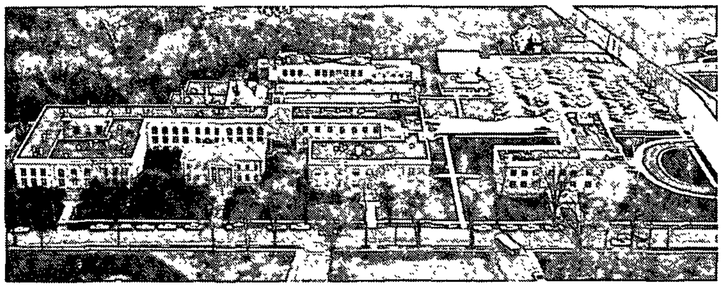

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THE KINETICS OF RESIDUAL DELIGNIFICATION IN SULFITE-ANTHRAQUINONE PULPING OF SOUTHERN PINE

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THE KINETICS OF RESIDUAL DELIGNIFICATION IN SULFITE-ANTHRAQUINONE PULPING OF SOUTHERN PINE

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ABSTRACT

An experimental study of the kinetics of residual delignification in the sulfite-anthraquinone pulping of southern pine is described. In the pH range 9-10.1, the rate of residual delignification depends on the concentration of lignin remaining in the pulp, the total sulfite concentration remaining in the liquor, the hydroxide ion concentration and the initial concentration of AQ. The orders with respect to each of these concentrations are estimated to be 2.0, 0.75, 0.18 and 0.1, respectively. The rate is decreased when total carbonate concentration is increased at a given level of pH and total sulfite concentration. As the pH is increased to values above 12, the kinetic behavior of the system changes and the rate increases.

INTRODUCTION

A knowledge of the chemical kinetics of wood pulping is of indisputable value in the development, control and optimization of pulping processes. Recognition of this fact has resulted in considerable research aimed at the development of kinetic descriptions of kraft pulping, but less effort has been devoted to achieving an understanding of the kinetics of the sulfite processes. This is particularly true of the alkaline sulfite-anthraquinone (SAQ) processes, which have made their appearance only within the last decade.

A little is known about the kinetics of neutral sulfite semichemical (NSSC) pulping (e.g., 1,2) and somewhat more about that of sulfite pulping in acidic liquors. Hagberg and Schoon (3), for example, showed that the acid sulfite delignification of spruce occurs in two stages. In the first, which extends to a lignin content of about 12%, the order of reaction with respect to lignin is 0.65 and in the second it increases to 1.58. Orders with respect to bisulfite ion and hydrogen ion are the same in both phases, 0.79 and 0.74, respectively. In the NSSC system, on the other hand, Kansal and Basu (2) observed orders of 1.75 with respect to lignin and 0.25 with respect to sulfite, when both were measured after the initial rapid delignification was complete.

The observation that delignification occurs in distinct phases having different rate constants parallels a similar one in studies of kraft pulping kinetics. There, however, all phases, initial, bulk and residual, are usually represented as being first order in lignin and of differing orders in hydroxide ion and hydrosulfide ion. The values of these orders and the corresponding rate constants have important implications for process design, especially when combined with a similar knowledge of the parameters governing carbohydrate degradation kinetics. This has been amply illustrated by the development of modified kraft cooking as a route to improved selectivity and lower unbleached lignin contents.

Sulfite-anthraquinone pulping may have similar potential for development into a low-lignin pulping process by suitable modifications. This is suggested by the extremely good selectivity apparent during its bulk phase. However, to realize any such potential, it will be necessary to find a means of avoiding the sharp deterioration in selectivity that accompanies the transition to the residual phase (4). A study of the kinetics of residual delignification is a good first step toward that goal; the results of such a study are reported here.

In a related investigation, Eagle and McDonough determined the rate law for SAQ bulk delignification of southern pine (5). During that part of the cook (22-9% lignin yield) the reaction orders with respect to lignin and sulfite are 2.2 and 0.5, respectively, and the activation energy is 34250 kcal/mole. That work also provided an estimate of the stoichiometric coefficient of sulfite: 0.533 g of sodium sulfite (expressed as Na_2O) were consumed for each g of lignin dissolved after the lignin yield had decreased by 4.2% (o.d. wood basis). The first 4.2% was dissolved with no apparent consumption of sulfite, a feature that is absent from the corresponding AQ-free system. These figures were used in the work described here to estimate the residual sulfite concentration as a function of degree of delignification.

