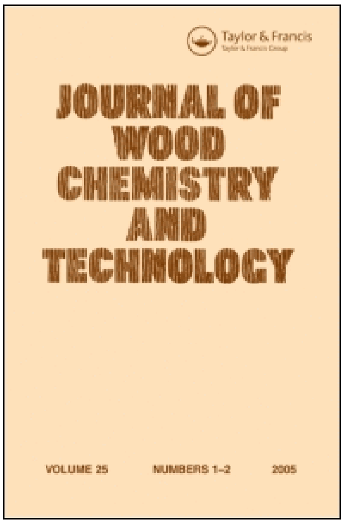

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OXIDATIVE PRETREATMENT WITH HYDROGEN PEROXIDE PRIOR TO ALKALINE PULPING

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ABSTRACT

Oxidative pretreatment of Southern pine wood with alkaline hydrogen peroxide increased its rate of delignification during subsequent kraft and soda-AQ pulping. Effective pretreatment required the removal of transition metals prior to oxidation at high pH (12), low temperature (50°C) and short reaction time (<45 min.). Compared with reference pulping, pretreatment with 1.4% H_2O_2 and 3.3% NaOH on wood reduced pulping time to 35 kappa number by 30 minutes (at 170°C). Pre-oxidation resulted in pulp with yield-kappa number and viscosity-kappa number relations equal to or greater than those of corresponding reference pulp.

For both kraft and soda-AQ pulp, bleachability, in terms of chemical charge and final viscosity, was unaffected by pre-oxidation while total bleached yield was increased by about 2% on wood. Handsheet strengths for unbleached and bleached kraft pulp were unaffected by oxidative pretreatment whereas those for unbleached soda-AQ pulp were improved to kraft-like levels. However bleached soda-AQ pulp strengths, both with and without pre-oxidation, were less than those of corresponding bleached kraft pulp.

INTRODUCTION

Oxidative pretreatments prior to alkaline pulping have been studied extensively on the laboratory scale, using such oxidants as peracetic acid (1,2), hydrogen peroxide (3,4), nitrogen dioxide (5-8), oxygen (9-10), potassium permanganate (11) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (12,13). The main aim in these studies has been to modify lignin in a way that increases its reactivity in fragmentation reactions, thus accelerating delignification. Pre-oxidation may further accelerate delignification by introducing hydrophilic functions in lignin enhancing its solubility. In some cases oxidative pretreatments increase pulp yield, presumably through stabilisation of carbohydrates toward alkaline peeling reactions.

The key to accelerating alkaline delignification through increased lignin reactivity lies in modifying its structure to enhance β-aryl ether cleavage in non-phenolic units. This scission is believed to strongly influence the rate of bulk lignin removal (15). Efforts to date have focused on replacing hydroxyl groups adjacent to the β-aryl ether link with substituents such as phenols (16), sulfonic acids (17) or carbonyls (18). Carbonyls are of interest here since they can be introduced through oxidative treatments.

Previous work on pre-oxidation with alkaline hydrogen peroxide has shown that it accelerates soda delignification; however, its effect on alkaline pulping systems in which strong nucleophiles are present, i.e.,kraft and soda-anthraquinone (AQ) pulping, is undetermined (3,4). While oxidised functions such as α- and γ- carbonyls in lignin promote side-chain cleavages in important non-phenolic β-aryl ether units (especially in the presence of hydrosulfide or anthrahydroquinone anions (19,20)), known reactions between native lignin structures and hydroperoxide anion do not generate these oxidised functions (21). On the other hand, radical species generated during peroxide decomposition, such as HOO· HO· and singlet O_2, are highly reactive electrophiles which may initiate such oxidations and thus affect the course of subsequent alkaline delignification (22).

All radical and ionic oxidants in the alkaline peroxide system are able to oxidise carbohydrate reducing end groups to more stable aldonic acids (23). This should help to reduce base-induced stepwise depolymerisation (peeling) reactions and increase carbohydrate retention during subsequent pulping. Unfortunately, radicals present, especially HO·, can also attack carbohydrates by oxidising hydroxyl groups along carbohydrate chains to carbonyls, thereby sensitizing polysaccharides to glycosidic bond cleavage by ß-eliminations (22). This not only lowers final pulp viscosity,but also promotes yield loss through stepwise depolymerisation of generated fragments with reducing endgroups (secondary peeling).

The purpose of the present work was to study the effects of peroxide pretreatment of wood prior to kraft and soda-AQ pulping. Effects on delignification kinetics, pulping selectivity, and pulp strengths and bleachability were examined. To achieve the greatest pre-oxidation effectiveness with hydrogen peroxide, radical reactions with carbohydrates must be minimised. Preferential reaction with lignin components will be favoured by complete penetration of wood with alkaline peroxide and controlled decomposition of peroxide to maintain low steady-state concentrations of radical species. In initial laboratory studies, wood meal (Southern pine) was used to ensure complete penetration of the chemicals into the wood, and teflon- lined equipment was chosen to reduce peroxide decomposition. The kraft process was selected to determine optimal pre-oxidation conditions.

