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RAPID D/Z AND Z/D STAGES FOR DELIGNIFICATION OF SOUTHERN PINE KRAFT PULP

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ABSTRACT

Partial replacement of chlorine dioxide with ozone in an initial delignification stage can provide bleach cost savings, extend ClO_2 generator capacity, and reduce the generation of bleach plant filtrate AOX and color. In addition, capital savings can be realized with the use of short retention times for both the D and Z stages. The purpose of the work described in this paper was to develop data for (D/Z) and (Z/D) delignification of southern pine in a way that takes advantage of the rapid reaction rates of both chlorine dioxide and ozone. A series of laboratory experiments was done with (D/Z)E and (Z/D)E delignification stages in a two-level factorial to determine the effects of retention times, order of chemical addition, total kappa factor, temperature, consistency, carryover, and level of ozone substitution on the extent of delignification of a southern pine kraft pulp. Only kappa factor, temperature, presence of carryover, and level of ozone substitution were found to be significant factors. Rapid D and Z stages (0.5-1 min) were as effective as longer retention time stages. Additional experiments were done to compare (D/Z)(EPO) and (Z/D)(EPO) stages to D(EPO) for determining the optimum level of ozone addition.

INTRODUCTION

Environmental regulations have required that U.S. mills switch to chlorine dioxide-based "elemental chlorine free" (ECF) bleaching processes to reduce the amount of chlorinated organic material in the effluent, as measured by its adsorbable organic halide (AOX) content. Since chlorine dioxide must be produced on-site in a generator with a given capacity, bleached mills must add additional generating capabilities or utilize alternative bleaching chemicals that do not present environmental problems. For mills producing high-value, high-brightness products, even the use of an ECF sequence with a high consumption of chlorine dioxide may result in levels of AOX production that are higher than desired or allowed. Some mills may also need to increase the value of their products by adding additional bleaching capacity to an existing bleach plant, or to increase the operating efficiency and reduce costs by adding additional stages. These changes can require a significant capital investment.

An alternative to increasing the capacity of a mill's chlorine dioxide generator is to replace part of the bleaching chemical requirements with ozone. Ozone (O_3) can be effectively combined with chlorine dioxide (ClO_2) in the first stage of a multistage plant. Studies by Lachenal and others showed that an initial (D/Z) stage at 3.5% consistency was effective with no washing or additional acidification needed between the D and Z stages.[1] Dillner and Tibbling used a medium-consistency (DZ) stage with sequential addition of the ozone only 5-20 seconds after initial chlorine dioxide addition.[2] The preferred conditions were a relatively low temperature for (DZ), a pH of about 4, and a gas pressure in the ozone stage of 10 bar.

The key to economical use of ozone as a partial replacement for chlorine dioxide is the replacement ratio, or how much chlorine dioxide can be replaced by a given amount of ozone to achieve the same amount of bleaching. The theoretical replacement ratio of ozone for chlorine dioxide based on oxidation equivalents is 1.7 kg ClO_2/kg O_3.[3] At the respective chemical costs for chlorine dioxide and ozone, the cost-effective replacement ratio is 1.5-1.7.

Chirat and Lachenal, in a study of hardwood pulp bleaching, showed that a replacement ratio of 1.6 kg ClO_2 /kg O_3 based on total chemical applied was achieved for a (D/Z)(EOP)DD sequence.[4] For a softwood pulp, the replacement ratio was 2.1 for a (D/Z)(EO)DED sequence. Additional studies by Chirat and others showed that the replacement ratio based on total chemical charge for a (D/Z)(EP)D sequence on a hardwood pulp was 1.8.[5] In another study, a series of pilot-plant trials with a northern softwood kraft pulp was done to demonstrate the effectiveness of operating (D/Z) stages at low consistency. In this case, a replacement ratio of 2 was achieved with full sequence ((D/Z)(EP)DED) bleaching.[6] A recent study with southern pine kraft pulps showed that the replacement ratio achieved for an O(D/Z)(EOP)DD sequence based on total chemical applied was 1.2.[7]

Several commercial systems employing (D/Z) or (Z/D) stages are running in mills around the world, all but one on hardwood pulp.[8,9,10] For the most part, these systems have resulted in significant decreases in bleach chemical costs and effluent AOX, COD, and color.

It is apparent from the above discussion that replacement ratios determined in different studies are significantly different from one another. The replacement ratio appears to depend on species, process conditions, and relative chemical charges. Furthermore, data on southern softwood kraft pulp are limited in the literature.

The research described here was directed toward identifying the process conditions under which ozone can be used as an effective replacement for part of the chlorine dioxide used in the bleaching of southern softwood kraft pulp, while simultaneously exploiting the previously demonstrated high reaction rate of chlorine dioxide in an initial delignification stage.[11] Since the reaction of ozone with residual lignin is also extremely fast, we envisioned (D/Z) or (Z/D) delignification stages with very short retention times and correspondingly reduced requirements for capital equipment. Such rapid (D/Z) or (Z/D) stages could be implemented by simply adding mixers and short retention tubes. A key element of such a strategy would be the freeing of the existing first-stage mixing and retention equipment for use as a brightening stage elsewhere in the bleach sequence. This would decrease total bleaching chemical cost and/or enable the brightness target to be raised, while simultaneously decreasing the rate of AOX generation.

