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**OXYGEN PULPING OF HARDWOODS AND SOFTWOODS
UNDER OXYGEN-RICH CONDITIONS**

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ABSTRACT

Red maple and loblolly pine were pulped at low consistency with air and alkali at 2550 psi. The pulps were then compared with high consistency oxygen pulps and with kraft pulps. Red maple chips gave a 65% yield pulp with the low consistency system which compared favorably in strength properties to a 50% yield kraft pulp, and was substantially better than a high consistency oxygen pulp from fiberized wood. The low consistency system also gave superior results with loblolly pine, but the strength properties still did not match those of the kraft reference pulps. The results demonstrate the advantage of pulping under conditions of high oxygen availability.

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INTRODUCTION

Oxygen pulping is one promising method of reducing the pollution problems associated with pulping with sulfur compounds. It is also compatible with simpler chemical recovery systems. However, one of the major difficulties is getting rapid and uniform reactions to occur due to the low solubility and slow rate of dissolution of oxygen in the alkaline cooking liquor.

This manuscript, submitted to Tappi for publication, describes results obtained using a laboratory system which operates under conditions which assure high oxygen availability. A hardwood and softwood are studied, and comparisons are made with more conventional oxygen pulping methods. Several distinct advantages of operating under oxygen-rich conditions are described.

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INTRODUCTION

Oxygen bleaching has become a practical alternative to more conventional bleaching methods, and has already reached the point of significant commercial use. On the other hand, oxygen pulping has not reached that stage yet, due to carbohydrate degradation and mass transfer problems of getting the oxygen to the site of reaction with lignin. Long reaction times or nonuniform pulping are often experienced.

Various approaches have been taken to solve these problems. Two-stage, soda-oxygen pulping, with fiberization is one approach which is widely used (1). Thin chips (ca. 1 mm) have been tried (2-4), as have compression-rolled chips (5). Often the reactions are carried out at high consistency to enhance the interaction of the wood with the gas phase (6), although low consistency with circulating liquor has also been used (7).

An area that has seen less attention is that of improving the rate of dissolution and solubility of oxygen in the cooking liquor. One novel approach which was successful for bleaching is to carry out the reaction at low consistency in a flow reactor consisting of a long pipe, injecting oxygen at strategic points (8). In this paper, we would like to present results obtained in a low-consistency system which uses air at 2550 psi and circulating liquor with a shower head to improve oxygen dissolution. These are compared with high-consistency pulping using pure oxygen under more conventional conditions. Both a hardwood (red maple) and softwood (loblolly pine) were studied.

EXPERIMENTAL

The system which was used for low-consistency pulping is shown in Fig. 1. It is based on equipment which was designed and built by Zimpro, Inc. Some of the technology has been patented (9). A steam-jacketed reactor and heat exchanger form a loop, with a packingless pump to circulate the liquor. A shower head aids in dissolving air, which is supplied from a compressor and maintained typically at 2550 psi. This corresponds to a partial pressure of oxygen of about 500 psi. Pure oxygen at this pressure could be a practical alternative for commercial use, although the fire and explosion hazard is reduced by using air. The wood sample is placed in a stainless steel mesh basket in the reactor. The liquor is based on what is typically obtained from a wet-combustion recovery system, and consisted of 9.9 g of Na_2CO_3 and 7.6 g of NaHCO_3 per liter. In most cases, 220 g of wood was pulped with 15 liters of liquor, giving a liquor-to-wood ratio of almost 70. Larger amounts of wood could be used without increasing the amount of liquor.

[Fig. 1 here]

High-consistency oxygen pulping was carried out in a Teflon-lined stainless steel vessel at ca. 25% consistency. Sodium carbonate (usually 10% on wood, as Na_2O) was used as alkali with pure oxygen at 130 or 300 psi. Kraft pulps were prepared in small rotating vessels immersed in an oil bath under conventional laboratory conditions. The kraft cooking conditions were a 4:1 liquor-to-wood ratio, 28% sulfidity, and 90 minutes to reach temperature. For red maple, 15% active alkali (as Na_2O), and 60 minutes at 180°C were used. For loblolly pine, 18% active alkali and 174°C were used for 34 and 75 minutes for the high and low kappa number pulps, respectively.