RESULTS AND DISCUSSION

Wood Meal Studies

Table 1 shows that oxidative pretreatment of wood meal with 2% H_2O_2 on wood at pH 13 significantly accelerated subsequent kraft delignification when compared with reference pulping without pretreatment, i.e. final kappa number was lowered 18 to 26 units. Similar alkaline pretreatment without peroxide had no effect on delignification and resulted in lower total yield. It should be noted that wood meal pulping experiments were performed at high liquor-to-wood ratio (40 dm^3/kg) in order to maintain nearly constant chemical concentration throughout the pulping period.

TABLE 1

Effect of Acid Washing and Magnesium Addition on Oxidative Pretreatment with 2% H_2O_2 (Southern Pine Wood Meal)

	Pretreatment[1]			Kraft Pulping[2]		
Acid Wash[3]	Mg^{2+} (M)	H_2O_2 Consumed (%)[4]	NaOH Consumed (%)[4]	Kappa No.	Total Yield (%)[4]	Viscosity (mPa.s)
Reference kraft						
No	None			52.7	48.1	18.9
Yes	None			53.8	48.4	22.1
Alkaline pretreated						
No	0.001	-	3.2	54.3	47.6	19.0
Yes	0.001	-	3.6	53.1	47.8	21.4
Pre-oxidised						
No	-	2.0	3.9	27.0	39.6	11.0
No	0.001	2.0	3.8	28.3	41.5	9.4
Yes	-	1.8	3.8	36.1	44.6	17.3
Yes	0.001	1.4	3.6	34.5	46.1	19.4

[1] Pretreatment: 0.04 M H_2O_2 (when indicated) & 0.5 M NaOH; 15 dm^3/kg; 45 minutes; 80°C.

[2] Kraft pulping: 23 g/l AA (as Na_2O); 25% sulfidity; 40 dm^3/kg; 955 H-factor.

[3] Soak at 25°C in 0.1 M HCl for 4 hours at 40 dm^3/kg. Water wash to neutral pH.

[4] Based on wood.

As controlled peroxide decomposition is likely to be important for effective pre-oxidation, the effects of removing catalytic transition metal ions from wood meal and adding magnesium stabiliser to the pretreatment liquor were examined. To remove metals, wood meal was soaked in dilute acid for several hours then washed to neutral pH with deionised water. This treatment reduced manganese content from 79 ppm to less than 1 ppm, copper content from 5 to 1 ppm, and iron content from 16 to 7 ppm.

Acid washing to remove metals had no effect on extents of delignification for either reference kraft pulping or pulping after alkaline pretreatment, although pulp viscosities were somewhat improved (Table 1). It was essential, however, to remove metals when using oxidative pretreatment, in order to obtain the benefit of increased delignification at acceptable levels of total yield and pulp viscosity. The presence of residual peroxide indicated that peroxide decomposition and consumption was more controlled when the concentration of metal ions was minimised. Inclusion of magnesium cation during pre-oxidation also contributed to improved pulping selectivity in terms of both yield-kappa number and viscosity-kappa number relations (Table 1).

The effects of varying pre-oxidation reaction conditions were studied using a system in which magnesium was added and also wood meal was acid washed. When initial pretreatment pH was reduced stepwise from 12.9 to 10.1, fastest delignification resulted at about pH 12 when alkali concentration was 0.1 M NaOH (Table 2). Pulping selectivity was relatively unaffected by pretreatment pH.

Varying peroxide level from 1 to 4% H_2O_2 on wood increased its consumption during pre-oxidation but had relatively little effect on final kappa number (Table 3). Since this series of pre-oxidations was run a higher pH than optimal (0.5 M rather than 0.1 M NaOH), the small decrease in kappa number with increased peroxide concentration may have been partly due to a pH effect, i.e., pH was lowered to nearer optimum level by the addition of acidic hydrogen peroxide.

Increasing pretreatment time and temperature above initial levels of 45 minutes and 80°C increased peroxide consumption, but not the extent of delignification during subsequent kraft pulping (Table 4). In this experimental series, delignification was improved only when pre-oxidation temperature was reduced to 70°C. Further study indicated that reaction temperatures and times as low as 50°C and 15 minutes resulted in effective pre-oxidation.

The response of oxidative pretreatment to changing conditions suggests that there may be two competing types of reactions between peroxide species and wood during pre-oxidation. Beneficial reactions appear to be both rapid and finite in nature since optimal pretreatment effect occurred at low temperature and was largely unaffected by increased peroxide consumption. These results suggest that oxidative reactions which accelerate delignification involve specific lignin structures and radical decomposition products. On the other hand, there seem to be rival reactions which reduce pretreatment benefits. These reactions are slower, and thus more extensive under harsher pretreatment conditions. They could possibly be attributed to excessive radical attack resulting from uncontrolled peroxide decomposition, or alternatively to mechanisms involving ionic species and high activation energies.

