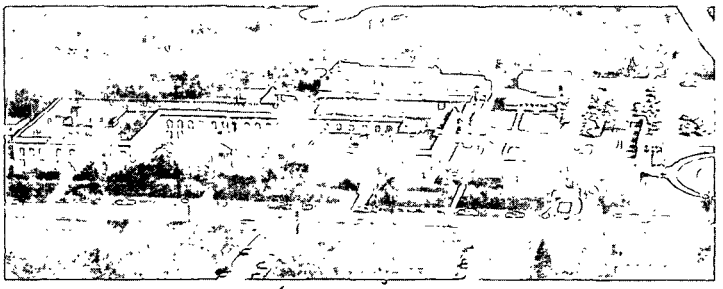

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OXIDATIVE PULPING OF SOFTWOODS

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INTRODUCTION

Pulp can be obtained in relatively high yields from loblloly pine by an oxidative process. In this, alkali impregnated chips are first reduced in size by fiberization in a pressurized refiner system. After that, lignin is modified by chlorine dioxide and removed in a further step by alkali.

It is shown that the use of more alkali results in less selective removal of lignin, whereas the use of more chlorine dioxide results in more selective removal of lignin.

At 72% yield sheet properties within 10% of those for a corresponding 56% yield kraft pulp are obtained; however, the cost of chlorine dioxide tends to be too high for this process to be economically feasible.

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Oxidative Pulping of Softwoods

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Abstract

Pulping process steps consist of fiberizing alkali-impregnated chips, lignin modification by chlorine dioxide, modified lignin removal by alkali and disk refining. Tests on loblolly pine showed: (1) more alkali for chip impregnation resulted in lower pulp yield without additional lignin removed, (2) more oxidant caused greater removal of lignin than carbohydrate, and (3) more alkali to remove modified lignin resulted in about equal removal of carbohydrate and lignin. Alkali and water impregnated chips fiberized at high consistency at 75 psig, then delignified with 4.5-7.5% chlorine dioxide followed by 8.0% sodium hydroxide gave 70-85% yield pulps, with Kappa no. 78-116. Strength properties improved as yield decreased, and alkali impregnation of chips was better than water. At 72% yield and 0.43-0.54 g/cc sheet densities, burst, breaking length, stretch, tear factor, tensile stiffness, ring crush and degrees-to-crack were within 10% of the corresponding 56% yield kraft pulp data with 0.53-0.63 g/cc sheet densities. Chlorine dioxide could be substituted on a chemical equivalent basis by chlorine dioxide/chlorine from a generator.

The objectives of this study included obtaining higher than normal pulp yields by selective delignification and eliminating objectionable emissions to the environment. Essential steps of the pulping process were adopted on the basis of work on chlorine dioxide-alkali pulping of hardwoods described previously (1). The first of these steps is chip fiberization on which preliminary studies already have been reported for softwoods (2).

In those earlier tests it was found that chip fiberization at a steam pressure corresponding to about 160°C resulted in significantly less fiber damage. However, evidence was obtained that after delignification, reduction in some papermaking properties had arisen from fiberization, in spite of retention of fiber length. This paper describes high-yield chlorine dioxide-alkali pulps obtained from loblolly pine chips that were fiberized at about 160°C after alkali impregnation.

RESULTS AND DISCUSSION

Process Tests, Pulp Lignin Contents and Yield

Tests made using alkali in the pretreatment before lignin modification by chlorine dioxide and subsequent alkali reaction to remove modified lignin, indicated that alkali pretreatment was of benefit since it meant greater lignin removal for the addition of a given amount of oxidant as shown in Fig. 1. This probably arises because alkali removed extractives that would otherwise consume oxidant.