RESULTS

Initial Factorial Study

An initial two-level factorial study was done in the laboratory to evaluate the effects of the main process variables on delignification efficiency. Subsequent testing could then focus on the significant process conditions. For these runs, a laboratory high-shear mixer was used for the D and Z stages. A simple extraction (E) stage was done following the (D/Z) or (Z/D) stages. The kappa number following the (D/Z)E or (Z/D)E stages was measured to determine the effectiveness of the process conditions. The factorial study had eight variables at two levels as shown in Table I.

Table I. Factor Levels for Initial Factorial

	Factor levels	
Variable	**-1**	**1**
Order	(Z/D)	(D/Z)
Total Kappa Factor*	0.15	0.25
O_3 substitution, %**	30	70
Temperature, °C	40	70
Consistency, %	3	10
Black Liquor Carryover, kg COD/ton	0	10
D stage time, min	0.5, 2***	30
Z stage time, min	0.5, 2***	5

*Total Kappa factor calculated as ((ClO_2 * 2.63)+ (O_3 * 4.47))/kappa number
**%O_3 substitution calculated as percentage of total kappa factor
***Time was 0.5 minutes when stage was first and 2 min. when stage was second

A 1/16 replicate of this 2^8 factorial was done, a total of 16 runs. The initial factorial results were then subjected to multiple regression analysis using the factor levels as defined in Table I for each of the independent variables. The experimental data are shown in Table II. Coded independent variables were used in this and subsequent analyses. The coding equation for each is shown in Table A.I in the Appendix. The degree of delignification (expressed as a fraction) after the E stage was used as the dependent variable rather than the E stage kappa number so that the results could be compared to later data sets that used pulps of different starting kappa numbers. The variables that had a significant effect (95% confidence interval) on the E stage kappa number were identified and are shown in Table A.II along with the R^2 value and mean square error term. The coefficients show the direction and estimated magnitude of each of the significant effects. The results show that delignification was adversely affected by lower kappa factor (KF), higher temperature, higher ozone substitution, and the presence of carryover. It is especially noteworthy that order of addition, consistency, and retention times in the D and Z stages did not have a significant effect on the degree of delignification.

A second set of runs was done with (D/Z)E and (Z/D)E at the center point conditions (zero coded variable levels), 0.20 KF, 50% O_3 substitution, and 55°C. Three additional (D/Z)E runs were done to determine the effect of retention time in the D and Z stages. Partial sequences DE and ZE at 0.25 KF were also done for comparison. These results are shown in Table III.

Table II. Results of Initial Factorial Study, 0.15 and 0.25 KF

Sequence	Total KF	% O_3 Sub.	%ClO_2	%O_3	Temp. °C	%Cons.	Carryover kg COD/ton	D time min.	Z time min.	Kappa No.
(D/Z)E	0.25	30	1.63	0.41	70	10	0	30	2	5.2
(D/Z)E	0.25	30	1.63	0.41	40	3	10	30	5	7.0
(D/Z)E	0.25	70	0.70	0.97	70	3	0	0.5	5	9.2
(D/Z)E	0.25	70	0.70	0.97	40	10	10	0.5	2	9.1
(D/Z)E	0.15	70	0.42	0.58	70	3	10	30	2	16.7
(D/Z)E	0.15	70	0.42	0.58	40	10	0	30	5	12.0
(D/Z)E	0.15	30	0.98	0.25	40	3	0	0.5	2	9.1
(D/Z)E	0.15	30	0.98	0.25	70	10	10	0.5	5	12.5
(Z/D)E	0.25	30	1.63	0.41	40	10	0	2	5	4.7
(Z/D)E	0.25	30	1.63	0.41	70	3	10	2	0.5	8.2
(Z/D)E	0.25	70	0.70	0.97	70	10	10	30	5	11.2
(Z/D)E	0.25	70	0.70	0.97	40	3	0	30	0.5	7.6
(Z/D)E	0.15	70	0.42	0.58	40	3	10	2	5	15.1
(Z/D)E	0.15	30	0.98	0.25	70	3	0	30	5	9.4
(Z/D)E	0.15	30	0.98	0.25	40	10	10	30	0.5	11.3
(Z/D)E	0.15	70	0.42	0.58	70	10	0	2	0.5	13.5

