Entrained black liquor solids and viscosity selectivity in oxygen delignification reinforced with hydrogen peroxide

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ABSTRACT *Results are reported from a study on the effects of entrained black liquor solids on the rate of delignification and on the viscosities of loblolly pine kraft pulps delignified with oxygen and oxygen reinforced with hydrogen peroxide (PO). The amounts of entrained solids ranged from 0 to 85 kg/o.d. metric ton of pulp at a consistency of 15%.*

Black liquor solids entrainment of up to about 30 kg/o.d. metric ton of pulp is beneficial, increasing the rates of oxygen delignification and PO delignification. However, black liquor solids entrained with the pulp affected the pulp viscosity. The overall selectivities (kappa number vs. viscosity) of oxygen- and PO-bleached pulps were slightly lower for pulps with entrained solids. Using hydrogen peroxide (0.5% on pulp) to reinforce the oxygen stage has yielded pulps lower in kappa number and equal in viscosity to oxygen-delignified pulps.

KEYWORDS
Black liquor
Brightness
Hydrogen peroxide
Kraft pulp
Kappa number
Oxygen delignification
Viscosity

A two-stage, hydrogen-peroxide-reinforced oxygen delignification (PO-PO) followed by chlorine dioxide (D) and hydrogen peroxide (P) bleaching has been suggested as a sequence to produce bleached kraft pulps (>85% ISO brightness) from loblolly pine (*1*, *2*). Such a process has the potential to significantly reduce the amount of chlorinated organics, particularly tetrachlorinated dibenzodioxins (TCDD) and dibenzofurans (TCDF), in both pulp and effluent. Coupled with other internal closure techniques, the process can be utilized to operate a cost-effective "closed-cycle" bleach plant (*3*, *4*).

For a two-stage, hydrogen-peroxide-reinforced oxygen delignification of kraft pulps, the mode of hydrogen peroxide charge is critical to achieve better selectivity (*1*, *2*). The first oxygen-delignification stage should be reinforced with hydrogen peroxide, whether or not the second stage is reinforced. The selectivity of oxygen or hydrogen-peroxide-reinforced oxygen (PO) delignification is defined here as the ratio of viscosity to the kappa number of the pulp (*5*). The black liquor solids entrained with the unbleached pulp as a result of inadequate washing of the brown-stock would therefore influence the selectivity of PO delignification to a great extent. Samuelson and Ojteg showed that NO_2/O_2 pretreatment of pulps and the selectivity of oxygen delignification of NO_2/O_2-pretreated pulps were influenced by black liquor carry-over or precipitated lignin with the pulps (*6*).

The purpose here is to report the results from a study into the effects of entrained black liquor solids on the rate of delignification and selectivity of oxygen-delignified and PO-delignified loblolly pine kraft pulps. Solids entrainment with the pulp is defined as the total weight of black liquor solids (both organic and inorganic) in the feedstock (unbleached pulp) and is expressed as a percentage of the pulp weight (*7*). In this study, the concentrations of entrained solids ranged from 0 to 85 kg/o.d. metric ton of pulp at a consistency of 15%.

Results and discussion

Table I lists the properties of the unbleached pulp and the consumption

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of chemicals at the oxygen-delignification and PO-delignification stages for five levels of black liquor solids entrainment. As a rule of thumb, 0.79 kg of total black liquor solids is equivalent to 0.57 kg of salt cake. Thus, a black liquor solids entrainment of 85 kg/o.d. metric ton of pulp (8.5% on pulp) is equivalent to a salt cake loss of 48.5 kg of Na_2SO_4/o.d. metric ton of pulp, and this has to be made up at chemical recovery. For a perspective, the black liquor solids entrainment (salt cake) with the pulp after a three-stage brownstock washing is about 25-35 kg (15-20 kg of Na_2SO_4/metric ton of pulp).

