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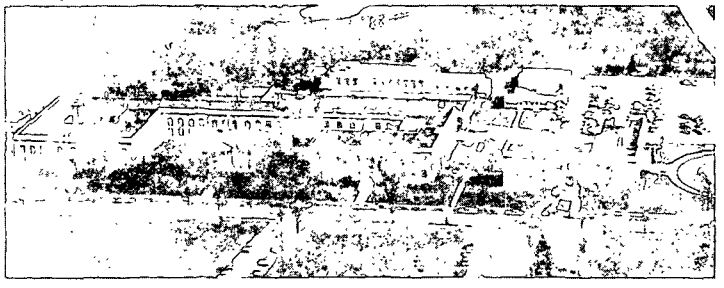

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USE OF CHLORINE DIOXIDE-ALKALI FOR HIGH YIELD PULPING

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INTRODUCTION

In the nonsulfur delignification of wood with chlorine dioxide-alkali to provide high-yield pulps, nonuniformity of oxidation across chips is overcome by pressurized fiberization of chips. Some aspects of minimizing mechanical damage to fibers during this operation are discussed in the following paper. Chlorine dioxide modifies lignin facilitating its removal by alkali in a two-step chlorine dioxide-alkali delignification process. This removes lignin more selectively than in the usual chemical pulping process so that much higher than normal yields of pulps are obtained. Examples are given for an unbleached softwood pulp and a bleached hardwood pulp which include comparisons of papermaking properties with the corresponding lower yield kraft pulps. The concept of a chlorine dioxide-alkali pulp mill system is outlined and reference is made to the current cost disadvantage arising from high energy input.

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ABSTRACT

In the nonsulfur delignification of wood with chlorine dioxide-alkali to provide high-yield pulps nonuniformity of oxidation across chips is overcome by pressurized fiberization. Subsequent limited reaction with chlorine dioxide, at least one quarter of which can be replaced by the chemical equivalent amount of chlorine, modifies lignin facilitating its removal by alkali at below 100°C. High-yield unbleached softwood and bleached hardwood pulps obtained in 72% and 57-60% yields, respectively, are compared with the corresponding 56% and 46-47% yield kraft pulps. Comparison of papermaking properties is made for three component furnishes including clay filler in the case of hardwood pulps. The concept of a chlorine dioxide-alkali pulp mill system is outlined with reference to high yield as well as environmental advantages and current cost disadvantages including high energy input.

INTRODUCTION

This review relates to studies in which two important objectives were:

to obtain higher than normal pulp yields by selective delignification, and to eliminate objectionable emissions to the environment.

As a part of the second objective the use of sulfur chemicals was excluded.

To achieve high pulp yields by selective delignification, attention was focussed on the use of chlorine dioxide as the main oxidant because of its effectiveness in selectively degrading lignin and its relatively favorable cost compared with other selective oxidants such as peracetic acid.

The essential steps of the pulping process now followed include:

chip fiberization,
lignin modification by an oxidant, and
modified lignin removal by alkali.

UNIFORMITY OF REACTION

When wood chips are reacted with oxidants like aqueous chlorine dioxide or acidified sodium chlorite, uniform reaction from outside to center, or, that is across the chip is generally difficult to achieve since the oxidant tends to react before it is transported into the wood chip. Such nonuniform reaction is illustrated in Figure 1 for an aspen chip. The less stained or lighter fibers are on the outer part of the chip which was delignified enough for the fibers to have separated. Further into the chip, delignification was significantly less and insufficient to permit fiber separation.

Figure 1. Cross section from the edge of an aspen chip after 120 hr at room temperature in acidified sodium chlorite showing nonuniform delignification. Sample embedded in butyl methacrylate; stained with Graff's "C" stain; magnification 180X.

CHIP FIBERIZATION

To achieve more uniform reaction, chips were fiberized or, that is, mechanically reduced to fiber bundles in disk refiners. In this operation the primary aims are to minimize mechanical damage to fibers, power consumption and undesirable

changes such as significant hydrolysis or lignin condensation. Unfortunately this poses a dilemma because with temperature elevation there is not only a trend toward plasticization of the lignin-rich middle lamella region between fibers which facilitates fiberization (1) but also a trend toward more wood hydrolysis and lignin condensation.

Investigations on hardwoods and softwoods were undertaken in pilot equipment, such as illustrated in Figure 2, in which the disk refiner operates at controlled pressures. Preheating water impregnated chips in the pressure vessel to progressively higher temperatures before fiberization showed that by increasing the temperature from near 130°C to about 160°C the degree of plasticization in the middle lamella region was sufficient for fiberization of chips without significant mechanical shortening of fibers. This was demonstrated by determination of fiber length distribution data, as discussed elsewhere (2,3). No significant amount of wood hydrolysis, for example, was detected at 160°C, presumably because the times at temperature were kept relatively short. Other advantages to increasing the temperature to 160°C have also been noted (2).

