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EFFECT OF KRAFT PULPING ON OXYGEN DELIGNIFICATION

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A THESIS

Submitted in Partial Fulfillment of the

Requirements for the Degree of

Doctor of Philosophy

(in Chemical Engineering)

The Graduate School

The University of Maine

May, 2002

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EFFECT OF KRAFT PULPING ON OXYGEN DELIGNIFICATION

By Haixuan Zou

Thesis Advisor: Dr. Joseph M. Genco

An Abstract of the Thesis Presented
in Partial Fulfillment of the Requirements for the
Degree of Doctor of Philosophy
(in Chemical Engineering)
May, 2002

The objective of the study reported here was to investigate experimentally the effect of the major Kraft pulping variables on the response of brownstock pulps to medium consistency oxygen delignification.

Kraft pulping was performed on mixed Northeastern hardwood chips in a laboratory rocking digester. Kraft pulps of kappa number 16 and 20 mL $KMnO_4$ were produced by pulping under a variety of conditions. The effective alkali (EA) charged to the digester was varied over the range of 12 to 21% while the sodium sulfide content of the pulping liquor was varied between 0 to 30% sulfidity. Cooking temperatures of 160 to 180 °C were investigated by varying the time at temperature as measured by the H-factor. Anthraquinone was used as a pulping catalyst at levels between 0 to 4%.

Conditions of low EA charge, low temperature, high sulfidity and high levels of anthraquinone led to pulps with high pulp yield. When the effective alkali charge in the digester was low, cooking at low temperature gave rise to pulps with high viscosity and improved selectivity in the Kraft pulping process.

The response variables following oxygen delignification were found to depend upon the cooking conditions applied in the digester. The kappa number versus time data could be fit to a classical power law model, indicative of lignin fragmentation occurring by an infinite number of parallel first order reactions (Schoon, 1982). There was a systematic increase in the oxygen delignification rate, as measured by a reduction in the kappa number and an increase in the Schoon rate constant, with decreasing brownstock pulp yield in the digester. The pulp selectivity, when measured as the change in pulp viscosity with changes in kappa number, increased with increasing pulp yield until a maximum was reached.

Chemical analysis of the carbohydrates in the pulps indicated that the loss in pulp yield in the digester was caused primarily by a reduction in the hemicellulose polymers as additional effective alkali was added or by cooking at higher temperature in the digester. The loss in pulp yield could be roughly correlated to the COD content of the residual spent liquor.

ACKNOWLEDGEMENTS

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I am grateful to the members of my advisory committee, Dr. Adriaan van Heiningen, Dr. Barbara J.W. Cole, Dr. Ray C. Fort, and Dr. John C. Hassler for their suggestions and consultation.

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INTRODUCTION

1.1. WOOD

Wood is the dominant fiber source in the pulp and paper industry in the world, although non-wood fiber material has seen increased development in the recent years. Wood can be simply classified as softwood and hardwood. Both softwoods and hardwoods consist of four major components: cellulose, hemicellulose, lignin, and extractives. The relative amounts of the components differ between softwoods and hardwoods and between species. Typical compositions of woods (percent) are shown in Figure 1.1 for softwoods and Figure 1.2 for hardwoods (Cole, B.J. 1999).

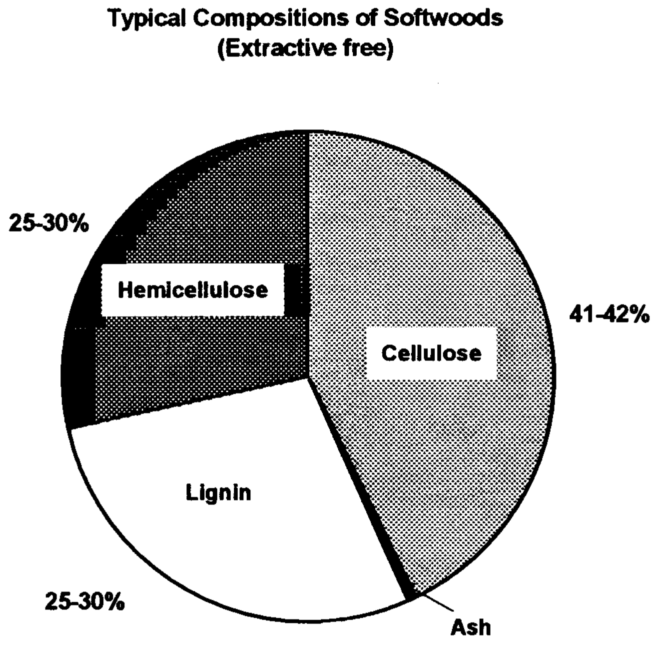


Figure 1.1. Typical compositions of softwoods (Cole, B.J. 1999).

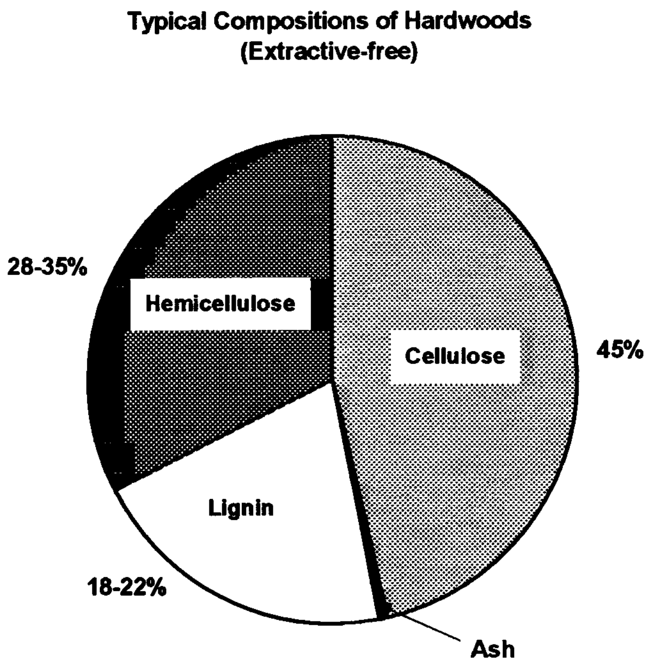


Figure 1.2. Typical compositions of hardwoods (Cole, B.J. 1999).

1.1.1. Cellulose

Cellulose is a polysaccharide consisting of β-D-glucose units linked together by 1-4 glycosidic bonds (Sjostrom, 1993). Cellulose is a linear polymer of β-(1→4)-D-glucopyranose units in ${}^4C_1$ conformation. It is the biggest component in both softwood and hardwood species (see Figure 1.1, 1.2). The structure of cellulose is shown in Figure 1.3. The degree of polymerization (DP) of cellulose in wood is approximately 10,000. In chemical pulping and bleaching, the objective is to separate the wood fiber without seriously degrading the cellulose chain.

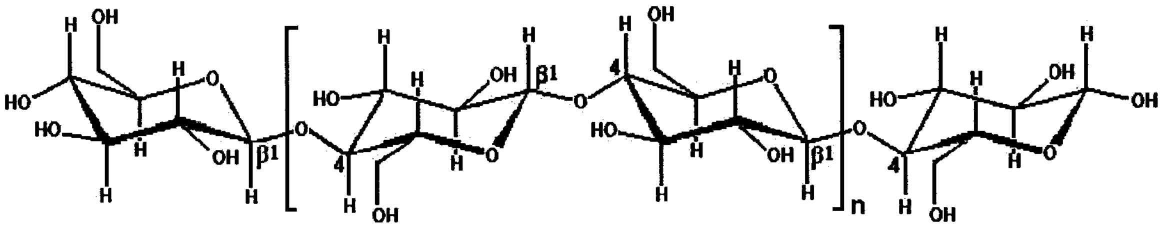


Figure 1.3. Cellulose structure (Sjöström, 1993).

1.1.2. Hemicellulose

Hemicelluloses are sugar polymer and very similar to cellulose in their make-up except that they are heterogeneous in their monosaccharide units and have a much shorter chain length. They all contain side chain or groups that lead to an amorphous structure. Each hemicellulose is composed of several carbohydrate monomers (arabinose, galactose, glucose, xylose, and mannose (heteropolysaccharides)) joined primarily by 1-4 glycoside bonds between monomer units. The hemicellulose polymers are non-crystalline and can generally be solubilized by base, but this removes the acetate side groups (de-esterification). The typical degree of polymerization of hemicellulose chains is about 100-200. Hemicelluloses play a very important role in pulping and bleaching processes. Typical hemicellulose monomer unit structures found in hardwood are shown in Figure 1.4. The principal hemicellulose component of hardwoods is glucuronoxylan, comprising 15-30% of wood. Glucomannan is the minor hemicellulose component of hardwoods, making up 1-3% of hardwoods. Their structures are illustrated in Figure 1.5.

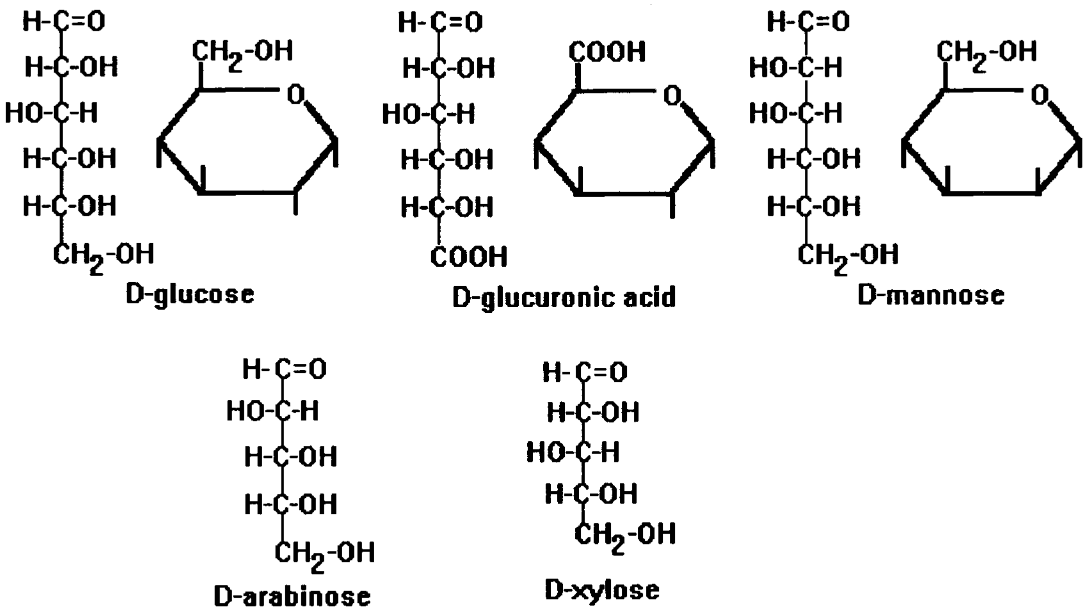
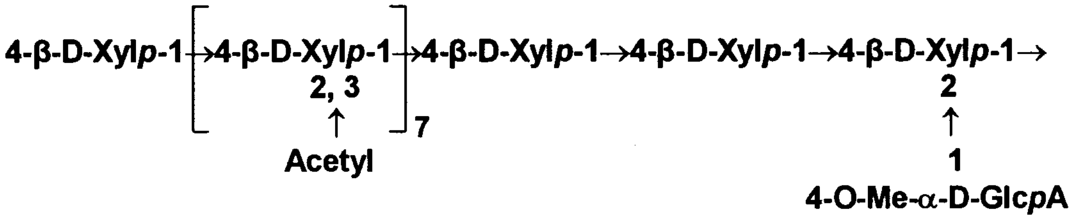


Figure 1.4. Hemicellulose monomer structure (Sjöström, 1993).

A.



$$\text{4-}\beta\text{-D-Xyl}p\text{-1}\left[\rightarrow\underset{\substack{2,3\\ \uparrow\\ \text{Acetyl}}}{\text{4-}\beta\text{-D-Xyl}p\text{-1}}\right]_7\rightarrow\text{4-}\beta\text{-D-Xyl}p\text{-1}\rightarrow\text{4-}\beta\text{-D-Xyl}p\text{-1}\rightarrow\underset{\substack{2\\ \uparrow\\ 1\\ \text{4-O-Me-}\alpha\text{-D-Glc}p\text{A}}}{\text{4-}\beta\text{-D-Xyl}p\text{-1}}\rightarrow$$

Repeating unit of 4-O-methylglucuronoxylan (glucuronoxylan).
Acetyl is (CH_3CO)

B.

4-β-D-Glc*p*-1→4-β-D-Man*p*-1→4-β-D-Glc*p*-1→4-β-D-Man*p*-1→4-β-D-Man*p*-1→

Repeating unit of hardwood glucomannan.

Figure 1.5. Hardwood hemicellulose structure (Sjöström, 1993).

1.1.3. Lignin

Lignin is a very complex polymer consisting of phenylpropane units (Figure 1.6) combined in a random formation. Coniferyl alcohol is the predominant lignin monomer found in softwoods. Both coniferyl and sinapyl alcohols are lignin monomers found in hardwood. The exact structure of lignin is not completely understood because of the random nature of the linkages between the phenylpropane units.

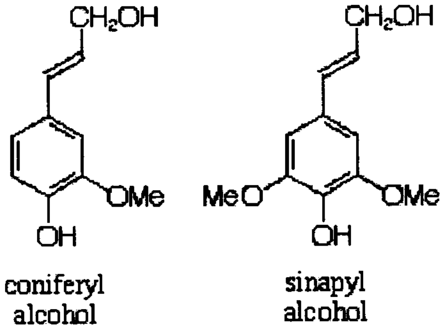


Figure 1.6. Monomers found in wood lignin.

However, several different types of linkages between lignin units have been identified. A widely accept proposed chemical structure of lignin is shown in Figure 1.7 (Brunow, 1998).

The objective of chemical pulping and bleaching is using specific amounts of chemicals to remove as much lignin as possible from wood to form pulp without damaging the fiber structure and losing hemicelluloses and cellulose.

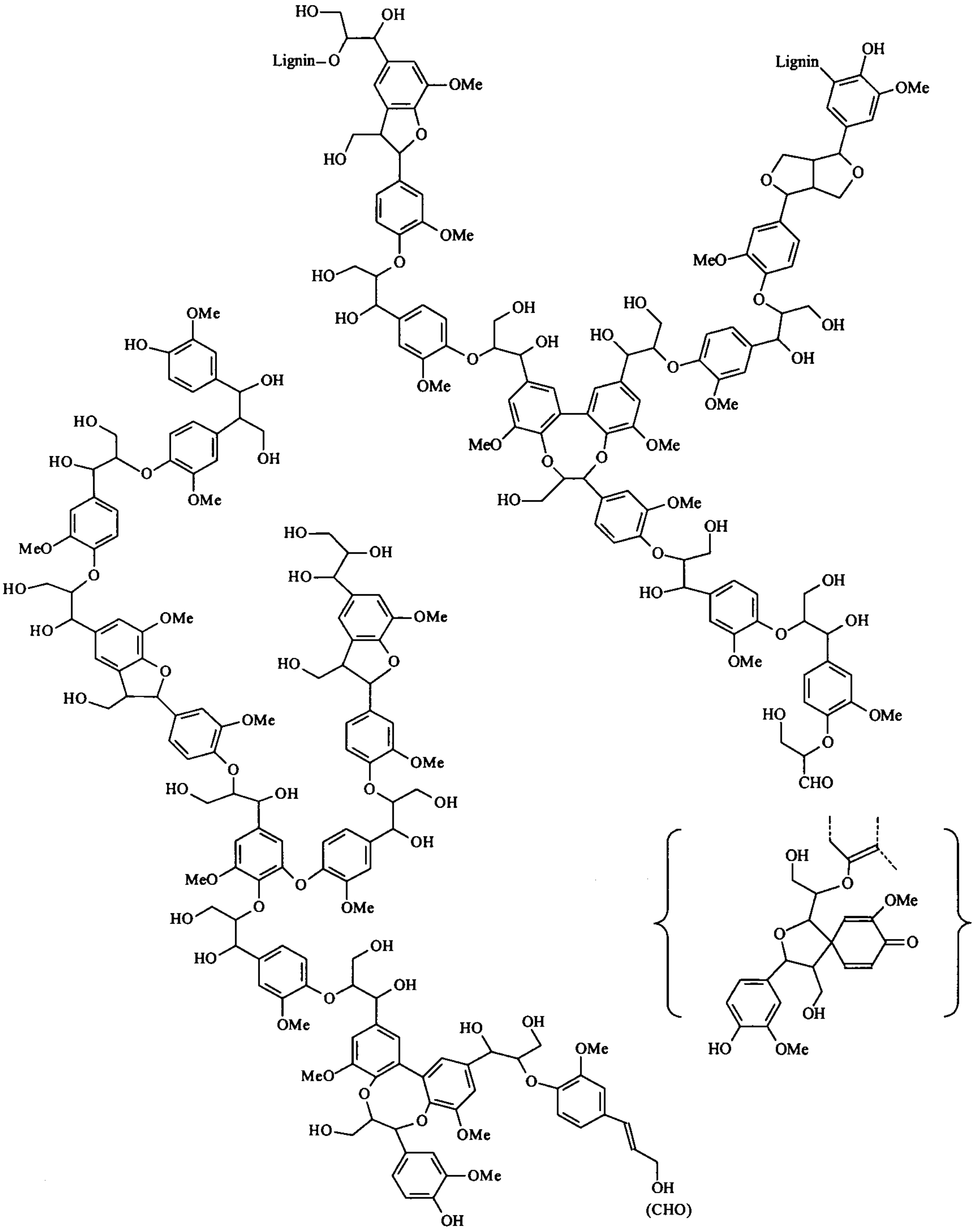


Figure 1.7. Lignin structure (Brunow, 1998).