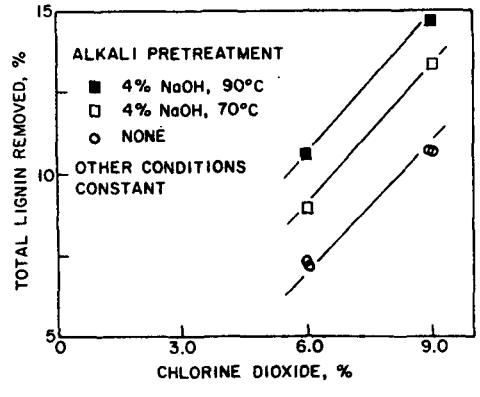

Fig. 1. Total Klason plus acid-soluble lignin removed from fiberized loblolly pine by chlorine dioxide-alkali with and without alkali pretreatment before oxidation and with other conditions held constant.

Preliminary experiments also showed that pulps of a particular yield could be obtained using chlorine dioxide-alkali delignification conditions different enough to affect costs, and with lignin contents different enough to affect pulp quality. Furthermore, unbleached pulps with papermaking properties could be obtained at over 70% yield. However, before consolidating quantitative data, tests were undertaken to settle a basis for pretreatment consisting of alkali impregnation of chips followed by fiberization in a pressurized refiner system, with a target pretreatment yield level of about 90%. This was the yield after the alkali pretreatment in Fig. 1.

Pretreatment conditions were defined on the basis of earlier chip fiberization studies as being at a steam pressure of 75 psig for up to about 5 minutes (2), following impregnation with varying amounts of alkali. The results obtained are given in Table I which includes the bases (A and B) for chip pretreatments used in subsequent tests.

Using earlier tests as a guide 4.5 and 9% were chosen as bracketing the amount of oxidant to be investigated. Then, check runs confirmed that material from pretreatments relating to A and B in Table I when delignified using a proposed range of chlorine dioxide-alkali conditions would give pulps in 65-85% yield. Examples of data obtained are presented in Fig. 2 and 3. In Fig. 2, based on pretreatment A followed by lignin modification with 9% chlorine dioxide, the choice of 90°C as the alkali reaction temperature was influenced by tests at 70 and 90°C as well as previous observations on hardwoods (1). Final pH was essentially dependent on the amount of alkali for reaction times of 30-120 minutes and, provided the reaction proceeded for 60 minutes, Kappa number was also essentially dependent on the amount of alkali.

Initial experiments were extended to more completely show the relative amount of lignin removal as functions of oxidant addition and pulp yield. Pretreatment conditions were as for A and B in Table I and chemical addition for two-step delignification was further defined on the basis of using 4-8% alkali for removal of modified lignin. Figure 3 shows there is an appreciable spread of Kappa numbers corresponding to each level of oxidant addition. This spread reflects the amount of alkali used in the impregnation of chips as well as after lignin modification in the alkali reaction.

Along with the spread in Kappa number for each amount of oxidant used there is a spread in yield. Hence, as shown in Fig. 3, at a particular yield Kappa number can vary considerably and much more than is normally encountered when kraft pulping. This arises

Table I. Alkaline Pretreatment Tests on Loblolly Pine Chips

Alkali impregnation:	Chips steamed twice at 15 psi for 2 min, then covered with NaOH solution for 30 min with 100 psig nitrogen over pressure and drained 30 min								
NaOH concn., g/l	initial	15.4			22.1			39.0	
	final	13.0			19.0			33.2	
NaOH uptake, %[a]		2.9			4.0			7.0	
Steaming at 75 psig:									
Minutes	2.5	5.0	7.5	1.25	2.5	5.0	1.25	2.5	5.0
Condensate/drip pH	10.4	9.6	8.8	12.0	11.8	11.8	—	12.0	12.3
Fiberization[b]:									
Yield, %	92.9	91.3	91.1	93.3	92.8	93.0 (Basis A)	88.2	87.0	86.7 (Basis B)

[a] All percentages on original o.d. chips, unless indicated otherwise.

[b] 12-Inch Sprout-Waldron refiner at atmospheric pressure.

from an interplay between the alkali pretreatment conditions, the amount of chlorine dioxide used for lignin modification and subsequent alkali reaction conditions, and, particularly relates to the steps in chlorine dioxide-alkali delignification being basically different.

