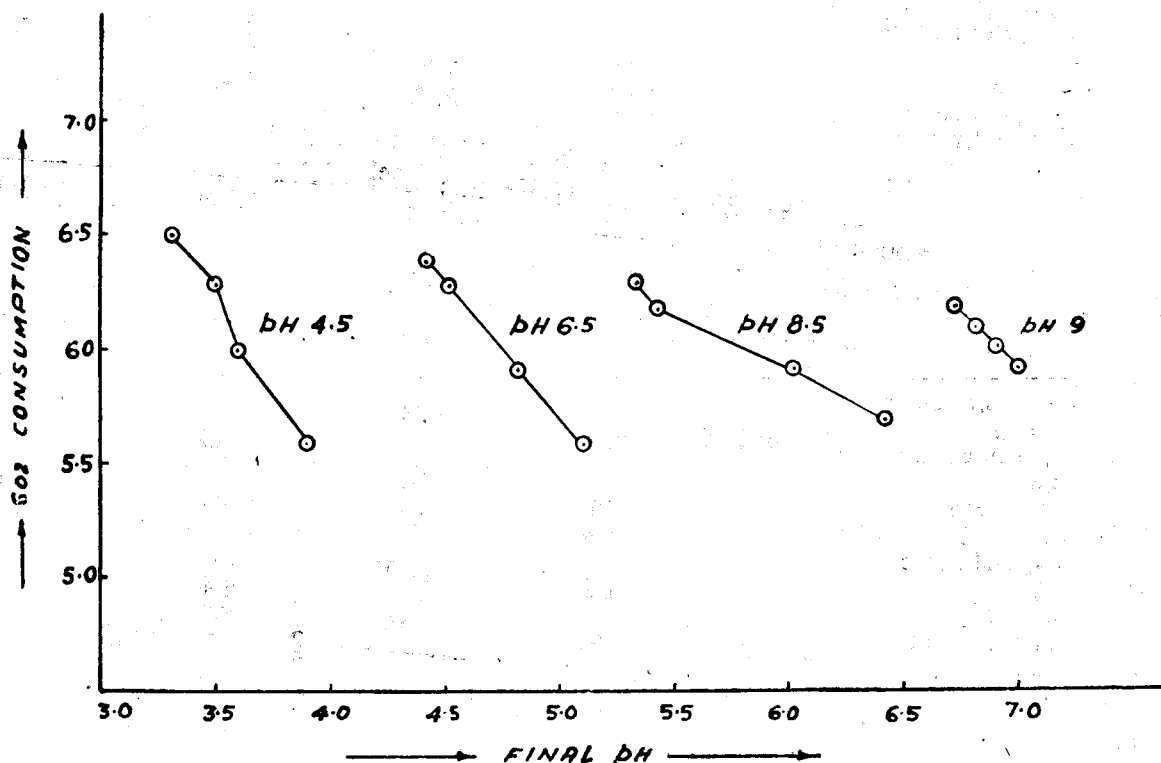


Fig. 1 Variation of SO_2 Consumption with Final pH

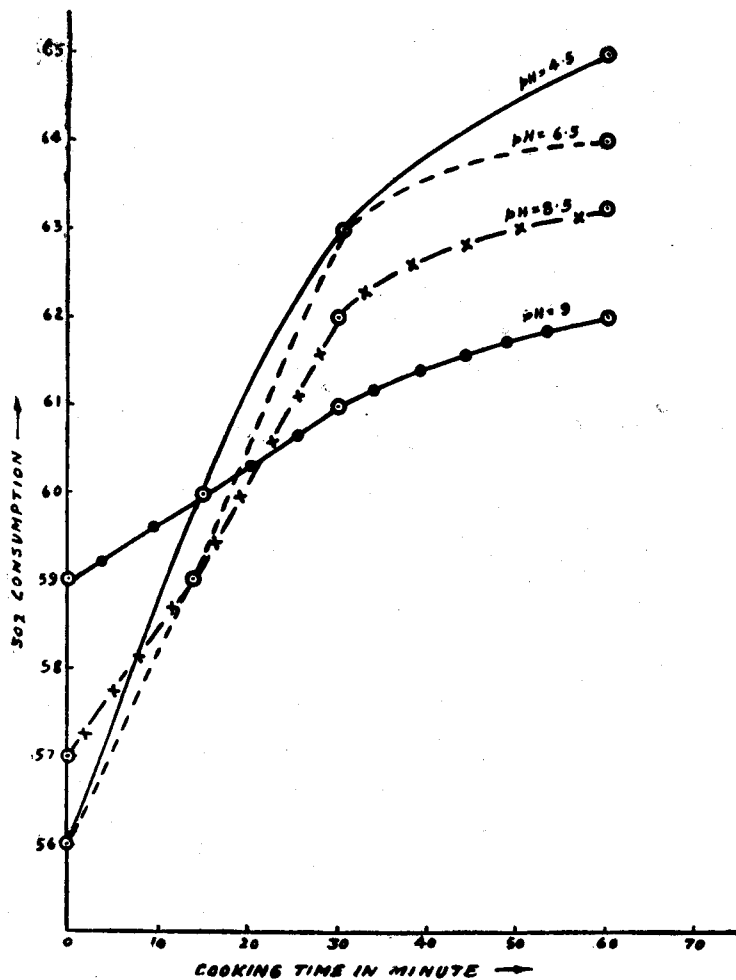