[http://www.helsinki.fi/~orgkm_ww/lignin_structure.html]

1.2. KRAFT PULPING

The objective of Kraft pulping is to chemically separate the fibers in wood (or other fibrous materials) and dissolve most of the lignin contained in the fiber walls. In the Kraft pulping process, a mixture of sodium sufide (Na_2S) and sodium hydroxide ($NaOH$) is used to pulp the wood and liberate the individual cellular elements. High pulp strength and wide adaptability have made the kraft process the most popular pulping process in the world.

The manner in which the Kraft pulping process is executed has a significant effect on pulp bleaching and oxygen delignification. The amount of reduced lignin remaining in the pulp will depend upon the conditions used in the pulping processes. Also, the chemical demand required to bleach the pulp to a given brightness value can be different even when the lignin content in the pulp is the same. In addition, variations in the hemicellulose content and structure resulting from different pulping conditions would be expected to have a significant effect on oxygen delignification and bleaching. To optimize the oxygen delignification process and the production of ECF or TCF-bleached pulps, a better understanding of the relationship between pulping and bleaching is required. Specifically, it is desired to study the effect of the parameters in the cooking process on oxygen delignification and in subsequent bleaching stages.

1.3. OXYGEN DELIGNIFICATION

Oxygen delignification is defined as the use of oxygen and alkali to remove a substantial fraction of the lignin from the unbleached pulp. This process is becoming increasingly important in modern pulp bleaching technology. Oxygen delignification kinetics are very important for understanding the reaction mechanism and in the design and control of oxygen delignification reactions. Extending oxygen delignification without loss of fiber strength and pulp yield will be an important topic in pulp bleaching research for the near future. A lower kappa number following an oxygen delignification stage results in a lower active chemical charge required to bleach the pulp. This results in savings in chlorine dioxide charge and other chemical requirements to achieve the target brightness. Furthermore, the effluents from an oxygen delignification stage can be recycled to the chemical recovery system. Consequently, the environmental impact from color, COD, AOX and BOD in bleach plant effluent is reduced (Parthasarathy, 1992). In addition, it is well known that an application of oxygen delignification at high kappa numbers can lead to an increase in pulp yield. The biggest drawback of an oxygen delignification system is that the selectivity of the process is low compared to ClO_2 bleaching so that commercially the delignification has been traditionally limited to about 50%. Another disadvantage is the high capital cost of installing an oxygen delignification system.

Oxygen delignification is practiced commercially using both medium consistency (10%-14%) and high concentration (25%-35%) technology; although, practically all new systems use medium consistency technology because the capital cost is lower. One- and two-stage medium consistency oxygen delignification systems are available commercially. Figure 1.8 shows a typical two-stage medium consistency oxygen delignification system. In this system, caustic, $MgSO_4$ and steam are added to the pulp prior to going to the standpipe of a medium consistency pump, which provides the motive power to the pulp and the total pressure in the oxygen delignification reactors. Oxygen

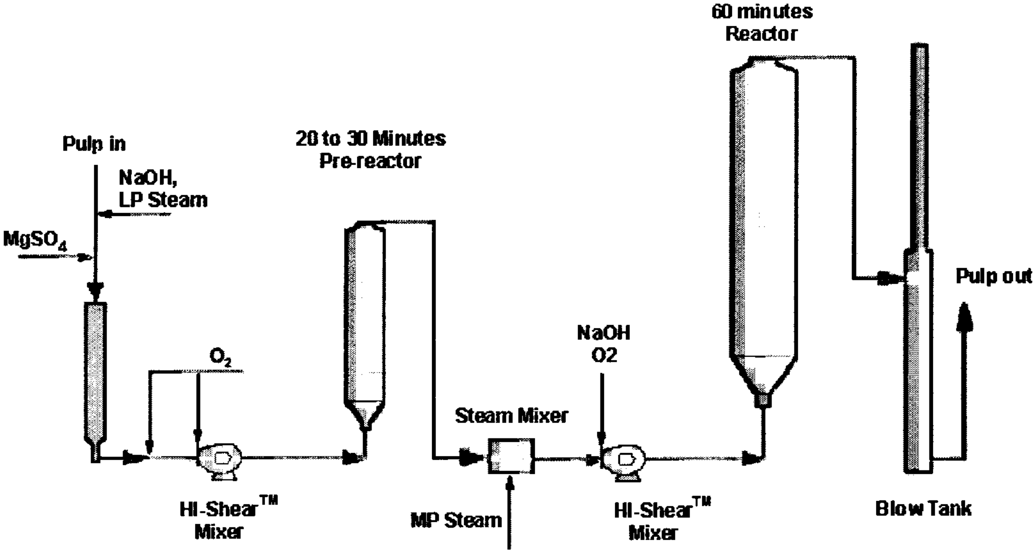


Figure 1.8. Two-stage medium consistency oxygen delignification system.

gas is then added to the pulp ahead of an oxygen mixer, which reduces the size of the oxygen gas bubbles and produces intimate contact between the pulp and oxygen. The pulp then proceeds through an up flow tower having a residual time of 20 to 30 minutes. Typically the temperature is 85 to 100 °C. The pulp then goes to a steam mixer where medium pressure (100 psig) steam is added to reach the desired reacting temperature. Additional caustic and oxygen are also added and mixed in a second high shear mixer. The pulp then proceeds through a second medium consistency reactor. In the second reactor the reaction time is typically 50 to 60 minutes. The pulp from the second medium consistency reactor goes to a blow tank where the off gases are released. The off gases consist of water vapor, carbon dioxide, carbon monoxide, nitrogen, unreacted oxygen, and any inert gases present in the oxygen initially. The pulp from the blow tank then proceeds to a post oxygen washing.

The kinetics of oxygen delignification is complex and varies for different wood species and pulping processes. Delignification proceeds rapidly during the first five to ten minutes of the oxygen stage, and then proceeds at a much slower rate for the remaining delignification time. The rate equation describing lignin removal is characterized by a high apparent reaction order with respect to the lignin content when expressed with a single region model (Schoon, 1982). The delignification kinetics are thought to be hindered by transfer of oxygen and alkali into the cell wall and by refractory residual lignin moieties present in the pulp resulting from the pulping conditions. A major unexplored area in oxygen bleaching is the relationship between delignification kinetics observed in the oxygen stage and the conditions present in the digester and other unit operations in the fiber line.

1.4. OBJECTIVE AND SCOPE

Few of the previous studies on oxygen delignification have focused on the effect of pulping process conditions. Rather, many have focused on optimizing the oxygen delignification process itself.

The objective of the present study was to determine the impact of the effective alkali (EA) level, cooking temperature in the digester and pulp yield on the performance of an oxygen stage. The effect of the pulp yield of the brownstock on the kinetics of oxygen delignification was studied by varying the hemicellulose content of the pulp. In this study, Northeastern hardwood Kraft pulps were used as the pulp of interest. The scope of this study was to obtain response curves for an oxygen stage using conventional hardwood kraft pulps. The pulps used in this investigation will had similar values for the kappa number but were produced in a kraft digester by varying the H-factor at various effective alkali (EA) levels or by varying cooking temperature. Pulps with high hemicellulose content were prepared by pulping with anthraquinone which functions as a pulping catalyst. Pulps of high hemicellulose content were investigated became preliminary work (Zou, 2000) showed that pulps with high xylan content were more difficult to delignify but had improved selectivity.

Chapter 2

LITERATURE REVIEW

2.1. KRAFT PULPING

Dahl first invented the Kraft pulping process at 1879 (Grace & Malcolm, 1989). Since its initial discovery the Kraft pulping process has developed tremendously and has become the leading pulping process in the pulping industry in the world. Advantages of the Kraft process are better pulp physical properties, shorter cooking time, insensitivity to wood species and supply, and efficient energy and chemical recovery capabilities.

2.1.1. Kraft Pulping Chemistry

The objective of kraft pulping is to chemically separate the fibers in wood (or other fibrous materials) and dissolve most of the lignin contained in the fiber walls. This is typically accomplished by using sodium hydroxide (NaOH) and sodium sulfide (Na_2S) liquor and cooking at a specific temperature for a given period of time. Appropriately 70 to 75% of the lignin in wood is located in the secondary wall of the fiber with the balance found in the middle lamella and the p-layer.

In Kraft pulping, fiber separation is achieved by dissolving the lignin that holds the fibers together in the middle lamella or the region between adjacent cells. The chemicals in the cooking liquor also penetrate the fiber walls and dissolve the lignin that exists there. The chemicals not only react with lignin but also react with the carbohydrate polymers that exist in the cell wall. The latter reactions are unwanted, since they degrade the carbohydrates to smaller, soluble molecules that lower yield and reduce fiber quality.

Since both solid and liquid phases are present, there are several steps that must be considered for the Kraft process (Wilder, 1964; Levenspiel, O., 1972):

1) Transport or movement (penetration and molecular diffusion) of chemicals into and air from the exterior of the chips;
2) Adsorption of the chemicals onto the reaction surfaces;
3) The actual chemical reaction step;
4) The desorption of reaction productions from the surfaces;
5) Diffusion of the dissolved reaction products to the exterior of the chip.

The slowest step in this process series controls its overall rate.

2.1.1.1. Reactions of Carbohydrates

During Kraft pulping both carbohydrate and lignin reactions occur. The reactions of the cellulose and hemicellulose polymers have been extensively studied by many researchers. The main carbohydrate reactions that occur in kraft pulping are deacetylation, peeling and stopping reactions, side chain elimination reaction, and random hydrolysis (Grace et al., 1989).

Deacetylation. Deacetylation reactions involve the saponification of acetyl groups in acetylated hemicelluloses, i.e., the galactoglucomannan in softwoods and 4-O-methyl-glucuronoxylan in hardwoods. Deacetylation reactions are rapid and quantitative.

Peeling reaction and stopping reaction. The peeling reaction, which results in a yield loss, occurs primarily during the heat-up period of the cook. In the peeling reaction, the terminal units of the polysaccharide chain are removed in a stepwise manner until a stopping reaction occurs that stabilizes the polysaccharide against further peeling. The carbohydrate material lost in peeling is converted to soluble acids, which reduce the effective alkali concentration of the cooking liquor. The polysaccharides, which have undergone a stopping reaction, are relatively stable until the high temperature portion of the cook is reached. The cessation of peeling may be due to a rearrangement of the reducing end group which makes it stable to peeling ("chemical stopping"), or because the reducing end group has become physically inaccessible to the alkaline reagent ("physical stopping"). The generally accepted mechanism for peeling reactions and two stopping reactions are shown in Figure 2.1.

Random cleavage of the main chain. During the Kraft pulping process, with removal of the side chains, the main carbohydrate chain is also cleaved. Random cleavage lowers the molecular weight of carbohydrates and also decreases yield by solubilization of the short ends cleaved off.

Removal of methyl and ultimately glucuronosyl groups. During the Kraft reactions, methyl and ultimately glucuronosyl groups are removed from the arabino (4-O-methyl-glucourono) xylans and 4-O-methyl-glucouronoxylans polymers.

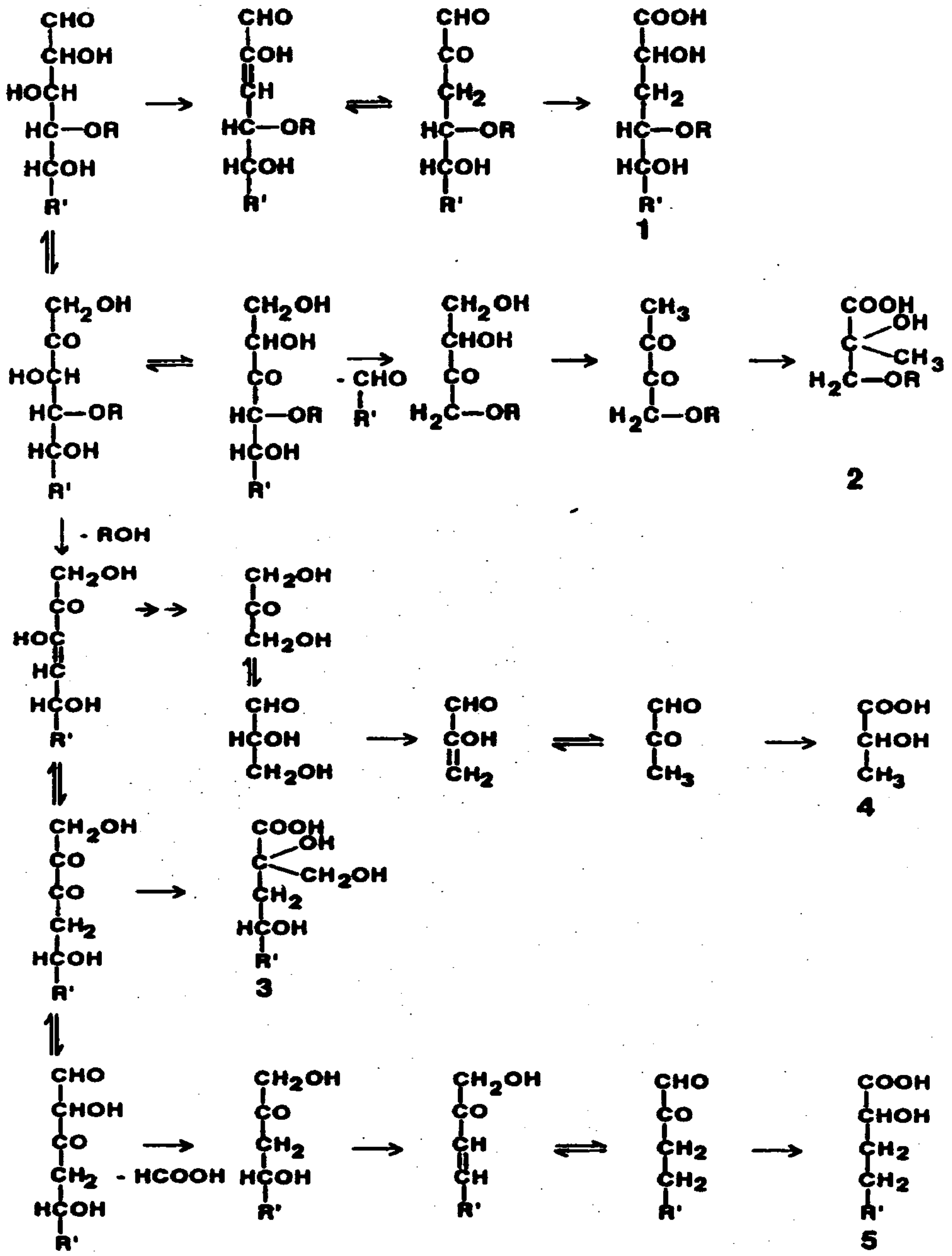


Figure 2.1. Peeling reaction and stopping reactions of polysaccharides. R—polysaccharide chain; R'—CH_2OH or H; (1)—3-deoxyhexonic acid end groups; (2)—2-C-methylglyceric acid end groups; (3)—3-deoxy-2-C-hydroxymethylpentonic acid; (4)—2-hydroxypropanoic acid; (5)—3,4-dihydroxypentanoic acid (Sjostrom, E., 1993).

2.1.1.2. Reaction of Lignin

The reactions of lignin during kraft pulping are complex and not completely understood. Lignin is basically a complex aromatic polymer built up of hydroxyphenylpropane units and is therefore phenolic in character. It is comprised of a heterogeneous, branched network system with no evident simple repeating unit. Therefore, it appears to be totally amorphous and is chemically bonded to the hemicelluloses. Generally, Kraft pulping involves mercaptation, alkaline hydrolysis, and alkaline condensation of lignin. The reaction of sulfur with lignin in the Kraft pulping is not completely understood, it appears to result in stabilizing phenolic groups thus preventing lignin condensation and aiding the cleavage of ether bonds between phenylpropane units that have free phenolic hydroxyl groups. Studies with model substances representing various structural units in lignin have largely clarified the delignification reactions in kraft pulping.

Cleavage of ether bonds. The main fragmentation reactions of lignin in kraft pulping are cleavage of α-aryl ether bonds in phenolic units and of β-aryl ether bonds in phenolic and non-phenolic units (Gierer, 1970). The main reactions are shown in Figure 2.2.

Cleavage of carbon-carbon bonds. A minor portion of lignin fragmentation during Kraft pulping can be ascribed to the cleavage of carbon-carbon bonds in side chains, between side chains, and in aromatic nuclei. Cleavage of carbon-carbon bonds can form formaldehyde that may enter lignin condensation reactions.

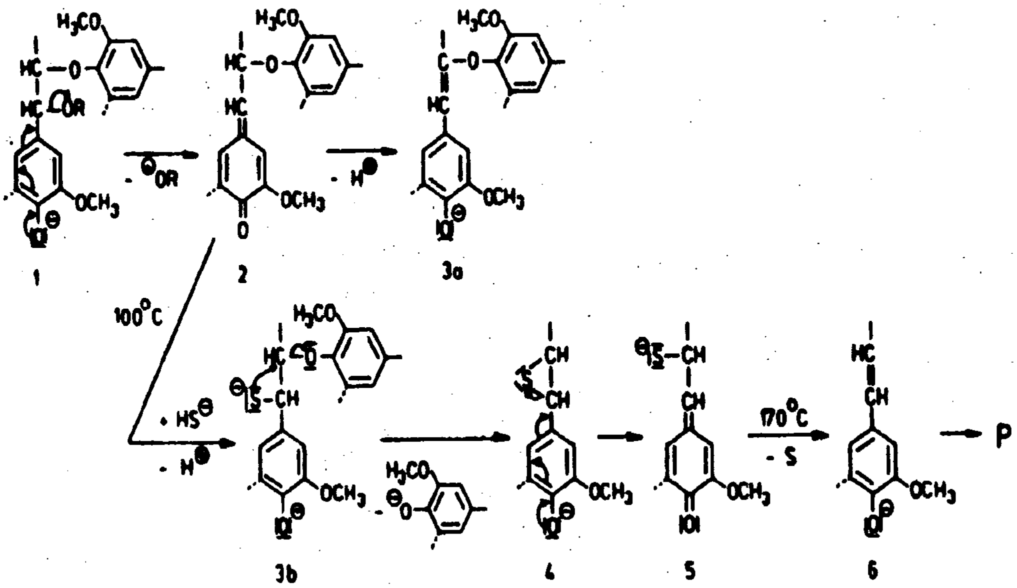


Figure 2.2. Main reactions of phenolic β-aryl ether structures during kraft pulping (Gierer, J., 1977).

