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A Study of the Kinetics of Delignification During the Early Stage of Alkaline Sulfite Anthraquinone Pulping

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A STUDY OF THE KINETICS OF DELIGNIFICATION DURING THE EARLY STAGE OF ALKALINE SULFITE ANTHRAQUINONE PULPING

A thesis submitted by

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ABSTRACT

Alkaline sulfite anthraquinone (ASAQ) pulping has shown great promise as an alternative to conventional kraft pulping. The process is capable of producing pulps of higher yield at a given lignin content than normal kraft pulping. The resulting pulps have many desirable properties; they are easily bleached, have high strength, and are easily refined. One problem with the process is that, at a kappa number of about fifty, the selectivity for delignification falls rapidly. The result is the inability to produce pulps of low lignin content with high strength out of the digester under normal pulping conditions.

The purpose of this thesis was to develop a mathematical model for the delignification kinetics of the early stage of ASAQ pulping. A novel approach was used to determine the behavior of the system. Experiments were carried out in a flow through reactor, and delignification kinetics determined by measuring the concentration of lignin in the liquor flowing through the reactor.

A description of the system has been developed based on the experimental work in this thesis which is consistent with the chemistry of delignification and the results of model compound work in the literature.

The rate law for the early stage of ASAQ pulping had the form

$$-\frac{dL}{dt} = \left\{k_0 + k_5\left[SO_3^{2-}\right]\left[AHQ^{2-}\right] + k_6\left[SO_3^{2-}\right]\left[OH^-\right] + k_7\left[OH^-\right] + k_8\left[AHQ^{2-}\right]\right\} L$$

The presence of a sulfite/AQ interaction term indicates that the delignification does not proceed by a simple set of parallel reactions, as has been indicated in the literature.

The selectivity of the initial stage of ASAQ pulping as studied in this thesis is maximized by keeping liquor pH at the low end of the range studied, and other liquor chemical concentrations high. High pulping temperatures favor delignification over carbohydrate degradation when both sulfite and anthraquinone are present in the liquor.

This thesis provides the first kinetic description of the early stage of ASAQ pulping. Further research into subsequent delignification phases may yield the information necessary to give the overall solution to increasing the selectivity of the ASAQ process.

ACKNOWLEDGEMENTS

Although the title page of this document shows only one name, many other persons were instrumental in bringing this work to fruition. My thesis advisory committee, Tom McDonough, Earl Malcolm and Dave Clay, were invaluable in providing ideas, direction, and motivation throughout the course of the thesis work. The staff of the Institute of Paper Chemistry, including the machine shop, millwrights, electricians, analytical chemistry, and the computer laboratory, provided assistance that cannot be measured, but is surely appreciated.

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Finally, the love and support of my family is gratefully acknowledged. My husband Jim, daughter Kara, and parents have provided the kind of help I really needed from time to time. This work could not have been completed without them.

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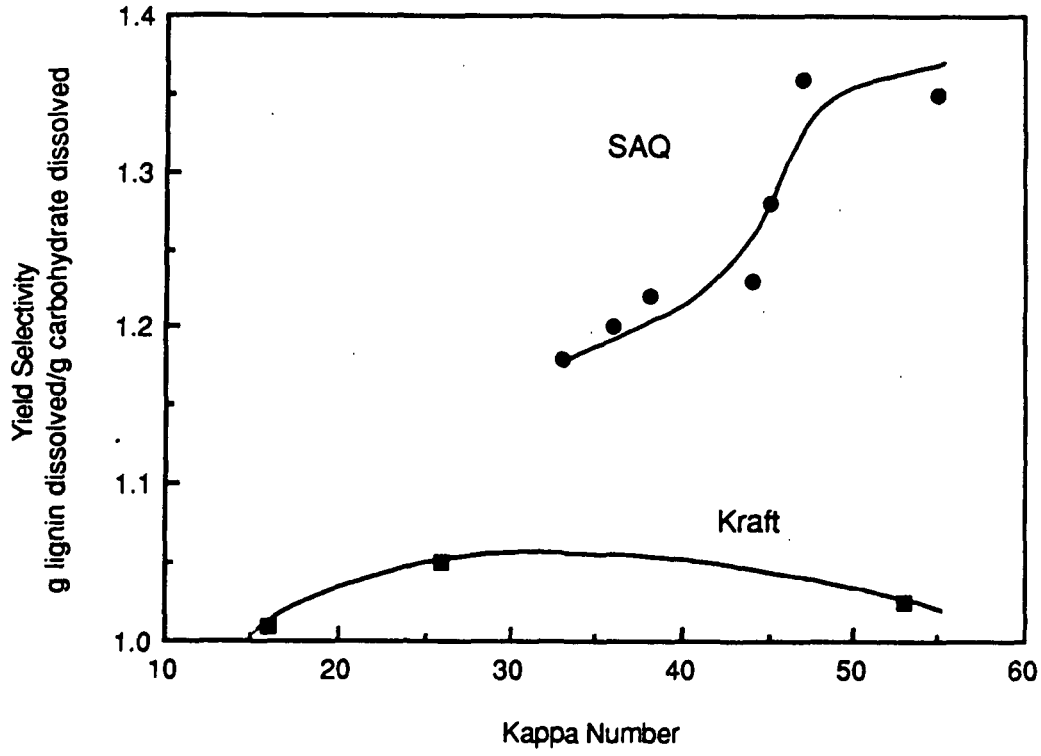
BACKGROUND

Alkaline sulfite anthraquinone (ASAQ) pulping has shown great promise as an alternative to conventional kraft pulping. The process produces pulps of higher yield at a given lignin content than normal kraft pulping. The resulting pulps have many desirable properties; they are easily bleached, have high strength, and are easily refined.

In spite of these advantages, ASAQ pulping has not found wide application, apparently because it requires a complex chemical recovery system and because the selectivity advantage over kraft pulping decreases at kappa numbers below about 50 (Fig. 1).

Figure 1. Selectivity advantage of delignification for ASAQ vs. Kraft pulping decreases with decreasing kappa number[9]



The large size of the selectivity advantage at kappa numbers greater than 50 suggests the possibility of modifying the process in such a way that the selectivity would be retained when pulping to much lower kappa numbers. If so, the resulting process would offer the possibility of selectively producing unbleached pulps of very low lignin contents without undue losses in yield or strength. Such pulps, unlike kraft pulps, could be bleached to high brightness with the application of relatively small amounts of bleaching chemicals. This is a very desirable goal, given the multitude of potential environmental problems associated with pulp bleaching.

The fact that this goal is achievable in principle has been demonstrated by pulping experiments conducted at high liquor–to–wood ratios[9] (and correspondingly high chemical charges). Pulps of kappa numbers as low as thirteen were produced at acceptable yield and strength levels by this method. Identification of other, more economical means of achieving the same objective depends upon gaining a better understanding of the kinetics of delignification and carbohydrate degradation during ASAQ pulping. Earlier work in this direction[27,28] suggests that initial phase kinetics are important. The present research was accordingly undertaken with the objective of defining rate laws for the early stages of delignification under alkaline sulfite anthraquinone pulping conditions.

The following sections summarize the background material for this thesis. A brief discussion of the sulfite/bisulfite system in aqueous solution is presented first, followed by a review of the fundamental chemistry of lignin as it pertains to the understanding of ASAQ pulping. A discussion of the kinetic considerations of importance to the thesis follows, including a look at the studies of ASAQ

kinetics in the literature. Finally, the theory behind the reactor modeling and fluorescence spectroscopy used in the thesis are covered.

THE BISULFITE/SUFITE SYSTEM

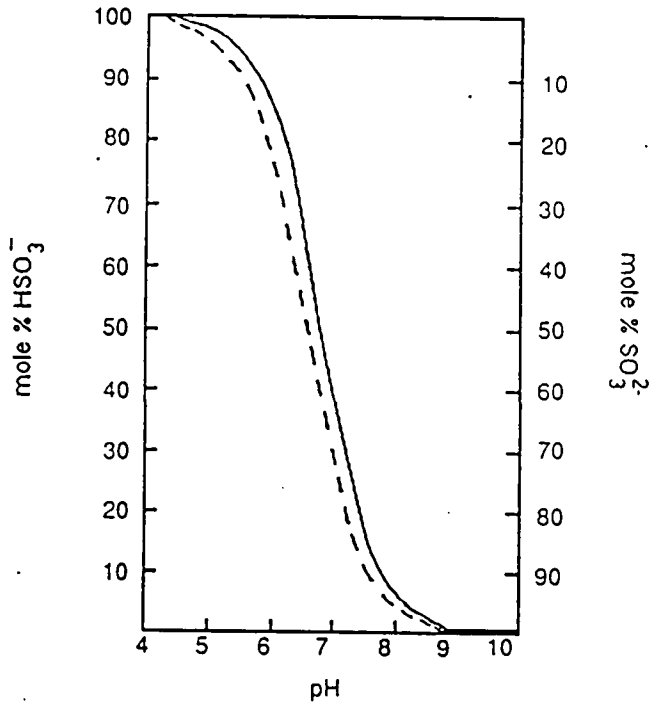
During neutral and alkaline sulfite pulping, the delignifying species are sulfite ions ($SO_3^{=}$), bisulfite ions (HSO_3^{-}), and hydroxide ions (OH^{-}). The equilibrium between the bisulfite and sulfite ions may be written

$$HSO_3^- \underset{K_a}{\rightleftharpoons} SO_3^{=} + H^+ \qquad \text{(A)}$$

The value of K_a for this equilibrium is 5.0×10^{-8} at 25°C. The concentrations of sulfite and bisulfite ions depend on the pH of the pulping medium as shown in Fig. 2.[4] As the pH of the liquor changes, the active delignifying species change as well. At pH 10 and 25°C, the ratio of sulfite ions to bisulfite ions is 500:1 (see Appendix 1 for calculations).

Temperature changes will also affect the values of both K_a and K_w, the equilibrium constant for the dissociation of water. When the solution temperature increases from 25°C to 150°C, K_a for the bisulfite/sulfite equilibrium increases to 7.8×10^{-8}. For the same temperature change, K_w increases from 10^{-14} to 7.8×10^{-12} (calculations for these values appear in Appendix 1). The net effect of these changes is an increase in the ionization of the water, giving an increased concentration of hydrogen ions in solution. This drives the equilibrium between bisulfite and sulfite to the left, resulting in a higher concentration of bisulfite ions in solution. The ratio of sulfite to bisulfite ions at 150°C is approximately 20:1 for a solution which corresponds to a pH of approximately 10 at room temperature.

Figure 2. Sulfite/bisulfite solution composition – dependence on pH
— = 10 g Na2O/liter, — — = 50 g Na2O/liter (after ref. 4)



DELIGNIFICATION CHEMISTRY

The fundamental chemistry of lignin degradation reactions are reviewed in this section. The discussion is limited to the reactions likely to be of importance during alkaline sulfite anthraquinone pulping.

Lignin is a complex three dimensional polymer (Fig. 3). The complexity of its structure may be better understood by representing it in terms of a generic arylpropane unit (Fig. 4) in which R may refer to hydrogen, aryl or alkyl and R_1 may represent an aroxyl, aryl, or alkyl group. The unit may be phenolic (R_2 = H) or non-phenolic (R_2 = adjacent unit). Varying the substituents R, R_1, and R_2 results in the ability to represent all prominent lignin structures, as shown in Fig. 5.

Figure 3. A representation of the lignin macromolecule (after ref. 1, diagram courtesy of R. Barkhau)

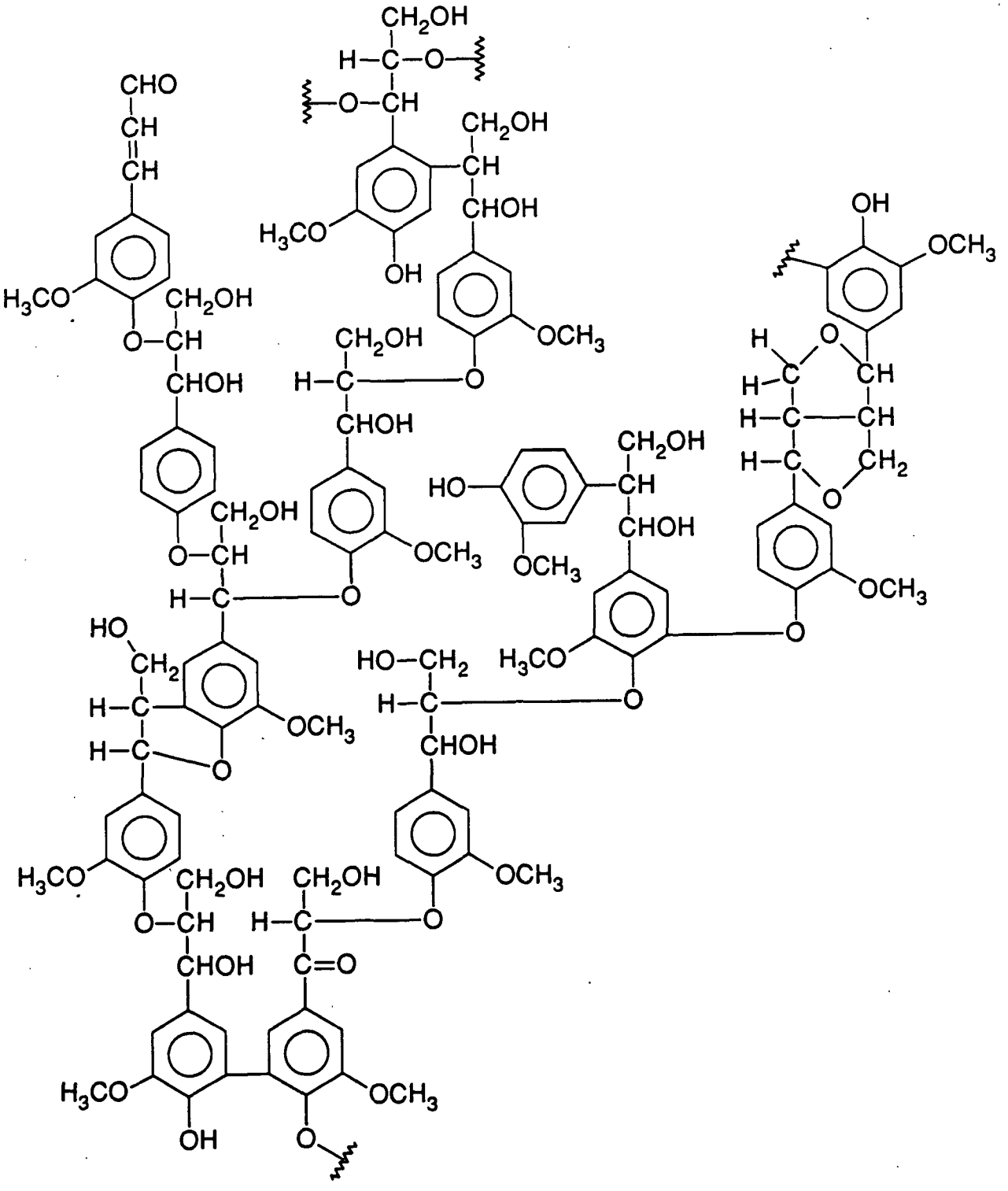
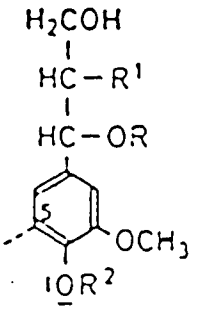
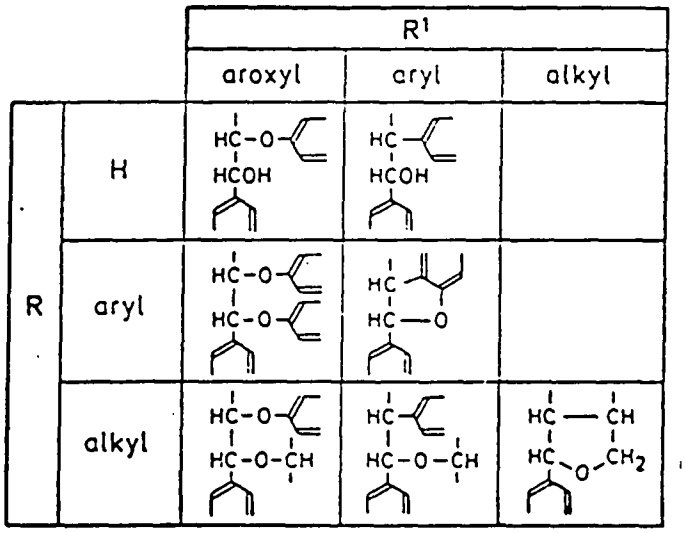


Figure 4. General arylpropane unit[2].



R = H, aryl or alkyl
R^1 = aroxyl, aryl or alkyl
R^2 = H, alkyl or aryl

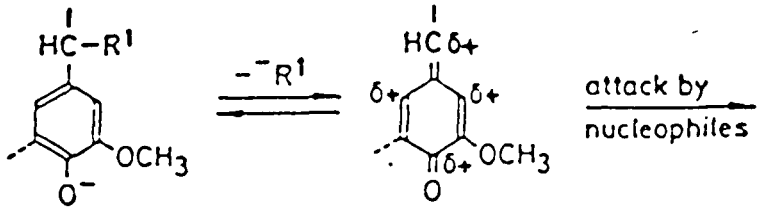
Figure 5. Common linkages in lignin[3].



Delignification is brought about by two types of structural changes in lignin: degradation by cleavage of interunit linkages to reduce molecular size, and the introduction of hydrophilic groups, rendering the fragments more soluble. During pulping, the reactions of lignin are primarily nucleophilic reactions.[2] The phenolic arylpropane unit can form the quinone methide

intermediate (Fig. 6), thus generating centers of electron deficiency. These centers (δ+ in Fig. 6) are the sites of nucleophilic attack during pulping.

Figure 6. Sites (δ+) of nucleophilic attack[2]



R^1 = OH, OAr or OAlk

Hydroxide, sulfite, and bisulfite may react with lignin by nucleophilic addition to the center of electron deficiency at the α carbon of the arylalkane unit in Fig. 7. This type of nucleophilic reaction is illustrated on the right side of Fig. 7 where N^{2-} represents a general nucleophile, and H_2N the protonated form of the nucleophile. The hydroxide may also abstract a proton from the hydroxyl group at the γ carbon of the propyl side chain, resulting in the unsaturated structure on the left side of Fig. 7.

Under alkaline conditions, non–phenolic units may be fragmented without the formation of the quinone methide intermediate. This reaction involves the participation of an adjacent hydroxyl group. The ionized hydroxyl group on the α carbon attacks the adjacent carbon atom, displacing the ether and forming the three membered oxirane intermediate. The cleavage of a β–aryl ether linkage by this neighboring group mechanism is illustrated in Fig. 8.

Figure 7. Competition between addition of nucleophile and proton abstraction[2]

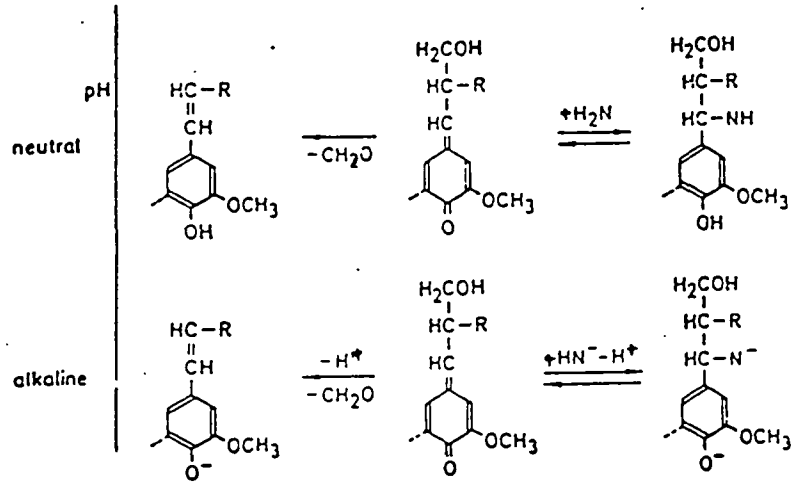
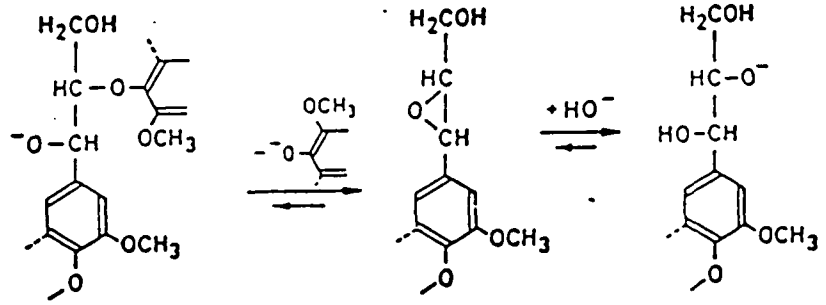


Figure 8. Neighboring group mechanism[2]

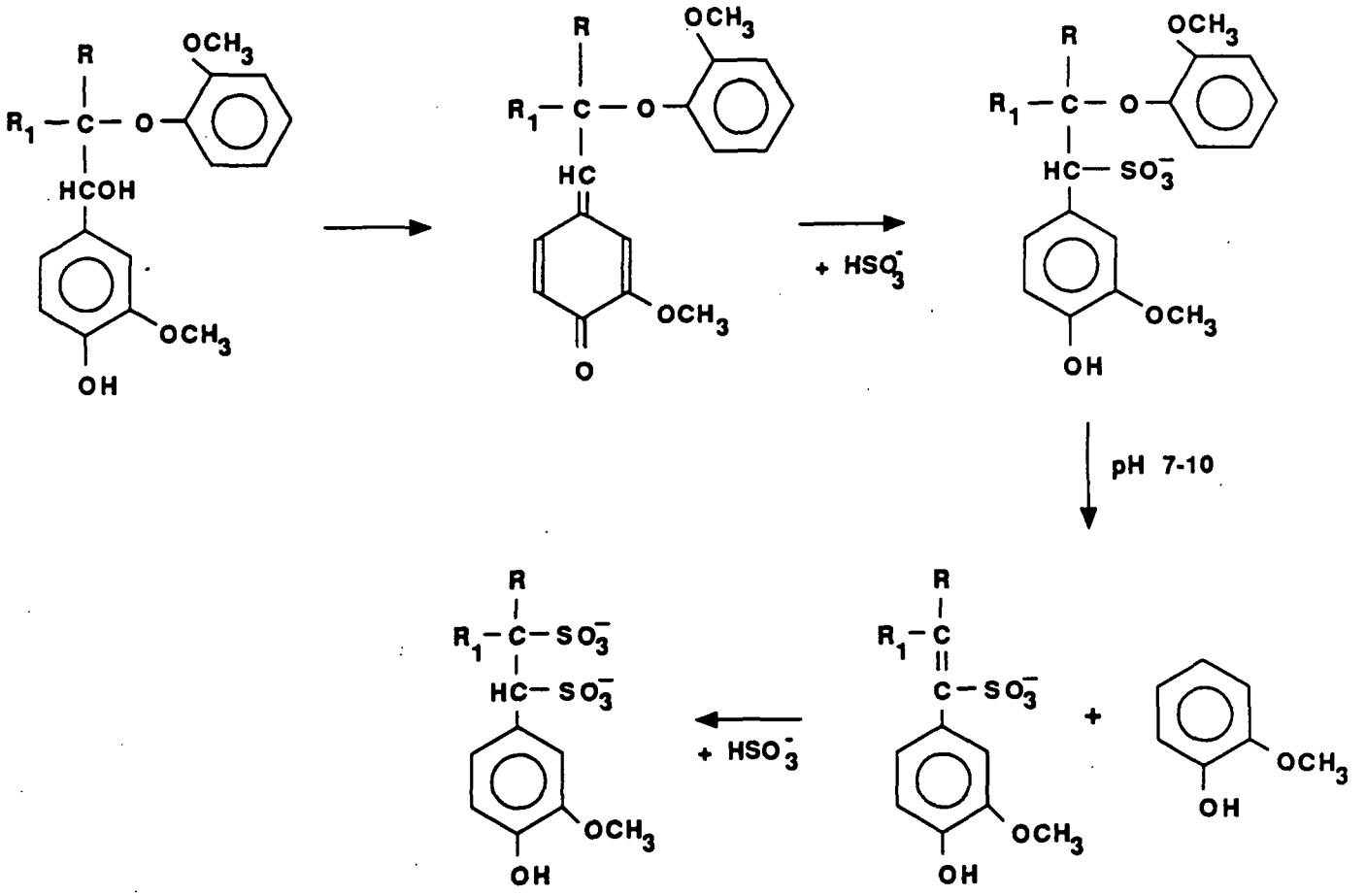


Under neutral sulfite conditions, the reactions of lignin are restricted to the phenolic units, with sulfonation of the benzylic carbon being the most important reaction.[3] Alpha-sulfonic acid groups which are present in beta-aryl ether structures accelerate the cleavage of the beta-aryl ether bond. The mechanism of the reaction involves the formation of the quinone methide intermediate, followed by sulfonation at the alpha carbon. Under neutral pulping conditions, the quinone methides are immediately trapped by the sulfite ions present to give the alpha-sulfonic acids as shown in Fig. 9. If the pH of the

pulping liquor is raised above the neutrality point, elimination reactions may follow sulfonation and produce the styrene structures shown in Fig. 9.

Under alkaline sulfite conditions, a non-phenolic beta-aryl ether containing an α carbonyl group quantitatively eliminated the beta substituent[3]. The remaining phenylpropane skeleton was partly sulfonated, and partly rearranged to different ketol structures. The condensation reactions of lignin

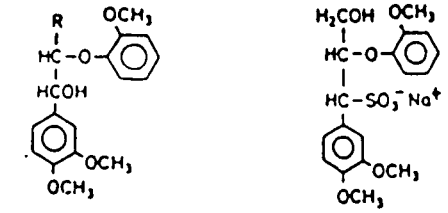
Figure 9. Reactions of phenolic β–aryl ether structures during sulfite pulping in the neutral to alkaline pH range (after ref. 3)



may be of less importance during alkaline sulfite delignification than during kraft pulping due to the sulfonation of the intermediate conjugated structures formed during the cook.

Ljunggren, Ljungquist and Wenger[5] studied the effect of α–substituents on the rate of cleavage of β–aryl ether structures in a lignin model compound. Sulfonation of the α–position of a non–phenolic lignin model compound as shown in Fig. 10 dramatically accelerated the rate of cleavage of the β–aryl ether bond under alkaline conditions. The kinetic data obtained in this study are shown in Table 1. It is readily seen that the sulfonated compound degrades at a higher rate at 119°C than the reference compound at 172°C.

Figure 10. Reference and sulfonated model compounds[5]



3 R = CH_2OH 1

Table 1. Rate constants for alkaline cleavage of the β–aryl ether[5]

Compound	Temperature °C	[OH] mole/liter	Observed Rate Constants for Guaiacol Formation 10^3 k, 1/minutes	Final Yield of Guaiacol (mole% of theoretical)
1	100	0.53	9.4	93
	119	0.51	41.0	98
	140	0.55	199.0	100
3	172	0.30	13.3	95

THE CATALYTIC EFFECT OF ANTHRAQUINONE

The effect of anthraquinone (AQ) on carbohydrate stabilization reactions was discovered in 1972 by Bach and Feihn[6], who used an AQ derivative (anthraquinone monosulfonate, AMS) for their experiments. The fact that AMS accelerated degradation reactions of lignin model compounds was later discovered by other workers. Holton[7] developed this concept further, using AQ itself, as well as several AQ derivatives. The use of AQ under alkaline conditions produced pulps of higher yield at a given kappa number than the kraft process.

Pulping studies on pine and eucalyptus by Cameron *et al.* [8] showed that the effectiveness of AQ in alkaline solutions was highly dependent on alkalinity. When sodium hydroxide/sodium carbonate mixtures were used as pulping liquors with a fixed addition of AQ, the kappa number of the pulp rose steadily as the proportion of carbonate increased (Fig. 11). When sodium carbonate constituted more than 50% of the alkali in the liquor, the AQ had no effect on the pulping rate. Based on this information, it was hypothesized that AQ would have no effect at the lower pH of the neutral sulfite process. In fact, the AQ had a remarkable effect on both the pine and the eucalyptus, giving kappa number reductions of 38% and 29% for the woods, respectively.

McDonough, VanDrunen and Paulson[9] experimented with low lignin ASAQ pulping. The first series of experiments was conducted at constant temperature and at a typical industrial liquor to wood ratio (4:1). They noted losses in both delignification rate and selectivity below kappa number 50 (Fig. 1). Their results for the dependence of kappa number, yield selectivity and viscosity selectivity on liquor composition are illustrated in Fig. 12–14. As can be seen from the ternary diagrams, pulping rates are lowest in pure Na_2SO_3 and highest

Figure 11. Response of pine to pulping with NaOH and Na_2CO_3[8]

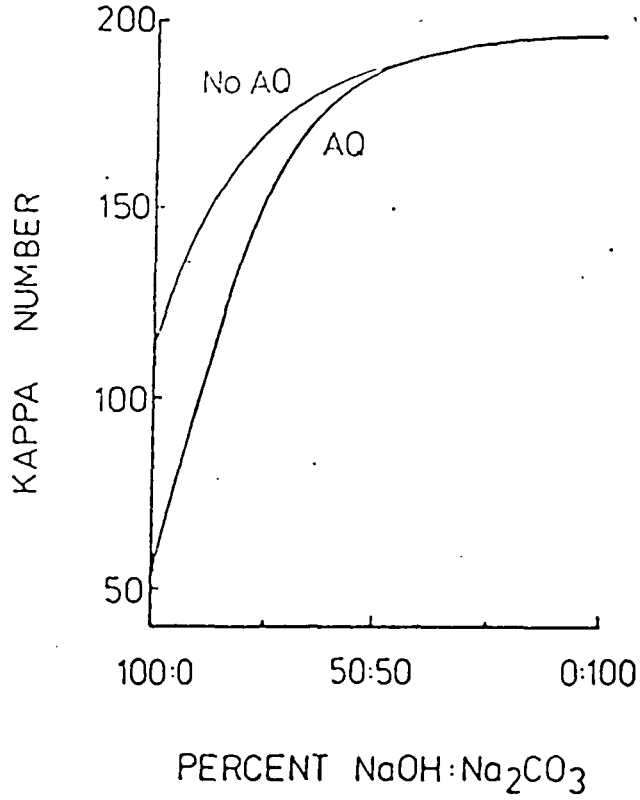


Figure 12. Contours of constant kappa number[9]

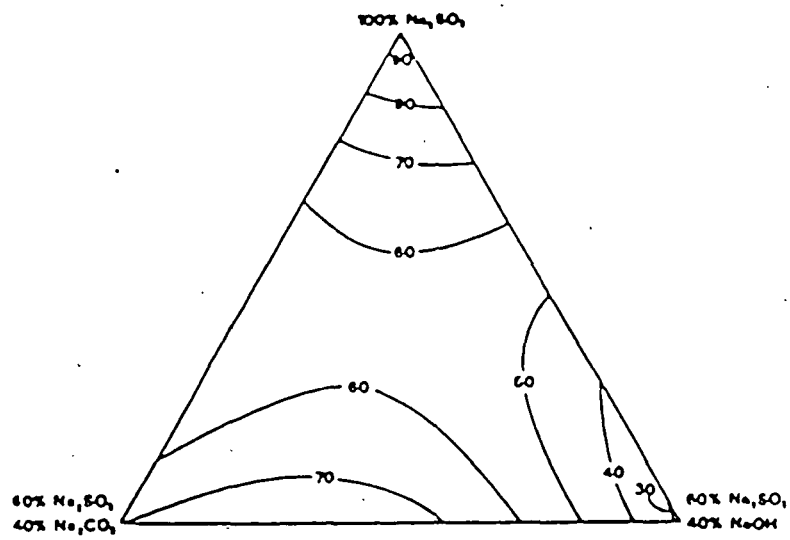


Figure 13. Contours of constant yield selectivity (g lignin dissolved/g carbohydrate dissolved)[9]

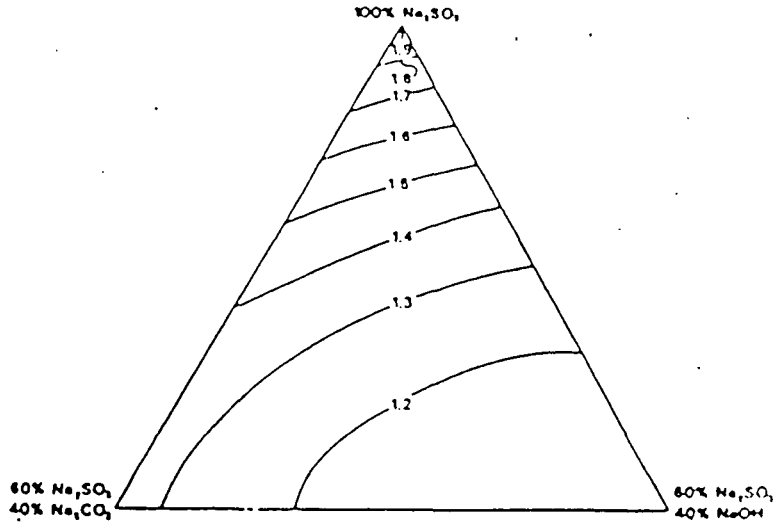
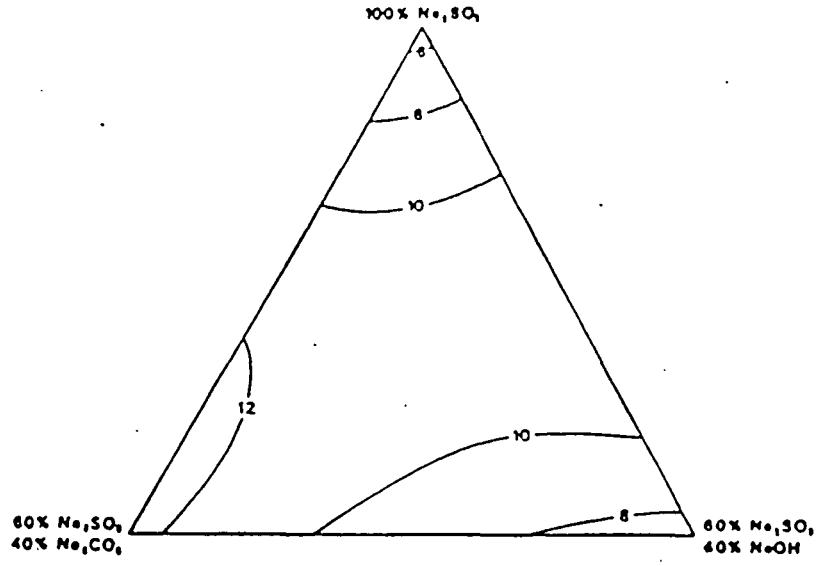
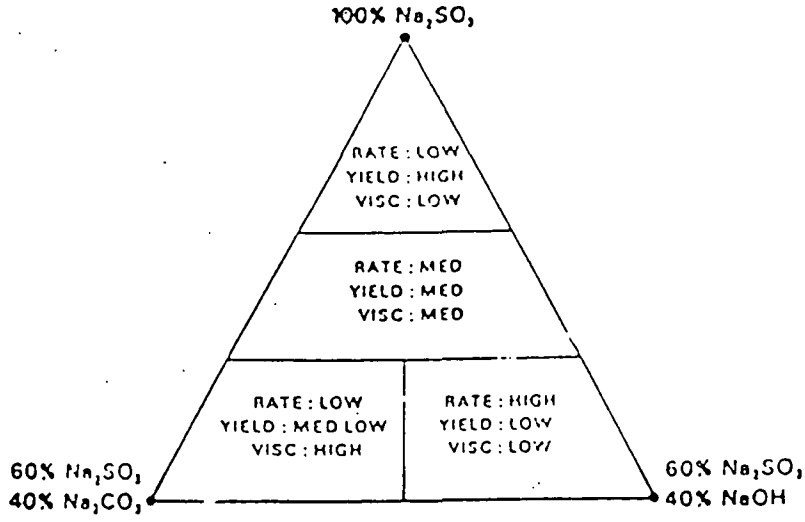


Figure 14. Contours of constant viscosity selectivity (10^{-4} x g lignin dissolved/mole glycosidic bonds broken in cellulose)[9]



in NaOH rich liquors. The yield selectivity is best in pure Na_2SO_3 and worst in high NaOH liquors, with the Na_2CO_3 rich liquors falling in between. The viscosity selectivity was highest in the carbonate rich liquors and poorest in the pure sulfite liquor. Fig. 15 summarizes these results. The effects on kappa number and yield were observed to be very non–linear in liquor pH.

Figure 15. Summary of chemical effects[9]



Interestingly, a second set of cooks performed at high liquor to wood ratio (and correspondingly, a high chemical charge) gave very different results. When the wood was cooked at the same temperature at a liquor to wood ratio of 20:1, the sulfite cooks gave low kappa numbers with pulp viscosities that were much higher than the comparable kraft cooks (Table 2). Carbohydrate yields were higher for the sulfite cooks than the corresponding kraft yields at both levels of sulfite liquor pH (10 and 13). The superiority of the high liquor–to–wood ratio, high chemical charge cooks may be attributed to any of several different factors. These include higher average concentrations of sulfite and/or AQ, a higher average pH, and lower average dissolved lignin concentration. A higher average

Table 2. Results of high liquor to wood ratio cooks[9]

	HLSAQ pH 10	HLSAQ pH 13	Kraft	HLK	HLKAQ
Initial Concentrations, g Na2O/l					
Sodium Sulfite	48	48	0	0	0
Sodium (Carbonate + Hydroxide)	12	12	37.5	37.5	37.5
Sodium Sulfide	0	0	12.5	12.5	12.5
Initial AQ Concentration, g/l	0.25	0.25	0.00	0.00	0.25
Maximum Temperature, °C	180	180	165	165	165
Time at Temperature, minutes	210	210	121	118	120
Liquor-to-wood ratio, ml/g	20	20	3.8	20	20
Initial pH	11.0	13.4	n.d.	n.d.	13.5
Final pH	10.0	13.1	n.d.	13.5	n.d.
Total Yield, % OD Wood	46.8	43.5	46.7	40.2	40.2
Rejects, % OD Wood	1.1	0.1	0.4	0.1	0.0
Kappa number	22.8	12.9	38.8	16.8	13.5
Carbohydrate Yield, % OD Wood	45.2	42.6	44.0	39.2	39.4
Viscosity, mPa s	51.9	25.0	37.4	14.1	13.6
Unbleached brightness	42.2	42.7	22.5	40.9	43.0

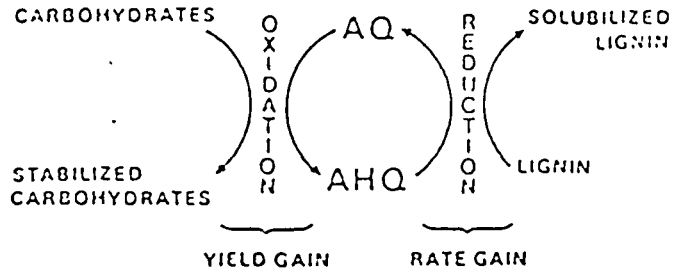
n.d. = not determined
Process designations: HLSAQ = high liquor-to-wood ratio sulfite-anthraquinone
HLK = high liquor-to-wood ratio kraft
HLKAQ = high liquor-to-wood ratio kraft-anthraquinone
All pulps prepared in a 50 l digester equipped with external circulation and indirect heating

sulfite concentration, for example, may result in more extensive lignin sulfonation, and hence greater "degradability" of the lignin (as suggested in previous model compound studies[5]). The development of rate laws for both the delignification and carbohydrate degradation reactions would allow these various possibilities to be distinguished from one another.

The generally accepted mechanism for promotion of delignification and carbohydrate stabilization during alkaline pulping is shown in Fig. 16. AQ reacts with carbohydrates, forming alkali stable saccharinic acids and AHQ. These saccharinic acids will no longer undergo "peeling" reactions[4], thus preserving the yield of the pulp. The AHQ reduces lignin, rendering it soluble and

regenerating AQ. This simple mechanism may apply only for limited times during kraft and strongly alkaline sulfite AQ pulping.

Figure 16. AQ–AHQ redox cycle[10]



The mechanism for the interaction of AQ with lignin has been the subject of many investigations in recent years. Two main theories have emerged: the adduct formation mechanism and the single electron transfer (SET) mechanism.

According to the adduct mechanism[12,13], the quinone methide intermediate is attacked by the AHQ dianion, resulting in a nucleophilic addition to the α carbon double bond, as shown in Fig. 17. The adduct then decomposes to various phenolic products. The stereochemistry of the adduct is shown in Fig. 18. It can be seen that the adduct is quite crowded, and steric hindrance would seem to preclude its participation in pulping reactions within the rigid wood matrix. The formation of the adduct with the lignin dissolved in the pulping liquor may be more favorable.

Figure 17. Nucleophilic attack on quinone methide by AQ[12]

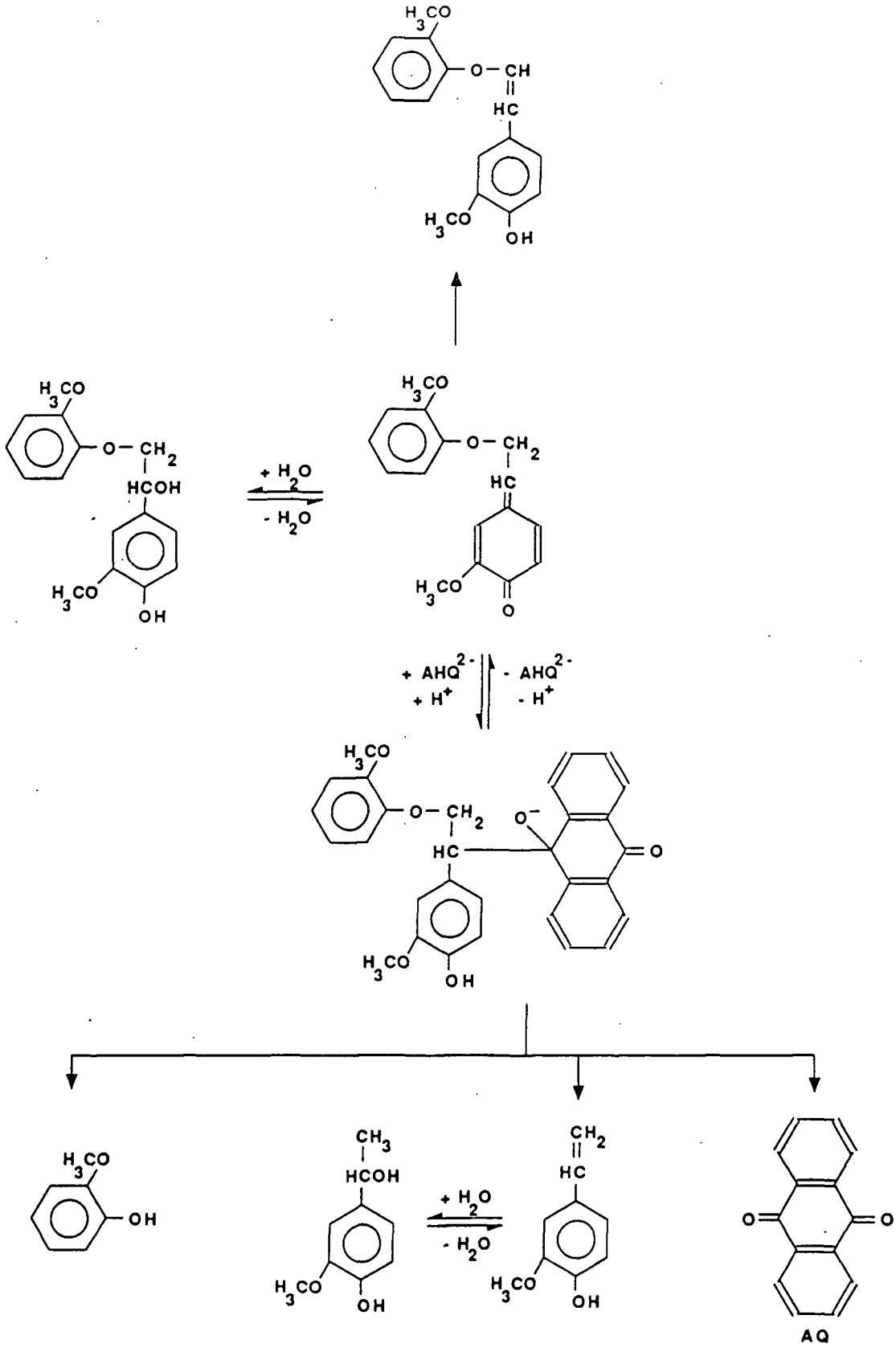
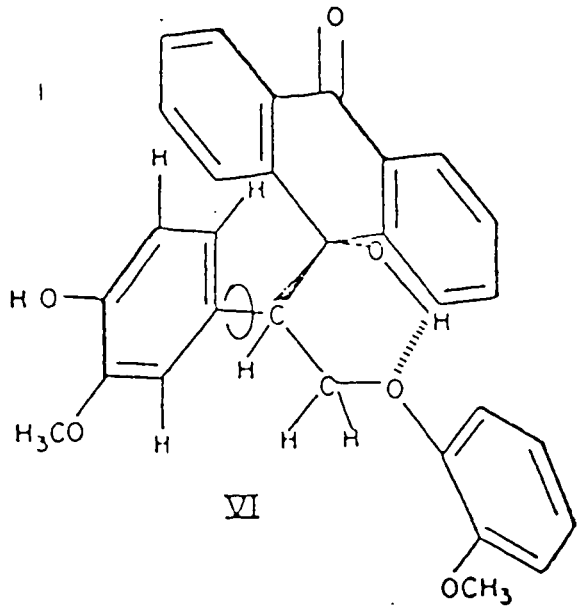


Figure 18. Stereochemical configuration of adduct[13]



VI

According to the single electron transfer mechanism, the AHQ acts as a carrier of electrons from carbohydrate to lignin. Dimmel *et al.* [14] have provided evidence to support this mechanism through the use of cyclic voltammetry. These studies, and the results of other studies using different techniques (which will not be reviewed here), give support to the SET mechanism theory.