Chip studies

Further pre-oxidation studies were performed under more conventional pulping conditions using wood chips and a lower liquor-to-wood ratio. Southern pine chips were first treated with acidified DTPA (diethylenetriaminepentaacetic acid) to reduce transition metal content to levels similar to those of acid-washed wood meal. Chip pretreatment involved rapid

TABLE 2

Effect of pH on Oxidative Pretreatment with 2% H_2O_2
(Southern Pine Wood Meal)

Oxidative Pretreatment[1]				Kraft Pulping[2]		
pH Init./ Final	NaOH Applied (M)	H_2O_2 Consumed (%)[3]	NaOH Consumed (%)[3]	Kappa No.	Total Yield (%)[3]	Viscosity (mPa.s)
Reference kraft						
None				53.8	48.4	22.1
Pre-oxidised						
12.9/12.8	0.5	1.4	3.6	34.5	46.1	19.4
12.4/11.8	0.1	1.3	3.3	31.8	45.6	20.1
11.8/9.6	0.05	1.3	2.2	38.2	46.7	19.0
11.2/10.4	0.015[4]	2.0	-	43.1	47.0	21.7
10.1/9.9	0.25[5]	2.0	-	44.8	46.9	21.4

[1] Pretreatment: 0.04 M H_2O_2, NaOH as indicated & 0.001 M Mg^{2+}; 15 dm^3/kg; 45 minutes, 80°C.

[2] Kraft pulping: 23 g/l AA (as Na_2O); 25% sulfidity; 40 dm^3/kg; 955 H-factor.

[3] Based on wood.

[4] Buffered with 0.49 M Na_2CO_3.

[5] Buffered with 0.38 M $NaHCO_3$.

impregnation under vacuum with hot alkaline peroxide solution followed by vapour-phase reaction under optimal conditions, as determined from wood meal studies. Concentrations of hydrogen peroxide and alkali were adjusted to give consumption levels similar to those for wood meal. Pretreated chips were not washed prior to pulping and alkali carry-over (typically 0.4% active alkali on wood) was accounted for in reported pulping charges.

At consumptions of 1.4% H_2O_2 and 3.3% NaOH, oxidative pretreatment with chips accelerated delignification for both kraft and soda-AQ pulping (Table 5). Pulping time at 170°C to reach 35 kappa number was reduced by about 30 minutes. As shown

TABLE 3

Effect of Hydrogen Peroxide Level on Oxidative Pretreatment (Southern Pine Wood Meal)

Oxidative Pretreatment[1]				Kraft Pulping[2]		
H_2O_2 Applied (M)	H_2O_2 Applied (%)[3]	H_2O_2 Consumed (%)[3]	NaOH Consumed (%)[3]	Kappa No.	Total Yield (%)[3]	Viscosity (mPa.s)
Reference kraft						
None				53.8	48.4	22.1
Pre-oxidised						
0.02	1.0	0.9	3.4	37.5	46.6	20.0
0.04	2.0	1.4	3.6	34.5	46.1	19.4
0.08	4.0	2.3	4.1	33.4	45.8	20.8

[1] Pretreatment: H_2O_2 as indicated, 0.5 M NaOH & 0.001 M Mg^{2+}; 15 dm^3/kg; 45 minutes; 80°C.

[2] Kraft pulping: 23 g/l AA (as Na_2O); 25% sulfidity; 40 dm^3/kg; 955 H-factor.

[3] Based on wood.

TABLE 4

Effect of Time and Temperature on Oxidative Pretreatment with 2% H_2O_2 (Southern Pine Wood Meal)

Oxidative Pretreatment[1]				Kraft Pulping[2]		
Temp. (°C)	Time (min.)	H_2O_2 Consumed (%)[3]	NaOH Consumed (%)[3]	Kappa No.	Total Yield (%)[3]	Viscosity (mPa.s)
Reference kraft						
None				53.8	48.4	22.1
Pre-oxidised						
70	45	1.1	3.1	30.9	45.3	19.6
80	45	1.3	3.3	31.8	45.6	20.1
80	90	1.5	3.4	36.9	46.3	19.7
90	45	1.7	3.5	34.0	45.6	16.8
90	90	1.8	3.8	36.1	45.7	17.9
100	45	1.9	3.8	36.9	45.8	18.0
100	60	1.9	4.0	37.8	45.7	19.2

[1] Pretreatment: 0.04 M H_2O_2, 0.1 M NaOH & 0.001 M Mg^{2+}; 15 dm^3/kg.

[2] Kraft pulping: 23 g/l AA (as Na_2O); 25% sulfidity; 40 dm^3/kg; 955 H-factor.

[3] Based on wood.

for kraft pulping, alkaline pretreatment without peroxide also accelerated delignification but to a lesser extent (Table 5).