Lignin condensation reactions. The major site of condensation reactions is the unoccupied C-5 position of phenolic units. Therefore, condensation occurs more easily during softwood kraft pulping, compared to hardwood. It has been found that, during conventional kraft pulping, the major structural changes occurring on the residual lignin are the progressive enrichment of carboxylic acids and condensed phenolic hydroxyl groups. Toward the end of Kraft pulping, the residual lignin contains much more C5 condensed phenolic hydroxyl groups than were present in the starting wood sample. Both C5 and C6 condensed phenolic hydroxyl units were found to be relatively stable toward oxygen delignification (Jiang and Argyropoulos, 1999). Examples of condensation reactions of lignin during Kraft pulping are shown Figure 2.3.

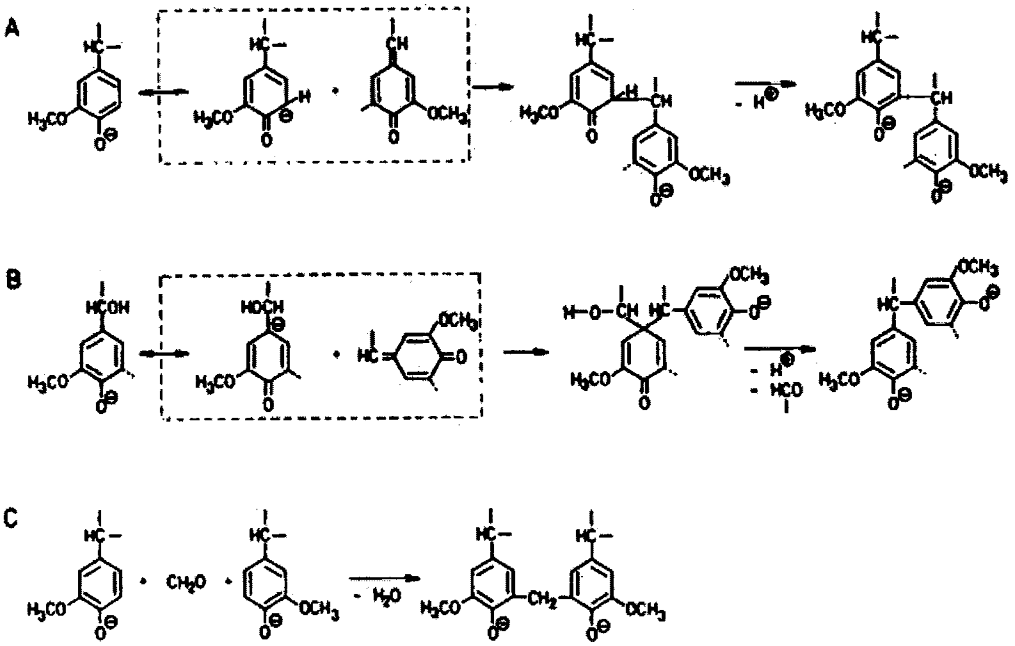


Figure 2.3. Examples of lignin condensation reactions during kraft pulping (Gierer, J., 1977).

2.1.2. Kraft Pulping with Anthraquinone

Holton (1977) reported that anthraquinone (AQ) not only can increase pulp yield, it also can increase the rate of delignification leading to lower lignin levels for equivalent cooking conditions. Great developments in the late 1980s and early 1990s have lead to the tremendously expanded use of AQ.

The generally accepted mechanism is that AQ functions in a redox sequence such as is illustrated in Figure 2.4. AQ cycles between its insoluble oxidized form and its soluble reduced form. First, AQ reacts with the reducing group of a carbohydrate thus stabilizing the carbohydrate against alkaline peeling reactions and producing the reduced soluble form of AQ (AHQ). Then, the AHQ reacts with the quinonemethide segment of the lignin polymer increasing the rate of delignification. The AHQ is also converted back to AQ at the same time and finishes a cycle reaction (Grace & Malcolm, 1989).

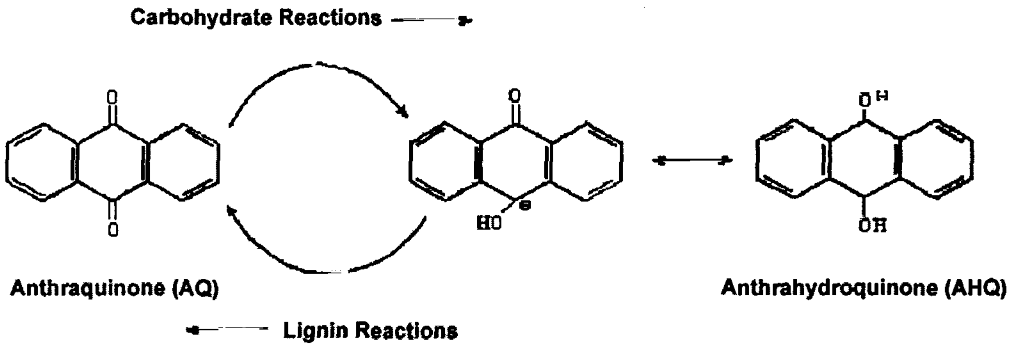
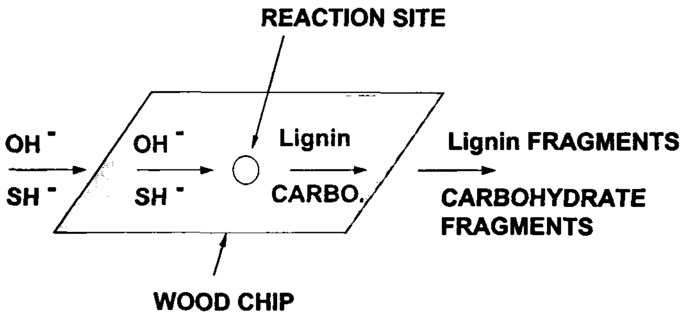


Figure 2.4. Mechanism for the reaction of anthraquinone in alkaline pulping (Grace and Malcolm, 1989).

2.1.3. Kraft Pulping Kinetics

2.1.3.1. Delignification Models

Grace and Malcolm (1989) presented an excellent review of the kinetics of Kraft pulping. Kraft delignification is a solid/liquid heterogeneous phase reaction. It is not a homogeneous process as sometimes inferred from the fit of empirical equations. The wood chips are porous solids and are impregnated with pulping liquor. Reactions proceeds continuously through the solid chip, most likely at different rates at different locations. Reactants diffuse in and products out as reaction proceeds in the porous system (Figure 2.5).



One or a combination of resistances can control the overall rate of delignification. Resistances of importance are the liquid film resistance, pore diffusional resistance, and chemical reaction resistances. Pore resistance and chemical reaction resistances expectedly play the dominant role.

The two active chemicals in the Kraft process, NaOH and Na_2S, have independent functions. The NaOH promotes hydrolysis of phenolic ether bonds of lignin and neutralized acids formed in the degradation of both lignin and carbohydrates. It is usually given in terms of the effective alkali (EA) defined by the equation

$$EA = (NaOH + 1/2Na_2S) \qquad (2.1)$$

NaOH arises both from caustic existing in the pulping liquor (white liquor) and because Na_2S can react with water.

$$Na_2S + H_2O = NaSH + NaOH \qquad (2.2)$$

$$NaSH + H_2O = H_2S + NaOH \qquad (2.3)$$

The factor of ½ arises because the Na_2S exists primarily in the form of hydrosulfide ion (HS^-) because reaction (2.3) above is suppressed and does not occur to any extent. SH^- ion reacts almost exclusively with lignin in a way that prevents condensation reactions from occurring. Sulfidized lignin reforms hydrosulfide ions. The sulfide thus has the effect of catalyzing or speeding delignification. The effect is particularly great up to 10% sulfidity defined by the equation

$$Sulfidity = [Na_2S/(Na_2S + NaOH)] \qquad (2.4)$$

Enhancement in the rate of delignification is slight for values of the sulfidity much over 30% (Rydholm, 1968). Commercial values in Northern America are typically in the range of 15% to 30%.

Numerous models have been proposed to describe the kinetics of the Kraft Process. There are three approaches to treating the kinetics of Kraft pulping. Most treat this heterogeneous kinetic problem with homogenous kinetic equations. Two examples of this approach are the model of Kerr (1970) and that of Edwards and Norberg (1973). More complicated models others include mass transfer effects (Johnsson, 1971; and Gustafson and Ricker, 1983) while some are purely empirical (Hatton, 1976; Tasman, 1981; and Lin, 1978). Perhaps the most fundamentally sound model is the degelation model of Yan (1981) who treated lignin as a random polymer and applied the Floy theory of trifunctional polymerization in reverse model lignin breakdown.

In the homogenous kinetic approach, which is most widely used, three periods of delignification are defined, an initial period, a bulk delignification period, and a final delignification period. The overall delignification rate has been expressed by pseudo-first order kinetic equations.

$$-\frac{dL}{dt} = k(L - L_d) \qquad (2.5)$$

where (L) is the lignin content often expressed as a % on wood, (L_d) is the residual or unreactive lignin that cannot be removed by the alkali conditions in the digester, and (k) is the first order rate constant which depends upon the experimental conditions. More complicated expressions include concentration terms for the hydroxyl ion (OH^-) included singly or in combination with the concentration of sulfide ion (SH^-) ion

$$-\frac{dL}{dt} = k \cdot L^a \cdot (OH^-)^b \cdot (HS^-)^c \qquad (2.6)$$

2.1.3.2. H-factor or Time at Temperature Factor

The applicability of simple first order exponential equations led to the so called H-factor (Vroom, 1957) which incorporates the effects of both time and temperature in one simple factor. At constant wood and liquor composition, the H-factor allows control of the pulp yield and lignin content by changing either the temperature or time, with the same H-factor producing the same pulp yield and kappa number. The residual or "floor" lignin content in equation (2.5) is taken to be zero and first order kinetics are assumed to apply.

$$\frac{dL}{dt} = k * L \qquad (2.7)$$

The reaction rate constant (k) in equation (2.5) is arbitrarily taken to be unity at 100 C and the values of (k) at other temperatures (T) is calculated on the basis of the Arrhenius relationship:

$$k = A \cdot e^{-E_a/RT} \qquad (2.8)$$

where A is the frequency factor and E_a is the activation energy. The activation energy (E_a) had been determined from previous research to by equal to 32 Kcal/mole for Kraft pulping and 35 Kcal/mole for a soda cook (0 sulfidity case). With these values and the reaction rate constant taken to be unity (k=1) at 100 °C, the frequency factor (A) can be determined so that the reaction rate constant becomes,

$$k = k_r = \exp(43.2 - 16{,}113/T) \qquad \text{(Kraft)} \qquad (2.9)$$

$$k = k_r = \exp(45.8 - 17{,}610/T) \qquad \text{(Soda)} \qquad (2.10)$$

where the subscript (r) on the rate constant denotes a "relative" rate, and the temperature (T) is given in degrees Kelvin. The H-factor was defined as the integral of the relative rate constant (k_r) with time

$$H = \int k_r dt = \int_0^{t_f} \exp(43.2 - 16{,}113/T)dt \text{ (Kraft)} \qquad (2.11)$$

where (t_f) is the final time. For the soda process a similar equation would be used. To evaluate the integral on the right side of equation (2.11), the time versus temperature history for the cooking cycle must be known (Figure 2.6).

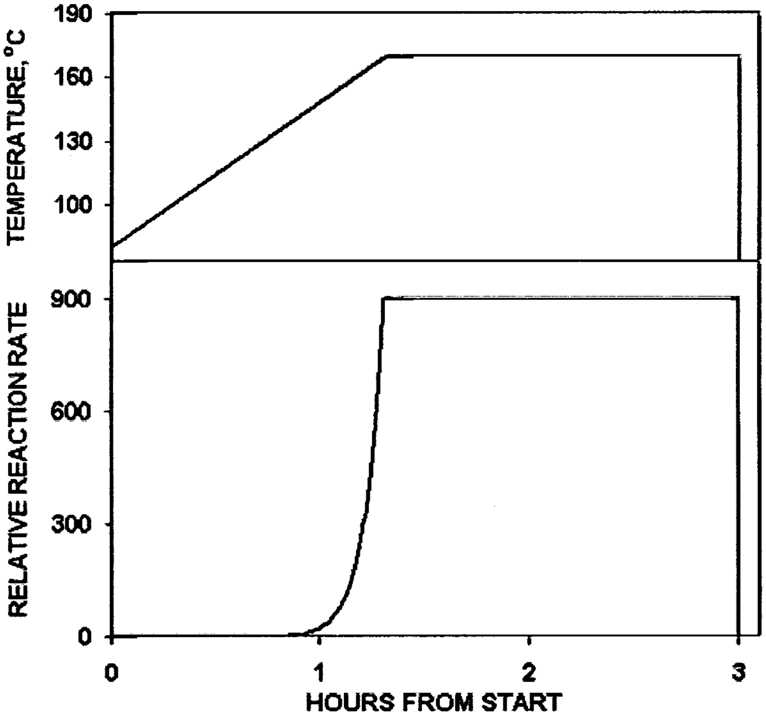


Figure 2.6. Relative reaction versus cooking time (Grace and Malcolm, 1989).

For a typical batch cooking cycle, the top of Figure 2.6 shows the time versus temperature curve, while the bottom curve shows the relative rates calculated from the equations for the temperature at selected time values. The H-factor is the area under the lower curve. Lastly, for illustration, Figure 2.7 shows the lignin content and pulp yield plotted against H-factor for three different temperature values for a Kraft cook at 31% sulfidity. The lignin content and pulp yield are single valued functions of the H-factor, and are independent of temperature.

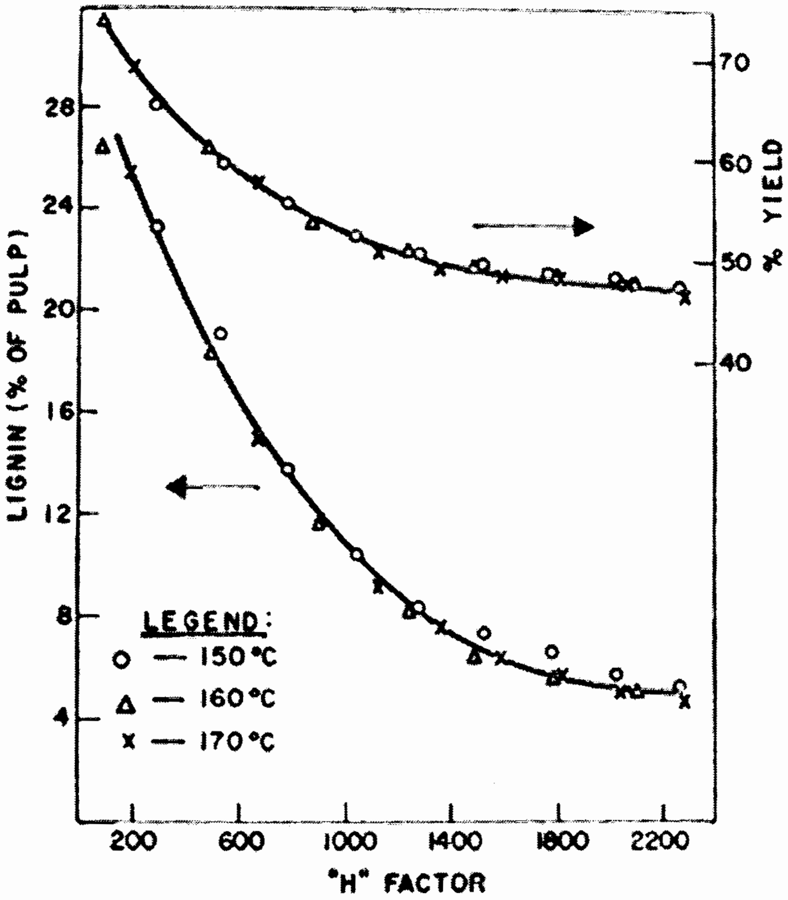


Figure 2.7. Pulp yield and lignin content versus H-factor at three temperatures (Grace and Malcolm, 1989).

2.1.3.3. Carbohydrate Removal during Kraft Pulping

Little research work was done on the kinetics of carbohydrate removal during Kraft pulping. A major work in the field of carbohydrate removal is the work of Aurell and Hartler (1965). Data are presented in Figures 2.8 and 2.9 for the yield of hemicellulose polymers as a function of pulping time and temperature. The loss of glucomannan is illustrated in Figure 2.8 and shows that this hemicellulose polymer is removed rapidly at the beginning of the cook, that is, for temperatures less than about 115 °C. At temperatures higher than 115 °C, that is when about 70% of the glucomannan is removed, the rate of removal drops off sharply and the glucomannan content of the pulp becomes constant. Also, there is essentially no effect of alkali concentration on the rate of glucomannan removal. To investigate the mechanism of the hemicellulose reactions, sodium borohydride was added to the pulping liquor prior to the cooking. Borohydride is a very powerful reducing agent and converts the carbonyl groups on the reducing end units to hydroxyl groups. This reaction stabilizes the carbohydrates and reduces peeling, which was seen to occur with the glucomannan even at elevated temperatures (see Figure 2.8). Thus, it was concluded that dissolution of glucomannan occurs primarily by peeling at elevated temperature. At low cooking temperatures (100 °C), the loss of glucomannan is thought to occur by dissolution in alkali since the sodium borohydride had no effect on the quantity dissolved.

