Effect of lignin content on ozone bleaching at medium consistency

Wei Su and Jeffery Hsieh

ABSTRACT: The effect of pulp lignin content on ozone bleaching at medium consistency was studied in the laboratory. A constant charge of ozone was applied to unbleached chemical pulps with varying lignin contents (kappa no. 10–50). The degree of delignification from ozone bleaching was measured as the drop in kappa number. Cellulose degradation from ozone bleaching was measured as the decrease in pulp viscosity. The results show a correlation between pulp lignin content and the efficiency of ozone bleaching. The best selectivity of ozone bleaching occurs at limited reduction of lignin content, thus highlighting the need for extended delignification prior to bleaching. The data presented in this report are potentially useful for developing an ozone-bleaching module for computerized simulation and optimization of ozone bleaching.

KEYWORDS: Consistency, kappa number, lignin content, medium consistency, multistage process, oxidative bleaching, ozone bleaching, ozonization, permanganate number, pulps, rheological properties, solids content, viscosity.

The future of the pulp and paper industry will largely depend on the industry's ability to control its impact on the environment. The bleaching process has been an area of particular concern, and much of current research has focused on the use of alternative bleaching agents. The use of ozone as a bleaching agent has been widely studied at low and high consistency. In this report, we present laboratory results from our study of ozone bleaching at medium consistency.

Ozone as a bleaching agent for cellulosic materials has been known for decades. Several patents and articles have already discussed ozone bleaching in relation to such critical factors as practical ozone bleaching *(1)*, the technique *(2)*, the action of ozone on cellulose *(3, 4)*, wood species *(5)*, pH and consistency *(6)*, and the commercial system using ozone bleaching *(7)*. However, ozone bleaching has generally been considered possible only at low or high pulp consistency in these patents and articles.

The objective of this work is to study the possibility of using ozone as a bleaching agent at medium consistency. The ozone-bleaching conditions used in this study were chosen on the basis of effectiveness and selectivity. Effectiveness was evaluated in terms of the efficiency of lignin removal, which was measured as reduction in kappa number. Selectivity was evaluated in terms of carbohydrate degradation, which was measured as the reduction in CED (cupriethylenediamine) pulp viscosity when pulp was bleached to a given kappa number.

Several variables—reactor type, bleaching conditions, ozone reaction time, temperature, pH, pulp consistency, ozone–oxygen flow rate, and ozone concentration—were studied in an effort to optimize the ozone-bleaching process. The experiments were conducted at the laboratory scale using a 2^3 factorial experimental design. The results were analyzed using Yate's algorithm to determine the main effects of the variables on ozone bleaching at medium consistency. Once the optimum ozone-bleaching conditions had been identified, these conditions were applied in the laboratory, and several

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experiments were performed to study the effect of pulp lignin content on ozone bleaching at medium consistency.

Experimental design

Considerable research at the laboratory and pilot scale has been conducted in recent years to determine the effectiveness of ozone in pulp bleaching. Past research shows that the use of ozone as a bleaching agent is most successful at pH 2–3, pulp consistency 25–46%, and temperatures below 60°C *(8)*. An extraction stage following the ozone stage improves bleachability. Pulp pretreatment with acid to control the pH before the ozone stage enhances lignin removal and reduces pulp degradation. Increasing the ozone charge has a positive effect on lignin removal and brightness, but pulp viscosity suffers significantly.

Pine kraft pulp prepared in a laboratory digester (M/K) was used in the bleaching experiments. Brownstocks were pretreated by washing in a chemical solution, followed by filtration and fluffing.

All experiments were conducted in the laboratory under bleaching conditions used by previous researchers. Ozone–oxygen gas (up to 4 L/min) for the bleaching experiments was produced in an ozone generator (Welsbach), which produces ozone by passing oxygen through a corona discharge. Ozone gas was continuously fed into the ozone reactor throughout the entire period of ozone reaction. The concentration of ozone during the experiments was tracked with an ozone monitor (PCI LC-12). This device measures the ultraviolet absorption of gas samples, and the ozone concentration is computed using Beer's law. The ozone charge on moisture-free pulp was determined by a chemical procedure. This was done by measuring the volume of exit gas bubbling through a 2% solution of potassium iodide in water. The solution was then acidified and titrated with sodium thiosulfate to determine the amount of ozone.