RESULTS AND DISCUSSION - RED MAPLE

Table I contains strength data for three oxygen pulps and a kraft pulp for comparison. The oxygen pulps were prepared at the 65% yield level to emphasize a major advantage (high yield) of oxygen pulping. All values are interpolated for the same sheet density. For high-consistency oxygen pulping, it is necessary to fiberize the wood before pulping, whereas the low-consistency, high-pressure air system works on a variety of starting materials, including standard hardwood chips.

[Table I here]

The fiberization was carried out at 160°C after impregnation with Na₂CO₃. A wide plate gap was used to minimize fiber damage. These conditions were chosen to be above the softening point for lignin to produce fiber bundles separated between fibers, rather than fragmenting fibers.

It can be seen that the two oxygen pulps from fiberized starting material gave similar strength properties. The main advantage of low consistency and high oxygen availability in this instance is a large reduction in pulping time, from 640 minutes to 250 minutes (both at 120°C). The oxygen pulp from chips required PFI milling to a lower freeness to reach the same sheet density, where it gave superior strength properties. Significantly, tear strength, which is always a problem with oxygen pulps, was considerably improved. Pulping chips did require an increase in time (340 min) and temperature (130°C), but 5/8 inch chips (ca. 4 mm thick) were pulped without rejects.

The oxygen pulps compare favorably with the kraft pulp, even at higher yield and kappa number. The fiberized samples gave strengths similar to the kraft pulp, while the oxygen pulp from chips appears even better. Tear strength, which is usually low with oxygen pulps, was lower from the fiberized samples, but comparably to the kraft pulp in the case of the oxygen pulp from chips. These differences suggest that the fiberization process, which is common to many oxygen pulping sequences, contributes to reduced strength.

Thus, it can be seen that the use of hardwood chips under conditions of low consistency and high oxygen availability offers a distinct advantage in oxygen pulping. The pulp produced is superior to those produced from fiberized wood, and very similar in strength properties to a kraft pulp from the same wood. The main disadvantage is the long cooking time required under the conditions used in this work. Higher temperatures might help, but nonuniformity of reaction begins to be a problem.

RESULTS AND DISCUSSION - LOBLOLLY PINE

Loblolly pine presents a more formidable challenge in oxygen pulping. The greatest degree of success in the literature has been with hardwoods. The lignin in softwoods is less reactive to the oxidation reactions. In addition, wood morphology and extractive content may well inhibit mass transfer of oxygen to the reaction site. Our results with loblolly pine confirmed these apprehensions.

Strength is the primary consideration with softwood chemical pulps. The kraft process gives very strong pulps, and must be used as the basis for comparison. With loblolly pine, chips gave too many rejects when pulped to useful kappa numbers for the accepts. Flakes of approximately 13 mm by 13 mm by 1.1 mm gave satisfactory results which are shown in the tables. Table II gives strength properties for high kappa number oxygen and kraft pulps.

Table III provides the same comparison for low kappa number pulps. Constant sheet density was again used as the basis of comparison, but similar patterns were observed at 500 freeness.

[Tables II and III here]

In the high kappa number loblolly pine pulps, a pattern similar to that observed in maple was obtained. Thus, the low consistency, high oxygen availability system applied to flakes gave the best oxygen results. However, even these best results fell short of the kraft strength properties. Approximately 25% more pulp was obtained, but even this is not enough to make up for the lower burst and tear strength in grades where strength is a requirement.

At low kappa number, it was necessary to add potassium iodide to obtain useable strength properties from high consistency oxygen pulping. At low consistency, similar strength properties were obtained without adding this stabilizer. Only a marginal improvement was observed in going to flakes, and all of these pulps fall far short of the strength properties of kraft. The yield advantage was about the same; about 25% more pulp was obtained under low consistency, high oxygen availability conditions on flakes, compared to kraft pulping of chips.

In going from high to low kappa number, all of the strength properties of the kraft pulps improved. On the other hand, in the oxygen pulps, only the tear factor appeared to increase consistently. Other strength properties were not improved except for the comparison for pulps with and without potassium iodide (first columns in Tables II and III). Thus, the additional carbohydrate degradation which accompanies further pulping negates the effect of lignin removal. Therefore, pulping to low kappa numbers does not appear to be advantageous in oxygen pulping.

Viscosity is considered by many to be a reasonable measure of the inherent strength potential of a pulp. In general, it reflects the molecular

weight of the carbohydrate fraction of the pulp (lignin is removed by sodium chlorite for high-kappa pulps). Typically, higher molecular weight means greater strength.