The dissolution of xylan is illustrated in Figure 2.9. By contrast, this figure shows that the xylan polymers are removed primarily at high temperature, above about 150 °C. Figure 2.9 also shows that the dissolution depends strongly on the concentration of alkali and the addition of sodium borohydride, the strong reducing agent does not significantly change the level of dissolution. These results were interpreted to mean that xylan polymers are not primarily removed by peeling but rather by simple dissolution in strong alkali.

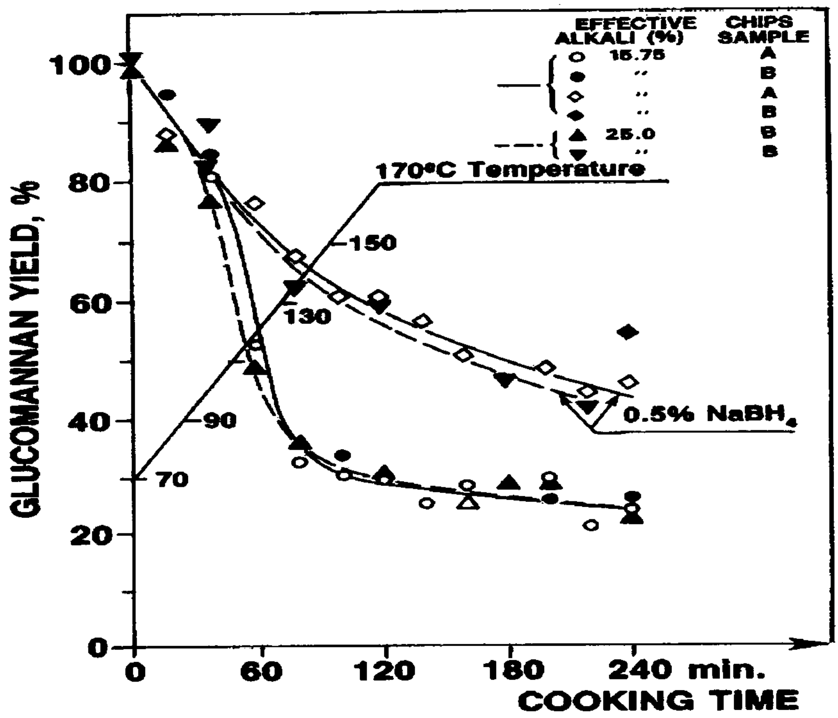


Figure 2.8. The removal of glucomannan during pine Kraft cooks (Aurell and Hartler, 1965).

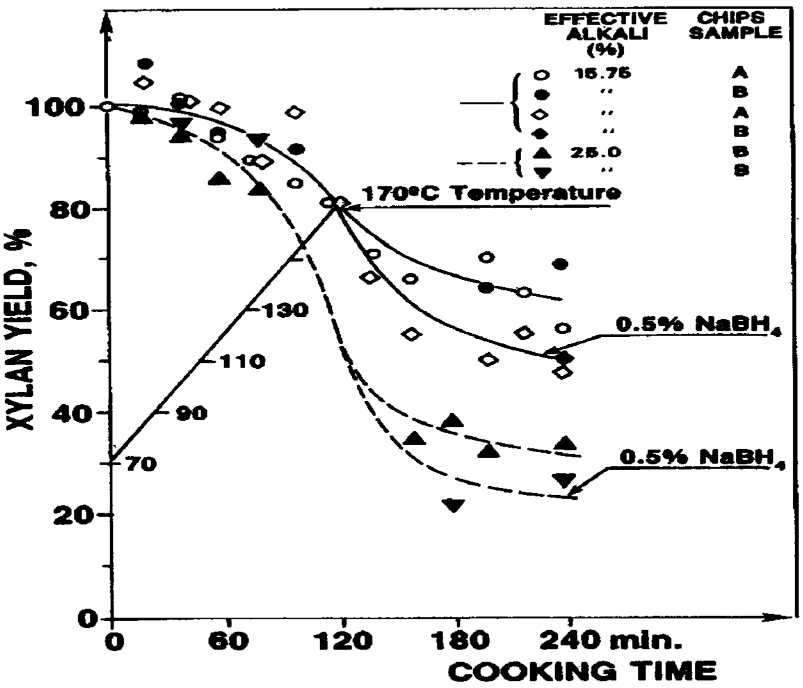


Figure 2.9. The removal of xylan during pine Kraft cooks (Aurell and Hartler, 1965).

2.2. OXYGEN DELIGNIFICATION

2.2.1. Pulp Bleaching Mechanism

Each bleaching reagent develops its own chemistry with residual lignin, when the bleaching is conducted in alkaline or in acid conditions. The common effect among the bleaching chemicals is that all are oxidants. During the bleaching process, it is believed that lignin degradation and solubilisation are the result of attack on the aromatic rings (Lachenal et al, 1999).

The general mechanism of oxidative bleaching can be described using the same global reaction shown in Figure 2.10, which is an oxidation reaction (Lachenal et al., 1999). Four electrons are exchanged in the formation of one muconic acid derivative from one aromatic ring. A subsequent alkaline stage is required when the oxidant is operating in acid conditions in order to hydrolyze the esters and solubilize the acid products.

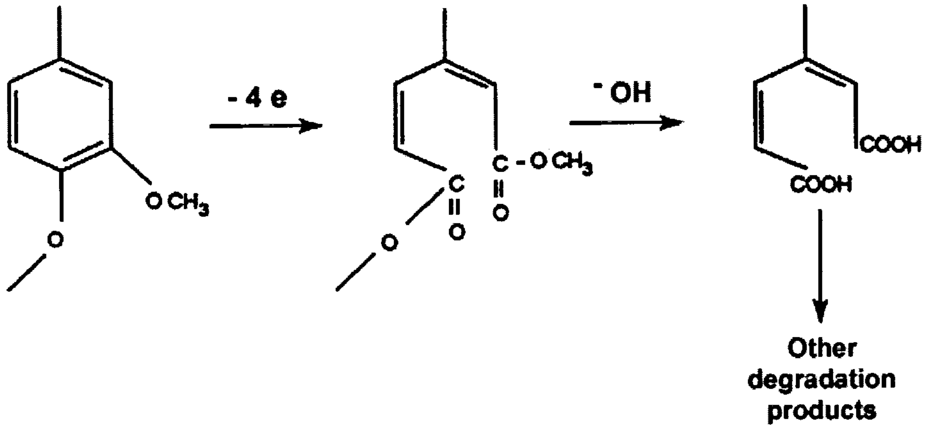


Figure 2.10. General mechanism of oxidative bleaching (Lachenal et al., 1999).

Chlorine Dioxide Bleaching. As a bleaching reagent, chlorine dioxide has a very high selectivity towards lignin. The reactions that take place during ClO_2 bleaching are shown in Figure 2.11. The aromatic ring is opened during reaction. No other ClO_2

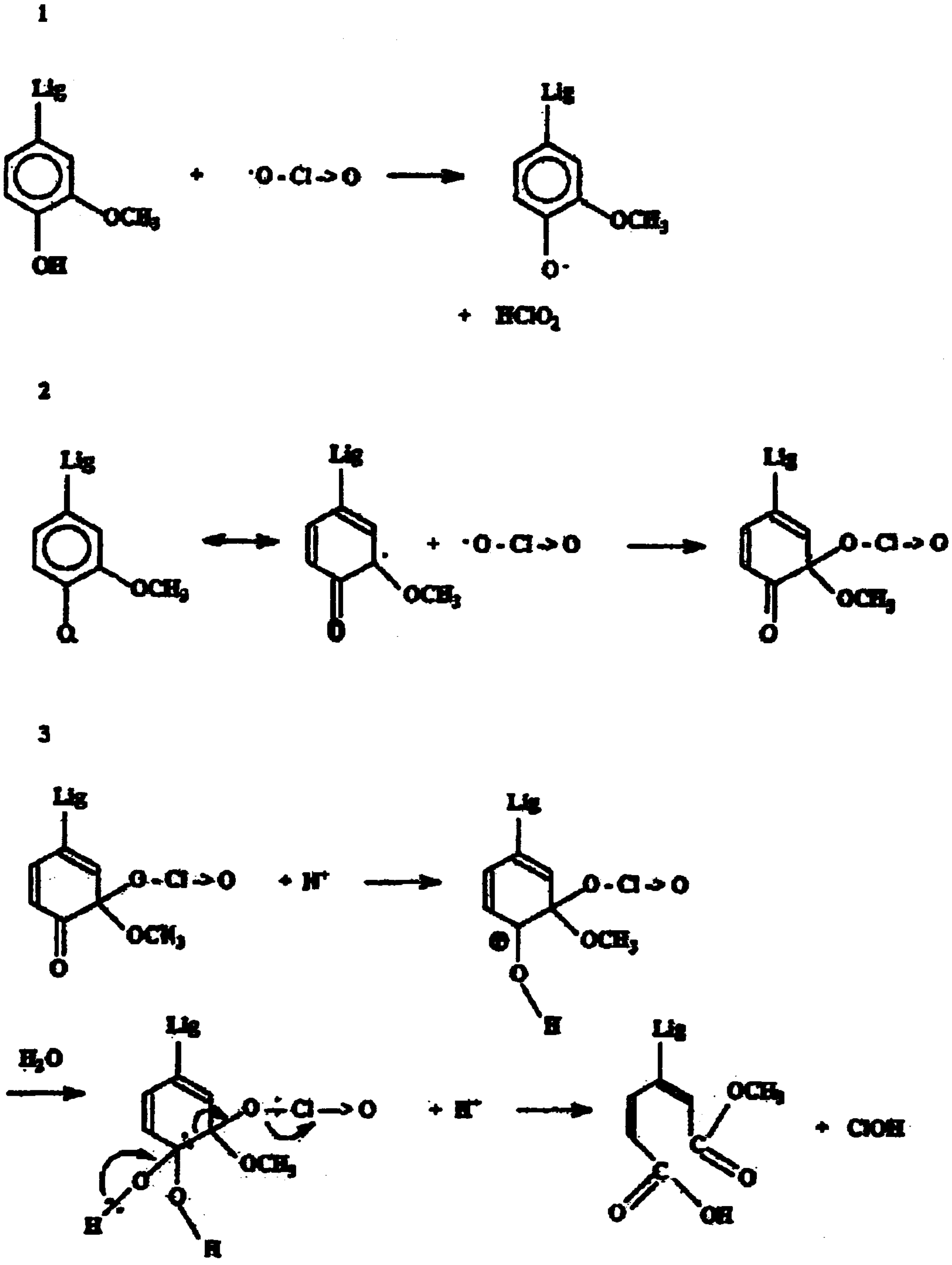


Figure 2.11. General mechanism for ClO_2 delignification.
1. Formation of a phenoxy radical; 2. Attack of a second ClO_2 molecule;
3. Acid catalyzed ring opening (Lachenal, D., 1999).

reaction that would lead to delignification has been described. The ClOH formed as a byproduct does react and should generate new free phenolic groups, which are the active sites for ClO_2 reaction (Lachenal, D.,1999).

Ozone Bleaching. Since it produces no toxic byproducts, ozone is a reagent that is gaining use as a bleaching chemical. Ozone is a strong electrophile that attacks aromatic rings and side-chain double bonds in lignin. Lignin degradation by opening of the aromatic rings is the most probable mechanism during bleaching. Double bonds on side chains should react even faster, of which the number is very small in residual lignin, however (Lachenal, D., 1999). The use of ozone as a bleaching reagent has the same limitation as oxygen and hydrogen peroxide. The same detrimental radicals also form during ozone bleaching, which results in poor selectivity in the bleaching. The reactions that take place during ozone bleaching are shown in Figure 2.12.

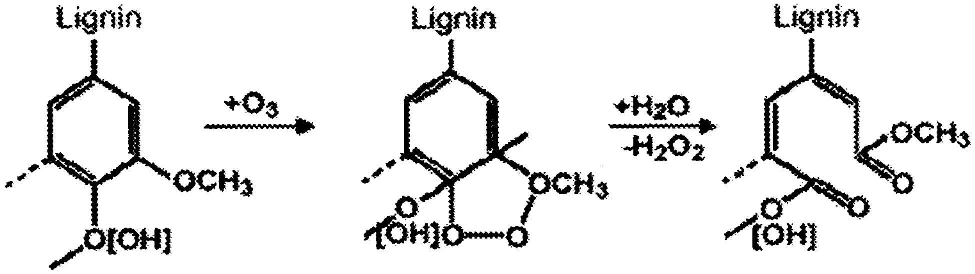


Figure 2.12. General mechanism for ozone delignification (Lachenal, 1999)

Hydrogen Peroxide Bleaching. Since it generates no toxic byproducts, hydrogen peroxide is an environmental friendly bleaching agent. Hydrogen peroxide bleaching is run under similar conditions to oxygen delignification. Because metal ions presenting in pulp and in solution catalyze the formation of hydroxyl free radicals from hydrogen peroxide, a pretreatment step in which a chelating agent is applied prior to peroxide bleaching is necessary. At high temperature (90-100 °C) H_2O_2 is thought to react in a similar way to oxygen except that OH^- radical not O_2 would initiate the reaction on the phenolic rings. H_2O_2 would initially decompose into radicals according to:

$$2\,H_2O_2 \Leftrightarrow \bullet OH + HOO\bullet + H_2O$$

Then again, ring opening would occur (Lachenal, D., 1999).

2.2.2. Oxygen Delignification Chemistry

2.2.2.1. Oxygen Chemistry

McDonough (1996) reviews oxygen delignification chemistry, which is quite complicated due to the complexity of the lignin structure, as well as the number of different oxygen species formed during the reaction. The mechanism of oxygen bleaching has been studied using model compounds by numerous investigators (Gierer and Imsgard, 1977; Ljunggren and Johansson, 1987; Johansson and Ljunggren, 1994) and by examining residual and dissolved lignin moieties (Berry and Fleming, 1987). Depending upon the pH, the oxygen molecule can be reduced to different species: HO_2^-, H_2O_2, $O_2\bullet^-$, $HO_2\bullet$, and $HO\bullet$ (Figure 2.13).

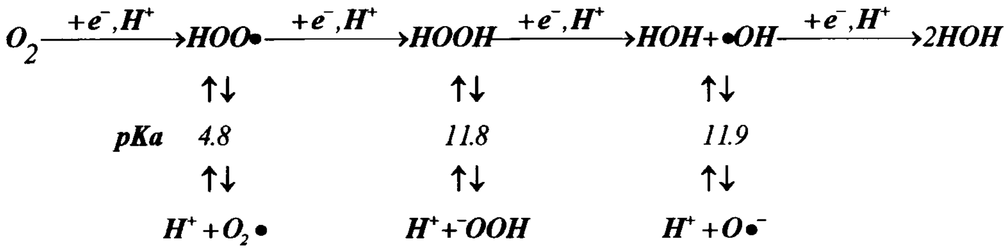
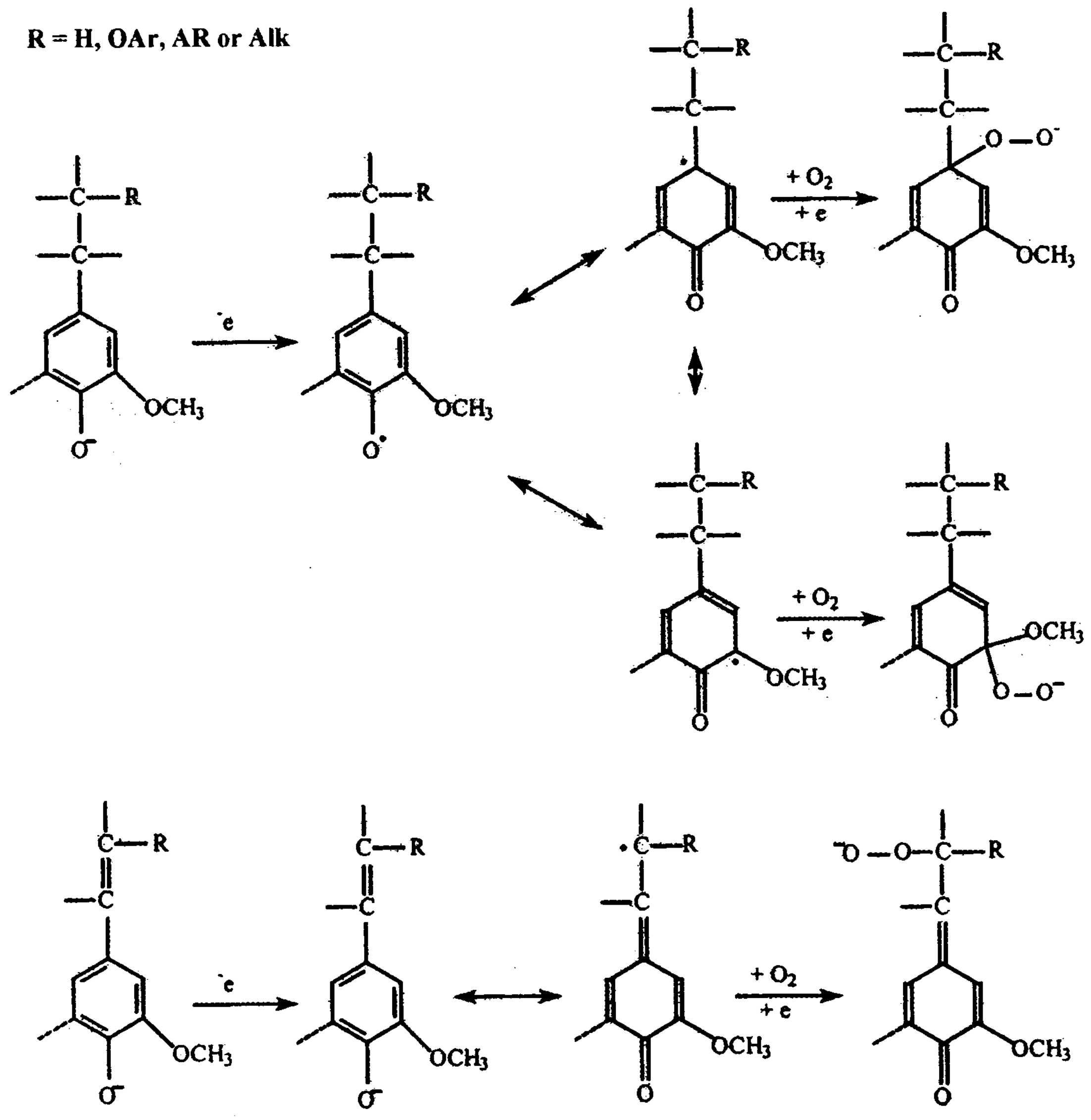


Figure 2.13. Stepwise reduction of oxygen (McDonough, 1996).