Initial Kappa 24.5

Table III. Results for (D/Z)E, (Z/D)E, DE, and ZE

Sequence	Total KF	% O_3 Sub.	%ClO_2	%O_3	Temp. °C	%Cons.	Carryover kg COD/ton	D time min.	Z time min.	Kappa No.
(D/Z)E	0.20	50	0.93	0.55	55	3	0	0.5	20	7.0
(D/Z)E	0.20	50	0.93	0.55	55	3	0	0.5	20	7.5
(D/Z)E	0.20	50	0.93	0.55	55	3	0	30	15	9.3
(D/Z)E	0.20	50	0.93	0.55	55	3	0	10	35	8.6
(D/Z)E	0.20	50	0.93	0.55	55	3	0	0.5	45	8.4
(Z/D)E	0.20	50	0.93	0.55	55	3	0	20	0.5	8.4
(Z/D)E	0.20	50	0.93	0.55	55	3	0	20	0.5	8.7
DE	0.25	0	2.33	0	70	3	0	30		5.4
ZE	0.25	100	0	1.38	70	3	0		30	14.5

Initial Kappa 24.5

(D/Z)(EPO), (Z/D)(EPO), and D(EPO)

Additional tests were done with a more aggressive (EPO) extraction stage following the (D/Z), (Z/D), and D stages. These results are shown in Table IV along with a direct comparison to the same partial sequence with only an E stage instead of (EPO).

The results from Table IV were combined with the results from Tables II and III and the entire data set was subjected to regression analysis. All process variables, their two-factor interactions, and their squared terms were included. The analysis showed that many of these terms were too small to be considered statistically significant. The results of a regression analysis that included only those variables determined to be statistically significant at the 95% confidence level are shown in Table A.III. The coefficient of each shows the magnitude and direction of the corresponding effect on degree of delignification. These results were in good agreement with the regression results of the initial factorial shown. Two additional terms were significant in this case. The squared term for percent substitution resulted from inclusion of the D(EPO) (zero substitution) data. It reflects the observation that the effect of substitution is absent at low substitution levels, but becomes increasingly negative as substitution is increased.

The presence of either an E or (EPO) stage is also accounted for. On average, the oxidatively reinforced extraction stage results in an extracted kappa number that is lower by 1.2 units.

Table IV. Effect of (EPO) Stage with D, (D/Z), and (Z/D)

Sequence	Total KF	% O_3 Sub.	%ClO_2	%O_3	D time min.	Z time min.	Kappa No.
(D/Z)E	0.25	50	1.16	0.69	0.5	30	5.8
(D/Z)(EPO)	0.25	50	1.16	0.69	0.5	30	3.9
(D/Z)E	0.20	50	0.93	0.55	0.5	30	9.5
(D/Z)(EPO)	0.20	50	0.93	0.55	0.5	30	6.8
(D/Z)E	0.15	50	0.70	0.41	0.5	30	10.8
(D/Z)(EPO)	0.15	50	0.70	0.41	0.5	30	7.8
(Z/D)E	0.25	50	1.16	0.69	30	0.5	5.9
(Z/D)(EPO)	0.25	50	1.16	0.69	30	0.5	3.9
(Z/D)E	0.20	50	0.93	0.55	30	0.5	9.2
(Z/D)(EPO)	0.20	50	0.93	0.55	30	0.5	6.2
(Z/D)E	0.15	50	0.70	0.41	30	0.5	11.3
(Z/D)(EPO)	0.15	50	0.70	0.41	30	0.5	7.5
D(EPO)	0.18	0	1.69		50		4.5
D(EPO)	0.15	0	1.40		50		5.6
D(EPO)	0.12	0	1.12		50		6.8
D(EPO)	0.10	0	0.93		50		7.9

Initial kappa 24.5
D, (D/Z), or (Z/D) stages – 45°C, 10% cons., no carryover

As in the initial regression, higher temperatures, higher percent ozone substitution, and the presence of carryover all result in higher extracted kappa number (decreased delignification efficiency). More notably, the effects of order of addition, consistency, and D and Z stage retention times were not significant. Rapid D and Z stages of less than one minute retention time can result in the same degree of delignification as longer stages.

The results from Table IV are shown in Figure 1, where percent delignification is plotted as a function of the total KF applied in the (D/Z), (Z/D), or D stages. At a given total KF, the D(EPO) sequence results in a greater delignification than the (D/Z)(EPO) and (Z/D)(EPO) sequences. The increase in delignification for the partial sequences with an (EPO) stage versus just an E stage is also apparent.

From other available data, it appeared that the best economics for chlorine dioxide replacement occur at relatively low ozone dosages, in the range of 0.2-0.3%. To examine this, another series of runs was done with (D/Z)(EPO) and (Z/D)(EPO) stages, limiting the ozone application to either 0.2 or 0.3%. The starting pulp for this was from the same source as the previous runs but the starting kappa number was somewhat lower at 21.6. The results are shown in Table V, together with the results of a series of D(EPO) runs on the same starting pulp for comparison. Two sets of (D/Z)(EPO) runs with and without 10-kg/ton black liquor carryover were also done