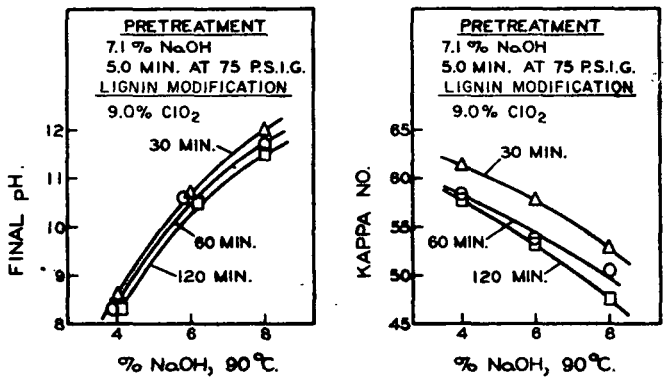

Fig. 2. Amount of alkali used in reaction after severest pretreatment and lignin modification of loblolly, showing corresponding final pH (left) and Kappa number (right).

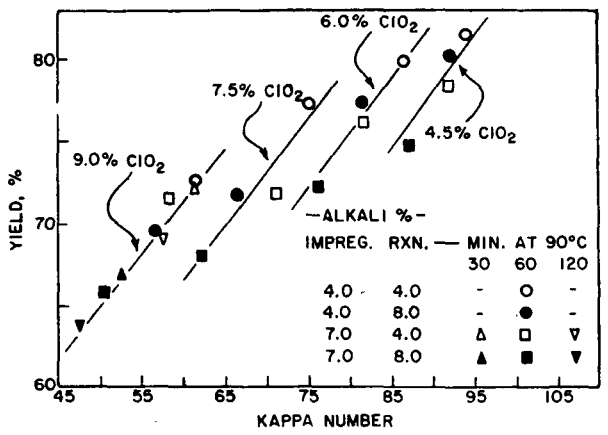

Fig. 3. Kappa numbers at different loblolly pine yield levels relating to pretreatment with 4.0 and 7.0% sodium hydroxide (A and B, Table I), lignin modification with 4.5-9.0% chlorine dioxide, reaction with 4.0 and 8.0% alkali at 90°C for times shown and with other conditions constant.

The function of the oxidation step is to modify lignin so that it becomes readily soluble in alkali whereas the main function of the subsequent alkali reaction is to remove modified lignin. However, because for economic reasons the amount of oxidant applied is very much less than in some earlier studies using excess sodium chlorite (2,3), lignin is degraded to a varying extent so that its solubility in alkali varies. Thus, in Fig. 3 lignin continues to be removed as the alkali conditions are made more severe, but this leads to an accompanying increased loss of carbohydrates which are nonresistant to alkali degradation so that delignification becomes less selective and pulp yield decreases.

One way to relate the extent of lignin removal to process conditions and pulp yield is presented in Fig. 4. For this lignin data are needed but deriving these from Kappa numbers is questionable. Although there is a straight line relationship between Kappa numbers and Klason lignin when using one pretreatment (A, Table I) the line was displaced sideways for the other pretreatment (B, Table I) so that the percentage of Klason lignin approximately equals Kappa number x 0.23 to 0.26. This slope is much different from that for the usual chemical pulps (4).

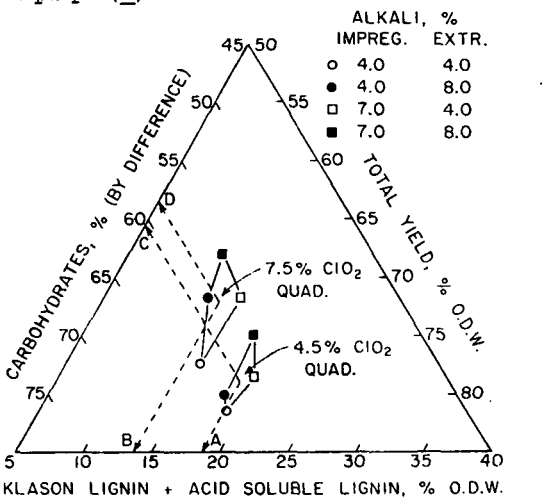

Fig. 4. Changes in yield and chemical composition of loblolly pine pulps for 4.5 and 7.5% chlorine dioxide and constant set of alkali conditions for each quadrilateral.