Fig. 2 Relationship Between SO_2 Consumption and Cooking Time

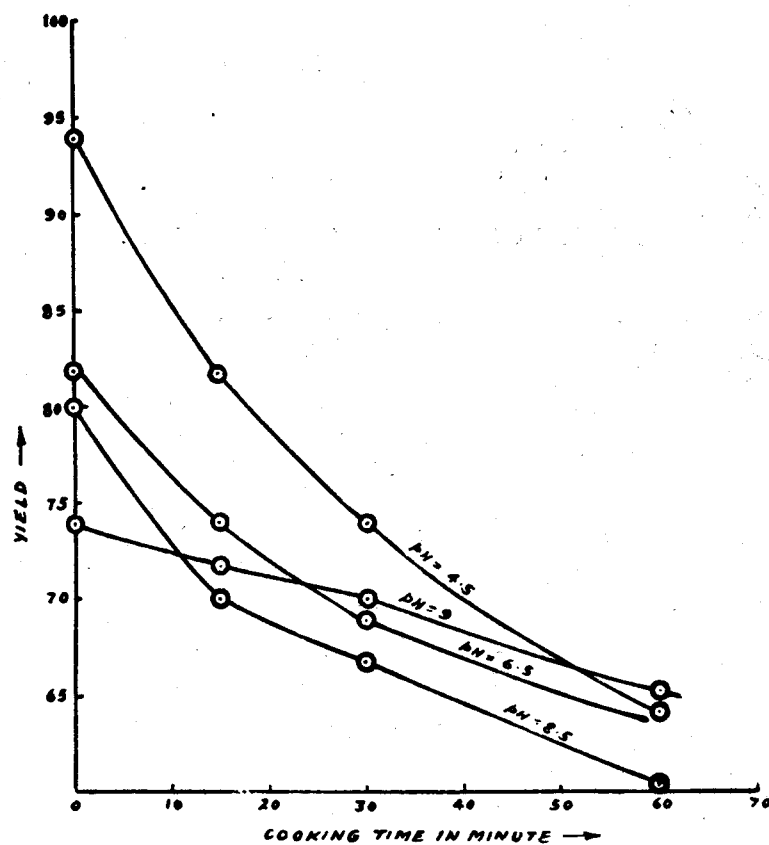


Fig. 3 Variation of Yield With Cooking Time.