The experimental part of the present study consisted of a series of microdigester cooks of 1 mm thick wafers (to eliminate mass transfer limitations) at high liquor-to-wood ratio (to keep liquor concentrations nearly constant). The cooks were done in sets of seven in a common oil bath. Within each set, all microdigesters were charged with aliquots of the same pulping liquor, so conditions were identical except for cooking time. One microdigester was cooled and opened 30 minutes after the bath reached its maximum temperature of 180°C and another at the end of each of six more 30-minute intervals. The pulps were fiberized, screened and washed, after which determinations of lignin content and yield were made. The principal experimental variables were cold liquor pH, sulfite concentration, and initial AQ concentration. One set of cooks was done at a high carbonate concentration to determine the effect of that variable.

RESULTS AND DISCUSSION

Initial conditions, lignin yields, pH values and estimated residual sulfite concentrations for all cooks are given in Table 1. In this section, the effect of each of the experimental variables is illustrated and discussed. This is followed by a description of an analysis of the data and the rate expression it produced.

Effect of pH

Figure 1 shows the effect of varying the initial cold pH of the pulping liquor over the range 9.5 to 13.4 at constant initial sulfite concentration

Table 1 Experimental pulping data

	Initial Conditions							
Set No.	pH	Cs, g/L	Total Na_2O, g/L	AQ, g/L	Time at 180°C, min	pH	Cs, g/L	Lignin Yield, % d.w.
156	9.0	44.6	56.5	0.25	30	9.02	39.9	10.13
					60	9.00	39.0	6.67
					120	8.99	38.3	3.90
					150	8.98	38.2	3.49
					180	8.98	37.9	2.39
					210	8.98	37.8	1.96
169	9.5	45.8	57.1	0.25	30	9.33	40.8	9.03
					60	9.31	40.1	6.37
					90	9.31	39.7	4.76
					120	9.29	39.4	3.74
					150	9.28	39.3	3.33
					180	9.28	39.2	2.75
					210	9.28	39.0	2.10
183	9.65	43.4	55.7	0.25	30	9.45	38.5	8.60
					60	9.43	37.6	5.39
					90	9.42	37.3	4.31
					120	9.41	37.1	3.51
					150	9.41	36.9	2.86
					180	9.41	36.8	2.48
					210	9.41	36.7	1.98
182	9.85	41.9	53.1	0.25	30	9.60	36.5	7.00
					60	9.60	36.0	5.05
					90	9.60	35.7	3.81
					120	9.60	35.5	3.11
					150	9.60	35.4	2.53
					180	9.61	35.3	2.16
					210	9.60	35.1	1.71
149	10.0	43.5	55.9	0.25	30	9.72	38.0	6.36
					60	9.67	37.4	4.00
					90	9.63	37.1	3.00
					120	9.63	36.9	2.28
					150	9.62	36.7	1.66
					180	9.62	36.6	1.24
					210	9.60	36.6	1.10
171	10.5	48.4	50.0	0.25	30	9.91	43.0	6.91
					60	9.90	42.2	4.00
					90	9.88	41.9	3.01
					120	9.87	41.8	2.51
					150	9.86	41.6	1.71
					180	9.86	41.5	1.42
					210	9.85	41.5	1.29
146	11.0	44.5	55.9	0.25	30	10.20	38.8	6.31
					60	10.10	38.1	3.54
					90	10.05	37.8	2.42
					120	10.00	37.6	1.76
					150	9.93	37.5	1.46
					180	9.92	37.5	1.16