I. 2^3 factorial experimental design of ozone-bleaching experiments at medium consistency *

Run No.	Pulp consistency, %		Ozone concentration, %		pH	
1	12	–	1.5	–	7	–
2	16	+	1.5	–	7	–
3	12	–	3.0	+	7	–
4	16	+	3.0	+	7	–
5	12	–	1.5	–	2	+
6	16	+	1.5	–	2	+
7	12	–	3.0	+	2	+
8	16	+	3.0	+	2	+

* 2^3 experimental design represents three variables at two levels

The success of any bleaching process can be measured across three domains: lignin removal, brightness improvement, and strength retention. Lignin removal can be measured by the reduction of kappa number. The kappa-number test is an indirect method to determine the lignin content of pulp. A linear relationship between kappa number and percent lignin content has been developed and proven explicitly *(9)* and is given by the equation:

$$\text{Lignin, \%} = 0.147 \times \text{kappa number}$$

The effects of ozone concentration, pulp consistency, and acid pretreatment of the pulp on ozone bleaching were studied through the use of a two-level experimental design. Data from the experiments were analyzed using Yate's algorithm. Each experiment was duplicated to minimize the error. The bleaching conditions and the design of experiments are given in **Table I**.

Results of factorial experiments

The experimental results of the 2^3 factorial design were averaged. The kappa-number results for the eight runs are presented in **Table II**. Corresponding results for pulp viscosity are given in **Table III**. The results for kappa number are plotted vs. reaction time in **Fig. 1** (Runs 1–4 at neutral pH) and in **Fig. 2** (Runs 5–8 at acid pH). Similarly, the results for pulp viscosity are plotted vs. reaction time in **Fig. 3** (neutral pH) and in **Fig. 4** (acid pH).

The effects of the three controlled variables—pulp consistency, ozone concentration, and pH—on kappa number are presented in **Fig. 5**. The effects of the controlled variables on pulp viscosity are plotted in **Fig. 6**. Yate's algorithm was used to calculate the effects plotted in both Figs. 5 and 6. The results of our experiments are in general agreement with reports published by other scientists.

Kappa number

The effectiveness of ozone bleaching at medium consistency, as measured by reduction in kappa number, is shown in Fig. 1 for the runs at neutral pH and two levels of pulp consistency and ozone concentration. The effects of pulp consistency and ozone concentration on bleaching are obvious. The curve for Run 4—carried out at higher levels of pulp consistency and ozone concentration—shows that both variables exert a very strong effect on the ozone reaction rate. Under these conditions, the ozone reaction takes place rapidly during the earlier stage of bleaching. The similarity of the curves for Runs 2 and 3 shows that ozone concentration and pulp consistency have almost the same impact on the ozone reaction rate.

Figure 2 shows kappa-number reduction during medium-consistency

II. Kappa-number reduction during ozone bleaching at medium consistency

Reaction time, min	*Run 1*	*Run 2*	*Run 3*	*Run 4*	*Run 5*	*Run 6*	*Run 7*	*Run 8*
0	36.61	36.61	36.61	36.61	36.61	36.61	36.61	36.61
15	31.08	28.54	28.29	22.67	30.50	26.70	28.40	21.90
30	25.72	21.15	20.31	12.27	25.72	19.53	20.45	11.79
45	20.73	13.49	12.43	8.61	20.72	12.39	12.43	7.87
60	17.65	9.22	8.05	5.46	16.35	7.80	6.35	5.46
75	14.60	7.60	6.57	4.81	13.55	6.01	5.10	4.56
90	11.87	5.94	5.31	3.80	11.00	4.43	4.01	3.67