With an increase in the black liquor solids entrained in the pulp from 0 to 85 kg/o.d. metric ton, the kappa number of the unbleached pulp increased to 34.0, a 5.3% increase over the reference pulp (kappa number 32.3). The viscosity of the pulps remained the same at 34.5 mPa·s except for the pulp with black liquor solids entrainment of 85 kg/o.d. metric ton, for which the viscosity was measured to be 33.5 mPa·s (Table I).

The consumption of chemicals at oxygen delignification and PO delignification are related directly to the concentration of black liquor solids entrained with the pulp. For example, in oxygen delignification, compared to the reference pulp with no entrained solids, a black liquor solids entrainment of 85 kg/o.d. metric ton of pulp doubled the oxygen consumption and increased the sodium hydroxide by about 50% (Table I). In PO delignification, as in oxygen bleaching, the consumption of oxygen, alkali, and hydrogen peroxide were all increased with the increase in the concentration of entrained black liquor solids. Hydrogen peroxide was completely consumed by the pulp with entrained black liquor solids of 85 kg/metric ton, and no residual hydrogen peroxide was detected. When the hydrogen peroxide charge was increased from 0.5-0.7% (o.d. pulp basis), 87% of the hydrogen peroxide was consumed by a similar pulp with entrained black liquor solids of 85 kg/metric ton.

The increased consumption of oxygen by pulps with entrained black liquor solids during oxygen delignification and PO delignification has been attributed to the oxidation of sodium sulfide in black liquor to sodium thiosulfate. On a stoichiometric basis, each mole of sodium sulfide oxidized would consume two moles of oxygen. The oxidation of organic components of the entrained black liquor also would result in additional consumption of oxygen. Increased consumption of NaOH during oxygen delignification and PO delignification was probably a result of higher concentration of acids formed from both pulp and black liquor. The NaOH would be consumed mostly in neutralization reactions. The tall oil with the black liquor would also consume a certain amount of alkali and contribute to the overall increase in the consumption of NaOH.

In PO delignification, the availability of hydrogen peroxide for useful reactions is the key factor in achieving better selectivity and is one of the reasons for the improved delignification and viscosity selectivity in PO delignification over oxygen delignification (*1, 2*). Any uncontrolled decomposition of hydrogen peroxide would severely restrict the overall selectivity of PO delignification. The selectivity of PO delignification of pulps would be affected therefore by the black liquor solids entrainment because of Na_2S in black liquor, which would initiate the decomposition of a substantial amount of hydrogen peroxide. Each mole of sodium sulfide decomposes four moles of hydrogen peroxide, so the carry-over of black liquor solids can exert an undue influence on the extent of delignification and on the selectivity of PO-delignified pulps. The oxidation of sodium sulfide by hydrogen peroxide or oxygen results in its conversion to sodium thiosulfate and sodium sulfate.

The presence of S^{2-}, $S_2O_3^{2-}$, and SO_4^{2-} anions in particular S^{2-} and $S_2O_3^{2-}$—promote the nucleophilic displacement on oxygen in hydrogen peroxide to hydroperoxyl anion (*8*). The subsequent disproportionation reaction between hydrogen peroxide and hy-

I. Pulp properties and chemical consumption

Black liquor solids, kg/metric ton	Kappa no.[a]	Viscosity,[a] mPa·s	Chemical consumption, % Oxygen	NaOH	NaOH adj.[b]	H_2O_2	H_2O_2 adj.[b]
Oxygen delignification							
0	32.3	34.5	1.7	2.1	52.5	...	...
20	32.5	34.4	2.1	2.6	65.0	...	...
25	32.7	33.9	2.1	2.7	67.5	...	...
30	33.1	34.1	2.2	2.7	67.5	...	...
42.5	33.6	34.3	2.4	2.9	72.5	...	...
85	34.0	33.5	3.2	3.2	80.0	...	...
Hydrogen-peroxide-reinforced oxygen delignification							
0	32.3	34.5	1.8	2.4	60.0	0.38	76.0
20	32.5	34.4	2.1	3.0	75.0	0.42	84.0
25	32.7	33.9	2.1	3.1	77.5	0.44	88.0
30	33.1	34.1	2.2	3.2	80.0	0.48	96.0
42.5	33.6	34.3	2.4	3.2	80.0	n.r.	n.r.
85	34.0	33.5	3.2	3.3	82.5	n.r.	n.r.
85[c]	34.2	33.7	3.2	3.5	87.5	0.62	88.6