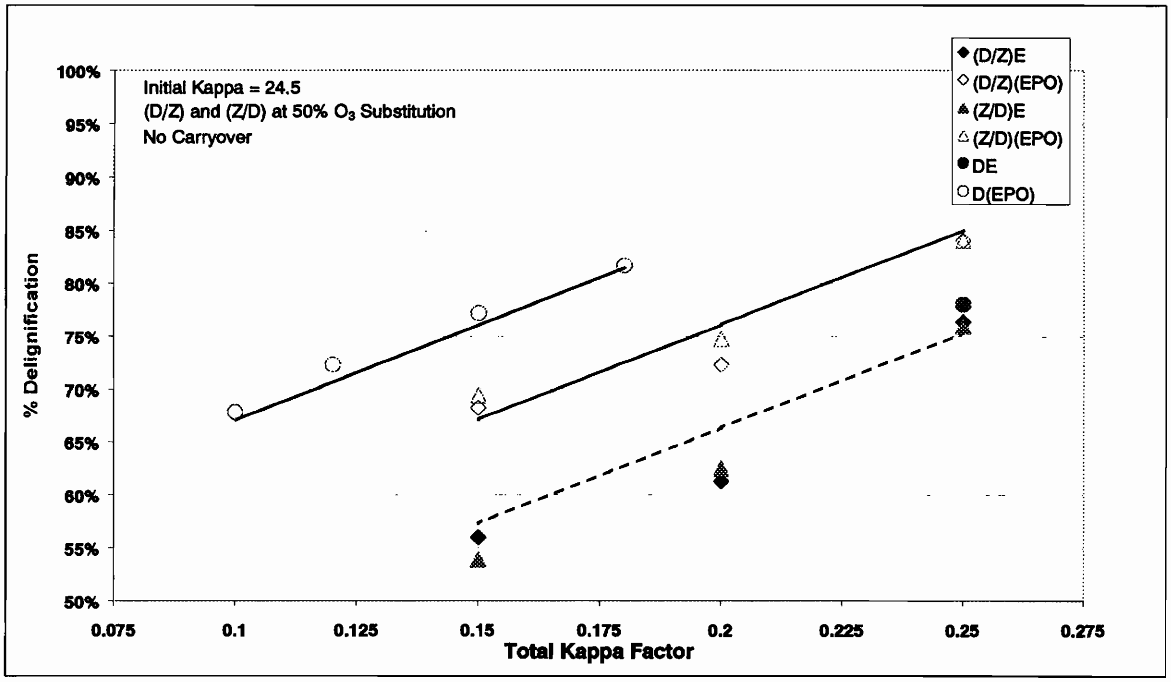

Figure 1. % Delignification vs. Total Kappa Factor for SW Kraft

Table V. Results for D(EPO), (D/Z)(EPO), (D/Z)(EPO)

Sequence	Total KF	% O_3 Sub.	$\%ClO_2$	$\%O_3$	Carryover kg COD/ton	D time min.	Z time min.	Kappa No.
(D/Z)(EPO)	0.19	22	1.23	0.2	0	0.5	30	2.8
(D/Z)(EPO)	0.18	34	0.99	0.3	0	0.5	30	2.9
(D/Z)(EPO)	0.19	22	1.23	0.2	10	0.5	30	4.0
(D/Z)(EPO)	0.18	34	0.99	0.3	10	0.5	30	4.6
(Z/D)(EPO)	0.10	40	0.5	0.2	10	30	0.5	8.7
(Z/D)(EPO)	0.12	31	0.75	0.2	10	30	0.5	7.1
(Z/D)(EPO)	0.16	25	1.0	0.2	10	30	0.5	5.1
(Z/D)(EPO)	0.12	50	0.5	0.3	10	30	0.5	7.1
(Z/D)(EPO)	0.15	40	0.75	0.3	10	30	0.5	5.9
(Z/D)(EPO)	0.18	34	1.0	0.3	10	30	0.5	3.8
D(EPO)	0.20	0	1.64		10	50		2.9
D(EPO)	0.18	0	1.47		10	50		3.7
D(EPO)	0.15	0	1.23		10	50		4.6
D(EPO)	0.15	0	1.23		10	50		4.5
D(EPO)	0.12	0	0.98		10	50		5.9

Initial kappa 21.6
D, (D/Z) or (Z/D) stages – 45°C, 10% cons.,

These data were also subjected to multiple regression analysis and the results are shown in Table A.IV. The delignification efficiency as a function of total KF is shown in Figure 2 along with the regression lines. As seen with the previous data, the delignification efficiency decreases with increasing ozone substitution and inclusion of carryover. This series of experiments revealed a significant effect of order of chemical addition, which varied as a function of KF. At high KF, (Z/D) was more effective than (D/Z) while at low KF, (D/Z) was more effective. This result, however, is based on a limited number of data points, particularly for (D/Z)(EPO). Again, there was no significant effect of the D stage or Z stage retention times, indicating that a 30-second stage is as effective as 30 minutes.