2.2.2.2. Reaction of Lignin

Model compounds have been used to study the reaction of lignin with oxygen under alkaline conditions (Gierer and Imsgard, 1977; Ljunggren and Johansson 1987; Johansson and Ljunggren, 1994; e.t.). Also, Berry and Fleming (1987) identified residual and dissolved lignin structures during oxygen bleaching. These studies have been summarized by McDonough (1996) and show that free phenolic hydroxyl groups play a major role in oxygen delignification. The phenolic group is ionized under strongly alkaline conditions, generating a site with high electron density, which undergoes transfer of a single electron to molecular oxygen or any of the available radical species. The degradation products from oxygen delignification are predominately organic acids and carbon dioxide (Miller et al., 1995). The suggested mechanism of oxygen delignification is shown in Figure 2.14 and 2.15 (McDonough, 1996).



R = H, OAr, AR or Alk

Figure 2.14. Initial reaction leading to oxygen delignification (McDonough, 1996).

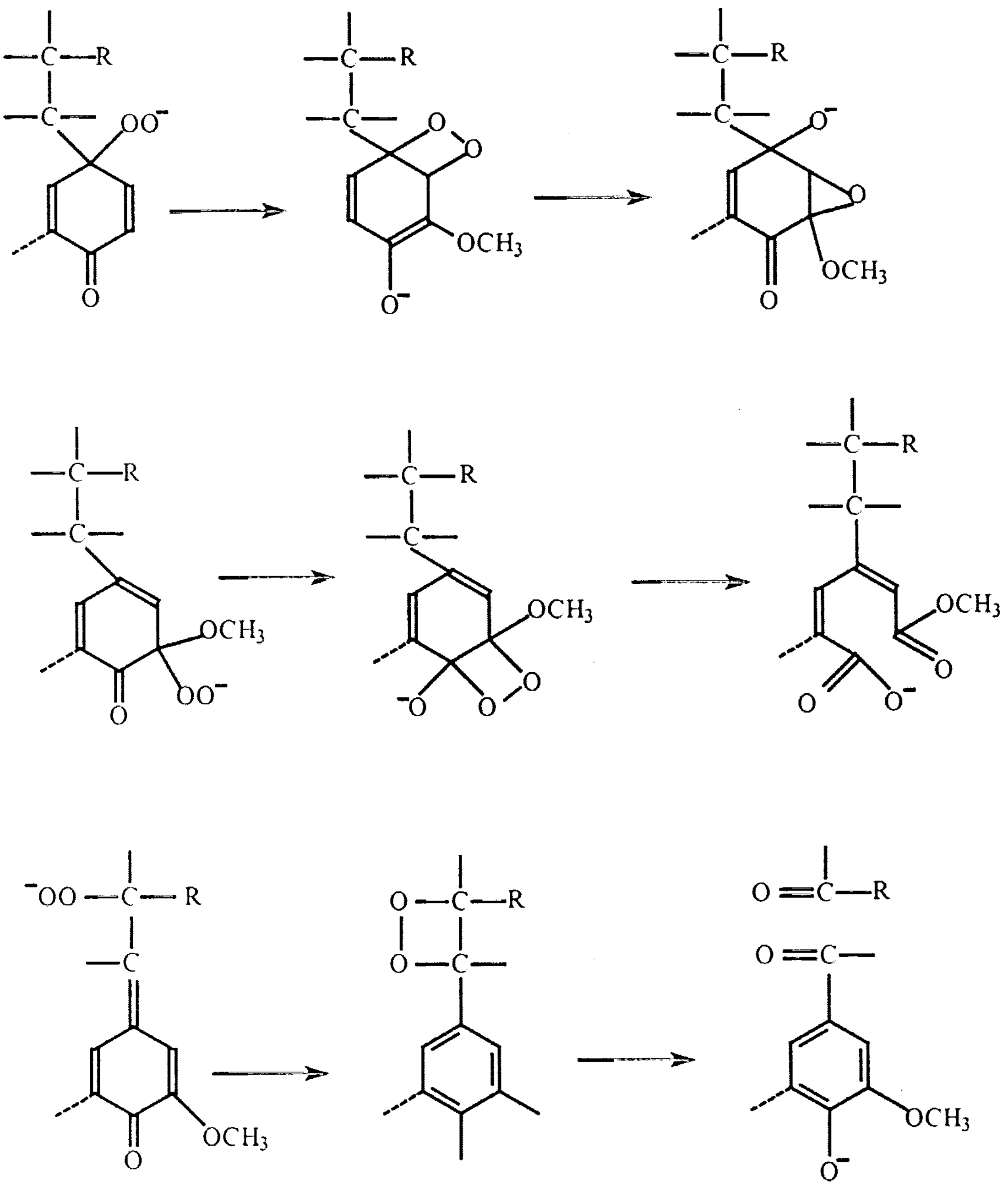


Figure 2.15. Reaction of intermediate (McDonough, 1996).

Johansson and Ljunggren (1994) studied the reactivity of lignin model compounds with oxygen in alkaline media and found that phenolic structures with a conjugated side chain, like stilbene and enol ethers, react very rapidly during oxygen bleaching, whereas structures like propylguaiacol and β-aryl ethers are more resistant. Some of the free radical reaction mechanisms were thought to produce new cross-linked structures that had lower reactivity than the precursors from which they were formed. The oxygen degradation kinetics for a wide variety of the lignin model compounds suspended in alkali solution could be fit to a high degree of confidence to first order kinetic equations. The various lignin model compounds, however, showed a wide range of first-order reaction coefficients.

Tamminen and Hortling (2001) investigated the effect of alkaline cooking method on the reactivity of lignin during subsequent oxygen delignification. Based upon isolated lignin structure, they reported that there were no major differences in lignin structure related to the cooking method and oxygen delignification. At the same kappa number level, they found that both the residual lignins in the alkaline pulp and that in the pulp following oxygen delignification were found to be very similar. So they suggested that lignin carbohydrate linkages play an important role in hindering delignification.

2.2.2.3. Reaction of Carbohydrates

Carbohydrate degradation is the main factor limiting the amount of lignin that can be removed during oxygen delignification. In the oxygen delignification process, carbohydrates are attacked to a greater extent than in the chlorination and alkali extraction processes.

Random chain cleavage and endwise secondary “peeling” reactions are two types of carbohydrate degradation reactions that occur during oxygen delignification. Random chain cleavage can occur at any point along the main chain to lower the molecular weight of the carbohydrate polymers. Endwise secondary “peeling” reactions occur by reactions at the aldehydic end of the carbohydrate chain and result in sugar units on the end of the chain being attacked and successively removed (Sjostrom, 1981). Although both of these reactions may occur during oxygen bleaching, random chain cleavage is more significant and reduces the intrinsic viscosity of the cellulose.

Random chain cleavage reactions are catalyzed by transition metal ions such as iron, manganese, and copper, which are present in unbleached pulp. These transition metals catalyze the formation of reactive, oxygen-based radicals, such as hydroxyl radicals, that randomly attack the cellulose chain, ultimately leading to chain breakage at the point of attack. The associated decrease in the average length of the cellulose chains manifests itself as a decrease in pulp viscosity and, if allowed to proceed far enough, as a decrease in pulp strength. Gierer (1997) proposed a possible reaction of hydroxyl radicals with carbohydrates which is shown in Figure 2.16.

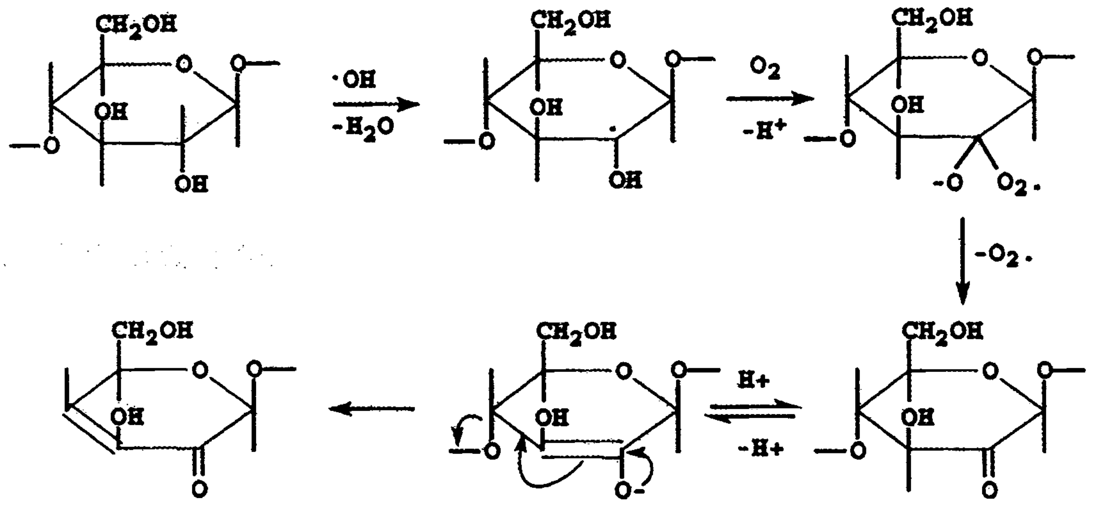


Figure 2.16. Reactions of hydroxyl radicals with carbohydrates (Gierer, 1997).

Guay (1999) used model compounds to study the carbohydrate degradation mechanism during oxygen delignification. He reported that no experimental evidence was found to support the mechanism shown in Figure 2.16. Rather, Guay (1999) proposed an alternative degradation mechanism based upon studies with methyl-β-D-cellubioside as a model compound. He suggests a possible degradation pathway that is summarized in Figure 2.17. Guay (1999) performed calculations that suggest the proposed mechanism is energetically favorable. Additionally, he also reports experimental evidence to support this mechanism.

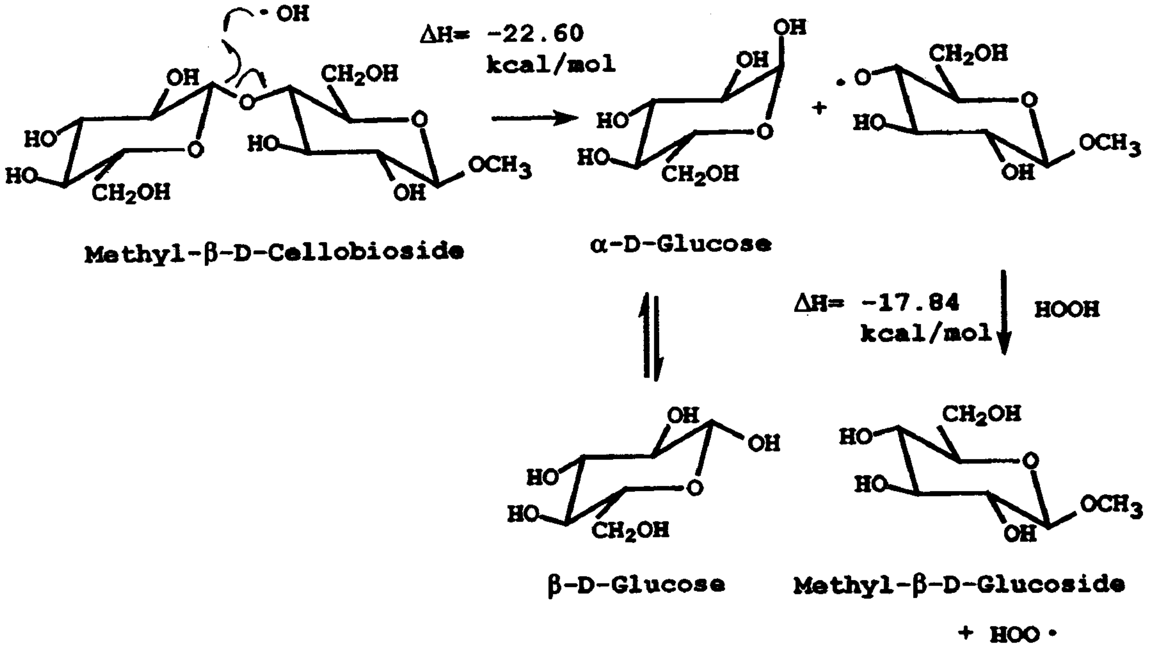


Figure 2.17. Methyl-β-D-glucoside and D-glucose formation (Guay, 1999).

The peeling reaction, which is responsible for decreasing the yield of the process, is usually of less importance in oxygen bleaching than random chain cleavage. In the oxygen delignification of kraft pulp, yield loss is generally not a serious problem. This occurs for two reasons. First, kraft pulps (because of their long previous exposure to strongly alkaline conditions in the digester) contain very few end units that have not been converted to the stable form by stopping reactions. The secondary reason is that oxygen itself converts reducing end groups to the stable oxidized form. However, peeling can become a problem if random chain cleavage is excessive because every chain breakage creates two new chain ends, one of which is a reducing end group.

2.2.2.4. Selectivity and Carbohydrate Protector

The rate of carbohydrate degradation has been linked to the presence of the hydroxyl free radicals that randomly attack the cellulose chain, ultimately leading to chain breakage at the point of attack. The hydroxyl radical is formed when hydrogen peroxide accepts an electron, to form a hydroxide ion and a hydroxyl radical (See Figure 2.13). The decomposition of hydrogen peroxide to hydroxyl free radicals and water is catalyzed by trace quantities of transition metals (Fe, Mn, Cu). Selectivity can be improved by using carbohydrate protectors, the most important commercially being the magnesium ion which ties up metal irons (McDonough, 1996). Magnesium ion has been used primarily with softwood pulp. In hardwood delignification, protectors are less frequently used, because the pulp coming from the digester has a higher viscosity. Lower alkali concentration gives better hardwood selectivity for the oxygen delignification process (Agarwal, 1996). Temperature does not seem to greatly lower selectivity, which indicates that oxygen delignification should be conducted at low alkali content but high temperature. Commercially, carbohydrate selectivity limits the drop in kappa number in an oxygen stage to about 50%, although new two-stage, medium-consistency systems are approaching 60% for softwood kraft pulp. Recently studies also show that adsorption of polymeric additives is a useful method in selectivity improvement during oxygen delignification (van Heiningen and Violette 2002).

2.2.2.5. Hexenuronic Acid

Buchert and co-workers (1996) have shown that the chemical structure of xylan is modified due to the conversion of methylglucuronic acid side groups to hexenuronic acid side groups in kraft pulping. Pulping conditions affect the amount of hexenuronic acid present in the pulp. Due to its reactivity, hexenuronic acid is readily degraded when ClO_2 or O_3 are used as bleaching reagents. However, pulps bleached with either H_2O_2 or O_2 contain high amounts of hexenuronic acid, which are resistant to attack under alkaline conditions. Also hexenuronic acid consumes potassium permanganate and thus gives an abnormally high kappa number (Li and Gellerstedt, 1997).

2.2.2.6. Mass Transfer

Oxygen delignifcation is a heterogeneous reaction involving three phases—solid (fiber), liquid (aqueous alkali solution), and gas (oxygen). Oxygen gas must cross the gas-liquid interface, diffuse through the liquid film surrounding the fiber, and finally diffuse into the fiber wall before reacting. This is illustrated in Figure 2.18. Increasing the mass transfer areas A_1 and A_2 are only partially effective because of the inherent slowness of the diffusion phenomena involved and the low solubility of oxygen in aqueous media.

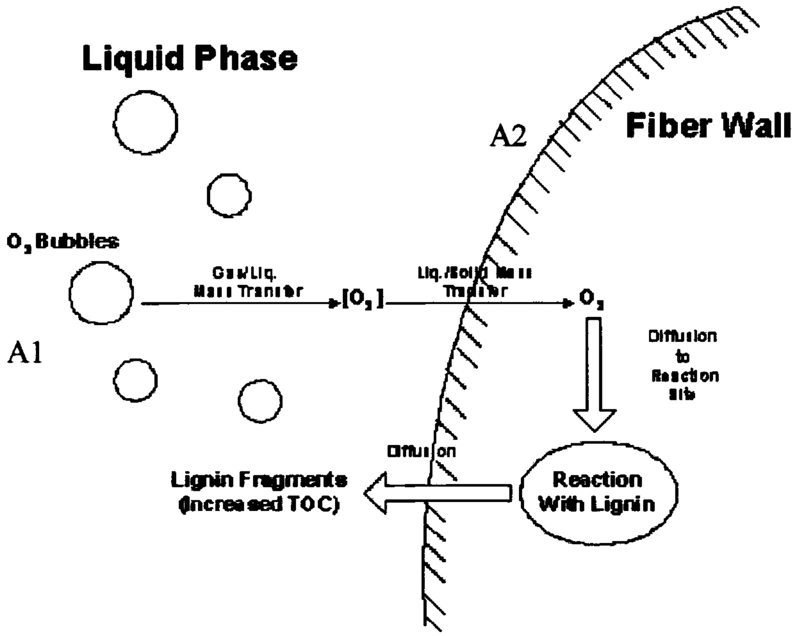


Figure 2.18. Mass transfer in oxygen delignification (Iribarne and Schroeder, 1997)

Hsu and Hsieh (1985) reported that the mass transfer resistance of oxygen in the gas phase is insignificant in comparison with the liquid phase resistance. The liquid phase resistance is high because of the low solubility of oxygen in the liquid phase. Hsu and Hsieh (1985) also found that the intra-fiber mass resistance was insignificant in comparison to the liquid phase mass transfer rate. Similarly, Agarwal et al. (1999) reported that there was no improvement in the oxygen delignification rate after the pulp had been refined, which suggests that the intra-fiber mass transfer effect does not influence the delignification rate.