					210	9.92	37.4	0.91
155	12.0	44.7	56.6	0.25	30	10.13	38.9	5.68
					60	10.13	38.4	3.52
					90	10.11	38.1	2.62
					120	10.09	37.9	1.85
					150	10.08	37.8	1.27
					180	10.08	37.7	1.11
					210	10.05	37.7	0.90
172	12.5	47.6	59.2	0.25	30	10.39	42.2	6.71
					60	10.35	41.6	4.57
					90	10.33	41.2	2.89
					120	10.31	41.0	2.33
					150	10.30	40.9	1.85
					180	10.27	40.8	1.43
					210	10.28	40.7	1.20
170	13.0	47.7	58.4	0.25	30	10.50	42.3	6.76
					60	10.46	41.6	3.94
					90	10.45	41.3	2.81
					120	10.42	41.1	2.07
					150	10.40	40.9	1.40
					180	10.40	40.9	1.27
					210	10.38	40.8	1.09
175	13.25	45.7	57.4	0.25	30	12.97	39.7	4.77
					60	12.93	39.1	2.30
					90	12.92	38.9	1.44
					120	12.86	38.8	1.25
					150	12.81	38.7	0.92
					180	12.76	38.7	0.76
					210	12.76	38.6	0.58
150	13.4	44.3	56.7	0.25	30	13.28	37.6	1.78
					60	13.24	37.3	0.73
					90	13.23	37.2	0.35
					120	13.22	37.2	0.23
					150	13.22	37.1	0.10
					180	13.17	37.1	0.05
					210	13.12	37.1	0.00
152	10.0	20.7	50.5	0.25	30	9.82	15.7	8.33
					60	9.81	15.2	6.42
					90	9.79	14.8	4.98
					120	9.77	14.5	4.06
					150	9.75	14.4	3.40
					180	9.74	14.2	2.96
					210	9.74	14.2	2.86
151	10.0	52.8	58.7	0.25	30	9.50	47.5	6.89
					60	9.46	46.7	4.23
					90	9.44	46.4	3.10
					120	9.43	46.2	2.01
					150	9.41	46.0	1.57
					180	9.40	46.0	1.38
					210	9.40	45.9	1.11
154	10.0	44.0	56.3	0.25	30	9.76	39.0	8.02
					60	9.72	38.2	5.24
					90	9.72	37.9	4.04
					120	9.71	37.6	2.94
					150	9.71	37.4	2.32
					180	9.70	37.3	1.92
					210	9.70	37.3	1.64
153	10.0	44.2	56.5	0.25	30	9.90	38.5	5.51
					60	9.86	37.9	3.35
					90	9.83	37.7	2.50
					120	9.80	37.5	1.89
					150	9.80	37.4	1.53
					180	9.79	37.4	1.25
					210	9.78	37.3	1.09
147	11.0	44.5	79.0	0.25	30	10.38	38.8	5.89
					60	10.36	38.4	4.11
					90	10.32	38.1	3.23
					120	10.31	37.9	2.28
					150	10.29	37.8	1.95
					180	10.28	37.7	1.71
					210	10.26	37.6	1.43

(44.6 ± 1.1 g Na_2O/L) and constant total Na_2O concentration (56.8 ± 0.8 g Na_2O/L). This resulted in average residual phase pH values ranging from 9.3 to 13.2. It is readily apparent that lower residual lignin levels are reached at a given cooking time as the pH is increased, but much of the difference is due to acceleration of delignification during the earlier part of the cook. The effect of pH on the rate of the residual phase is smaller. A possibly more important effect is the change in rate behavior seen as the final pH is increased from 10 to 13. At the higher levels the shape of the curves is different, being more concave and suggestive of a higher order with respect to lignin. A change in kinetics over this interval may be attributed to the incursion of additional delignification mechanisms. Soda-AQ delignification reactions are expected to occur in parallel with alkaline sulfite-AQ reactions at pH values in excess of about 12.

