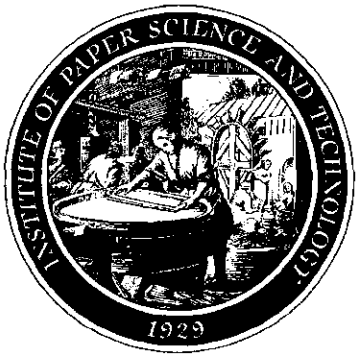

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Improved Bleaching Performance with Reduced Cost: Optimizing ECF Bleaching Technologies with a Poor Man's O

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INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY
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IMPROVED BLEACHING PERFORMANCE WITH REDUCED COST: OPTIMIZING ECF BLEACHING TECHNOLOGIES WITH A POOR MAN'S O

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ABSTRACT

ECF bleaching technologies now represent a globally accepted bleaching method that has minimal environmental impacts. The challenge that remains is how these ECF bleaching technologies can be utilized to minimize capital and operating costs. Our research has shown that the use of a D(E+O)* or (E+O)D(E+O)* sequence on pre- and post-O_2 pulps can efficiently remove lignin. Furthermore, this bleaching procedure is relatively insensitive to the presence of bleach plant effluent and black liquor carryover. This paper quantifies the impact of black liquor carryover and shows the effects of reinforcing a poor man's oxygen stage with hydrogen peroxide in an attempt to improve bleaching performance.

INTRODUCTION

Bleached chemical pulp production has undergone dramatic changes in the past several years. Environmental concern that is manifested in changing market demands and more stringent environmental regulations is one of the most important drivers of these changes in bleaching technologies. In an effort to improve the overall environmental impact of bleached chemical pulp operations, the pulp and paper industry has begun to implement a series of process changes including use of oxygen delignification technologies, fortification of extraction stages with oxygen and hydrogen peroxide, and improved brownstock washing [1-3]. In addition, the industry has had to find alternatives to elemental chlorine as a bleaching agent [4]. Hence, the demand for elemental chlorine-free (ECF) bleaching technologies, such as chlorine dioxide, hydrogen peroxide and oxygen, has been on the rise. Although these ECF bleaching technologies have been shown to address environmental concerns and produce pulps with desirable quality properties, the conversion in bleaching operations has been accompanied by increased costs [5]. Clearly, the challenge that now needs to be addressed is how ECF bleaching technologies can be utilized to minimize capital and operating costs. Several research groups have begun to address this issue and publications by Tait [6], Stapley et al. [7], Null and Cenatempo [8], Kimbrell [9], and Chakar et al. [10], are certainly indicative of this endeavor.

Several researchers have focused on extending the performance of oxygen delignification technologies, thereby providing improved costs. These researchers have noted that it is possible to improve pulp yields by halting the kraft cook at a high kappa number (i.e., 40-50 for SW kraft) before the selectivity of the kraft cook decreases in the terminal phase [10-14]. Magnotta et al. have reported improved selectivity with an extended oxygen OO system on high kappa kraft pulps. They showed that an OO system can increase yields ~4% prior to ECF bleaching [11]. Parthasarathy took a different approach by coupling modified kraft cooking conditions such as polysulfide, anthraquinone, and surfactant-based chip penetrants to gain bleached pulp yields (as much as 4-6%) when pulping was ceased at a kappa number of 40-50 [14]. The observed yield benefits of extended oxygen delignification technologies could lower overall operating costs compared to conventional systems by reducing the wood requirement [11]. In addition, the yield increases are further amplified by reducing the organic load on the recovery furnace, which offers the potential for significant production increases in a recovery boiler-limited mill while increasing environmental benefits.

A mini, (E+O), or poor man's oxygen system provides an alternative approach to utilizing oxygen delignification technologies. This system usually removes less lignin but requires less capital investment than a typical oxygen delignification system and is easily retrofitted to existing pulp bleaching operations [10]. Equipment and conditions required for a mini oxygen stage are similar to those currently applied in oxygen and hydrogen peroxide-reinforced extraction stages in the bleach plant [15]. Typically, a mini oxygen delignification stage uses an upflow tube with a retention of about 30 minutes, oxygen pressure of 80-90 psig, 1% NaOH, held at 70-80°C [5]. McKenzie reported that the commercial use of a mini oxygen system has produced low AOX pulps with no loss of production due to recovery or recausticizing bottlenecks. In addition, the mini oxygen stage provided approximately 25% delignification prior to a conventional oxygen stage [16].