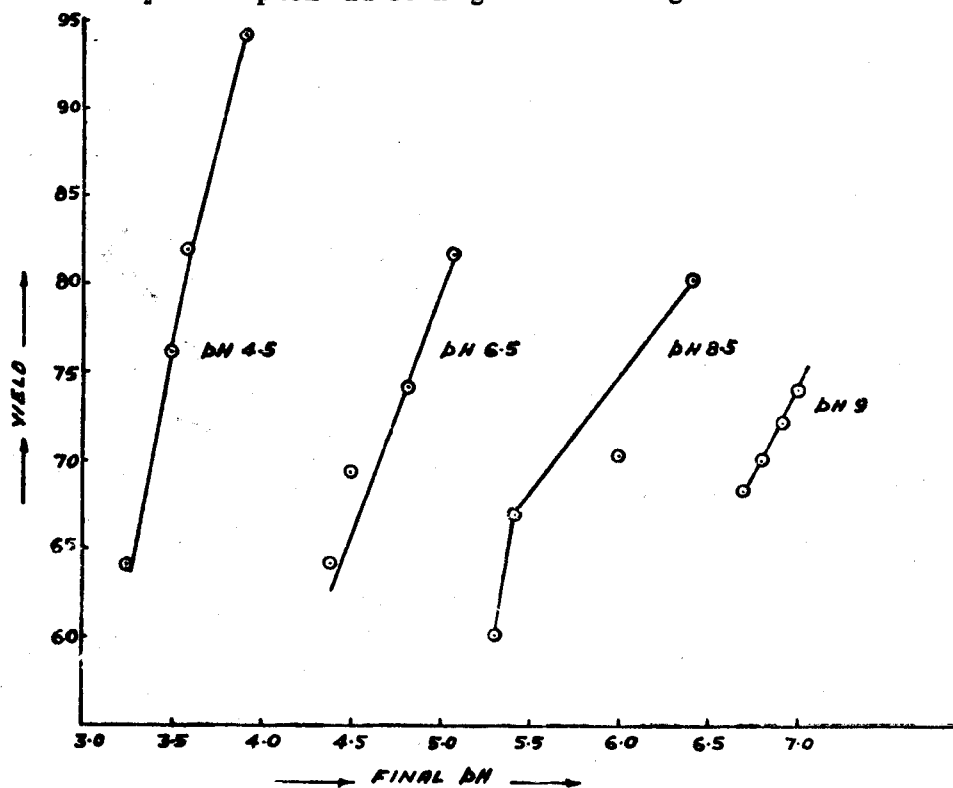


Fig. 4 Relationship Between Yield and Final pH

lignin has direct relationship i.e. klason lignin content increases as yield increases from 65 to 94 percent. Delignification in N.S.S.C. pulping is less in comparison to sulphite pulping. Abnormally high value of lignin content in N.S.S.C. cooked holocellulose i.e. from 1.01 to 2.6 percent indicates (i) some sort of condensation reaction taking place (ii) degradation of carbohydrate dominates over lignin, removal during cooking at 153°C which is responsible for its high percentage.

EFFECT OF pH AND COOKING TIME ON ALPHA-CELLULOSE

It is seen from Fig. 7 that there is more or less uniform increase in alpha-cellulose content (60.5 to 85%) as cooking time increases from 0 to 60 minutes at 153°C. Percentage of alphacellulose is maximum at pH 8.5 followed by that at pH 6.5, while at pH 4.5, it is minimum in comparison to sulphite pulping carried out at higher pH, while in N.S.S.C. pulping there is less gradual increase in alpha-cellulose content (74.5 to 78.6%). This is due to the retention of hemicellulose and less dissolution and hydrolysis of low molecular weight polysaccharide during N.S.S.C. pulping. Fig. 8 shows that yield is inversely proportional to alpha