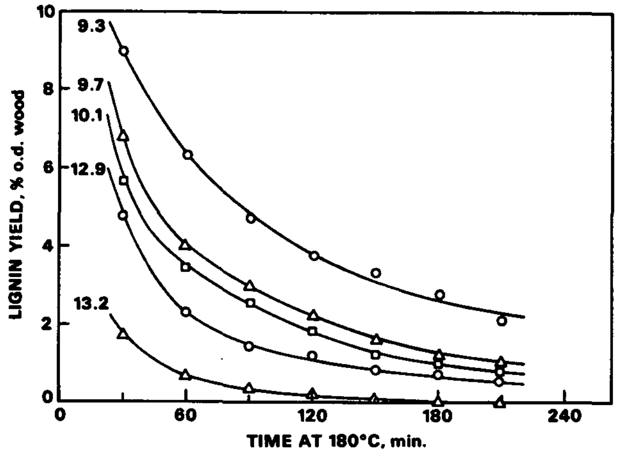

Fig. 1 Residual lignin yield *vs.* time at various pH values. Sets 149, 150, 155, 169, and 175. pH values shown are averages for the interval shown. Initial liquor pH ranged from 9.5 to 13.4. See Table 1 for details.

It may be noted in passing that the data of Fig. 1 demonstrate the delignification potential of sulfite-AQ systems. Lignin yields on the order of 1% (kappa number about 12) can be reached in times at temperature ranging from 1-3 hours.

Effect of Sulfite Concentration

The effect of varying the total sulfite concentration (Na_2SO_3 and $NaHSO_3$, added together and expressed as equivalent Na_2O) is illustrated by Fig. 2, which compares the results obtained in sets 151 (45.9-47.5 g/L total sulfite as Na_2O, pH 9.4-9.5) and 152 (14.2-15.7 g/L total sulfite as Na_2O, pH 9.7-9.8). Residual delignification is substantially accelerated by increasing the concentration of SO_2 in the liquor.

The dashed lines in the figure represent the predictions of a kinetic model, further described below, which was obtained as a least squares fit to nearly all of the data in Table 1. In the development of this model, estimates of sulfite concentration as a function of pulping time within each set of cooks were used. Although the variation was not large, because of the high liquor-to-wood ratio used, this provided some additional information upon which to base a quantitative estimate of the dependence of rate on sulfite concentration. It also avoided inaccuracies which would be incurred by assuming that sulfite concentration remained truly constant within sets.

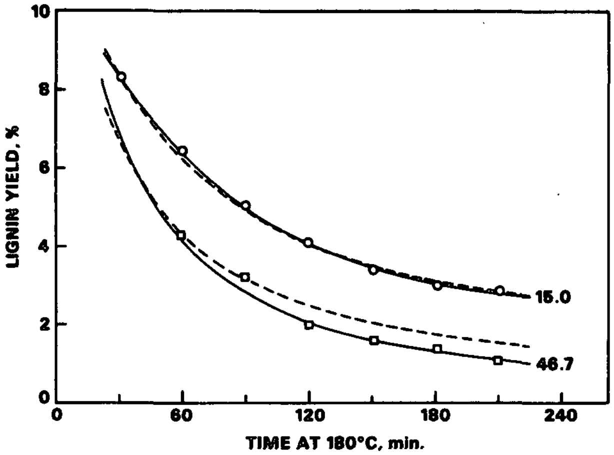

Fig. 2 Residual lignin yield *vs.* time at two different total sulfite concentrations. Sets 151 and 152. Sulfite concentrations are averages over the period shown. Initial total sulfite concentrations 20.7 and 52.8 g/L as Na_2O.

Effect of AQ Concentration

Figure 3 compares the rates of residual delignification at two different levels of AQ addition. These corresponded to concentrations of 0.1 and 0.5 g/L. At the higher concentration, the lignin yield was significantly lower at any given cooking time, but the effect was due mainly to an acceleration of the earlier part of the cook. The rate of residual delignification was not greatly affected.

Effect of Carbonate Concentration

In the pH interval 9-12, the inorganic components of the pulping liquor are sodium sulfite, sodium carbonate and sodium bicarbonate. It is known that liquors made from sulfite and carbonate pulp faster than those containing only sulfite. This could simply be the result of the buffering capacity of carbonate-bicarbonate mixtures, or it could reflect an additional, more active, role of carbonate in the pulping reactions. To distinguish between these possibilities, sets of cooks were done with liquors of similar pH and sulfite concentration, but different concentrations of total carbonate (Na_2CO_3 and $NaHCO_3$ expressed as Na_2O and added together). The results are presented in Fig. 4 and show that carbonate decelerates delignification in the residual phase. This is probably the result of an ionic strength effect and indicates that the major beneficial effect of carbonate is to prevent rapid pH drops which would slow down the AQ-assisted sulfite pulping reactions.

