High Yield Pulp Production by Modified Sulfite Process

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INTRODUCTION

During recent years there has been an increasing interest in high yield pulp production. High yield pulp has already been obtained by mechanical, chemi-mechanical and semichemical pulping proocesses, but these pulp contain more lignin than the conventional chemical pulp. Therefore, refining and beating have little effect on fibrillation of pulp fiber, and the strength of paper therefrom is relatively low. Consequently, a process for making high yield pulp, which is easily refined and beaten to produce a high strength paper, is desired.

This paper discusses a new pulping process, so-called sulfomethylation process, in which sodium sulfite and formaldehyde are used as the softening agents of coarse pulp and wood chips.

SOFTENING AGENT

Sodium sulfite, formaldehyde and water react to make sodium hydroxymethylsulfonate by the following reaction:

$$Na_2SO_3 + CH_2O + H_2O \rightleftarrows HOCH_2SO_3Na + NaOH$$

A pH range 12.4 to 12.7 of the resulting aqueous solution suggests that about 10% by weight of the original sodium sulfite is converted to sodium hydroxymethylsulfonate under the preparative conditions described later. Consequently, the aqueous solution contains sodium sulfite, formaldehyde, sodium hyroxymehhylsulfonate and sodium hydroxide.

The softening agent prepared as above reacts with lignin in wood. Details of the reaction have not been confirmed, but it seems that (i) formaldehyde is added to the aromatic ring in lignin to form a methylol group and then the methylol group is sulfonate with sodium sulfite; (ii) ortho position of phenolic hydroxyl group in lignin is directly sulfomethylated with sodium hydroxymethylsulfonate; and (iii) in addition to the above, the benzylalcoholic hydroxyl group of side chain in lignin should be sulfonated according to the sulfonation mechanism of lignin (1). These reactions are summarized in **Fig. 1.**

In cooking, the lignin which does not combine with carbohydrate is partly dissolved in the cooking solution, while the lignin which combines with carbohydrate is converted to the hydrophilic and soft state by sulfomethylation and sulfonation. The resulting cooked chips may be easily defiberized mechanically without fiber shortening and specific fiber damage. Furthermore, fiber containing such a type of lignin may be easily fibrillated by refining and beating.

EXPERIMENTAL

Raw Material

Spruce (Picea jezoensis) and beech (Fagus crenata) wood meals, thoroughly extracted with alcohol-benzene (1 : 2), were used for the preliminary cooking test.

Larch (Larix Kaempferi) refiner groundwood, which was treated by the classifier to remove to fine portion, was used as the pre-defiberized material. Removal of the fine portion was to increase the freeness of pulp, and to elucidate the behaviour of beating.

Fir (Abies mariyana) and mixed hardwoods chips were also submitted to cooking. Mixed hardwoods chips which were fractionated by screen having hole with 13 and 31 diameters, consist of

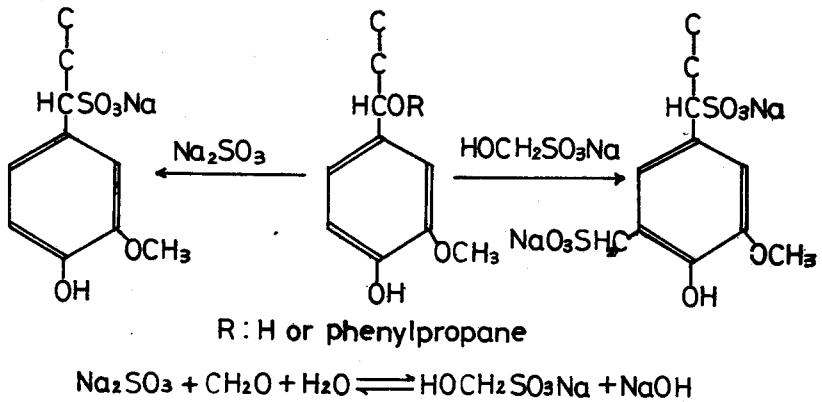

Fig. 1. Sulfonation and sulfomethylation of lignin.

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30% of oak (Quercus serrata), 20% of maple (Acer mono), 19% of elm (Ulmus davidiana), 15% of basswood (Tilia japonica), 9% of sen (Kalopanax septemlobus) and 7% of alder (Alnus japonica). These hardwoods are native to Hokkaido, Japan.

Cooking

Two types of cooking methods were adopted here. One way, liquid phase cooking, was carried out under elevated temperature and pressure with the aqueous solution of sodium sulfite and formaldehyde. Wood chips were pre-soaked in the cooking solution for 30 min. under reduced pressure of 30 — 40 mm Hg. Wood-to-liquor ratio was 1 : 6. In another way by Laboratory Defibrator (Defibrator Co., Sweden), the wood chips were pre-soaked in the cooking solution under the reduced pressure of 30 —40 mm Hg., then excess solution was removed, and subsequently the chips were heated by steam as in the conventional vapor phase cooking. Wood-to-liquor ratio was 1 : 2.5 after the relief of excess solution. In this case, the cooking time could be decreased appreciably.