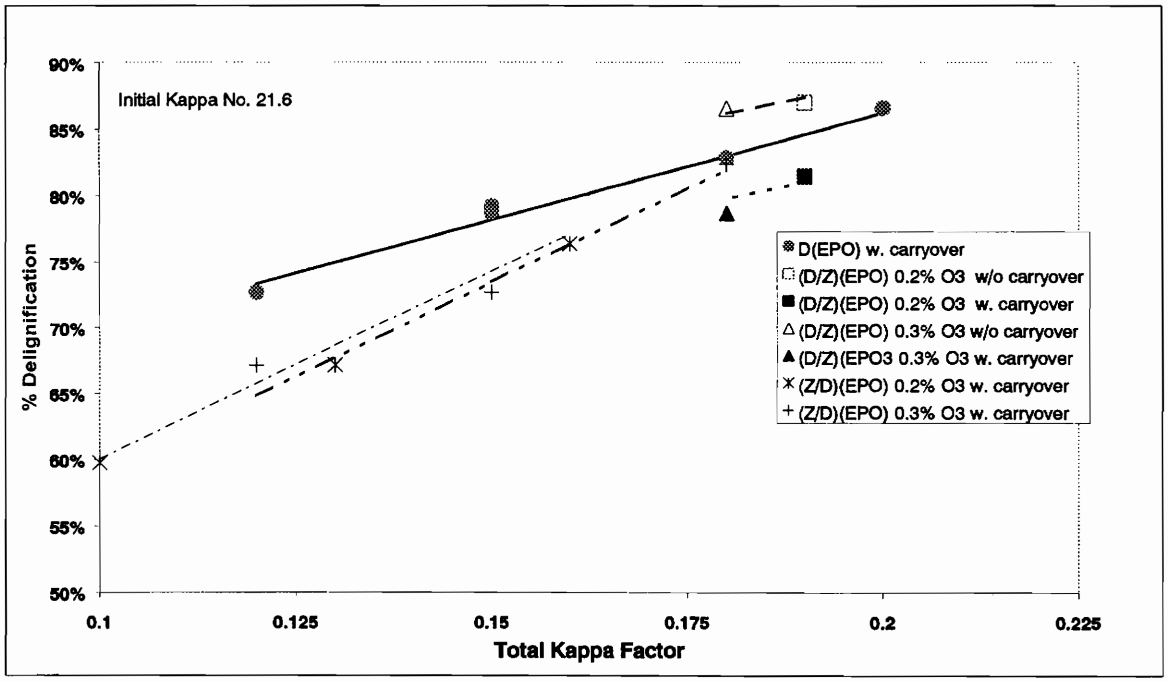

Figure 2. % Delignification vs. Total Kappa Factor for 21 Kappa SW pulp

To better define the effects of KF, level of ozone addition, order of chemical addition, and black liquor carryover, an additional factorial experiment was done with a third pulp sample. This pulp was from the same mill as that used for all of the previous tests, and had a kappa number of 25.5. The factor levels are shown in Table VI and the results are shown in Table VII.

The results of regression analysis of the Table VII data are shown in Table A.V. They agree with the previous data as to the significant effects. The presence of carryover results in a higher (EPO) kappa number but the effect decreases with increasing KF. The percent delignification is shown in Figure 3 as a function of total KF for the data of Table VII, together with the calculated regression lines.

Table VI. Factor Levels for (D/Z)(EPO) and (Z/D)(EPO) Factorial

	Factor levels		
Variable	**-1**	**0**	**1**
Order	(Z/D)		(D/Z)
ClO_2 .%	0.8	1.2	1.6
O_3, %	0.2		0.3
Black Liquor Carryover, kg COD/ton	0		10

Table VII. Results for (D/Z)(EPO) and (Z/D)(EPO) Factorial

Sequence	Total KF	% O_3 Sub.	%ClO_2	%O_3	Carryover kg COD/ton	Kappa No.
(D/Z)(EPO)	0.12	29.8	0.8	0.2	0	8.3
(D/Z)(EPO)	0.14	38.9	0.8	0.3	0	7.5
(D/Z)(EPO)	0.12	29.8	0.8	0.2	10	10.8
(D/Z)(EPO)	0.14	38.9	0.8	0.3	10	10.6
(D/Z)(EPO)	0.16	22.1	1.2	0.2	0	4.7
(D/Z)(EPO)	0.18	29.8	1.2	0.3	0	4.6
(D/Z)(EPO)	0.16	22.1	1.2	0.2	10	7.4
(D/Z)(EPO)	0.18	29.8	1.2	0.3	10	6.3
(D/Z)(EPO)	0.20	17.5	1.6	0.2	0	4.1
(D/Z)(EPO)	0.22	24.2	1.6	0.3	0	3.3
(D/Z)(EPO)	0.20	17.5	1.6	0.2	10	5.1
(D/Z)(EPO)	0.22	24.2	1.6	0.3	10	4.5
(Z/D)(EPO)	0.12	29.8	0.8	0.2	0	8.4
(Z/D)(EPO)	0.14	38.9	0.8	0.3	0	7.8
(Z/D)(EPO)	0.16	22.1	1.2	0.2	0	6.8
(Z/D)(EPO)	0.18	29.8	1.2	0.3	0	5.4
(Z/D)(EPO)	0.16	22.1	1.2	0.2	10	7.8
(Z/D)(EPO)	0.18	29.8	1.2	0.3	10	7.2
(Z/D)(EPO)	0.20	17.5	1.6	0.2	0	4
(Z/D)(EPO)	0.22	24.2	1.6	0.3	0	3.6
(Z/D)(EPO)	0.20	17.5	1.6	0.2	10	4.8
(Z/D)(EPO)	0.22	24.2	1.6	0.3	10	4.3