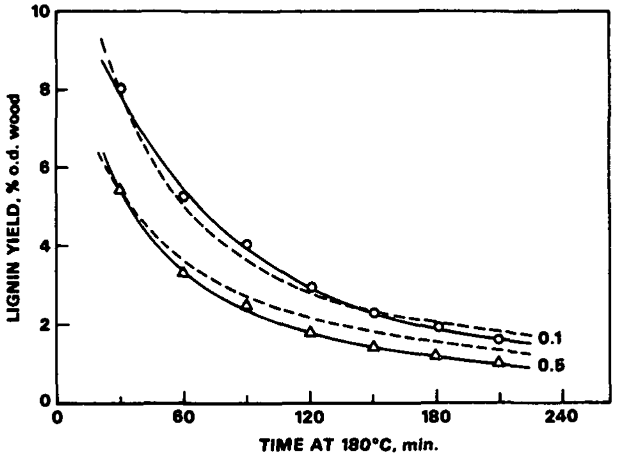

Fig. 3 Residual lignin yield vs. time at two different initial anthraquinone concentrations. Sets 153 and 154. AQ concentrations shown correspond to the amount of AQ added at the start of the cook. Total sulfite concentrations 38.1 ± 0.9 g/L as Na_2O. Total Na_2O concentration 56.4 ± g/L. pH 9.8 ± 0.1.

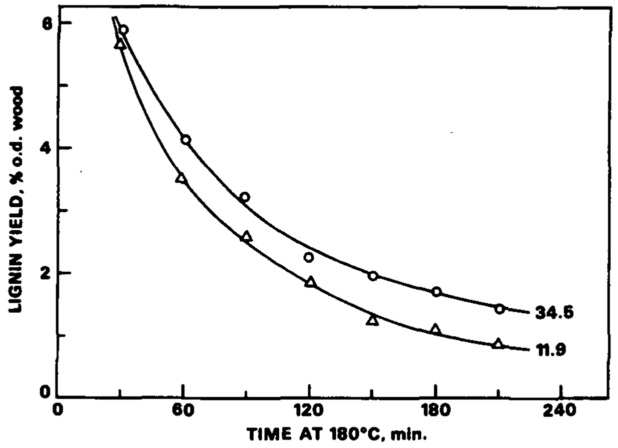

Fig. 4 Residual lignin yield vs. time at two different total carbonate concentrations. Sets 147 and 155. Total sulfite concentration 38.3 ± 0.7 g/L Na_2O. pH 10.1-10.4 over the interval shown.

A Kinetic Model

An empirical rate expression was obtained by least squares analysis of data in Table 1. On the basis of the above discussion, and by analogy with earlier investigations, it was assumed at the outset that the rate could be considered proportional to the product of the concentrations of residual lignin, total sulfite, hydroxide ion and AQ, each raised to its own power. The proportionality constant and exponents were then estimated from the data, but only after excluding results obtained at pH values higher than 12 (Sets 150, 170, 172 and 175) and at unusually high carbonate concentrations (Set 147). The former exclusion was made in view of the likely inability of such a model to describe the complexity of simultaneous soda-AQ and sulfite-AQ reactions, and the latter because insufficient data were available to include an ionic strength effect in the model.

The parameters were obtained by a combination of two subroutines (DVERK and ZXMIN) from the IMSL library (6) and a simple pattern search. A candidate parameter set was chosen and the rate expression integrated for each experimental run with DVERK, using as boundary conditions the concentrations existing after 30 minutes at temperature. The sum of squared deviations of the integrated expression from the data points was calculated and accumulated as the integration proceeded. ZXMIN, a quasi-Newton method function minimization routine then chose a new parameter set and the cycle repeated until the sum of squared deviations was minimized. In practice, ZXMIN often supplied parameters that could not feasibly be handled by DVERK, which responded by terminating abortively. As a result, the final choice of parameters was made by a systematic search in a region identified by initial trials with ZXMIN.