III. Pulp-viscosity reduction during ozone bleaching at medium consistency

Reaction time, min	*Run 1*	*Run 2*	*Run 3*	*Run 4*	*Run 5*	*Run 6*	*Run 7*	*Run 8*
0	41.07	41.07	41.07	41.07	41.07	41.07	41.07	41.07
15	35.12	30.12	32.04	28.56	35.12	31.05	30.48	27.62
30	29.65	20.54	21.93	18.27	29.98	25.41	23.19	19.75
45	24.56	13.99	15.63	10.46	25.33	21.06	19.56	14.23
60	19.30	9.20	8.50	6.75	21.46	17.47	16.74	12.26
75	15.30	6.70	6.57	4.63	18.34	14.48	13.66	11.02
90	11.44	4.53	5.31	3.89	15.86	12.89	12.68	10.36

ozone bleaching at pH 2. The similarity of the curves in Figs. 1 and 2 indicates that the acid pretreatment did not affect the efficiency of lignin removal. The ozone charge on a moisture-free pulp basis is in the range of 0.5–1.0%.

The effects of pulp consistency, ozone concentration, and pH on the rate of the bleaching reaction were evaluated by applying Yate's algorithm to analyze the results of the factorial experiments. Figure 5 shows the calculated effects of these variables on kappa number. Pulp consistency and ozone concentration had similar and strong effects on kappa-number reduction. As seen in Fig. 5, the effects change with reaction time, and the maximum effects in these experiments occurred during the first 30–45 min of reaction. It is apparent that the acid pretreatment of the pulp had little effect on the effectiveness of ozone bleaching in reducing pulp kappa number.

Pulp viscosity

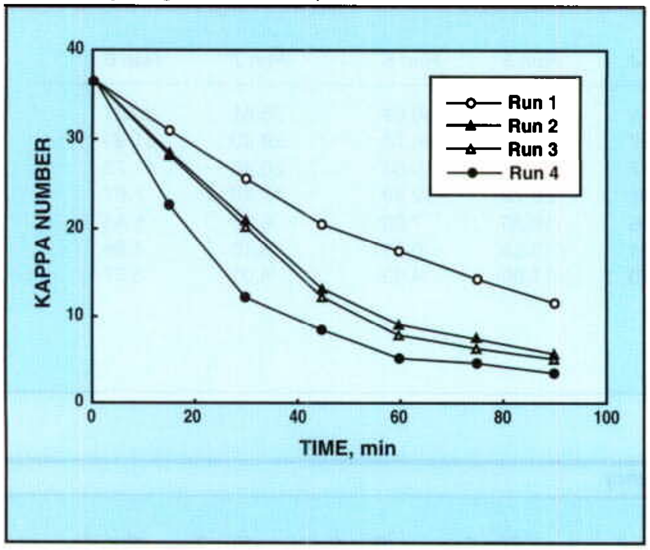
The selectivity of ozone bleaching at medium consistency, as measured by changes in CED viscosity, is shown in Fig. 3 for the runs at neutral pH and two levels of consistency and ozone concentration. The curves for Runs 2, 3, and 4 show that both consistency and ozone concentration strongly affect the ozone reaction rate. The results for pulp viscosity in Fig. 3 at neutral pH are consistent with the corresponding kappa-number runs of Fig. 1. However, the viscosity results for the runs in Fig. 4 at pH 2 differ from those of the corresponding kappa-number runs in Fig. 2. While acid pretreatment had no apparent effect on delignification, the selectivity of ozone bleaching with acid pretreatment is much better than without pretreatment. Without pretreatment, pulp viscosity dropped to 4 cP at 90 min of ozone reaction, as seen in Fig. 3. With pretreatment, pulp viscosity only dropped to 10 cP at 90 min, as seen in Fig. 4.

The calculated effects (Yate's algorithm) of pulp consistency, ozone concentration, and pH on pulp viscosity are shown in Fig. 6. The results show that pH is the variable with a positive effect on the selectivity of ozone bleaching. Clearly, the acid pretreatment of pulp has a very strong impact on the reduction of pulp viscosity during ozone bleaching. Figure 6 also shows that the effect of pH on pulp viscosity increased with reaction time during these factorial experiments. Pulp viscosity suffered losses at all levels of pulp consistency, ozone concentration, and reaction time, although these losses were mitigated by acid pretreatment of pulp.