DELIGNIFICATION

Although aqueous chlorine dioxide can selectively delignify wood the amount of oxidant needed makes the cost prohibitive for pulp production. Furthermore, much of the oxidant is consumed in additional reaction with lignin that has already been degraded to the point where it is soluble in alkali, as discussed with reference to Figure 3.

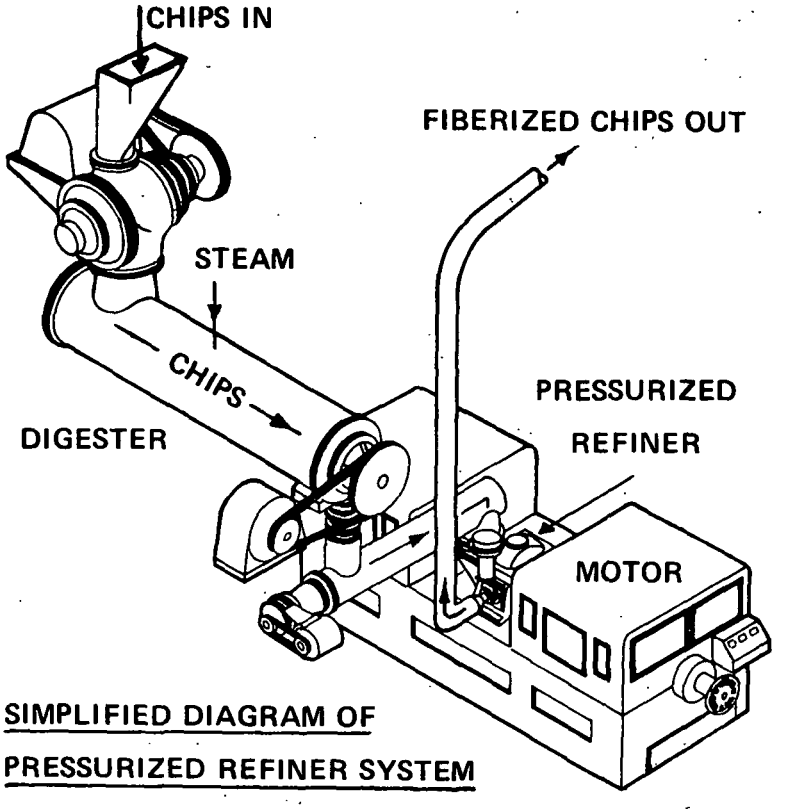

Figure 2. Diagram of pressurized refiner system with pressure vessel or digester through which chips are fed to a double disk refiner before discharge to atmosphere.

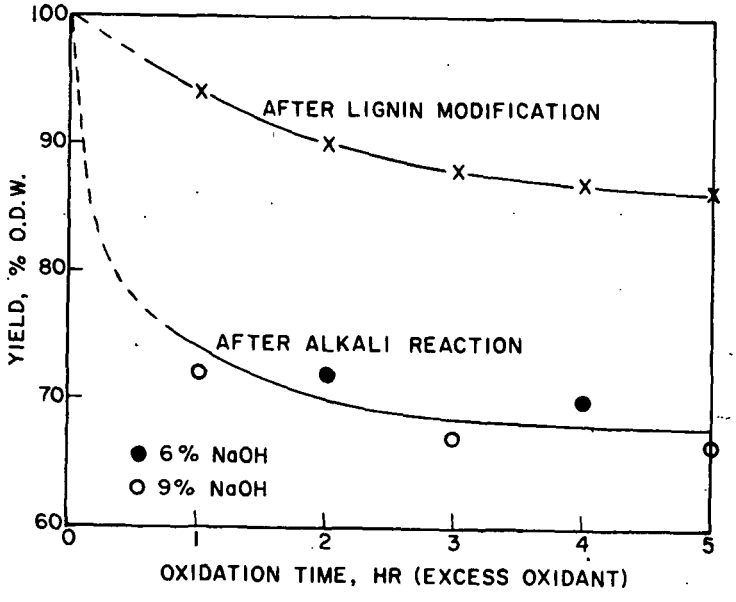

Figure 3. Yields after reaction of fiberized aspen chips at 50°C with excess acid chlorite (upper curve) and subsequent reaction with sodium hydroxide at 50°C for 1 hr (lower curves).