Initial Kappa 25.5
(D/Z) or (Z/D) stages – 50°C, 10% consistency,

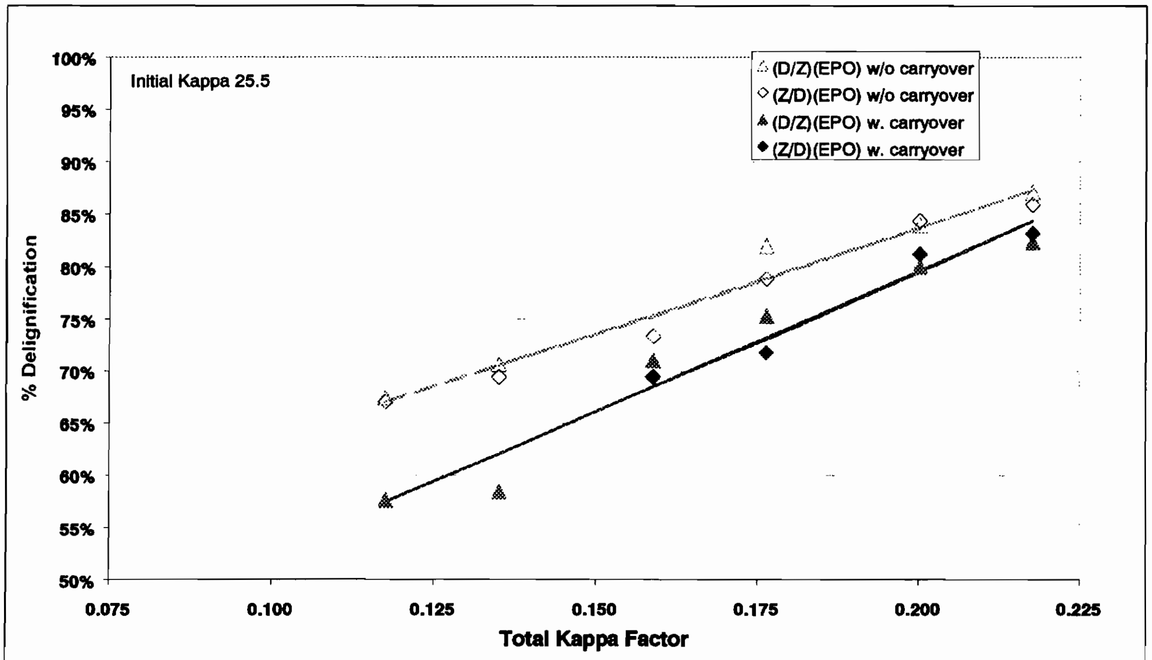

Figure 3. % Delignification vs. Total Kappa Factor for (D/Z)(EPO) and (Z/D)(EPO) Factorial

Final Analysis and Replacement Ratio Calculations

The data of Tables II, III, IV, V and VI were combined into a single data set and subjected to a final regression analysis. Comparison of each data set to the others showed that the kappa 21.6 pulp appeared to delignify more readily than the other two even though all pulps came from the same mill source. Variations in the pulping conditions for this pulp probably account for the difference in bleachability. This pulp difference was accounted for in the final regression analysis by an additional independent ("dummy") variable which was set to a value of 1 for experiments on the kappa 21.6 pulp and 0 for all other experiments.

The results of the regression analysis are shown in Table VIII, which includes only those effects that were significant at the 95% confidence level. The coefficients show the magnitudes and directions of the effects on the fractional degree of delignification and, as in previous Tables, are in terms of the independent variables coded as shown in Table A.I. These results are in good agreement with the regression results of each of the data subsets discussed above, in that the degree of delignification is decreased by increasing ozone substitution and temperature, as well as by the inclusion of black liquor carryover. The two interaction terms quantify the observation that the detrimental effect of black liquor carryover is smaller when the kappa factor is high and/or when the caustic extraction stage is fortified with peroxide and oxygen. Similarly, they again show that the effects of D and Z retention times, order of chemical addition, and consistency are all too small to be considered significant, within the ranges studied.

Table VIII. Regression Analysis of Combined Degree of Delignification Data From All Experiments

Variable (coded)	Coefficient	R^2	Error
Kappa factor	0.0952	0.9688	0.0227
% Substitution	-0.0736		
(EPO) Stage	0.0668		
Carryover	-0.0345		
Temperature	-0.0213		
KF*Carryover	0.0102		
(EPO)*Carryover	0.0126		
$(\% \text{ Substitution})^2$	-0.0150		
Kappa 21.6 Pulp	0.0701		
Intercept	0.6641		

The coefficients in Table VIII define an equation that describes the dependence of the fractional degree of delignification on the levels of all of the process variables examined in this study. The equation was used to construct the series of curves as shown in Figure 4 for the case of 40°C in the D, (D/Z), or (Z/D) stages, 10 kg COD/ton black liquor carryover, and an (EPO) stage. This figure may be used to show how the replacement ratio of ozone for chlorine dioxide at a given degree of delignification (or extracted kappa number) can be determined from the regression model.