These effects were more clearly demonstrated in second-order kinetic plots of delignification (Figure 1). The rate of delignification when pulping alkaline pretreated chips was intermediate between those for reference kraft pulping and pulping pre-oxidised chips. Ratios of rate constants determined from regression slopes indicated that pre-oxidation accelerated kraft delignification by 50% and that one third of this improvement was attributable to the alkalinity of the pretreatment.

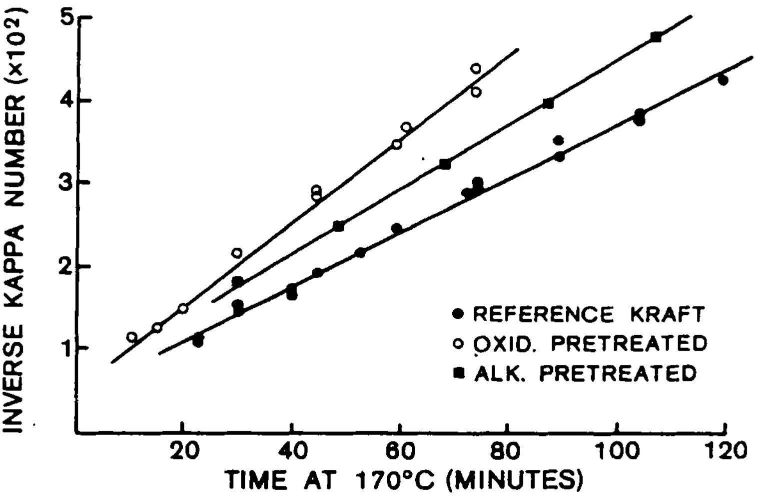

FIGURE 1 - Effect of pretreatment on kinetics for kraft delignification.

Regressions:

Ref. kraft $(K\#)^{-1} = 0.0046 + 3.23 \times 10^{-4}(t)$; $r = 0.99$

Oxid. pretreat. $(K\#)^{-1} = 0.0059 + 4.90 \times 10^{-4}(t)$; $r = 0.99$

Alk. pretreat. $(K\#)^{-1} = 0.0060 + 3.83 \times 10^{-4}(t)$; $r = 0.99$.

Alkaline pretreatments, both with and without peroxide, resulted in increased alkali concentrations during subsequent pulping of pretreated chips (Figure 2). Alkali consumption during pretreatment (3% NaOH on wood) reduced the large alkali demand normally observed during initial phases of alkaline pulping. Thus higher alkali concentrations were present to accelerate important bulk-phase delignification.

TABLE 5

Effect of Oxidative Pretreatment on Alkaline Pulping (Southern Pine Chips)

	Pretreatment[1]		Pulping			
Pulp Type	H_2O_2 Consumed (%)[2]	NaOH Consumed (%)[2]	Time @ 170°C (min.)	Kappa No.	Total Yield (%)[2]	Viscosity (mPa.s)
Kraft[3]						
Reference	----- None	------	73	34.8	46.2	29.7
Reference	----- None	------	45	52.2	48.2	34.8
Alk. pretreat.	-	3.1	45	44.1	47.7	-
Pre-oxidised	1.4	3.3	45	34.3	47.0	31.3
Soda-AQ[4]						
Reference	----- None	------	100	36.3	46.5	14.1
Pre-oxidised	1.4	3.3	70	36.0	46.7	15.5

[1] Impregnate with 0.3 M H_2O_2, 0.5 M NaOH & 0.001 M Mg^{2+} at 6 dm^3/kg; react 45 minutes at 50°C.

[2] Based on wood.

[3] Kraft pulping: 20% AA (as Na_2O); 25% sulfidity; 5 dm^3/kg; 80 minutes to 170°C.

[4] Soda-AQ pulping: 20% AA (as Na_2O); 0.1% AQ on wood; 5 dm^3/kg; 80 minutes to 170°C.

Pulping selectivity, in terms of yield-kappa number relations, was not significantly improved by pre-oxidation (Figure 3). Special attention was directed at the low kappa region where kraft pulping characteristically loses selectivity due to a reduction in delignification relative to carbohydrate degradation (24). Pre-oxidation had no effect on the kappa number at which selectivity decreased, (indicated by increased regression slope in Figure 3). Apparently, gains in carbohydrate stability through oxidative conversion of native reducing end groups were offset by increased lability toward alkaline chain cleavage and secondary peeling.

Pulping selectivity, in terms of viscosity-kappa number relations, was however improved by pre-oxidation, especially at kappa number greater than 35 (Figure 4). Over 10 units of viscosity were gained by oxidative pretreatment prior to kraft pulping to 45 kappa number, i.e., 44 versus 33 mPa.s.