In Figure 3 the upper curve shows a falling yield, mainly due to lignin removal, as reaction with excess oxidant continues. However, at relatively high yields of 95% and above there is a rapid increase to 20-22% in the amount of material readily soluble in alkali (lower curve). Analyses have shown that 55-70% of this material consists of significantly modified lignin and its removal by alkali without further consumption of oxidant is achieved below 100°C under conditions mild enough to avoid excessive loss of carbohydrate material, especially hemicelluloses.

Thus delignification is achieved on a two-step basis using chlorine dioxide-alkali with limited oxidant availability restricting the extent of degradation of lignin before alkali reaction and with process conditions, particularly temperature and alkalinity, favoring retention of more than the usual amount of carbohydrates, thereby leading to higher yields of pulp.

HIGH-YIELD UNBLEACHED SOFTWOOD PULP

Investigations on softwoods have shown that for reaction with a given amount of chlorine dioxide, lignin removal is greater when there is an alkali extraction beforehand, and from a series of preliminary experiments with alkali impregnation of chips before fiberization it was possible to bracket process conditions in an area of more specific potential interest. Bracketing was on the basis that it may be necessary to use as much as 6 to 9% chlorine dioxide to obtain a pulp with a desirable level of strength properties and as little as about 4.5% in obtaining a 75% yield pulp to get into an economic ballpark.

Both of these points were recognized in a series of experiments using 4.5 and 7.5% chlorine dioxide for which changes in yield and chemical composition of pulps are presented in Figure 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.

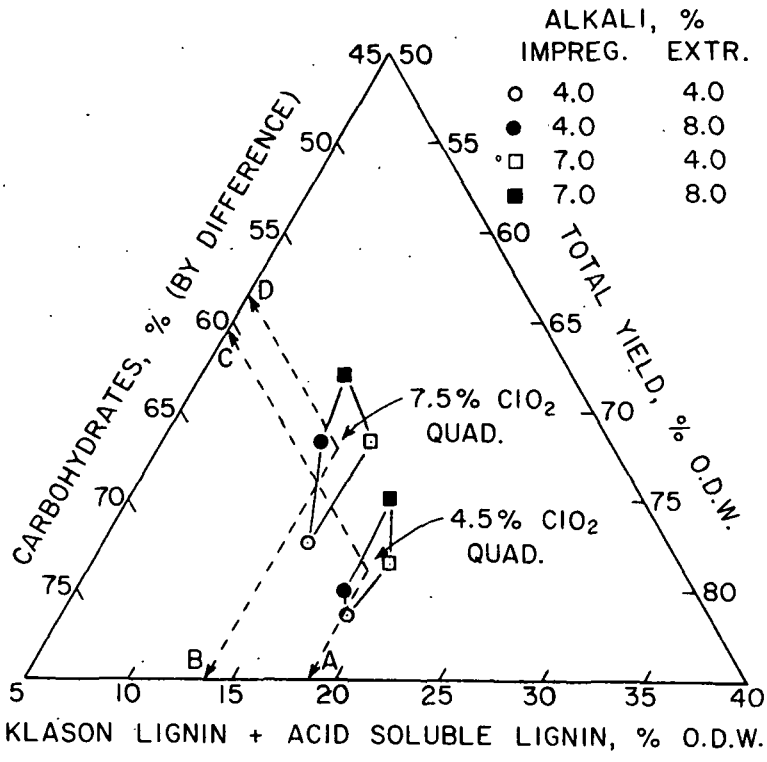

Figure 4. Changes in yield and chemical composition of loblolly pine pulps for 4.5 and 7.5% chlorine dioxide (o.d.w. basis) and constant set of alkali conditions for each quadrilateral.

The set of results for each amount of oxidant is represented in Figure 4 by a quadrilateral. 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 yield with about equal removal of carbohydrate and lignin (open → closed points).

Papermaking properties of a series of pulps obtained within the yield range covered in Figure 4 were more favorable as yield decreased and at 70-75% yield were about comparable to a 56% yield kraft pulp from the same pine chips, as illustrated in Table 1. A noteworthy difference is the lower density range for sheets from the 72% yield oxidative pulp. As a consequence comparison at

similar sheet density results in superior bonding properties for the oxidative pulp. Also, sheets from this pulp were significantly cleaner and had a much lower shive content.