Suckling studied the effect of anthraquinone on the cleavage of beta-aryl ethers in the presence of sulfite.[15] Anthraquinone accelerated the cleavage of phenolic ethers, but not the non-phenolic compounds. This does not, the author purports, explain the acceleration of the bulk phase of pulping observed in the presence of AQ, but does explain the accelerating effect of AQ during the initial phase of pulping. During the bulk phase, the cleavage of non-phenolic interunit bonds is required. This, together with sulfonation, is postulated to result in the dissolution of lignin during the bulk phase.

The result of the experiments conducted was the reaction scheme shown in Fig. 19. Reactions with the methylated model compound 2 gave negligible yields of guaiacol. The phenolic model compound 1 had a much greater extent of fragmentation. Model compound 1 was shown to be degraded by two parallel and competing reaction pathways: one involving sulfite only, the other pathway limited by the reaction of AQ with the quinone methide. This general reaction mechanism is in agreement with results obtained by Eagle and McDonough[27], which will be discussed further in the next section. Eagle's work covered bulk phase ASAQ pulping; the fact that the reaction mechanism postulated by Suckling (Fig. 19) agrees with the kinetic result of Eagle's work is inconsistent with Suckling's postulate that his mechanism explains acceleration of lignin degradation only during the initial phase of ASAQ pulping.

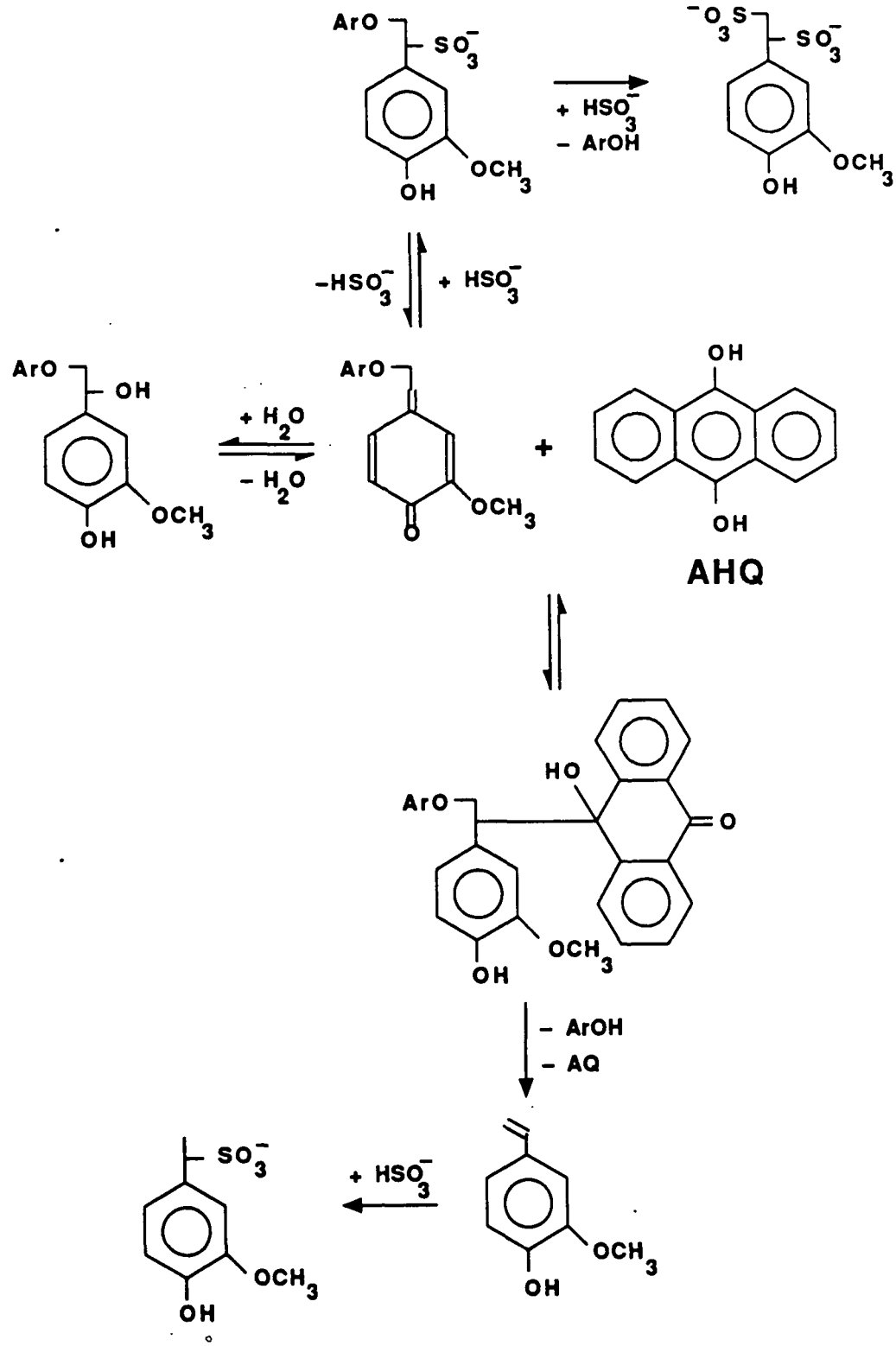
KINETICS

An understanding of the existing knowledge of the kinetics of various delignification processes is relevant to the goals of this thesis. We will begin with a discussion of the kinetics of the sulfonation of wood.

Sulfonation of Wood

Heitner, Beatson and Atack[16] studied the effects of several variables on the rate of sulfonation of black spruce wood chips at pH 7. The results of their study indicate that the rate of sulfonation is first order with respect to the concentrations of "sulfonatable" sites in the lignin and total SO_2 (the total sulfite concentration expressed as an equivalent weight of SO_2), with an activation energy of about 63 kJ $mole^{-1}$ ($\approx$15 kcal $mole^{-1}$). Lignin removal from the chips

Figure 19. Scheme for ASAQ reactions of lignin model compounds[15]

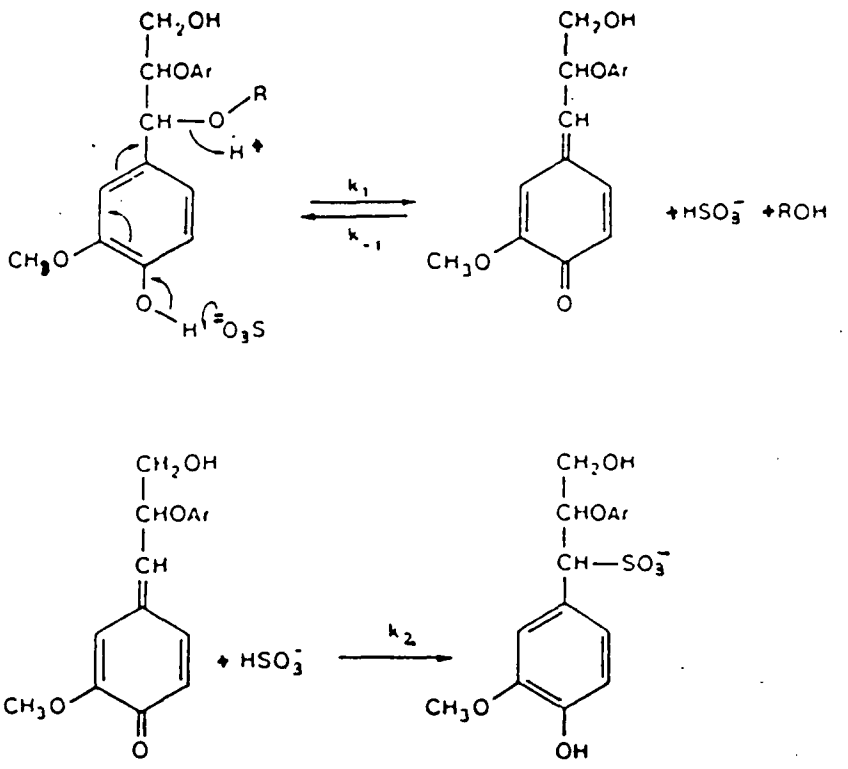


was independent of both the total SO_2 concentration and the sulfonate content of the wood.

A mechanism for the reaction between the sulfite and the wood was presented. The formation of the quinone methide intermediate was postulated to be promoted by the sulfite, as shown in Fig. 20. The addition of bisulfite to the quinone methide intermediate would follow rapidly. This mechanism would follow the rate law

$$\text{Rate of sulfonation} = \frac{k_2 k_1}{k_{-1} + k_2[SO_2]}(S_p - S)[SO_2]^2 \qquad (1)$$

Figure 20. Sulfite promoted formation of quinone methide[16]



where k_1, k_{-1}, and k_2 are temperature dependent rate constants, S_p is a "plateau" sulfonate content of the wood, S is the sulfonate content of the wood at time t (S_p and S are both expressed as a percentage based on the original wood), and $[SO_2]$ is

the total SO_2 concentration. If $k_{-1} << k_2 [SO_2]$, the reaction will be first order in total SO_2, as observed. This was believed to be a reasonable assumption, since sulfite is four orders of magnitude more nucleophilic than water, and water was present in concentrations only 500 times greater than that of sulfite at the lowest sulfite concentrations used. There is some doubt as to the plausibility of this mechanism. The reaction presented is a simple acid/base reaction, and if this mechanism plays an important role, other buffers might be expected to behave in the same way.

A subsequent study by the same group of authors[17] looked at the effects of temperature and total SO_2 concentration on the rate of sulfonation at pH 4. It was postulated that the sulfonation reaction at this pH proceeds by two mechanisms, one which involves a quinone methide intermediate and is dependent on the total SO_2 concentration, and one which is independent of the total SO_2 concentration and involves a carbonium ion intermediate. The combined result of these two mechanisms is a sulfonation rate which is proportional to $[\text{total } SO_2]^{0.4}$.

These mechanisms are shown in Fig. 21. Scheme 1 illustrates the postulated interaction of sulfite with the quinone methide intermediate. The reaction involves the formation of the quinone methide from the phenolic lignin units, followed by slow sulfite attack. The formation of quinone methides may seem to be precluded at pH 4, but in experiments with methylated wood meal (blocking the path for the formation of the quinone methide), the sulfonation rate was shown to be greatly reduced, as shown in Fig. 22. The fact that the sulfonation rate was not reduced to zero by methylation of the wood indicates that another, independent mechanism for sulfonation must be operating under these conditions. The mechanism postulated is shown as

Scheme 2 in Fig. 21. This mechanism would be independent of total SO_2 if the rate limiting step was the formation of the carbonium ion.

Figure 21. Mechanisms for sulfonation at pH 4[17]

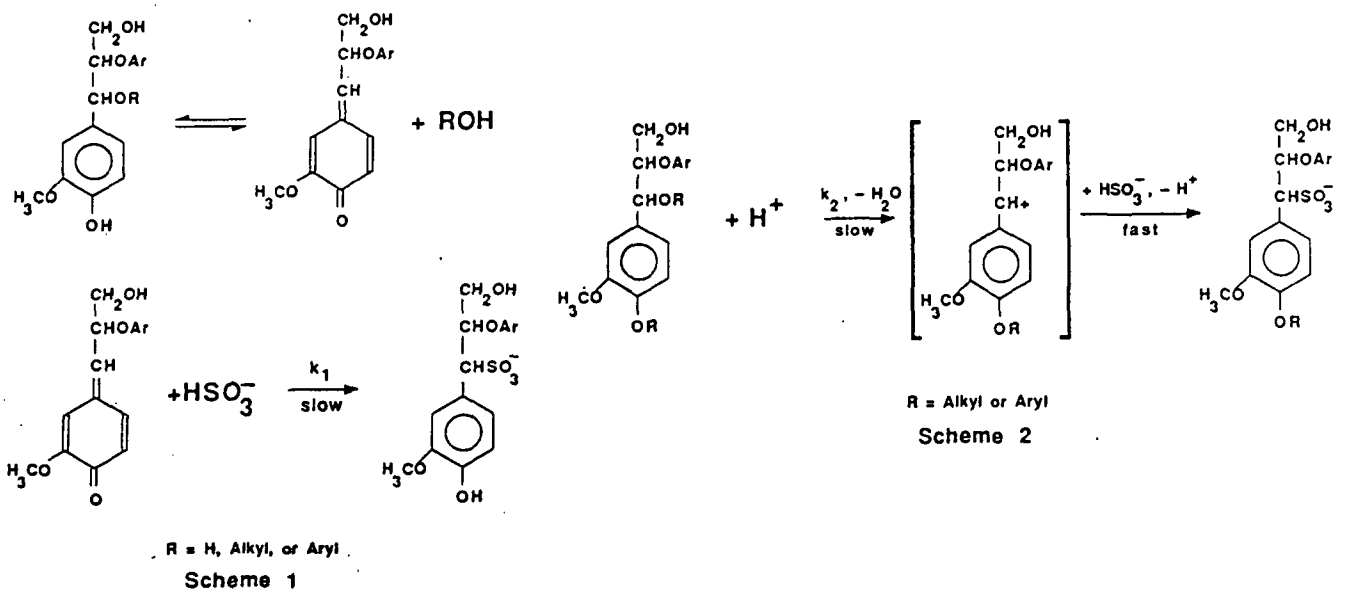
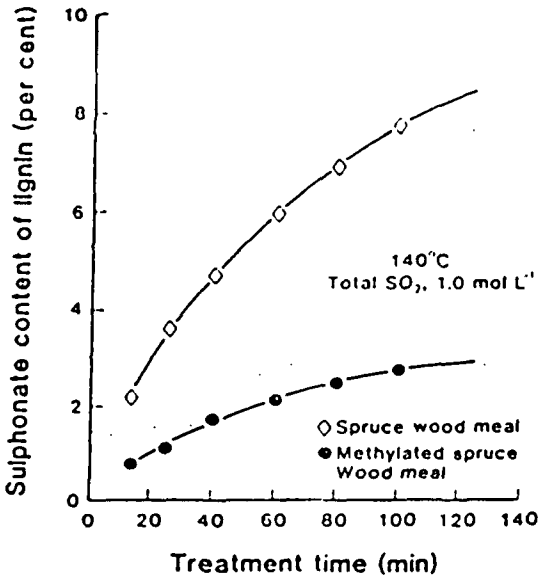


Figure 22. Methylation of wood meal inhibits sulfonation of lignin in wood[17]



The yield loss and lignin removal rates at pH 4 were independent of total SO_2 concentration. High total SO_2 concentrations promoted sulfonation, but had no effect on pulp yield. Increasing the reaction temperature increased both the sulfonation rate and the yield loss. The best method of obtaining pulps with high sulfonate contents, based on these results, would be to use liquors with high total SO_2 concentrations. The rate of sulfonation was less dependent on total SO_2 at pH 4 than at pH 7, so the sulfonation rate enhancement from an increase in total SO_2 concentration will be smaller at the lower pH.

Kraft Pulping

Kraft pulping is probably the single most widely studied pulping process, with wide application throughout the paper industry. The process has many highly desirable properties; it is capable of pulping almost any fibrous material, produces pulps which are strong and amenable to use in many different products, and has a well proven chemical recovery cycle. The disadvantages of the process are as well known as the advantages: a relatively low yield for the desired pulp lignin content, difficult bleaching, and various environmental concerns. Many studies of the kinetics of kraft pulping have been undertaken in the effort to improve the performance of the process. The results of these studies show the utility of kinetics in providing direction for process improvements.

The kraft pulping of pine may be divided into three distinct kinetic phases. The initial phase is characterized by a very rapid drop in the carbohydrate yield, a slow removal of lignin (relative to the rate of carbohydrate removal), and the consumption of a large amount of alkali. The bulk phase gives a much higher ratio of lignin removed to carbohydrate removed. The final, or residual phase is

similar to the initial phase in that the lignin removal is slow relative to the degradation of carbohydrates.

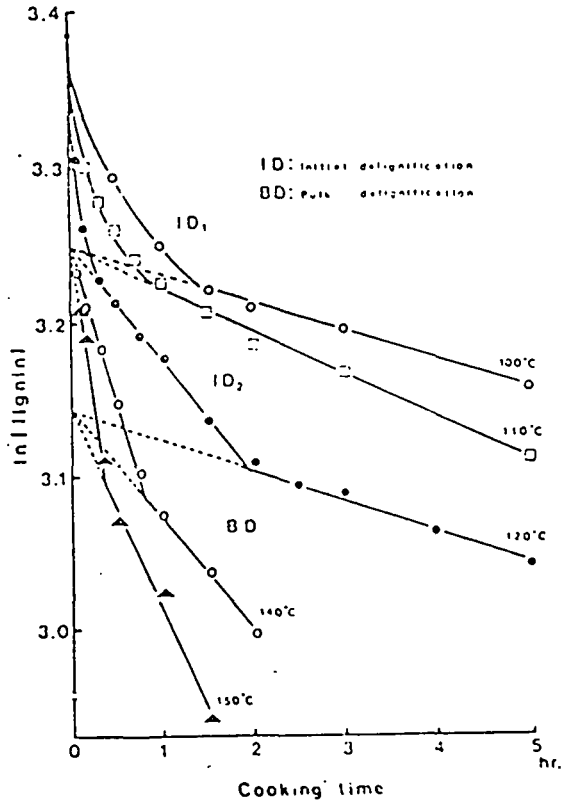
Olm and Tistad[18] reported one of the earliest studies of the initial phase of kraft delignification. This study showed that there is a very significant difference in the dependence of the rates of delignification and carbohydrate degradation on the chemical composition of the pulping liquor. The rate of delignification was shown to be independent of the liquor composition, while the rate of carbohydrate loss increases with increasing effective alkali. The delignification rate decreased if there was a drastic decrease in the sulfidity of the liquor. The carbohydrate loss was independent of the liquor sulfidity. The delignification rate was directly proportional to the lignin content of the wood.

Kondo and Sarkanen[19] reported findings on the initial phase of kraft and soda–AQ pulping. They found that the initial phase of both the kraft and soda–AQ cooks consisted of two kinetically distinguishable phases, which they called the ID_1 and ID_2 phases (Fig. 23). The ID_1 phase was very rapid and of indeterminate order. The ID_2 phase was slightly slower and was first order in lignin. The apparent activation energy for the ID_2 phase of kraft pulping was 73 kJ $mole^{-1}$(≈17.4 kcal $mole^{-1}$).

The result of kinetic studies by researchers at STFI[20] has been an improved method for the operation of continuous digesters, in which the concentration of alkali is kept low during the initial period, and increased as the maximum pulping temperature is reached. This method has resulted in higher pulp viscosities at a given pulp lignin content from industrial digesters.

Many kinetic models of the kraft process have appeared in the literature. One of the most comprehensive is that presented by Burazin[21]. His model was a

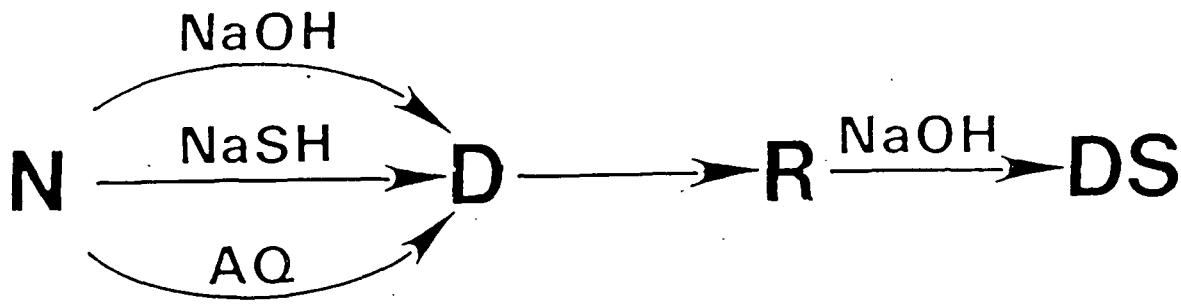
Figure 23. Two kinetically distinct regions of the initial phase of kraft pulping[19]



dynamic representation of the process, with reactions of hydroxide, sulfide, and anthraquinone with both lignin and carbohydrates accounted for. The model also included heat and mass transfer effects. The best reaction network model for delignification was a parallel/series reaction network, shown in Fig. 24, where N represents the "native" lignin in the wood, D is dissolved lignin, R is residual lignin, and DS represents dissolved solids. The rate of the AQ reaction pathway was determined to be proportional to the square root of the AQ concentration.

The square root dependence on AQ concentration is in agreement with several studies published by Werthemann.[22–24] One of his most significant

Figure 24. Burazin's delignification reaction network[21]



findings was that sulfide and anthraquinone exhibit markedly different kinetic behaviors in delignification.[24] The rate of lignin dissolution was shown to be directly proportional to the sulfide concentration, while being proportional to the square root of the AQ charge. Some arguments[23] were presented to suggest that the square root dependency is a result of the stoichiometry of the lignin/AQ interaction, *i.e.*, each molecule of AQ may contribute to a reaction at each of two lignin sites.

Bolker and Abbot[25] presented a description of the results of experiments with several different additives for soda pulping. The four additives studied were AQ, amine, hydrosulfide, and ethanol. The relative molar effectiveness of the four additives tested was determined by plotting the molar concentration of one additive against the molar concentration of another at a given kappa number under fixed conditions of time, temperature, etc. The values thus obtained are shown in Table 3, where the molar effectiveness of ethanol has been set equal to 1. The delignification rate proved to be first order in hydrosulfide ion and proportional to the square root of the AQ charge.

Table 3. Molar effectiveness of additives[25]

Additive	Relative Molar Effectiveness
Ethanol	1
Amine	2.5
Hydrosulfide	15-25
Anthraquinone	1000-3000

The rate expression found for the AQ delignification was

$$\frac{dL}{dt} = -\left(k_S + k_{AQ}[AQ]^{0.5}[OH^-]^{1.2}\right)L^2 \qquad (2)$$

Addition of AQ gave an apparent activation energy of 149 kJ $mole^{-1}$. The apparent activation energy for soda delignification is approximately 130 kJ per mole. Thus, AQ cannot be considered a true catalyst for delignification since it does not decrease the activation energy of the lignin degradation reactions.

A general mechanism was proposed for the action of AQ in the delignification, shown in Fig. 25. Each of the three steps in the mechanism was considered in an effort to determine the explanation for the additive's efficacy. The three steps may be written as follows:

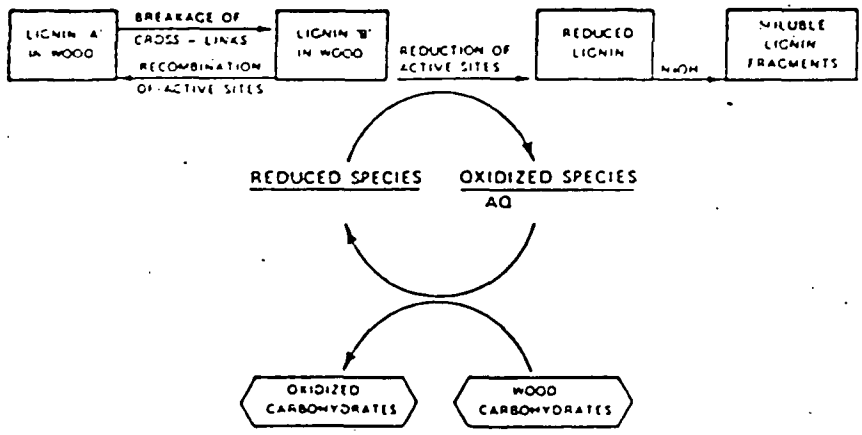
$$\text{Step 1} \quad L_A + OH^- \rightleftharpoons L_B$$

$$\text{Step 2} \quad L_B + AQ \longrightarrow L_C$$

$$\text{Step 3} \quad L_C + OH^- \longrightarrow L_D$$

where L_A is lignin "A" in the wood, L_B is lignin "B" in the wood, L_C is the reduced lignin, and L_D represents the soluble lignin fragments (refer to Fig. 25).

Figure 25. General mechanism for AQ reactions[25]



If step one were the rate controlling step, the rate equation should contain terms in OH^- and lignin. The presence of the AQ term may be due to its rapidly reacting with L_B, thus reducing the reversion to L_A. This would result in a net acceleration of the forward reaction without changing the apparent activation energy.

If step two were the rate limiting step, the rate law would contain terms in lignin, hydroxide, and AQ. The high molar effectiveness of AQ should be reflected in a decrease in the apparent activation energy, which was not observed in the experiments. Step two was thus eliminated as a possible rate controlling step.

If step three were rate–controlling, the rate law should again contain terms in lignin and hydroxide, and the activation energies would be similar. A large difference in pre–exponential factors was observed, indicating that the additive concentration term may appear as a result of the fact that the rate of formation of L_C will depend on the rate of step two. The overall reaction rate would then increase because the concentration of the intermediate L_C increased, while the

activation energy of the slowest step (step 3) remains the same. In other words, the accelerating effect of AQ may not be due to a lowering of the potential energy barrier to reaction, but to an increase in the number of molecular collisions which result in the bond–breaking reaction.

The observations of both a higher value for the collision factor and no decrease in the activation energy for the reaction prompted the authors to select step three as the rate controlling step in the process.

Alkaline Sulfite Anthraquinone Pulping

There have been several studies of the kinetics of the ASAQ process presented in the literature. The studies will be discussed in this section.

Ojanen, Tulppala and Virkola[26] made one of the earliest attempts to develop a kinetic description of the ASAQ process. They compared the response of pine and birch chips under "neutral" sulfite conditions in the presence of AQ. The results of their experiments with pine are shown in Tables 4 and 5. A kinetic analysis of the data in Table 5 was performed, using a rate law of the form

$$r_L = \frac{dL}{dt} = kC^a L^b \qquad (3)$$

where C is the concentration of the cooking liquor, L is the unreacted lignin (% on wood), and k is the rate coefficient. According to the author, "since the initial chemical charge and the size and direction of change were the same", C^a was assumed to be constant. The data in Table 5 show that up to 81% of the Na_2SO_3 was consumed. It is clear that C^a was not constant, and that this was not a good

Table 4. Reaction conditions for cooks[26]

Cooking Temp., °C	Time at Temp., minutes	Wood Raw Material	Total Yield, %	% Rejects	Kappa Number
170	240	pine	58.2	4.0	44.2
175	180	pine	57.6	2.8	41.8
180	130	pine	55.5	3.1	37.9
175	180	pine	58.8	4.0	41.6
175	160	pine	59.8	5.3	45.5
175	120	pine	60.9	7.1	49.8
175	135	birch	67.0	12.9	54.8
175	165	birch	64.3	7.8	49.4
175	240	birch	60.1	1.9	46.6
175	210	birch	63.7	2.3	40.1

Rate of temperature increase = 1 C/min
liquor/wood = 4.5
Sodium sulfite = 20% on OD wood, sodium carbonate = 4% on OD wood (both expressed as NaOH), AQ = 0.1% on OD wood

Table 5. Data for kinetic analysis[26]

Cooking time minutes	Cooking Temperature, °C	Total Yield %	Chlorine Number	Waste Liquor pH	Waste Liquor Sulfite consumed, %
5	85	84.5	30.9	10.3	-
25	105	85.5	30.7	9.8	1.5
55	135	84.1	30.4	9.5	5.6
75	155	81.5	29.6	9.4	11.8
95	175	74.5	25.3	9.5	32.4
115	175	68.8	17.8	9.4	45.3
135	175	67.0	15.4	9.6	55.0
135	175	62.3	12.5	9.4	62.9
185	175	61.3	11.4	9.4	68.1
215	175	60.4	10.8	9.4	69.5
245	175	60.3	10.7	9.3	74.8
275	175	56.1	9.4	9.2	76.8
315	175	54.8	7.5	9.0	81.1

assumption. No allowance was made for the fact that the temperature of the cook was not constant. The final expression used in the evaluation of the data was

$$\frac{dL}{dt} = -k L^b \qquad (4)$$

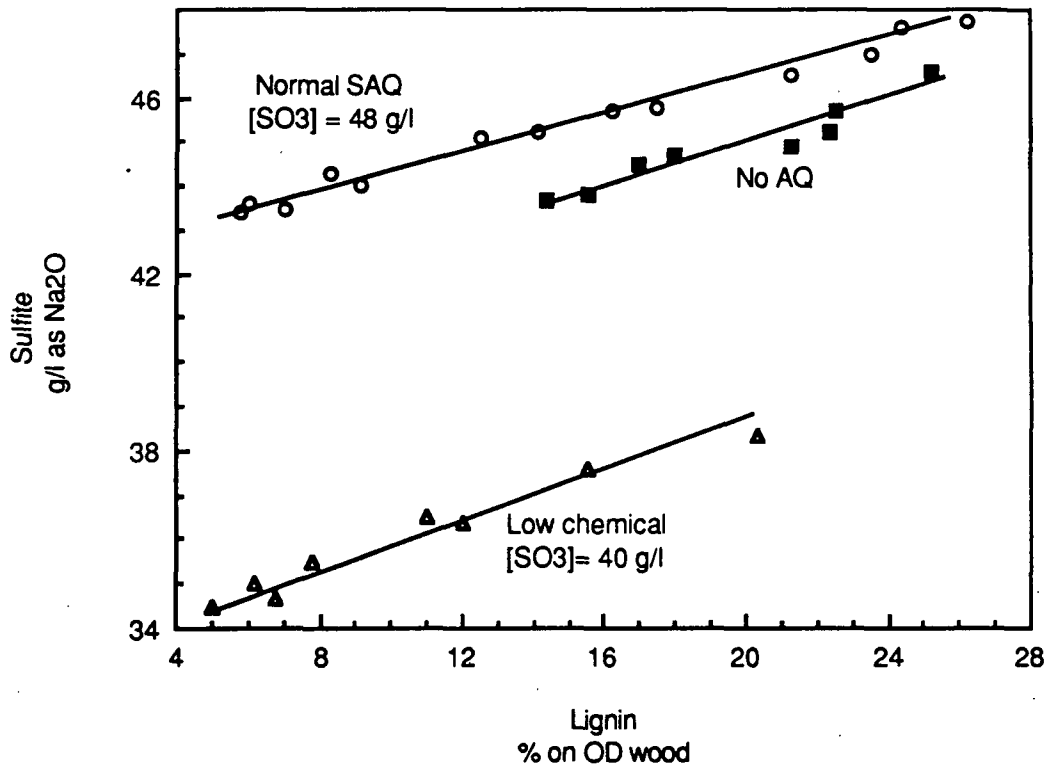
Values for the exponent b and the rate coefficient k were calculated for the bulk and residual phases of delignification, as shown in Table 6. Given the limitations on the accuracy of these numbers, it is difficult to draw any meaningful conclusions from these data.

Table 6. Values for rate coefficient and lignin exponent[26]

Delignification stage	b	k x 10^2
Pine		
bulk	0.356	5.80
residual	0.877	2.01
Birch		
bulk	0.437	3.45
residual	1.227	0.77

Eagle and McDonough[27] conducted a kinetic study of the ASAQ pulping of loblolly pine. The study was restricted to pH 10, and covered the temperature range from 160 °C to 180 °C. A liquor to wood ratio of 20:1 to 25:1 made the assumption of constant liquor concentrations more reasonable. The experiments were performed with very thin wood shavings to minimize mass transfer effects. There was evidence that AQ is not a catalyst for the normal sulfite reactions, but instead reacts with, or enables reactions with, species not normally attacked by sulfite alone. Fig. 26 shows the relationship between the unreacted sulfite and the amount of lignin remaining in the pulp. The plot for the AQ–free cooks extrapolates through the initial conditions (48 g/l sulfite as Na_2O, 32.3% lignin on dry wood); the plots for the cooks containing AQ suggest that 4.5 to 5.5% of the original lignin was dissolved without any measurable reaction with sulfite.

Figure 26. Unreacted sulfite vs. lignin remaining in pulp[27]



The model which gave the best fit for the data was a parallel reaction scheme, with a rate law of the form

$$-\frac{dL}{dt} = A_1 e^{-E_1/RT} L^{n_1} + A_2 e^{-E_2/RT} L^{n_2}$$

where reaction 1 represents reactions without AQ, and reaction 2 is reactions of AQ only. The values obtained for the constants in this equation are shown in Table 7. The apparent reaction order in lignin is quite high, and the activation energy for delignification was greater than that previously reported for kraft pulping.

Table 7. Values for kinetic parameters for bulk phase ASAQ pulping[27]

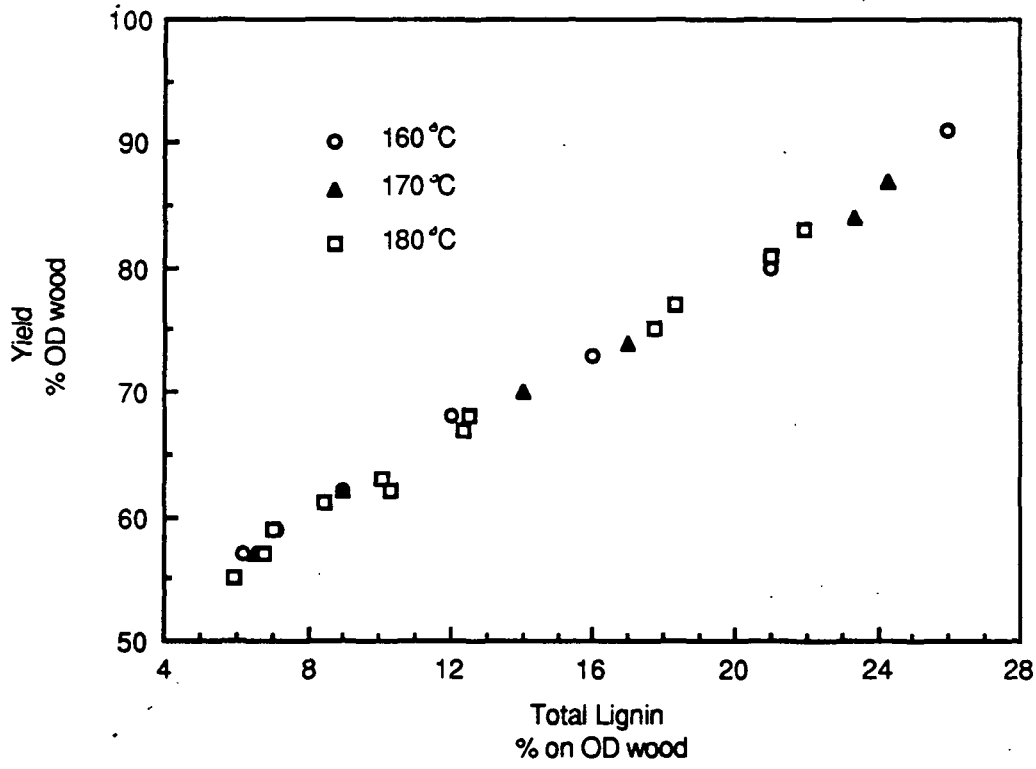
(1) = reactions without AQ, (2) = reactions of AQ only

Activation Energy kcal/gmole	29.15 (1) 37.00 (2)
Pre-exponential Factor	1.389 x 10^10 (1) 1.102 x 10^15 (2)
Lignin Exponent	2.4 (1) 2.4 (2)

The authors also made the observation that there was a very strong linear correlation between the pulp yield and lignin content over the range of 5–22% lignin on original wood, as shown in Fig. 27. The implication is that the lignin and carbohydrate are removed in the mass ratio of 1.7:1. This mass ratio was independent of temperature, suggesting that the lignin and carbohydrate are removed as a complex, or by some reaction mechanism involving both species (barring the unlikely possibility of two independent reactions with the same activation energies).

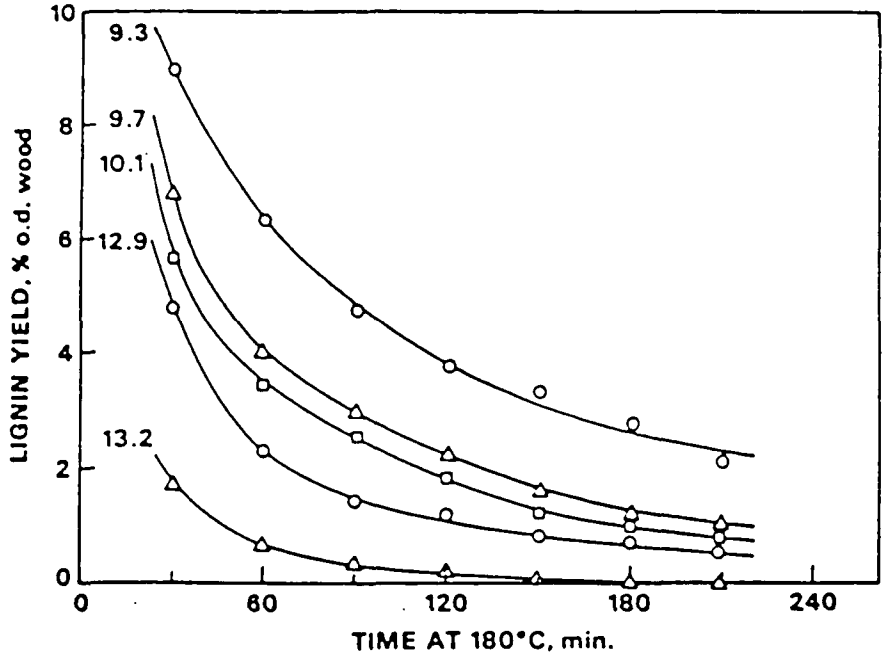
McDonough[28] summarized the results of an extensive study of the kinetics of the residual phase of ASAQ pulping. The rate of residual delignification was found to be dependent on four variables: the concentration of lignin remaining in the pulp, the total sulfite concentration, the hydroxide ion concentration, and the initial concentration of anthraquinone. The rate was most strongly influenced by the lignin concentration, with a reaction order of 2.0, while the orders in sulfite, hydroxide, and initial AQ were estimated to be 0.75, 0.18 and 0.10, respectively. While the dependence on [OH^-] is relatively weak, it was observed that the kinetic behavior of the system changed as the pH increased

Figure 27. Linear relationship between pulp yield and lignin content shown to be independent of temperature[27]



from 10 to 13. The higher pH levels changed the shape of the lignin yield *vs.* time curves, as shown in Fig. 28. More curvature is apparent in the curves at higher pH, suggesting a higher reaction order with respect to lignin. The "incursion of additional delignification mechanisms", in particular the occurrence of soda–AQ reactions in parallel with the sulfite reactions at higher pH, was postulated to contribute to this change in kinetics.

Figure 28. Effect of pH on residual delignification[28] (labels on curves indicate average pH over the cook)



Sulfite concentration was shown to have a significant effect on the residual delignification rate, as seen in Fig. 29. The pH over the course of the two experiments shown varied from 9.4 to 9.8. The dashed lines in the figure represent the predictions of a kinetic model obtained from the data presented in the report. The initial anthraquinone concentration did not affect the residual delignification rate, but influenced the final pulp lignin content by accelerating an earlier portion of the cook (Fig. 30).

The residual delignification rate decreased with an increase in total carbonate concentration (at a given level of pH and sulfite concentration). This effect was said to be the result of an ionic strength effect. All cooks in this study were done at the same temperature, so no estimate of the activation energy was possible.

Figure 29. Effect of sulfite concentration on residual delignification[28] (average sulfite concentration during the cook = 15.0 and 46.7 g/l total sulfite expressed as equivalent Na_2O)

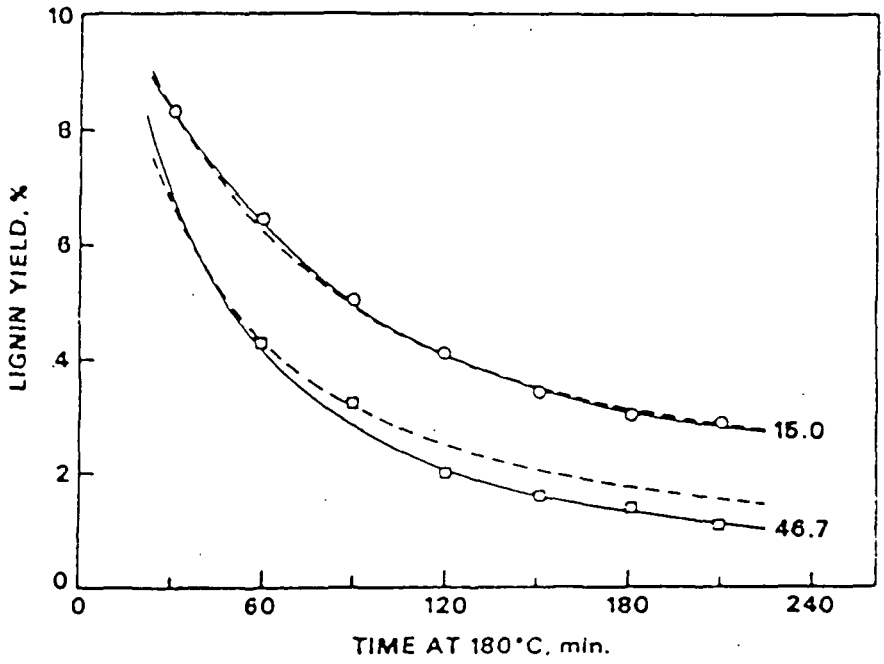
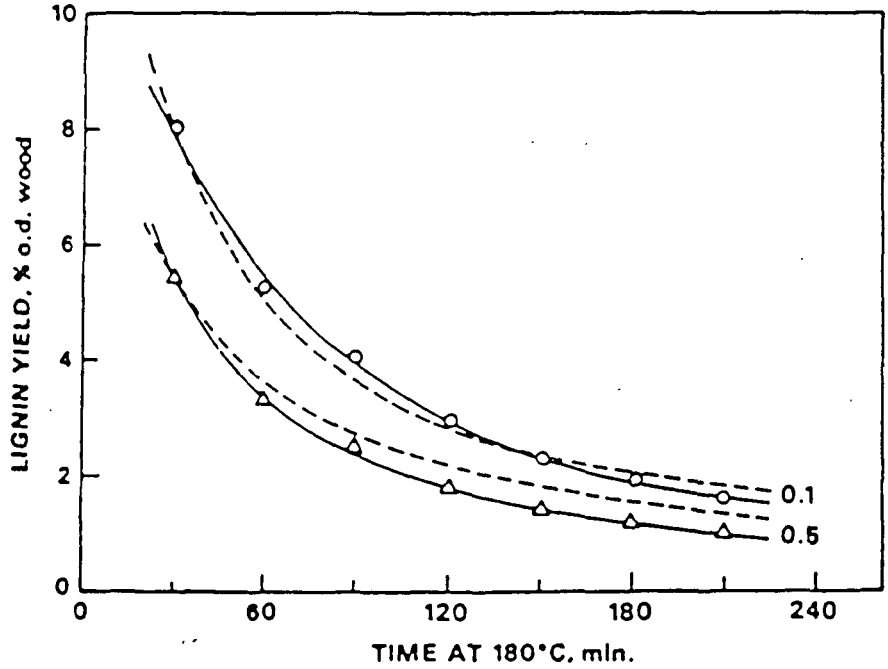


Figure 30. Effect of initial anthraquinone concentration (0.1 and 0.5 g/l) on residual delignification[28]



We have seen that there is a significant body of knowledge concerning the kinetics of pulping reactions. A description of the kinetics of ASAQ which is more detailed than that described above would prove useful in the continued improvement of the process. The effect of controllable parameters on the initial phase of ASAQ pulping is completely unknown. This was the goal of this thesis. The techniques used to approach this goal require some background knowledge, presented in the following sections.