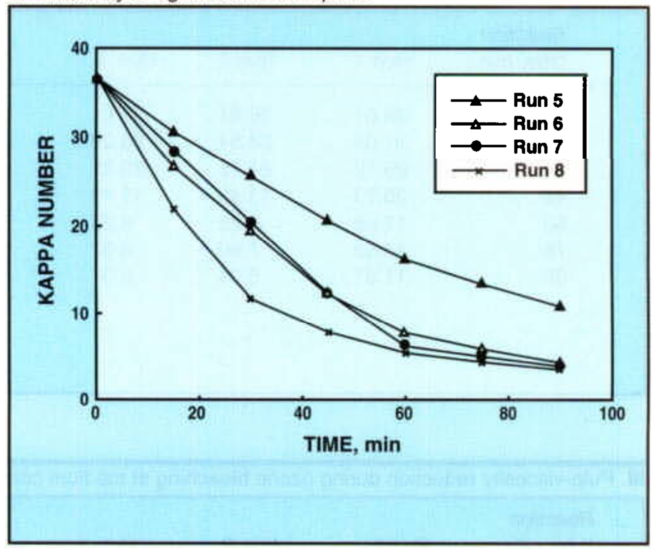
Effect of lignin content on ozone bleaching

The optimum ozone-bleaching conditions at medium consistency, as determined by the factorial experiments, are given in **Table IV**.