Chemical charges (on o.d. pulp basis) at the oxygen stage:
NaOH = 4%, $MgSO_4$ = 0.5% and with PO, H_2O_2 = 0.5%. The partial pressure of oxygen was 760 kPa (at 25°C).
[a]Mean value of four measurements (standard error < 10%).
[b]Percent consumption in terms of chemical charge; adjusted for the residual alkali with the pulp from the entrained black liquor solids.
[c]H_2O_2 = 0.7% on pulp.
n.r. = no residual hydrogen peroxide in the spent liquor; complete consumption of H_2O_2 by pulp (0.5%).

II. Properties of oxygen-delignified and PO-delignified kraft pulps at different levels of black liquor solids entrainment

Black liquor solids, kg/metric ton	Kappa number[a]				Viscosity,[a] mPa•s	Brightness,[a] % ISO
	Init.	Final	Difference	Reduction, %		
Oxygen delignification						
0	32.3	15.9	16.4	50.8	21.4	34.2
20	32.5	15.3	17.2	52.9	20.6	35.1
25	32.7	15.0	17.7	54.1	20.3	34.6
30	33.1	15.5	17.6	53.2	20.2	34.5
42.5	33.6	16.2	17.4	51.8	19.4	34.2
85	34.0	16.6	17.4	51.2	19.0	34.0
Hydrogen-peroxide-reinforced oxygen delignification						
0	32.3	13.2	19.1	59.1	21.3	36.9
20	32.5	13.0	19.5	60.0	19.8	37.1
25	32.7	13.1	19.6	59.9	19.3	37.0
30	33.1	13.4	19.7	59.5	19.0	36.9
42.5	33.6	14.0	19.6	58.3	19.0	37.3
85	34.0	14.5	19.5	57.4	18.5	36.3
85[b]	34.2	14.0	20.2	59.1	19.5	37.4

[a]Mean value of four measurements (standard error < 10%).
[b]Hydrogen peroxide charge was increased to 0.7% on o.d. pulp.

droperoxyl anion tends to accelerate the decomposition of hydrogen peroxide (*8*). According to Edwards (*8*), the decomposition of hydrogen peroxide by nucleophiles in aqueous solution is a cumulative function of reactivity constants, mainly double basicity (*9*) and polarizability (*10*). Next to I^-, the anions S^{2-}, HS^-, and $S_2O_3^{2-}$, respectively, have the highest nucleophilic strengths to decompose hydrogen peroxide (*8, 11, 12*). Jencks and Carriuolo (*11*) and Edwards (*8*) determined the rate of decomposition of hydrogen peroxide by I^- and S^{2-} anions, respectively, and found that the rates are nearly the same [$k = 7.0 \times 10^{-1}$ L/(mole•s)]. On the other hand, according to Jencks and Carriuolo (*11*), the rate of decomposition of hydrogen peroxide by $S_2O_3^{2-}$ anions is slower by almost twice the order of magnitude [$k = 2.5 \times 10^{-2}$ L/(mole• s)] in comparison to S^{2-} anions. Nevertheless, among the nucleophiles studied by them, I^-, S^{2-}, and $S_2O_3^{2-}$ anions, respectively, had the highest rate constants, next only to thiourea, which decomposed hydrogen peroxide instantaneously.