Recent research efforts have focused on extending the capabilities of the poor man's oxygen delignification technologies. Some modifications to the process involve the addition of other oxidative chemicals, such as hydrogen peroxide, as well as the use of multiple stages [15]. Histed has proposed using an enhanced poor man's oxygen stage to achieve higher levels of delignification. The enhanced poor man's oxygen, which is a 0.05 kappa factor D pretreatment stage followed by a higher than normal temperature in the (E+O) stage, can achieve approximately 50% delignification [17]. Chakar et al. demonstrated that (E+O) treatment of a 26.6 kappa number softwood resulted in 13-25% delignification, depending on the caustic charge. These researchers also showed that the delignification effects of the (E+O) treatment were improved dramatically if the caustic was divided in half and the pulp was treated with a low charge of chlorine dioxide after an initial mini oxygen stage [10]. Dyer et al. further examined the benefits of an enhanced poor man's oxygen stage. They demonstrated that a (E+O)$D_{0.05}$(E+O) had 6% more delignification than a $D_{0.05}$(E+O)(E+O). The authors attributed this enhanced

delignification to the initial (E+O) stage removing easily oxidized lignin prior to the low kappa factor charge of chlorine dioxide [5].

In an effort to further extend the performance of a poor man's oxygen stage, it would be useful to investigate the impact of black liquor carryover on this ECF bleaching technology. Dissolved material in an oxygen stage, unlike that from chlorination and following extraction stages, is uncontaminated by chloride ions. It can therefore be routed back to the recovery furnace, where it becomes a source of energy instead of a pollutant [18, 19].

Enz and Emmerling reported that a raw black liquor solids addition of 65 kg/o.d. ton had no impact on the delignification or pulp physical properties of a commercial oxygen delignification system. In fact, this stability allowed the mill to use a low average dilution factor to the brownstock washing system [20]. Several researchers have investigated the impact of inefficient washing systems on laboratory oxygen delignification systems. There is some evidence that small amounts of black liquor carryover might benefit an oxygen delignification system. Bokstrom and Norden [12], Miller [21], Parthasarathy [22], and Parsad et al. [23] reported increases in delignification at the addition rates used in their studies. The apparent reason for this increase in delignification is due to residual alkali left in the carryover. However, several other research groups have found that black liquor carryover impacts both alkali and oxygen consumption due to the competing reactions between pulp lignin and dissolved material in the liquor [24, 25]. This lowers the delignification rate and may even enhance the selectivity of the oxygen delignification system [18, 19, 26-29]. Although there has been a significant contribution to the effects of black liquor carryover on an oxygen delignification system, the effects on a mini oxygen system and other ECF bleaching technologies are not yet clear. This paper further examines a poor man's oxygen stage incorporated with chlorine dioxide, hydrogen peroxide, and chelating stages in an attempt to elucidate the impact of black liquor carryover on the overall performance of these ECF bleaching technologies.

EXPERIMENTAL

Materials

A series of three commercial SW kraft pulps were employed for the mini oxygen delignification studies in this paper. Two preoxygen stage pulps had kappa numbers of 26.3 and 24.2, respectively, while a postoxygen pulp had a kappa number of 8.9. The preoxygen pulps had respective viscosity values of 27.4 and 26.5 cP while the postoxygen pulp had a viscosity value of 21.0 cP. Prior to the mini oxygen delignification studies, the pulps were extensively washed until the wash water was pH neutral and colorless. All chemicals employed for these studies, with the exception of chlorine dioxide, were purchased commercially and used as received.

Metals Analysis of Pre- and Post-O_2 Pulps

Nonprocess elements of the kappa 24.2 and 8.9 SW kraft pulp were determined using standard ICP methods [30, 31]. Table I summarizes the results of the ICP analysis.

Table I. Metals analysis of pre- and post-O_2 pulps

Metal	24.2 Kappa Pre-O_2 SW Kraft Pulp (ppm)	8.9 Kappa Post-O_2 SW Kraft Pulp (ppm)
Fe	12	10
Co	<1	<1
Mn	36	32
Mg	510	482
Ni	2	<1
Cu	<1	13
Cr	<1	<1
Na	1310	280
Ca	1315	1555
K	86	94

Mini Oxygen Delignification

A 1000-mL capacity Parr reactor equipped with a stirrer, a pressure gauge, a heating mantle, and connected to a Parr 4842 temperature controller was charged with 20.0 grams of never-dried fibers (solids basis). The pulp consistency was adjusted to 10% by adding distilled water. Table II summarizes the delignification conditions.