2.2.3. Oxygen Delignification Kinetics

Most kinetics models for oxygen delignification are empirical in which the rate of delignification is considered to be proportional to the lignin content expressed as the kappa number (K), hydroxide ion concentration [OH$^-$] and oxygen pressure (P_{O2}) expressed in the form of a "power law". This is given by an equation of the form:

$$-r_a = -\frac{dK}{dt} = k[OH^-]^m [P_{O_2}]^n K^q \qquad (2.13)$$

The constant m, n and q are determined empirically from experimental data. The reaction rate coefficient *k* depends on the temperature and is given by Arrhenius equation:

$$k = A\exp(-\frac{E_A}{RT}) \qquad (2.14)$$

where (E_A) is the activation energy, (R) is the gas constant and (T) is the absolute temperature.

Based on equations (2.13) and (2.14), oxygen delignification kinetics have been described by using one and two region kinetic equations (Olm and Teder, 1979). Guven and co-worker (1996) present a summary of kinetic models proposed by a number of authors. Guven (1996) also investigated the two rate periods for ten southern hardwood species. Guven (1996) conducted experiments at 90°C, 2.5% NaOH, 100 psig and reaction times of 5 and 60 minutes. She concluded that data for the first and second delignification phases could be correlated to the kraft cooking conditions and the response variables of the brownstock pulp. The data for the initial rate period could be correlated in terms of the H-factor, the residual effective alkali, the kappa number and the fiber coarseness. The data for the second rate period could be fit to the initial effective alkali used in the kraft cook, the kappa number, the fiber coarseness and the pulp yield.

2.2.3.1. Olm and Teder's Model

Some investigators have treated oxygen delignification by considering that the drop in kappa number takes place over two distinct time periods, a rapid initial step followed by a long period during which the kappa number drops very slowly (Figure 2.18). The two different reaction periods are assumed to be related to the various lignin linkages comprising its structure, which have been shown by Johansson and Ljunggren (1994) to have widely different half lives when exposed to oxygen in alkaline medium.

The most widely accepted two regions kinetic model is that of Olm and Teder (1979) who assumed pseudo, first-order kinetics equations in terms of the kappa number. They defined the initial kappa number (K_0) as the sum of quickly (K_{01}) and slowly (K_{02}) eliminated lignin (Figure 2.19).

$$K_0 = K_{01} + K_{02} \tag{2.15}$$

Equation (2.15) was applied to the two regions in the form of two first-order kinetic expressions. The corresponding two-region delignification equation for softwood proposed by Olm and Teder (1979) is,

$$-\frac{dK}{dt}=k_1[OH^-]^{0.1}[P_{O_2}]^{0.1}K_1+k_2[OH^-]^{0.3}[P_{O_2}]^{0.2}K_2 \qquad (2.16)$$

where k_1 and k_2 are the rate constant in the initial and final phases respectively and K_1 and K_2 are the “fast” and “slowly” eliminated lignin. As an alternative to the two-region representation, the same data can be represented by the one-region global model (2.17).

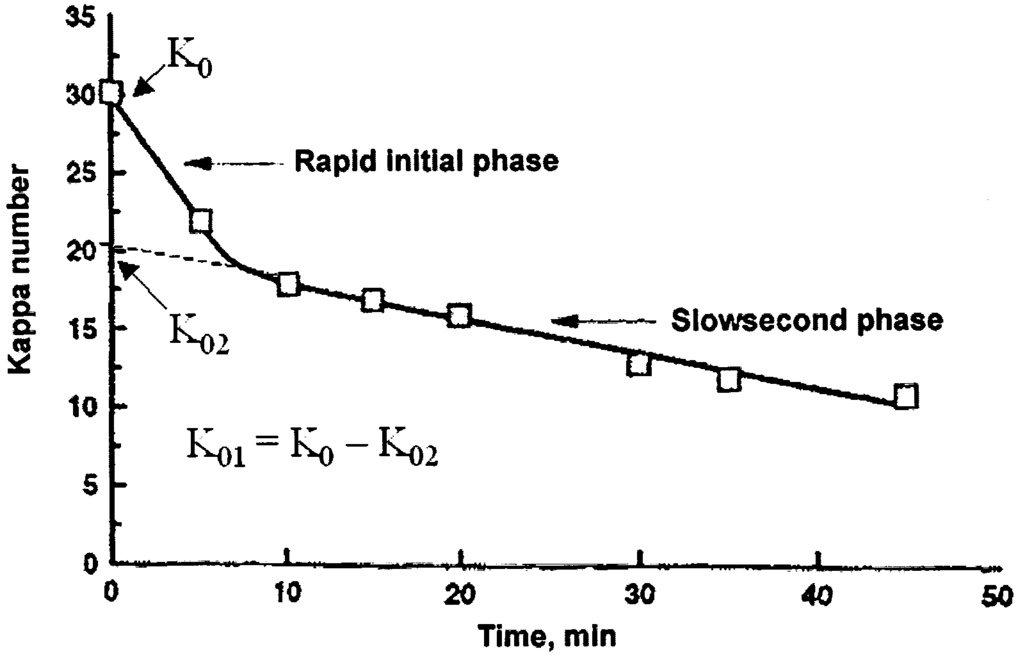


Figure 2.19. Two-region oxygen delignification (Olm and Teder, 1979).

Kovasin et al. (1987) applied the one region model to Olm and Teder (1979) data and obtained the equation,

$$-\frac{dK}{dt}=k[OH^-]^{0.6}[P_{O_2}]^{0.5}K^{3.2} \qquad (2.17)$$

Kovasin et al. (1987) used equation (2.17) and developed an algorithm for sizing medium-consistency oxygen delignification towers.

2.2.3.2. Hsu and Hsieh's Model

Hsu and Hsieh (1987, 1988) carried out delignification experiments in an agitated reactor at "ultra-low" consistency (0.4%) to eliminate the effect of alkali concentration change and also to eliminate liquid phase mass transfer restriction during the oxygen delignification process. Hsu and Hsieh (1987) studied the effect of alkali concentration, temperature, and the oxygen pressure on delignification as well as on carbohydrate degradation. Based on their experiments carried out at 0.4% consistency, they proposed a single stage kinetic model given by equation (2.18).

$$-\frac{dK}{dt} = 0.24\exp(-\frac{8.3\cdot 10^7}{RT})\cdot[P_{O_2}]^{0.89}[OH^-]^{1.0}K^{6.27} \qquad (2.18)$$

They also fit the data to the two-stage model (2.19) and found that the two-stage model fit the data better than the single-region model.

$$-\frac{dK}{dt} = 2.46\exp(-\frac{3.6\cdot 10^7}{RT})\cdot[P_{O_2}]^{0.35}[OH^-]^{0.78}K^{3.07}[u(t)-u(t-2)]$$

$$+143.449\exp(-\frac{7.1\cdot 10^7}{RT})\cdot[P_{O_2}]^{0.74}[OH^-]^{0.7}K^{3.07}u(t-2) \qquad (2.19)$$

In equation (2.19), *u(t)* is the unity function. They also found that decreasing the consistency from 0.4 to 0.3 and 0.2% did not affect the kappa number reduction, which led them to conclude that the effect of fiber entanglement on the overall delignification rate was eliminated in this low range of consistency.

2.2.3.3. Agarwal's Model

Agarwal and co-workers (1996) performed a detailed investigation of the oxygen delignification kinetics for mixed southern hardwoods using mill-cooked pulp. The kappa number versus time data were fit to a power law rate equation of apparent order "q" by following the method suggested by Schoon (1982).

$$-r_a = -\frac{dK}{dt} = kK^q \qquad (2.20)$$

The reaction rate constant (k) was correlated to the initial alkali concentration [OH^-, g/liter], temperature (T, K), activation energy (E_A, kJ/mole) and oxygen pressure (P_{O2}, psig) by the equation

$$k = 6.59x10^6 \exp(-107.2/RT)\left[OH^-\right]^{0.92} P_{O_2}^{0.53} \qquad (2.21)$$

The three primary process variables affecting the kappa number decrease are, in decreasing order of importance, (1) temperature, (2) alkali concentration, and (3) oxygen pressure. An attractive feature of the power-law model, equations (2.20) and (2.21), is that it can be integrated simply to give an expression that can be used readily for estimating the kappa number drop with time under various reaction conditions.

$$K = \left[\frac{1}{K_0^{q-1}} + (q-1)kt\right]^{-\frac{1}{(q-1)}}, q \neq 1 \qquad (2.22)$$

Agarwal and coworkers (1996) found that the reaction order q for mixed southern hardwoods was 7.7. This extremely high rate order suggests that the delignification process is hindered in the second reaction period, as seen by the flattening of the kappa number versus time curve. This hindrance could be due to a number of factors; solid state mass transfer of oxygen and caustic into the cell wall, by lignin condensation reactions, or by the presence of carbohydrates such as xylans that are bound to lignin groups and are resistant to delignification under alkaline conditions.

2.2.3.4. Schoon's Interpretation of the High Rate Order

High apparent reaction orders have been observed with respect to the lignin content in kinetic studies of various bleaching processes. Schoon (1982) has shown that a power law equation results when polymer degradation occurs via an infinite number of first-order reactions proceeding in parallel with various moieties in the structure of the polymer. Refractory lignin groups would have low first-order reaction rate coefficients and could account for the slow second-rate period. Figure 2.20 illustrates hindered delignification for a pure extraction stage and an oxygen stage, each operating with northeastern softwood kraft pulp at 100 °C with 2.5% caustic. The extraction and the oxygen stages are the same except that the oxygen pressure was 0 psig in the extraction stage and 100 psig in the oxygen stage. Both curves can be fit to a high degree of confidence to the power law model. The apparent reaction order (q) in the extraction stage at 0 psig is 24, whereas operating with oxygen at 100-psig-oxygen pressure the apparent order is 5.2. The lower apparent order "q" results because the lignin structure is less resistant to the conditions present in the oxygen stage (Zou, 2000).

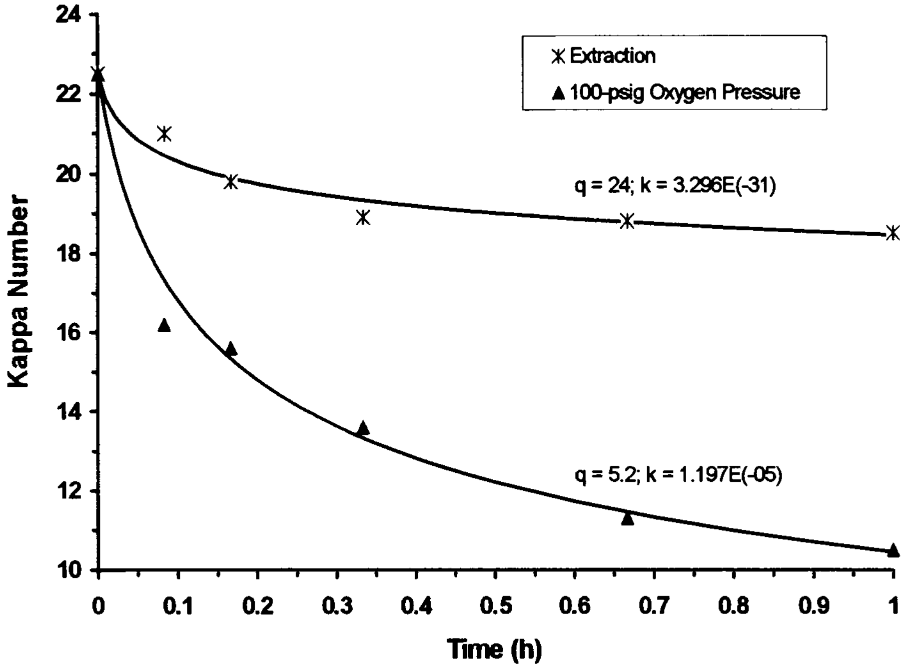


Figure 2.20. Delignification of softwood in a pure extraction stage and an oxygen bleaching stage, each at 100 °C with 2.5% alkali (Zou, 2000).

Schoon also defined a frequency function f(k) of the rate constant, with f(k) as the fraction of the rate constants having values between k and k+dk. This frequency function was defined by equation,

$$\int_0^\infty f(k)dk = 1 \qquad (2.23)$$

The distribution function F(a, b) is defined as the fraction of the rate constants with the values between k = a and k = b and is given by,

$$F(a,b) = \int_a^b f(k)dk \qquad (2.24)$$

Schoon defined a reaction of the α^{th} order which is the net effect of a large number of parallel first order reactions. This is given by equation (2.25), which has the same form as the power law equation that was used by previous workers to define the kinetics of oxygen delignification. The effects of temperature, alkali concentration, and pressure are incorporated into single rate constant k_a.

$$-\frac{dL}{dt} = k_a \cdot L^{\alpha} \tag{2.25}$$

where,

L = the total lignin content,

α = reaction order, determined experimentally,

k_α = rate constant, determined experimentally.

Predicated upon equation (2.25), Schoon derived an expression for the function f(k), which explains the observed rate order α. Schoon's function is given as equation (2.26).

$$f(k) = \frac{q^{\frac{1}{\alpha-1}} k^{\frac{2-\alpha}{\alpha-1}}}{\Gamma(\frac{1}{\alpha-1})} \cdot \exp(-qk) \tag{2.26}$$

In Schoon's theory the value of q depends on α, k_α and L_0 (the lignin content at the start of the reaction) and is given by equation (2.15).

$$q = [(\alpha-1)k_a \cdot L_0^{\alpha-1}]^{-1} \tag{2.27}$$

The assumption of a large number of parallel first order reactions with different rate constants, given by a distribution function, can adequately explain the observed delignification response. The lignin fractions having a high value for the rate constant contribution to the rapid initial phase of the reaction, while the fractions having a very low rate constant contribute to the slow second phase.

2.2.4. Carbohydrate Degradation Kinetics

2.2.4.1. Olm and Teder's Model

Olm and Teder (1979) expressed the carbohydrate degradation kinetics during oxygen delignification by two zero order reactions (See Figure 2.21). The kinetic expression is,

$$dm_n/dt = k_3[OH^-]^{0.2}P_{O_2}^{0.8} + k_4[OH^-]^{0.6}P_{O_2}^{0.1} \qquad (2.28)$$

where m_n is number average molecular weight and k_3 and k_4 are the rate constant for the first- and second-rate periods.

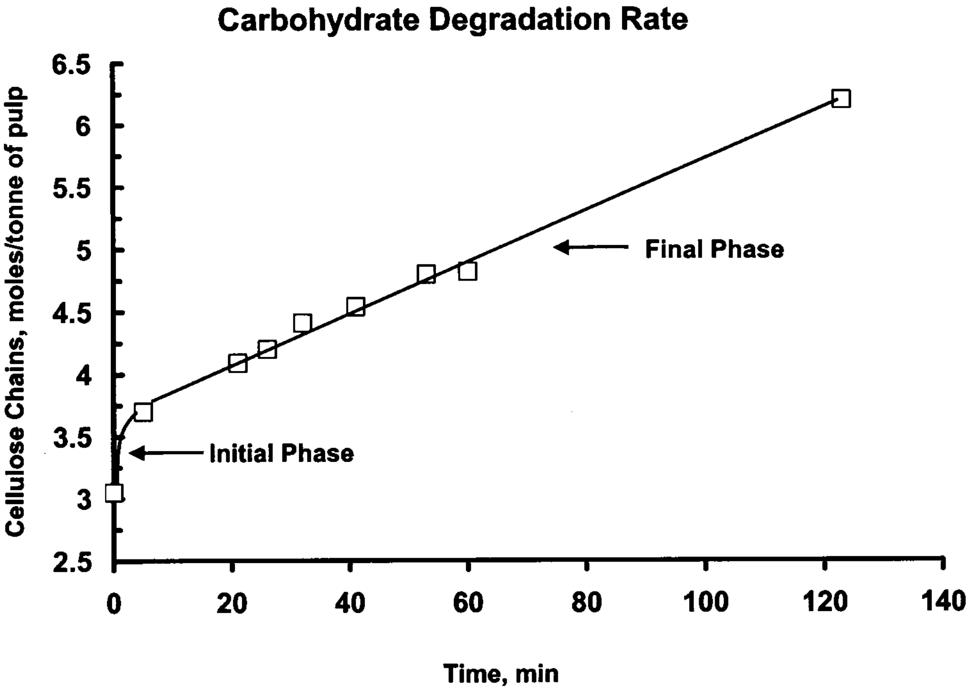


Figure 2.21. Carbohydrate degradation (Olm and Teder, 1979).