Refining

In the liquid phase cooking, the cooked chips were defiberized in 8-in. Bauer Bros. laboratory single disk refiner, once with plate No. 8117 at a 0.002-in. clearance and twice with plate No. 8114 at a 0.001-in. clearance. The knots were removed on a vibrating flat screen having 0.016-in. slots. In the vapor phase cooking, the cooked chips were defiberized in Laboratory Defibrator at 150°C for 2 min., and then knots were removed.

Physical Properties of Pulp Sheet

The pulp thus obtained was beaten by a Lampen mill, and then prepared into handsheet. Physical properties of pulp sheet were tested according to TAPPI Standards.

TABLE I. Cooking Results of Spruce and Beech Wood Meals

Wood species	Cooking time, min.	pH of waste liquor	Yield, %	Klason lignin %
Spruce			100	28.0
„	30	7.8	90.9	24.3
„	60	7.7	88.3	24.0
„	180	7.6	86.4	18.2
Beech			100	22.4
„	30	7.4	81.4	18.4
„	60	7.3	79.3	15.6
„	180	7.2	75.4	14.3

RESULTS AND DISCUSSION

Cooking of Wood Meal

Cooking solution was prepared from 40 g. of sodium sulfite and 9.5 g of formaldehyde per liter, and the pH value of the solution was 12.4. Spruce and beech wood meals were cooked at 160°C for 30 — 180 min. As is evident from **Table I,** delignification with the solution of sodium sulfite and formaldehyde was not significant. This result suggests that lignin-carbohydrate linkage was rather stable because the pH value was maintained alkaline during cooking.

Cooking of Refiner Groundwood

The object of this experiment was to explore how the physical properties of pre-defiberized chips are improved by the treatment with the solution of sodium sulfite and formaldehyde. Kvisgaard (2) and Dahm (3) have treated groundwood with sodium hydroxide and sodium sulfite. They showed that the breaking length of treated groundwood could be improved considerably, especially in the case of sulfite treatment.

Cooking solution was prepared from 50 g of sodium sulfite and 11 g of formaldehyde per liter and the pH value of the solution was 12.7. Cooking was carried out 110°C — 150°C for 120 min. The pulp thus obtained was beaten in Lampen mill and prepared into handsheet. For comparative purpose, the same procedure as above was carried out, except that the cooking solution contained only sodium hydroxide (4g/l), and cooked yield at 150°C for 120 min. was 86.4% based on classified refiner goundwood.

Cooking conditions and results are shown in **Table II.** The beating of pulp (I, II and III) by Lampen mill was much easier than the original pulp, as shown

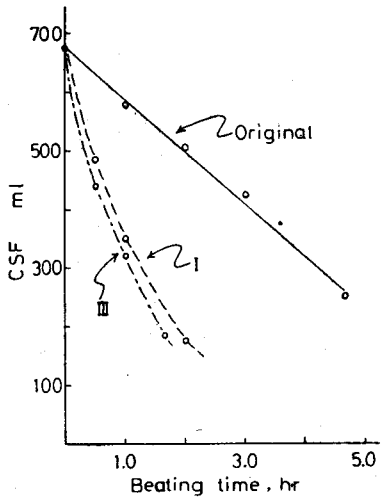

Fig.2. Canadian Standard freeness for various beating time.

in **Fig. 2.** This result shows that the pulp thus obtained had become hydrophilic by sulfomethylation and sulfonation of lignin. Further evidence for this concept are also supported by the distribution of fiber lengths of beaten pulp.

Strength properties of pulp sheet are sumarized in **Table III.** When the cooking temperature was increased from 110°C to 150°C, the strength of pulp sheet was improved, especially in the breaking length. Pulp treated wiht sodium hydroxide was much inferior to that with sodium sulfite and formaldehyde in strength properties, especially in the breaking length and burst factor.

Cooking of Wood Chips

It has been studied how the pH value of cooking solution influenes on the cooking results of wood chips. Three kind of cooking solution were prepared by mixing sodium sulfite 0—50g, sodium bisulfite 0—40 g and formaldehyde 11 g per liter. Mixed hardwoods chips were cooked at 150°C for 120 min. **Tables IV and V** show the results obtained at three different pH levels of the cooking solution. The results suggest that, in order to develop the strength properties, the cooking solution must be alkaline. Within a range of experiments, best result was obtained by a cooking solution of pH 12.7.

Tables VI and VII show some of the results of fir and mixed hardwoods chips by liquid phase and vapor phase cookings. All of the cookings were carried out with a solution containing 50 g of sodium sulfite and 11 g of formaldehyde per liter at 150°C for 39 — 120 min. in the liquid phase cooking, and for 4 — 8 min. in the vapor phase cooking. In order to clarify the efficiency of the addition of formaldehyde, the same procedure as above was carried out except that the cooking solution contained only so-

TABLE II. Cooking Results of Larch Refiner Groundwood.