Table II. Mini oxygen bleaching conditions

Stage	O_2 Pressure/ psi	NaOH/ %	H_2O_2/ %	$MgSO_4$/ %	Temp./ °C	Time/ Min.
(E+O)	90	1.25	-	0.1	80.0	20.0
(E+P+O)	90	1.25	0.5	0.1	80.0	20.0
O	90	2.50	-	0.1	105.0	60.0

Chlorine Dioxide Stages

The chlorine dioxide (D) stages were performed on 20.0 grams of never-dried fibers (solid basis) at 10% consistency in sealed plastic bags immersed in a constant temperature water bath. Table III summarizes the experimental conditions for these stages.

Table III. Chlorine dioxide stage conditions

Stage	Kappa Factor	Exiting pH	Temp./ °C	Time/ min.
D	0.05	2.2	70.0	30.0
D	0.20	2.2	70.0	30.0

Pulp Characterization

Delignified pulps were analyzed for kappa number following TAPPI Method T 236 cm-85 [32]. Typical experimental standard deviations for the preoxygen pulps were determined to be 0.09 and 0.08 for the postoxygen pulps. Pulp viscosity values were determined in accordance with TAPPI Method T 230 om-89 [33] and standard deviations for the preoxygen pulps were 0.6 and 0.2 for the pre- and postoxygen pulps, respectively. Pulp brightness measurements were reported as ISO brightness and were performed in accordance with TAPPI Method T 525 om-92 [34]. Typical brightness standard deviations for the preoxygen pulps were determined to be 0.1 and 0.08 for the postoxygen pulps. The handsheets for these measurements were made using TAPPI Method T 218 sp-97 [35]. Nonprocess elements of the pre- and postoxygen pulps were determined using standard ICP methods [30, 31].

RESULTS AND DISCUSSION

Mini O_2 and Black Liquor Carryover

Previous studies reported by Chakar et al. [10] and others [17, 36, 37] have shown that the delignification effects of a mini oxygen treatment are improved if the caustic charge is split into two and the pulp is oxidized with a low charge of chlorine dioxide. Furthermore, Dyer et al. [5] have shown that there are no significant detrimental impacts on a (E+O)$D_{0.05}$(E+O) sequence when not employing interstage washing. These studies are beneficial to understanding the advantages of an enhanced poor man's oxygen stage although the conditions employed for these studies may not mimic an actual bleach plant setting. As a result, the impact of black liquor carryover on mini oxygen delignification as well as other ECF bleaching technologies is not fully understood [12, 18-29]. In addition, the advantages of an enhanced poor man's oxygen sequence have not been explored on postoxygen delignified kraft pulps.

This study explores the impact of black liquor carryover on mini oxygen delignification as part of a sequence using chlorine dioxide. The experimental conditions were selected from previous literature reports [5, 10, 38]. The consistency of all the stages was maintained at 10% while a constant charge of magnesium sulfate in the mini oxygen stages was employed to minimize the number of experimental variables. The mini oxygen delignification studies were maintained at an oxygen pressure of 90 psi and were stirred at a constant rate throughout the experiment. Black liquor was added to the pulp at two different charges, 2 and 10 kg solids per o.d. ton of pulp. There was no interstage washing employed in any of the studies employing black liquor carryover. These results were then compared to control studies that did not employ any black liquor or bleach plant effluent.

The delignification response for the 26.3 kappa SW kraft pulp under varying mini oxygen delignification conditions is summarized in Figure 1. It is interesting to observe that the black liquor carryover seemed to enhance delignification under most cases except where the chemical charge was high, i.e., $D_{0.20}$(E+O)(E+O) and (E+O)$D_{0.20}$(E+O). The mild conditions of the (E+O)(E+O) sequence yielded 43% delignification for both 2 and 10 kg/ton of black liquor carryover and 35% delignification with no carryover. The increase in delignification with the addition of black liquor is presumably due to residual alkali left in the carryover [12, 21-23]. The use of a low charge of ClO_2 and splitting the caustic charge between two (E+O) stages significantly improved the response of the pulp toward delignification in the second (E+O) stage, as was also reported by Chakar et al. [10]. However, the increase in delignification compared to the (E+O)(E+O) sequence was 6% and 10% for the 2 and 10 kg/ton carryover levels, respectively, while an 18% increase in delignification is apparent for pulp having interstage washing and no carryover. This effect is presumably due to partial consumption of ClO_2 by the black liquor carryover, thereby decreasing the overall efficiency of this bleaching agent. The

delignification response using 10 kg/ton carryover was often lower than that of a 2 kg/ton black liquor carryover charge. It would seem reasonable that this decreased delignification can be attributed to an increase in the total number of competing reactions between pulp lignin and dissolved material in the black liquor, as was reported by earlier researchers [24, 25].