In Fig. 4 for each level of oxidant a constant set of four alkali conditions was used for chip impregnation and modified lignin removal, with temperature, time, and consistency held constant. The set of results for each amount of oxidant is represented in Fig. 4 by a quadrilateral and for simplification quadrilaterals corresponding to other amounts of oxidant have been omitted. From the positions of the quadrilaterals it will be apparent that increased use of oxidant caused greater lignin removal (A→B) than carbohydrate removal (C→D). Also, greater impregnation of chips with alkali results in lower pulp yield without additional lignin removal (circles → squares) and greater use of alkali to remove modified lignin resulted in lower pulp yields with about equal removal of carbohydrate and lignin (open → closed points).

Pulps and Their Evaluation

To produce pulps for evaluation a plan was developed based on process steps as in the above to cover strengths at least comparable with a high-yield kraft pulp on the one hand, and on the other hand reasonable costs. Earlier work had indicated that it may be necessary to use as much as 9% chlorine dioxide to obtain a pulp with the strength properties desired, and as little as 4.5% chlorine dioxide to economically produce a 75% yield pulp, prior to the recent historical dramatic rise in energy costs.

Process conditions used to produce five pulps in 70-86% yield using 4.5 and 7.5% chlorine dioxide as detailed in Table II were based on the results already discussed. Chip fiberization was in a 36-inch double disk pressurized refiner and after delignification, because the point of fiber liberation, as discussed by McGovern (5), had not been reached mechanical action or primary refining was needed to achieve fiber separation.

Primary refined pulps were dewatered in a centrifuge with recycle of white water until clear to prevent loss of fines. A significant reduction in the amount of power was noted when primary refining these pulps compared with the amount needed for the kraft cooked chips providing a 56% yield reference pulp. Illustrative chart strips are shown in Fig. 5.

Pulps produced as in Table II were beaten in a PFI mill to provide data as in Table III. This shows that for the four pulps derived from alkali impregnated chips, burst, breaking length, stretch, tensile stiffness, ring crush and crease cracking resistance were greater as yield decreased, and a similar but less clear trend occurred for sheet density and tear. The 70% yield and Kappa No. 78 pulp derived from chips which had been only water impregnated before fiberization (Pulp 0/70) had generally lower strength values than the comparable pulp with Kappa No. 78 derived from chips which had been alkali impregnated before fiberization. This indicates that with alkali-impregnation of chips, when fiberizing at a steam pressure of 75 psig there is a significant reduction in the amount of mechanical damage to fibers, which is in addition to the reduction observed previously as a consequence of fiberization at 75 psig rather than at lower steam pressures (2).

During primary refining the plate gap needed to reduce shives to fibers without significant reduction in freeness was much less for the chlorine dioxide-alkali pulps at the highest yield level, than for the 56% high-

Table II. Chlorine Dioxide-Alkali High-Yield Pulping Process Data for Loblolly Pine

Process step	Related Data					
Chip pretreatment	Impregnation	A[a]		B[a]		Water
	Fiberization pressure, psig (°C)	75(160)[b]		75(160)[b]		75(160)[b]
	Alkali conditioning	No		No		Yes[c]
	Yield, %	93.0[d]		86.7[d]		86.0
Lignin modification[e]	Chlorine dioxide, %	4.5	7.5	4.5	7.5	7.5
Alkali reaction[f]	Sodium hydroxide, %	8.0	8.0	8.0	8.0	8.0
	Yield, %	86	77	80	72	70
	Kappa no.	106	79	116	78	78
	Klason lignin, % o.d. pulp	22.5	16.7	22.6	16.0	15.8
Primary refining[g]	Canadian freeness, ml	725	720	720	730	600
	Pulp code	A/86	A/77	B/80	B/72	0/70

[a]Alkali impregnation of chips using aqueous sodium hydroxide as in bases A and B in Table I.