REACTOR MODELING

The use of a flow reactor in the study of reaction kinetics offers some significant advantages. The liquor composition and reaction temperature may be controlled to constant levels, making the mathematical treatment of the resulting data easier.

Although much consideration is given in the reactor design to achieving ideal flow behavior, there will almost always be some non–ideal nature to the flow through the reactor. The extent of non–ideal flow behavior in the reactor was determined using the technique of residence time distribution measurement. The development of the theory behind this method may be found in the chemical reaction engineering text by Levenspiel[29].

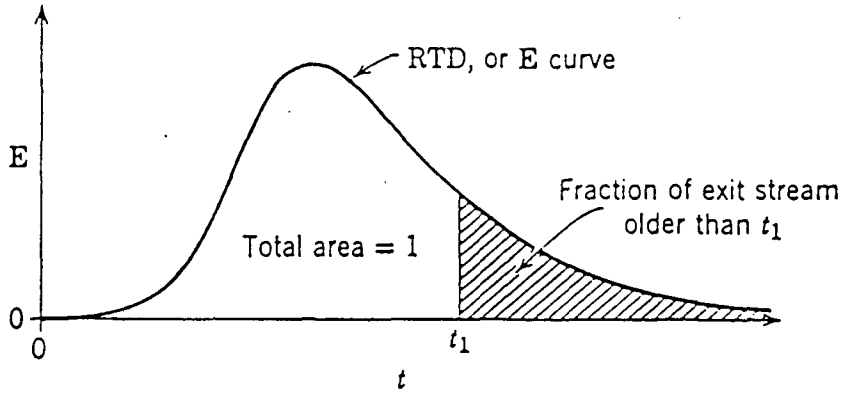
Elements of fluid taking different routes through a reactor will require different lengths of time to pass through the vessel. The distribution of these times for the stream of fluid leaving the reactor vessel is called the exit age distribution E, or the residence time distribution (RTD) of the fluid.

It is convenient to represent the RTD in such a way that the area under the curve is unity, or

$$\int_0^\infty E\,dt = 1 \tag{6}$$

This procedure is known as normalizing the distribution. Fig. 31 shows a typical distribution in normalized form.

Figure 31. Normalized residence time distribution



Since we wish to characterize the extent of nonideal flow by using this exit age distribution, we need some way to evaluate E for the flow. This is accomplished using a stimulus–response technique; the system is disturbed by a known stimulus and its response is measured. In the case of the flow reactor used in this work, the stimulus was a fluorescing tracer dye input to the fluid entering the vessel. The response was determined by the measurement of the fluorescence of discrete samples taken at the reactor outlet. The technique is described in more detail in the Experimental Section of this report. Theoretically, any type of input signal could be used for this measurement. A step or pulse signal, however, is easily treated mathematically. In the determination of the residence time distribution of the reactor vessel for this thesis, a pulse input of tracer dye was used.

Suppose that, with no tracer dye present anywhere in the reactor, an instantaneous ideal pulse of highly concentrated dye is injected at the reactor inlet. The normalized plot of tracer dye concentration at the reactor outlet versus time is called the C curve. The normalization is performed by dividing the measured concentration points by the area under the entire concentration–time curve. For a closed vessel, measurement of the C curve gives the exit age distribution directly, that is,

$$C = E \tag{7}$$

The calculation of the mean residence time and the derivation of a flow model for the reactor involves the use of some simple statistics calculated from the experimentally determined E distribution.

From n discrete measurements of the tracer dye concentration at the reactor outlet, the mean residence time is calculated using the following equation:

$$\bar{t} = \frac{\sum_{i=1}^{n} t_i C_i \Delta t}{\sum_{i=1}^{n} C_i \Delta t} \tag{8}$$

where

$\bar{t}$ = mean residence time

C_i = concentration of tracer dye

t_i = time at which concentration C_i is measured

Δt = time interval between measurements

Another important quantity of the distribution is its spread, commonly measured by the variance, σ^2:

$$\sigma^2 = \frac{\sum_{i=1}^{n} (t_i - \bar{t})^2 C_i \Delta t}{\sum_{i=1}^{n} C_i \Delta t} \tag{9}$$

The variance represents the square of the spread of the distribution, and is useful for matching experimental curves to one of a family of theoretical curves for flow models.

One model which finds widespread use in describing nonideal flow is the tanks in series model. In this model, it is imagined that the fluid flows through a series of equal volume ideal stirred tanks, and the one parameter in the model is N, the number of tanks in the chain. For N tanks in series, it can be shown that

$$E_\theta = N\bar{t}_i E = \frac{N(N\theta)^{N-1}}{(N-1)!} e^{-N\theta} \tag{10}$$

where

$\bar{t}_i$ = mean residence time in one tank

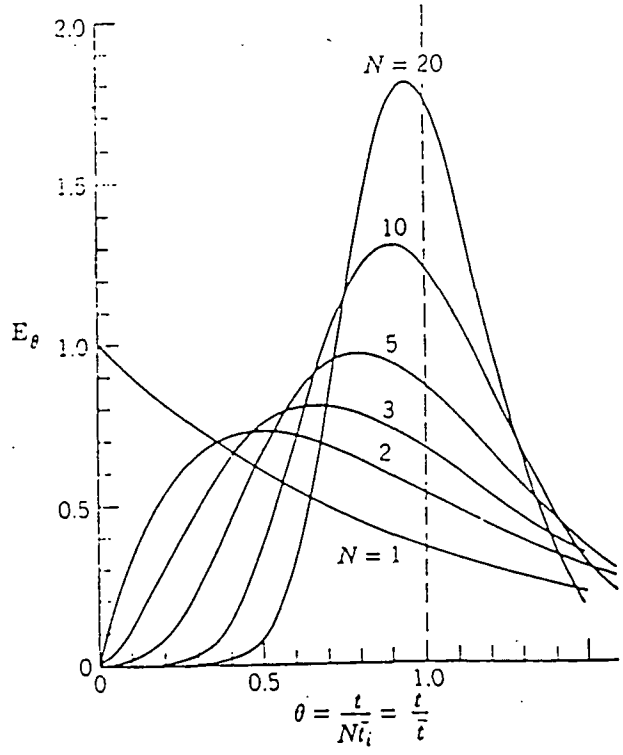
$\bar{t} = N\bar{t}_i$ = mean residence time in the N tank system

$$\bar{\theta}_i = \frac{t}{\bar{t}_i} = \frac{Nt}{\bar{t}} \quad , \quad \bar{\theta} = \frac{t}{\bar{t}} = \frac{t}{N\bar{t}_i}$$

This equation describes a set of curves, shown in Fig. 32. Their mean and variance are found to be

$$\bar{t} = N\bar{t}_i, \quad \sigma^2 = N\bar{t}_i^2 = \frac{\bar{t}^2}{N} \tag{11}$$

Figure 32. RTD curves for the tanks-in-series model



Therefore, from the experimentally determined values for $\bar{t}$ and σ^2, we may calculate N, the number of stirred tanks to be used in the flow model for the reactor. The flow behavior of the liquor through the reactor may thus to be modeled as the flow through a series of equal volume, perfectly mixed stirred tank reactors.

A mass balance on the dissolved lignin in the reactor gives

mass of lignin in inlet liquor – mass of lignin in outlet liquor
= lignin entering liquor by reaction + lignin accumulated in liquor

In symbolic form, the mass balance becomes

$$\frac{dL_i}{dt} = \frac{L_{i-1} - L_i}{\bar{t}_i} - r_L \qquad (12)$$

where

$\frac{dL_i}{dt}$ = lignin accumulation in the liquor in the i^{th} reactor

L_{i-1} = lignin concentration at the i^{th} reactor inlet

L_i = lignin concentration at the i^{th} reactor outlet

$\bar{t}_i$ = i^{th} reactor time constant or mean residence time

r_L = lignin reaction rate (rate of removal from the wood)

The accumulation of lignin in the flowing pulping liquor in the reactor used for this study is described by a set of N of these equations.

If there is a negligible change in liquor composition from the reactor inlet to outlet, and it is assumed that the delignification rate may be expressed as some function of the liquor composition (i.e., $r_L = f([SO_3^{=}], AQ, [OH^-])$), then it is clear that the delignification rate, and thus the lignin content of the wood, will be uniform throughout the reactor. The removal of lignin from the wood may therefore be described with a single batch delignification equation:

$$\frac{dL}{dt} = -r_L \tag{13}$$

Since all rate constants are to be calculated based on a unit of reactor volume, a single equation such as equation 8 will describe the appearance of lignin in the liquor by chemical reaction. This equation, combined with the N liquor flow equations, is the set of equations used as the mathematical model of the reactor.

$$\frac{dL_{wood}}{dt} = -r_L$$

$$\frac{dL_1}{dt} = \frac{L_0 - L_1}{\bar{t}_1} - r_L \,, \quad \frac{dL_2}{dt} = \frac{L_1 - L_2}{\bar{t}_2} - r_L \ldots \frac{dL_N}{dt} = \frac{L_{N-1} - L_N}{\bar{t}_N} - r_L$$

Using this set of equations with a known form of the rate law, r_L, the outlet concentration profile for dissolved lignin may be predicted for the reactor. Conversely, if the outlet concentration profile is measured, the rate law

describing the delignification rate may be obtained. The latter approach has been taken in this thesis.

We now have a technique which may be used to determine the rate law for delignification occurring inside the reactor, provided that we are able to measure the lignin concentration in the liquor at the reactor outlet. The technique developed for this purpose used fluorescence spectroscopy. Some general, introductory remarks on the fluorescence technique will be presented in the next section.

FLUORESCENCE SPECTROSCOPY

Fluorescence spectroscopy is an optical technique that has many desirable properties for its use in measuring lignin content of solutions. With the use of appropriate sample handling procedures, the technique produces a linear response over several orders of magnitude in concentration.

There are two types of fluorescence spectra: excitation spectra and emission spectra. Excitation spectra show the intensity of the emitted light at one wavelength as a function of the wavelength of the exciting light. For simple molecules at low concentration, the excitation spectrum has the same shape as the absorption spectrum. This similarity follows from the physical laws for fluorescence phenomena:

$$Q = I_A \Phi_f = (I_0 - I_T)\, \Phi_f \qquad (14)$$

where

Q = intensity of the emitted light
I_A = absorbed portion of the incident light
I_0 = intensity of the incident light
I_T = intensity of the transmitted light
Φ_f = quantum efficiency for fluorescence

Using the Beer-Lambert relationship,

$$I_T = I_0 e^{(-(\ln 10)\ \varepsilon\ b\ c)} \tag{15}$$

where

ε = molar absorptivity
b = sample path length
c = concentration in moles/liter

the following equation results:

$$Q = I_0(1 - e^{-(\ln 10)\ \varepsilon\ b\ c})\Phi_f \tag{16}$$

Expansion of the exponential term gives

$$Q = I_0((\ln 10)\ \varepsilon\ b\ c)\ (1 - (\ln 10)\ \varepsilon\ b\ c\ /2 + ((\ln 10)\ \varepsilon\ b\ c)^2/6+...)\Phi_f \tag{17}$$

If the absorbance is small, the equation simplifies to

$$Q = I_0\ ((\ln 10)\ \varepsilon\ b\ c)\ \Phi_f \tag{18}$$

This equation is true when the absorbance of the solution is small. The intensity of the emitted light (Q) is proportional to the absorbance (εbc); if $I_0\Phi_f$ is constant, then the excitation spectrum has the same shape as the absorption spectrum. Φ_f is normally a constant, independent of excitation wavelength, and I_0 may be kept constant by electronic compensation. All spectra and spectral data presented in this report are corrected for variation in the intensity of the excitation source.

Emission spectra are obtained by keeping the excitation wavelength constant and measuring the intensity of the emitted light as a function of wavelength. The emission spectra for simple molecules tend to be mirror images of the excitation spectra.

The equations derived above indicate that the intensity of the light emitted by a fluorescing compound is linearly related to the concentration of that compound in solution. Lignin is known to be a highly absorbing species, and its fluorescence properties have been used to measure its concentration in solution.

Baumgartner and coworkers[30] used the strong fluorescence of lignin to trace kraft mill effluent from an ocean outfall. The fluorescence of the lignin in seawater was found to be linear over two orders of magnitude in concentration. The exact concentrations were not given.

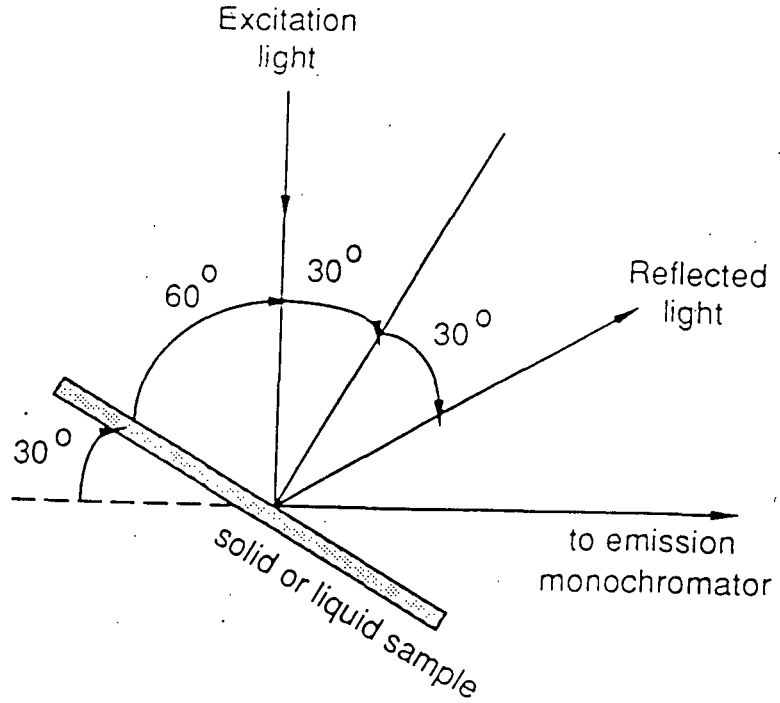
Almgren and his coworkers[31] used a fluorescence method to study the concentrations of spent sulfite liquors in the Baltic Sea. They found that the relative fluorescence intensities showed a linear relationship with concentration from 0.05 p.p.m. up to 7-8 p.p.m. in a standard 1 cm cuvette. Higher concentrations resulted in a self-quenching of the fluorescence.

Fluorescence of pulping liquors should be a very useful tool for use in the control of pulp mills. Bublitz[32] reports on attempts to use fluorescence as a means for controlling digesters. The technique worked well in laboratory studies, but was inconsistent in the mill environment. Specifically, the correlations between the fluorescence behavior of the pulping liquors and various cooking parameters in an acid sulfite mill were inconsistent. The problems encountered were explained by the inability of the mill to accurately control parameters such as liquor to wood ratio, acid strength, and chip charge. Better correlations were observed in a kraft mill with a continuous digester, where better process control was practiced.

Horvath and coworkers[33], using liquor samples generated as a part of this thesis, showed that fluorescence may behave in a linear way up to relatively high

concentrations. Use of a backscattering sample holder configuration (Fig. 33) was necessary for these lignin concentration ranges. The fluorescence of the pulping liquors (using this sample configuration) was linearly related to concentration up to about 1000 ppm; at this point, self-quenching of the fluorescence began (refer to the Experimental section of this report for details). This concentration, however, proved to be sufficiently high to allow the measurement of liquors from high liquor-to-wood ratio cooks without a dilution step.

Figure 33. Backscattering sample holder configuration



PROBLEM STATEMENT AND THESIS OBJECTIVES

The review of the literature in this area has shown that there is a general lack of knowledge of the kinetics of the delignification occurring during alkaline sulfite anthraquinone pulping. There has been no study directed at the early stage of pulping, and limited work in the bulk and residual phases. Kinetic descriptions of the various phases of delignification will provide the ability to optimize the ASAQ process to produce pulps of low lignin content at acceptable yield and strength levels.

The goal of this thesis, then, was to provide a mathematical model of the early stage of delignification during ASAQ pulping. If possible, a reaction network was to be developed which was consistent with the mathematical model and with current knowledge of lignin chemistry.

RESULTS AND DISCUSSION

APPROACH

The goal of this study was to quantify the effects of several parameters on the rate of delignification during the initial stage of ASAQ pulping. The general approach used has been alluded to in previous sections. The pulping reaction was carried out in a flow–through reactor, and the concentration of dissolved lignin in the outlet liquor was measured by fluorescence spectroscopy as a function of time. This lignin concentration profile was then compared to predicted profiles based on postulated rate equations. The rate equation which gave the best fit to all of the observed data was chosen to be representative of the process.

The steps involved in the process of obtaining the best model were:

1. Measure the fluorescence of the pulping liquor as a function of time at selected levels of temperature and liquor composition

2. Convert the fluorescence profile to a lignin concentration profile

3. Use the mathematical model of the reactor to calculate values for an apparent first order delignification rate constant

4. Regress the rate constants obtained in (3) from a series of experiments against the liquor composition variables to determine the complete form of the rate law

Steps 1 and 2 are described in the Experimental section of this report. Steps 3 and 4 are described in more detail below.

The flow model for the reactor, as described in the reactor modeling section of this report (five perfectly mixed stirred tank reactors in series), was used to mathematically describe the flow of liquor through the reactor. A simple kinetic model, first order in lignin, was used as the rate law needed for the delignification at constant liquor composition. The first order model was the simplest kinetic rate law that was consistent with the observed lignin concentration profiles at the reactor outlet. These profiles showed a decrease in the lignin concentration in the liquor with time, indicating some form of dependence of the delignification rate on the lignin content of the pulp. Models of different orders in lignin (1/2 and 2) were tried, but resulted in inferior fits to the data.

The first order model had the form

$$-\frac{dL}{dt} = k\,L \qquad (19a)$$

$$k = A\,e^{-E/RT} \qquad (19b)$$

where L is the lignin concentration in the wood, and k is the Arrhenius rate coefficient, determined by an activation energy, E, and pre–exponential factor, A.

The activation energy and pre–exponential factor were manipulated to obtain the best fit for the data at a given liquor composition, using data for all three temperatures at that liquor composition. In this way, the best values of E and A were obtained for each liquor composition. Values for the rate coefficient were then calculated from the activation energies and pre–exponential factors.

The manipulation of E and A and the minimization of the sum of the squared deviations of the model from the data points were performed using a FORTRAN program on the Burroughs A6F mainframe computer. The source code is listed in Appendix 3. The approach was to set values for E and A using DO loops,

and calculate the sum of squared deviations for each pair of parameter values. A coarse grid pattern search was performed initially, narrowing the range of E and A until a precision of four significant figures was obtained. The best fitting set of values for the parameters was chosen based on the minimization of the sum of squared deviations. The fit of the model was more sensitive to changes in the activation energy than changes in the pre–exponential factor, as shown in Appendix 9.

Analyses of variance were performed on the first order rate coefficients for all data, grouped by experimental category (sulfite only, AQ only, sulfite + AQ). The complete analyses of variance and tables of means are presented in Appendix 4. All main effects and two factor interactions were significant at the 99% confidence level.

The results for all experiments are shown in Tables 8–10. The effects of the controlled variables on the average rate coefficients are shown in Fig. 34–36. The rate constants (k135) plotted in these figures are rate constants determined at 135°C for each liquor composition. The effect of temperature on the value of the rate constants is assumed to be exponential (equation 19b).

Fig. 34 and 35 show that, in the presence of only sulfite or only anthraquinone, liquor pH has a much more pronounced effect on the average value for the rate constant than does the concentration of the other delignifying chemical in solution. At pH 10, the level of sulfite or AQ present in the system has relatively little effect on the rate constant for the delignification.

There is an interesting comparison possible between Fig. 34 and 35. Comparing the values for the rate constants at zero concentration in the sulfite only experiments with the corresponding AQ only experiments, we may estimate the

Table 8. Results of sulfite only experiments

Sulfite, M	pH	Temp,°C	Yield, %ODW	Lig Yield, %	k, 1/min	Activation Energy, cal/mole	Pre-exponential Factor
0	10	120	96.83	26.87%	0.0013	13490	4.57E+04
		135	92.38	25.60%	0.0027		
		150	89.61	22.17%	0.0045		
	13	120	88.94	26.36%	0.0016	14290	1.67E+05
		135	84.55	24.30%	0.0042		
		150	80.27	19.84%	0.0059		
0.1	10	120	96.64	26.64%	0.0013	15040	2.93E+05
		135	91.54	25.63%	0.0024		
		150	88.10	23.00%	0.0045		
	13	120	88.59	26.02%	0.0018	13440	6.21E+04
		135	79.91	24.17%	0.0044		
		150	75.34	20.15%	0.0062		
0.5	10	120	96.21	26.56%	0.0014	15170	3.66E+05
		135	92.07	25.41%	0.0026		
		150	86.51	22.70%	0.0049		
	13	120	84.00	25.30%	0.0023	13100	5.06E+04
		135	81.30	23.38%	0.0052		
		150	78.39	18.97%	0.0077		

NOTE: No glucose present in these experiments

Table 9. Results of anthraquinone only experiments

AQ, mM	pH	Temp, °C	Yield, %ODW	Lig Yield, %	k, 1/min	Activation Energy, cal/mole	Pre-exponential Factor
0	10	120	96.74	26.64%	0.0015	11760	5.61E+03
		135	92.3	25.79%	0.0028		
		150	89.73	22.75%	0.0044		
	13	120	88.75	24.61%	0.0030	12330	2.26E+04
		135	84.44	21.98%	0.0054		
		150	80.48	17.48%	0.0092		
0.05	10	120	96.55	26.64%	0.0021	11800	8.02E+03
		135	91.62	25.63%	0.0037		
		150	88.18	23.00%	0.0062		
	13	120	88.65	26.02%	0.0028	12090	1.57E+04
		135	79.85	24.17%	0.0050		
		150	75.32	20.15%	0.0085		
0.1	10	120	96.12	25.44%	0.0021	11960	9.69E+03
		135	91.96	24.16%	0.0036		
		150	86.59	21.12%	0.0062		
	13	120	83.79	24.25%	0.0031	12510	2.98E+04
		135	81.36	21.86%	0.0056		
		150	78.31	17.29%	0.0098		
0.2	10	120	96.62	25.94%	0.0022	11500	5.79E+03
		135	92.31	23.39%	0.0038		
		150	89.51	20.34%	0.0063		
	13	120	89.07	24.06%	0.0035	12010	1.73E+04
		135	84.55	21.53%	0.0061		
		150	80.11	15.80%	0.0103		

NOTE: Glucose present in these experiments at a concentration of 0.06 M

Table 10. Results of sulfite + anthraquinone experiments

Sulfite, M	AQ, mM	pH	Temp, °C	Yield, %ODW	Lig Yield, %	k, 1/min	Activation Energy, cal/mole	Pre-exponential Factor
0.1	0.05	10	120	96.83	25.72%	0.0020	20160	3.21E+09
			135	92.43	23.62%	0.0039		
			150	89.54	19.77%	0.0074		
		13	120	88.87	25.22%	0.0025	20650	5.72E+09
			135	84.63	22.83%	0.0050		
			150	80.18	16.81%	0.0097		
	0.1	10	120	96.49	25.99%	0.0020	19610	1.40E+09
			135	91.50	23.21%	0.0040		
			150	88.07	18.58%	0.0075		
		13	120	88.59	25.53%	0.0028	19920	2.50E+09
			135	80.09	20.96%	0.0057		
			150	75.35	15.25%	0.0109		
	0.2	10	120	96.31	25.59%	0.0021	20410	3.81E+09
			135	91.82	22.75%	0.0042		
			150	86.71	19.90%	0.0080		
		13	120	83.91	24.47%	0.0032	20560	5.98E+09
			135	81.28	20.93%	0.0065		
			150	78.40	14.05%	0.0127		
0.5	0.05	10	120	96.82	26.47%	0.0018	19840	2.10E+09
			135	92.27	24.13%	0.0036		
			150	89.61	20.46%	0.0069		
		13	120	88.73	25.12%	0.0029	19350	1.50E+09
			135	84.49	20.14%	0.0059		
			150	80.28	15.29%	0.0113		
	0.1	10	120	96.60	25.78%	0.0021	20590	5.50E+09
			135	91.48	22.66%	0.0043		
			150	88.27	19.44%	0.0082		
		13	120	88.62	24.37%	0.0033	20620	7.01E+09
			135	79.89	18.79%	0.0068		
			150	75.21	13.20%	0.0131		
	0.2	10	120	96.28	25.73%	0.0024	19920	3.20E+09
			135	92.12	22.23%	0.0049		
			150	86.39	17.16%	0.0094		
		13	120	84.05	23.86%	0.0036	20130	4.31E+09
			135	81.41	20.12%	0.0073		
			150	78.33	11.08%	0.0143		

NOTE: Glucose present in these experiments at a concentration of 0.06 M

Figure 34. Effect of liquor composition on rate coefficient at 135°C – sulfite only experiments

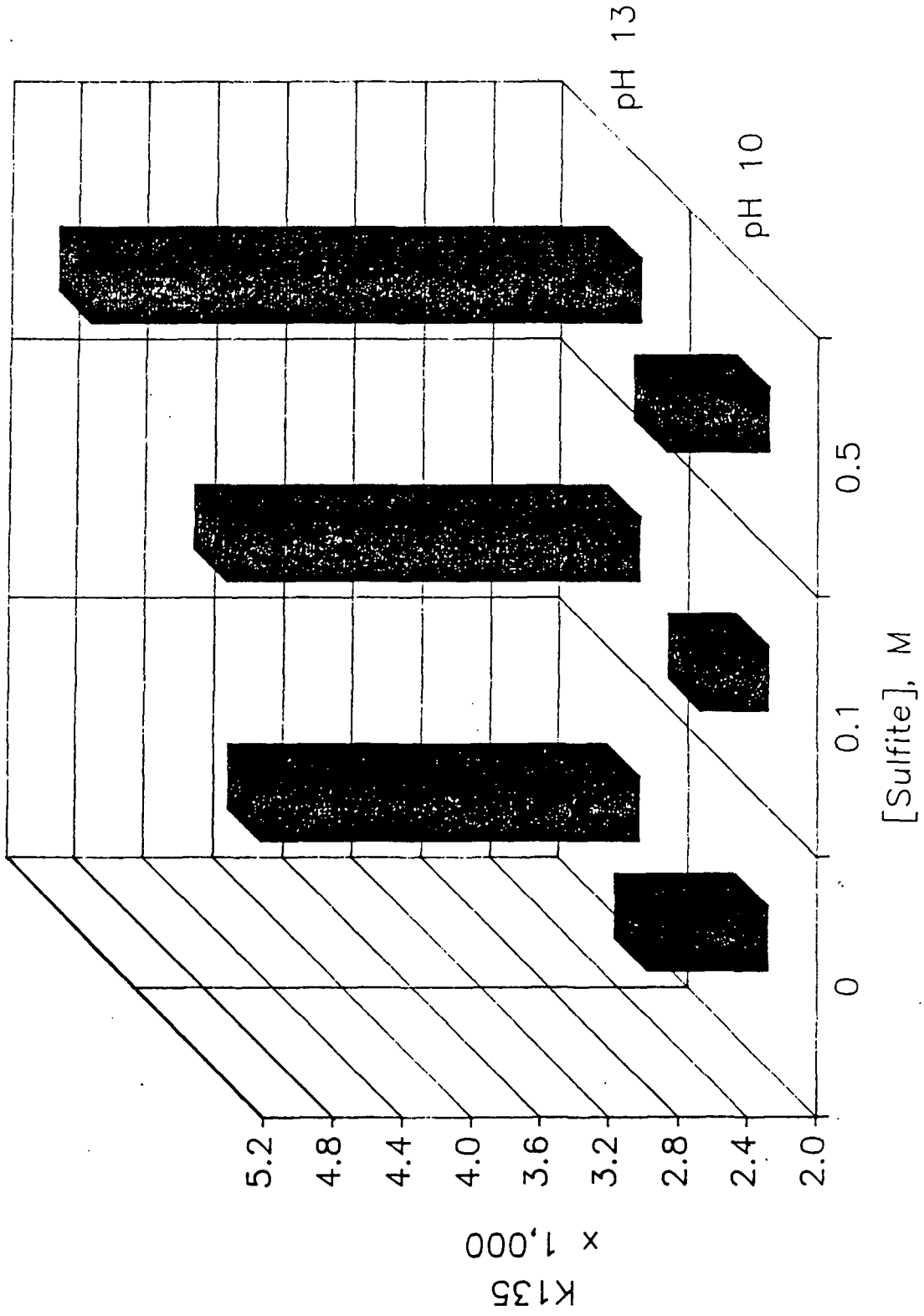


Figure 35. Effect of liquor composition on rate coefficient at 135°C – AQ only experiments

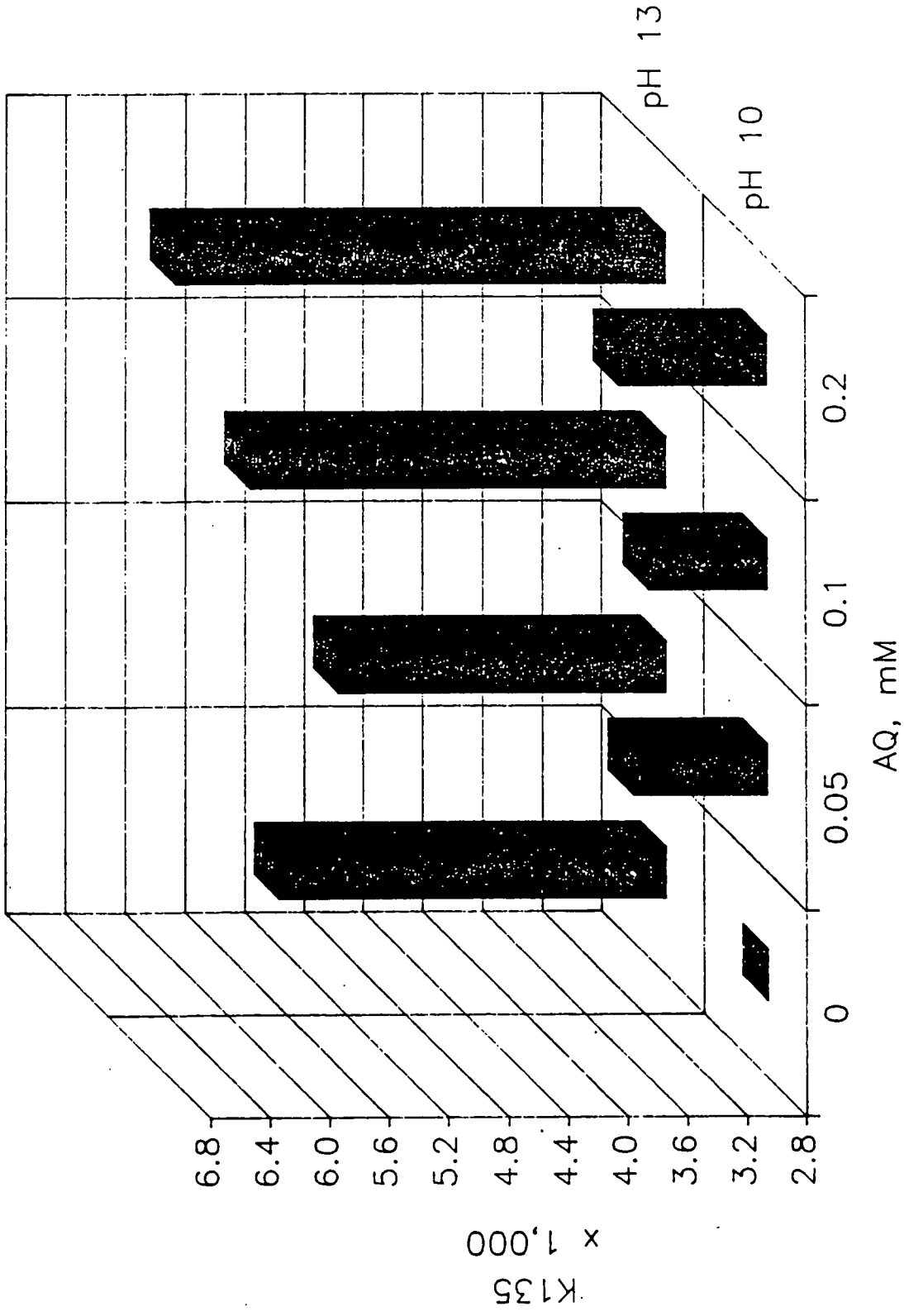
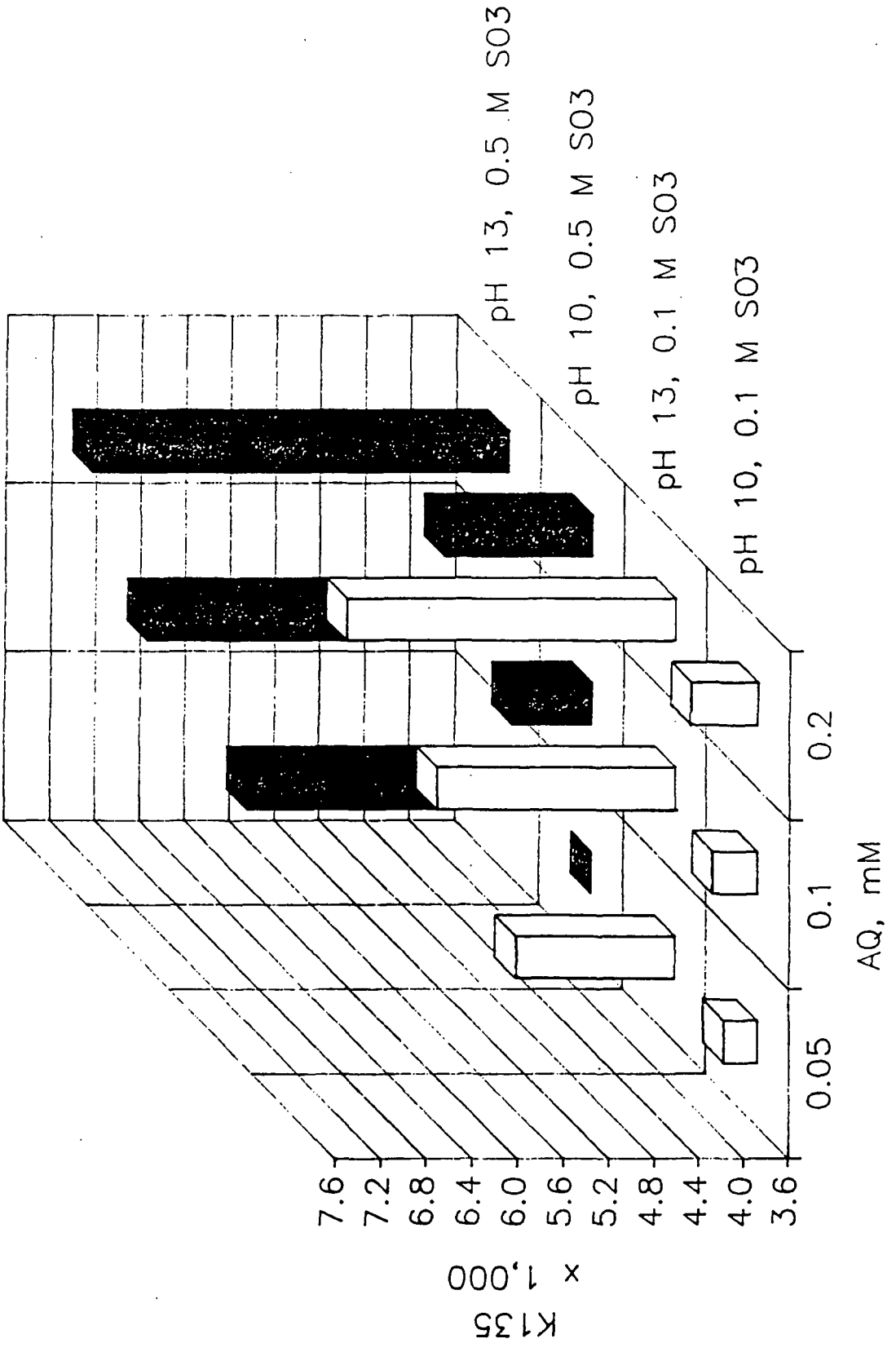


Figure 36. Effect of liquor composition on rate coefficient at 135°C – sulfite + AQ experiments



effect of glucose on the rate of delignification in the absence of other delignifying agents. At pH 10, the rate constant in the absence of glucose (from the sulfite only experiments) is 0.0027 minutes^{-1}; the rate constant with glucose in the system (from the AQ only experiments) has the value of 0.0028 minutes^{-1}. The effect of glucose on the delignification at pH 10 is therefore negligible.

At pH 13, however, the rate constants in the absence and presence of glucose are 0.0042 minutes^{-1} and 0.0054 minutes^{-1}, respectively. The increase in the rate constant at pH 13 is consistent with observations made in experiments with a β–aryl ether lignin model compound by Fullerton[35]. The model compound experiments were conducted in 1.0 *N* NaOH, and increasing the amount of glucose in the system from zero to ten equivalents increased the amount of cleavage of the β–aryl ether bond from 14% to 53%. "Equivalent" is not clearly defined in this article, but it is logical to assume that it is defined on a molar basis (one mole of glucose per mole of model compound). Converting the equivalent to a mass basis (necessary for use in the experiments with wood) gives one equivalent corresponding to about 0.61 gram glucose per gram lignin model compound.

During the pulping experiments with the flow reactor in which the liquor contained glucose (the AQ only and the sulfite + AQ experiments), the sugar was present in an amount which was roughly three equivalents, based on the amount of lignin present in the wood in the reactor. This amount of glucose would be expected to increase the delignification rate by a factor of approximately two, based on Fullerton's experiments. The observed increase in the average rate constant was 0.0042 minutes^{-1} to 0.0054 minutes^{-1}, a factor of approximately 1.3. The agreement with Fullerton's data is good, especially since the experiments were conducted at a lower pH. Still lower values of pH would be expected to reduce the effect of glucose on the system, as observed in the flow reactor experiments at pH 10.

The glucose in the system at pH 13 may therefore have an effect on the values for the rate constants from the experiments at that pH. Since there is clearly such a strong glucose/pH interaction, this effect would likely be reflected in inflated values for the terms in the final mathematical models (for the AQ only and sulfite + AQ experiments) which contain a hydroxide concentration. In the absence of glucose, these terms may have a lower value. From the data presented in this thesis, it impossible to distinguish a glucose/sulfite interaction from a glucose/hydroxide interaction.

It is also possible for the glucose to participate in reactions with bisulfite. The aldehyde functionality in the glucose may be oxidized to an aldonic acid, while the bisulfite is reduced to thiosulfate:

$$2\ R\text{–}CHO + 2\ HSO_3^- \rightarrow 2\ R\text{–}COOH + S_2O_3^{2-} + H_2O \qquad \text{(B)}$$

R = glucose residue

If this reaction were occurring to any significant extent, two phenomena should have been observed during the experiments:

1) The AQ would not have been readily reduced to the soluble AHQ since the glucose would have been consumed by reaction with bisulfite

2) A lower sulfite concentration should have been measured by the Palmrose titration, used to check final sulfite concentrations of all liquors

Neither of these phenomena were observed; it is thus concluded that the consumption of sulfite and glucose by reaction with each other is negligible.

Using the three independent liquor composition variables (sulfite concentration, AQ concentration, cold pH), a stepwise regression was performed on the data, starting with the polynomial model

$$k_{obs} = k_1[SO_3^{2-}] + k_2[OH^-] + k_3[AHQ^{2-}] + k_4[SO_3^{2-}][OH^-] + k_5[SO_3^{2-}][AHQ^{2-}] + k_6[AHQ^{2-}][OH^-] \quad (20)$$

using only the terms appropriate for the experimental category. Separate regressions were performed for the data obtained at each of the three temperatures studied. The significant terms in the regression equation were used to model the dependence of the first order rate coefficient on liquor composition. This model was then used to predict the rate coefficient for each experimental condition. These steps were performed for each experimental category.

It must be emphasized that the concentrations appearing in equation 20 are not necessarily representative of the actual composition of the liquor in the reactor. The concentrations used in this equation are based on room temperature measurements. The fact that the pulping experiments are conducted at temperatures significantly greater than 25°C leads to changes in the equilibria in the solution, as discussed in the Background section of this report.

Increasing the temperature from 25°C to 150°C makes very little difference in the value of K_a for the bisulfite/sulfite equilibrium (from 5.0×10^{-8} to 7.8×10^{-8}), but changes the value for K_w substantially (from 10^{-14} to 7.8×10^{-12}). The increase in the ionization of water molecules at the higher temperature generates a higher concentration of hydrogen ions in solution. The increase in the H^+ concentration will drive the bisulfite/sulfite equilibrium toward the bisulfite, resulting in a higher concentration of bisulfite ions and a lower concentration of sulfite ions at the higher temperature.

It should be noted in advance that all models include an intercept term, k_0, which is not equal to zero. This can be rationalized by keeping in mind that these experiments represent the very early stages of a pulping reaction. Early experiments during this thesis showed that there is a significant portion of the lignin initially present in the wood that is soluble in hot water. These intercept terms, therefore, may be considered as a measure of the rate of delignification in water alone (in the absence of delignifying agents such as $SO_3^=$, OH^-, AQ, etc.). During subsequent delignification stages (bulk and residual phases), such an intercept term might be interpreted as the lignin removal rate during earlier delignification phase(s). The value of the intercept term was independent of the model chosen for the regression of the data from all experimental categories (Appendix 5), supporting the hypothesis that the intercept may be interpreted as a measure of the lignin removal rate in water alone.

The next step would have been to propose a reaction network which was consistent with the regression model for the delignification. This proved to be difficult, requiring several assumptions which were not completely consistent with the chemistry of lignin as summarized in the Background section of this report. What are presented below, therefore, are simply the mathematical models for the delignification, with some speculation as to the significance of the terms in the models. The models for each experimental category will be discussed separately.

SULFITE ONLY DELIGNIFICATION MODEL

The sulfite only model has the form

$$-\frac{dL}{dt} = \left\{k_{0,S} + k_1\left[SO_3^{2-}\right]\left[OH^-\right] + k_2\left[OH^-\right]\right\} L \qquad (21)$$

The values for k_0, k_1 and k_2 are given in Table 11 from the regression of this rate law at the three temperatures evaluated.

Table 11. Values for coefficients in sulfite only model

Temperature	120 C		135 C		150 C	
Rate Constant	Parameter Estimate	95% Conf. Interval	Parameter Estimate	95% Conf. Interval	Parameter Estimate	95% Conf. Interval
K0,S gm lignin/minute	0.0013	± 0.00010	0.0026	± 0.00022	0.0046	± 0.00032
K1, gm lignin•liter^2/mol OH•mol SO3•minute	0.0136	± 0.00433	0.0199	± 0.01060	0.0351	± 0.01543
K2, gm lignin•liter/mol OH•minute	0.0035	± 0.00159	0.0126	± 0.00388	0.0161	± 0.00563
R^2	0.991		0.993		0.987	

The degradation of lignin by hydroxide is expected, based on knowledge of the chemistry of lignin. The sulfite/hydroxide interaction term may arise due to an increase in the reactivity of the lignin as a result of sulfonation, with the sulfonated lignin degraded by reaction with the hydroxide.

ANTHRAQUINONE ONLY DELIGNIFICATION MODEL

The AQ only experiments were modeled by the rate law

$$-\frac{dL}{dt} = k_{0,AQ} + k_3\left(AHQ^{2-}\right) + k_4\left[OH^-\right] L \qquad (22)$$

where (AHQ^{2-}) is the concentration of AHQ in mmoles/liter. In this case, the values for k_0, k_3 and k_4 are given in Table 12.

Table 12. Values for coefficients in anthraquinone only model

Temperature	120 C		135 C		150 C	
Rate Constant	Parameter Estimate	95% Conf. Interval	Parameter Estimate	95% Conf. Interval	Parameter Estimate	95% Conf. Interval
K0,AQ gm lignin/minute	0.0017	± 0.00031	0.0031	± 0.00049	0.0051	± 0.00100
K3, gm lignin•liter/mmol AHQ•minute	0.0028	± 0.00221	0.0043	± 0.00357	0.0074	± 0.00735
K4, gm lignin•liter/mol NaOH•minute	0.0113	± 0.00327	0.0205	± 0.00530	0.0370	± 0.01088
R^2	0.947		0.956		0.943	

The reaction of the lignin with AQ has a lower activation energy than the degradation by hydroxide. This result conflicts with earlier observations of the action of AQ during the bulk phase of soda delignification[25], where the activation energy for the AQ reactions was actually higher than that for the hydroxide. The AQ appears to be acting as a true catalyst in these experiments, providing a reaction pathway of significantly lower energy. The pre-exponential factor for the AQ reactions, however, is two orders of magnitude lower than that for the hydroxide reactions. Although the AQ reactions are of lower energy, fewer of the lignin molecules may be degraded by these reactions.