It is evident from the rate constant values that in a hydrogen-peroxide-reinforced oxygen delignification of pulps with entrained black liquor solids, the hydrogen peroxide should be charged only after the addition of oxygen, so that much of the Na_2S in entrained black liquor solids be converted to $Na_2S_2O_3$. In addition to the nucleophiles, other impurities present with the black liquor, particularly transition metals, would also affect the stability of hydrogen peroxide and would further its decomposition. Therefore, nucleophilic displacement on oxygen as well as uncontrolled homolytic decomposition of hydrogen peroxide by black liquor solids, particularly sulfide and other sulfur species, would increase the concentration of hydroxyl and hydroperoxyl radicals and would affect the selectivity.

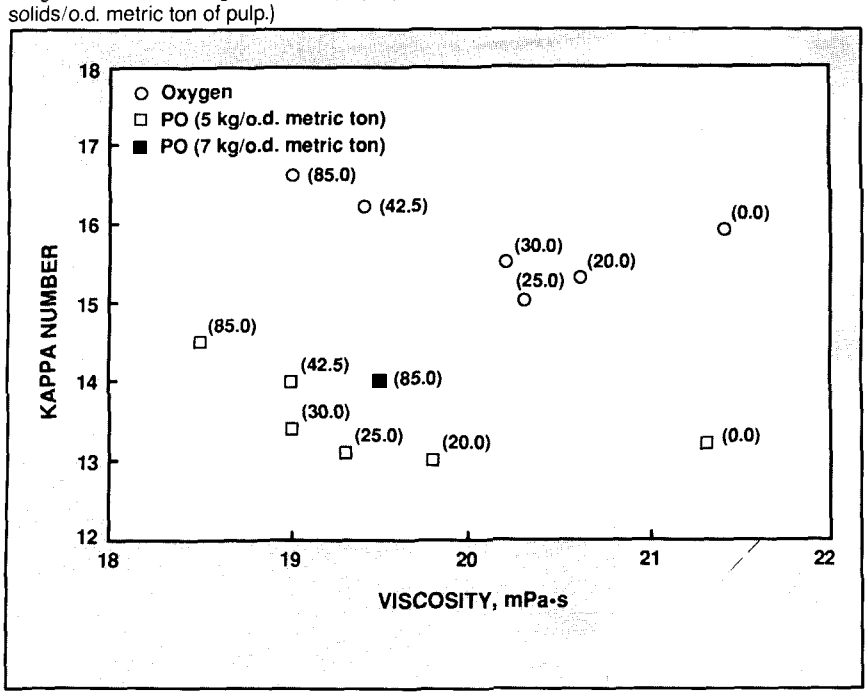
A large concentration of radicals, particularly hydroxyl radicals, results in the degradation not only of lignin but also of carbohydrates, leading to enhanced delignification but reduced pulp viscosity. The degradation reactions generate more acids and consume more alkali at PO delignification. This has been explicitly demonstrated for the PO delignification of pulps (Table I). From a chemical consumption point of view, beyond certain limits of black liquor solids carry-over, increased black liquor solids entrainment with the pulp is detrimental to oxygen delignification and especially to PO delignification and would restrict the availability of oxygen and hydrogen peroxide for useful reactions.

The properties of oxygen-delignified and PO-delignified pulps are listed in **Table II**. Under constant chemical charges, reinforcement of the oxygen stage with hydrogen peroxide has improved the extent of delignification by as much as 17%. Reinforcement of oxygen delignification with 0.5% hydrogen peroxide (o.d. pulp basis) has resulted in a kappa number reduction of about 60%. Under the same conditions, the kappa number reduction in oxygen-delignified pulp was about 51%. Hydrogen peroxide reinforcement of oxygen delignification has resulted not only in pulp with reduced kappa number (13.2) but also in a pulp equal in viscosity to oxygen-delignified pulp of kappa no. 15.9. The PO pulps were brighter by about 3% ISO points than the oxygen-bleached pulps.