2.2.4.2. Iribarne and Schroeder's Model

Iribarne and Schroeder (1997) suggested that due to the different methods of evaluating the molecular weight (m_n) or to a relatively low resolution in their experiment, it was not necessary to use two parallel equations to obtain the apparent zero-order kinetics as proposed by Olm and Teder (1979). Rather, Iribarne and Schroeder (1997) described carbohydrate degradation kinetics during the oxygen delignification stage by a single zero-order equation,

$$dm_n/dt = 7\times 10^{10}\cdot e^{-78/RT}[OH^-]^{0.3}P_{O_2}^{0.4} \tag{2.29}$$

2.2.4.3. Kubes's G-factor Model

The G-factor model described by Kubes et al. (1983) was originally developed for use with the kraft pulping process, but it may also be used to analyze carbohydrate degradation data. Kubes et al. (1983) showed that the random cleavage of cellulose and other carbohydrates could be expressed in terms of the weight average degree of polymerization [DP_t]. In the G-factor model, the change in the reciprocal of the degree of polymerization can be expressed in terms of the reaction rate coefficient (k) for a bimolecular reaction occurring between the hydroxyl ion [OH^-] and the concentration for the number of glycosidic bonds, and the reaction time (t), see equation (2.30).

$$\frac{1}{DP_t}-\frac{1}{DP_0}=\frac{k\cdot t}{[Gly]} \tag{2.30}$$

where,

DP_o = initial weight average degree of polymerization,

DP_t = weight average degree of polymerization at time t,

k = Arrhenius rate constant, reflecting temperature influence,

t = time,

Gly = (Concentration of glycosidically bonded monomers)/(MW of monomer);

Predicated upon equation (2.30), Kubes et al. (1983) showed that the viscosity loss (η) is a straight line when plotted as (1/η) versus the time (t) at maximum temperature.

$$\frac{1}{\eta_t} - \frac{1}{\eta_0} = \int_0^t k_{vis}(t)dt \qquad (2.31)$$

where

η_o = initial intrinsic viscosity, cc/g

η_t = intrinsic viscosity at time t, cc/g

k_{vis}= Arrhenius rate constant, reflecting temperature influence.

2.2.5. Factors Affecting Oxygen Delignification

2.2.5.1. Initial Kappa Number

It has been shown that a pulp with a higher initial kappa number or lignin content will possess a greater fraction of easily removed lignin fragments. Poukka et al. (1999) reported that for softwood kraft pulp, the degree of delignification resulting from oxygen delignification increases as the kappa number from the digester increases, even when alkali dosage per kappa unit is lowered. Similarly, Agarwal et al. (1999) also has shown that for southern hardwood kraft pulps, those pulps with higher initial kappa number would have lower resistance to oxygen delignification. In their study, the pulps with higher initial kappa number had higher reaction rates (-dK/dt) compared to similar pulps with low initial kappa number.

2.2.5.2. Time and Temperature

At a fixed alkali concentration, the decrease in the kappa number with time exhibits two distinct stages, an initial rapid kappa number drop followed by a slower one that extends for a prolonged period of time. Also, delignificaton is considerably accelerated by an increase in temperature, but the selectivity decreases. Figure 2.22 illustrates the effect of temperature on the oxygen delignification of mixed southern hardwood kraft pulp.

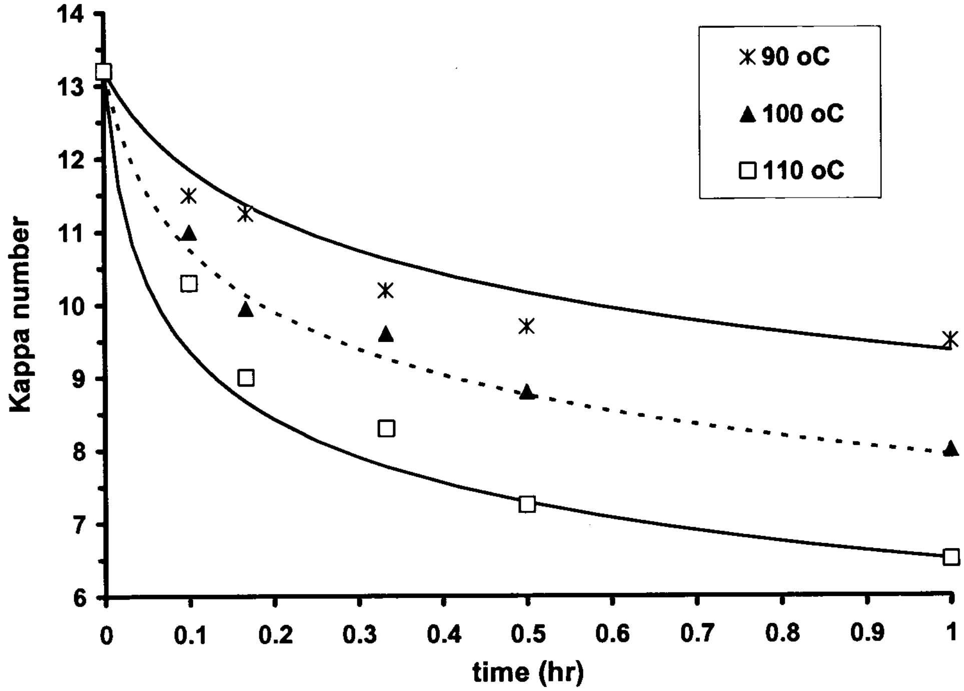


Figure 2.22. Effect of time and temperature on oxygen delignification (Agarwal, 1999).

2.2.5.3. Alkali Concentration

Increasing the NaOH charge results in a higher delignification rate and lower selectivity. Figure 2.23 and 2.24 illustrate this relation for data on the oxygen delignification of Canadian softwood kraft pulp published by Liebergott et al. (1985).

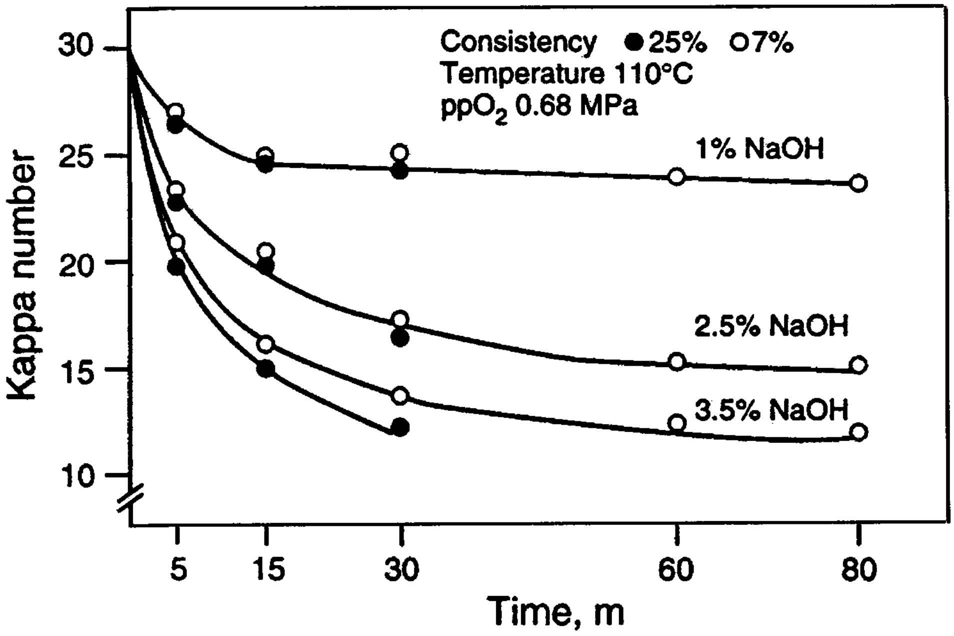


Figure 2.23. Effect of alkali charge on delignification (Liebergott, et al., 1985).

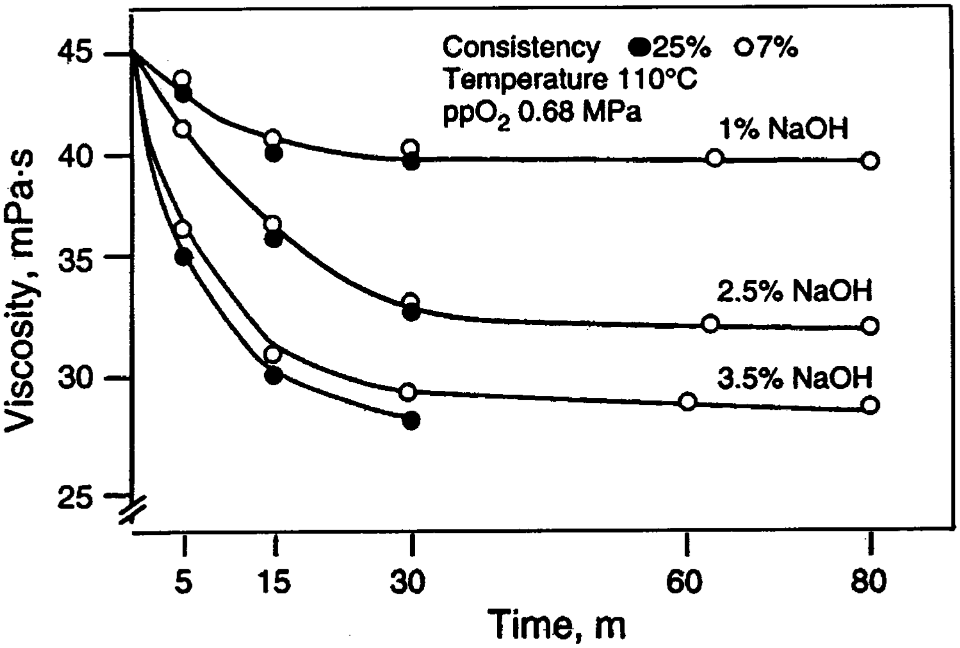


Figure 2.24. Effect of alkali charge on viscosity drop (Liebergott, 1985).

2.2.5.4. Oxygen Pressure

Increasing the oxygen pressure in the reactor will improve reaction speed and delignification. However, beyond a minimum value, the effect of oxygen pressure is small in comparison to the effects brought about by changing alkali charge and temperature. Generally, in the absence of an excess of alkali, increases in oxygen pressure have relatively little effect on delignification once a threshold value is reached -- about 60 psig in the case of southern hardwood kraft pulp shown in Figure 2.25.

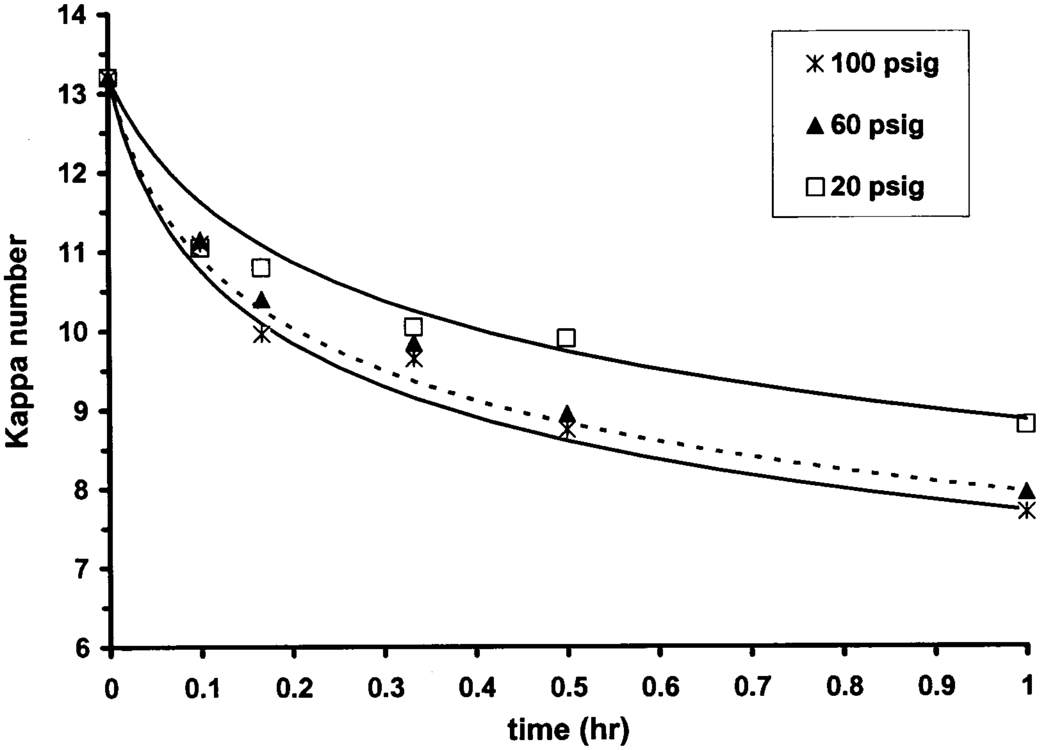


Figure 2.25. Effect of oxygen pressure on delignification (Agarwal, 1999).

2.2.5.5. Consistency

Oxygen delignification is a heterogeneous reaction system consisting of three phases—solid (fiber), liquid (aqueous alkali solution), and gas (oxygen). The process has an inherent drawback in that the solubility of oxygen in alkaline solution is low. Therefore, to decrease the mass transfer limitation for the transport of oxygen from the gas to the liquid phase, a large interfacial area is required between the gas and the liquid phase. One approach to solving this problem is to remove most of the free liquid phase.

When oxygen bleaching was first introduced, the only means of achieving this was to operate the system at high consistencies (28- 30%). This has the two-fold effect of providing a large gas-liquid interfacial area and also reducing the thickness of the liquid layer through which oxygen must diffuse to reach the fiber. Also, the amount of potentially oxidizable dissolved organic material going to the oxygen reactor is reduced as the consistency is raised. Raising the consistency has the further advantage of reducing the amount of water that must be heated to the reaction temperature. However, this required a press to dewater the pulp prior to the oxygen stage, which means a substantial capital investment. The other disadvantage resulting from high consistency processing is the tendency of the pulp to catch fire in the oxygen reactor (Markam and Magnotta, 1981).

In the late 1970s, high-shear mixing devices were developed that could efficiently disperse oxygen gas in pulp as very small bubbles in the 10-14% consistency range. This development led to the rapid implementation of the medium consistency (10-14%) oxygen delignification process. Currently, most of the oxygen delignification systems are operated at medium consistencies. As previously mentioned, the main advantage of a medium consistency system over a high consistency system is that no special dewatering equipment is needed.

Despite its far-reaching equipment and process implication, the effect of consistency at fixed alkali charge is relatively small. If the alkali concentration is held constant, and there is sufficient mixing to disperse the oxygen and caustic into the pulp, there is little difference between low consistency and medium consistency oxygen delignification. This was substantiated by Agarwal and co-workers (1999).

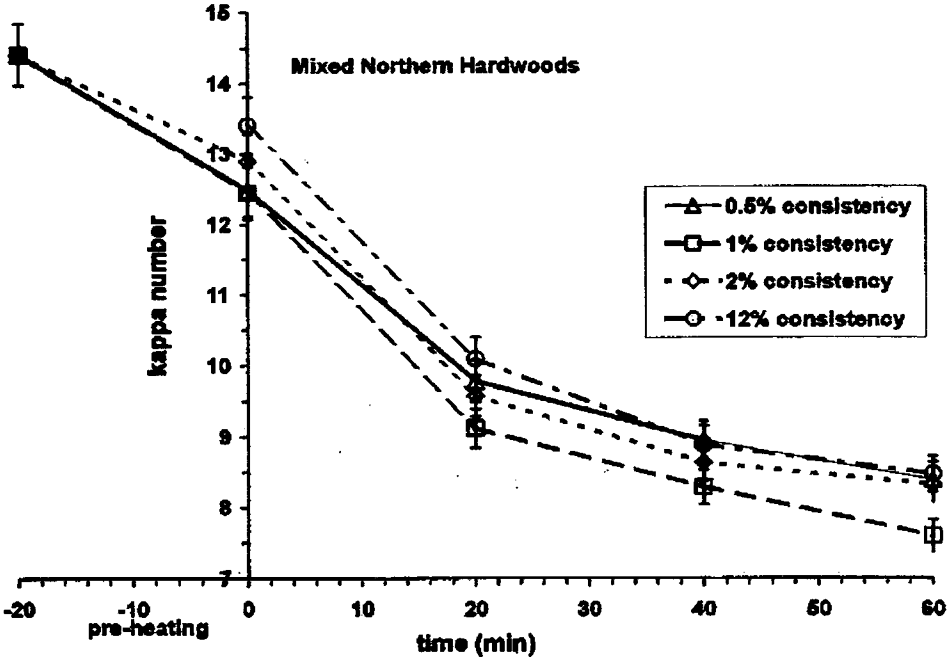


Figure 2.26 Effect of consistency on oxygen delignification (Agarwal, 1999)

Agarwal and co-workers (1999) studied the effect of pulp consistency on oxygen delignification and found that there was little difference between 0.5% and 12% consistency. Figure 2.26 illustrates this point with data for mixed Northern hardwood kraft pulp.

2.2.5.6. Additives

Van Tran (2000) studied the additives in enhancing the delignification degree of a hardwood kraft pulp in the oxygen stage. He reported that surfactants DTPA (diethylenetriamine pentaacetate) and TAED (tetraacetylethylene diamine) improved the delignification, KAQ (alkaline solution of disodium salt of 1, 4-dihydro-9, 10-dihydroxy anthracene) and oxone (potassium peroxymonosulfate) decreased the delignification degree, and AQ and urea maintained the delignification degree.

2.3. EFFECT OF KRAFT PULPING ON BLEACHING AND OXYGEN DELIGNIFICATION

Digester operating conditions would be expected to affect the response variables in oxygen delignification and subsequent bleaching stages. Fundamental process variables in Kraft pulping are wood species -- as it affects the morphology and chemical composition, chip thickness--as it relates to penetration, concentration of hydroxyl (OH^-), sulfide ($S^{=}$) and bisulfide (HS^-) ions which depend upon the chemicals charge and the liquor to wood ratio, cooking time, and temperature (H-factor) in the digester. In mill practice numerous industrial variables control the outcome of the digestion process in addition to the fundamental cooking variables. These mill variables such as wood aging, moisture content, effectiveness of steaming, and others would most likely affect the response variables in oxygen delignification and pulp bleaching. Important response variables such as kappa number drop, viscosity, COD and alkali consumption would be affected by the mill variables. Varying the cooking conditions not only affects the final kappa number (lignin content) leaving the digester but also results in different properties for the lignin and hemicellulose at a target kappa number. These differences in chemical structure would be expected to affect oxygen delignification and subsequent bleaching of pulps.