As the amount of ozone substitution is increased, the total KF in the first stage has to increase to maintain the same degree of delignification. The increase is very slight at low substitution levels, but becomes increasingly significant as the substitution level is increased. This is illustrated in Figure 4 by the horizontal line at 82% delignification (corresponding to a D(EPO) partial sequence at 0.20 KF) and the line at 72% delignification (corresponding to a D(EPO) partial sequence at 0.15 KF). The points show the calculated total KFs that are required at the 10, 20, and 30% substitution levels. At low levels of substitution (<10%) there is little change in the required total KF, so the replacement ratio would be close to the theoretical amount of 1.7 kg ClO_2/kg O_3 based on oxidation equivalents. However, as the amount of substitution is increased, the total KF has to be increased and the replacement ratio will decrease. The calculated replacement ratios for each of these cases are shown in Table IX, using a starting kappa number of 25 as an example. High replacement ratios are favored by a high KF and low percent O_3 substitution.

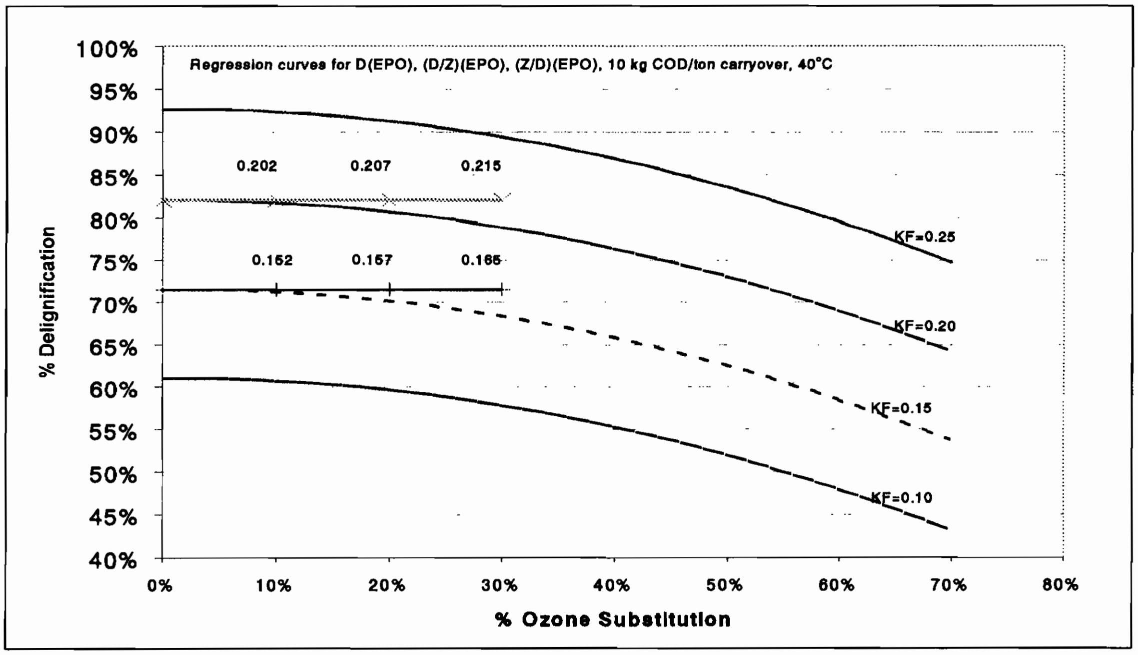

Figure 4. Regression Curves for % Delignification vs. % Ozone Substitution

Table IX. Calculated Replacement Ratios for (D/Z)(EPO) with Carryover

% Delignification	(EPO) Kappa No.*	Total Kappa Factor	% O_3 Substitution	% ClO_2	% O_3	Replacement Ratio kg ClO_2/kg O_3
82%	4.5	0.200	0	1.90	0.00	
		0.202	10	1.72	0.11	1.6
		0.207	20	1.57	0.23	1.4
		0.215	30	1.43	0.36	1.3
72%	7.0	0.150	0	1.43	0.00	
		0.152	10	1.30	0.08	1.5
		0.157	20	1.19	0.18	1.3
		0.165	30	1.10	0.28	1.2

*Assuming initial kappa number = 25

EXPERIMENTAL

Pulp

Southern softwood pulp from a mill with conventional batch kraft cooking was used for all testing. Three samples were acquired from the same mill at different times and had initial kappa nos. of 24.5, 21.6, and 25.5. The pulp was well washed in the lab and thickened to 30% consistency. Black liquor was added to the stages that included carryover at a level of 10 kg COD/ton.