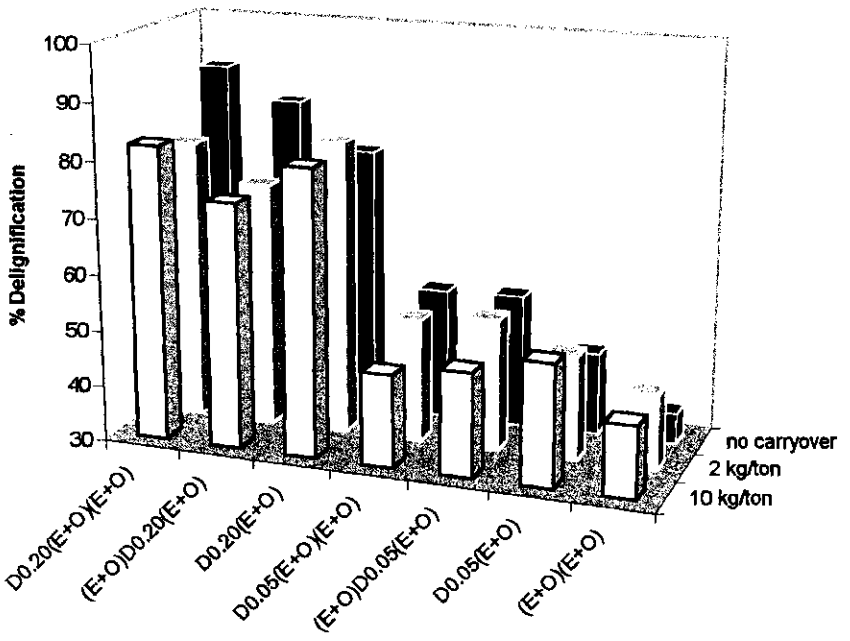

Figure 1. Mini oxygen delignification responses for a 26.3 kappa SW kraft pulp with no carryover, 2 kg/ton carryover, and 10 kg/ton carryover. The pulps having no carryover involved interstage washing while the pulps having added carryover involved no interstage washing.

The viscosity losses for the no carryover, 2 kg/ton, and 10 kg/ton carryover SW kraft pulps are summarized in Figure 2. The initial viscosity of this pulp was 33.2 cP. As expected, the viscosity loss for the $D_{0.05}$(E+O)(E+O) sequence is smaller than that for the (E+O)$D_{0.05}$(E+O) sequence due to the placement of the first (E+O) stage in the sequence. Interestingly, the viscosity losses increased as a function of the amount of carryover in the pulp. It is anticipated that black liquor carryover introduces transition metal ions to the pulp. These transition metal ions can then form radicals, leading to degradation of the carbohydrates. The (E+O)$D_{0.05}$(E+O) sequence yielded a greater viscosity loss than the (E+O)(E+O) sequence, although it provided improved delignification. This could be attributed to the selectivity of the intermediate chlorine dioxide stage.