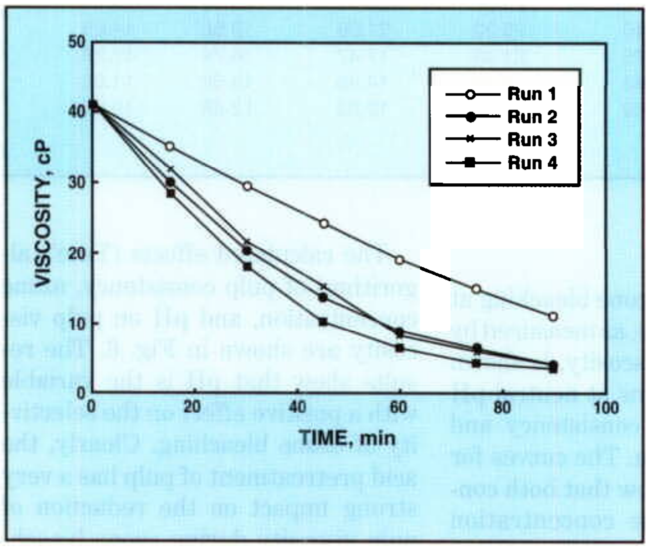
1. Efficiency of lignin removal at pH 7



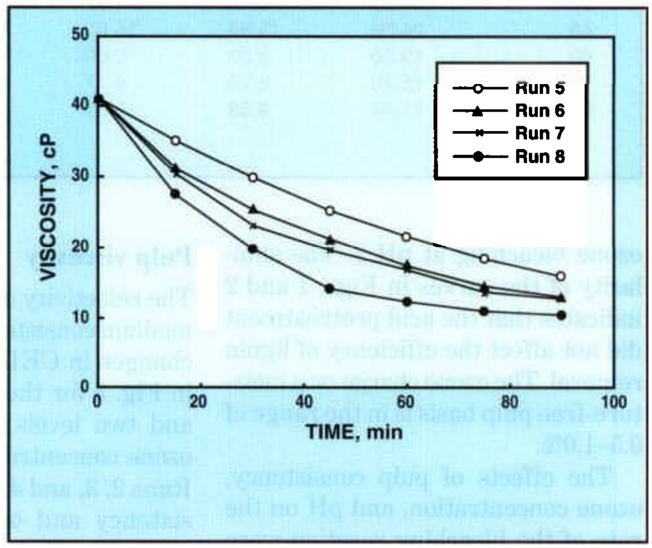
2. Efficiency of lignin removal at pH 2



3. Efficiency of pulp-viscosity reduction at pH 7



4. Efficiency of pulp-viscosity reduction at pH 2



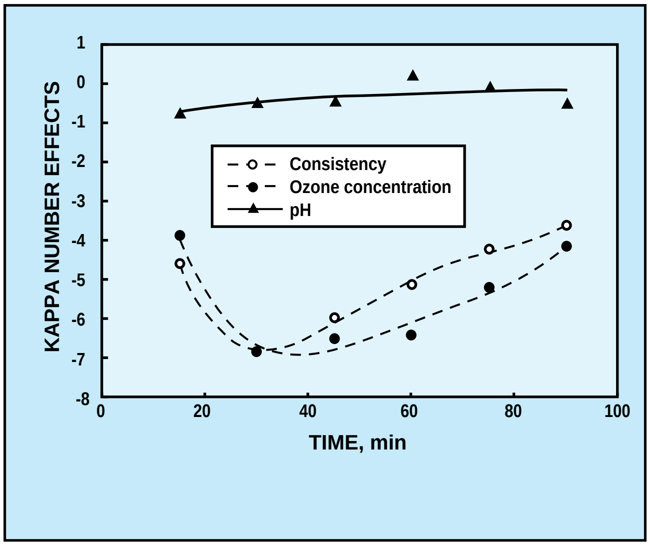
Brownstock kraft pulp samples of varying kappa number and viscosity were prepared for ozone-bleaching experiments at the optimized conditions listed in Table IV. Kappa number and viscosity were measured using TAPPI T 236 cm-85 and T 230 om-89, respectively.

All pulp samples were bleached using optimum procedures and the conditions outlined in Table IV. The bleached pulps were then analyzed to determine the effect of lignin content on ozone bleaching at medium consistency. This was done by measuring pulp kappa number and viscosity and comparing these values with the values of the unbleached samples. The results in **Table V** demonstrate that the bleached kappa number and viscosity relied heavily on the initial values for the unbleached pulp. Table V shows that kraft pulps can be bleached with ozone to kappa no. 3–6 at a viscosity in the range of 7–14 cP.

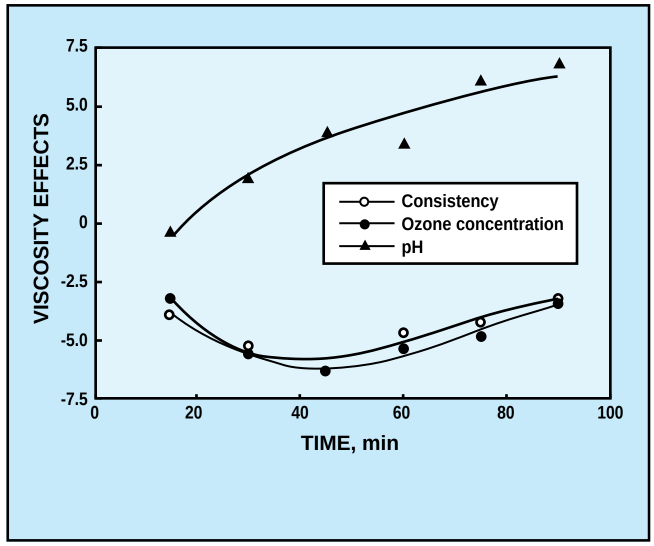
Figure 7 is a plot of viscosity vs. kappa number before ozone bleaching. There is a clear linear correlation between pulp lignin content and pulp viscosity. **Figure 8** is a plot of viscosity vs. kappa number after ozone bleaching. The curve in Fig. 8 shows the existence of a correlation between lignin content and viscosity, but it is not a linear correlation. **Figure 9**, which combines Figs. 7 and 8, clearly shows that the linear correlation before ozone reaction switches to a nonlinear correlation after ozone reaction.