D, Z, (D/Z), (Z/D) Stages

Chlorine dioxide (D) and ozone (Z) stages were done in a CMS 2040 High Intensity Mixer from CRS Reactor Engineering. Chlorine dioxide (ClO_2) was prepared from the reaction of sodium chlorite ($NaClO_2$) with sulfuric acid (H_2SO_4). Chlorine dioxide solution was injected into the reactor from a liquid injection cylinder. Ozone was prepared from oxygen in a PCI model ozone generator. The ozone was compressed with a diaphragm compressor and stored in a gas injection cylinder. The ozone concentration was determined by UV measurement in a PCI ozone analyzer. The required amount of ozone was injected into the reactor bowl from the injection cylinder. The pulp was mixed at 2500 rpm during ozone addition and at 500 rpm during chlorine dioxide addition. The pulp was washed and thickened upon completion of the stage. The exit pH and residual chlorine dioxide were measured on a sample of filtrate.

E and (EPO) Stages

Extraction (E) stages were done in sealed plastic bags in a water bath. Reinforced extraction stages (EPO) were done in a pressurized reactor having a horizontal mixing shaft. The reactor was sealed and pressurized with oxygen to the 60 psig. The oxygen pressure was then decreased during the reaction to simulate an up-flow bleach tower. The reaction conditions were:

E stages – 1.8% NaOH, 10% consistency, 60 minutes, 70°C
(EPO) stages - 2.0% NaOH, 0.5% H_2O_2, 10% consistency, 60 minutes, 70°C, initial O_2 pressure 60 psig

The pulp was thoroughly washed and thickened prior to additional processing. The exit pH and residual chemical were measured on a sample of filtrate. Kappa number and viscosity were determined on the pulps according to TAPPI procedures.

CONCLUSION

The laboratory results have shown that (D/Z) and (Z/D) stages with D and Z retention times of less than one minute are effective as a first delignification stage for a southern pine kraft pulp. The order of addition, (D/Z) or (Z/D), does not have a significant effect nor was there a significant difference between 3 or 10% consistency applications. The degree of delignification is increased by increasing the total KF (D and Z stage chemical charges combined) and by the use of an (EPO) stage instead of an E stage. Increased temperatures adversely affect the delignification of (D/Z) or (Z/D) stages, presumably due to the temperature dependence of ozone decomposition. The presence of black liquor carryover decreases the degree of delignification but the effect of carryover is less at higher KFs and when an (EPO) stage is used instead of an E stage. Maximum replacement ratios of 1.6-1.7 are achieved with low ozone substitution (10%) at high total KFs (>0.2). However, even at 30% substitution, ozone can replace 30% more than its own weight of chlorine dioxide.

There are additional environmental benefits of using ozone beyond the straight cost replacement consideration, such as achieving reduced AOX and color. Operating mill installations have also shown that with efficient high-shear mixers, the replacement ratios achieved are typically higher than those demonstrated in the laboratory.

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APPENDIX

Table A.I. Coding of Independent Variables for Regression Analysis

Variable	Coding	Range of Values	
Order	-1 or 1	(Z/D) = -1	(D/Z) = 1
Carryover	-1 or 1	0 kg COD/ton = -1	10 kg COD/ton = 1
(EPO) stage	-1 or 1	E stage = -1	(EPO) stage = 1
Consistency	-1 or 1	3% = -1	10% = 1
Kappa 21.6 pulp	0 or 1	Kappa 21.6 pulp =1	Other pulps = 0
Kappa factor	(KF-0.2)/0.05	0.10 KF = -2	0.25 KF = 1
% O_3 Substitution	(Sub. – 0.5)/0.2	0 = -2.5	0.70 = 1
Temperature	(Temp.- 55)/15	30^oC = -1	70^oC = 1
D or Z stage time	(Time – 25)/25	0 min. = -1	50 min. = 1

Table A.II. Regression Results of Fractional Delignification of Initial Factorial

Variable (coded)	Coefficient	R^2	Error
Kappa factor	0.0954	0.983	0.0208
% Substitution	-0.0689		
Temperature	-0.0256		
Carryover	-0.0520		
Intercept	0.587		

Table A.III. Regression Results of Fractional Delignification of all Kappa 24.5 Data

Variable (coded)	Coefficient	R^2	Error
Kappa factor	0.0899	0.962	0.0262
% Substitution	-0.0743		
Temperature	-0.0234		
Carryover	-0.0483		
(EPO) stage	0.0489		
$(\% \text{ Substitution})^2$	-0.0153		
Intercept	0.648		

Table A.IV. Regression Results of Fractional Delignification of Kappa 21.6 Data

Variable (coded)	Coefficient	R^2	Error
Kappa factor	0.0804	0.986	0.012
% Substitution	-0.0125		
Order	-0.0328		
Carryover	-0.0320		
Order*KF	-0.0545		
Intercept	0.863		

Table A.V. Regression for Fractional Delignification for Kappa 25.5

Variable (coded)	Coefficient	R^2	Error
Kappa factor	0.110	0.9735	0.0157
% Substitution	-0.0253		
Carryover	-0.0769		
(%Sub.)xCarryover	-0.0395		
Intercept	0.781		