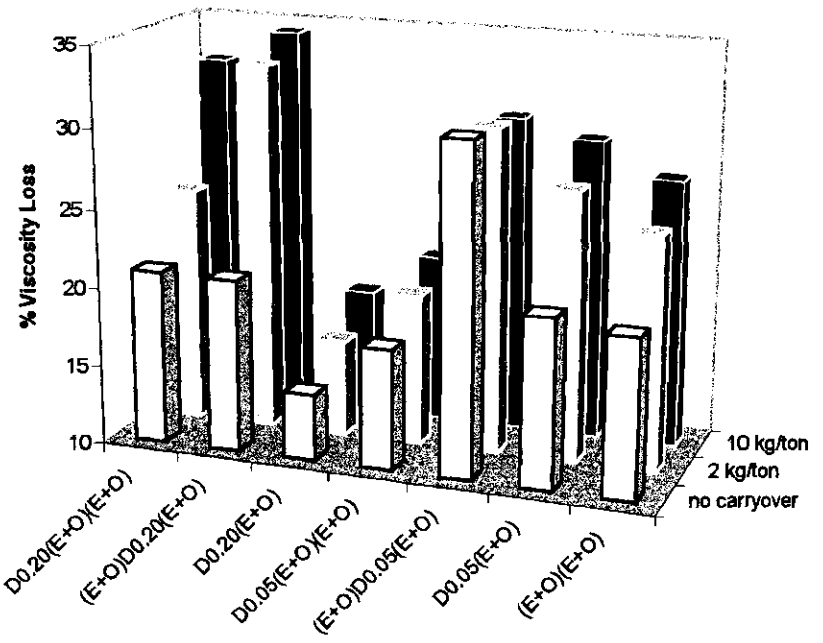

Figure 2. Mini oxygen delignification pulp viscosity losses (%) for a 26.3 kappa SW pulp with no carryover, 2 kg/ton, and 10 kg/ton black liquor carryover. The pulps having no carryover involved interstage washing while the pulps having added carryover involved no interstage washing.

Figure 3 presents the selectivity (defined as Δkappa/Δviscosity) data for the no carryover, 2 kg/ton, and 10 kg/ton carryover SW kraft pulps. In general, the selectivity decreases as a function of black liquor carryover load. This observation is contrary to results reported by others [18, 19, 26-29]. However, the conditions used in those studies indicate that much higher levels of carryover were used. In addition, the carryover used in those studies may have been model compounds or black liquor with low metals content. The selectivity of the (E+O)$D_{0.05}$(E+O) sequence is much lower than that for the

$D_{0.05}$(E+O)(E+O) sequence, due primarily to the large change in viscosity that was brought about by the placement of the (E+O) sequence. As a result, the selectivity of the (E+O)$D_{0.05}$(E+O) sequence is comparable to that of a (E+O)(E+O) sequence. Meanwhile, the sequences involving high kappa factor D stages were the most selective of this study, due to their high delignification compared to the other sequences employed in this study.

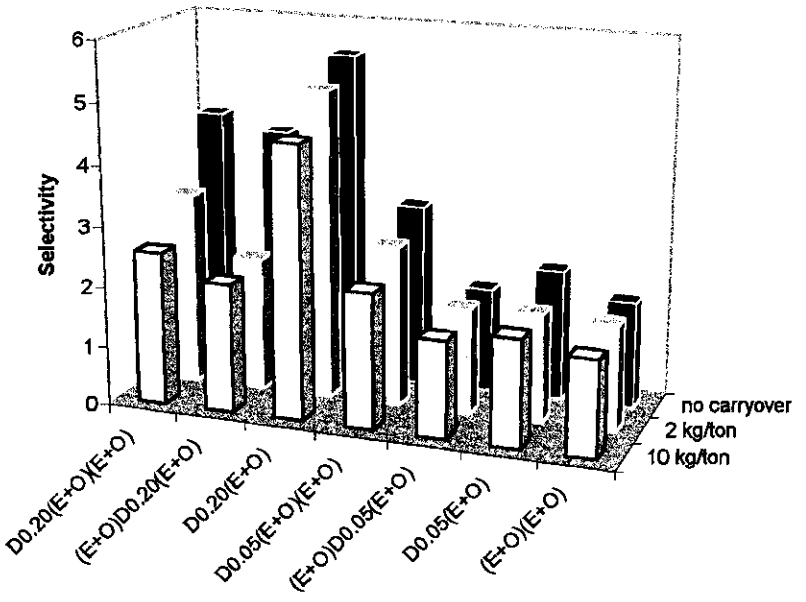

Figure 3. Mini oxygen delignification selectivity (Δkappa/Δviscosity) of SW kraft pulp with no carryover, 2 kg/ton, and 10 kg/ton black liquor carryover. The pulps having no carryover involved interstage washing while the pulps having added carryover involved no interstage washing.

Mini O_2 Reinforced with H_2O_2

In an effort to further enhance a poor man's oxygen stage, this study was extended to investigate the impact of black liquor carryover on a mini oxygen delignification system reinforced with hydrogen peroxide for both pre- and postoxygen delignified SW kraft pulps. The consistency of all the stages was maintained at 10% while a constant charge of magnesium sulfate in the mini oxygen stages was employed to minimize the number of experimental variables. The mini oxygen delignification studies were maintained at an oxygen pressure of 90 psi and were stirred at a constant rate throughout the experiment. Black liquor was added to the pulp at only one level, 10 kg solids per o.d. ton of pulp. There was no interstage washing employed in any of the studies employing black liquor

carryover. These results were then compared to control studies that did not employ any black liquor or bleach plant effluent.