The resulting expression was

$$-dL/dt = 1.2\times10^{-3}(L)^{2.0}(Cs)^{0.75}(OH)^{0.18}(CAQo)^{0.1},$$

in which

L = lignin yield, % o.d. wood,

t = time, min,

Cs = Total sulfite concentration, g/L, as Na_2O,

OH = $10^{(pH-14)}$, where pH is measured at 25°C, and

CAQo = AQ charged per unit volume of liquor, g/L.

The order in lignin was clearly higher than 1, as shown by marked curvature in logarithmic plots of lignin yield versus time for all sets. In minimizing the sum of squared deviations of the calculated values from the data, it was observed that a lignin exponent of 2.0 gave a better fit than either 1.9 or 2.1. There was no apparent justification for including a lignin "floor level" as an additional parameter that has been cited as necessary in some other delignification models (7).

The order in total sulfite of 0.75 is not as firmly fixed by the data as the order in lignin. Only two sets of runs were done at sulfite concentrations appreciably outside the 37-40 g/L range, which resulted in a noticeable correlation between the sulfite exponent and the rate constant; within limits, different combinations of the two parameters gave fits of similar quality. Nevertheless, it can be said that values of the sulfite exponent outside the range 0.6-0.9 gave significantly poorer fits.

The hydroxide exponent of 0.18 also showed some correlation with other parameters, but gave much better fits in the range 0.16-0.20 than elsewhere. With reference to this term in the equation, it should also be noted that it is probably more a reflection of effects of the state of ionization of certain species (lignin phenolic groups and bisulfite ion, for example) than of active participation by the hydroxide ion itself. Another point worth noting is that the state of ionization of these species at pulping temperature is quite different from that indicated by a cold pH measurement.

The AQ term is also somewhat formalistic. Expressing the concentration as amount of material added per unit volume of liquor does not directly address the possibilities that the proportion dissolved or the proportion surviving may vary, or that the concentration based on wood is more relevant than that based on liquor. Until further research answers these questions, the simplification employed here is both necessary and justified by the usefulness of the approximate expression obtained. The value of 0.1 for the exponent reflects a range of possible values within the range 0.05-0.15 and indicates a relatively weak dependence of residual delignification rate on AQ concentration over the range 0.1-0.5 g/L.

Figure 5 allows an assessment of the predictive ability of the model. Additional comparisons of model and experiment are included in Fig. 2 and 3. Although the agreement with observed values is far from perfect, it is sufficiently good to make the model useful for simulation of process alternatives and for guiding future research. Among its implications is that, within the pH range 9-10, the major leverage for accelerating residual delignification is the residual sulfite concentration. Possible methods of applying this finding are now under study in our laboratory.

EXPERIMENTAL

Wafers 1 mm thick were cut from disks of southern yellow pine, tentatively identified as loblolly pine, Pinus taeda. These were air dried for storage and their moisture content was accurately determined, Analysis (8) showed that the wood contained 31.0% Klason lignin and 0.8% acid soluble lignin. The extractives content (TAPPI Test Method T 204 os-76) was 4.5%. Average specific gravity (green volume basis) was 0.411.

Liquors were prepared by absorbing CO_2 in solutions containing the calculated amounts of sodium sulfite and sodium hydroxide until the desired pH was reached. The liquors were potentiometrically titrated with standard acid before and after CO_2 addition.

Prior to pulping, the wafers were vacuum impregnated with pulping liquor at room temperature and transferred to 500 mL cylindrical microdigesters. These were mounted on a rack in a thermostatically controlled oil bath; during pulping, the microdigesters were continuously rotated end over end. The temperature of the bath was raised to 90°C, held there for 15 minutes, and then raised to 180°C linearly over a period of 90 minutes.