Pulp	Cooking temp., °C	pH of waste liquor	Yield, %	Klason lignin, %
Original			100	26.9
I	110	9.4	95.9	24.7
II	130	8.5	92.7	23.6
III	150	7.9	89.1	19.6

TABLE III. Strength Properties of Larch Refiner Groundwood Handsheets

Pulp	CSF, ml	Basis wt. g/m²	Density, g/cm³	Breaking Length, km	Tear factor	Burst factor	MIT folding
	680	73.8	0.38	1.5	60.2	1.1	3
Origial	330	68.9	—	2.2	29.6	1.0	4
	487	62.7	0.59	2.9	52.6	1.4	5
I	350	66.9	0.62	3.9	35.9	1.5	4
	220	58.4	0.68	4.6	38.7	2.2	9
	469	66.0	0.65	3.9	53.0	1.6	4
II	347	65.5	0.68	4.0	42.5	1.7	13
	226	64.5	0.72	4.4	41.8	2.4	13
	445	65.3	0.73	5.1	62.1	2.8	41
III	324	66.5	0.81	5.6	49.0	2.8	59
	231	66.0	0.82	6.0	46.3	3.3	42
IV NaOH treated	242	73.4	—	3.4	39.2	1.4	28

TABLE IV. Cooking Conditions and Results at Different pH Levels of Solution.

	Comp. of cooking solution, a						
Pulp	Na_2SO_3 g/l	$NaHSO_3$ g/l	PH	Total yield, %	Screened yield, %	Screenings %	CSF, c ml
V	0	40	4.6(3.5)b	79.5	71.5	8.0	630
VI	25	20	11.9(6.7)	80.8	72.3	8.5	625
VII	50	0	12.7(7.7)	79.8	72.7	7.1	580

a: 0.396 mole sulfite plus 0.370 mole formaldehyde.
b: Data in parenthesis show pH value after cook.
c: CSF of screened pulp.

TABLE V. Strength Properties ofMixed Hardwood Pulp Handsheets.

Pulp	CSF, ml	Basis wt., g/m²	Density, g/cm³	Breaking length, km	Tear factor	Burst factor	MIT folding
V	325	63.7	0.46	2.8	32.1	1.2	2
VI	315	64.9	0.60	5.6	57.6	3.3	33
VII	310	63.6	0.67	5.9	66.0	3.9	52

TABLE VI. Cooking Conditions and Results of Fir and Mixed Hardwood.

Pulp	Wood species	Cooking method	Cooking time, min/a	pH of solution before	pH of solution after	Total yield, %	Screened yield, %	Screenings %
VIII	Fir	LP,Na_2SO_3	120	9.4	7.8	91.6	71.2	20.4
IX	Fir	LP,Na_2SO_3 +CH_2O	120	12.7	8.0	87.7	76.4	11.3
X	Mixed hardwood	LP,Na_2SO_3	30	9.4	7.0	85.3	82.3	3.0
XI			120	9.4	7.0	80.9	76.9	4.0
XII	Mixed hardwood	LP	30	12.7	7.9	84.7	80.9	3.8
XIII		Na_2SO_3 +CH_2O	120	12.7	7.6	75.7	71.9	3.8
XIV	Mixed hardwood	VP	4	12.7	9.6b	83.7	71.7	12.0
XV		Na_2SO_3 +CH_2O	8	12.7	9.1b	83.3	65.0	18.3

LP: Liquid phase cooking, VP: Vapor phase cooking.
a: at maximum temperature of 150°C.
b: After defibration.

TABLE VII. Strength Properties of Fir and Mixed Hardwoods Pulp Handsheets.

Pulp	CSF ml	Basis wt. g/m^2	Density g/cm^3	Breaking length, km	Burst factor	MIT folding	Brightness, Hunter, %
VIII	500	63.4	0.48	2.5	1.1	2	32.1
IX	450	60.2	0.52	3.8	1.7	5	36.4
X	305	63.6	0.57	4.5	2.3	8	43.2
XI	310	59.0	0.67	5.9	3.6	35	40.0
XII	305	61.6	0.62	6.1	3.5	35	44.2
XIII	310	61.3	0.69	6.6	4.1	58	43.2
XIV	330	63.1	0.57	4.5	2.5	7	49.8
XV	325	63.1	0.58	4.5	2.3	9	48.8

dium sulfite. As shown in **Table VII**, the development of the strength properties was obtained by the addition of formaldehyde (IX > VIII or XII, and XIII > X or XI). Although this cooking process appears to be more suitable in hardwood than in softwood, further experiments along this line are in progress. Within a range of experiments, the pulp by vapor phase cooking was superior in brightness and inferior in the trength properties to the pulp by liquid phase cooking.

CONCLUSION

The foregoing laboratory results indicate the possibilities of upgrading the pulp properties by this pulping process, in which sodium sulfite and formaldehyde are used as the softening agents of coarse pulp and wood chips. However, there are still far from optimum cooking and defibration conditions, and these are now under way. Bleaching of this new pulp is also remained to be studied.

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