The delignification response for the preoxygen with no carryover as well as the pre- and postoxygen delignified SW kraft pulps with 10 kg/ton of black liquor carryover is summarized in Figure 4. The kappa 26.3 pre-O_2 pulps with no black liquor carryover exhibited a greater extent of delignification than the kappa 24.2 pre-O_2 pulps with carryover, as was also observed in our earlier study. In addition, the 24.2 kappa pre-O_2 pulp exhibited a greater extent of delignification than that of the 8.9 kappa post-O_2 pulp except in the case of the O_2 treatment. This effect is presumably due to the nature of the residual lignin in the post-O_2 pulp. This lignin is further oxidized than the lignin in the pre-O_2 pulps and is thus more resistant to additional oxidation. The extent of delignification was proportional to the amount of hydrogen peroxide in the bleaching sequence. As the hydrogen peroxide was decreased, the extent of delignification also decreased. It is interesting to observe the differences in delignification for the (E+O+P)$D_{0.05}$(E+O) and (E+O)$D_{0.05}$(E+O+P) sequences. Although there was a difference observed in delignification for these two sequences for the pre-O_2 pulps with no carryover, there was no apparent difference for either the pre- or post-O_2 pulps having added black liquor carryover. This further suggests that there are competing reactions occurring between the pulp lignin and dissolved material in the black liquor, thereby leading to a lower bleaching effectiveness [24, 25].

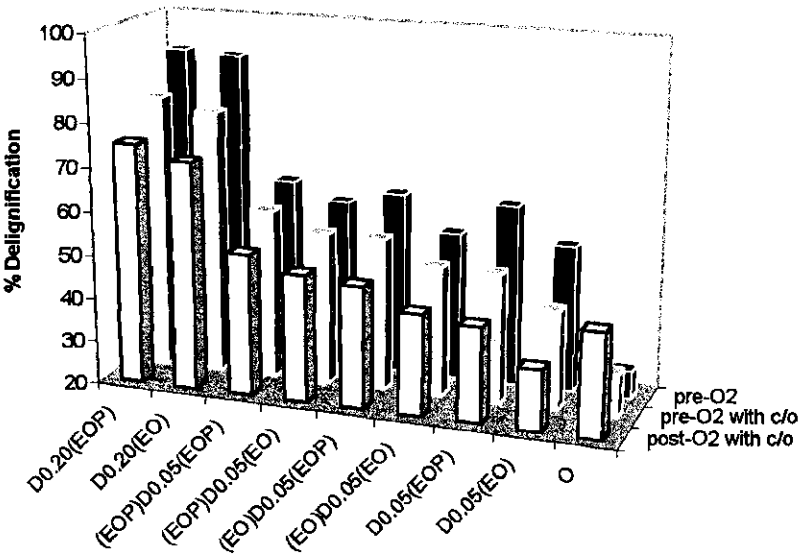

Figure 4. Delignification responses (%) for a pre-O_2 pulp with no black liquor carryover and a pre-O_2 and post-O_2 SW kraft pulp with 10 kg/ton of black liquor carryover. The pulps having no carryover involved interstage washing while those having added carryover employed no interstage washing.

The changes in pulp viscosity for the 27.4 cP pre-O_2 pulps with no carryover as well as the 26.5 cP pre-O_2 and 21.0 cP post-O_2 SW kraft pulps with 10 kg/ton of black liquor carryover are summarized in Figure 5. Although the extent of delignification increased with greater amounts of hydrogen peroxide, the loss in viscosity is also greater for increasing amounts of hydrogen peroxide. This effect is presumably due to the decreased selectivity of hydrogen peroxide under increased oxygen pressure. In general, a greater viscosity loss was observed for both pre-O_2 pulps when compared to that for the post-O_2 pulps. It is interesting to observe that the viscosity loss was often greater for the pre-O_2 pulps with no carryover than for the pre- and post-O_2 pulps with added carryover. This effect further reinforces the theory that there are competing reactions between pulp lignin and the dissolved material in the black liquor [24, 25]. The black liquor may indirectly protect the carbohydrates from degradation by providing these competing reaction pathways. However, this effect was not observed for the post-O_2 SW kraft pulp treated with another oxygen stage.