The black liquor solids entrainment had a positive influence on the oxygen delignification and improved the extent of delignification (**Fig. 1**). An additional delignification of about 4% was observed for the pulp with black liquor solids entrainment of 30 kg/o.d. metric ton. When the solids entrainment was increased above 3% (>30 kg/o.d. metric ton), a small drop in the delignification rate was observed, but this drop in delignification did not affect the overall removal of lignin from the pulp. As a matter of fact, the removal of lignin from pulps with entrained black liquor solids was higher than with the oxygen-delignified reference pulp having no entrained black liquor solids.

In PO delignification, in contrast

1. The influence of entrained black liquor solids on the kappa number and viscosity of oxygen-delignified and PO-delignified kraft pulps (Numbers in the parentheses are kg of black liquor solids/o.d. metric ton of pulp.)



III. Chemical components in Southern pine black liquor

pH	11.80
Total dry solids in black liquor, %	21.84
Organic matter,[a,b] %	69.78
Inorganic matter,[b] %	30.22
Alkali as Na_2O, g/L	
NaOH	6.40
Na_2S[c]	3.42
(% on dry solids)	(1.57)
Na_2CO_3	30.53
Na_2SO_4	0.65
$Na_2S_2O_3$	5.80
Total titratable	40.35
Active alkali	9.82
Total sodium, g/L	67.13
Total sulfur, g/L	11.02

[a]% = 100%—sulfated ash as NaOH, % of total solids.
[b]Organic and inorganic matters were determined on the basis of dry total solids.
[c]Sodium sulfite was determined after reducing all the sulfur compounds.

with oxygen delignification, the carryover of black liquor solids resulted in only marginal improvements in the extent of delignification (Fig. 1). Improvements in kappa number reduction were observed up to black liquor solids of 30 kg/o.d. metric ton of pulp, beyond which the delignification was slower than in the reference pulp. In oxygen delignification, improvements in lignin removal were observed for the entire range of black liquor solids entrainment; in PO delignification, the entrained solids lowered the rate of delignification after 30 kg of black liquor solids entrainment (Fig. 1). The decrease in the rate of PO delignification can be compensated by increasing the charge of hydrogen peroxide. Upon increasing the hydrogen peroxide charge from 0.5% to 0.7% on o.d. pulp, the selectivity of PO delignification of pulp with 85 kg of black liquor solids entrainment was improved to that of a pulp with entrained black liquor solids of 30–42.5 kg/o.d. metric ton (Fig. 1).

The viscosities of both oxygen-delignified and PO-delignified pulps were affected by the entrained black liquor solids. These viscosity losses were significant in comparison with the reference pulps. At a black liquor solids entrainment of 85 kg/o.d. metric ton of pulp, the viscosity losses were 11.2% for oxygen-delignified pulps and 13.1% for PO-delignified pulps. The brightnesses of oxygen-delignified and PO-delignified pulps were not affected by the entrained black liquor solids.

Improvements in the rate of delignification but reductions in viscosity suggest that the controlled decay of oxygen and hydrogen peroxide and the subsequent generation of radicals are important in improving the selectivity of oxygen delignification and PO delignification. The findings reported here are in agreement with the results reported by Magnotta and Courchene (*7*) for the oxygen delignification of West Coast softwood kraft pulps (kappa no. 59.4).

Summary

Black liquor solids entrainment of up to about 30 kg/o.d. metric ton of pulp is beneficial, increasing the rate of oxygen delignification and PO delignification. However, black liquor solids entrained with the pulp affected the pulp viscosity. Therefore, the overall selectivities of oxygen- and PO-bleached pulps were slightly lower for pulps with black liquor solids entrainment as compared to the reference pulp containing no carryover solids. Despite the reduced selectivity of PO delignification with increased black liquor solids entrainment, reinforcement of the oxygen stage with hydrogen peroxide (0.5% on pulp) has resulted in pulps lower in kappa number and equal in viscosity to oxygen-delignified pulps.