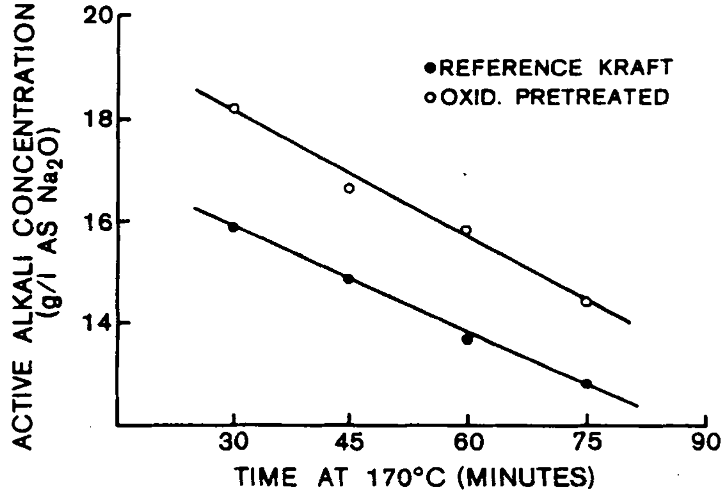

FIGURE 2 - Effect of oxidative pretreatment on residual active alkali concentration during kraft pulping.

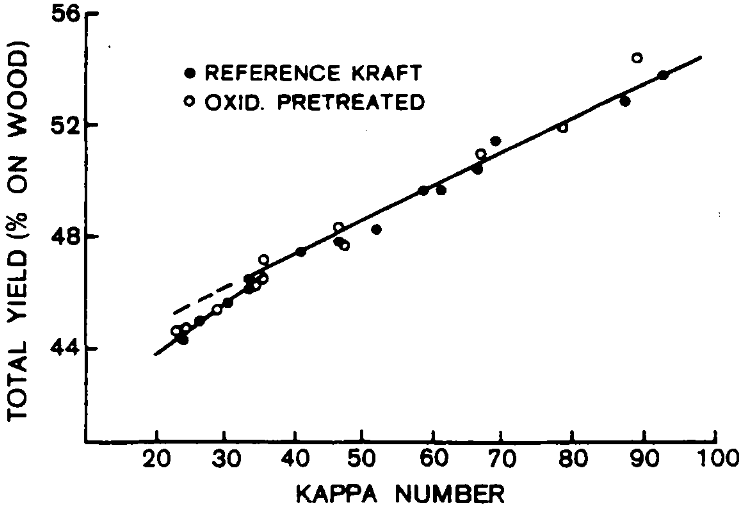

FIGURE 3 - Effect of oxidative pretreatment on yield-kappa number relations for kraft pulping.

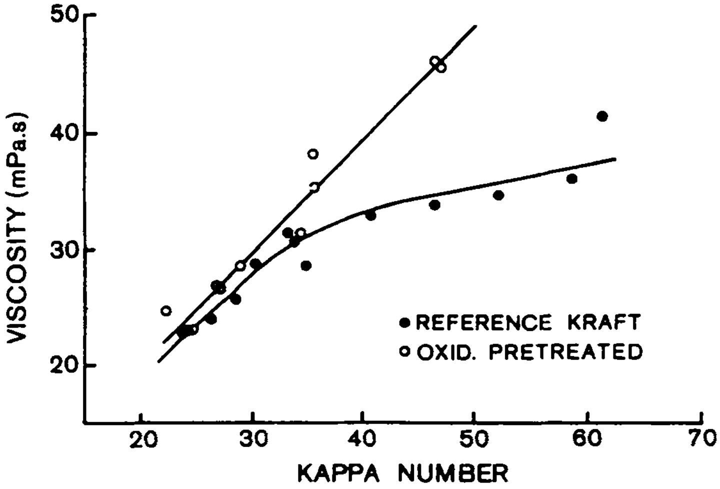

FIGURE 4 - Effect of oxidative pretreatment on viscosity-kappa number relations for kraft pulping.

In order to examine the effects of pre-oxidation on pulp strength properties, full handsheet evaluations were performed on kraft reference and pre-oxidised pulps at about 45, 35 and 27 kappa number. A similar pair of soda-AQ pulps at 36 kappa number was also evaluated. Handsheet strengths, as indicated by tear index at 90 N.m/g tensile index, were similar for all kraft pulp pairs despite differences in pulp viscosity (Table 6). Extended kraft pulping to low kappa number (27) for either reference or pre-oxidised pulp resulted in reduced pulp strength. At 35 kappa number, soda-AQ pulp from pre-oxidised chips was stronger than reference soda-AQ pulp and similar in strength to corresponding kraft pulp (Table 6).