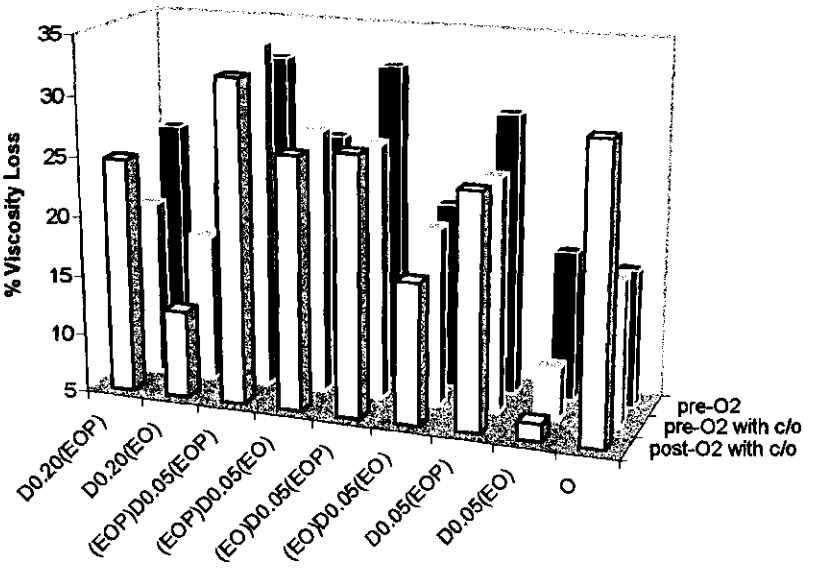

Figure 5. Viscosity losses (%) for a 27.4 cP pre-O_2 pulp with no black liquor carryover and a 26.5 cP pre-O_2 and 21.0 cP post-O_2 SW kraft pulp with 10 kg/ton of black liquor carryover. The pulps having no carryover involved interstage washing while those having added carryover employed no interstage washing.

Figure 6 presents the selectivity (defined as Δkappa/Δviscosity) data for the pre-O_2 pulps with no carryover and the pre- and post-O_2 SW kraft pulps with black liquor carryover. In general, the selectivity decreased when comparing the pre-O_2 pulps with no carryover to the pre-O_2 pulps with 10 kg/ton carryover. This effect is presumably due to the extent of delignification outweighing the viscosity loss for the pulps with no black liquor carryover. In addition, the selectivity decreased when comparing the pre-O_2 pulps with carryover to that of the post-O_2 pulps with carryover. The reason for this is presumably due to the nature of the residual lignin. The residual lignin remaining in the post-O_2 pulps may be more difficult to oxidize than the residual lignin in the pre-O_2 pulps, thereby reducing the overall selectivity. An exception to this is observed in both the $D_{0.20}$(E+O) and $D_{0.05}$(E+O) sequences. These short sequences actually improved the selectivity of the post-O_2 over the pre-O_2 pulps with carryover and without carryover.

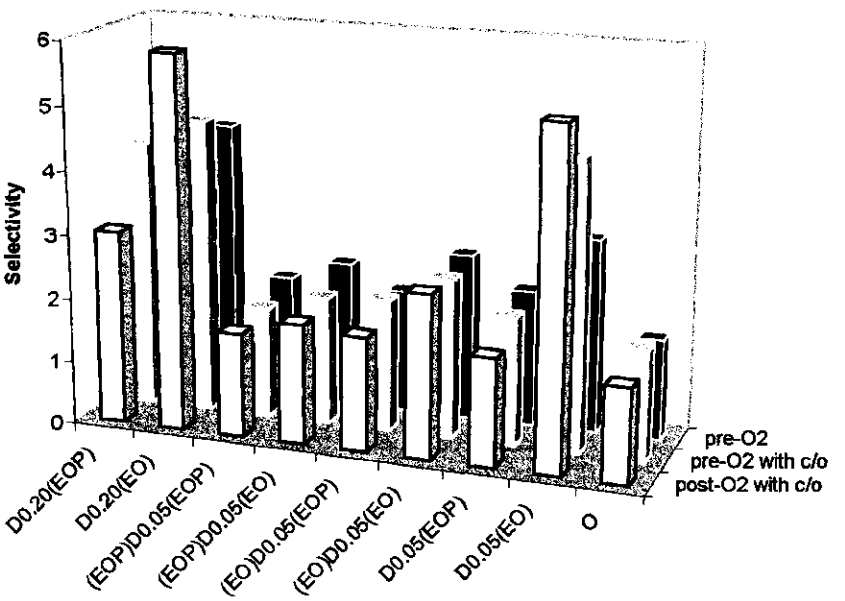

Figure 6. Selectivity responses for a pre-O_2 pulp with no black liquor carryover and a pre-O_2 and post-O_2 SW kraft pulp with 10 kg/ton of black liquor carryover. The pulps having no carryover involved interstage washing while those having added carryover employed no interstage washing.