Experimental procedures

The chemical components of the black liquor are listed in **Table III**. Loblolly pine kraft pulp from a commercial source (kappa no. 32) was used as the feedstock. The unbleached pulp was washed free of alkali by soaking for 24 h in deionized water, filtering, and centrifuging. These steps were repeated three times.

The oxygen delignification was performed in an Autoclave Engineers, Inc., bolted-closure, packless autoclave (about 1.08 L), having provisions to inject chemicals (gas or liquid) during the experiment. For each batch, an excess of NaOH was mixed with 100 g of pulp (o.d. basis), and the consistency was adjusted to 5%. After a retention period of 60 min, the pulp was pressed to a consistency of 25%. The filtrate was analyzed for the residual alkali concentration. Any deficiency in alkali charge was made up by adding calculated amounts of NaOH to the pulp. Appropriate

amounts of $MgSO_4$ (0.5%) and amounts of black liquor corresponding to dry solid charges of 25, 30, 35, 42.5 and 85 kg/o.d. metric ton of pulp were added to the pulp along with NaOH.

The pulp consistency was adjusted to 20%, the pulp was loaded to the reactor, and the reactor was charged with hydrogen peroxide. The final consistency of the pulp after mixing with H_2O_2 was 15%. The reactor was pressurized with oxygen to 760 kPa (110.3 psig), and the contents were heated to 110°C. The time to reach the cooking temperature of 110°C was about 10 min, and this temperature was kept constant for all the runs. Delignification was carried out for 30 min at 110°C. At the end of the reaction, the pulp was discharged after relieving the reactor pressure. Before the pulp was washed with tap water, the spent liquor was collected and analyzed for the concentration of residual alkali and hydrogen peroxide. After the pulp was washed thoroughly with tap water, it was hand pressed and centrifuged. Then it was fluffed and stored at 4°C.

Kappa number, pulp viscosity, and residual alkali and hydrogen peroxide concentrations were measured by TAPPI Test Methods. (Pulp viscosity is reported as 0.5 CED, or cupriethylenediamine viscosity of 0.5% pulp, by TAPPI Test Method T 230 om-82.) Brightness was measured in Elrepho 2000 (Ahiba Datacolor) at $\lambda = 457$ nm, following ISO procedures 2469 and 2470.□

Literature cited

1. Parthasarathy, V. R., Sundaram, V. M., Jameel, H., Gratzl, J., and Klein, R., 1989 International Symposium on Wood and Pulping Chemistry, TAPPI PRESS, Atlanta, p. 107.
2. Parthasarathy, V. R., Sundaram, V. M., Jameel, H., Gratzl, J., and Klein, R., 1989 Pulping Conference, Book 2, TAPPI PRESS, Atlanta, p. 539.
3. Rapson, W. H., Pulp Paper Mag. Can. 68(12): T635(1967).
4. Isbister, J. A., Reeve, D. W., and Rapson, W. H., The closed-cycle concept kraft mill at Great Lakes Paper Company Limited, PIMA (Aug.): 23(1978).
5. Croon, I. and Andrews, D. H., Tappi 54(11): 1893(1971).
6. Samuelson, O. and Ojteg, U., Tappi J. 75(2): 141(1990).
7. Magnotta, V. L. and Courchene, C. E., 1982 Pulping Conference Proceedings, TAPPI PRESS, Atlanta, p. 309.
8. Edwards, J. O., Peroxide Reaction Mechanism, Interscience Publishers, New York, 1962, p. 168.
9. Edwards, J. O., J. Am. Chem. Soc. 76: 1540(1954).
10. Edwards, J. O., J. Am. Chem. Soc. 78: 1819(1956).
11. Jencks, W. P. and Carriuolo, J., J. Am. Chem. Soc. 82: 1778(1960).
12. Satterfield, C. N., Reid, R. C., and Briggs, D. R., J. Am. Chem. Soc. 76: 3922(1954).

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