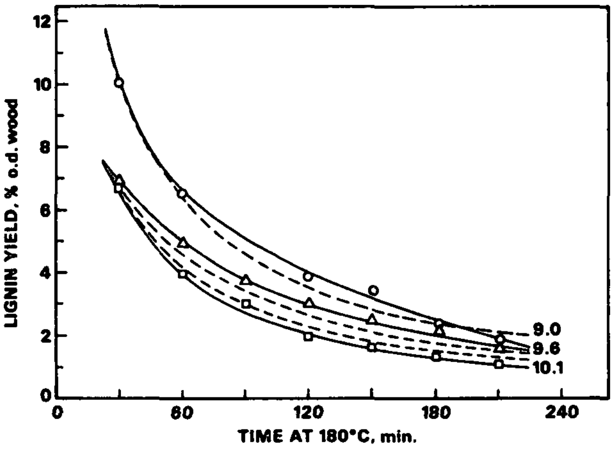

Fig. 5 Comparison of observed (data points and solid lines) and calculated (dashed lines) residual lignin yields at different pH values. Sets 155, 156, and 182. pH values shown are averages for the interval shown.

At the end of the cook the microdigester was removed from the bath, rapidly cooled with steam and water showers, and opened. A sample of the liquor was removed for titration and the cooked wafers were fiberized in a Waring blender. The pulp was then washed, dewatered, weighed, and sampled for determination of moisture and kappa number.

Some of the pulps, together with additional samples from previous research (9), were analyzed for Klason and acid soluble lignin (8). Regression analysis then yielded a linear relationship between kappa number and total lignin content, which was subsequently used to infer values for the lignin content of all of the experimental pulp samples. The data for this regression are shown in Table 2, and the equation obtained was

$$Lp = -1.07 + 0.193 \text{ (kappa no.)}$$

in which Lp is the regression estimate of the sum of the Klason and acid soluble lignin contents, expressed as a percentage of the o.d. pulp weight. Lignin yield was obtained as the product of Lp and the fractional pulp yield.

CONCLUSIONS

1. In sulfite-anthraquinone pulping of southern pine, the rate of residual delignification in the pH range 9.0-10.1 depends on the concentration of lignin remaining in the pulp, the pH of the liquor, and the concentrations of sulfite sulfur and anthraquinone in the liquor. The rate of lignin removal shows a second order dependence on remaining lignin content.

2. The rate depends more strongly on residual sulfite concentration than on the concentration of hydroxide ion or initial anthraquinone concentration. The orders with respect to these concentrations are estimated to be 0.75, 0.18 and 0.10, respectively.

3. The observed effects can be summarized in an approximate rate expression of the simple power law type. It incorporates the above reaction orders and a rate constant of 1.2×10^{-3}.

4. The rate decreases when the total carbonate concentration is increased at a given pH and total sulfite concentration.

5. As the pH is increased above 12, the kinetic behavior of the system changes and the rate increases.

Table 2 Kappa No. - Lignin Regression Data and Results

Cook No.	Klason Lignin, % o.d. pulp	Acid-Soluble Lignin, % o.d. pulp	Total Lignin, % o.d. pulp	Lp Kappa Number
142-1	4.0	0.8	4.8	30.4
142-2	5.5	3.8	9.3	52.1
142-6	6.8	9.4	16.2	93.0
143-1	10.2	1.2	11.4	67.8
143-4	11.0	1.3	12.3	71.0
143-5	8.8	10.0	18.8	97.8
144-1	4.4	0.9	5.3	27.4
144-3	6.6	4.4	11.0	55.0
160	1.0	0.7	1.7	12.9
161	1.2	1.2	2.4	22.8
167	3.6	2.0	5.6	41.0
173	0.8	2.0	2.8	20.7
174	0.9	0.8	1.7	11.7
180	3.8	3.4	7.2	45.2
181	5.0	2.3	7.3	45.5

Regression equation: $Lp = -1.07 + 0.193$ (Kappa).
Correlation coefficient, $r = 0.989$.
Standard error of estimate, $s = 0.81$.
Confidence interval (95%) for estimated value of Lp at Kappa No. 46.3: 7.85 ± 0.45.

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