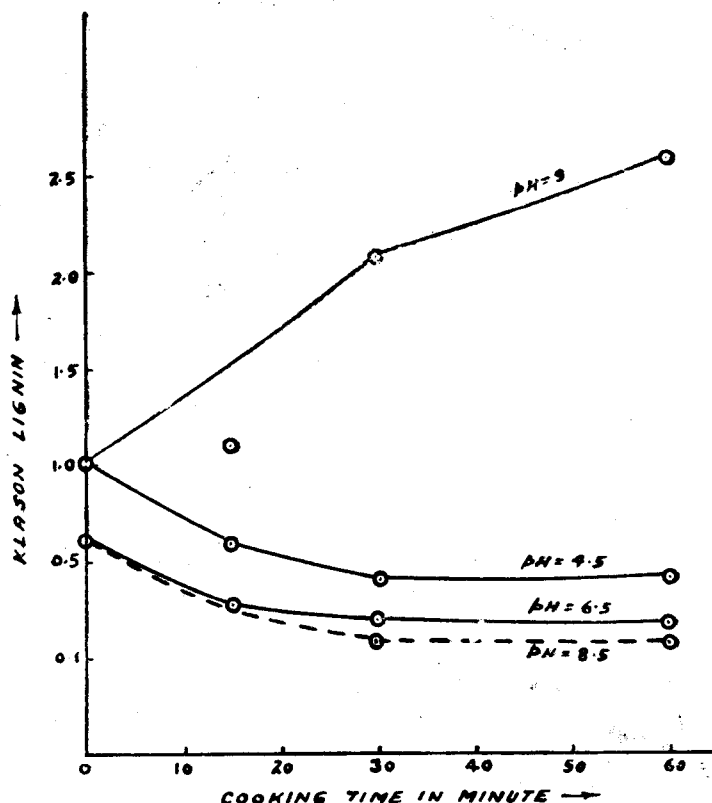


Fig. 5 Relationship Between Klason Lignin and Cooking Time

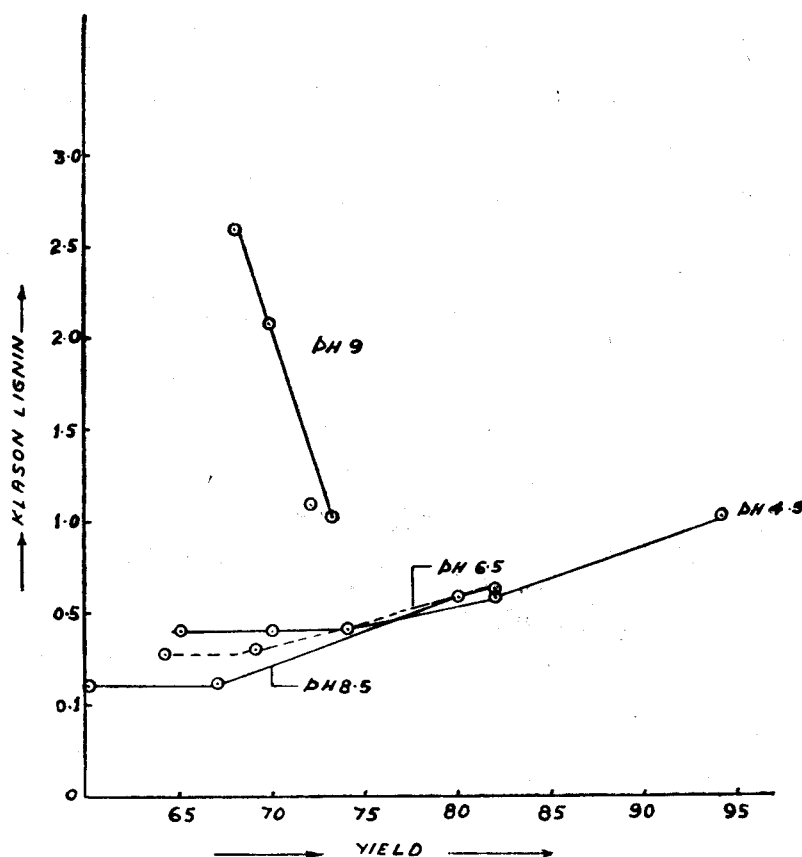


Fig. 6 Relationship Between Klason Lignin and Yield

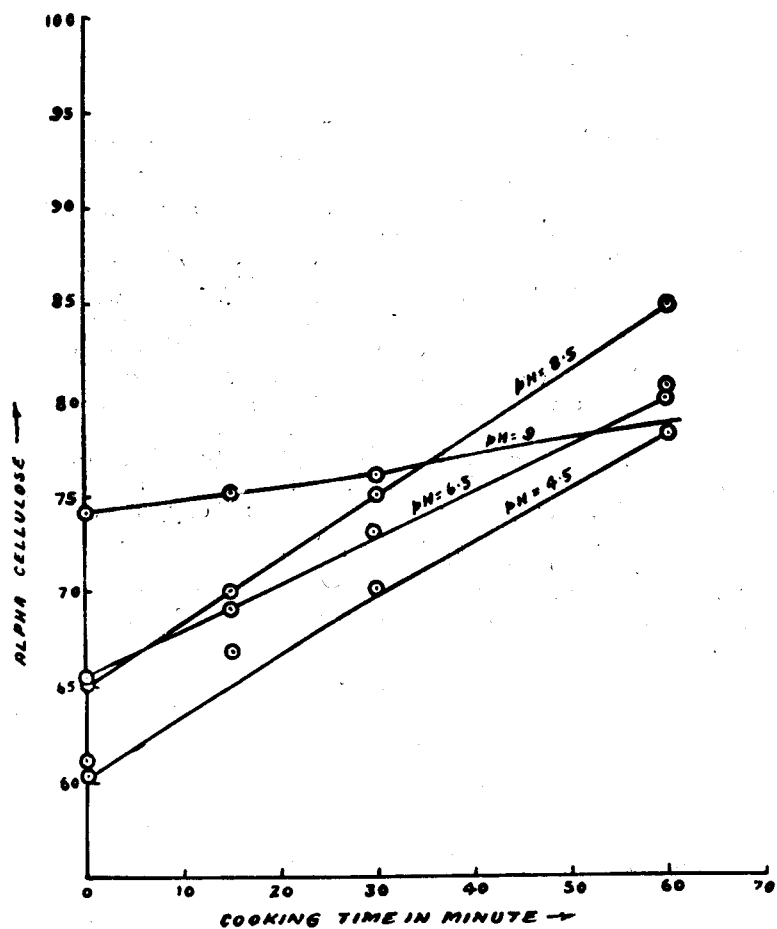


Fig. 7 Relationship Between Alpha Cellulose and Cooking Time

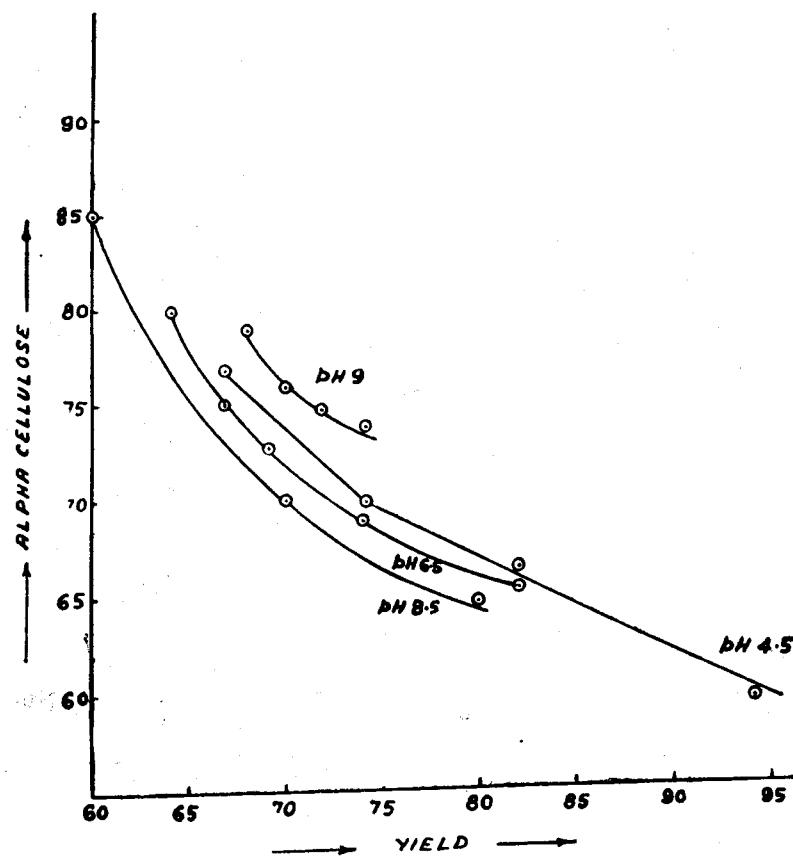


Fig. 8 Relationship Between Alpha Cellulose and Yield

cellulose content i.e. alpha-cellulose content increases considerably as yield decreases from 94% to 65%.

EFFECT OF pH AND COOKING TIME ON PENTOSANS

Fig. 9 shows that Pentosans (derived from xylose and arabinose) in holocellulose decrease from 16.15 to 5.1 percent as cooking time increases. This is due to the formation of more volatile furfural from xylose while pentosans value in N.S.S.C. cooked holocellulose is high in comparison to sulphite cooked holocellulose which indicates that most of the lower molecular weight polysaccharides are retained in holocellulose, cooking time has less effect on degradation of pentosan content during N.S.S.C. pulping. Fig. 10 shows that as yield increases from 60 to 94 percent, pentosans content increases. It is maximum at pH 4.5 followed by at pH 6.5 and 8.5.