With high-yield pulps, such as OA pulps, the appreciable hemicellulose content tends to lower the viscosity. Chemical degradation also contributes to lower viscosity. Hence, oxygen pulps have viscosities which are much lower than typical kraft pulps. This was indeed the case in the present work.

Loblolly pine viscosities were found to drop very quickly in OA pulping. At high consistency, the viscosity dropped from 36.3 to 7.6 in 10 minutes at 120°C. During this time the yield dropped only from 81.0 to 73.1. After that, a trend was noted toward lower viscosities at lower yields. The data are plotted in Fig. 2. High-consistency results are kept separate from low consistency. Each set gave a straight line despite the fact that pulping conditions varied considerably within each set. The following equations were obtained from linear regression analysis:

$$\text{High consistency: Viscosity} = -3.8 + 0.155 \text{ yield } (r^2 = 0.90)$$

$$\text{Low consistency: Viscosity} = -5.1 + 0.224 \text{ yield } (r^2 = 0.98)$$

[Fig. 2 here]

Within the parameter range investigated, these two equations predict higher viscosities at low consistency. Also shown in Fig. 2 are viscosities for two high-consistency cooks which contained potassium iodide. It can be seen that these viscosities are much higher than the other high-consistency viscosities. The low-consistency pulps are intermediate in viscosity.

These viscosity results provide a partial explanation for the observation that strength properties did not improve appreciably as lignin was removed in going from high to low kappa number pulps. During this time, viscosity was also decreasing, which counteracted the effect of lignin removal.

CONCLUSIONS

The low-consistency, high oxygen availability system offers a definite advantage in oxygen/alkali pulping. Higher viscosities, greater strength properties, and faster cooking are obtained. The ability to use chips or flakes provides a method of avoiding the mechanical damage associated with fiberization. Hardwoods can be successfully pulped under these conditions, giving strength properties similar to kraft. Loblolly pine, however, and probably softwoods in general, do not give properties comparable to kraft. The low consistency system provides the greatest advantage at high kappa numbers, where oxygen pulps have the best properties, and where potassium iodide was not used at high consistency. The two factors which appear to affect strength properties the most are mechanical damage during fiberization and chemical carbohydrate degradation during pulping. These factors combine to make oxygen pulping of softwoods of marginal use.

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Table I. Comparison of Red Maple Oxygen and Kraft Pulps^a

Pulp type	O ₂ ^b	O ₂ ^c	O ₂ ^d	kraft
Consistency	high	low	low	high
Starting material	fib'd	fib'd	chips	chips
Yield, % (kappa number)	65 (72)	65 (72)	65 (75)	50 (14)
Canadian freeness, ml	550	400	325	560
Breaking length, km	5.3	5.4	6.7	5.3
Burst factor	25	28	37	24
Tear factor (Elmendorf)	47	41	54	51
Zero-span b.l., km	11.8	12.2	19.0	21.0

^aAll strength values interpolated for 0.60 sheet density.

^bCooking conditions: twice using 5.2% Na₂CO₃ as Na₂O, 100 min to and 320 min at 120°C, 130 psi oxygen pressure measured at 100°C each time.

^cCooked once at 130°C for 250 min with liquor:wood ratio of 68.

^dCooked once at 120°C for 340 min with liquor:wood ratio of 34.

Table II. Strength Properties for High-Kappa Oxygen and Kraft Pulps from Loblolly Pine^a

Pulp type	O ₂ ^b	O ₂ ^c	O ₂ ^d	kraft
Consistency	high	low	low	high
Starting material	fib'd	fib'd	flakes ^e	chips
Yield, % (kappa number)	59.5 (74)	61.8 (80)	65.1 (70)	51.7 (78)
Canadian freeness, ml	240	330	505	445
Breaking length, km	7.2	8.3	9.5	11.0
Burst factor	44	53	60	85
Tear factor (Elmendorf)	65	68	77	123
Zero-span b.l., km	12.1	13.5	15.3	19.8

^aAll strength values interpolated for 0.60 sheet density.

^bCooked 15 hr at 120°C and 300 psi initial O₂ pressure using 6% Na₂CO₃ as Na₂O.

^cCooked 3.3 hr at 130°C and 2550 psi air pressure.

^dCooked 4.0 hr at 130°C and 2550 psi air pressure.

^eKappa and strength values after removal of 16.1% rejects.