The changes in brightness for the pre-O_2 pulps with no carryover as well as the pre-O_2 and post-O_2 SW kraft pulps with 10 kg/ton of black liquor carryover are summarized in Figure 7. The changes in brightness follow trends similar to the delignification responses illustrated earlier. The kappa 26.3 pre-O_2 pulp with no black liquor carryover exhibited a

greater brightness change for all treatments than the kappa 24.2 pre-O_2 pulp with carryover. In addition, the 24.2 kappa pre-O_2 pulp exhibited a greater brightness change than the 8.9 kappa post-O_2 with the exception of the O_2 treatment. It is interesting to observe that the brightness change was based on the exiting bleaching stage. This observation is most notable in the sequences involving three stages. Those sequences ending with an (E+O+P) stage often increased the brightness compared to those ending in an (E+O) stage, presumably due to the ability of the hydrogen peroxide to react with and destroy chromophores remaining in the pulp.

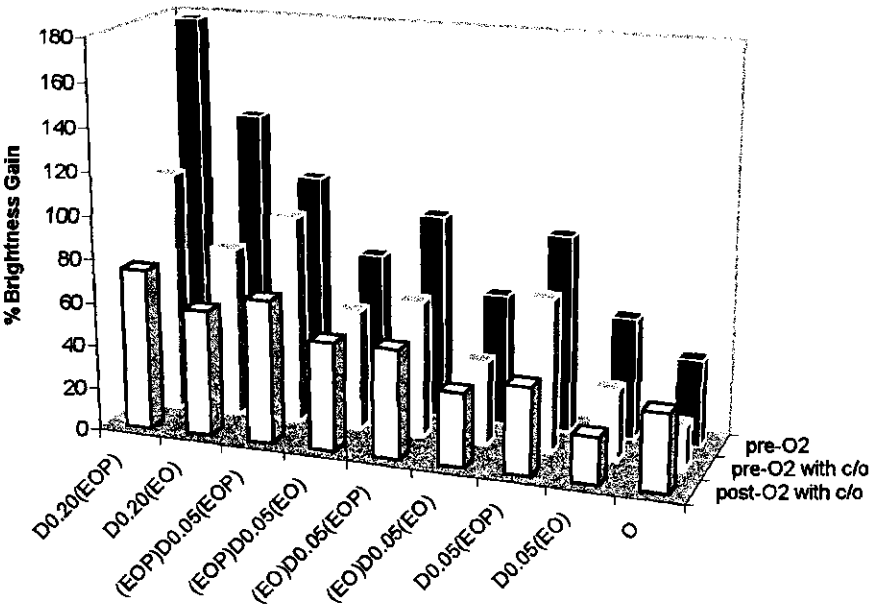

Figure 7. Changes in brightness(%) for a pre-O_2 pulp with no black liquor carryover and a pre-O_2 and post-O_2 SW kraft pulp with 10 kg/ton of black liquor carryover. The pulps having no carryover involved interstage washing while those having added carryover employed no interstage washing.

SUMMARY

The mini oxygen delignification studies with black liquor carryover confirmed that using a poor man's O to remove lignin from kraft pulps continues to be a promising technology. Analysis of the mini O_2 systems indicated that these technologies had superior performance with pre-O_2 pulps when compared to post-O_2 SW kraft pulps. Furthermore, these studies confirmed the proposed benefits of splitting the charge of the mini O in two and further oxidizing the pulp with a low kappa factor chlorine dioxide stage. Analysis of the mini oxygen systems reinforced with hydrogen peroxide revealed

that the addition of hydrogen peroxide in the last stage of a (E+O)*D(E+O)* sequence had a greater impact on bleaching performance than if placed in the front of the sequence. These studies also confirmed that black liquor carryover has little or no effect on the final pulp physical properties. However, the modest levels of black liquor carryover employed in this study may not be entirely indicative of an actual bleach plant. Hence, future studies within our research group will address this issue and will be reported in the near future.

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