EFFECT OF pH AND COOKING TIME ON ACIDIC SUGAR

Acidic sugar in holocellulose is approximately 3.68% but with cooking time it decreases gradually from 3.62 to 0.21% (Fig. 11). Uronic acid decreases less (i.e. 3.62 to 3.55) at pH 4.5, (3.6 to 2.55%) at pH 6.5. The chances of less decrease in uronic acid content during sulphite cooking at pH 4.5, 6.5 is due to the electron attracting ability of the carboxyl groups or carbonyl groups or due to the different conformation and stereo-chemistry of sugars (i.e. mannose xylose (no C-6). In the case of carboxyl group, this results in a partial positive charge on C-1 glycosidic oxygen which would repel the approach of the hydrated hydrogenion, thus increasing the resistance of this bond towards acid hydrolysis, while uronic acid at pH 8.5 is too low i.e. from 1.04 to 0.21%. Neutral sulphite pulping does not have much effect on uronic acid. The

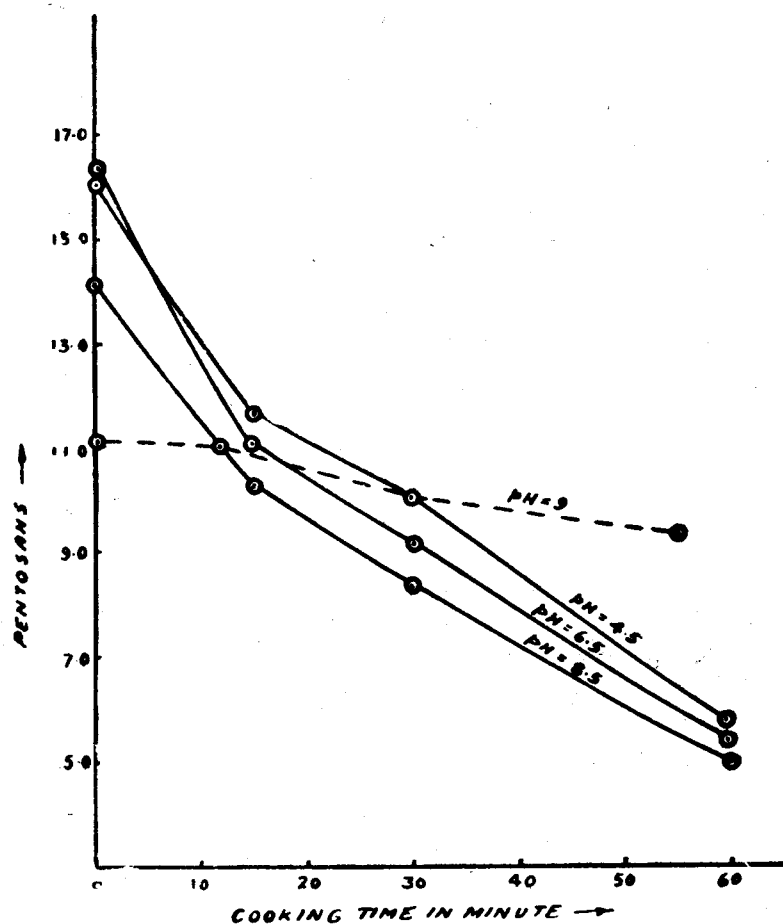


Fig. 9 Variation of Pentosans with Cooking Time

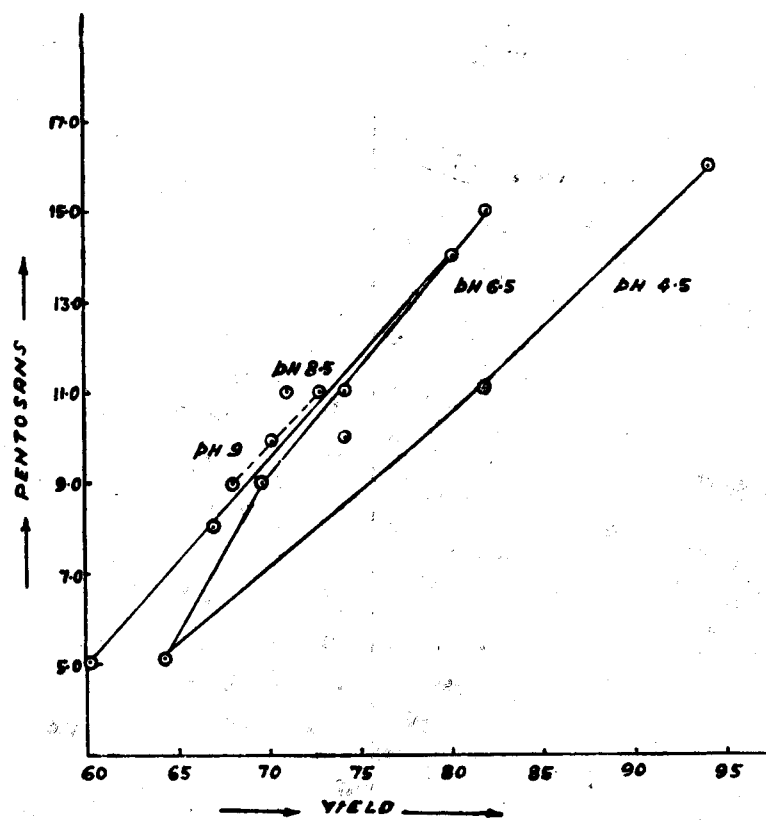


Fig. 10 Variation of Pentosans with Yield