Figure 10 shows the analysis of ozone-bleaching selectivity at the optimized conditions. The low values for the ratio of viscosity–kappa number represent the best ozone-bleaching selectivity. As seen in Fig. 10, the best selectivity occurs at little

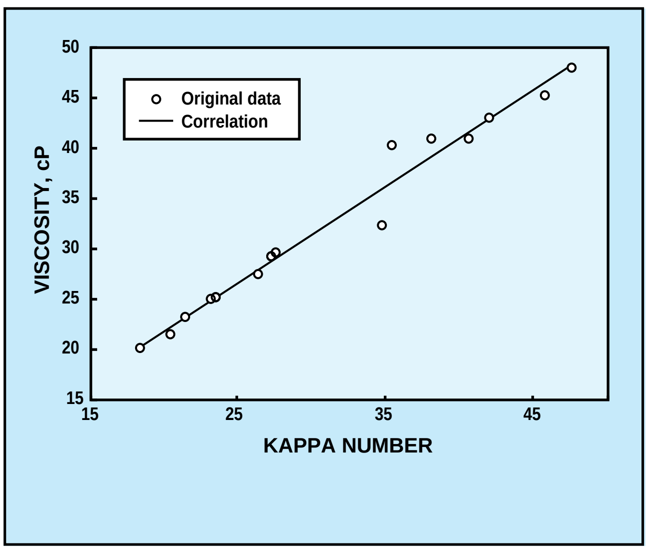
5. Analysis of kappa-number effects (Yate's algorithm)



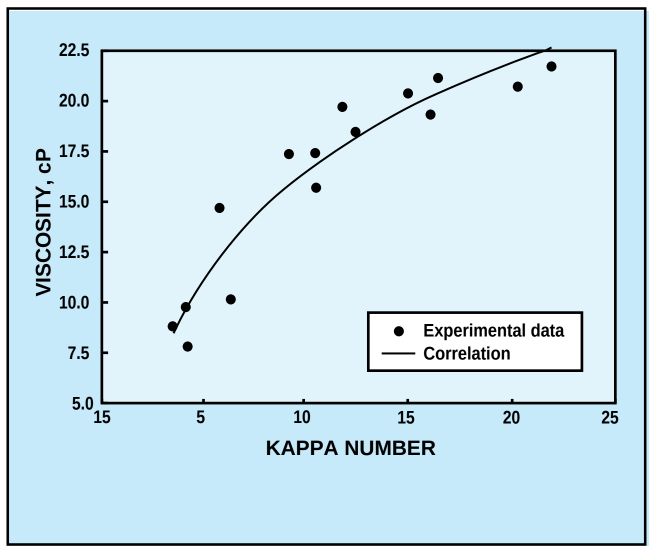
6. Analysis of viscosity effects (Yate's algorithm)



7. Viscosity vs. kappa number before bleaching



8. Viscosity vs. kappa number after bleaching



IV. Optimum ozone-bleaching conditions at medium consistency

Temperature	30°C
Pretreatment by acetic acid	pH 2
Pulp consistency	16%
Ozone concentration	3%
Reaction time	30 min

reduction of lignin content, or no more than 65% lignin reduction. Consequently, extended delignification (i.e., low-kappa-number pulps) and multistage bleaching will be required to obtain full brightness for medium-consistency pulps treated with ozone.

Conclusions

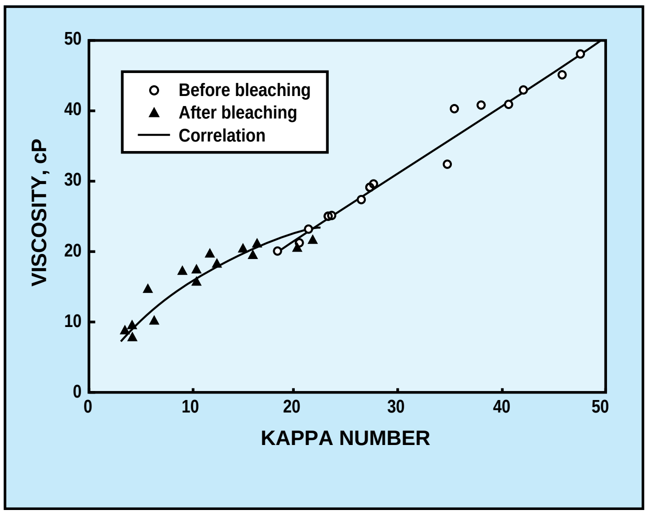
Research has shown that ozone can be used to eliminate or partially replace chlorine for bleaching of pulp. Most of this research has focused on ozone bleaching at low or high consistency. In this study, we examined the effect of pulp lignin content on ozone bleaching at medium consistency.