TABLE 6

Effect of Oxidative Pretreatment on Unbleached Alkaline Pulp Handsheet Strengths

Pulp Type	Kappa No.	Viscosity (mPa.s)	95% Confidence Interval for Tear Index @ 90 N.m/g Tensile Index ($mN.m^2/g$)
Kraft			
Reference	43.8	33.3	15.9 ± 1.7
Pre-oxidised	46.3	43.9	16.6 ± 3.9
Reference	33.5	31.1	17.7 ± 2.2
Pre-oxidised	35.3	33.5	17.3 ± 1.3
Reference	26.4	25.4	14.7 ± 0.9
Pre-oxidised	28.5	28.7	14.0 ± 1.2
Soda-AQ			
Reference	36.3	14.1	14.4 ± 1.4
Pre-oxidised	36.0	15.5	18.1 ± 1.2

Bleachability

Kraft and soda-AQ pulps (~35 kappa number) from reference and pretreated chips were fully bleached under similar conditions with either a (C+D)EDED or an O(C+D)ED sequence (Table 7). Compared with reference pulps, pulps from pre-oxidised chips were of similar final brightness and viscosity while total yields were improved by 2% on wood. Treatment yields after both oxygen delignification and chlorine bleaching were higher for pulps from

TABLE 7

Effect of Oxidative Pretreatment on Alkaline Pulp Bleachability (Unbleached Kappa Number ~ 35)

Sequence	Applied Chemical[1]			Bleach Results		
	Cl_2 (%)	ClO_2 (%)	NaOH (%)	Brightness (GE)	Total Yield (%)[2]	Viscosity (mPa.s)
			KRAFT PULP			
(C+D)EDED						
Reference	3.2	1.8	4.4	86	42.1	27.6
Pre-oxidised	2.9	1.7	4.2	87	44.0	24.7
O/(C+D)ED						
Reference	1.2	1.1	6.4	87	42.2	17.8
Pre-oxidised	1.3	1.1	6.4	86	43.9	16.7
			SODA-AQ PULP			
(C+D)EDED						
Reference	3.3	1.8	4.5	85	41.9	13.3
Pre-oxidised	3.2	1.8	4.5	85	43.7	14.1

[1] Based on pulp.

[2] Based on wood.

oxidatively pretreated chips, thus indicating that some pre-oxidation effects on carbohydrates had carried over from pulping to influence subsequent oxidative bleach treatments. Unbleached handsheet brightnesses were 2 to 4 points higher for pulps from pre-oxidised chips but unfortunately these benefits did not translate into higher final brightness after similar bleaching.

Handsheet analysis showed that bleached kraft and kraft/O_2 pulp strengths were unaffected by oxidative pretreatment (Figure 5). Fully bleached soda-AQ pulp, on the other hand, had lower strength when pre-oxidation was employed (Figure 5). This was opposite to the trend shown by unbleached soda-AQ pulp where pre-oxidation led to greater overall strength at 36 kappa number (Table 6). After bleaching, confidence intervals for tear index at 90 N.m/g tensile index were 18.6 ± 1.0 and 17.2 ± 0.5 mN.m^2/g for reference and pretreated soda-AQ pulp, respectively. The

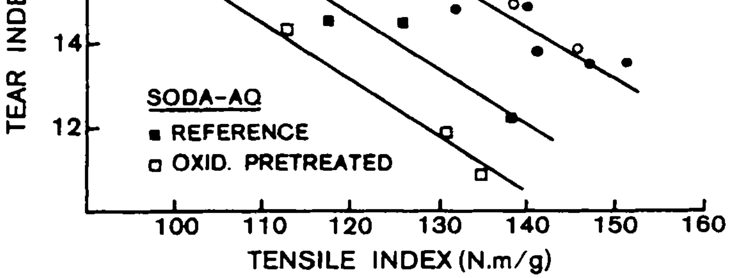

FIGURE 5 - Effect of oxidative pretreatment on bleached pulp strengths.

reference soda-AQ pulp increased substantially in tear versus tensile strength after bleaching. This effect is common for most pulps when carefully bleached in the laboratory (25). Pre-oxidation, however, somehow prevented this from occurring for soda-AQ pulp.

Potential Applications

The aim of oxidative pretreatment with hydrogen peroxide was to improve delignification and selectivity. These benefits could in turn be utilised in the mill to:

(i) increase pulp production from existing equipment,
(ii) extend delignification in the digester to lower kappa number,
(iii) improve pulp quality through less carbohydrate degradation.

Work here has demonstrated that pre-oxidation can help to achieve objective (i) by shortening pulping cycles in the digester and increasing bleached pulp yield. Retro-fitting a pretreatment system would be relatively simple since it uses non-pressurised equipment and chemicals required are compatible with existing recovery processes. Effective treatment to remove metals from wood chips prior to pre-oxidation, however, would be difficult to achieve economically on an industrial scale. In addition the high cost of hydrogen peroxide and sodium hydroxide must be considered. The cost of the latter as well as its impact on the sodium/sulfur balance in the recovery system might be overcome by use of new recovery technologies. For example, Tampella's TRP (26) can efficiently regenerate kraft pulping liquor as well as provide a side stream of pure alkali suitable for oxidative pretreatment or oxygen bleaching.

Attempts to employ pre-oxidation to extend delignification while maintaining pulp quality were not successful. At 27 kappa number, kraft pulp strength, as indicated by tear index at 90 N.m/g tensile index, was diminished both with and without pre-oxidation.