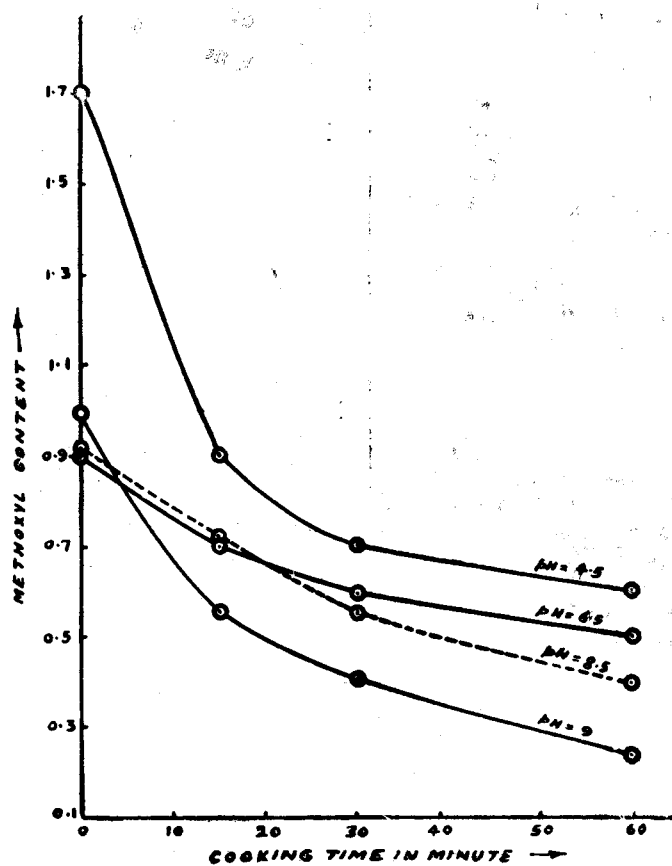


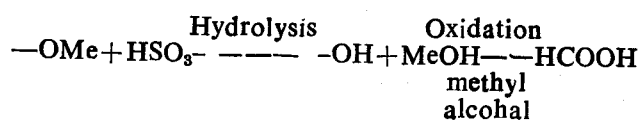
Fig. 11 Variation of Uronic Anhydride with Cooking Time

values in N.S.S.C. cooked holocellulose varies from 3.6 to 2.77% which is very much near to original holocellulose value i.e. 3.6%.

EFFECT OF pH AND COOKING TIME

ON METHOXYL AND ACETYL GROUPS

Eucalyptus tereticornis holocellulose originally contained 3.36% methoxyl content. This can be seen from Table I, II, III, IV that methoxyl value decreases considerably on pulping. Fig. 12 shows that with cooking time, methoxyl value decreases from 1.7 to 0.64%, 0.96 to 0.50%, 1.94 to 0.4%, 1.0 to 0.24% as cooks were carried out at different pH levels. This is due to the hydrolysis of —OMe group in methyl alcohol and finally into formic acid as follows :



Similarly, holocellulose has 1.01% acetyl content which was also hydrolysed during pulping into acetic acid and was responsible for the acidity of residual liquor. Absence of acetyl content in cooked holocellulose indicates the complete hydrolysis of acetyl group during pulping.