SULFITE + ANTHRAQUINONE DELIGNIFICATION MODEL

The sulfite + AQ experiments were successfully modeled by the rate law

$$-\frac{dL}{dt} = \left\{k_{0,SAQ} + k_5\left[SO_3^{2-}\right]\left[AHQ^{2-}\right] + k_6\left[SO_3^{2-}\right]\left[OH^-\right] + k_7\left[OH^-\right] + k_8\left[AHQ^{2-}\right]\right\} L \quad (23)$$

Values for the coefficients in equation 23 are shown in Table 13. The regression of the sulfite + AQ experimental rate coefficients against this model gave an overall coefficient of determination of 0.97.

Table 13. Values for coefficients in sulfite + anthraquinone model

Temperature	120 C		135 C		150 C	
Rate Constant	Parameter Estimate	95% Conf. Interval	Parameter Estimate	95% Conf. Interval	Parameter Estimate	95% Conf. Interval
K0,SAQ gm lignin/minute	0.0017	± 0.00021	0.0033	± 0.00045	0.0062	± 0.00088
K5, gm lignin•liter^2/mol SO3•mmol AQ•minute	0.0028	± 0.00456	0.0058	± 0.00927	0.0115	± 0.01797
K6, gm lignin•liter^2/mol SO3•mol OH•minute	0.0081	± 0.00854	0.0165	± 0.01734	0.0322	± 0.03361
K7, gm lignin•liter/mol OH•minute	0.0074	± 0.00319	0.0157	± 0.00646	0.0314	± 0.01253
K8, gm lignin•liter/mmol AQ•minute	0.0026	± 0.00203	0.0056	± 0.00414	0.0112	± 0.00804
R^2	0.966		0.968		0.97	

It is interesting to note that the model for the SAQ experiments reduces to the models for the sulfite only or AQ only experiments when the appropriate concentration terms are set to zero. This may seem to imply that the sulfite and AQ

react with the lignin along separate, parallel pathways. This observation would be consistent with the results of earlier studies of the ASAQ process (*e.g.*, Suckling[15] and Eagle[27]). The presence of the sulfite/AQ interaction term casts some doubt on this hypothesis. Its significance may be interpreted using the argument presented above for the sulfite/hydroxide interaction term in the sulfite only model.

There is also a possibility for interaction between the sulfite and the anthraquinone which is independent of the lignin. The nature of this interaction may involve a transfer of electrons from the sulfite to the AQ, resulting in an overall increase in the concentration of the AHQ. Although possible, this theory is not supported by AQ solubility experiments by Storgard–Envall and Dimmel[36], where a sodium sulfite/sodium carbonate solution was shown to have a very limited extent of reaction with AQ, dissolving less than 5% of the AQ charged in the experiment.

These models (equations 21–23) were used to predict values for the rate coefficients for all experiments for their respective experimental categories. The predicted values agree very well with the observed values (Fig. 37).

The final models (equations 21–23, as appropriate) were used to predict outlet concentration profiles for all experiments. Modeling was accomplished using the FORTRAN program described earlier in this section (Appendix 3). Plots of all experiments (data and predicted profiles) are shown in Appendix 7. A representative plot is presented here as Fig. 38.

Figure 37. Predicted vs. observed rate coefficients

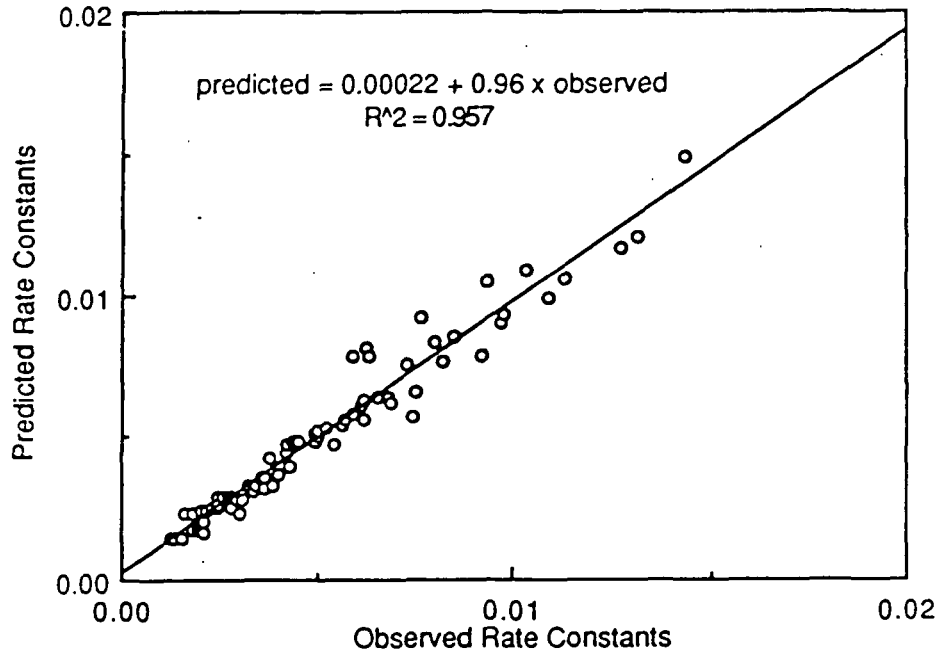
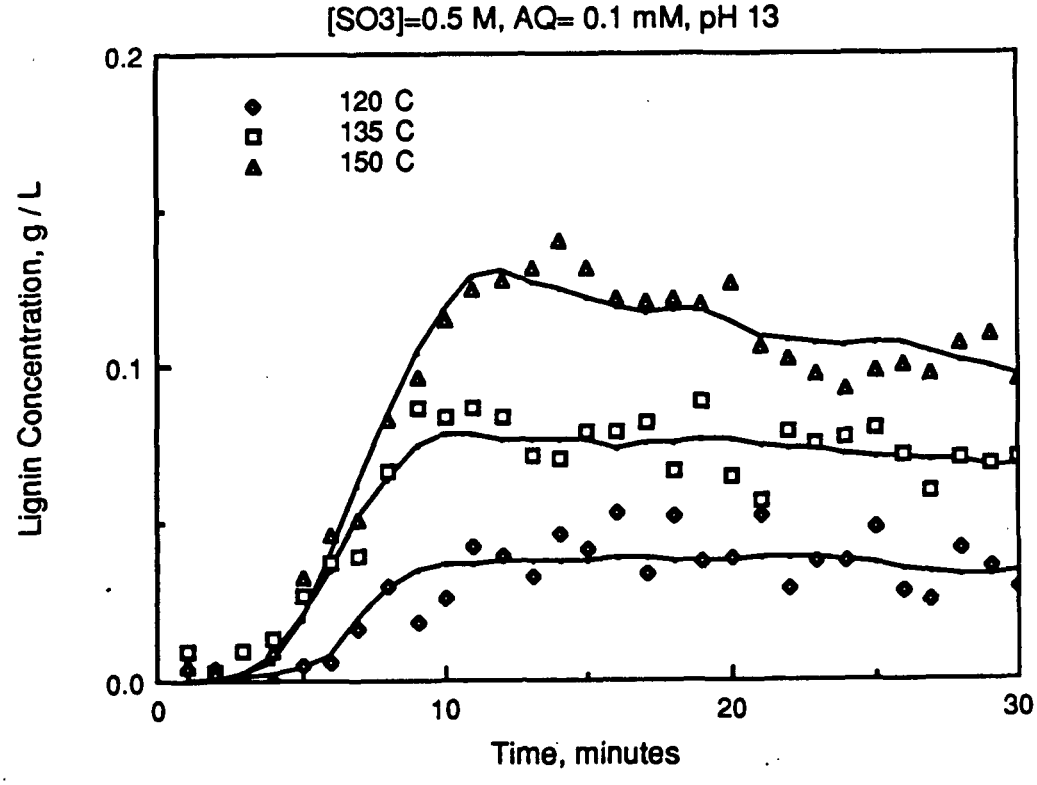


Figure 38. Example plot of experimental data with predicted concentration profiles



USEFULNESS AND LIMITATIONS OF THE DELIGNIFICATION MODELS

It is clear from the discussion above that mechanistic inferences should not be drawn from these models. The equations presented above are regressions of rate constants obtained from lignin concentration profiles against liquor concentration values measured at room temperature. These models are needed for comparisons with models developed for other delignification phases and for carbohydrate degradation. Such comparisons will allow optimization of the pulping process for extended delignification without undue carbohydrate degradation.

CARBOHYDRATE DEGRADATION KINETICS

The same approach as was used to determine which liquor composition variables had a significant effect on the delignification rate constants was used to study the effects on the first order rate constants for carbohydrate loss. Since only two data points per experiment were available (initial and final carbohydrate contents), the conclusions that may be drawn from this analysis are limited. A more complete discussion of the results of this analysis appears in Appendix 10.

The analysis indicated that the rate of carbohydrate degradation in the AQ only experiments depended on both the hydroxide concentration and the AQ concentration. In the sulfite only and sulfite + AQ experiments, however, the carbohydrate degradation depended only on the hydroxide concentration. The fact that the anthraquinone concentration term does not appear in the carbohydrate degradation model for the sulfite + AQ experiments is a significant result. During the initial phase in the presence of sulfite, the anthraquinone's selectivity enhancement effect is due to acceleration of delignification reactions, not to the prevention of carbohydrate degradation.

IMPLICATIONS FOR ALKALINE SULFITE ANTHRAQUINONE PULPING

The strong dependence of the delignification rate on liquor concentrations during the initial phase provides some clues as to the reasons for loss in selectivity during ASAQ pulping. The rate law determined for ASAQ's early stage

$$-\frac{dL}{dt} = \left\{k_0 + k_5\left[SO_3^{2-}\right]\left[AHQ^{2-}\right] + k_6\left[SO_3^{2-}\right]\left[OH^-\right] + k_7\left[OH^-\right] + k_8\left[AHQ^{2-}\right]\right\}L$$

shows two terms which depend on the concentration of sulfite in solution. As the sulfite concentration drops during the course of a normal, low liquor–to–wood ratio cook, the magnitude of these two terms will drop, resulting in a decrease in the rate of delignification.

Anthraquinone also appears in two terms in the delignification rate law. Any loss in the amount of AQ available will decrease the rate of delignification substantially.

The pH of the pulping liquor will affect both the delignification and the carbohydrate degradation rates. If the pH of the liquor falls more slowly than the concentrations of sulfite and AQ in the liquor, the carbohydrate degradation would continue at a slowly decreasing rate, while the delignification rate decreased rapidly.

The loss in selectivity during ASAQ pulping, based on the forms of the rate laws for the early stage of the process, may be attributed primarily to a decrease in the delignification rate relative to the rate of carbohydrate degradation. It does not appear that an increase in the carbohydrate degradation rate is likely, but this possibility cannot be ruled out without further investigations of the bulk and residual phases of pulping under ASAQ conditions.

CONCLUSIONS

Delignification during the early stage of ASAQ pulping may be described by a relatively simple dependence on reaction conditions. The delignification is first order in lignin, sulfite concentration, hydroxide concentration, and anthraquinone concentration.

The carbohydrate degradation rate was modeled as a first order process. Results indicate that high reaction temperatures favor delignification over carbohydrate degradation. The only liquor composition variable which affected the carbohydrate content of the ASAQ pulps was the liquor pH, with increases in pH giving increased degradation rates.

Comparison of the results of the delignification and carbohydrate degradation models indicates that, during the initial phase in the presence of sulfite, the anthraquinone's selectivity enhancement effect is due to acceleration of delignification reactions, not to the prevention of carbohydrate degradation.

The use of a flow-through reactor for these studies, and the novel approach taken in the analysis of the data generated represents a significant advance in the technology that has been applied to the study of pulping kinetics. The approach was made possible by the development of a technique (using fluorescence spectroscopy) which allowed the measurement of dissolved lignin concentration profiles at the reactor outlet, giving much more information from a single experiment than is possible with a batch system.

EXPERIMENTAL MATERIALS AND METHODS

PREPARATION OF WOOD SHAVINGS

The wood shavings used for the pulping experiments were prepared by splitting logs of loblolly pine and using a power jointer to plane shavings from the flat surfaces of the quarter logs. The shavings were collected and allowed to air dry overnight. The shavings were classified using coarse wire screens, with the fractions retained on the 1/4" and 1/2" screens used for the experiments. The average thickness of the shavings was 0.303 mm. Shavings were stored in a large plastic bag at 4°C until extracted.

Shavings were extracted with a 2:1 mixture of benzene:ethanol in a large soxhlet extractor for a minimum of fifteen cycles of solvent, taking about eight hours. Extracted shavings were allowed to air dry for at least twenty-four hours in a fume hood. The dried, extracted shavings were stored in polyethylene bags at 4°C until used for pulping experiments.

PREPARATION OF PULPING LIQUORS

All liquors were prepared using distilled water which was deoxygenated by boiling for at least ten minutes and allowing to cool under nitrogen.

Sulfite Liquors

Reagent grade (98.7%) sodium sulfite (Na_2SO_3) was weighed to the nearest 0.01 gram and dissolved in deoxygenated water (giving an initial pH of 10.0 ± 0.1). The pH of the solution was adjusted by addition of 6.45 N sodium hydroxide solution drop by drop until the desired pH was obtained. Final liquor concentrations were verified by the Palmrose titration procedure as modified by Eagle[27] (Appendix 11).

Anthraquinone Liquors

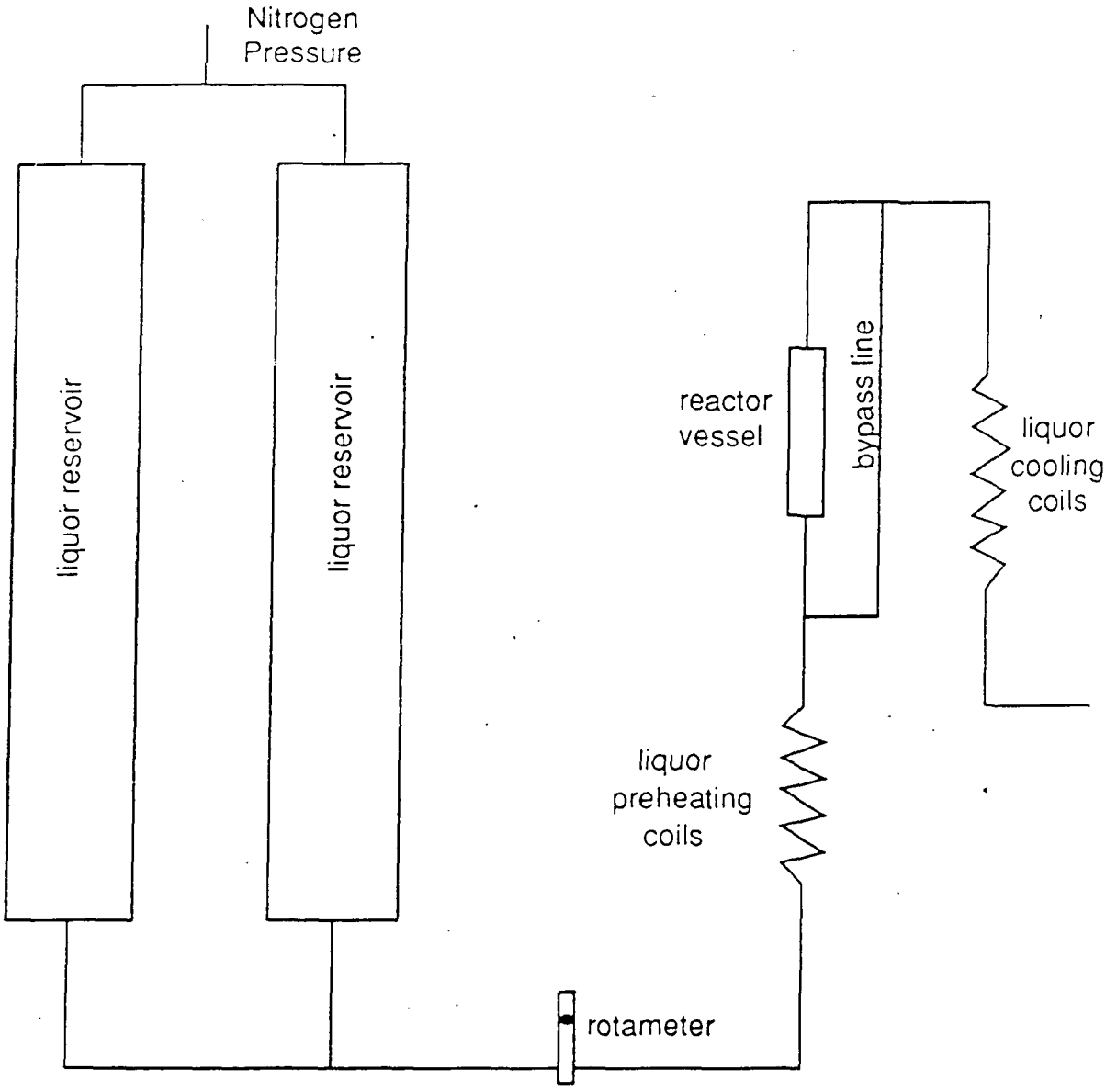
A base solution of 0.1 M sodium hydroxide and 0.06 M glucose (pH 13) was prepared in warm deoxygenated water. The solution was kept at 50-60 °C while stirring in a 1000 ml filtering flask, kept free from air by sweeping the space above the solution with nitrogen. Powdered anthraquinone (97%), was weighed to the nearest 0.0001 gram and added to the heated solution. The solution was stirred for two to three hours to allow the anthraquinone to be converted to its soluble reduced form, anthrahydroquinone. Liquor pH was adjusted by bubbling carbon dioxide through the solution while stirring until the desired pH was reached. Concentrations were verified on selected samples using the gas chromatographic technique developed by Wiseman[34]. Representative data from these determinations is presented in Appendix 2.

For the AQ-free control experiments, the base solution was prepared in the same manner, without the addition of anthraquinone. No glucose was used in the solutions for the control experiments in the sulfite only experimental category (refer to Results section for details on the experimental categories).

THE FLOW THROUGH REACTOR

A schematic diagram of the flow through reactor system is shown in Fig. 39. Pulping liquor is supplied to the reactor from two twelve liter reservoirs, with flow maintained by pressurizing the reservoirs with oxygen–free nitrogen. The liquor flows through a rotameter (for indication of flow rate) and into the liquor preheating coils. The stainless steel tubing is wound into coils which fit tightly around two cartridge heaters (1000 W each). Thermal contact between the heaters and the tubing was enhanced by the application of heat transfer putty to seal each coil and heater into one solid unit.

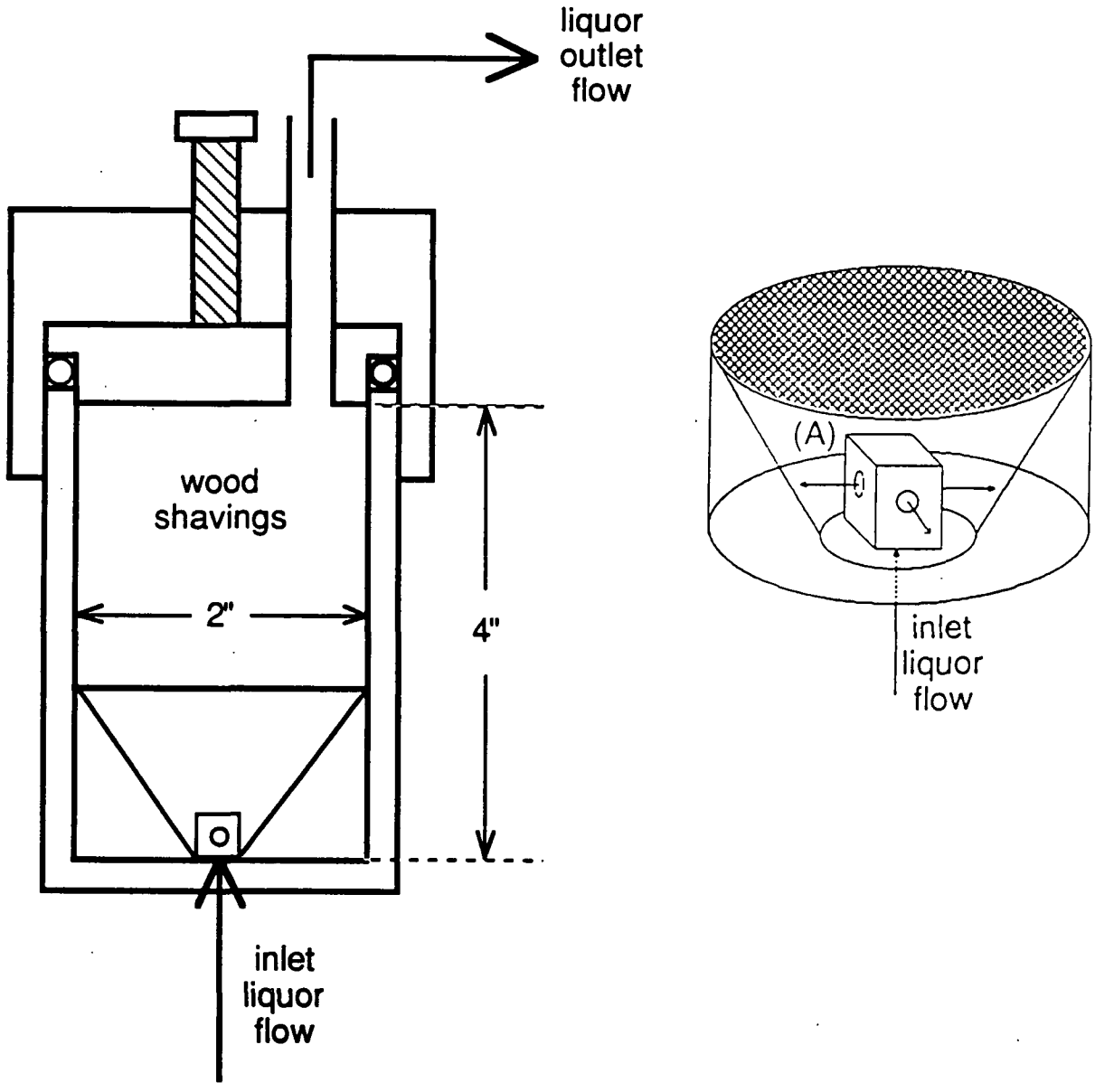
Figure 39. Flow through reactor system – schematic diagram



The temperature of the liquor at the outlet from these heaters is controlled by adjustment of the voltage supplied to the heaters using a variable voltage supply (VARIAC). From the liquor preheating section, the liquor may bypass the reactor (such as during startup of the system), or be directed to the reactor using a three–way valve.

The reactor vessel is constructed of stainless steel. The reactor is two inches in diameter (I.D.) and four inches long. The liquor flow is distributed across the reactor by the inlet device shown schematically in Fig. 40. The liquor enters the reactor through a flow divider (A), which directs the flow radially toward the inside

Figure 40. Reactor vessel and liquor inlet design



of a conical fitting in the bottom of the reactor. The conical fitting was turned from a solid stainless steel bar, two inches in diameter, so that it fit snugly in the bottom of the reactor. A screen on the top of the conical inlet device holds the wood shavings in place.

The liquor exiting the reactor is cooled by flowing through coils immersed in a water bath, with the flow rate through the system controlled by a needle valve at the outlet for the cooling coils. Samples of the liquor for testing were taken done at this point.

RESIDENCE TIME DISTRIBUTION EXPERIMENTS

The residence time distribution for the reactor vessel filled with wood shavings was determined experimentally by injecting 0.1 ml of 1000 ppm fluorescien dye at the reactor inlet. Samples were taken at the outlet from the cooling coils at fifteen second intervals for the first five minutes, and at thirty second intervals thereafter. The fluorescence of these samples was measured. This fluorescence profile is normalized such that the area under the curve is equal to one. The resulting profile is known as the E-curve, and from its properties the reactor vessel's behavior may be calculated as described in the Reactor Modeling section of this report. Data from three independent RTD experiments are presented in Appendix 2.

PULPING EXPERIMENTS

Preliminary Batch Cooks

The first set of pulping experiments were performed to generate liquor samples with varying lignin concentrations to be used in the evaluation of methods for the determination of lignin concentration in solution.

Two sets of cooks at a liquor to wood ratio of 10:1 were performed. The experimental conditions are summarized in Table 14. All cooks were performed at 180°C. Samples of the liquors from these cooks were sent to the National Bureau of Standards for fluorescence testing, and later evaluated with a commercially available fluorescence spectrophotometer (as described below).

Table 14. Results from preliminary cooks

Sulfite g/l as Na2O	Total Alkali g/l as Na2O	AQ Conc'n mM	Time at Temp. minutes	Pulp Yield %ODW	Hypo Number	Total Lignin %ODP
18	48	1	0	61.81	15.7	17.1
18	48	1	60	53.41	11.2	11.5
18	48	1	120	51.55	9.9	9.7
18	48	1	180	49.44	9.1	8.9
36	48	1	0	65.66	16.4	18
36	48	1	60	52.82	8.1	8.2
36	48	1	120	49.91	5.9	5.7
36	48	1	180	47.53	4.4	4.7

M & K Digester Cooks

Two cooks were performed in the M & K digester in the Pulping Laboratory to generate a large quantity of ASAQ liquor for use in the calibration of the fluorescence technique. Cooking conditions and results are summarized in Table 15.

Table 15. Results of cooks in M & K digester

Sulfite g/l as Na2O	Total Alkali g/l as Na2O	AQ Conc'n mM	Time at Temp. minutes	Pulp Yield %ODW	Hypo Number	Total Lignin %ODP
15	40	0.25	60	32.5	1.2	1.21
15	40	0.25	120	39.5	2.08	2.15

Flow Through Reactor Cooks

The main body of experimental data came from cooks performed in the flow through reactor described earlier. The specific method of operation is described here.

The extracted wood shavings were impregnated with liquor before cooking by immersing a weighed (to the nearest 0.0001 gram) wood sample in the liquor and applying vacuum for five minutes, relieving, and reapplying until no bubbles were being removed from the shavings (about an additional five minutes). The shavings sank to the bottom of the jar during this procedure, an indication of good penetration of liquor into the shavings. The shavings were then placed into the reactor, with care taken to eliminate air bubbles in the wood bed. The reactor was sealed and attached to the flow system.

Flow of the cooking liquor commenced with the liquor bypassing the reactor. The reactor was not preheated independently. When the liquor reached the desired temperature, the flow was directed to the reactor, and the heaters to the reactor turned on. This procedure resulted in a very rapid increase in the reactor temperature (Fig. 41). This temperature profile was recorded and used explicitly in the modeling of the reaction kinetics. Liquor samples (approximately four milliliters each) were taken at one minute intervals during the run. These samples were tested for fluorescence and titrated for sulfite concentration if required.

TESTING OF PULPS

The lignin content of the pulps from the flow through reactor was determined by the Hypo Number method (TAPPI Standard T–253). The hypo number method was chosen because the method is more accurate at high lignin contents than the kappa number procedure, and the results are linearly related to the total lignin content (Klason + acid soluble) of the pulp, as shown in Fig. 42. None of the pulps contained more than 1.5% acid soluble lignin, with the low lignin content pulps containing less than 0.5% acid soluble lignin. The equation for

Figure 41. Temperature profile of pulping run

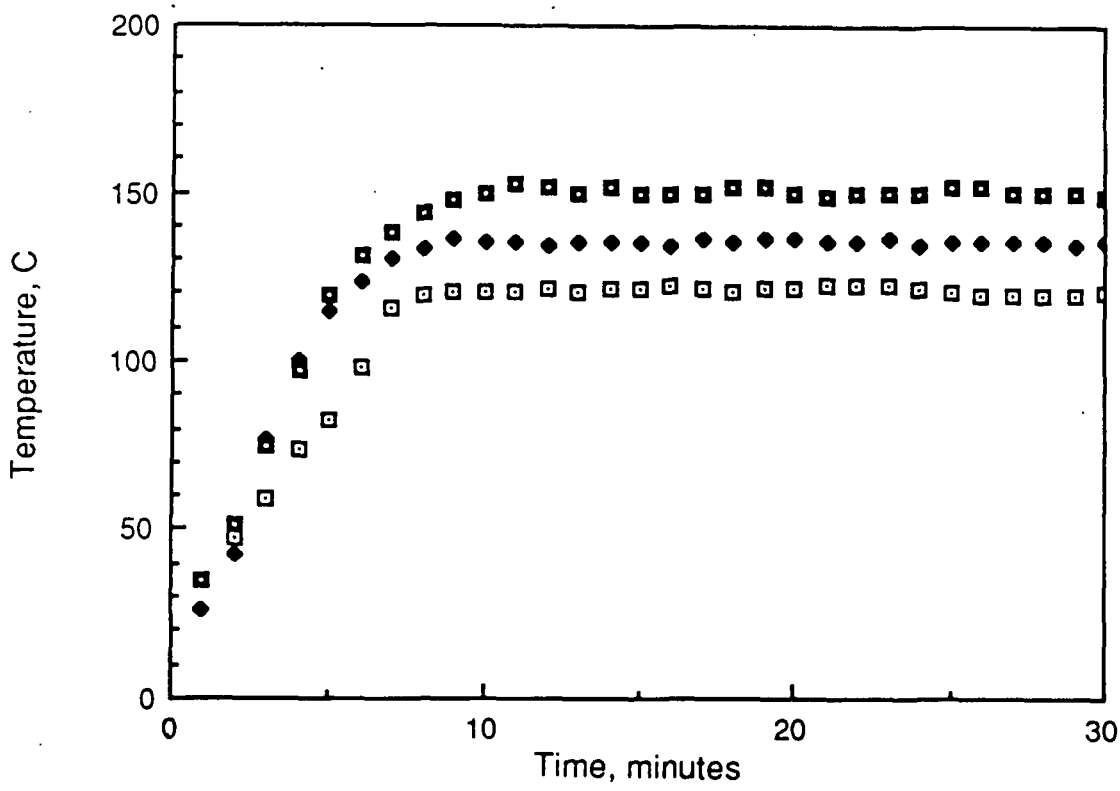
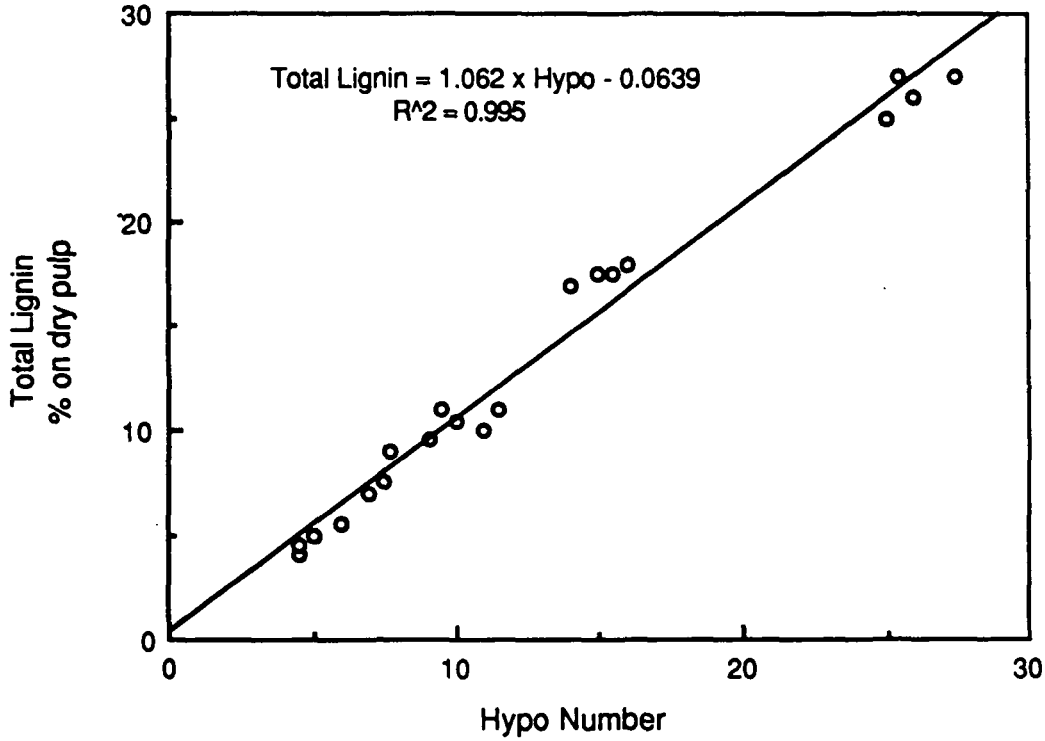


Figure 42. Linear relationship between Hypo Number and lignin content of pulps



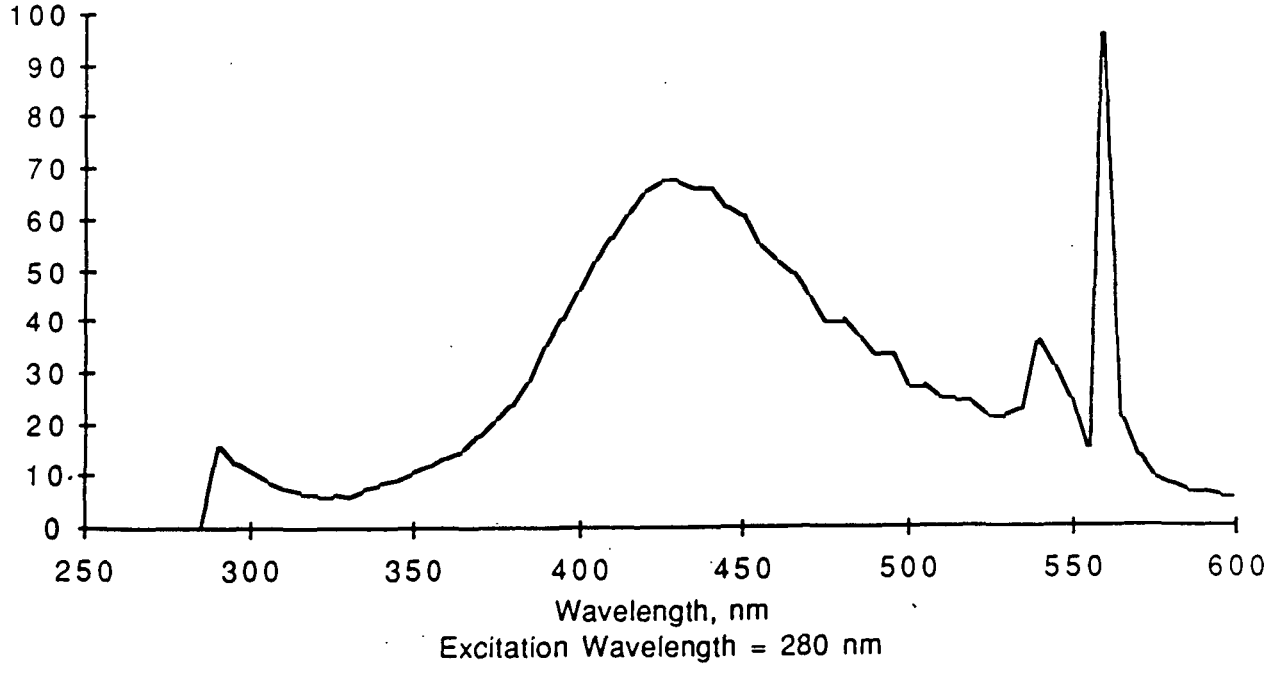
the line in Fig. 42 was used to determine the lignin content of the pulps from the FTR experiments.

Moisture content of the wood and pulps was determined by weighing a sample to the nearest 0.0001 gram and drying under vacuum at 105°C to constant weight.

TESTING OF RESIDUAL LIQUORS

The emission spectrum of a typical ASAQ liquor from this thesis (liquor from a cook in the M & K digester) is shown in Fig. 43. The excitation wavelength used for this spectrum was 280 nm. The spectrum has a broad peak at 425 nm; these wavelengths (280 nm for excitation and 425 nm for emission) were used for the measurement of the fluorescence of the liquors from the flow through reactor.

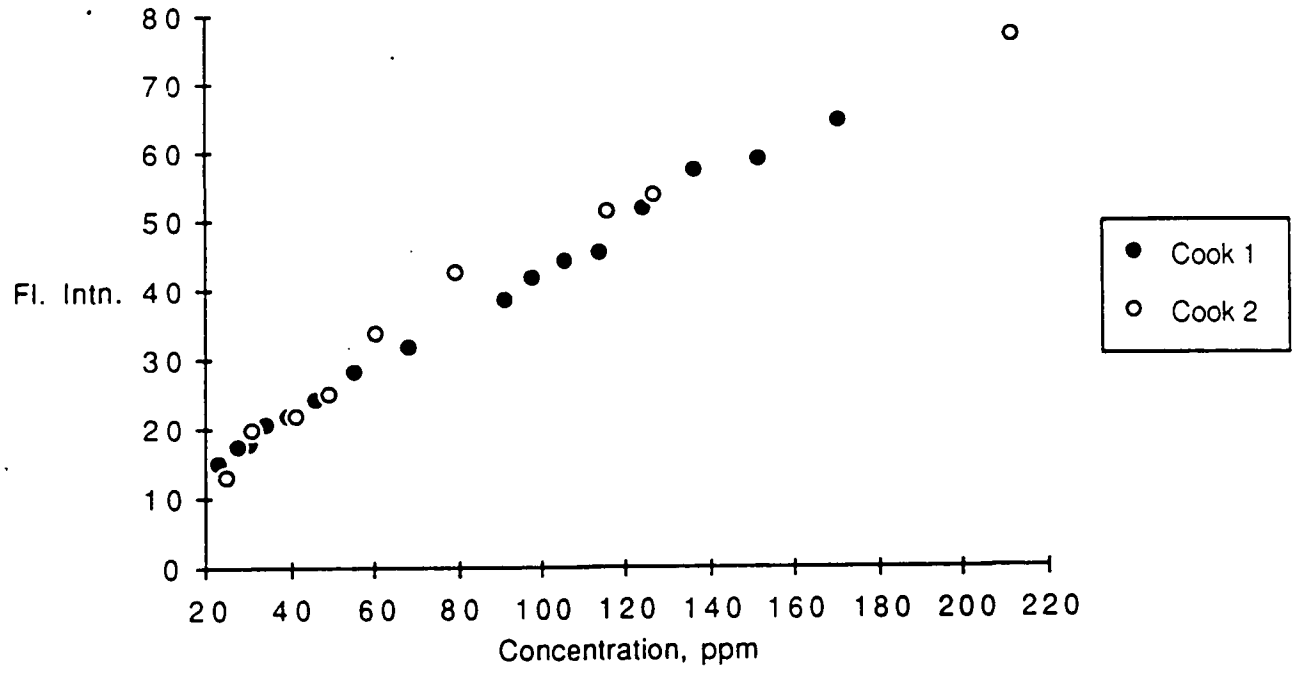
Figure 43. Emission spectrum for ASAQ liquor



Samples of liquor taken from the outlet of the cooling coils were tested for fluorescence using a Perkin–Elmer LS–5B Spectrophotometer. The same liquor samples were titrated for sulfite content (when appropriate) using the Palmrose titration procedure (Appendix 11). The cold (room temperature) pH of the liquor samples was determined using a semi–micro combination pH electrode.

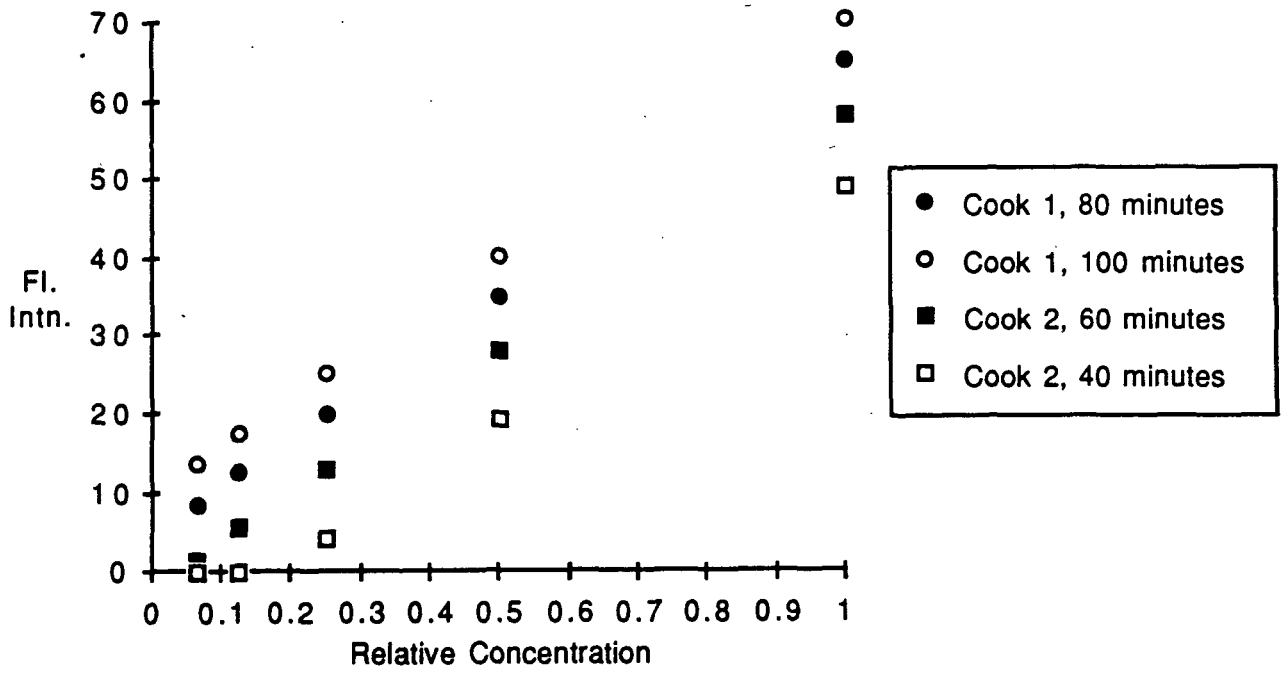
Fig. 44 shows the results of the two high liquor-to-wood ratio cooks performed in the M&K digester. The data were obtained by taking a sample of the cooking liquor after pulping (which therefore determines the lignin concentration in solution) and performing successive dilutions on that sample. The fluorescence was seen to be linear in concentration over an order of magnitude in concentration. The concentration range shown in Fig. 44 includes the lignin concentrations expected (and obtained) at the reactor outlet.

Figure 44. Lignin concentration from control cooks



Liquor samples taken earlier in the M & K cooks were tested for fluorescence by successive dilution. It is not possible to determine the actual lignin concentration in solution for these samples. However, the decrease in fluorescence intensity for a given dilution should be the same as for the liquor sample discussed in the preceding paragraph (*i.e.*, the slope of the relative concentration *vs.* fluorescence plot should remain the same) if there is no change in the fluorescent behavior of the lignin fragments in solution as a function of the extent of delignification. This was indeed the case, as shown in Fig. 45. For these liquors, a 50% decrease in lignin concentration results in about a 40% decrease in relative fluorescence intensity.

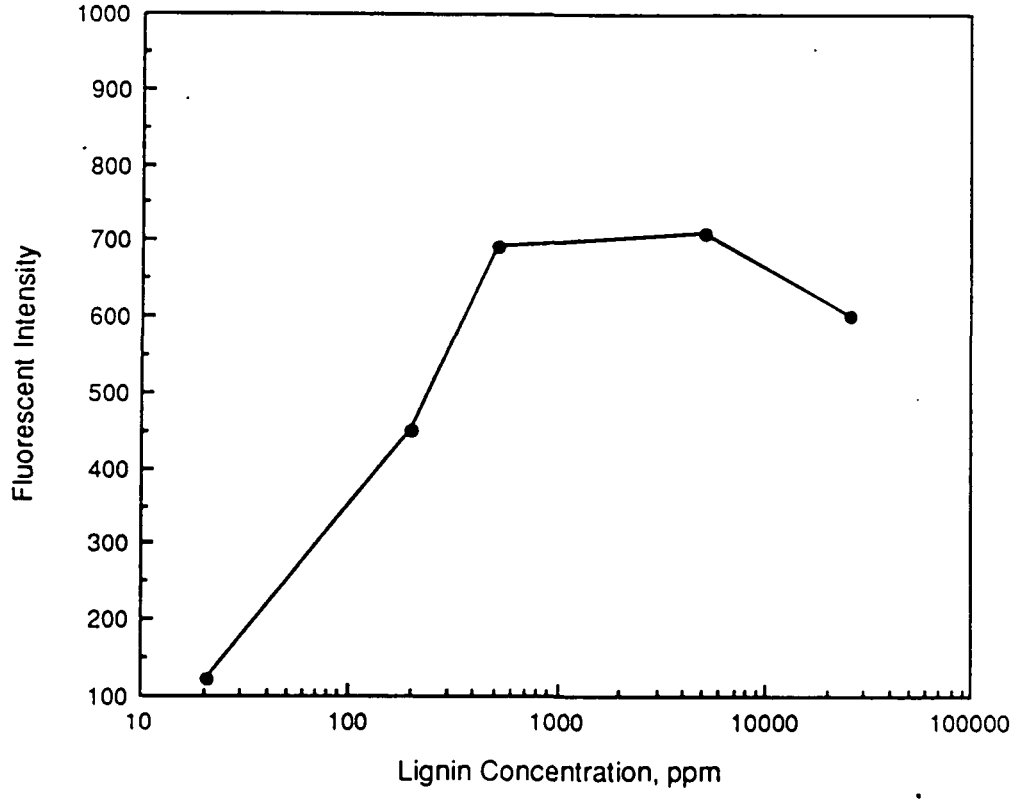
Figure 45. Relative changes in fluorescence for M & K liquor samples



The linear response range of the fluorescence technique used in this thesis extends to 1000 ppm, where "self-quenching" begins to occur (Fig. 46). The concentration of the fluorescing species in solution becomes high enough that the emitted light is reabsorbed by molecules in solution before the light can escape the sample cell. Further increases in concentration above this level gives no increase in

the fluorescence intensity from the solution, and may even result in a decrease in the intesity of the emitted light, as observed in Fig. 46.