Based on our experimental results, ozone bleaching can be carried out at medium consistency, thus eliminating the need for a fluidizing mixer and pressurizing-gas facilities. However, satisfactory pulp brightness cannot be achieved by only one stage of ozone bleaching, since the long time of reaction allows the ozone to attack the carbohydrates. Previous studies have shown that ozone treatment seems to be more aggressive toward lignin, behaving more like a delignifying agent than a bleaching agent *(10)*. The best selectivity of ozone bleaching occurs at limited reduction of lignin content. In our experiments, the best selec-

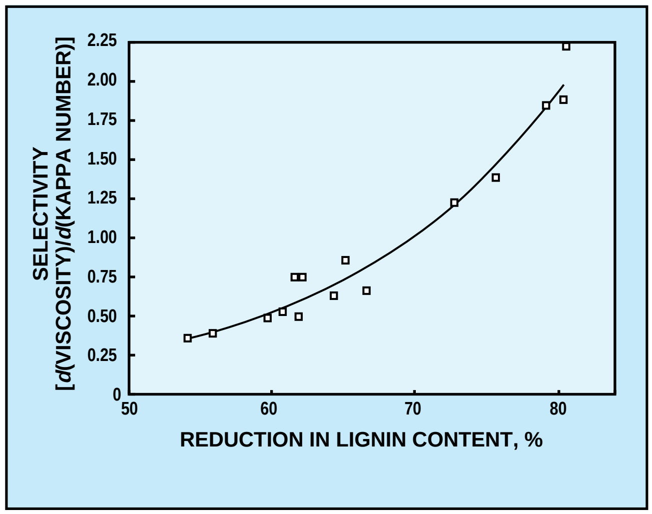
V. Bleaching results

Stock No.	*Kappa number*		*Pulp viscosity, cP*	
	Before bleaching	*After bleaching*	*Before bleaching*	*After bleaching*
1	18.32	3.57	20.12	8.74
2	20.44	4.26	21.49	7.28
3	21.37	4.21	23.21	9.71
4	23.36	6.37	25.15	10.16
5	23.51	5.74	25.30	14.66
6	26.36	9.18	27.51	17.32
7	27.30	10.48	29.40	15.72
8	27.52	10.44	29.67	17.44
9	34.74	12.37	32.51	18.43
10	35.36	11.79	40.22	19.75
11	38.01	14.92	41.12	20.43
12	40.55	16.33	41.15	21.17
13	41.93	15.96	43.27	19.43
14	45.74	20.18	45.44	20.78
15	47.47	21.76	48.31	21.78

9. Viscosity vs. kappa number before and after ozone bleaching



10. Ozone-bleaching selectivity as a function of reduction in lignin content



tivity occurs at less than 65% lignin reduction. Extended delignification of pulps to low kappa numbers will be required to obtain a fully bleached pulp.

Ozone alone generally cannot bleach a pulp above 80% brightness. Consequently, ozone must be used in combination with other bleaching agents (oxygen, peroxides, and chlorine dioxide) to achieve a 90+% brightness. Ozone is best applied in the early stages of a bleaching sequence. An ozone stage (Z stage) can be used to replace the chlorination stage in pulp bleaching, as in ZED, OZED, OZP, OZEP, ZEDED, or OZEDED sequences. Our laboratory will be conducting further experiments to investigate the effects of pretreatment by oxygen, nitrogen, and enzyme before ozone bleaching at medium consistency.

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