Table 1

PFI MILL EVALUATIONS OF HIGH-YIELD
CHLORINE DIOXIDE-ALKALI AND KRAFT PULPS

	Loblolly Pine Pulps	
	72% Yield Oxidative	56% Yield Kraft
Kappa number	80	85
Mill counter rev.	450-1650	450-1650
Canadian Freeness, ml	705-240	705-205
Handsheet density, g/cc	0.43-0.54	0.53-0.63
Burst factor	36-50	39-55
Breaking length, km	5.6-7.8	5.9-8.0
Stretch, %	2.4-2.8	2.4-3.3
Tensile stiffness, Et, kg/cm	350-435	385-430
Tear factor (Elmendorf)	123-92	128-98
Modified ring crush, lb/in.	5.5-6.1	5.6-6.1
Degrees-to-crack	47-50	53-49

Process conditions for obtaining the oxidative pulp in Table 1 are set out in Table 2. Apart from chip fiberization, the pulping process is carried out at normal pressure which is one of its advantages.

It is known from additional experiments that chlorine dioxide addition can be reduced by using the chemical equivalent amount of 6.6% chlorine dioxide and 3.6% chlorine which directly relates to the composition of the output from a

chlorine dioxide generator (4). However, a further reduction in chlorine dioxide addition would be needed for economic reasons and at the same time some trade-off in pulp quality would appear to be a possibility for linerboard grades of pulp.

Table 2

SOFTWOOD PULPING PROCESS DATA

Process Step	Related Data	
Chip impregnation and fiberization	Sodium hydroxide, % o.d. chips	11.7
	Steam pressure, psig (°C)	75(160)
	Time at pressure, min.	5.0
	Total load, brake hp. days/o.d. ton	3.2
Lignin modification[a]	Chlorine dioxide, %	7.5
	Temperature, °C	25→35
Alkali reaction[a]	Sodium hydroxide, %	8.0
	Temperature, °C	90
	Yield, %	72
	Kappa number	78

[a]Reaction time, 60 min at 8-12% consistency.

A primary refining step after alkali reaction was carried out in the same way as a similar step needed for obtaining the high-yield kraft pulp. However, power consumption was about one fourth for the former which would probably compensate for the power needed for chip fiberization.

HIGH-YIELD BLEACHED HARDWOOD PULP

Using essentially a similar approach to that above, with some variation in process details which have been discussed previously (2), hardwood pulps have been obtained in about 65% yield and bleached to high brightness in D/C-E-D stages.

Bleached pulp yield was 57-60% or 24-28% greater than the 46-47% yield in a control experiment producing a bleached red maple kraft pulp from the same chips.

Pulp evaluation data presented previously (2) show that the oxidative pulp has some differences from the corresponding kraft pulp. These differences, which include a higher drainage resistance and higher sheet density in the initial stages of beating, are seen as possible disadvantages where there is some inflexibility of attitudes toward pulp evaluation as is sometimes encountered in the pulp commodity market. However, the data in Table 3 illustrate the comparability of results obtainable through a flexible approach to furnish formulation which is possible under practical papermaking conditions.

Table 3

PAPERMAKING RESULTS WITH SIZED FURNISHES OF BLEACHED PULPS INCLUDING CLAY FILLER

Fiber Furnish: 30% bleached softwood kraft
70% bleached red maple as shown

	Red Maple Pulp	
	57-60% Yield Oxidative	46-47% Yield Kraft
Furnish:		
Canadian freeness, ml	400	380
Filtr. resist., $R \times 10^{-8}$, cm/g (ΔP = 10 cm H_2O)	1.7	1.5
Filler content, % o.d. sheet	14	8
Sheet density, g/cc	0.50	0.48
TAPPI brightness, %	83	83
Spec. scattering coeff., 650 nm	397	416
Breaking length, km (MD)	4.8	4.6
Tensile stiffness, Et, kg/cm (MD)	330	263
Tear factor (Elmendorf) (MD)	88	86

The furnishes for the two papermaking trials providing the data in Table 3 were formulated on the basis of a series of preliminary tests and trade-off the inherently higher bonding characteristic of the oxidative pulp for a gain in light scattering by increasing the clay filler content. There was no significant difference in the drainage properties of the two mixed furnishes. Also, other data in Table 3 show a close similarity in sheet properties. Thus, the 57-60% yield oxidative red maple pulp was successfully substituted for the corresponding conventional 46-47% yield bleached kraft pulp.

CLOSED-PROCESS SYSTEM

The above patented pulping process (5) consisting of chip treatment and two-step delignification is a part of the concept of a sulfur-free mill system outlined in Figure 5. This is based on our earlier discussions (6) and some aspects of recycling inorganic components within this system have been elaborated upon by others (7).