Figure 46. Self quenching of the liquor



DETERMINATION OF LIGNIN CONCENTRATION PROFILES

The concentration of lignin in the liquor leaving the reactor was determined from the fluorescence measurement on the liquor samples. A typical fluorescence/time profile is shown in Fig. 47. These measurements were converted to concentration values by noting that the area under this curve is proportional to the mass of lignin removed from the wood during the pulping run (Fig. 48). This follows if, for the i^{th} liquor sample, the lignin concentration in solution is proportional to the fluorescence of the sample:

$$L_i = k \cdot F_i \qquad (27)$$

Figure 47. Typical fluorescence/time profile

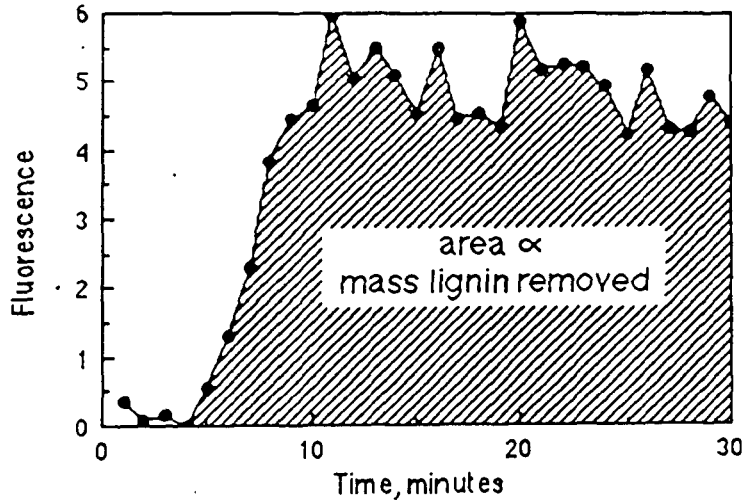
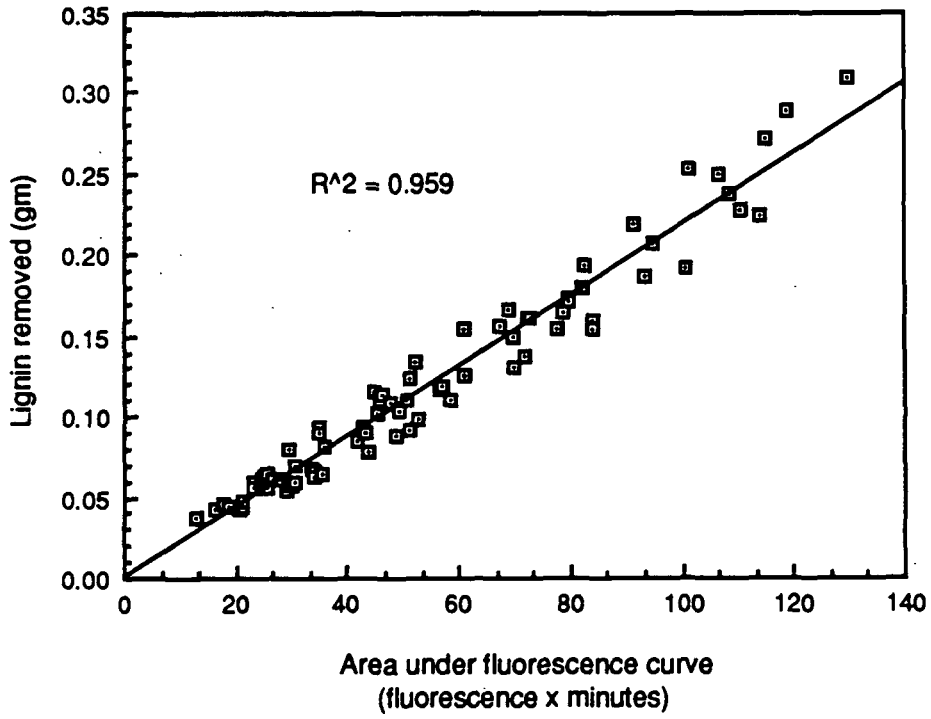


Figure 48. Linear relationship between area under fluorescence curve and lignin removed from wood



The mass of lignin removed is

$$M_{L_i} = L_i \cdot \Delta v_i = k \cdot F_i \cdot \Delta v_i \qquad (28)$$

For a constant flow rate v_0, $\Delta v_i = v_0 \Delta t_i$, and

$$M_{L_i} = k \cdot F_i \cdot v_0 \cdot \Delta t_i \tag{29}$$

Summing over all the samples taken,

$$\sum_i M_{L_i} = \sum_i k \cdot F_i \cdot v_0 \cdot \Delta t_i = k \cdot v_0 \cdot \sum_i F_i \cdot \Delta t_i \tag{30}$$

where

$\sum_i M_{L_i}$ = total mass of lignin removed

$\sum_i F_i \cdot \Delta t_i$ = area under fluorescence/time curve

A conversion factor was determined, based on this relationship, to convert the fluorescence measurements to concentration units. This conversion factor (CF)

$$CF = \frac{\text{mass of lignin removed}}{\text{area under curve}} \tag{31}$$

has the units of [grams of lignin*(fluorescence*time)$^{-1}$]. When the individual fluorescence measurements are multiplied by this conversion factor, a mass flow rate of lignin is obtained. This mass flow rate was converted to a lignin concentration by dividing by the liquor flow rate in liters/min, resulting in a concentration having the units of [grams lignin/liter].

The conversion factor obtained as described above is independent of experimental conditions (Appendix 12). Therefore, an average value for the conversion factor was calculated, and that value used to convert all fluorescence data to lignin concentration data.

The possibility of interference from the anthraquinone in solution was checked by obtaining the fluorescence spectra of a solution of anthrahydroquinone

and a slurry of anthraquinone. The excitation and emission spectra of the anthraquinone are shown in Figs. 49 and 50. The spectra of AQ and AHQ were not distinguishably different. The anthraquinone produced no measurable excitation maxima around 280 nm, and no emission in the vicinity of 425 nm. These were the wavelengths used for measuring lignin fluorescence in the pulping liquors. It was concluded that the presence of anthraquinone would have no effect on the measurement of lignin concentration.

Figure 49. Excitation spectrum for anthraquinone

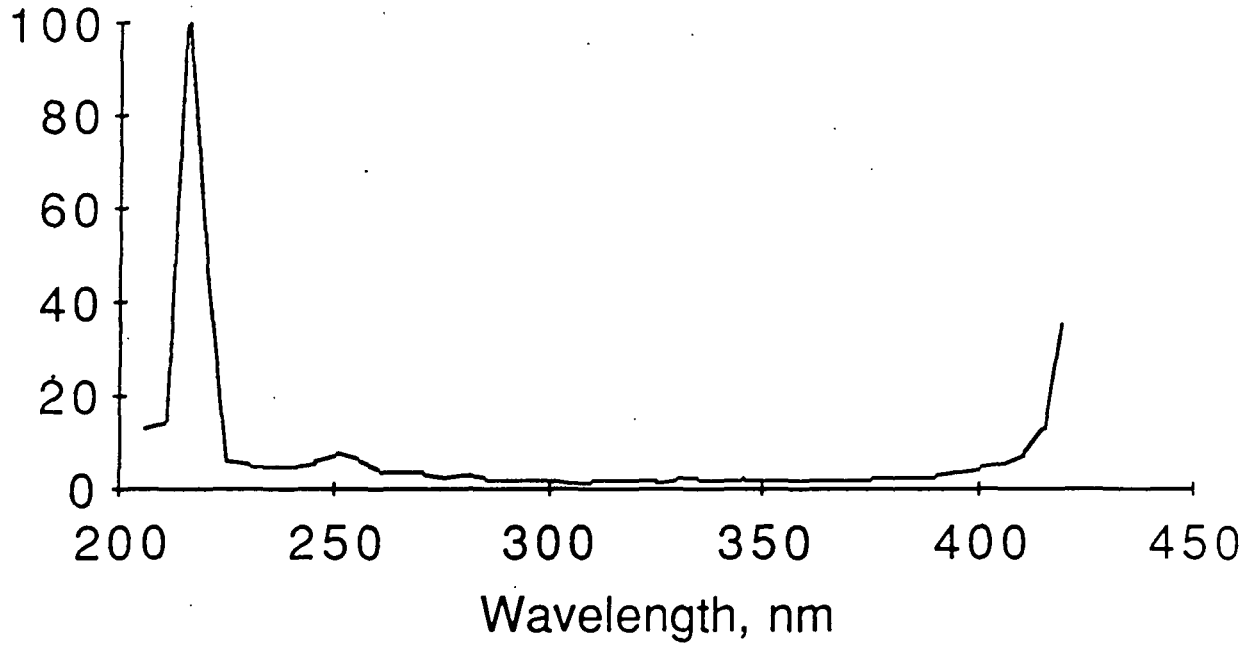
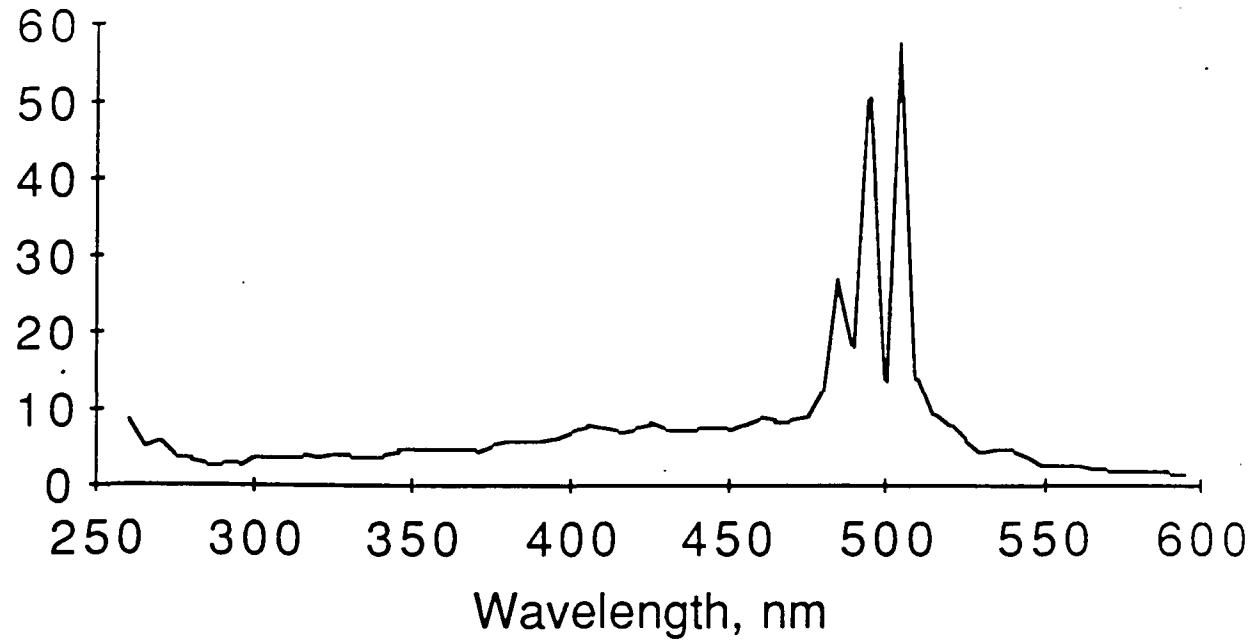


Figure 50. Emission spectrum for anthraquinone



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APPENDIX 1

EQUILIBRIUM CONSIDERATIONS

We first wish to determine the dependence of the distribution of ionic species as a function of pH for a diprotic acid, H_2SO_3. The simplest approach is to express the concentration of the three forms (H_2SO_3, HSO_3^-, and SO_3^{2-}) in terms of any one of them, and find the fraction of each by dividing by their sum. Expressing the concentrations in terms of HSO_3^-, we have

$$[H_2SO_3] = \frac{[HSO_3^-][H^+]}{K_1} \tag{A1}$$

$$[SO_3^{2-}] = \frac{[HSO_3^-]K_2}{[H^+]} \tag{A2}$$

where $K_1 = 1.0 \times 10^{-2}$ and $K_2 = 5.0 \times 10^{-8}$. The term $[H_2SO_3]$ is taken to be equal to the actual H_2SO_3 plus the dissolved (hydrated) SO_2 which has not reacted to form H_2SO_3. Now, if the total sulfite in all different forms is denoted by *s*, then

$$s = [H_2SO_3] + [HSO_3^-] + [SO_3^{2-}] \tag{A3}$$

Combining equations A1–A3 we obtain

$$s = [HSO_3^-]\left(\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]}\right) \tag{A4}$$

and the relative proportions of the three species in solution are therefore

$$[H_2SO_3] : [HSO_3^-] : [SO_3^{2-}] = \frac{[H^+]}{K_1} : 1 : \frac{K_2}{[H^+]} \tag{A5}$$

At a solution pH of 10, the ratio of bisulfite to sulfite ions in solution is

$$[HSO_3^-] : [SO_3^{2-}] = 1 : \frac{K_2}{[H^+]} = \frac{5 \times 10^{-8}}{10^{-10}} = 1 : 500$$

For the acid–base equilibrium

$$HSO_3^- \underset{K}{\rightleftharpoons} SO_3^{2-} + H^+$$

the dependence of the equilibrium constant K on temperature may be expressed as

$$\frac{d}{dT}(\ln K) = \frac{\Delta H^{\varnothing}}{RT^2} \tag{A6}$$

where

$$\Delta H^{\varnothing} = \Delta H^{o}_{f,products} - \Delta H^{o}_{f,reactants} \tag{A7}$$

with reactants on the left and products on the right side of the reaction as written. ΔH_f^0 (the standard enthalpy of formation) for many ions and compounds may be found in the CRC Handbook of Chemistry and Physics (59th Ed., pp. D67–D77). For the substances in the equilibrium above, the values are

$$\Delta H^0_{f,HSO_3^-} = -150.09 \frac{kcal}{g \cdot mole}$$

$$\Delta H^0_{f,SO_3^{2-}} = -149.20 \frac{kcal}{g \cdot mole}$$

$$\Delta H^0_{f,H^+} = 0 \frac{kcal}{g \cdot mole}$$

so that the enthalpy change for the equilibrium as written becomes

$$\Delta H^{\varnothing} = \Delta H^0_{f,SO_3^{2-}} + \Delta H^0_{f,H^+} - \Delta H^0_{f,HSO_3^-} = 0.89 \frac{kcal}{g \cdot mole}$$

Integrating equation A6 with respect to temperature gives

$$\ln\left(\frac{K_{T_f}}{K_{T_i}}\right) = -\frac{\Delta H}{R}\left(\frac{1}{T_f} - \frac{1}{T_i}\right) \tag{A8}$$

where

K_{T_f} = equilibrium constant at T_f

K_{T_i} = equilibrium constant at T_i

At T_i = 25°C, the equilibrium constant for the reaction above is 5×10^{-8}. Using equation A8, the equilibrium constant at 150°C would be

$$\ln\left(\frac{K_{150°C}}{5 \times 10^{-8}}\right) = -\frac{0.89}{1.98}\left(\frac{1}{423\ K} - \frac{1}{298\ K}\right)$$

$$K_{150°C} = 7.8 \times 10^{-8}$$

Analogous calculations for the change in the value for K_w, the dissociation constant for water, over the same temperature range gives

$$K_{W,150°C} = 7.78 \times 10^{-12}$$

since

$$\Delta H^{\varnothing} = 13.36 \frac{kcal}{g \cdot mole},\ K_{W,25°C} = 10^{-14}$$

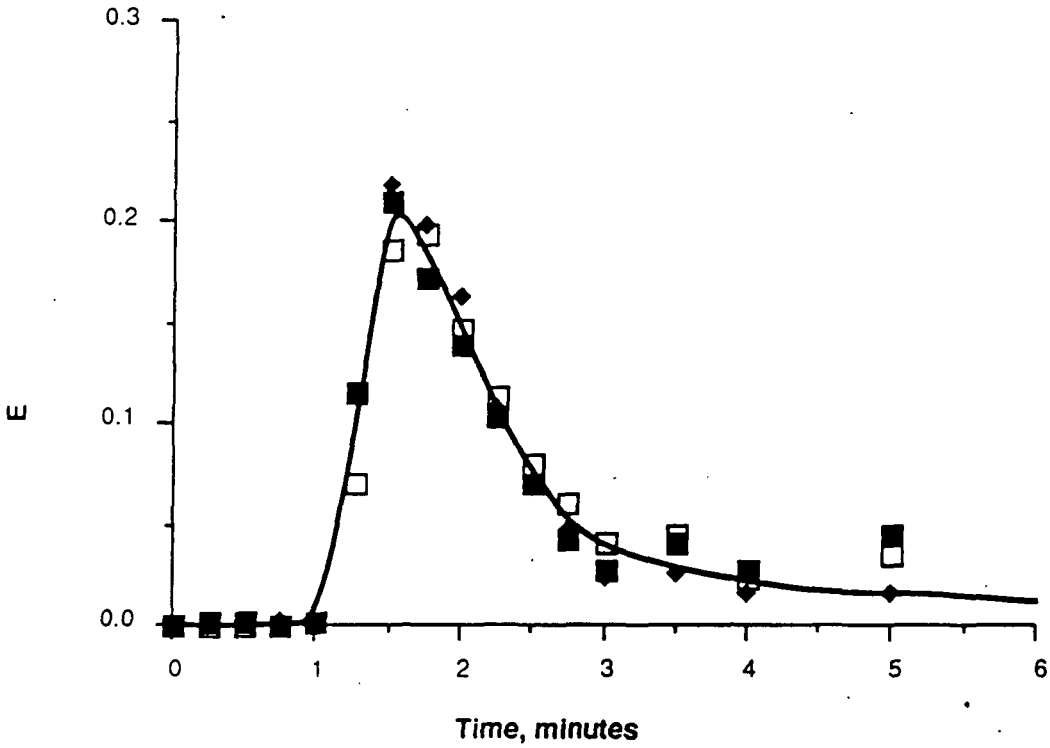
for the dissociation of water.

APPENDIX 2

EXPERIMENTAL DATA

The following table presents three sets of the fluorescence data used to determine the residence time distribution for the reactor vessel. The fluorescence data were normalized to make the area under the fluorescence/time curve equal to one, and the mean residence time and variance of the distribution were calculated as discussed in the reactor modeling section of this report. A plot of the data, with the predicted RTD for five CSTR's in series, follows the table.

Time, *minutes*	E	E	E
0.00	0.000	0.000	0.000
0.25	0.006	0.003	0.008
0.50	0.006	0.005	7.000
0.75	0.006	0.005	0.004
1.00	0.007	0.004	0.005
1.25	0.007	0.109	0.113
1.50	0.171	0.208	0.202
1.75	0.178	0.190	0.159
2.00	0.137	0.156	0.122
2.25	0.106	0.104	0.098
2.50	0.076	0.068	0.071
2.75	0.060	0.047	0.043
3.00	0.043	0.025	0.030
3.50	0.041	0.029	0.030
4.00	0.031	0.020	0.022
5.00	0.023	0.026	0.025
fbar =	2.11	1.89	2.07
variance =	0.907	0.581	1.049
N (# tanks) =	4.93	6.17	4.11



The following tables present the results of the experiments in the flow through reactor.

Sulfite only experiments – no glucose is present in these liquors

Sulfite, M	pH	Temp,°C	Yield, %ODW	gm lig diss	gm lig in pulp	%LODP	Hypo number	Lig Yield, %	gm ODP
0	10	120	96.83	0.0381	0.4800	27.75%	26.13	26.87%	1.7298
	10	135	92.38	0.0624	0.4695	27.71%	26.10	25.60%	1.6945
	10	150	89.61	0.1234	0.4009	24.74%	23.31	22.17%	1.6203
	13	120	88.94	0.0478	0.4778	29.64%	27.91	26.36%	1.6119
	13	135	84.55	0.0846	0.4372	28.74%	27.06	24.30%	1.5213
	13	150	80.27	0.1655	0.3582	24.71%	23.28	19.84%	1.4494
0.1	10	120	96.64	0.0437	0.4935	27.57%	25.96	26.64%	1.7900
	10	135	91.54	0.0608	0.4621	28.00%	26.37	25.63%	1.6507
	10	150	88.10	0.1108	0.4244	26.10%	24.59	23.00%	1.6261
	13	120	88.59	0.0559	0.4883	29.37%	27.66	26.02%	1.6622
	13	135	79.91	0.0931	0.4664	30.25%	28.48	24.17%	1.5418
	13	150	75.34	0.1613	0.3674	26.75%	25.20	20.15%	1.3736
0.5	10	120	96.21	0.0421	0.4577	27.60%	26.00	26.56%	1.6582
	10	135	92.07	0.0662	0.4692	27.60%	26.00	25.41%	1.6999
	10	150	86.51	0.1196	0.4306	26.24%	24.71	22.70%	1.6414
	13	120	84.00	0.0639	0.4362	30.11%	28.36	25.30%	1.4485
	13	135	81.30	0.1082	0.4497	28.75%	27.08	23.38%	1.5641
	13	150	78.39	0.1944	0.3675	24.20%	22.80	18.97%	1.5187

Sulfite, M	pH	Temp,°C	gm lig in wood	gm ODW	gm carb wood	gm carb pulp	KC*	Selectivity**
0	10	120	0.5181	1.7864	1.2683	1.2498	0.00049	2.056
	10	135	0.5319	1.8343	1.3024	1.2250	0.00204	0.807
	10	150	0.5244	1.8082	1.2838	1.2194	0.00172	1.916
	13	120	0.5256	1.8124	1.2868	1.1342	0.00421	0.313
	13	135	0.5218	1.7993	1.2775	1.0841	0.00547	0.438
	13	150	0.5237	1.8057	1.2820	1.0913	0.00537	0.867
0.1	10	120	0.5371	1.8522	1.3151	1.2966	0.00047	2.366
	10	135	0.5230	1.8033	1.2803	1.1886	0.00248	0.663
	10	150	0.5353	1.8457	1.3104	1.2017	0.00289	1.019
	13	120	0.5442	1.8764	1.3322	1.1740	0.00422	0.353
	13	135	0.5595	1.9293	1.3698	1.0754	0.00807	0.316
	13	150	0.5288	1.8233	1.2945	1.0062	0.00840	0.559
0.5	10	120	0.4998	1.7235	1.2237	1.2005	0.00064	1.815
	10	135	0.5355	1.8464	1.3109	1.2307	0.00211	0.826
	10	150	0.5502	1.8974	1.3472	1.2107	0.00356	0.877
	13	120	0.5001	1.7244	1.2243	1.0123	0.00634	0.301
	13	135	0.5580	1.9240	1.3660	1.1144	0.00679	0.430
	13	150	0.5619	1.9375	1.3756	1.1512	0.00594	0.866

NOTE: No glucose present in these experiments

* KC = first order rate constant for carbohydrate degradation, 1/minutes

** selectivity = gm lignin dissolved/gm carbohydrate dissolved

AQ only experiments – glucose is present at a concentration of 0.06 M in these experiments. The glucose and AQ concentrations were determined only on the original liquor, not on the effluent from the reactor.

AQ, mM	pH	Temp, °C	Yield, %ODW	gm lig diss	gm lig in pulp	%LODP	Hypo number	Lig Yield, %	gm ODP
0	10	120	96.74	0.0422	0.4757	27.54%	25.93	26.64%	1.7274
		135	92.3	0.0589	0.4732	27.94%	26.32	25.79%	1.6937
		150	89.73	0.1132	0.4116	25.35%	23.88	22.75%	1.6238
	13	120	88.75	0.0795	0.4461	27.73%	26.12	24.61%	1.6085
		135	84.44	0.1263	0.3954	26.03%	24.52	21.98%	1.5192
		150	80.48	0.2081	0.3158	21.72%	20.47	17.48%	1.4540
0.05	10	120	96.55	0.0437	0.4938	27.60%	25.99	26.64%	1.7895
		135	91.62	0.0608	0.4619	27.97%	26.34	25.63%	1.6515
		150	88.18	0.1108	0.4244	26.08%	24.56	23.00%	1.6273
	13	120	88.65	0.0559	0.4879	29.35%	27.64	26.02%	1.6623
		135	79.85	0.0931	0.4665	30.27%	28.51	24.17%	1.5410
		150	75.32	0.1613	0.3674	26.75%	25.20	20.15%	1.3732
0.1	10	120	96.12	0.0613	0.4382	26.47%	24.93	25.44%	1.6557
		135	91.96	0.0893	0.4460	26.28%	24.75	24.16%	1.6972
		150	86.59	0.1497	0.4009	24.39%	22.98	21.12%	1.6438
	13	120	83.79	0.0819	0.4186	28.94%	27.26	24.25%	1.4461
		135	81.36	0.1373	0.4203	26.87%	25.31	21.86%	1.5642
		150	78.31	0.2269	0.3349	22.08%	20.80	17.29%	1.5172
0.2	10	120	96.62	0.0547	0.4635	26.85%	25.29	25.94%	1.7265
		135	92.31	0.1028	0.4288	25.34%	23.87	23.39%	1.6920
		150	89.51	0.1567	0.3678	22.72%	21.41	20.34%	1.6190
	13	120	89.07	0.0895	0.4359	27.01%	25.44	24.06%	1.6138
		135	84.55	0.1345	0.3876	25.46%	23.99	21.53%	1.5221
		150	80.11	0.2381	0.2849	19.72%	18.59	15.80%	1.4449

AQ, mM	pH	Temp, °C	gm lig in wood	gm ODW	gm carb wood	gm carb pulp	KC*	Selectivity**
0	10	120	0.5178	1.7856	1.2678	1.2517	0.00042	2.629
		135	0.5322	1.8350	1.3029	1.2205	0.00218	0.715
		150	0.5248	1.8097	1.2849	1.2122	0.00194	1.557
	13	120	0.5256	1.8124	1.2868	1.1624	0.00339	0.639
		135	0.5217	1.7991	1.2774	1.1237	0.00427	0.822
		150	0.5239	1.8066	1.2827	1.1381	0.00399	1.439
0.05	10	120	0.5375	1.8534	1.3159	1.2957	0.00052	2.156
		135	0.5227	1.8025	1.2798	1.1895	0.00244	0.674
		150	0.5352	1.8454	1.3102	1.2029	0.00285	1.033
	13	120	0.5438	1.8751	1.3313	1.1744	0.00418	0.356
		135	0.5597	1.9299	1.3702	1.0745	0.00810	0.315
		150	0.5287	1.8231	1.2944	1.0058	0.00841	0.559
0.1	10	120	0.4995	1.7225	1.2230	1.2174	0.00015	11.060
		135	0.5352	1.8456	1.3104	1.2512	0.00154	1.509
		150	0.5505	1.8984	1.3479	1.2430	0.00270	1.427
	13	120	0.5005	1.7259	1.2254	1.0276	0.00587	0.414
		135	0.5576	1.9226	1.3650	1.1439	0.00589	0.621
		150	0.5618	1.9374	1.3756	1.1822	0.00505	1.174
0.2	10	120	0.5182	1.7869	1.2687	1.2630	0.00015	9.573
		135	0.5316	1.8330	1.3014	1.2632	0.00099	2.689
		150	0.5245	1.8087	1.2842	1.2512	0.00087	4.748
	13	120	0.5254	1.8118	1.2864	1.1779	0.00294	0.825
		135	0.5221	1.8002	1.2781	1.1345	0.00397	0.936
		150	0.5231	1.8037	1.2806	1.1600	0.00330	1.974

NOTE: Glucose present in these experiments at a concentration of 0.06 M

* KC = first order rate constant for carbohydrate degradation, 1/minutes

** selectivity = gm lignin dissolved/gm carbohydrate dissolved

Sulfite + AQ experiments – glucose is present at a concentration of 0.06 M in these experiments. The glucose and AQ concentrations were determined only on the original liquor, not on the effluent from the reactor.

Sulfite, M	AQ, mM	pH	Temp, C	Yield, %ODW	gm lig diss	gm lig in pulp	%LODP	Hypo number	Lig Yield, %	gmODP
0.1	0.05	10	120	96.83	0.0586	0.4598	26.57%	25.02	25.72%	1.7308
			135	92.43	0.0987	0.4330	25.55%	24.07	23.62%	1.6945
			150	89.54	0.1670	0.3576	22.08%	20.81	19.77%	1.6199
		13	120	88.87	0.0685	0.4574	28.38%	26.73	25.22%	1.6117
			135	84.63	0.1110	0.4110	26.98%	25.41	22.83%	1.5234
			150	80.18	0.2200	0.3036	20.97%	19.76	16.81%	1.4476
	0.1	10	120	96.49	0.0559	0.4818	26.93%	25.37	25.99%	1.7889
			135	91.5	0.1043	0.4184	25.37%	23.90	23.21%	1.6494
			150	88.07	0.1922	0.3430	21.10%	19.89	18.58%	1.6253
		13	120	88.59	0.0651	0.4796	28.82%	27.14	25.53%	1.6641
			135	80.09	0.1551	0.4047	26.18%	24.66	20.96%	1.5460
			150	75.35	0.2504	0.2778	20.24%	19.08	15.25%	1.3723
	0.2	10	120	96.31	0.0589	0.4412	26.57%	25.02	25.59%	1.6607
			135	91.82	0.1154	0.4199	24.78%	23.34	22.75%	1.6946
			150	86.71	0.1725	0.3776	22.96%	21.63	19.90%	1.6447
		13	120	83.91	0.0782	0.4223	29.16%	27.46	24.47%	1.4481
			135	81.28	0.1551	0.4025	25.75%	24.26	20.93%	1.5628
			150	78.4	0.2894	0.2718	17.92%	16.90	14.05%	1.5172
0.5	0.05	10	120	96.82	0.0452	0.4729	27.34%	25.75	26.47%	1.7298
			135	92.27	0.0894	0.4426	26.15%	24.63	24.13%	1.6927
			150	89.61	0.1543	0.3698	22.84%	21.52	20.46%	1.6194
		13	120	88.73	0.0703	0.4551	28.31%	26.66	25.12%	1.6074
			135	84.49	0.1595	0.3626	23.84%	22.46	20.14%	1.5211
			150	80.28	0.2537	0.2829	19.04%	17.96	15.29%	1.4855
	0.1	10	120	96.6	0.0581	0.4645	26.68%	25.14	25.78%	1.7405
			135	91.48	0.1170	0.4181	24.77%	23.33	22.66%	1.6880
			150	88.27	0.1793	0.3846	22.02%	20.75	19.44%	1.6553
		13	120	88.62	0.0892	0.4699	27.50%	25.90	24.37%	1.7085
			135	79.89	0.1862	0.3424	23.51%	22.16	18.79%	1.4562
			150	75.21	0.2719	0.2272	17.55%	16.56	13.20%	1.2945
	0.2	10	120	96.28	0.0629	0.4947	26.72%	25.17	25.73%	1.8510
			135	92.12	0.1313	0.4307	24.13%	22.73	22.23%	1.7853
			150	86.39	0.2250	0.3259	19.86%	18.72	17.16%	1.6409
		13	120	84.05	0.0919	0.4263	28.38%	26.73	23.86%	1.5018
			135	81.41	0.1712	0.3883	24.72%	23.29	20.12%	1.5706
			150	78.33	0.3092	0.1912	14.15%	13.35	11.08%	1.3517

Sulfite, M	AQ, mM	pH	Temp, C	gm lig in wood	gmODW	gm carb wood	gm carb pulp	KC*	Selectivity**
0.1	0.05	10	120	0.5184	1.7875	1.2691	1.2710	0.00005	30.724
			135	0.5317	1.8333	1.3016	1.2615	0.00104	2.459
			150	0.5246	1.8091	1.2845	1.2622	0.00058	7.516
		13	120	0.5259	1.8136	1.2877	1.1543	0.00364	0.514
			135	0.5220	1.8001	1.2781	1.1124	0.00463	0.670
			150	0.5236	1.8054	1.2818	1.1440	0.00379	1.596
	0.1	10	120	0.5377	1.8540	1.3163	1.3071	0.00023	6.067
			135	0.5228	1.8026	1.2798	1.2309	0.00130	2.133
			150	0.5352	1.8455	1.3103	1.2824	0.00072	6.879
		13	120	0.5447	1.8784	1.3337	1.1844	0.00396	0.436
			135	0.5598	1.9303	1.3705	1.1413	0.00610	0.677
			150	0.5282	1.8213	1.2931	1.0946	0.00556	1.261
	0.2	10	120	0.5000	1.7243	1.2243	1.2195	0.00013	12.334
			135	0.5352	1.8456	1.3104	1.2748	0.00092	3.240
			150	0.5501	1.8968	1.3467	1.2672	0.00203	2.168
		13	120	0.5005	1.7258	1.2253	1.0258	0.00592	0.392
			135	0.5576	1.9227	1.3651	1.1603	0.00542	0.757
			150	0.5612	1.9352	1.3740	1.2454	0.00328	2.250
0.5	0.05	10	120	0.5181	1.7866	1.2685	1.2569	0.00031	3.869
			135	0.5320	1.8345	1.3025	1.2501	0.00137	1.707
			150	0.5241	1.8072	1.2831	1.2496	0.00088	4.609
		13	120	0.5254	1.8116	1.2862	1.1524	0.00366	0.525
			135	0.5221	1.8003	1.2782	1.1585	0.00328	1.332
			150	0.5366	1.8504	1.3138	1.2026	0.00295	2.282
	0.1	10	120	0.5225	1.8018	1.2793	1.2761	0.00008	18.153
			135	0.5351	1.8452	1.3101	1.2699	0.00104	2.911
			150	0.5438	1.8753	1.3315	1.2908	0.00103	4.406
		13	120	0.5591	1.9279	1.3688	1.2386	0.00333	0.685
			135	0.5286	1.8227	1.2941	1.1138	0.00500	1.032
			150	0.4991	1.7212	1.2221	1.0673	0.00451	1.757
	0.2	10	120	0.5575	1.9225	1.3650	1.3563	0.00021	7.257
			135	0.5620	1.9380	1.3760	1.3545	0.00052	6.123
			150	0.5508	1.8994	1.3486	1.3150	0.00084	6.704
		13	120	0.5182	1.7868	1.2686	1.0755	0.00550	0.476
			135	0.5595	1.9293	1.3698	1.1824	0.00490	0.914
			150	0.5005	1.7257	1.2252	1.1605	0.00181	4.776

NOTE: Glucose present in these experiments at a concentration of 0.06 M
* KC = first order rate constant for carbohydrate degradation, 1/minutes
** selectivity = gm lignin dissolved/gm carbohydrate dissolved

The table below presents representative results of determinations of anthraquinone concentrations in solution by the gas chromatographic method of Wiseman[34]. All solutions have a total volume of 1000 ml.

gm 97% AQ Powder	gm AQ actual	Target Conc'n, mM	GC Conc'n mM
0.0108	0.0104	0.0499	0.0495
0.0106	0.0103	0.0494	0.0500
0.0108	0.0104	0.0499	0.0490
0.0215	0.0209	0.1004	0.0985
0.0214	0.0208	0.1001	0.0999
0.0428	0.0415	0.1993	0.2011
0.0434	0.0421	0.2022	0.2007

The following tables present representative outlet liquor concentration profiles for sulfite concentration and pH.

Sulfite only experiments

Inlet Liquor Concentrations

Sulfite, M	0.1	0.1
pH	10	13
AQ, mM	0	0
Temp, °C	150	150

Outlet Liquor Concentrations

Time, min	Sulfite, M	pH	Sulfite, M	pH
1	0.101	10.04	0.099	12.98
2	0.099	10.00	0.101	13.00
3	0.099	10.01	0.101	13.01
4	0.101	10.00	0.098	12.99
5	0.098	10.00	0.099	12.96
6	0.098	10.02	0.097	12.94
7	0.096	9.94	0.098	12.97
8	0.094	9.98	0.099	12.96
9	0.098	9.96	0.098	12.95
10	0.099	10.00	0.099	12.98
15	0.099	10.02	0.101	12.98
20	0.099	10.00	0.099	13.01
25	0.101	10.01	0.099	13.00
30	0.099	10.03	0.099	13.00

Sulfite + AQ experiments

Inlet Liquor Concentrations

Sulfite, M	0.1	0.1
pH	10	13
AQ, mM	0.2	0.2
Temp,°C	150	150

Outlet Liquor Concentrations

Time, min	Sulfite, M	pH	Sulfite, M	pH
1	0.101	10.00	0.099	13.00
2	0.099	10.02	0.101	13.03
3	0.099	10.01	0.101	13.01
4	0.101	10.00	0.098	13.00
5	0.095	10.00	0.099	12.95
6	0.098	10.03	0.097	12.93
7	0.098	9.95	0.098	12.96
8	0.094	9.98	0.099	12.95
9	0.098	9.97	0.098	12.99
10	0.099	10.00	0.099	13.00
15	0.101	10.00	0.101	13.00
20	0.099	10.01	0.099	13.01
25	0.101	10.00	0.099	12.99
30	0.099	10.03	0.099	12.98

APPENDIX 3

FORTRAN PROGRAM USED FOR MATHEMATICAL MODELING

The source code for the solution of the differential equations which describe the flow and kinetic behavior of the reactor is listed below.

```
#FILE (KBIASCA)OVERALL/MODEL2 ON STUDENTS
100 $SET ERRLIST OWN LINEINFO
200 $RESET FREE LIST
300 FILE  6(KIND=REMOTE,MAXRECSIZE=22,BLOCKSIZE=22,MYUSE=IO)
400 FILE  8(KIND=PRINTER)
500 FILE
65(KIND=DISK,TITLE='OUTPUT',MYUSE=OUT,PROTECTION=SAVE)
600 FILE
67(KIND=DISK,TITLE='OUTLET/PREDICT',MYUSE=OUT,PROTECTION=SA
VE)
700 FILE
69(KIND=DISK,TITLE='MODEL/DATA',MYUSE=IN,PROTECTION=SAVE,
800     &  DEPENDENTSPECS=TRUE)
900 $ INCLUDE "*IMSL/UERSET"
1000 $ INCLUDE "*IMSL/UERTST"
1100 $ INCLUDE "*IMSL/UGETIO"
1200 $ INCLUDE "*IMSL/ZSRCH"
1300 $ INCLUDE "*IMSL/ZXMJN"
1400 $ INCLUDE "*IMSL/ZXMWE"
1500 $ INCLUDE "*IMSL/DVERK"
1600 $ INCLUDE "*IMSL/USPKD"
1700 $ INCLUDE "SUB/CSTR5/OH3"
1800 $ INCLUDE "PARAMETER/VALUES"
2100      EXTERNAL FCN
2200 $ INCLUDE "MODEL/COMMON"
2300       DIMENSION WORK(100),IWORK(4),C(24),W(7,10),Y(7),TEMP(30,50),
2400     &
CLIG(30),CLIGIN(50),TOTSO3(50),TEMPK(30,50),MFLIG(30,50),PHIN(50)
2700      TOL=0.0001
2800      IND=1
2900      N=7
```

```
3000      NW=7
3200      READ(69,/)NR
3300      DO 5 I1=1,NR
3400       READ(69,/)TOTSO3(I1),PHIN(I1),AQIN(I1),CLIGIN(I1)
3500        DO 10 I=1,30
3600         READ(69,/)TEMP(I,I1),MFLIG(I,I1)
3800         TEMPK(I,I1)=TEMP(I,I1)+273.15
4200   10    CONTINUE
4300    5  CONTINUE
4330      DO 28 MN=10,20,5
4340       A(1)=MN*10**12
4350      DO 29 M=260,285,5
4360       AE(1)=M*100.
4400              SSR=0
4500               DO 100 NN=1,NR
4600                IND=1
4700                X=0
4710                 OH(NN)=10**(PHIN(NN)-14)
4720                 SO3(NN)=TOTSO3(NN)
4800                Y(1)=CLIGIN(NN)/0.1
4900                Y(2)=0.0
5000                Y(3)=0.0
5100                Y(4)=0.0
5200                Y(5)=0.0
5300                Y(6)=0.0
5400                Y(7)=0.0
5700               DO 30 L=1,30
5800                TK(L)=TEMPK(L,NN)
5900                CLIG(L)=MFLIG(L,NN)
6300                XEND=FLOAT(L)
7100                 CALL DVERK(N,FCN,X,Y,XEND,TOL,IND,C,NW,W,IER)
7200                IF (IND.LT.0.OR.IER.GT.0) GOTO 20
7300                 SSR=SSR+(CLIG(L)-Y(7))**2
7399 C               WRITE(6,/)L,CLIG(L),Y(7)
7400   30            CONTINUE
7500  100             CONTINUE
7600           WRITE(65,/)A(1),AE(1),SSR
7700   29      CONTINUE
7800   28     CONTINUE
7900   27    CONTINUE
```

```
8000  26 CONTINUE
8100     STOP
8200  20 CONTINUE
8300      WRITE(6,227)IND,TOL,N,W,Y(1),Y(2)
8400  227 FORMAT(4F15.8)
8500     STOP
8600     END
```

Following is the subroutine containing the form of the differential equations; this subroutine is called by the IMSL routine DVERK.

```
#FILE (KBIASCA)SUB/CSTR5/OH3 ON STUDENTS
8700      SUBROUTINE FCN(N,X,Y,YPRIME)
8800 $ INCLUDE "MODEL/COMMON"
8900      REAL TAU,L0,K,K1,K2,K3,K4,K5,K6,K7,K8,K9,R,YPRIME(7),Y(7)
9000     DATA L0,TAU,R/0,0.4,1.98/
9100     K1=A(1)*EXP(-AE(1)/(R*TK(L)))
10000     YPRIME(1)=-K1*Y(1)
10200     YPRIME(3)=(L0-Y(3))/TAU+K1*Y(1)
10500     YPRIME(4)=(Y(3)-Y(4))/TAU+K1*Y(1)
10800     YPRIME(5)=(Y(4)-Y(5))/TAU+K1*Y(1)
11100     YPRIME(6)=(Y(5)-Y(6))/TAU+K1*Y(1)
11400     YPRIME(7)=(Y(6)-Y(7))/TAU+K1*Y(1)
11700     RETURN
11800     END
```

The common block containing all variables shared by different parts of the program is listed below.

```
FILE (KBIASCA)MODEL/COMMON ON STUDENTS
10500     COMMON
10800     &       SO3IN(30,50)
10810     &,      HSO3IN(30,50)
10820     &,      SO3(30)
10830     &,      HSO3(30)
10900     &,      AQIN(50)
11000     &,      TK(30)
11500     &,      DP(5)
11800     &,      L
```

```
11900   &,    NN
12000   &,    CY(30)
12100   &,    A(10)
12200   &,    AE(10)
12300   &,    OH(30)
```

An example data file is listed below. Each data file contains information on three experiments at three different temperatures (120°C, 135°C, and 150°C) with the liquor composition information on the first line for each experiment.

```
#FILE (KBIASCA)SAQ/DATA/A1/S1/PH13/CORR ON STUDENTS
100 3,  %Number of experiments in this data file
200 0.1, 13.02, 0.1, 0.51934,  %[SO3], liquor pH, AQ (mM), initial grams of lignin
300 35.0, 0.01372995,
400 48.0, 0.01354248,
500 59.0, 0.01062433,
600 74.0, 0.00732783,
700 83.0, 0.01066148,
800 98.0, 0.00684661,
900 116.0, 0.08278563,
1000 119.0, 0.151469930001,
1100 120.0, 0.213119260001,
1200 120.0, 0.20185336,
1300 120.0, 0.2228641,
1400 121.0, 0.22506943,
1500 120.0, 0.19764346,
1600 121.0, 0.156779180001,
1700 121.0, 0.218969539999,
1800 122.0, 0.19638033,
1900 121.0, 0.152012320001,
2000 120.0, 0.19651783,
2100 121.0, 0.1943785,
2200 121.0, 0.146540739999,
2300 122.0, 0.21749651,
2400 122.0, 0.217950280001,
2500 122.0, 0.2300416,
2600 121.0, 0.15514065,
```