[b]Chip fiberization at 35-40% consistency in No. 418 Bauer pressurized refiner fitted with 36325/36326 0.10-inch taper plates after 5 min at pressure.

[c]Fiberized chips heated 5 min at 75 psig with 5.3% NaOH at 37% consistency.

[d]Yields based on quantitative data in Table I.

[e]Reaction 60 min at 8% consistency, 25→35°C.

[f]Reaction 60 min at 12% consistency, 90°C; Kappa no. determined after primary refining.

[g]Modified Model No. 105-A 12-in. Sprout-Waldron refiner fitted with No. 17,804 plates and operated under constant conditions, including 0.005-in. plate gap.

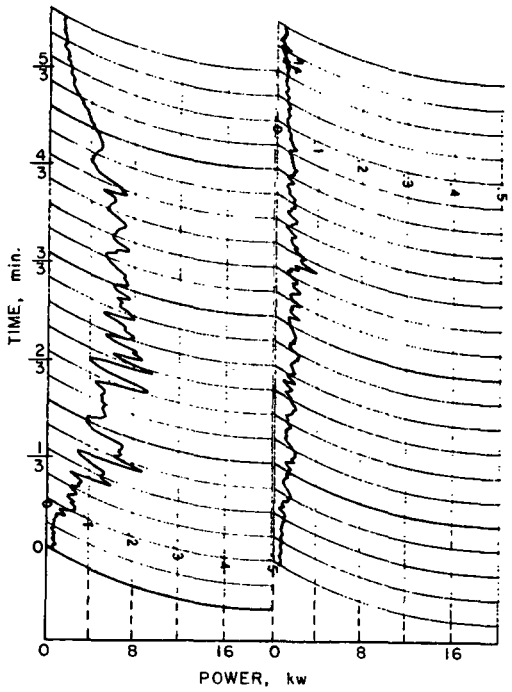

Fig. 5. Typical chart strips from Easterline Angus Model AW watt-hour meter showing readings for 56% yield kraft pulp (left) and 80% yield chlorine dioxide-alkali pulp (right) during primary refining under similar conditions. Chart speed: 3 in./min; plate gap: 0.018 in.

yield kraft reference pulp. However, the 72% yield oxidative pulp (B/72), which was similar in color to the kraft, could be primary refined to a relatively shive-free pulp with a greater plate gap permitting comparison with the kraft reference pulp as in Table IV. This shows that the 72% yield chlorine dioxide-alkali pulp beats to comparable freeness levels at essentially the same rate as the 56% yield kraft. Furthermore, although handsheet densities of the oxidative pulp are 15-20% below those for the kraft, various sheet properties including tear factor range from being near comparable to only about 10% below those for kraft. The results clearly demonstrate that by more selective delignification it is possible to obtain a 25% greater amount of oxidative pulp with papermaking properties nearly comparable to those for a high-yield kraft.

Plots of burst factor vs. filtration resistance showed that at constant burst the benefits of higher pulp yields as in Tables III and IV are associated with somewhat greater filtration resistance than for the high-yield kraft reference pulp. The result is that at about 45 burst factor, for example, higher yield and lower oxidant consumption are traded for greater filtration resistance.

Partial substitution of chlorine dioxide by chlorine was investigated for the case corresponding to the 72% yield pulp (B/72) in Table II. No significant differences were observed in pulp yield or evaluation data when the chlorine dioxide for lignin modification was substituted by the chemical equivalent amount of chlorine dioxide and chlorine containing up to at least 45% chlorine by weight. This means the oxidant could consist of a mixture of chlorine dioxide and chlorine such as obtained from a chlorine dioxide generator.