Thus, it can be concluded from the above discussion that klason lignin, pentosans, methoxyl groups, uronic acid continuously decrease as cooking time increases. Degradation of pentosans and cellulose, dehydration of pentose sugars into volatile furfural, decarboxylation of uronic acid and hydrolysis of 1-4-B glycosidic bonds of hexoses and pentoses into simple monomer and hydrolysis of methoxyl and acetyl groups into methyl alcohol and acetic acid respectively, are maximum at 153°C at 3 hrs. and minimum at 2 hours cooking at 153°C, while alpha cellulose contents increase as the cooking time increases gradually. Besides this, pH of cooking liquor plays an important role during pulping processes. In sulphite pulping yield decreases from 94 to 64% as pH increases from 4.5 to 8.5. Percentage of alpha-cellulose increases from 60.5 to 85% as pH increases. Degradation, hydrolysis and dissolution of sugars like pentoses and hexoses are prominent reactions during acidic range of sulphite pulping i.e. at pH 4.5, while hydrolysis redox-reaction, decarboxylation are prominent at neutral and alkaline pH i.e. 6.5, and 8.5 respectively. Thus, this type of sulphite pulping is useful for making rayon grade pulp where retention of hemicellulose is less.

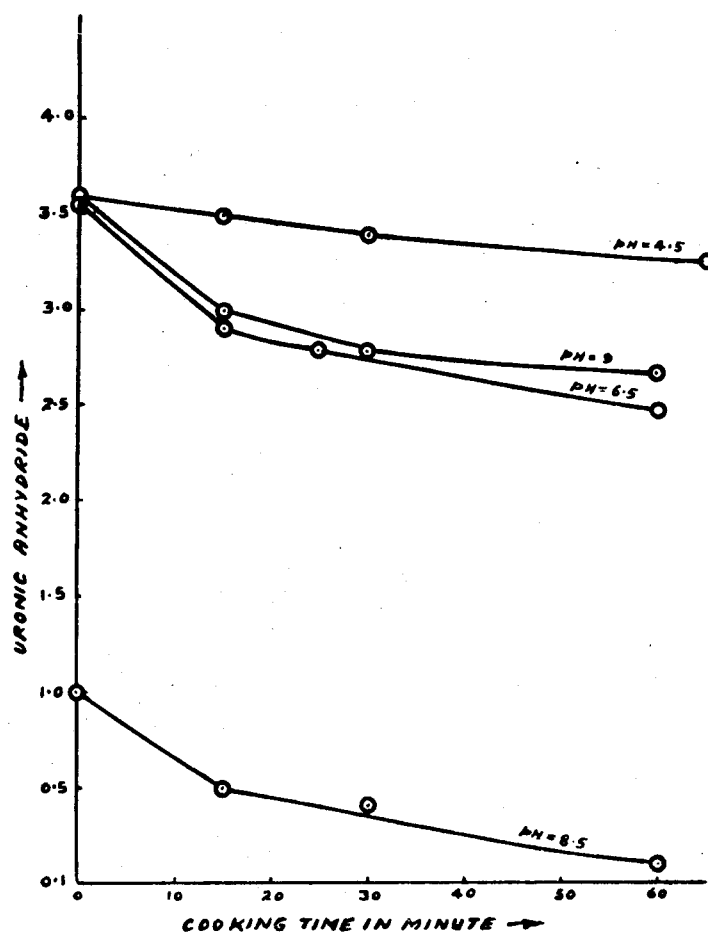


Fig. 12 Relationship Between Methoxyl Content and Cooking Time

Cooking time and pH play minor role on N.S.S.C. cooked holocellulose and they retain as much hemicellulose as possible during pulping. This indicates that degradation, dehydration, decomposition dissolution, hydrolysis and redox reaction of holocellulose are less prominent during N.S.S.C. pulping. Thus, this type of pulping is useful in making corrugated paper board because pulp yield is high and pulp is strong due to retention of hemicellulose.

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