When kraft pulping pre-oxidised wood to greater than 35 kappa number, the large viscosity improvement may allow environmentally favourable modifications to conventional processing without sacrifice of pulp quality. It is well known that viscosity-pulp strength relations are non-linear and that, above a certain threshold viscosity, large increases in pulp viscosity result in little improvement in strength (27). Nevertheless, high viscosity in unbleached pulp is useful, since there is a reserve of viscosity above the threshold value to buffer the effects of using less polluting, but also less viscosity-selective methods, to further remove lignin. Such methods include treatment with non-chlorine compounds, for example oxygen, ozone, or hydrogen peroxide. The three-stage process of pre-oxidation, kraft pulping to high kappa number, and further delignification with a non-chlorine treatment, produces bleachable-grade pulp which is lower in kappa number, but similar in viscosity, to conventional pulp, prepared in one stage by kraft pulping to about kappa number 30.

Pre-oxidation was shown to similarly improve delignification rate, viscosity and total yield with soda-AQ pulping. For unbleached soda-AQ pulp, pulp strengths were also increased by pre-oxidation and were similar to those of corresponding kraft pulp. This latter improvement overcomes one of the major drawbacks of using soda-AQ pulping with softwoods and thus enhances its attractiveness as a non-sulfur alternative to kraft production of unbleached pulp. The data base for soda-AQ pulping, however, was limited here and more extensive study is required to fully define the scope of oxidative pretreatment with this process.

CONCLUSIONS

Oxidative pretreatment with hydrogen peroxide significantly accelerated kraft delignification. Kinetic studies showed that pre-oxidation increased the rate of kraft pulping by 50% over that for similar pulping of untreated chips. About one-third of the rate increase was attributable to alkali consumption during pretreatment while the rest was due to the action of hydrogen peroxide. When producing bleachable-grade pulp of 35 kappa number, oxidative pretreatment reduced pulping time at maximum temperature (170°C) by 30 minutes. Effective pretreatment was achieved with consumptions of 1.4% H_2O_2 and 3.3% NaOH on wood.

As with most pre-oxidations, pretreatment with hydrogen peroxide led to reduced pulp viscosity after a given pulping period. Since kappa number was also substantially reduced over the same period, viscosity - kappa number relations for pulps from pre-oxidized chips were equal to or better than those for reference pulps. Yield-kappa number relations were similarly affected. The greatest improvement in selectivity for viscosity was achieved when pulping was terminated at high kappa number.

Effective pretreatment depends on controlling decomposition of hydrogen peroxide. This was achieved by removing catalytic metal ions prior to pretreatment and using mild reaction conditions. Near-optimal conditions were high pH (12), low temperature (50°C) and short reaction time (<45 minutes). Increased hydrogen peroxide consumption did not lead to improved pretreatment effects. Beneficial pre-oxidation reactions appear to be limited and consume only small amounts of peroxide.

Handsheet strengths of unbleached kraft pulps from pre-oxidised chips were similar to those of corresponding reference pulp. When pulping to 35 kappa number, pre-oxidation improved unbleached soda-AQ pulp strength to kraft-like levels.

The bleachability of kraft, kraft/O_2 and soda-AQ pulp was unaffected by oxidative pretreatment with hydrogen peroxide.

Handsheet strengths of bleached kraft and kraft/O_2 pulps were unaffected by pre-oxidation while those of bleached soda-AQ pulp were slightly diminished. Treatment yields after chlorine-based bleaching and oxygen deliginification were greater for pulp from pre-oxidised chips. Compared with yield for bleached reference pulp, total yield from pre-oxidised chips was increased by about 2% on wood.

EXPERIMENTAL

Wood Source

The wood material was air-dried loblolly pine (Pinus taeda) at 440 kg/m^3 basic density. Wood meal was prepared with a Wiley Mill fitted with a 2.0-mm screen then classified with a Ro-Tap testing sieve shaker. The accepted sample passed 40 mesh (425 µm) and was retained on 60 mesh (250 µm). Chips were screened on a Williams classifier and the accepted sample passed 7/8 mesh and was retained on 3/8 mesh.

Wood Meal Experiments

To remove metals from wood meal, air-dried samples were soaked in 0.1 M HCl for 4 hours at 40:1 dm^3/kg liquor-to-wood ratio and 25°C. Treated wood meal was washed with deionized water to neutral pH then air-dried for storage at room temperature.

Wood meal pretreatments were performed in a 200-ml teflon-lined autoclave fitted with magnetic stirring and heated in a temperature-controlled glycol bath. Wood meal (10 g o.d.) and alkali solution were heated to the desired temperature prior to injection of concentrated H_2O_2 to give a final liquor-to-wood ratio of 15:1 dm^3/kg. After reaction, the autoclave was rapidly cooled in ice water. Pretreated wood meal was washed with distilled water to neutral pH and residual liquor was analysed for peroxide (iodometric titration) and alkali (TAPPI Standard T 613) contents.