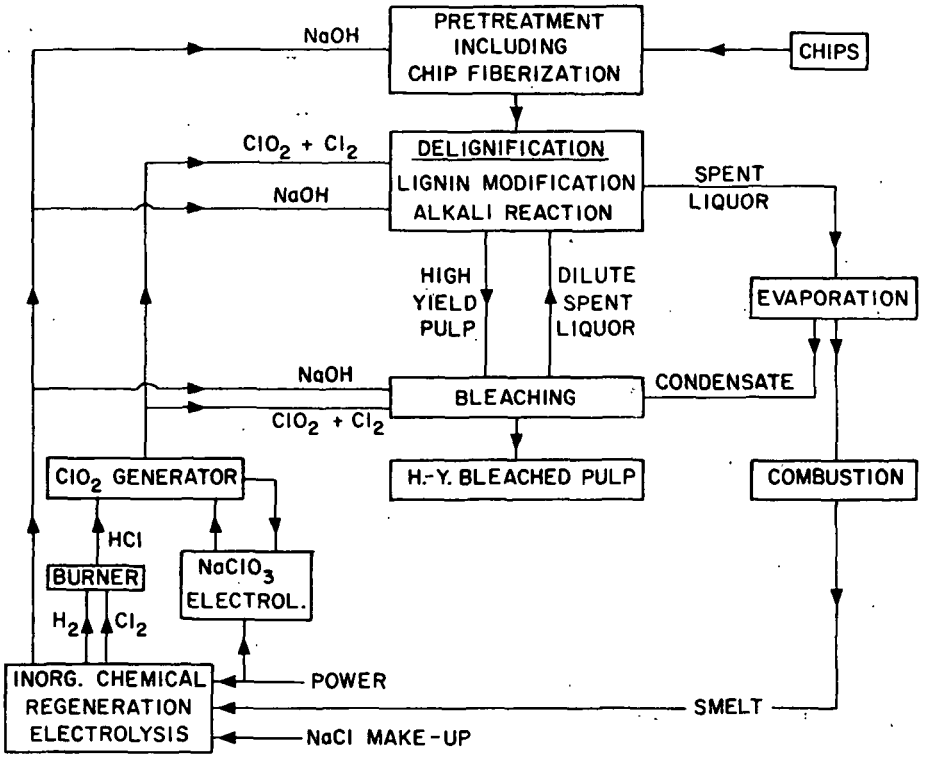

Figure 5. Flow chart of mill system for chlorine dioxide-alkali pulping process with chemical recycle.

Potential advantages of the system in Figure 5 in addition to high yields of pulp, include no odor and no bleach plant effluent, the elimination of which poses a significant problem (8). Development of this kind of system has now progressed to the stage where a pilot plant has been constructed at Kasugai in Japan (9,10).

Although the aspects of environmental protection and high-yield pulp provide incentives to pursue this development these benefits are gained at the cost of a relatively high energy input for electrolysis. The recent dramatic rise in energy costs is an adverse factor for the economic prospects of this system and some further significant cost reduction is now needed unless wood costs advance relative to energy costs. Conceivably capital cost reductions could be achieved by using the kind of equipment recently developed for displacement bleaching (11). Such equipment might enable the chemical process steps from fiberized chips to bleached pulp to be carried out in multistage reactors, thereby facilitating a reduction in oxidant consumption and the lowering of plant capital costs compared with current conventional pulping and bleaching plants.

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LITERATURE CITED

1. Nicholls, G. A., Wood Sci. Technol., 4, 292 (1970).

2. Nicholls, G. A., R. G. Jamieson, and V. J. Van Drunen, Tappi 58(5), 105 (1975).

3. Nicholls, G. A., R. G. Jamieson, and V. J. Van Drunen, TAPPI Alkaline Pulping Conference, Williamsburg, VA: (Oct., 1975).

4. Partridge, H. D., E. S. Atkinson, and R. C. Buser, Pulp Pap. Mag. Can., 73(8), 77 (1972).

5. Thompson, N. S., G. A. Nicholls, and S. T. Han, U.S. Patent 3,829,357 to Institute of Paper Chemistry (August 13, 1974).

6. Whitney, R. P., N. S. Thompson, G. A. Nicholls, and S. T. Han, Pulp Pap. 43(8), 68 (1969).

7. Rapson, W. H., U.S. Patent 3,755,068 to Erco Envirotech Ltd. (August 28, 1973).

8. Nicholls, G. A., Tappi, 56(3), 114 (1973).

9. Asaoka, Hiroshi, Jap. Pulp Pap. 13(1), 53 (1975).

10. Anon., ibid. 11 (4), 12 (1974).

11. Gullichsen, Johan, Tappi, 57(10), 111 (1974).