Table III. Strength Properties for Low-Kappa Oxygen and Kraft Pulps from Loblolly Pine^a

Pulp type	O ₂ ^b high ^e	O ₂ ^c low	O ₂ ^d low ^{f,g}	kraft high chips
Starting material	fib'd	fib'd	flakes	
Yield, % (kappa number)	53.8 (43)	52.6 (39)	58.9 (39)	46.9 (33)
Canadian freeness, ml	405	640	600	300
Breaking length, km	8.2	7.3	7.9	11.6
Burst factor	60	50	46	90
Tear factor (Elmendorf)	98	88	88	133
Zero-span b.l., km	15.1	14.0	15.4	22.3

^aAll strength values for 0.60 sheet density.

^bCooked 4.0 hr at 140°C and 300 psi O₂ pressure.

^cCooked 6.0 hr at 130°C and 2550 psi air pressure.

^dCooked 6.5 hr at 130°C and 2550 psi air pressure.

^eCook included 10% KI on o.d. wood basis.

^fKappa and strength values after removal of 0.5% rejects.

^gExtrapolated strength values (all others interpolated).

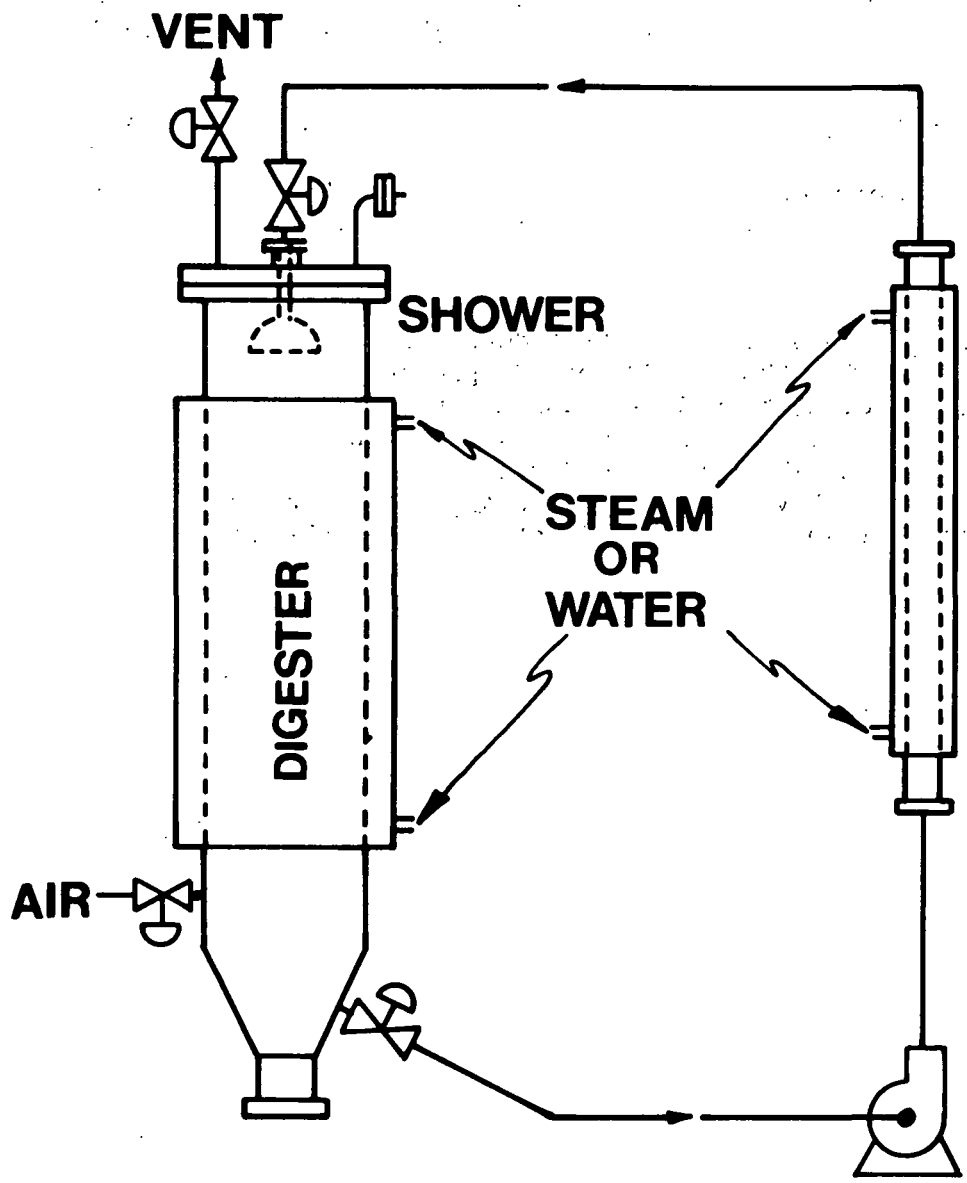


Figure 1. Low Consistency Reactor

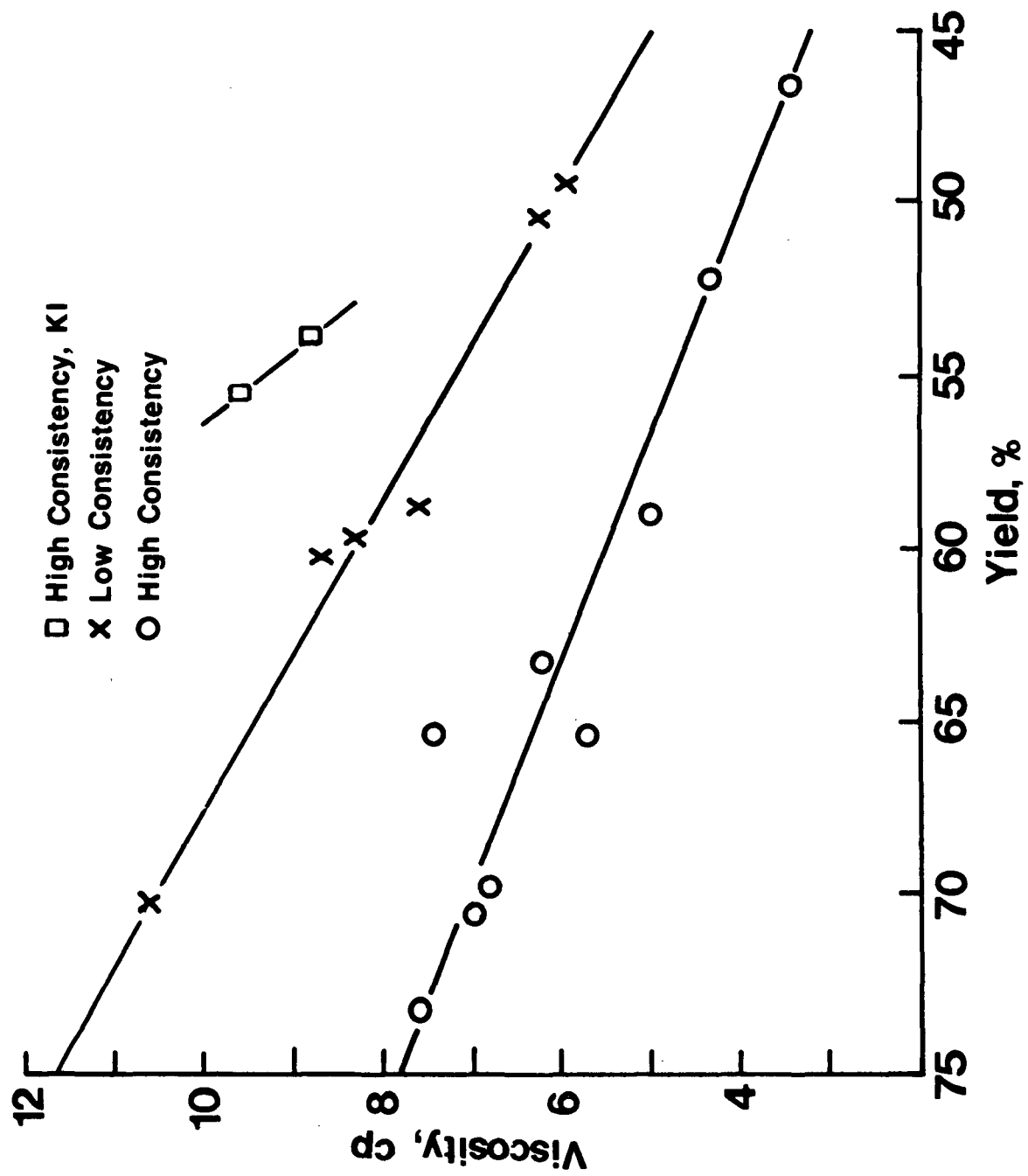


Figure 2. Viscosity vs. Yield for High and Low Consistency OA Pulps from Loblolly Pine