Alkaline pulping was performed in a 450-ml stirred autoclave at 40:1 dm^3/kg and 170°C maximum temperature. For pretreated wood meal, chemical application levels were calculated on the original sample weight. Active alkali, sulfidity and AQ levels were as noted. Anthraquinone was reduced and solubilized with warm aqueous glucose prior to liquor addition (1:1.3 mole ratio of AQ to glucose). Wood meal and pulping liquor were soaked at room temperature under vacuum for 30 minutes to aid penetration. Heatup to maximum temperature was 90 minutes. After reaction, the reactor was rapidly cooled in ice water. Water-washed pulp was analysed for total yield (gravimetric), kappa number (TAPPI Standard T 236) and viscosity (TAPPI Standard T 230). All unbleached pulp samples were delignified with acid chlorite prior to viscosity determinations (27). In some cases residual active alkali in the spent pulping liquor was also determined (TAPPI Standard T 625).

Chip Experiments

To remove metals from wood chips, air-dried samples were soaked under vacuum in 0.1 N H_2SO_4 and 0.003 M Na_5-DTPA for 4 hours at 8:1 dm^3/kg and 25°C. Treated chips were centrifuged then washed with distilled water for three cycles. Each cycle consisted of a 2 hour soak in water at 8:1 dm^3/kg and 25°C followed by centifugation. After the final wash, chips were air-dried and stored at room temperature.

For chip pretreatment, air-dried samples (150 g o.d.) were reacted in a 2-litre glass kettle fitted with inlet lines, heating mantle and thermocouple. After chips were loaded to the preheated kettle, alkaline peroxide liquor at the desired reaction temperature was drawn into the kettle for a 2-minute impregnation period under vacuum at 6:1 dm^3/kg. Excess impregnation liquor was then drawn off and the reaction was continued in the vapour phase. Residual impregnation and chip liquors were analysed for peroxide and alkali content.

Alkaline pulping was performed wth 150 g o.d. samples (based on original wood for pretreated chips) in 2.8-litre autoclaves at 5:1 dm^3/kg and 170°C maximum temperature. Four reactors were heated in one pulping cycle in a circulating hot-air oven. Active alkali, sulfidity and AQ levels were as noted. Chips and pulping liquor were soaked at room temperature under vacuum for 30 minutes to aid penetration. Heatup to maximum temperature was 80 minutes. After reaction, autoclaves were rapidly cooled in cold water. Pulped chips were disintegrated by a propeller stirrer prior to screening on a 0.25-mm slotted flat screen. Screened pulp was centrifuged and fluffed before analysis for total yield, kappa number and viscosity. Black liquor was analysed for residual active alkali.

Bleaching

For oxygen delignification, pulp (150 g o.d.) was impregnated with 5% NaOH and 0.1% Mg^{2+} by soaking for 15 minutes at 5% consistency then pressing to 20% consistency. Exact application levels of alkali were determined by acid titration of the pressate. After fluffing, impregnated pulp was loaded in 2.8-litre autoclaves which were then purged of air and pressurised with 690 kPa of room-temperature oxygen. Charged reactors were heated in a circulating hot-air oven to 110°C in 50 minutes and held for 30 minutes. After reaction, the reactors were rapidly cooled in cold water. Oxygen-treated pulp was washed with tap water then centrifuged and fluffed prior to storage at 4°C. Pulp was analysed for yield, kappa number and viscosity.

For chlorination, pulp (150 g o.d.) was reacted in a plastic bag for 1 hour at 3% consistency and 25°C. Available chlorine charge (percent on o.d. pulp) was calculated as 0.20 x kappa number. Exactly 10% of total available chlorine was supplied as chlorine dioxide mixed with chlorine water just prior to application. Chlorinated pulp was washed with tap water then hand-squeezed prior to further treatment. Residual bleach liquor was analysed for available chlorine (TAPPI Standard T 611).

For alkaline extraction, pulp was reacted in a plastic bag for 1 hour at 10% consistency and 70°C. Applied NaOH (percent on original pulp) was approximately 0.5 x percent available chlorine for E_1-stage and 0.5% NaOH for E_2-stage. Extracted pulp was washed with tap water then hand-squeezed prior to further treatment. The E_1-pulp was analysed for extracted kappa number.

For chlorine dioxide treatment, pulp was reacted with ClO_2 in a plastic bag for 3 hours at 10% consistency and 70°C. In the D_1-stage, 1.0% ClO_2 and 0.4% NaOH (on original pulp) was applied. In the D_2-stage, 0.5% ClO_2 (on original pulp) was applied. Pulp was washed with tap water after treatment. D_1-pulp was sampled for brightness (TAPPA Standard T 218) then hand-squeezed prior to further treatment. After the D_2-stage, pulp was centrifuged and fluffed prior to storage at 4°C. This pulp was analysed for bleach yield, brightness and viscosity.

Handsheet Analysis

Handsheet analysis was performed according to standard TAPPI procedures after beating pulp in the PFI mill (20.5 g o.d.) at 10% consistency with an applied load of 3.7 N/mm.

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