2700 120.0, 0.196444929999,
2800 119.0, 0.09539287,
2900 119.0, 0.164774749999,
3000 119.0, 0.130701960001,
3100 119.0, 0.08156582,
3200 120.0, 0.169333330001,
3300 0.1, 13.05, 0.1, 0.56101, %[SO3], liquor pH, AQ (mM), initial grams of lignin
3400 26.0, 0.01329539,
3500 43.0, 0.00233211,
3600 77.0, 0.02591748,
3700 100.0, 0.04286189,
3800 115.0, 0.07609657,
3900 123.0, 0.14112858,
4000 130.0, 0.220688449999,
4100 133.0, 0.326597990001,
4200 136.0, 0.414402390001,
4300 135.0, 0.519494509999,
4400 135.0, 0.466889830001,
4500 134.0, 0.46973402,
4600 135.0, 0.395762689999,
4700 135.0, 0.40532912,
4800 135.0, 0.4297583,
4900 134.0, 0.37208073,
5000 136.0, 0.37863752,
5100 135.0, 0.28442106,
5200 136.0, 0.33894792,
5300 136.0, 0.431922350001,
5400 135.0, 0.33496715,
5500 135.0, 0.296112669999,
5600 136.0, 0.339990410001,
5700 134.0, 0.27714701,
5800 135.0, 0.266662579999,
5900 135.0, 0.213720989999,
6000 135.0, 0.30093152,
6100 135.0, 0.262608360001,
6200 134.0, 0.219385619999,
6300 135.0, 0.21689707,
6400 0.1, 13.02, 0.1, 0.54267, %[SO3], liquor pH, AQ (mM), initial grams of lignin

6500 35.0, 0.01275558,
6600 51.0, 0.01004353,
6700 75.0, 0.01257739,
6800 97.0, 0.03456319,
6900 119.0, 0.1349875,
7000 131.0, 0.267821429999,
7100 138.0, 0.481642729999,
7200 144.0, 0.70144677,
7300 148.0, 1.01359954001,
7400 150.0, 1.14717465,
7500 152.0, 1.28156901999,
7600 151.0, 1.20256131999,
7700 150.0, 0.837129,
7800 151.0, 0.8318593,
7900 150.0, 0.80061554,
8000 150.0, 0.69211356,
8100 150.0, 0.68193382,
8200 151.0, 0.67238217,
8300 151.0, 0.61272328,
8400 150.0, 0.57959692,
8500 149.0, 0.48507658,
8600 150.0, 0.486289160001,
8700 150.0, 0.443911419999,
8800 150.0, 0.41285294,
8900 151.0, 0.354894419999,
9000 151.0, 0.34654778,
9100 150.0, 0.3282434,
9200 150.0, 0.2618423,
9300 150.0, 0.335152240001,
9400 149.0, 0.26218064,

Appendix 4

Analysis of Variance on Delignification Rate Constants

Analysis of Variance for Delignification Rate Constants – Sulfite only experiments

Source	DF	Sum–Squares	Mean–Square	F-Ratio
A (Sulfite)	2	1.436E-06	7.180E-07	38.3**
B (pH)	1	1.050E-05	1.050E-05	560**
AB	2	8.356E-07	4.178E-07	22.3**
C (Temperature)	2	4.784E-05	2.392E-05	1275**
AC	4	3.460E-07	8.651E-08	4.6
BC	2	1.855E-06	9.277E-07	49**
ABC	4	7.505E-08	1.876E-08	
TOTAL(Adj)	17	6.289E-05		

** = significant at the 99% confidence level

Table Of Means

Term	Value	Count	Mean
Grand Mean		18	0.0036
A: SULFITE			
	0	6	0.0038
	.1	6	0.0034
	.5	6	0.0040
B: PH			
	10	9	0.0028
	13	9	0.0044
C: TEMPERATURE			
	120	6	0.0016
	135	6	0.0036
	150	6	0.0056
AB: SULFITE,PH			
	0,10	3	0.0029
	0,13	3	0.0039
	.1,10	3	0.0027
	.1,13	3	0.0041
	.5,10	3	0.0030
	.5,13	3	0.0051

Term	Value	Count	Mean
AC: SULFITE,TEMPERATURE			
	0,120	2	0.0015
	0,135	2	0.0035
	0,150	2	0.0052
	.1,120	2	0.0016
	.1,135	2	0.0034
	.1,150	2	0.0054
	.5,120	2	0.0018
	.5,135	2	0.0039
	.5,150	2	0.0063
BC: PH,TEMPERATURE			
	10,120	3	0.0013
	10,135	3	0.0026
	10,150	3	0.0046
	13,120	3	0.0019
	13,135	3	0.0046
	13,150	3	0.0066
ABC: SULFITE,PH,TEMPERATURE			
	0,10,120	1	0.0013
	0,10,135	1	0.0027
	0,10,150	1	0.0045
	0,13,120	1	0.0016
	0,13,135	1	0.0042
	0,13,150	1	0.0059
	.1,10,120	1	0.0013
	.1,10,135	1	0.0024
	.1,10,150	1	0.0045
	.1,13,120	1	0.0018
	.1,13,135	1	0.0044
	.1,13,150	1	0.0062
	.5,10,120	1	0.0014
	.5,10,135	1	0.0026
	.5,10,150	1	0.0049
	.5,13,120	1	0.0023
	.5,13,135	1	0.0052
	.5,13,150	1	0.0077

Analysis of Variance for Delignification Rate Constants – AQ only experiments

Source	DF	Sum–Squares	Mean–Square	F-Ratio
A (AQ)	3	3.230E-06	1.076E-06	16.1**
B (pH)	1	3.141E-05	3.141E-05	470.6**
AB	3	1.732E-06	5.774E-07	8.65*
C (Temperature)	2	1.041E-04	5.208E-05	780.3**
AC	6	5.769E-07	9.615E-08	<1.0
BC	2	6.773E-06	3.386E-06	50.7**
ABC	6	4.004E-07	6.674E-08	
TOTAL(Adj)	23	1.483E-04		

** = significant at the 99% confidence level

* = significant at the 95% confidence level

Table of Means

Term	Value	Count	Mean
Grand Mean		24	0.0049
A: AQ			
	0	6	0.0044
	.05	6	0.0047
	.1	6	0.0051
	.2	6	0.0054
B: PH			
	10	12	0.0037
	13	12	0.0060
C: TEMPERATURE			
	120	8	0.0025
	135	8	0.0045
	150	8	0.0076
AB: AQ,PH			
	0,10	3	0.0029
	0,13	3	0.0059
	.05,10	3	0.0040
	.05,13	3	0.0055
	.1,10	3	0.0040
	.1,13	3	0.0062
	.2,10	3	0.0041
	.2,13	3	0.0066

Term	Value	Count	Mean
AC: AQ,TEMPERATURE			
	0,120	2	0.0023
	0,135	2	0.0041
	0,150	2	0.0068
	.05,120	2	0.0025
	.05,135	2	0.0043
	.05,150	2	0.0073
	.1,120	2	0.0026
	.1,135	2	0.0046
	.1,150	2	0.0079
	.2,120	2	0.0028
	.2,135	2	0.0049
	.2,150	2	0.0083
BC: PH,TEMPERATURE			
	10,120	4	0.0020
	10,135	4	0.0035
	10,150	4	0.0058
	13,120	4	0.0031
	13,135	4	0.0055
	13,150	4	0.0094
ABC: AQ,PH,TEMPERATURE			
	0,10,120	1	0.0015
	0,10,135	1	0.0028
	0,10,150	1	0.0044
	0,13,120	1	0.0030
	0,13,135	1	0.0054
	0,13,150	1	0.0092
	.05,10,120	1	0.0021
	.05,10,135	1	0.0037
	.05,10,150	1	0.0062
	.05,13,120	1	0.0028
	.05,13,135	1	0.0050
	.05,13,150	1	0.0085
	.1,10,120	1	0.0021
	.1,10,135	1	0.0036
	.1,10,150	1	0.0062
	.1,13,120	1	0.0031
	.1,13,135	1	0.0056
	.1,13,150	1	0.0098

Term	Value	Count	Mean
ABC: AQ,PH,TEMPERATURE			
	.2,10,120	1	0.0022
	.2,10,135	1	0.0038
	.2,10,150	1	0.0063
	.2,13,120	1	0.0035
	.2,13,135	1	0.0061
	.2,13,150	1	0.0103

Analysis of Variance for Delignification Rate Constants – Sulfite + AQ experiments

Source	DF	Sum-Squares	Mean-Square	F-Ratio
A (Sulfite)	1	4.141E-06	4.141E-06	169**
B (AQ)	2	1.042E-05	5.214E-06	213**
AB	2	5.424E-07	2.712E-07	11.1
C (pH)	1	5.114E-05	5.114E-05	2088**
AC	1	1.388E-06	1.388E-06	57**
BC	2	1.020E-06	5.101E-07	20.8**
ABC	2	5.414E-07	2.707E-07	11.0
D (Temperature)	2	3.378E-04	1.689E-04	6897**
AD	2	1.160E-06	5.802E-07	23.7**
BD	4	3.125E-06	7.812E-07	31.9**
ABD	4	1.621E-07	4.054E-08	1.66
CD	2	1.502E-05	7.514E-06	307**
ACD	2	3.866E-07	1.933E-07	7.9
BCD	4	3.557E-07	8.894E-08	3.6
ABCD	4	9.798E-08	2.449E-08	
TOTAL(Adj)	35	4.273E-04		

** = significant at the 99% confidence level

Table of Means

Term	Value	Count	Mean
ALL		36	0.0059
A: SO3			
	.1	18	0.0056
	.5	18	0.0062
B: AQ			
	.05	12	0.0052
	.1	12	0.0059
	.2	12	0.0066
C: PH			
	10	18	0.0047
	13	18	0.0071
D: TEMPERATURE			
	120	12	0.0026
	135	12	0.0052
	150	12	0.010

Term	Value	Count	Mean
AB: SO3,AQ			
.1,.05	6	5.068E-03	
	.1,.1	6	0.0055
	.1,.2	6	0.0061
	.5,.05	6	0.0054
	.5,.1	6	0.0063
	.5,.2	6	0.0070
AC: SO3,PH			
	.1,10	9	0.0046
	.1,13	9	0.0066
	.5,10	9	0.0048
	.5,13	9	0.0076
BC: AQ,PH			
	.05,10	6	0.0043
	.05,13	6	0.0062
	.1,10	6	0.0047
	.1,13	6	0.0071
	.2,10	6	0.0052
	.2,13	6	0.0079
AD: SO3,TEMPERATURE			
	.1,120	6	0.0024
	.1,135	6	0.0049
	.1,150	6	0.0094
	.5,120	6	0.0027
	.5,135	6	0.0055
	.5,150	6	0.011
BD: AQ,TEMPERATURE			
	.05,120	4	0.0023
	.05,135	4	0.0046
	.05,150	4	0.0088
	.1,120	4	0.0026
	.1,135	4	0.0052
	.1,150	4	0.010
	.2,120	4	0.0028
	.2,135	4	0.0057
	.2,150	4	0.011
ABC: SO3,AQ,PH			
	.5,.2,10	3	0.0056
	.5,.2,13	3	0.0084

Term	Value	Count	Mean
ABD:	SO3,AQ,TEMPERATURE		
	.1,.05,120	2	0.0022
	.1,.05,135	2	0.0045
	.1,.05,150	2	0.0085
	.1,.1,120	2	0.0024
	.1,.1,135	2	0.0048
	.1,.1,150	2	0.0092
	.1,.2,120	2	0.0026
	.1,.2,135	2	0.0054
	.1,.2,150	2	0.010
	.5,.05,120	2	0.0024
	.5,.05,135	2	0.0047
	.5,.05,150	2	0.0091
	.5,.1,120	2	0.0027
	.5,.1,135	2	0.0055
	.5,.1,150	2	0.011
	.5,.2,120	2	0.0030
	.5,.2,135	2	0.0061
	.5,.2,150	2	0.012
ACD:	SO3,PH,TEMPERATURE		
	.1,10,120	3	0.0020
	.1,10,135	3	0.0040
	.1,10,150	3	0.0077
	.1,13,120	3	0.0028
	.1,13,135	3	0.0057
	.1,13,150	3	0.011
	.5,10,120	3	0.0021
	.5,10,135	3	0.0043
	.5,10,150	3	0.0081
	.5,13,120	3	0.0033
	.5,13,135	3	0.0067
	.5,13,150	3	0.013

Term	Value	Count	Mean
BCD: AQ,PH,TEMPERATURE			
	.05,10,120	2	0.0019
	.05,10,135	2	0.0037
	.05,10,150	2	0.0072
	.05,13,120	2	0.0027
	.05,13,135	2	0.0055
	.05,13,150	2	0.010
	.1,10,120	2	0.0021
	.1,10,135	2	0.0041
	.1,10,150	2	0.0079
	.1,13,120	2	0.0031
	.1,13,135	2	0.0062
	.1,13,150	2	0.012
	.2,10,120	2	0.0023
	.2,10,135	2	0.0045
	.2,10,150	2	0.0087
	.2,13,120	2	0.0034
	.2,13,135	2	0.0069
	.2,13,150	2	0.014
ABCD: SO3,AQ,PH,TEMPERATURE			
	.1,.05,10,120	1	0.0020
	.1,.05,10,135	1	0.0039
	.1,.05,10,150	1	0.0074
	.1,.05,13,120	1	0.0025
	.1,.05,13,135	1	0.0050
	.1,.05,13,150	1	0.0097
	.1,.1,10,120	1	0.0020
	.1,.1,10,135	1	0.0040
	.1,.1,10,150	1	0.0075
	.1,.1,13,120	1	0.0028
	.1,.1,13,135	1	0.0057
	.1,.1,13,150	1	0.0110
	.1,.2,10,120	1	0.0021
	.1,.2,10,135	1	0.0042
	.1,.2,10,150	1	0.0080
	.1,.2,13,120	1	0.0032
	.1,.2,13,135	1	0.0065
	.1,.2,13,150	1	0.013
	.5,.05,10,120	1	0.0018

Term	Value	Count	
ABCD:	SO3,AQ,PH,TEMPERATURE		
	.5,.05,10,135	1	0.0036
	.5,.05,10,150	1	0.0069
	.5,.05,13,120	1	0.0029
	.5,.05,13,135	1	0.0059
	.5,.05,13,150	1	0.011
	.5,.1,10,120	1	0.0021
	.5,.1,10,135	1	0.0043
	.5,.1,10,150	1	0.0082
	.5,.1,13,120	1	0.0033
	.5,.1,13,135	1	0.0068
	.5,.1,13,150	1	0.013
	.5,.2,10,120	1	0.0024
	.5,.2,10,135	1	0.0049
	.5,.2,10,150	1	0.0094
	.5,.2,13,120	1	0.0036
	.5,.2,13,135	1	0.0073
	.5,.2,13,150	1	0.014

Appendix 5

Analysis of Variance on Intercept

Analysis of Variance for Intercept

Source	DF	Sum–Squares	Mean–Square	F-Ratio
A(MODEL)	20	3.380E-05	1.690E-06	0.36
ERROR	42	1.959E-04	4.666E-06	
TOTAL(Adj)	62	2.297E-04		

Table of Means for Intercept

Term	Value	Count	Mean
ALL		63	0.0036
A: MODEL			
	1	3	0.0026
	2	3	0.0028
	3	3	0.0032
	4	3	0.0031
	5	3	0.0028
	6	3	0.0028
	7	3	0.0033
	8	3	0.0032
	9	3	0.0042
	10	3	0.0037
	11	3	0.0047
	12	3	0.0043
	13	3	0.0032
	14	3	0.0023
	15	3	0.0044
	16	3	0.0051
	17	3	0.0042
	18	3	0.0043
	19	3	0.0037
	20	3	0.0037
	21	3	0.0031

APPENDIX 6

ANALYSIS OF VARIANCE ON CARBOHYDRATE DEGRADATION

RATE CONTANTS

NOTE: F–ratios have been tabulated only when significant at the 95% level or higher.

Analysis of Variance for Carbohydrate Degradation Rate Constants – Sulfite Only Experiments

Source	DF	Sum-Squares	Mean-Square	F-Ratio
A(SULFITE)	2	5.031E-06	2.516E-06	
B(PH)	1	8.196E-05	8.196E-05	91.73**
AB	2	1.367E-06	6.835E-07	
C(TEMP)	2	1.363E-05	6.815E-06	7.63*
AC	4	3.467E-06	8.668E-07	
BC	2	4.223E-07	2.112E-07	
ABC	4	3.574E-06	8.935E-07	
TOTAL(Adj)	17	1.094E-04		

** = significant at the 99% confidence level
* = significant at the 95% confidence level

Table of Means

Term	Value	Count	Mean
Grand Mean		18	0.004
A: SULFITE			
	0	6	0.0032
	0.1	6	0.0044
	0.5	6	0.0042
B: PH			
	10	9	0.0018
	13	9	0.0061
C: TEMP			
	120	6	0.0027
	135	6	0.0045
	150	6	0.0046
AB: SULFITE,PH			
	0,10	3	0.0014
	0,13	3	0.005
	.1,10	3	0.0019
	.1,13	3	0.0069
	.5,10	3	0.0021
	.5,13	3	0.0064

Term	Value	Count	Mean
AC: SULFITE,TEMP			
	0,120	2	0.0024
	0,135	2	0.0038
	0,150	2	0.0035
	.1,120	2	0.0023
	.1,135	2	0.0053
	.1,150	2	0.0056
	.5,120	2	0.0035
	.5,135	2	0.0045
	.5,150	2	0.0048
BC: PH,TEMP			
	10,120	3	0.0053
	10,135	3	0.0022
	10,150	3	0.0027
	13,120	3	0.0049
	13,135	3	0.0068
	13,150	3	0.0066

Term	Value	Count	Mean
ABC: SULFITE,PH,TEMP			
	0,10,120	1	0.0005
	0,10,135	1	0.002
	0,10,150	1	0.0017
	0,13,120	1	0.0042
	0,13,135	1	0.0055
	0,13,150	1	0.0054
	.1,10,120	1	0.0005
	.1,10,135	1	0.0025
	.1,10,150	1	0.0029
	.1,13,120	1	0.0042
	.1,13,135	1	0.0081
	.1,13,150	1	0.0084
	.5,10,120	1	0.0006
	.5,10,135	1	0.0021
	.5,10,150	1	0.0036
	.5,13,120	1	0.0063
	.5,13,135	1	0.0068
	.5,13,150	1	0.0059

Analysis of Variance for Carbohydrate Degradation Rate Constants – AQ Only Experiments

Source	DF	Sum-Squares	Mean-Square	F-Ratio
A(AQ)	3	1.915E-05	6.386E-06	9.89**
B(PH)	1	7.565E-05	7.565E-05	8.73*
AB	3	6.593E-06	2.197E-06	
C(TEMP)	2	1.126E-05	5.633E-06	117.18**
AC	6	5.360E-06	8.934E-07	
BC	2	6.167E-07	3.083E-07	
ABC	6	3.873E-06	6.456E-07	
TOTAL(Adj)	23	1.225E-04		

** = significant at the 99% confidence level

* = significant at the 95% confidence level

Table of Means

Term	Value	Count	Mean
Grand Mean		24	0.0032
A: AQ			
	0	6	0.0027
	0.05	6	0.0044
	0.1	6	0.0035
	0.2	6	0.0020
B: PH			
	10	12	0.0014
	13	12	0.0049
C: TEMP			
	120	8	0.0022
	135	8	0.0037
	150	8	0.0036

AB: AQ,PH			
	0,10	3	0.0015
	0,13	3	0.0039
	.05,10	3	0.0019
	.05,13	3	0.0069
	.1,10	3	0.0015
	.1,13	3	0.0056
	.2,10	3	0.0007
	.2,13	3	0.0034
Term	Value	Count	Mean
AC: AQ,TEMP			
	0,120	2	0.0019
	0,135	2	0.0032
	0,150	2	0.0030
	.05,120	2	0.0024
	.05,135	2	0.0053
	.05,150	2	0.0056
	.1,120	2	0.0030
	.1,135	2	0.0037
	.1,150	2	0.0039
	.2,120	2	0.0015
	.2,135	2	0.0025
	.2,150	2	0.0021
BC: PH,TEMP			
	10,120	4	0.0003
	10,135	4	0.0018
	10,150	4	0.0021
	13,120	4	0.0041
	13,135	4	0.0056
	13,150	4	0.0052

Term	Value	Count	Mean
ABC: AQ,PH,TEMP			
	0,10,120	1	0.0004
	0,10,135	1	0.0022
	0,10,150	1	0.0019
	0,13,120	1	0.0034
	0,13,135	1	0.0043
	0,13,150	1	0.0040
	.05,10,120	1	0.0005
	.05,10,135	1	0.0024
	.05,10,150	1	0.0029
	.05,13,120	1	0.0042
	.05,13,135	1	0.0081
	.05,13,150	1	0.0084
	.1,10,120	1	0.0002
	.1,10,135	1	0.0015
	.1,10,150	1	0.0027
	.1,13,120	1	0.0059
	.1,13,135	1	0.0059
	.1,13,150	1	0.0051
	.2,10,120	1	0.0002
	.2,10,135	1	0.0010
	.2,10,150	1	0.0009
	.2,13,120	1	0.0029
	.2,13,135	1	0.0040
	.2,13,150	1	0.0033

Analysis of Variance for Carbohydrate Degradation Rate Constants – Sulfite + AQ Experiments

Source	DF	Sum-Squares	Mean-Square	F-Ratio
A(SO3)	1	1.406E-07	1.406E-07	
B(AQ)	2	3.174E-07	1.587E-07	
AB	2	3.737E-06	1.868E-06	
C(PH)	1	1.138E-04	1.138E-04	94.8**
AC	1	4.769E-08	4.769E-08	
BC	2	1.016E-06	5.084E-07	
ABC	2	2.144E-06	1.072E-06	
D(TEMP)	2	3.656E-06	1.828E-06	
AD	2	4.392E-07	2.196E-07	
BD	4	1.649E-06	4.122E-07	
ABD	4	3.262E-06	8.156E-07	
CD	2	3.962E-06	1.981E-06	
ACD	2	3.425E-08	1.712E-08	
BCD	4	3.082E-06	7.707E-07	
ABCD	4	4.802E-06	1.200E-06	
TOTAL(Adj)	35	1.421E-04		

** = significant at the 99% confidence level

Term	Value	Count	Mean
Grand Mean		36	0.0025
A: SO3			
	0.1	18	0.0026
	0.5	18	0.0025
B: AQ			
	0.05	12	0.0026
	0.1	12	0.0025
	0.2	12	0.0024
C: PH			
	10	18	0.0007
	13	18	0.0043

Term	Value	Count	Mean
D: TEMP			
	120	12	0.0022
	135	12	0.0030
	150	12	0.0023
AB: SO3,AQ			
	.1,.05	6	0.0023
	.1,.1	6	0.0030
	.1,.2	6	0.0025
	.5,.05	6	0.0030
	.5,.1	6	0.0021
	.5,.2	6	0.0023
AC: SO3,PH			
	.1,10	9	0.0008
	.1,13	9	0.0044
	.5,10	9	0.0007
	.5,13	9	0.0042
BC: AQ,PH			
	.05,10	6	0.0006
	.05,13	6	0.0046
	.1,10	6	0.0009
	.1,13	6	0.0041
	.2,10	6	0.0006
	.2,13	6	0.0042
AD: SO3,TEMP			
	.1,120	6	0.0022
	.1,135	6	0.0030
	.1,150	6	0.0025
	.5,120	6	0.0023
	.5,135	6	0.0029
	.5,150	6	0.0021

Term	Value	Count	Mean
BD: AQ,TEMP			
	.05,120	4	0.0020
	.05,135	4	0.0033
	.05,150	4	0.0027
	.1,120	4	0.0025
	.1,135	4	0.0027
	.1,150	4	0.0023
	.2,120	4	0.0023
	.2,135	4	0.0029
	.2,150	4	0.0020
CD: PH,TEMP			
	10,120	6	0.0002
	10,135	6	0.0010
	10,150	6	0.0010
	13,120	6	0.0043
	13,135	6	0.0049
	13,150	6	0.0037
ABC: SO3,AQ,PH			
	.1,.05,10	3	0.0005
	.1,.05,13	3	0.0040
	.1,.1,10	3	0.0010
	.1,.1,13	3	0.0049
	.1,.2,10	3	0.0007
	.1,.2,13	3	0.0043
	.5,.05,10	3	0.0007
	.5,.05,13	3	0.0052
	.5,.1,10	3	0.0009
	.5,.1,13	3	0.0033
	.5,.2,10	3	0.0005
	.5,.2,13	3	0.0041

Term	Value	Count	Mean
ABD: SO3,AQ,TEMP			
	.1,.05,120	2	0.0018
	.1,.05,135	2	0.0028
	.1,.05,150	2	0.0022
	.1,.1,120	2	0.0030
	.1,.1,135	2	0.0032
	.1,.1,150	2	0.0027
	.1,.2,120	2	0.0017
	.1,.2,135	2	0.0030
	.1,.2,150	2	0.0028
	.5,.05,120	2	0.0021
	.5,.05,135	2	0.0037
	.5,.05,150	2	0.0031
	.5,.1,120	2	0.0020
	.5,.1,135	2	0.0023
	.5,.1,150	2	0.0019
	.5,.2,120	2	0.0029
	.5,.2,135	2	0.0027
	.5,.2,150	2	0.0013
ACD: SO3,PH,TEMP			
	.1,10,120	3	0.0001
	.1,10,135	3	0.0010
	.1,10,150	3	0.0012
	.1,13,120	3	0.0043
	.1,13,135	3	0.0050
	.1,13,150	3	0.0039
	.5,10,120	3	0.0003
	.5,10,135	3	0.0011
	.5,10,150	3	0.0008
	.5,13,120	3	0.0044
	.5,13,135	3	0.0048
	.5,13,150	3	0.0034

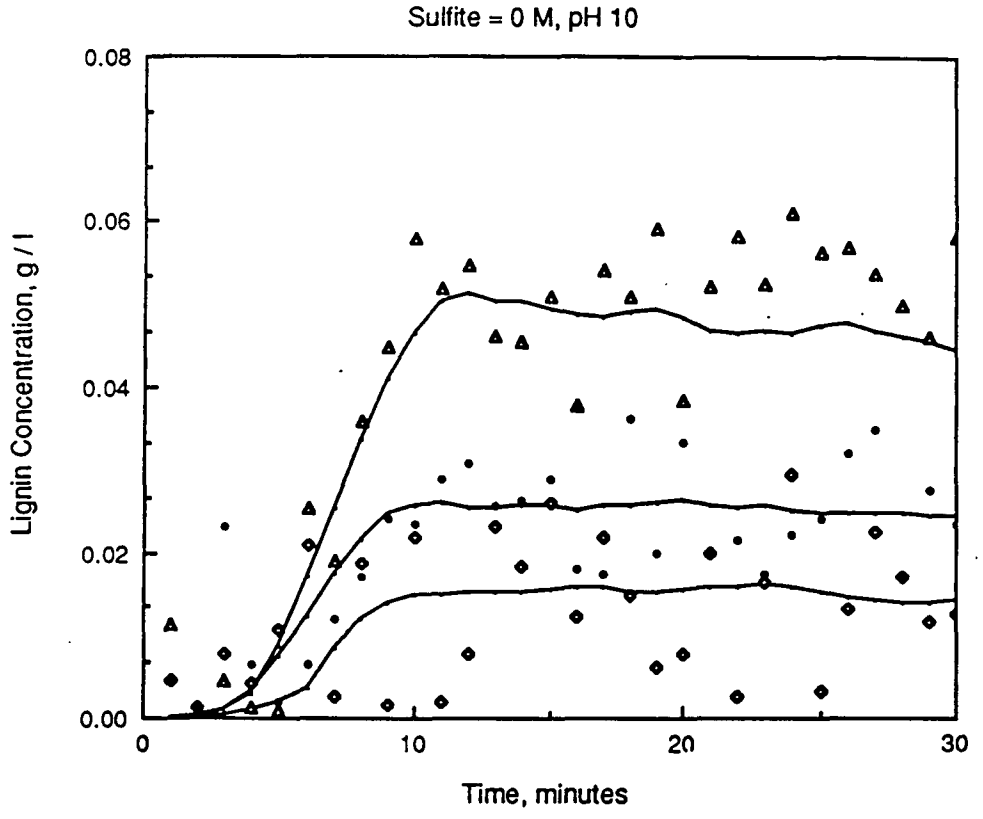
Term	Value	Count	Mean
BCD: AQ,PH,TEMP			
	.05,10,120	2	0.0001
	.05,10,135	2	0.0012
	.05,10,150	2	0.0007
	.05,13,120	2	0.0038
	.05,13,135	2	0.0054
	.05,13,150	2	0.0047
	.1,10,120	2	0.0002
	.1,10,135	2	0.0011
	.1,10,150	2	0.0015
	.1,13,120	2	0.0048
	.1,13,135	2	0.0044
	.1,13,150	2	0.0031
	.2,10,120	2	0.0001
	.2,10,135	2	0.0008
	.2,10,150	2	0.0009
	.2,13,120	2	0.0044
	.2,13,135	2	0.0050
	.2,13,150	2	0.0032
ABCD: SO3,AQ,PH,TEMP			
	.1,.05,10,120	1	0.0000
	.1,.05,10,135	1	0.0010
	.1,.05,10,150	1	0.0006
	.1,.05,13,120	1	0.0036
	.1,.05,13,135	1	0.0046
	.1,.05,13,150	1	0.0038
	.1,.1,10,120	1	0.0001
	.1,.1,10,135	1	0.0009
	.1,.1,10,150	1	0.0020
	.1,.1,13,120	1	0.0059
	.1,.1,13,135	1	0.0054
	.1,.1,13,150	1	0.0033
	.1,.2,10,120	1	0.0001
	.1,.2,10,135	1	0.0010
	.1,.2,10,150	1	0.0010
	.1,.2,13,120	1	0.0033

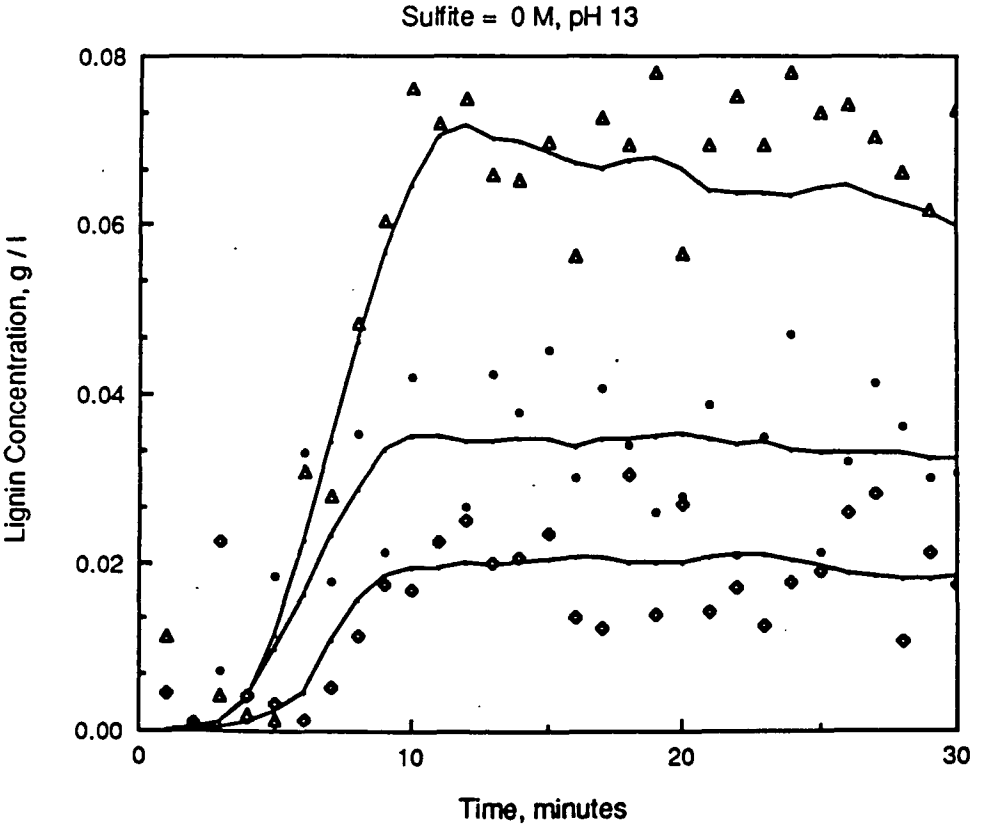
Term	Value	Count	Mean
ABCD:	SO3,AQ,PH,TEMP		
	.1,.2,13,135	1	0.0050
	.1,.2,13,150	1	0.0045
	.5,.05,10,120	1	0.0002
	.5,.05,10,135	1	0.0013
	.5,.05,10,150	1	0.0007
	.5,.05,13,120	1	0.0040
	.5,.05,13,135	1	0.0061
	.5,.05,13,150	1	0.0056
	.5,.1,10,120	1	0.0003
	.5,.1,10,135	1	0.0014
	.5,.1,10,150	1	0.0009
	.5,.1,13,120	1	0.0037
	.5,.1,13,135	1	0.0033
	.5,.1,13,150	1	0.0030
	.5,.2,10,120	1	0.0002
	.5,.2,10,135	1	0.0005
	.5,.2,10,150	1	0.0008
	.5,.2,13,120	1	0.0055
	.5,.2,13,135	1	0.0049
	.5,.2,13,150	1	0.0018

APPENDIX 7

PLOTS OF EXPERIMENTAL DATA

The following figures contain the experimental data plotted with predicted lignin concentration profiles. The symbols represent the three temperatures used in the experiments: diamonds are for 120°C, filled circles are for 135°C, and triangles are for 150°C.


Sulfite = 0 M, pH 10
Lignin Concentration, g / l
0.08
0.06
0.04
0.02
0.00
0
10
20
30
Time, minutes


Sulfite = 0 M, pH 13
Lignin Concentration, g / l
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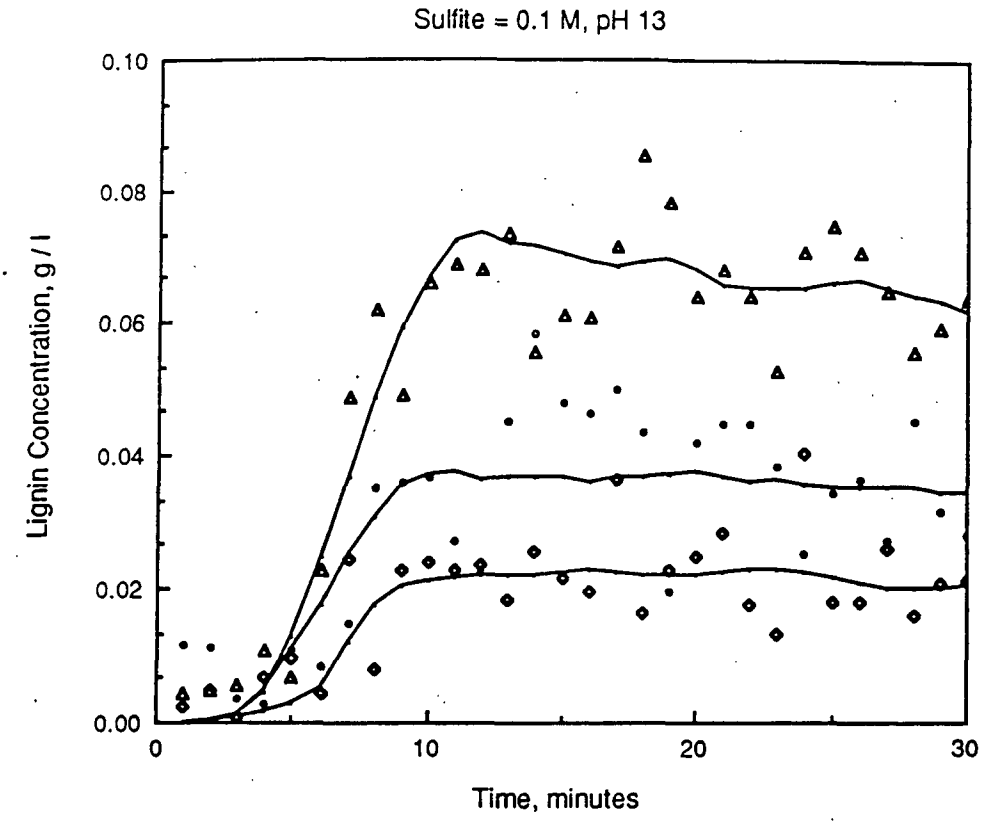
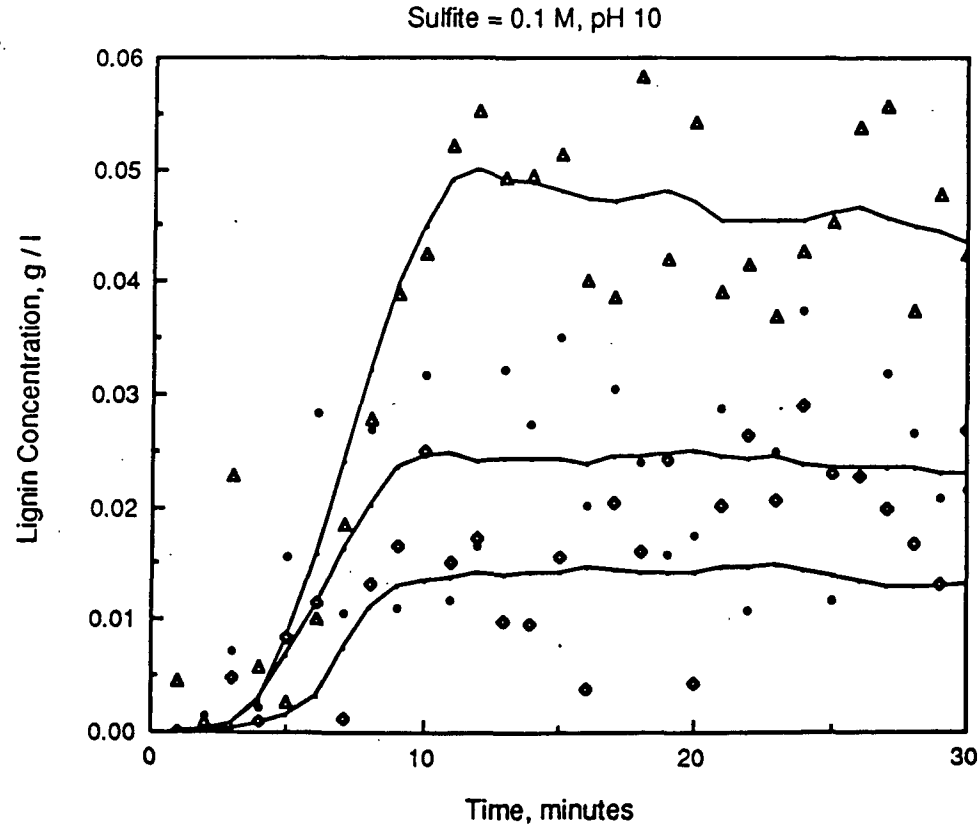
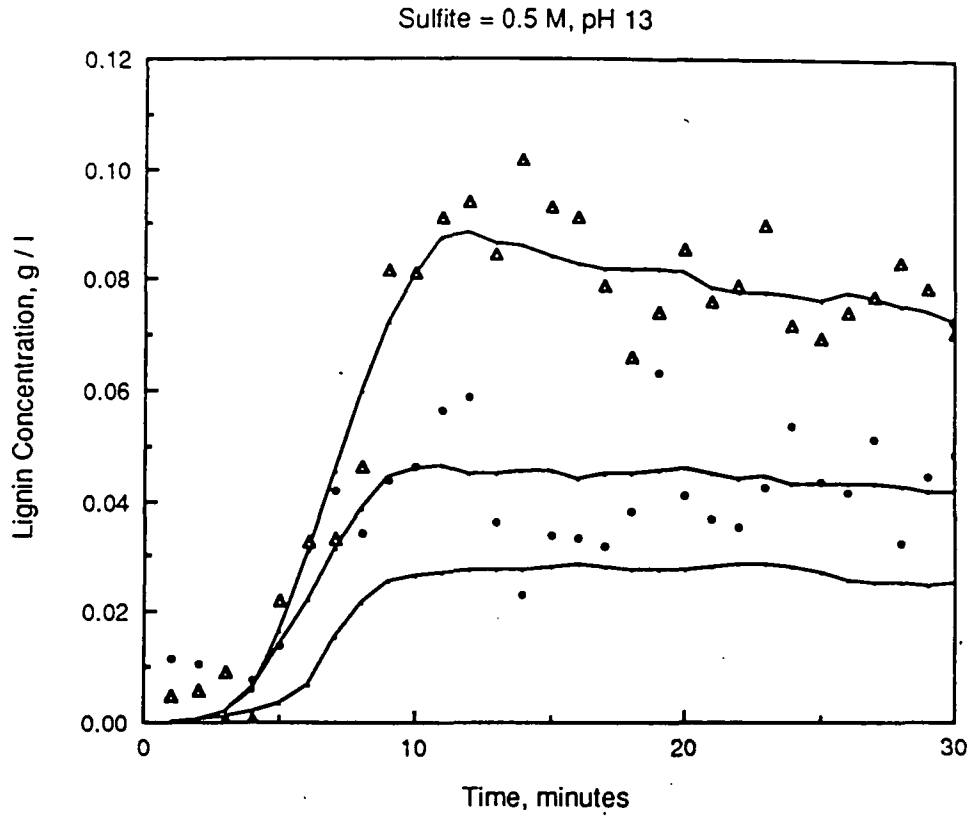
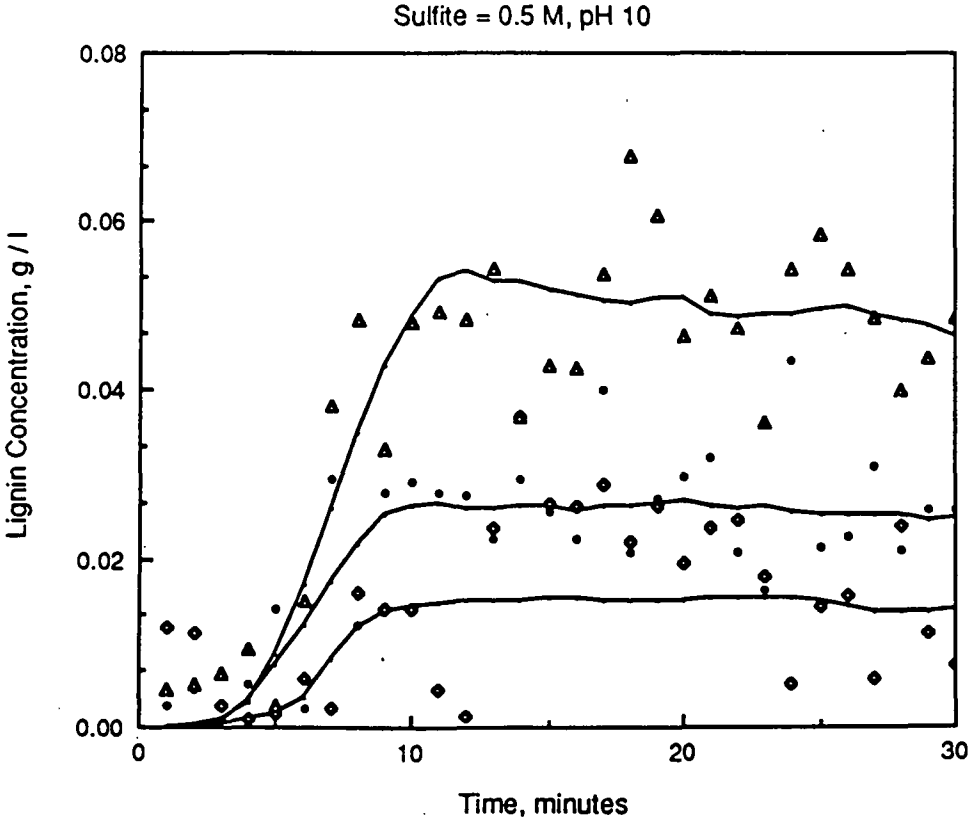
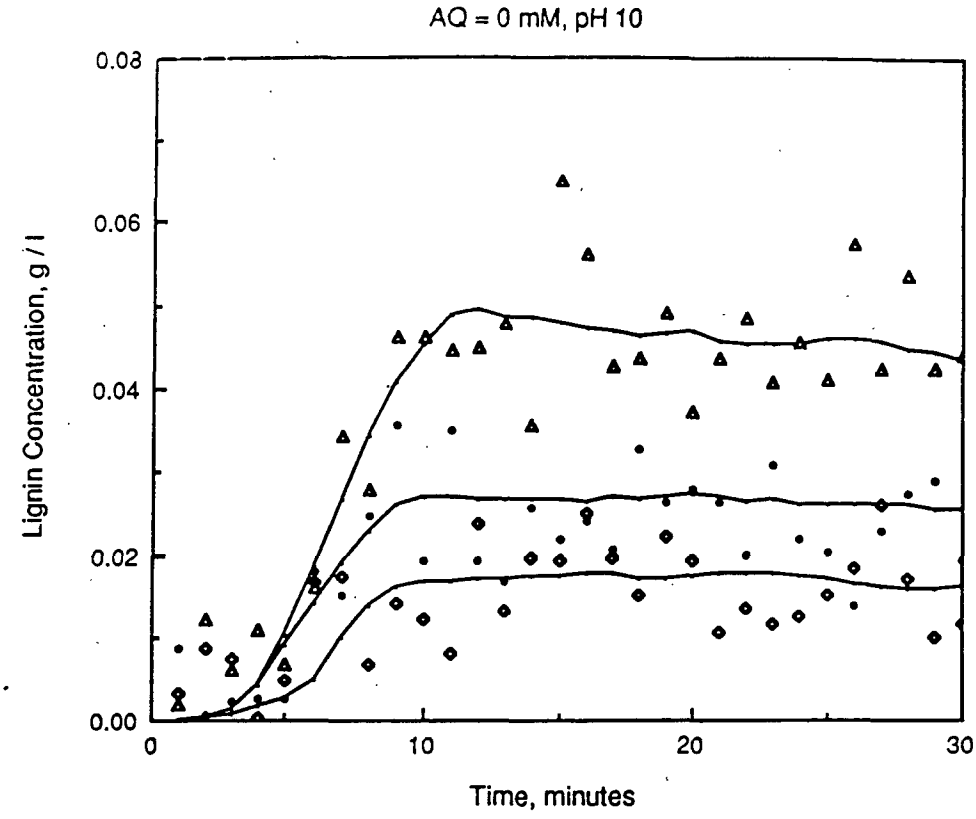
0.06
0.04
0.02
0.00
0
10
20
30
Time, minutes