Table III. Handsheet Test Data[a] for Pulps Produced as in Table II

Pulp code (Table II)	A/86	B/80	A/77	B/72	0/70
Kappa no.	106	116	79	78	78
PFI mill[b], counter rev.	450-1650	450-1650	450-1650	450-1650	50-750
Canadian freeness, ml	600-200	680-225	600-195	650-230	530-210
Handsheet drainage time, sec	4.8-6.0	4.7-5.9	4.8-6.5	4.7-6.0	4.9-6.4
Filtr. resist. $R \times 10^{-8}$ cm/g (ΔP=10 cm H_2O)[c]	0.39-2.0	0.27-1.8	0.40-1.8	0.33-1.4	0.52-1.4
Handsheet density, g/cc	0.39-0.51	0.38-0.51	0.47-0.57	0.44-0.54	0.46-0.55
Burst factor	18-27	22-35	30-40	39-50	35-45
Breaking length, km	3.5-5.1	3.9-6.3	5.0-6.7	5.8-7.5	5.5-7.2
Stretch, %	1.8-2.0	1.9-2.4	2.3-2.7	2.5-2.8	2.3-2.7
Tear factor (Elmendorf)	72-57	106-76	81-65	116-90	104-83
Tensile stiffness, Et, kg/cm	286-371	296-424	340-424	380-438	379-442
Modified ring crush, lb/in.[d]	4.7-5.7	4.7-5.8	5.2-6.0	5.4-6.6	5.0-5.6
Degrees-to-crack[e]	40-36	46-43	50-44	52-47	48-46

[a] Handsheets of 1.2 g prepared according to TAPPI Standard Method T 205 m-58 except as noted.

[b] Load, 3.4 kg; 10% consistency; 40 g o.d. pulp (follows primary refining with 0.005-in. plate gap).

[c] Means of duplicates using constant-rate filtration apparatus (6), for composite sample from two beater runs.

[d] According to TAPPI Standard Method T 472 m-51, except each test piece wrapped around 0.597-in. diameter mandrel with overlap glued and loading edges dipped into molten paraffin wax.

[e] Handsheets of 6.28 g (i.e., 69 lb/100 sq ft) made in British handsheet mold, pressed 5 min. at 50 psig and dried on steam drum at 230-235°F and tested according to method of Whitsitt and McKee (7).

Table IV. Comparison of Handsheet Test Data for High-Yield Chlorine Dioxide-Alkali and Kraft Loblolly Pine Pulps

Pulp[a]	72% Yield oxidative (Table II)				56% Yield kraft[b]			
Primary refining plate gap, 0.001 in.	0.018				0.018			
Canadian freeness, ml	740				720			
PFI mill, counter rev.	450	750	1150	1650	450	750	1150	1650[c]
Canadian freeness, ml	710	620	390	240	710	625	400	205
Handsheet drainage time, sec	4.6	4.8	5.2	5.9	4.4	4.8	5.3	7.1
Filtr. resist. $R \times 10^{-8}$ cm/g (ΔP=10 cm H_2O)	0.22	0.40	0.87	1.6	0.26	0.38	0.92	2.25
Handsheet density, g/cc	0.43	0.47	0.50	0.54	0.53	0.55	0.60	0.63
Burst factor	36	42	46	50	39	47	54	55
Breaking length, km	5.6	6.4	7.2	7.8	5.9	6.8	7.6	8.0
Stretch, %	2.4	2.5	2.7	2.8	2.4	2.9	3.1	3.3
Tensile stiffness, Et, kg/cm	350	380	415	435	385	400	420	430
Tear factor (Elmendorf)	123	110	97	92	128	118	105	98
Modified ring crush, lb/in.	5.5	5.7	6.2	6.1	5.6	6.0	6.1	6.1
Degrees-to-crack	47	47	48	50	53	51	51	49

[a] Testing methods as in Table III.

[b] Kappa No. 86.

[c] Single evaluation, other data are means of duplicates.

Taking the above into account a chlorine dioxide-alkali pulp was produced at 75% yield, using 5.0% chlorine dioxide plus 2.7% chlorine and compared with a 57% high-yield kraft reference pulp. Both pulps had similar runnability on a 12-inch wide web former. The sheets from the more beaten and lower freeness oxidative pulp had properties substantiating the above data, were similar in color to the high-yield kraft sheets, and were significantly cleaner.

The concept of a mill system based on the above process of producing oxidative pulps has been described recently (8). However, the amount of oxidant needed for this process is an unfavorable cost factor under current conditions of relatively higher energy costs.

ACKNOWLEDGMENTS

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