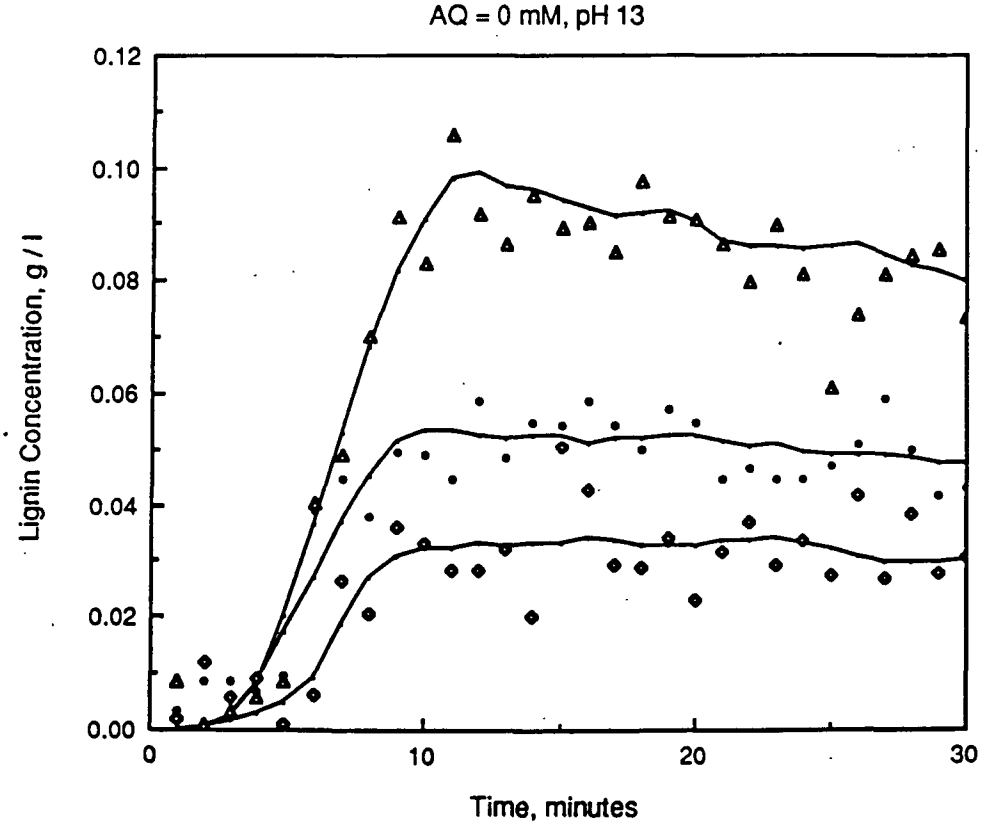

Sulfite = 0.1 M, pH 13
Lignin Concentration, g / l
0.10
0.08
0.06
0.04
0.02
0.00
0
10
20
30
Time, minutes

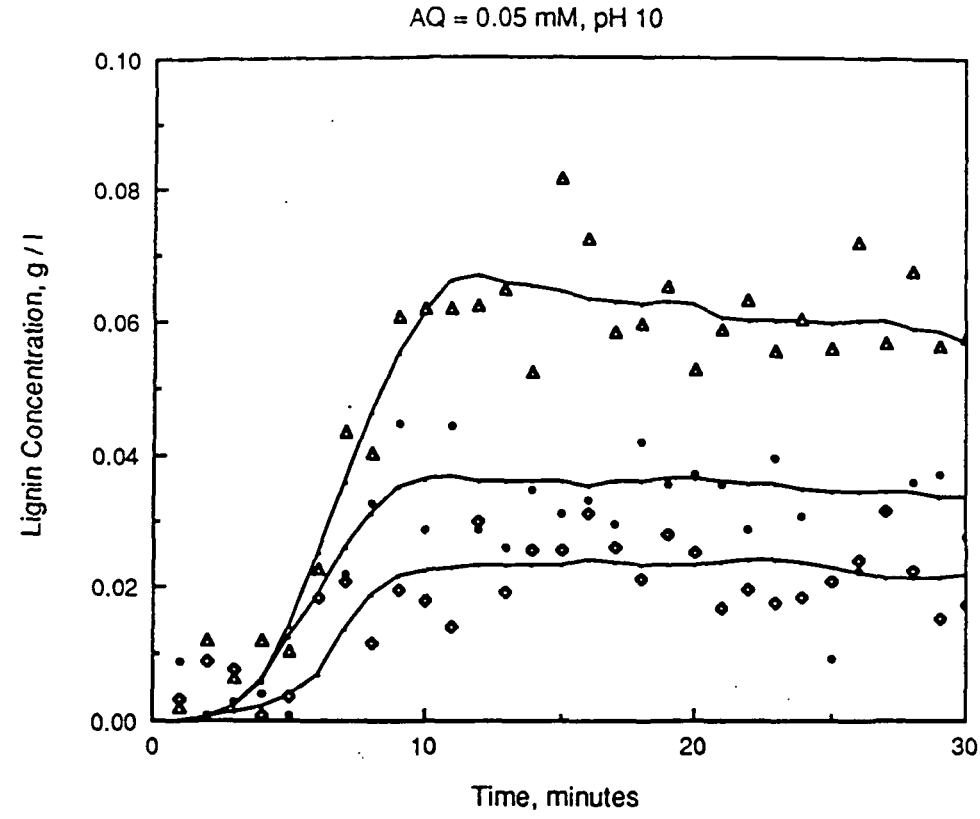

Sulfite = 0.1 M, pH 10
Lignin Concentration, g / l
0.06
0.05
0.04
0.03
0.02
0.01
0.00
0
10
20
30
Time, minutes

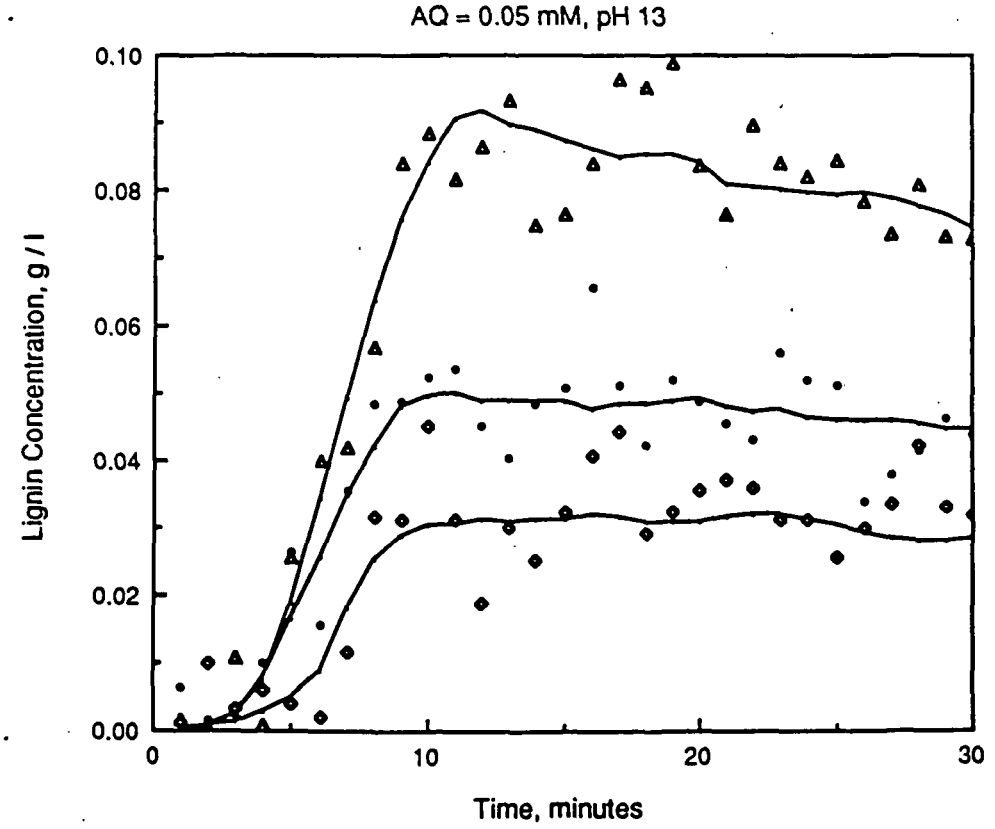

Sulfite = 0.5 M, pH 13
Lignin Concentration, g / l
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
10
20
30
Time, minutes

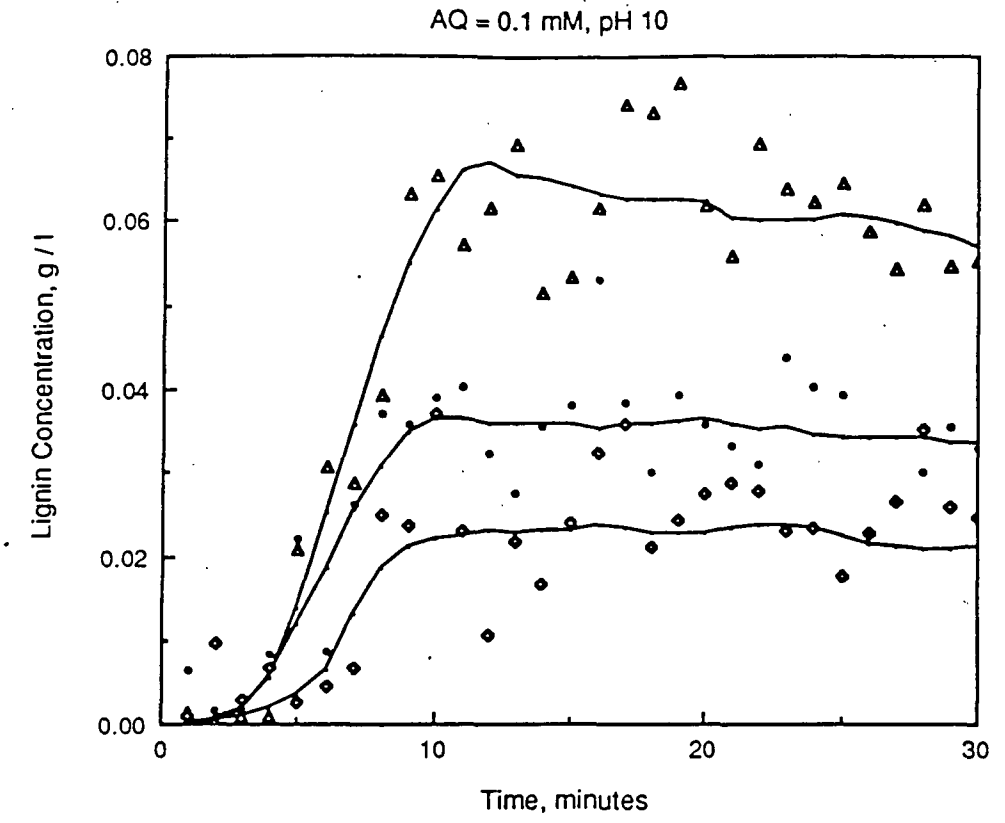

Sulfite = 0.5 M, pH 10
Lignin Concentration, g / l
0.08
0.06
0.04
0.02
0.00
0
10
20
30
Time, minutes

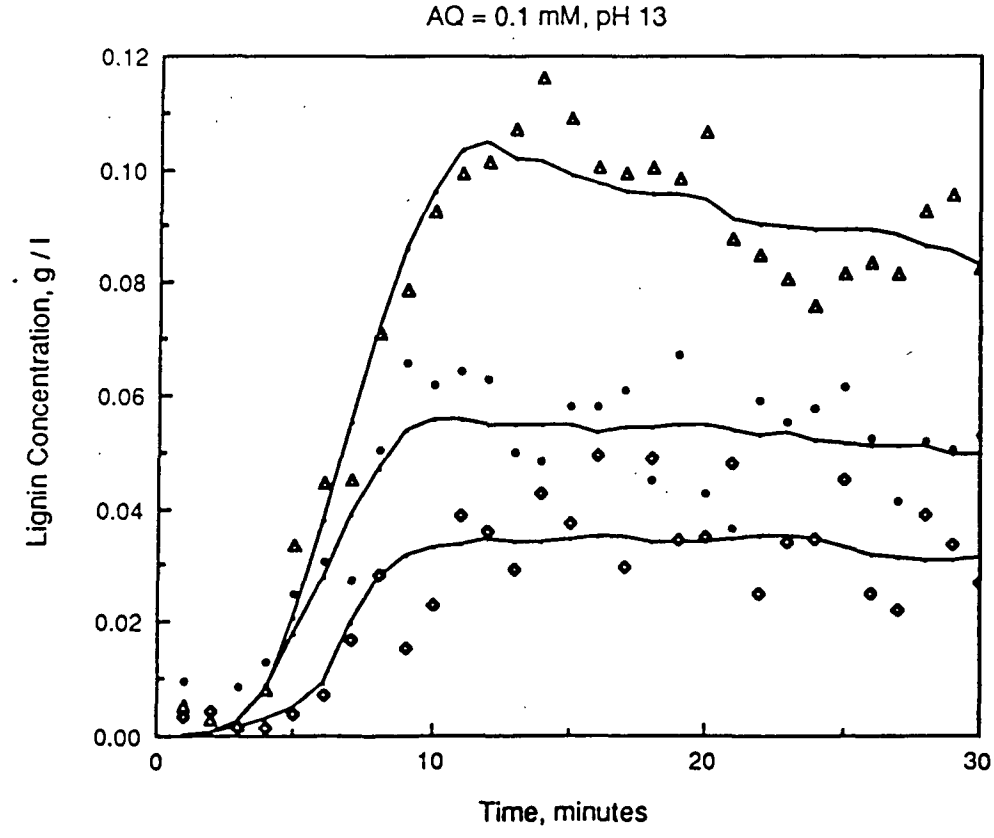

AQ = 0 mM, pH 10
Lignin Concentration, g / l
0.00
0.02
0.04
0.06
0.08
0
10
20
30
Time, minutes

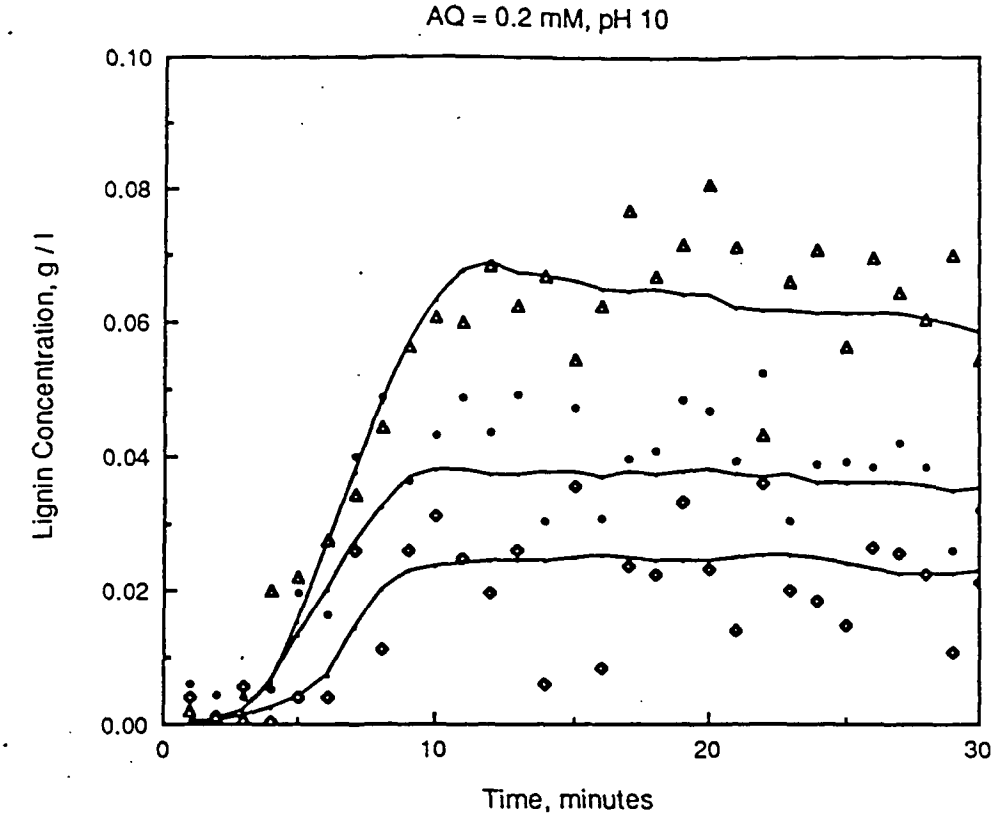

AQ = 0 mM, pH 13
Lignin Concentration, g / l
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0
10
20
30
Time, minutes

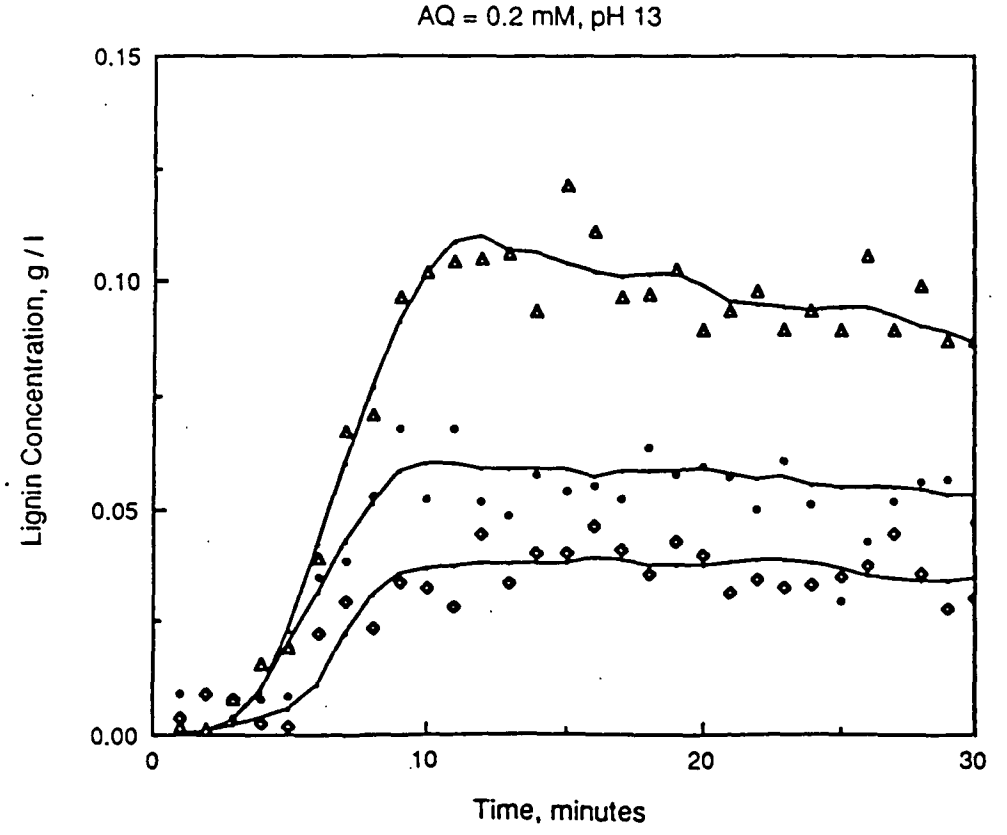

AQ = 0.05 mM, pH 10
Lignin Concentration, g / l
0.10
0.08
0.06
0.04
0.02
0.00
0
10
20
30
Time, minutes

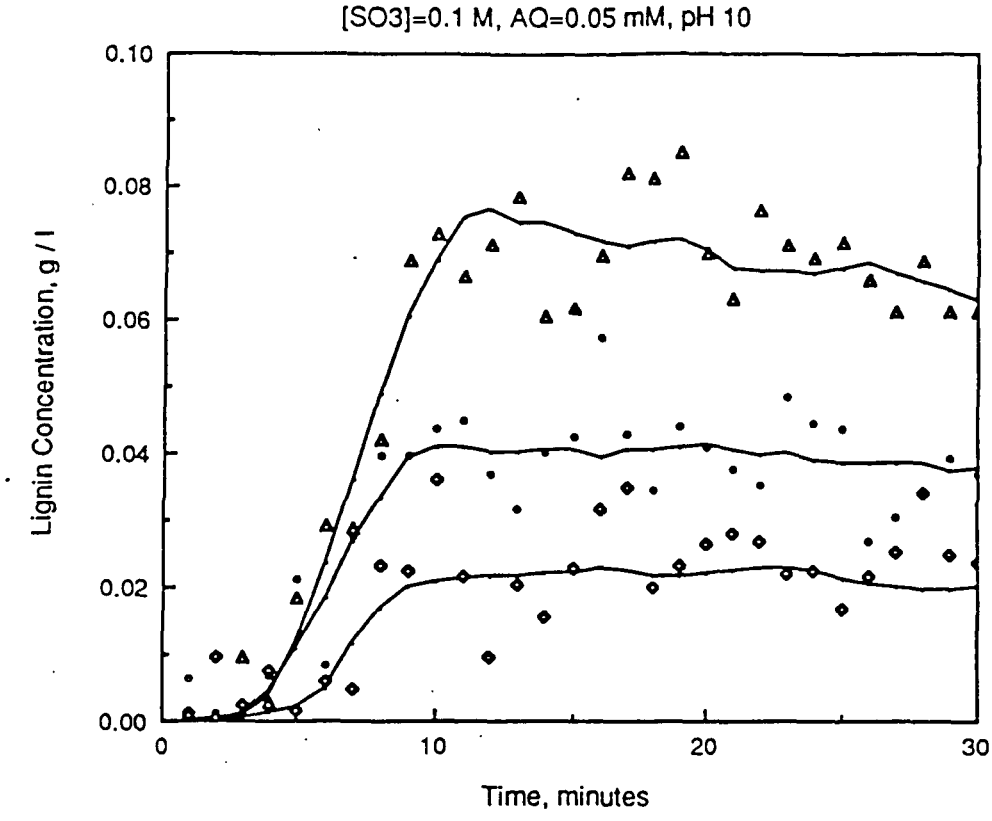

AQ = 0.05 mM, pH 13
Lignin Concentration, g / l
0.10
0.08
0.06
0.04
0.02
0.00
0
10
20
30
Time, minutes

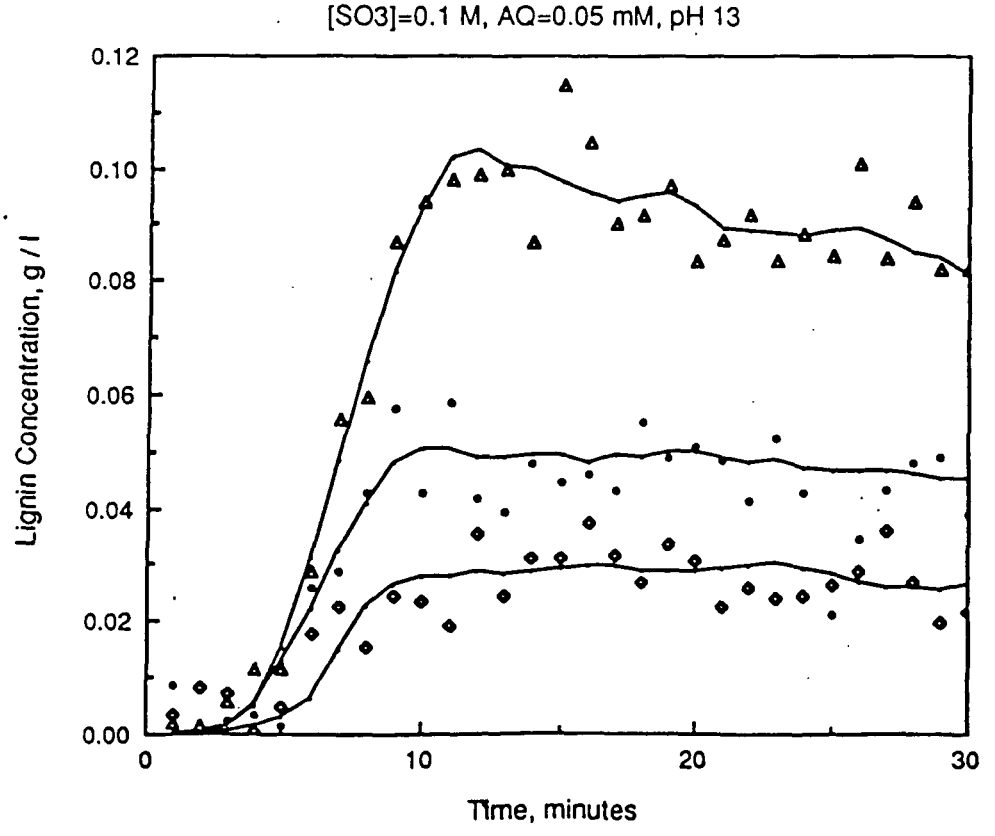

AQ = 0.1 mM, pH 10
Lignin Concentration, g / l
0.08
0.06
0.04
0.02
0.00
0
10
20
30
Time, minutes

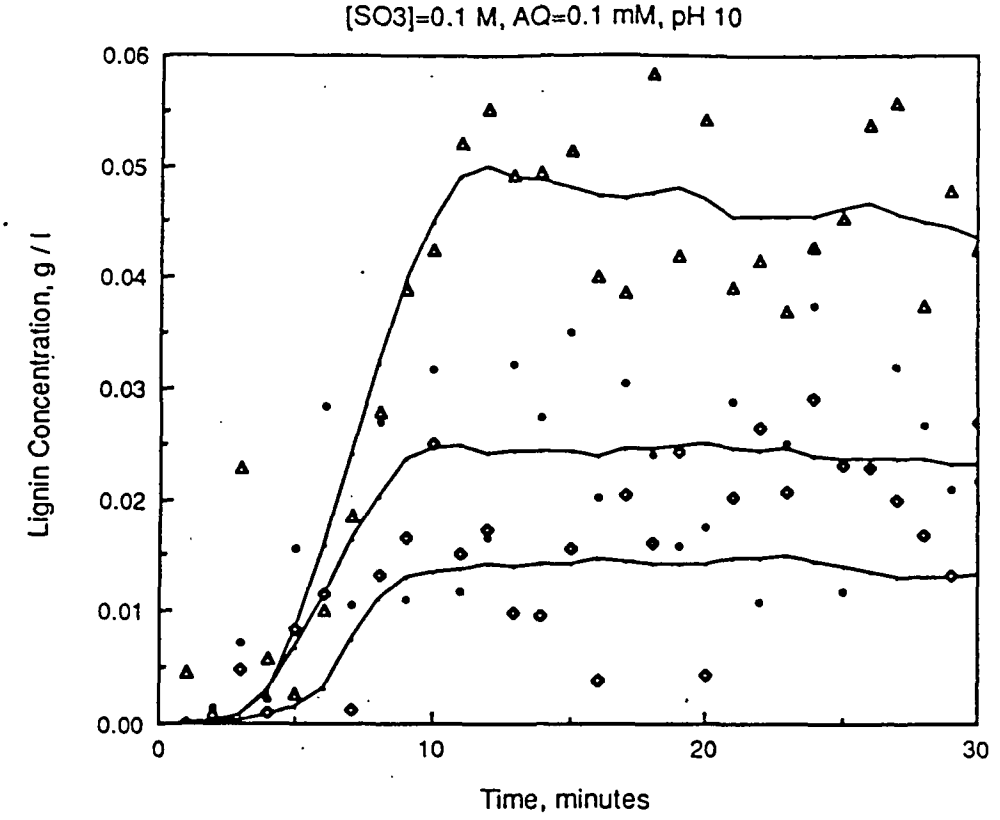

AQ = 0.1 mM, pH 13
Lignin Concentration, g / l
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
10
20
30
Time, minutes

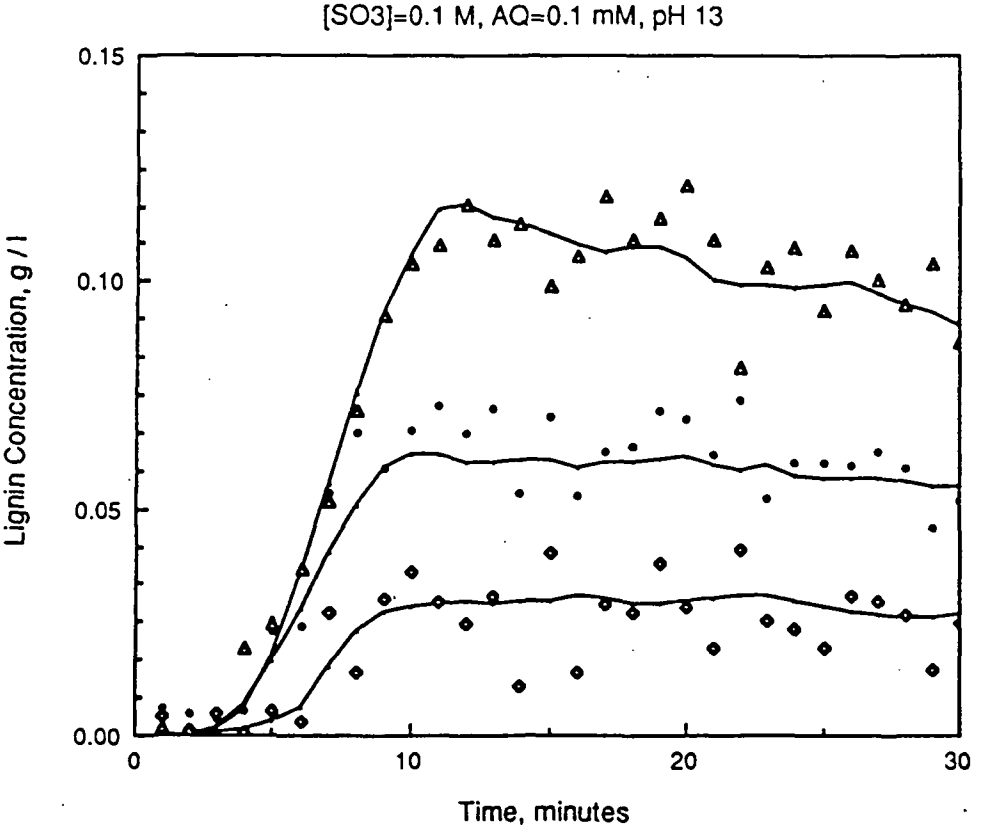

AQ = 0.2 mM, pH 10
Lignin Concentration, g / l
0.10
0.08
0.06
0.04
0.02
0.00
0
10
20
30
Time, minutes

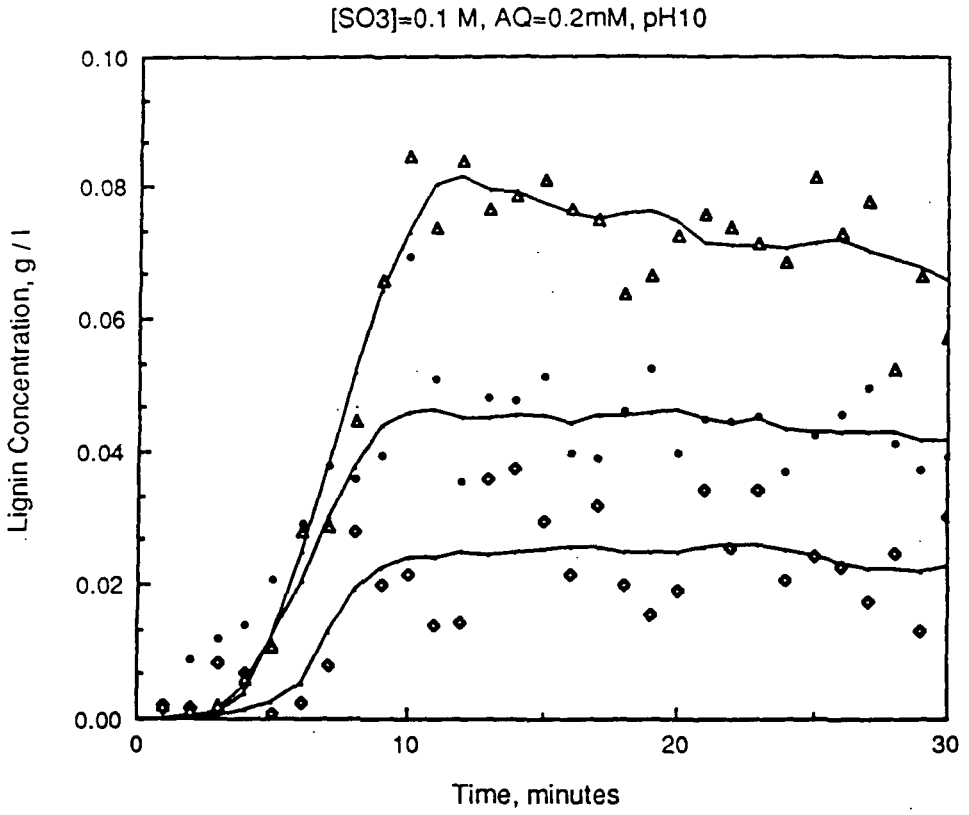

AQ = 0.2 mM, pH 13
Lignin Concentration, g / l
0.15
0.10
0.05
0.00
0
10
20
30
Time, minutes

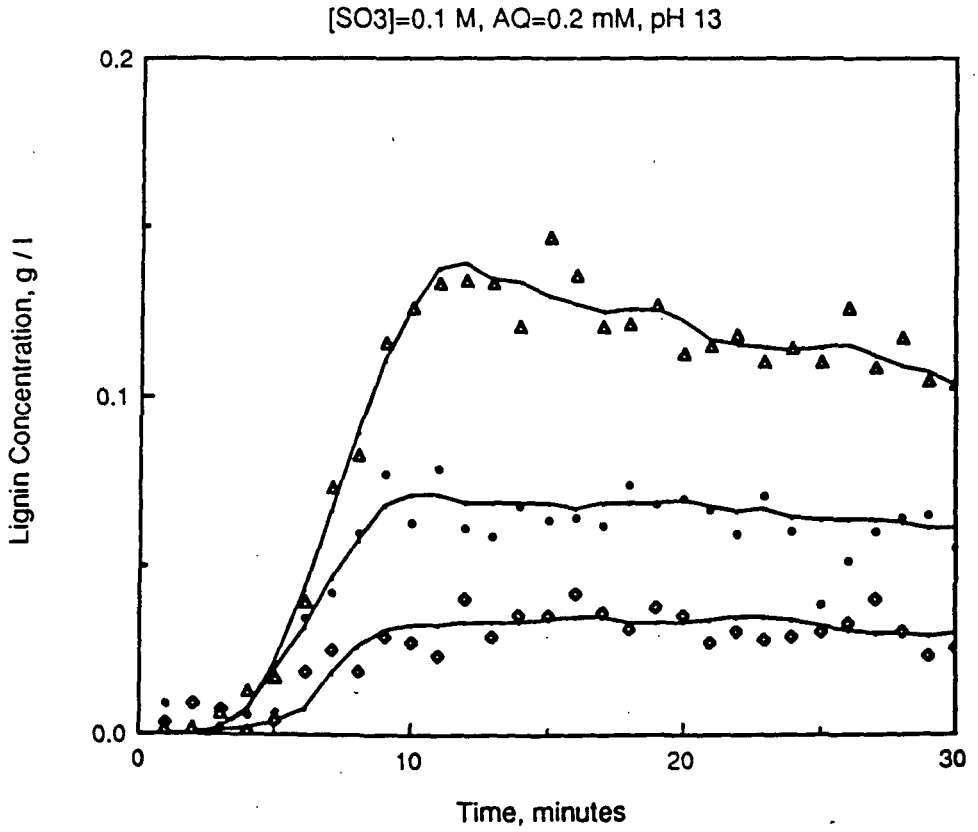

[SO3]=0.1 M, AQ=0.05 mM, pH 10
Lignin Concentration, g / l
0.10
0.08
0.06
0.04
0.02
0.00
0
10
20
30
Time, minutes

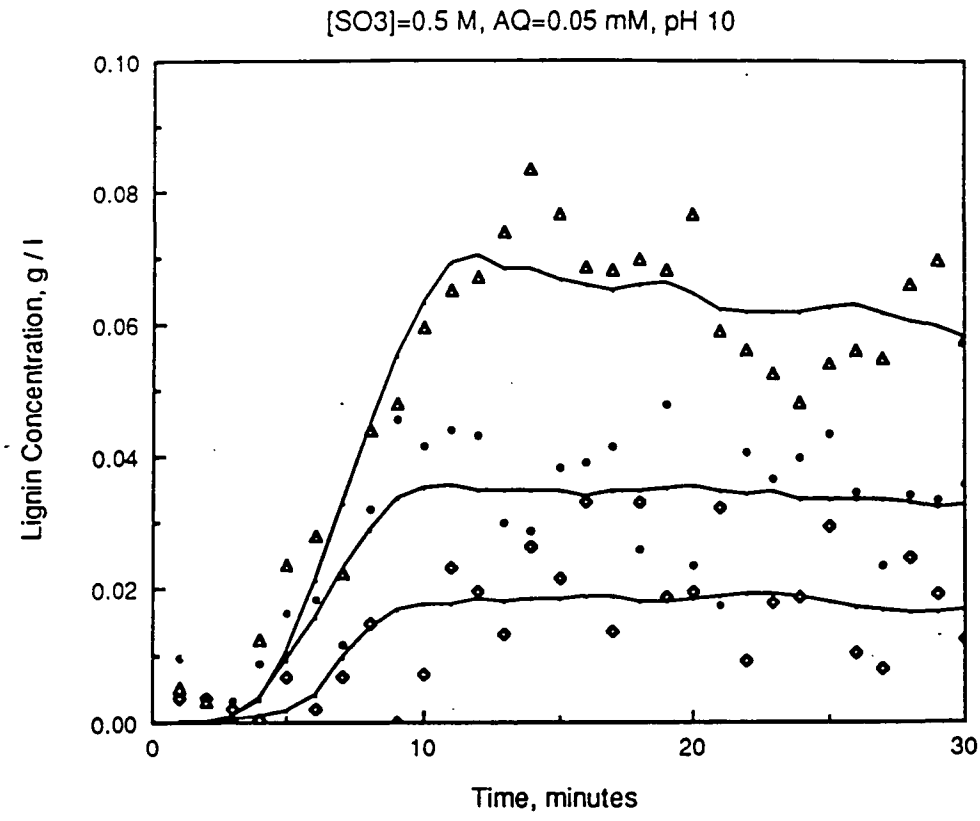

[SO3]=0.1 M, AQ=0.05 mM, pH 13
Lignin Concentration, g / l
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
10
20
30
Time, minutes

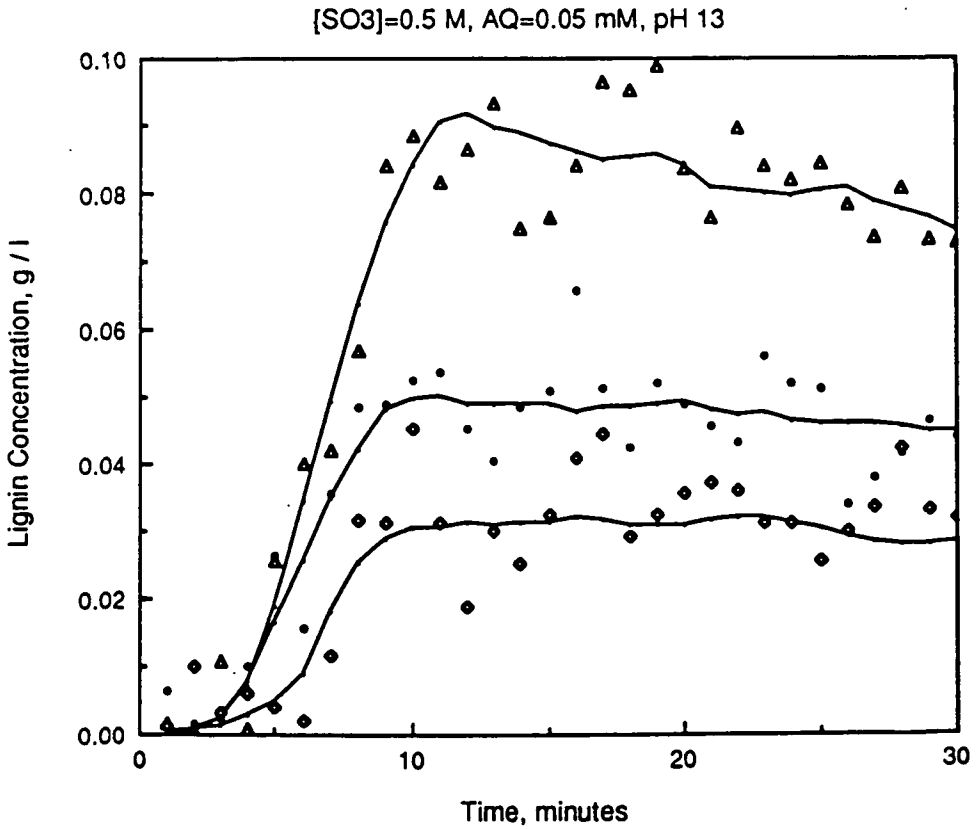

[SO3]=0.1 M, AQ=0.1 mM, pH 10
Lignin Concentration, g / l
0.06
0.05
0.04
0.03
0.02
0.01
0.00
0
10
20
30
Time, minutes

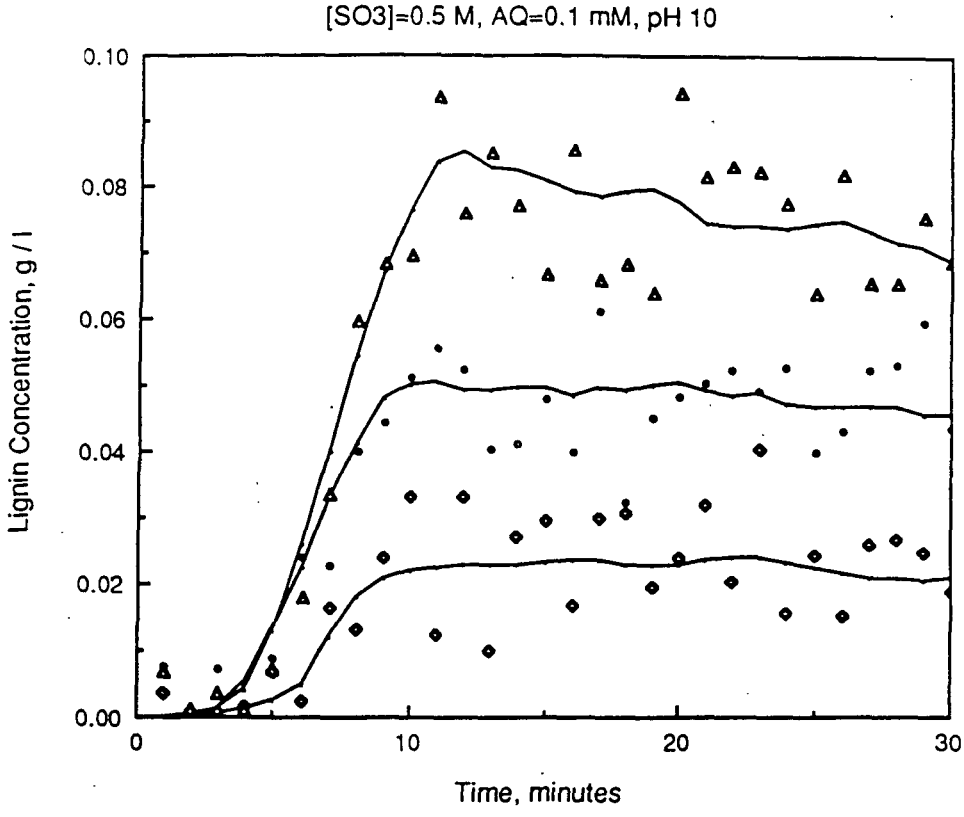

[SO3]=0.1 M, AQ=0.1 mM, pH 13
Lignin Concentration, g / l
0.15
0.10
0.05
0.00
0
10
20
30
Time, minutes

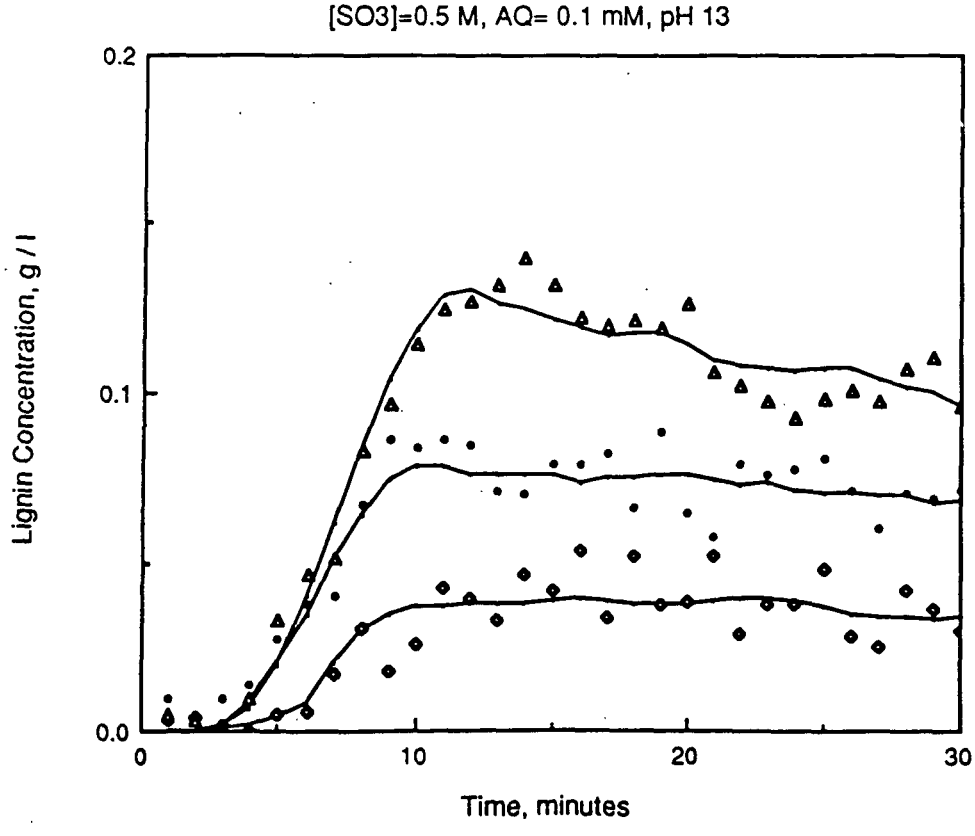

[SO3]=0.1 M, AQ=0.2mM, pH10
Lignin Concentration, g / l
0.10
0.08
0.06
0.04
0.02
0.00
0
10
20
30
Time, minutes

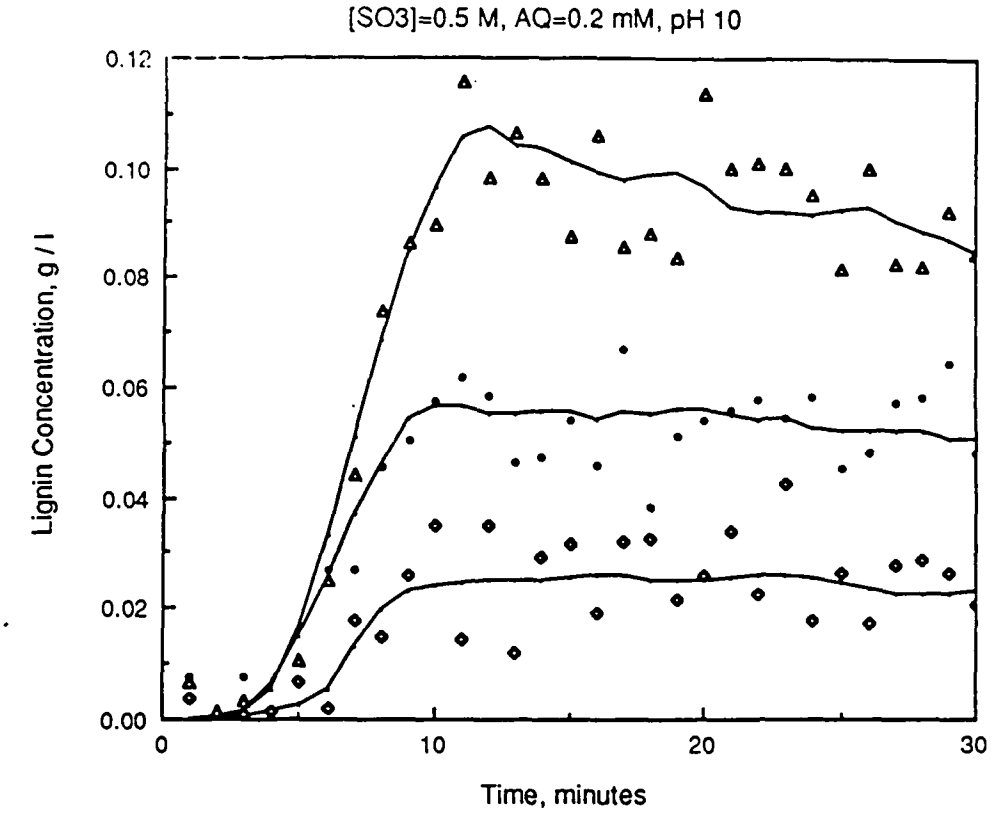

[SO3]=0.1 M, AQ=0.2 mM, pH 13
Lignin Concentration, g / l
0.2
0.1
0.0
0
10
20
30
Time, minutes

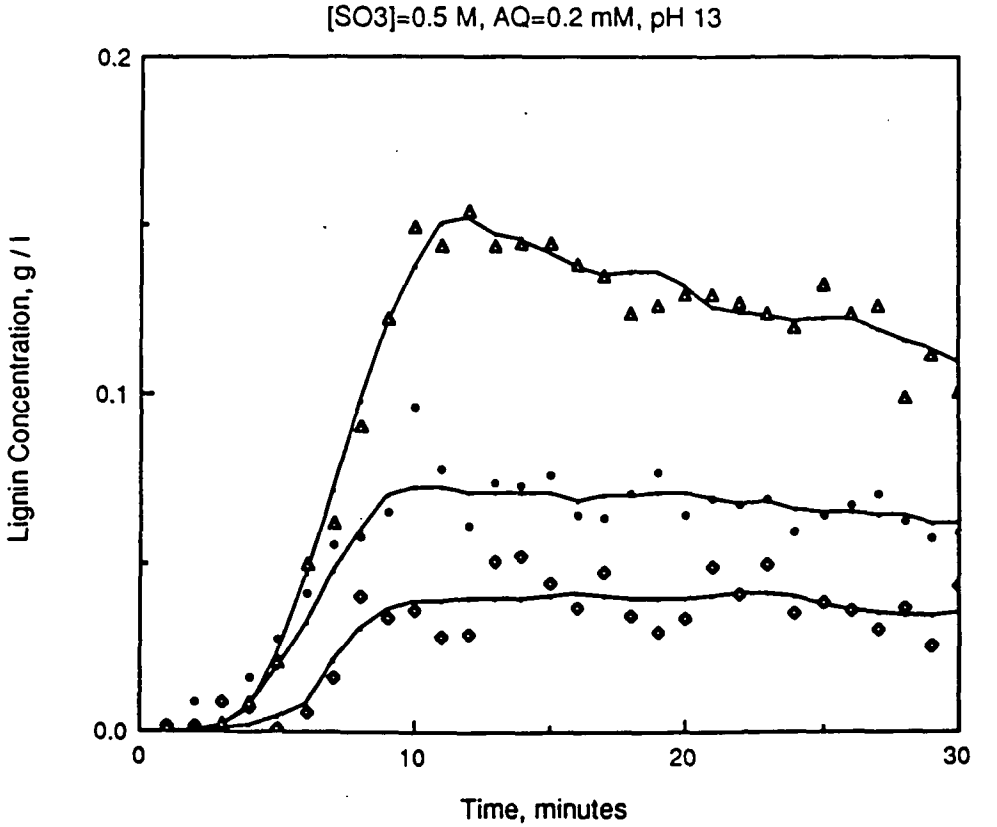

[SO3]=0.5 M, AQ=0.05 mM, pH 10
Lignin Concentration, g / l
0.10
0.08
0.06
0.04
0.02
0.00
0
10
20
30
Time, minutes


[SO3]=0.5 M, AQ=0.05 mM, pH 13
Lignin Concentration, g / l
0.10
0.08
0.06
0.04
0.02
0.00
0
10
20
30
Time, minutes


[SO3]=0.5 M, AQ=0.1 mM, pH 10
Lignin Concentration, g / l
0.10
0.08
0.06
0.04
0.02
0.00
0
10
20
30
Time, minutes


[SO3]=0.5 M, AQ= 0.1 mM, pH 13
Lignin Concentration, g / l
0.2
0.1
0.0
0
10
20
30
Time, minutes


[SO3]=0.5 M, AQ=0.2 mM, pH 10
Lignin Concentration, g / l
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
10
20
30
Time, minutes


[SO3]=0.5 M, AQ=0.2 mM, pH 13
Lignin Concentration, g / l
0.2
0.1
0.0
0
10
20
30
Time, minutes

Appendix 8

Analyses of Variance

Pulp Yield and Lignin Yield

Analysis of Variance – Pulp Yield – Sulfite only experiments

Source	DF	Sum–Squares	Mean–Square	F-Ratio
A(SULFITE)	2	19.81949	9.909747	3.74
B(PH)	1	436.1098	436.1098	164**
AB	2	5.151483	2.575741	<1.0
C(TEMP)	2	234.9712	117.4856	44.3**
AC	4	8.714649	2.178662	<1.0
BC	2	.4780087	.2390044	<1.0
ABC	4	10.60335	2.650836	
TOTAL(Adj)	17	715.848		

** = significant at the 99% confidence level

Table of Means

Term	Value	Count	Mean
ALL		18	87.3
A: SULFITE			
	0	6	88.8
	0.1	6	86.7
	0.5	6	86.4
B: PH			
	10	9	92.2
	13	9	82.4
C: TEMP			
	120	6	91.9
	135	6	87.0
	150	6	83.0
AB: SULFITE,PH			
	0,10	3	92.9
	0,13	3	84.6
	.1,10	3	92.1
	.1,13	3	81.3
	.5,10	3	91.6
	.5,13	3	81.2

Term	Value	Count	Mean
AC: SULFITE,TEMP			
	0,120	2	92.9
	0,135	2	88.5
	0,150	2	84.9
	.1,120	2	92.6
	.1,135	2	85.7
	.1,150	2	81.7
	.5,120	2	90.1
	.5,135	2	86.7
	.5,150	2	82.5
BC: PH,TEMP			
	10120	3	96.6
	10135	3	92.0
	10150	3	88.1
	13120	3	87.2
	13135	3	81.9
	13150	3	78.0
ABC: SULFITE,PH,TEMP			
	0,10,120	1	96.8
	0,10,135	1	92.4
	0,10,150	1	89.6
	0,13,120	1	88.9
	0,13,135	1	84.6
	0,13,150	1	80.3
	.1,10,120	1	96.6
	.1,10,135	1	91.5
	.1,10,150	1	88.1
	.1,13,120	1	88.6
	.1,13,135	1	79.9
	.1,13,150	1	75.3
	.5,10,120	1	96.2
	.5,10,135	1	92.1
	.5,10,150	1	86.5
	.5,13,120	1	84.0
	.5,13,135	1	81.3
	.5,13,150	1	78.4

Analysis of Variance – Pulp Yield – AQ only experiments

Source	DF	Sum–Squares	Mean–Square	F-Ratio
A(AQ)	3	29.19519	9.731731	5.01*
B(PH)	1	537.2333	537.2333	279**
AB	3	8.243324	2.747775	1.43
C(TEMP)	2	290.7583	145.3791	75**
AC	6	9.885448	1.647575	<1.0
BC	2	1.013658	.5068289	<1.0
ABC	6	11.52586	1.920977	
TOTAL(Adj)	23	887.8551		

** = significant at the 99% confidence level

* = significant at the 95% confidence level

Table of Means

Term	Value	Count	Mean
ALL		24	87.6
A: AQ			
	0	6	88.7
	0.05	6	86.7
	0.1	6	86.4
	0.2	6	88.7
B: PH			
	10	12	92.4
	13	12	82.9
C: TEMP			
	120	8	92.0
	135	8	87.3
	150	8	83.5
AB: AQ,PH			
	0,10	3	92.9
	0,13	3	84.6
	.05,10	3	92.1
	.05,13	3	81.3
	.1,10	3	91.6
	.1,13	3	81.2
	.2,10	3	92.8
	.2,13	3	84.6

Term	Value	Count	Mean
AC: AQ,TEMP			
	0,120	2	92.7
	0,135	2	88.4
	0,150	2	85.1
	.05,120	2	92.6
	.05,135	2	85.7
	.05,150	2	81.8
	.1,120	2	90.0
	.1,135	2	86.7
	.1,150	2	82.5
	.2,120	2	92.8
	.2,135	2	88.4
	.2,150	2	84.8
BC: PH,TEMP			
	10,120	4	96.5
	10,135	4	92.0
	10,150	4	88.5
	13,120	4	87.6
	13,135	4	82.6
	13,150	4	78.6
ABC: AQ,PH,TEMP			
	0,10,120	1	96.7
	0,10,135	1	92.3
	0,10,150	1	89.7
	0,13,120	1	88.8
	0,13,135	1	84.4
	0,13,150	1	80.5
	.05,10,120	1	96.6
	.05,10,135	1	91.6
	.05,10,150	1	88.2
	.05,13,120	1	88.7
	.05,13,135	1	79.9
	.05,13,150	1	75.3
	.1,10,120	1	96.1
	.1,10,135	1	92.0
	.1,10,150	1	86.6
	.1,13,120	1	83.8
	.1,13,135	1	81.4
	.1,13,150	1	78.3

Term	Value	Count	Mean
ABC: AQ,PH,TEMP			
	.2,10,120	1	96.6
	.2,10,135	1	92.3
	.2,10,150	1	89.5
	.2,13,120	1	89.1
	.2,13,135	1	84.6
	.2,13,150	1	80.1

Analysis of Variance – Pulp Yield – Sulfite + Anthraquinone experiments

Source	DF	Sum–Squares	Mean–Square	F-Ratio
A(SO3)	1	3.367E-04	3.367E-04	<1.0
B(AQ)	2	9.473719	4.736859	1.14
AB	2	28.77859	14.3893	3.47
C(PH)	1	872.5117	872.5117	210**
AC	1	1.770E-02	1.770E-02	<1.0
BC	2	2.612989	1.306495	<1.0
ABC	2	7.233241	3.616621	<1.0
D(TEMP)	2	467.925	233.9625	56.4**
AD	2	1.893E-02	9.467E-03	<1.0
BD	4	4.419961	1.10499	<1.0
ABD	4	12.3933	3.098325	<1.0
CD	2	.8342386	.4171193	<1.0
ACD	2	1.605E-02	8.025E-03	<1.0
BCD	4	5.66929	1.417322	<1.0
ABCD	4	16.58129	4.145322	
TOTAL(Adj)	35	1428.487		

** = significant at the 99% confidence level

Table of Means

Term	Value	Count	Mean
ALL		36	87.3
A: SO3			
	0.1	18	87.3
	0.5	18	87.3
B: AQ			
	0.05	12	87.7
	0.1	12	87.6
	0.2	12	86.6
C: PH			
	10	18	92.2
	13	18	82.4
D: TEMP			
	120	12	91.8
	135	12	87.0
	150	12	83.0

Term	Value	Count	Mean
AB: SO3,AQ			
	.1,.05	6	88.7
	.1,.1	6	86.4
	.1,.2	6	86.7
	.5,.05	6	86.7
	.5,.1	6	88.7
	.5,.2	6	86.4
AC: SO3,PH			
	.1,10	9	92.2
	.1,13	9	82.3
	.5,10	9	92.2
	.5,13	9	82.4
BC: AQ,PH			
	.05,10	6	92.5
	.05,13	6	83.0
	.1,10	6	92.3
	.1,13	6	82.8
	.2,10	6	91.9
	.2,13	6	81.3
AD: SO3,TEMP			
	.1,120	6	91.9
	.1,135	6	86.9
	.1,150	6	83.1
	.5,120	6	91.8
	.5,135	6	87.0
	.5,150	6	83.0
BD: AQ,TEMP			
	.05,120	4	92.7
	.05,135	4	87.2
	.05,150	4	83.3
	.1,120	4	91.4
	.1,135	4	87.5
	.1,150	4	83.8
	.2,120	4	91.4
	.2,135	4	86.2
	.2,150	4	82.1

Term	Value	Count	Mean
CD: PH,TEMP			
	10,120	6	96.6
	10,135	6	91.9
	10,150	6	88.1
	13,120	6	87.1
	13,135	6	82.0
	13,150	6	78.0
ABC: SO3,AQ,PH			
	.1,.05,10	3	92.9
	.1,.05,13	3	84.6
	.1,.1,10	3	91.6
	.1,.1,13	3	81.2
	.1,.2,10	3	92.1
	.1,.2,13	3	81.2
	.5,.05,10	3	92.0
	.5,.05,13	3	81.3
	.5,.1,10	3	92.9
	.5,.1,13	3	84.5
	.5,.2,10	3	91.6
	.5,.2,13	3	81.3
ABD: SO3,AQ,TEMP			
	.1,.05,120	2	92.9
	.1,.05,135	2	88.5
	.1,.05,150	2	84.9
	.1,.1,120	2	90.1
	.1,.1,135	2	86.6
	.1,.1,150	2	82.6
	.1,.2,120	2	92.6
	.1,.2,135	2	85.7
	.1,.2,150	2	81.7
	.5,.05,120	2	92.5
	.5,.05,135	2	85.8
	.5,.05,150	2	81.7
	.5,.1,120	2	92.8
	.5,.1,135	2	88.4
	.5,.1,150	2	84.9
	.5,.2,120	2	90.2
	.5,.2,135	2	86.8
	.5,.2,150	2	82.4

Term	Value	Count	Mean
ACD: SO3,PH,TEMP			
	.1,10,120	3	96.6
	.1,10,135	3	91.9
	.1,10,150	3	88.2
	.1,13,120	3	87.1
	.1,13,135	3	81.9
	.1,13,150	3	77.9
	.5,10,120	3	96.5
	.5,10,135	3	92.0
	.5,10,150	3	88.0
	.5,13,120	3	87.1
	.5,13,135	3	82.0
	.5,13,150	3	78.0
BCD: AQ,PH,TEMP			
	.05,10,120	2	96.7
	.05,10,135	2	92.0
	.05,10,150	2	88.8
	.05,13,120	2	88.7
	.05,13,135	2	82.4
	.05,13,150	2	77.8
	.1,10,120	2	96.6
	.1,10,135	2	92.0
	.1,10,150	2	88.2
	.1,13,120	2	86.3
	.1,13,135	2	82.9
	.1,13,150	2	79.3
	.2,10,120	2	96.4
	.2,10,135	2	91.8
	.2,10,150	2	87.3
	.2,13,120	2	86.3
	.2,13,135	2	80.7
	.2,13,150	2	76.8
ABCD: SO3,AQ,PH,TEMP			
	.1,.05,10,120	1	96.8
	.1,.05,10,135	1	92.4
	.1,.05,10,150	1	89.5
	.1,.05,13,120	1	88.9
	.1,.05,13,135	1	84.6
	.1,.05,13,150	1	80.2

Term	Value	Count	Mean
ABCD:	SO3,AQ,PH,TEMP		
	.1,.1,10,120	1	96.3
	.1,.1,10,135	1	91.8
	.1,.1,10,150	1	86.7
	.1,.1,13,120	1	83.9
	.1,.1,13,135	1	81.3
	.1,.1,13,150	1	78.4
	.1,.2,10,120	1	96.6
	.1,.2,10,135	1	91.5
	.1,.2,10,150	1	88.3
	.1,.2,13,120	1	88.6
	.1,.2,13,135	1	79.9
	.1,.2,13,150	1	75.2
	.5,.05,10,120	1	96.5
	.5,.05,10,135	1	91.5
	.5,.05,10,150	1	88.1
	.5,.05,13,120	1	88.6
	.5,.05,13,135	1	80.1
	.5,.05,13,150	1	75.4
	.5,.1,10,120	1	96.8
	.5,.1,10,135	1	92.3
	.5,.1,10,150	1	89.6
	.5,.1,13,120	1	88.7
	.5,.1,13,135	1	84.5
	.5,.1,13,150	1	80.3
	.5,.2,10,120	1	96.3
	.5,.2,10,135	1	92.1
	.5,.2,10,150	1	86.4
	.5,.2,13,120	1	84.1
	.5,.2,13,135	1	81.4
	.5,.2,13,150	1	78.3

Analysis of Variance – Lignin Yield – Sulfite only experiments

Source	DF	Sum-Squares	Mean-Square	F-Ratio
A(SULFITE)	2	1.05541	.5277051	28.55**
B(PH)	1	14.38266	14.38266	778**
AB	2	.738131	.3690655	19.96**
C(TEMP)	2	83.94164	41.97082	2270**
AC	4	.3961924	9.904E-02	5.36
BC	2	3.624725	1.812363	97.9**
ABC	4	7.392E-02	.0184824	
TOTAL	17	104.2127		

** = significant at the 99% confidence level

Table of Means

Term	Value	Count	Mean
ALL		18	24.1
A: SULFITE			
	0	6	24.2
	0.1	6	24.3
	0.5	6	23.7
B: PH			
	10	9	25.0
	13	9	23.2
C: TEMP			
	120	6	26.3
	135	6	24.7
	150	6	21.1
AB: SULFITE,PH			
	0,10	3	24.9
	0,13	3	23.5
	.1,10	3	25.1
	.1,13	3	23.4
	.5,10	3	24.9
	.5,13	3	22.6

Term	Value	Count	Mean
AC: SULFITE,TEMP			
	0,120	2	26.6
	0,135	2	25.0
	0,150	2	21.0
	.1,120	2	26.3
	.1,135	2	24.9
	.1,150	2	21.6
	.5,120	2	25.9
	.5,135	2	24.4
	.5,150	2	20.8
BC: PH,TEMP			
	10,120	3	26.7
	10,135	3	25.5
	10,150	3	22.6
	13,120	3	25.9
	13,135	3	24.0
	13,150	3	19.7
ABC: SULFITE,PH,TEMP			
	0,10,120	1	26.9
	0,10,135	1	25.6
	0,10,150	1	22.2
	0,13,120	1	26.4
	0,13,135	1	24.3
	0,13,150	1	19.8
	.1,10,120	1	26.6
	.1,10,135	1	25.6
	.1,10,150	1	23.0
	.1,13,120	1	26.0
	.1,13,135	1	24.2
	.1,13,150	1	20.2
	.5,10,120	1	26.6
	.5,10,135	1	25.4
	.5,10,150	1	22.7
	.5,13,120	1	25.3
	.5,13,135	1	23.4
	.5,13,150	1	19.0

Analysis of Variance – Lignin Yield – AQ only experiments

Source	DF	Sum–Squares	Mean–Square	F-Ratio
A(AQ)	3	20.28867	6.76289	73**
B(PH)	1	41.71208	41.71208	453**
AB	3	3.267571	1.08919	11.85**
C(TEMP)	2	135.358	67.67902	736**
AC	6	2.451695	.4086159	4.44*
BC	2	7.483386	3.741693	40.71**
ABC	6	.5514708	.0919118	
TOTAL(Adj)	23	211.1129		

** = significant at the 99% confidence level

* = significant at the 95% confidence level

Table of Means

Term	Value	Count	Mean
ALL		24	22.9
A: AQ			
	0	6	23.2
	0.05	6	24.3
	0.1	6	22.4
	0.2	6	21.8
B: PH			
	10	12	24.2
	13	12	21.6
C: TEMP			
	120	8	25.5
	135	8	23.6
	150	8	19.7
AB: AQ,PH			
	0,10	3	25.1
	0,13	3	21.4
	.05,10	3	25.1
	.05,13	3	23.4
	.1,10	3	23.6
	.1,13	3	21.1
	.2,10	3	23.2
	.2,13	3	20.5

Term	Value	Count	Mean
AC: AQ,TEMP			
	0,120	2	25.6
	0,135	2	23.9
	0,150	2	20.1
	.05,120	2	26.3
	.05,135	2	24.9
	.05,150	2	21.6
	.1,120	2	24.8
	.1,135	2	23.0
	.1,150	2	19.2
	.2,120	2	25.0
	.2,135	2	22.5
	.2,150	2	18.1
BC: PH,TEMP			
	10,120	4	26.2
	10,135	4	24.7
	10,150	4	21.8
	13,120	4	24.7
	13,135	4	22.4
	13,150	4	17.7
ABC: AQ,PH,TEMP			
	0,10,120	1	26.6
	0,10,135	1	25.8
	0,10,150	1	22.8
	0,13,120	1	24.6
	0,13,135	1	22.0
	0,13,150	1	17.5
	.05,10,120	1	26.6
	.05,10,135	1	25.6
	.05,10,150	1	23.0
	.05,13,120	1	26.0
	.05,13,135	1	24.2
	.05,13,150	1	20.2
	.1,10,120	1	25.4
	.1,10,135	1	24.2
	.1,10,150	1	21.1
	.1,13,120	1	24.3
	.1,13,135	1	21.9
	.1,13,150	1	17.3

Term	Value	Count	Mean
ABC: AQ,PH,TEMP			
	.2,10,120	1	25.9
	.2,10,135	1	23.4
	.2,10,150	1	20.3
	.2,13,120	1	24.1
	.2,13,135	1	21.5
	.2,13,150	1	15.8

Analysis of Variance – Lignin Yield – Sulfite + AQ experiments

Source	DF	Sum–Squares	Mean–Square	F-Ratio
A(SO3)	1	.5852314	.5852314	1.31
B(AQ)	2	16.73989	8.369947	18.7**
AB	2	3.719105	1.859552	4.16
C(PH)	1	72.73253	72.73253	162.7**
AC	1	.1166833	.1166833	<1.0
BC	2	5.939893	2.969947	6.6
ABC	2	.5745634	.2872817	<1.0
D(TEMP)	2	446.3408	223.1704	499**
AD	2	2.052084	1.026042	2.29
BD	4	4.234021	1.058505	2.36
ABD	4	3.520947	.8802369	1.96
CD	2	22.50834	11.25417	25.2**
ACD	2	.2284855	.1142428	<1.0
BCD	4	1.150683	.2876708	<1.0
ABCD	4	1.787499	.4468748	
TOTAL(Adj)	35	582.2309		

** = significant at the 99% confidence level

Table of Means

Term	Value	Count	Mean
ALL		36	21.3
A: SO3			
	0.1	18	21.4
	0.5	18	21.2
B: AQ			
	0.05	12	22.0
	0.1	12	21.6
	0.2	12	20.4
C: PH			
	10	18	22.7
	13	18	19.9
D: TEMP			
	120	12	25.3
	135	12	21.9
	150	12	16.7

Term	Value	Count	Mean
AB: SO3,AQ			
	.1,.05	6	22.3
	.1,.1	6	21.3
	.1,.2	6	20.7
	.5,.05	6	21.6
	.5,.1	6	21.9
	.5,.2	6	20.0
AC: SO3,PH			
	.1,10	9	22.8
	.1,13	9	20.1
	.5,10	9	22.7
	.5,13	9	19.7
BC: AQ,PH			
	.05,10	6	22.8
	.05,13	6	21.1
	.1,10	6	23.2
	.1,13	6	20.0
	.2,10	6	22.2
	.2,13	6	18.6
AD: SO3,TEMP			
	.1,120	6	25.2
	.1,135	6	21.9
	.1,150	6	17.2
	.5,120	6	25.5
	.5,135	6	21.8
	.5,150	6	16.3
BD: AQ,TEMP			
	.05,120	4	25.6
	.05,135	4	22.7
	.05,150	4	17.6
	.1,120	4	25.4
	.1,135	4	22.0
	.1,150	4	17.4
	.2,120	4	24.9
	.2,135	4	21.0
	.2,150	4	15.2

Term	Value	Count	Mean
CD: PH,TEMP			
	10,120	6	25.9
	10,135	6	23.1
	10,150	6	19.2
	13,120	6	24.8
	13,135	6	20.6
	13,150	6	14.3
ABC: SO3,AQ,PH			
	.1,.05,10	3	23.0
	.1,.05,13	3	21.6
	.1,.1,10	3	22.7
	.1,.1,13	3	19.8
	.1,.2,10	3	22.6
	.1,.2,13	3	18.8
	.5,.05,10	3	22.6
	.5,.05,13	3	20.6
	.5,.1,10	3	23.7
	.5,.1,13	3	20.2
	.5,.2,10	3	21.7
	.5,.2,13	3	18.4
ABD: SO3,AQ,TEMP			
	.1,.05,120	2	25.5
	.1,.05,135	2	23.2
	.1,.05,150	2	18.3
	.1,.1,120	2	25.0
	.1,.1,135	2	21.8
	.1,.1,150	2	17.0
	.1,.2,120	2	25.1
	.1,.2,135	2	20.7
	.1,.2,150	2	16.3
	.5,.05,120	2	25.8
	.5,.05,135	2	22.1
	.5,.05,150	2	16.9
	.5,.1,120	2	25.8
	.5,.1,135	2	22.1
	.5,.1,150	2	17.9
	.5,.2,120	2	24.8
	.5,.2,135	2	21.2
	.5,.2,150	2	14.1

Term	Value	Count	Mean
ACD: SO3,PH,TEMP			
	.1,10,120	3	25.7
	.1,10,135	3	23.0
	.1,10,150	3	19.7
	.1,13,120	3	24.7
	.1,13,135	3	20.9
	.1,13,150	3	14.7
	.5,10,120	3	26.1
	.5,10,135	3	23.2
	.5,10,150	3	18.7
	.5,13,120	3	24.8
	.5,13,135	3	20.4
	.5,13,150	3	13.9
BCD: AQ,PH,TEMP			
	.05,10,120	2	25.9
	.05,10,135	2	23.4
	.05,10,150	2	19.2
	.05,13,120	2	25.4
	.05,13,135	2	21.9
	.05,13,150	2	16.0
	.1,10,120	2	26.0
	.1,10,135	2	23.4
	.1,10,150	2	20.2
	.1,13,120	2	24.8
	.1,13,135	2	20.5
	.1,13,150	2	14.7
	.2,10,120	2	25.8
	.2,10,135	2	22.4
	.2,10,150	2	18.3
	.2,13,120	2	24.1
	.2,13,135	2	19.5
	.2,13,150	2	12.1
ABCD: SO3,AQ,PH,TEMP			
	.1,.05,10,120	1	25.7
	.1,.05,10,135	1	23.6
	.1,.05,10,150	1	19.8
	.1,.05,13,120	1	25.2
	.1,.05,13,135	1	22.8
	.1,.05,13,150	1	16.8

Term	Value	Count	Mean
ABCD:	SO3,AQ,PH,TEMP		
	.1,.1,10,120	1	25.6
	.1,.1,10,135	1	22.8
	.1,.1,10,150	1	19.9
	.1,.1,13,120	1	24.5
	.1,.1,13,135	1	20.9
	.1,.1,13,150	1	14.1
	.1,.2,10,120	1	25.8
	.1,.2,10,135	1	22.7
	.1,.2,10,150	1	19.4
	.1,.2,13,120	1	24.4
	.1,.2,13,135	1	18.8
	.1,.2,13,150	1	13.2
	.5,.05,10,120	1	26.0
	.5,.05,10,135	1	23.2
	.5,.05,10,150	1	18.6
	.5,.05,13,120	1	25.5
	.5,.05,13,135	1	21.0
	.5,.05,13,150	1	15.3
	.5,.1,10,120	1	26.5
	.5,.1,10,135	1	24.1
	.5,.1,10,150	1	20.5
	.5,.1,13,120	1	25.1
	.5,.1,13,135	1	20.1
	.5,.1,13,150	1	15.3
	.5,.2,10,120	1	25.7
	.5,.2,10,135	1	22.2
	.5,.2,10,150	1	17.2
	.5,.2,13,120	1	23.9
	.5,.2,13,135	1	20.1
	.5,.2,13,150	1	11.1

APPENDIX 9

MODEL SENSITIVITY ANALYSIS

The table presented below illustrates the change in the sum of the squared deviations of the observed lignin concentration values from the predicted lignin concentration values. The values presented are from the three experiments performed at a sulfite concentration of 0.1 M, an anthraquinone concentration of 0.2 mM, and pH 10.

	Activation Energies, kcal/mole								
	20200	20250	20300	20350	20400	20450	20500	20550	20600
1.00E+09	0.7746	0.6406	0.5073	0.3820	0.3053	0.4850	0.5626	0.7425	0.9726
1.50E+09	0.7420	0.5408	0.3417	0.2961	0.2756	0.5108	0.5983	0.6437	0.6784
2.00E+09	0.8775	0.7842	0.5742	0.3951	0.1938	0.2179	0.3794	0.5204	0.6197
2.50E+09	0.4429	0.3447	0.2969	0.1533	0.1431	0.3888	0.5314	0.6335	0.8235
3.00E+09	0.4001	0.3965	0.2579	0.2488	0.0550	0.2602	0.2966	0.4696	0.5398
3.50E+09	0.4228	0.2306	0.2176	0.1336	0.0285	0.1224	0.2632	0.4772	0.5497
4.00E+09	0.4163	0.2567	0.0625	0.0455	0.0155	0.0212	0.2541	0.4209	0.4306
4.50E+09	0.8076	0.6157	0.5195	0.2816	0.0815	0.1389	0.3438	0.3554	0.4581
5.00E+09	0.4465	0.3502	0.3417	0.1406	0.1076	0.2917	0.3363	0.4903	0.5652
5.50E+09	0.6832	0.6071	0.3820	0.2586	0.1678	0.4160	0.6292	0.7561	0.8724
6.00E+09	0.7057	0.5160	0.4626	0.2665	0.2397	0.2854	0.5086	0.7570	0.9718

APPENDIX 10

CARBOHYDRATE DEGRADATION KINETICS

The same approach as was used to determine which liquor composition variables had a significant effect on the delignification rate constants was used to study the effects on the first order rate constants for carbohydrate loss. Since only two data points per experiment were available (initial and final carbohydrate contents), the conclusions that may be drawn from this analysis are limited. The first order rate constant was calculated using the data shown in Appendix 2. The mass of lignin in the pulp was calculated based on the Hypo Number measurement, and the mass of carbohydrate material obtained by the difference between the total pulp mass and the mass of lignin. The original wood in the experiments was 29% lignin and 71% carbohydrate material.

The models presented below contain terms ($k_{C,0}$) corresponding to intercepts in the regression equation which are not equal to zero. These terms may be justified using the same arguments presented above for the intercept terms in the delignification models.

SULFITE ONLY EXPERIMENTS

The carbohydrate degradation rate constants for the sulfite only experiments are shown in Table A1. The analysis of variance performed on these data (Appendix 6) gave only two significant effects; temperature was significant at the 95% confidence level, and the liquor pH was significant at the 99% confidence level. Regression of these rate constants against the hydroxide concentration in the liquor resulted in the rate equation

$$\frac{dC}{dt} = -\left(k_{C,0} + k_{C,1}[OH^-]\right)C \qquad (A9)$$

where C is the carbohydrate content of the wood or pulp. The overall coefficient of determination for this model was 0.86. Values for the rate constants in this equation are presented in Table A2. The rate constants do not give a linear Arrhenius plot (ln k vs. 1/T), so no activation energy was evaluated. The model accounts for less of the variability in the rate constants at higher temperatures than at low temperatures. This trend is seen in the other two experimental categories as well.

Table A1. Rate constants for carbohydrate degradation for sulfite only experiments

Sulfite, M	pH	Temp,°C	KC*	Selectivity**
0	10	120	0.00049	2.056
		135	0.00204	0.807
		150	0.00172	1.916
	13	120	0.00421	0.313
		135	0.00547	0.438
		150	0.00537	0.867
0.1	10	120	0.00047	2.366
		135	0.00248	0.663
		150	0.00289	1.019
	13	120	0.00422	0.353
		135	0.00807	0.316
		150	0.00840	0.559
0.5	10	120	0.00064	1.815
		135	0.00211	0.826
		150	0.00356	0.877
	13	120	0.00634	0.301
		135	0.00679	0.430
		150	0.00594	0.866

* KC = first order rate constant for carbohydrate degradation, 1/minutes
** selectivity = gm lignin dissolved/gm carbohydrate dissolved

Table A2. Constants in carbohydrate degradation model for sulfite only experiments

Temperature, °C	KC0	KC1	R^2
120	0.0005	0.0439	0.9052
135	0.0022	0.0457	0.8996
150	0.0027	0.0385	0.7623

Anthraquinone Only Experiments

The rate constants for carbohydrate degradation in the AQ only experiments are shown in Table A3. Analysis of variance on these rate constants showed three significant effects. Temperature and anthraquinone concentration were significant at the 99% confidence level, and the liquor pH was significant at the 95% confidence level. Regression analysis of the rate constants resulted in the following model:

$$\frac{dC}{dt} = -\left(k_{C,0} + k_{C,2}[OH^-] - k_{C,3}[AQ]\right)C \qquad (A10)$$

An overall coefficient of determination for this model was calculated as 0.74. Values for the constants in this equation are presented in Table A4. The AQ reaction has a pre–exponential factor of 3.47×10^6, with an activation energy of 16,460 kcal/mole. This reaction reduces the degradation rate of the carbohydrates, as would be expected. The hydroxide reaction rate constants decrease slightly with temperature.

Sulfite + Anthraquinone Experiments

Table A5 shows the values for the carbohydrate loss rate constants for the sulfite + AQ experiments. The analysis of variance for these data showed that only the liquor pH had a significant effect on the rate of carbohydrate loss (at the 99% confidence level). Regression of the simple model

$$\frac{dC}{dt} = -\left\{k_{C,0} + k_{C,4}[OH^-]\right\}C \qquad (A11)$$

gave an overall coefficient of determination of 0.83, with values for the constants shown in Table A6. These constants decrease with increasing temperature, with an activation energy of -5120 kcal/mole.

Table A3. Rate constants for carbohydrate degradation for anthraquinone only experiments

AQ	pH	Temp	KC*	Selectivity**
0	10	120	0.00042	2.629
		135	0.00218	0.715
		150	0.00194	1.557
	13	120	0.00339	0.639
		135	0.00427	0.822
		150	0.00399	1.439
0.05	10	120	0.00052	2.156
		135	0.00244	0.674
		150	0.00285	1.033
	13	120	0.00418	0.356
		135	0.00810	0.315
		150	0.00841	0.559
0.1	10	120	0.00015	11.060
		135	0.00154	1.509
		150	0.00270	1.427
	13	120	0.00587	0.414
		135	0.00589	0.621
		150	0.00505	1.174
0.2	10	120	0.00015	9.573
		135	0.00099	2.689
		150	0.00087	4.748
	13	120	0.00294	0.825
		135	0.00397	0.936
		150	0.00330	1.974

* KC = first order rate constant for carbohydrate degradation, 1/minutes
** selectivity = gm lignin dissolved/gm carbohydrate dissolved

Table A4. Constants in carbohydrate degradation model for anthraquinone only experiments

Temperature, °C	KC0	KC2	KC3	R^2
120	0.0005	0.0379	0.0020	0.8541
135	0.0024	0.0377	0.0071	0.7565
150	0.0028	0.0310	0.0086	0.6047

Table A5. Rate constants for carbohydrate degradation for sulfite + anthraquinone experiments

Sulfite	AQ	pH	Temp	KC*	Selectivity**
0.1	0.05	10	120	0.00005	30.724
			135	0.00104	2.459
			150	0.00058	7.516
		13	120	0.00364	0.514
			135	0.00463	0.670
			150	0.00379	1.596
	0.1	10	120	0.00023	6.067
			135	0.00130	2.133
			150	0.00072	6.879
		13	120	0.00396	0.436
			135	0.00610	0.677
			150	0.00556	1.261
	0.2	10	120	0.00013	12.334
			135	0.00092	3.240
			150	0.00203	2.168
		13	120	0.00592	0.392
			135	0.00542	0.757
			150	0.00328	2.250
0.5	0.05	10	120	0.00031	3.889
			135	0.00137	1.707
			150	0.00088	4.609
		13	120	0.00366	0.525
			135	0.00328	1.332
			150	0.00295	2.282
	0.1	10	120	0.00008	18.153
			135	0.00104	2.911
			150	0.00103	4.406
		13	120	0.00333	0.685
			135	0.00500	1.032
			150	0.00451	1.757
	0.2	10	120	0.00021	7.257
			135	0.00052	6.123
			150	0.00084	6.704
		13	120	0.00550	0.476
			135	0.00490	0.914
			150	0.00181	4.776

* KC = first order rate constant for carbohydrate degradation, 1/minutes

** selectivity = gm lignin dissolved/gm carbohydrate dissolved

Table A6. Constants in carbohydrate degradation model for sulfite + anthraquinone experiments

Temperature, °C	KC0	KC4	R^2
120	0.0002	0.0418	0.8967
135	0.0010	0.0386	0.9016
150	0.0010	0.0264	0.6809

The fact that the anthraquinone concentration term does not appear in the carbohydrate degradation model is a significant result. During the initial phase in the presence of sulfite, the anthraquinone's accelerating effect is due to acceleration of delignification reactions, not to the prevention of carbohydrate degradation.

APPENDIX 11

THE PALMROSE SULFITE TITRATION PROCEDURE

The sulfite concentration of the liquor samples taken during the run is determined as follows:

1. A standardized solution of 0.026 M potassium iodate is used for the titration, prepared from reagent grade KIO_3.

2. 75 ml distilled water, 10 ml 0.5 M H_2SO_4, and 2 ml KI are placed in a 125 ml Erlynmeyer flask and mixed well.

3. Using a volumetric pipette, 2.00 ml residual liquor is added to the flask and mixed. A few drops of starch indicator are added, and the resulting solution titrated with the KIO_3 until the first intense blue appears.

4. The volume of KIO_3 is recorded, and converted to a concentration of sulfite using the equation developed by Eagle:

$$\text{Sulfite (g/l as } Na_2O) = 93 \bullet [KIO_3] \bullet \text{ml } KIO_3 \text{ titrated}$$

This concentration may then be converted to the units desired for the analysis.

Appendix 12

Analysis of Variance on Conversion Factor

Analysis of Variance for Conversion Factor – All Data Combined

Source	DF	Sum–Squares	Mean–Square	F-Ratio
A(SO3)	2	4.340E-07	2.170E-07	2.83
B(AQ)	3	4.278E-07	1.426E-07	1.86
AB	6	2.089E-07	3.483E-08	0.45
C(PH)	1	9.952E-09	9.952E-09	0.13
AC	2	5.781E-08	2.890E-08	0.38
BC	3	4.610E-08	1.536E-08	0.20
ABC	6	2.962E-07	4.938E-08	0.64
D(TEMP)	2	2.007E-07	1.003E-07	1.31
AD	4	4.425E-07	1.106E-07	1.44
BD	6	6.667E-07	1.111E-07	1.45
ABD	12	4.183E-07	3.486E-08	0.45
CD	2	8.107E-08	4.053E-08	0.53
ACD	4	2.693E-07	6.733E-08	0.88
BCD	6	1.450E-07	2.418E-08	0.31
ABCD	12	3.822E-07	3.185E-08	0.41
TOTAL	77	4.695E-06		