2.3.1. Effect of Cooking Temperature

Backstrom, M. et al. (1996) studied the influence of cooking temperature in modified softwood Kraft pulping. They found that the bleachability in the TCF-bleaching sequence according to the AZQP* sequence (A—acid treatment, Z—ozone stage, Q—

EDTD chelating stage, P*--peroxide with magnesium-ions addition) and the pulp viscosity for fully bleached pulps are improved when the cooking temperature was decreased from 175 °C to 155 °C. These effects are compared in Figure 2.27 and Figure 2.28. They also found that lowering the cooking temperature could improve pulp yield and reduce the number of revolutions in a PFI mill to reach a given tensile index (reducing refining energy).

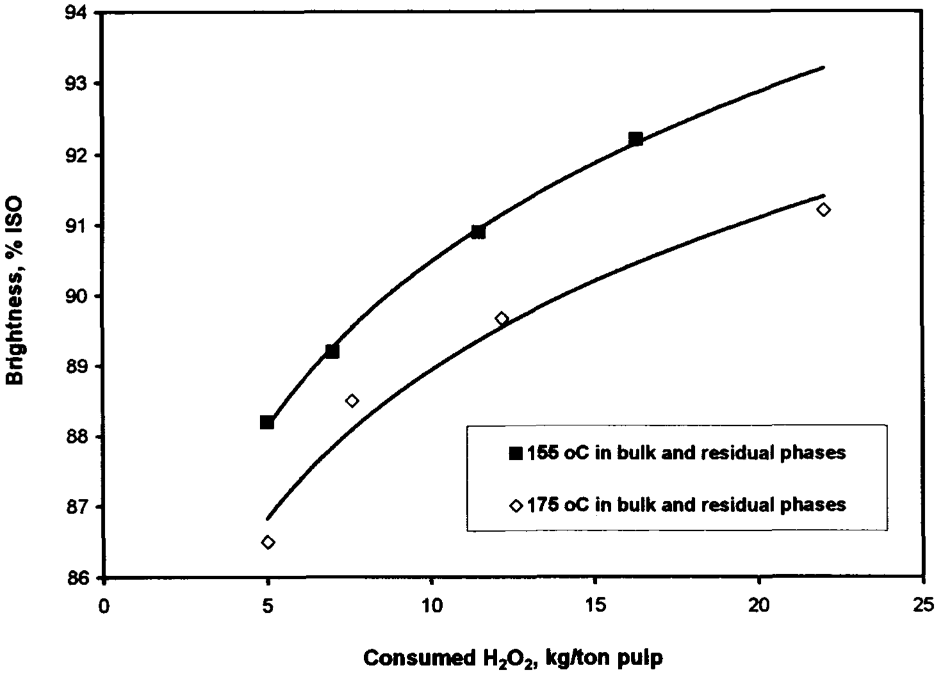


Figure 2.27. ISO-brightness versus hydrogen peroxide consumption for pulps produced at 155 °C and 175 °C in both bulk and residual phases (Backstrom, 1996).

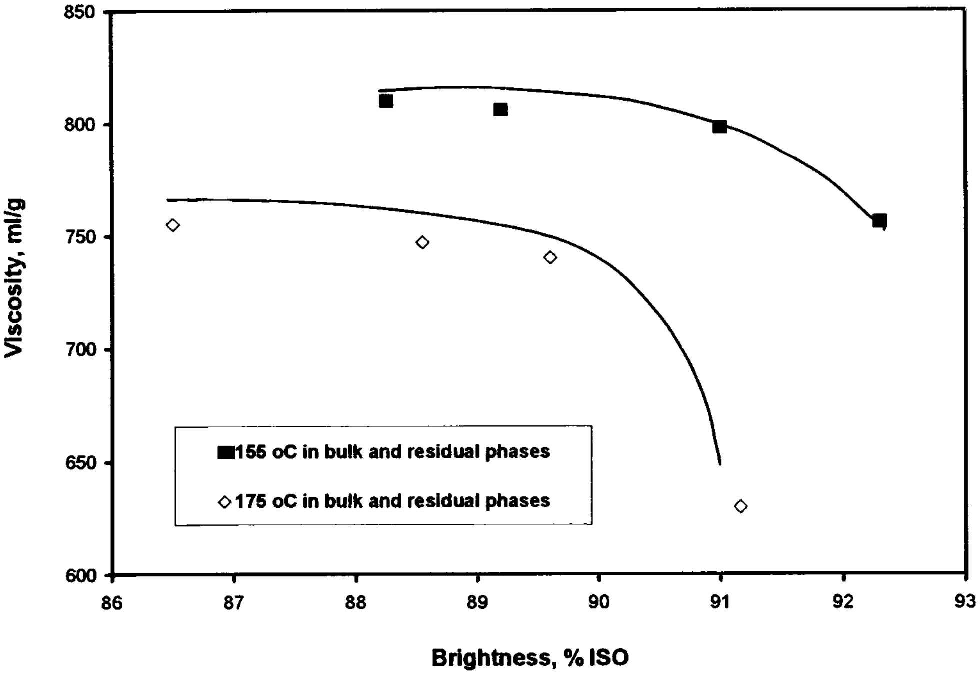


Figure 2.28. Viscosity versus ISO-brightness for pulps produced at 155 °C and 175 °C in both bulk and residual phases (Backstrom, 1996).

Gustavsson et al. (1999) present contradictory results in the study of the bleachability of softwood Kraft pulp using the QPQP*(*-with Mg^{++} addition) bleaching sequence. They reported that the bleachability was improved by increasing the cooking temperature for low and medium [OH^-] charges, but found no differences at high [OH^-] charge; compare Figure 2.29 and Figure 2.30. An increase in temperature together with a high [OH^-] and [SH^-] led to a deterioration in process selectivity whereas the process selectivity was not affected when the [OH^-] concentration was low and [SH^-] concentration was high (Figure 2.31). When both the [OH^-] and [SH^-] concentrations were low; an increase in the cooking temperature improved the process selectivity.

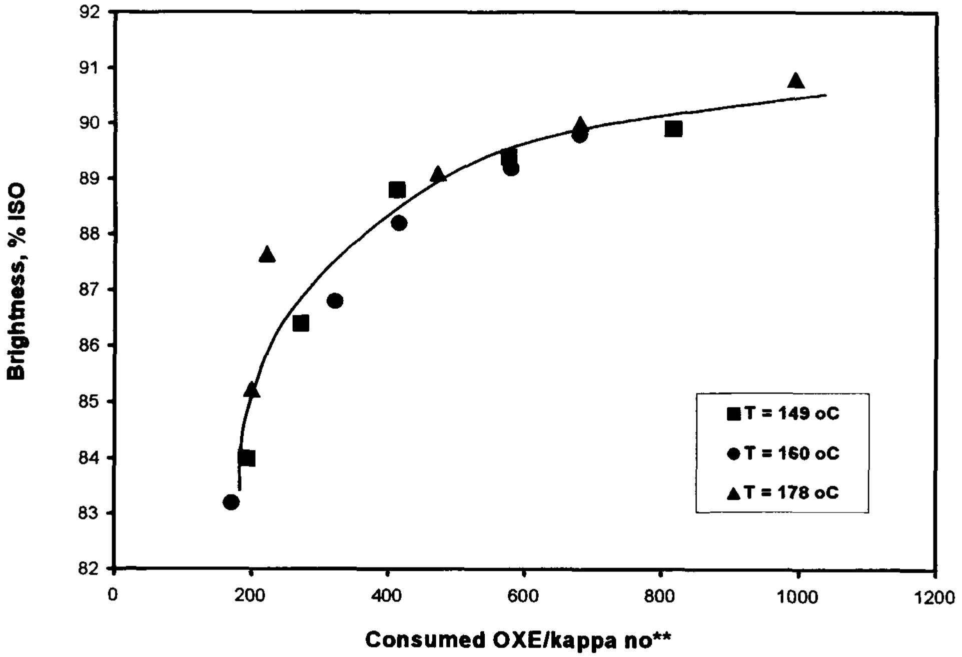


Figure 2.29. Brightness versus consumed OXE/kappa number**(**kappa number has been corrected with the hexenuronic acid content). Softwood Kraft pulps which were produced at [OH⁻]=0.5 mol/l and [SH⁻]=0.5 mol/l and at different temperatures were bleached using QPQP*(*-with Mg^{++}) (Gustavsson, 1999).

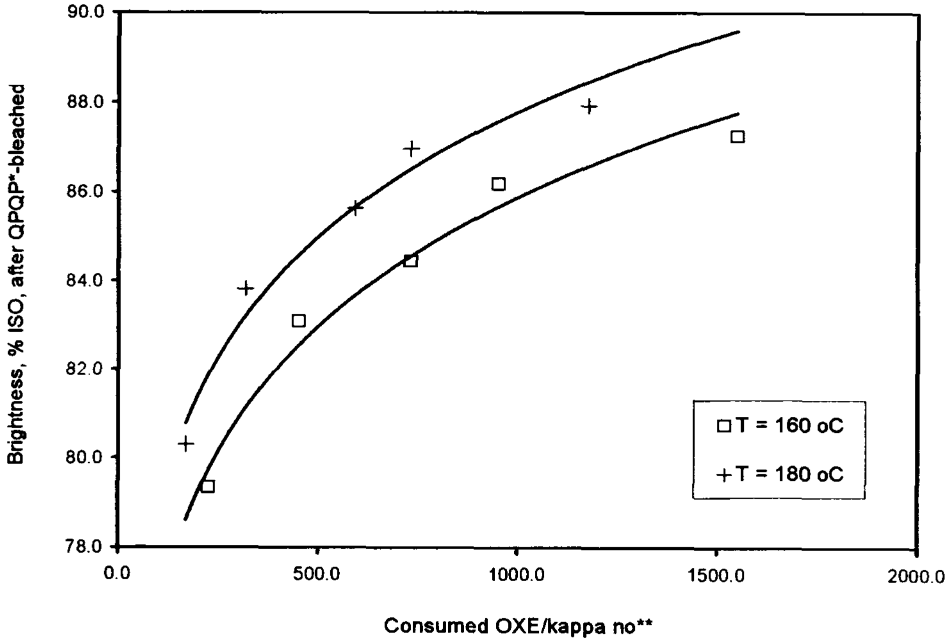


Figure 2.30. Brightness versus consumed OXE/kappa number**(**kappa number has been corrected with the hexenuronic acid content) QPQP*(*with Mg^{++})-bleached pulps produced at [OH⁻]=0.55 mol/l and [SH⁻]=0.075 mol/l and at different temperatures (Gustavsson, 1999).

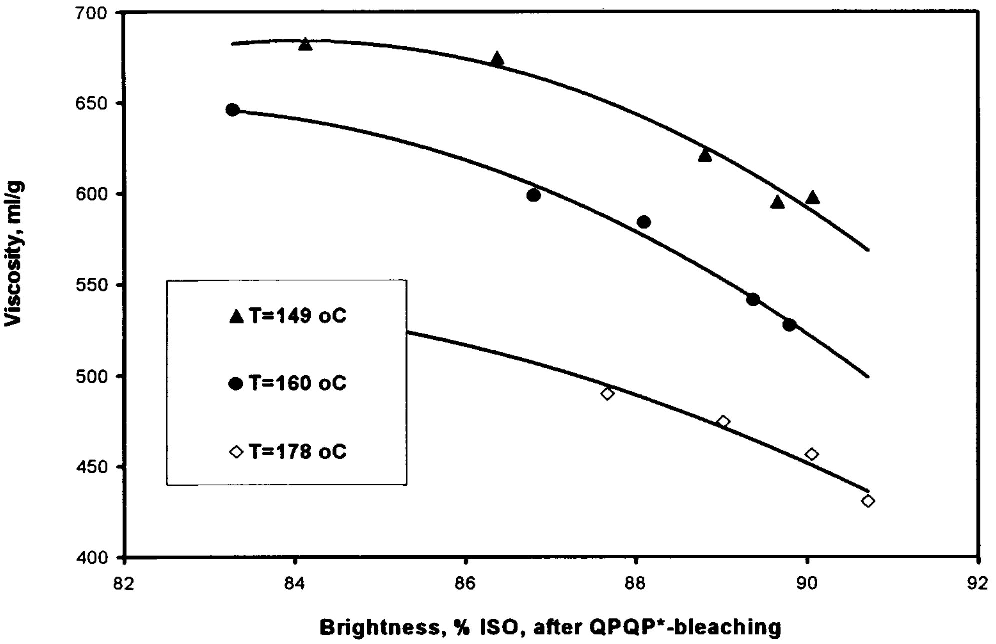


Figure 2.31. Viscosity versus. brightness for QPQP*-bleached pulps produced at [OH⁻] =1.5 mol/l and [SH⁻]=0.5 mol/l and at different temperatures (Gustavsson, 1999).

Chen, Y. (1995) studied the effect of cooking temperature in conventional birch Kraft pulp on oxygen delignification. He reported that the oxygen delignification efficiency was improved by increasing the cooking temperature from 170 °C to 180 °C. He suggested that the different cooking temperature resulted in a different structure for the residual lignin. The residual lignin in pulp cooked at higher temperature was more easily degraded during oxygen delignification than lignin in pulp cooked at a lower temperature.

2.3.2. Effect of Alkali Concentration

Many studies have shown that increasing the effective alkali charge improves the unbleached pulp brightness and the bleachability of the brownstock pulp (Svedman et al. 1995; Kettunen et al. (1997); Sjostrom (1998); Gustavsson et al. (1999).

Svedman et al. (1995) used a super batch digester to investigate the influence of white-liquor charge in the cooking stage on delignification, cooking selectivity, oxygen delignification, ECF bleachability and pulp quality. They reported that the higher the alkali concentration during cooking, the better is the pulp bleachability.

Kettunen et al. (1997) studied the effect of the EA concentration profile in the cooking stage on softwood Kraft pulping and ECF bleaching (DEDED). They found that when the EA concentration was increased throughout the cooking stage the following trends were observed:

- H-factor to achieve a target kappa number decreased,
- pulp yield decreased,
- rejects decreased,
- strength properties increased,
- brightness of the brownstock increased,
- bleachability of the brownstock increased,
- beatability or revolutions in the PFI mill to reach a target tensile strength decreased slightly,
- viscosity decreased, and
- hexenuronic acid content decreased.

Kettunen et al. (1997) also indicated that if the cooking stage EA profile was modified in such a manner that the alkali concentration at the beginning of cook was relatively low and the concentration was increased only at the end of the cook, pulp yield loss was minimized and the viscosity increased.

Rawat and McDonough (1998) found that increasing the EA gave birch Kraft pulp higher ECF bleachability, lower total yield, high rejects and lower viscosity. But the high-EA maple pulp had much higher bleachability than its low-EA counterpart at similar yield, reject and viscosity levels.

Sjostrom (1998) and Gustavsson et al. (1999) reported that a maximum in softwood bleachability using the QPQP*(*with Mg^{++}) sequence was seen for the pulp when it was cooked with an intermediate alkali concentration ($[OH^-] = 1.0$ mol/l). The process selectivity reached a maximum for the pulps produced at the intermediate alkali concentration (Figure 2.32 and Figure 2.33).

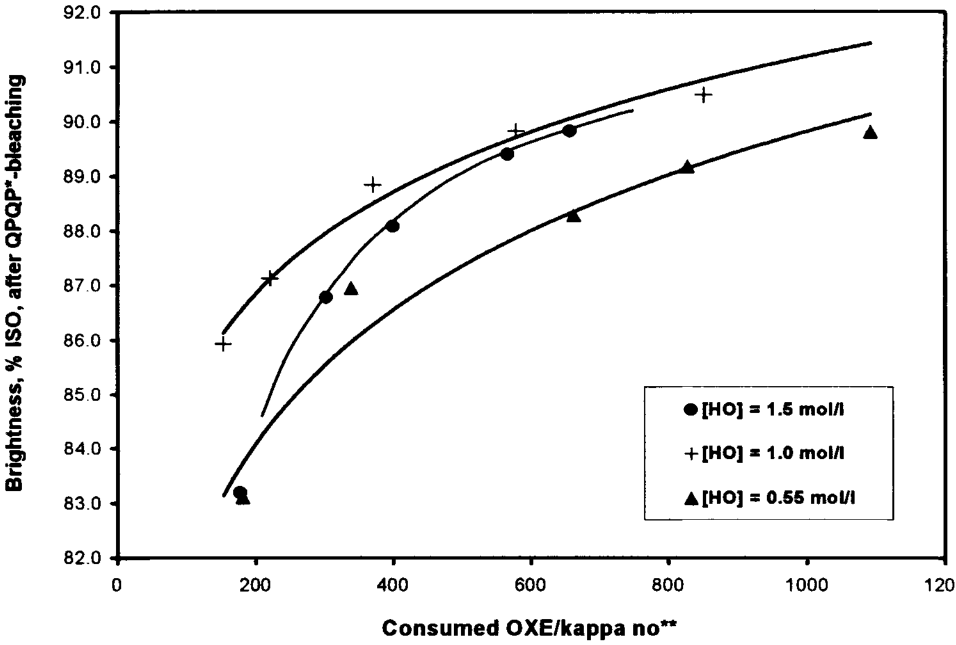


Figure 2.32. Brightness versus consumed OXE/kappa number QPQP-bleached pulps produced at $[SH^-]$=0.5 mol/l and at different $[OH^-]$ (Gustavsson, 1999).

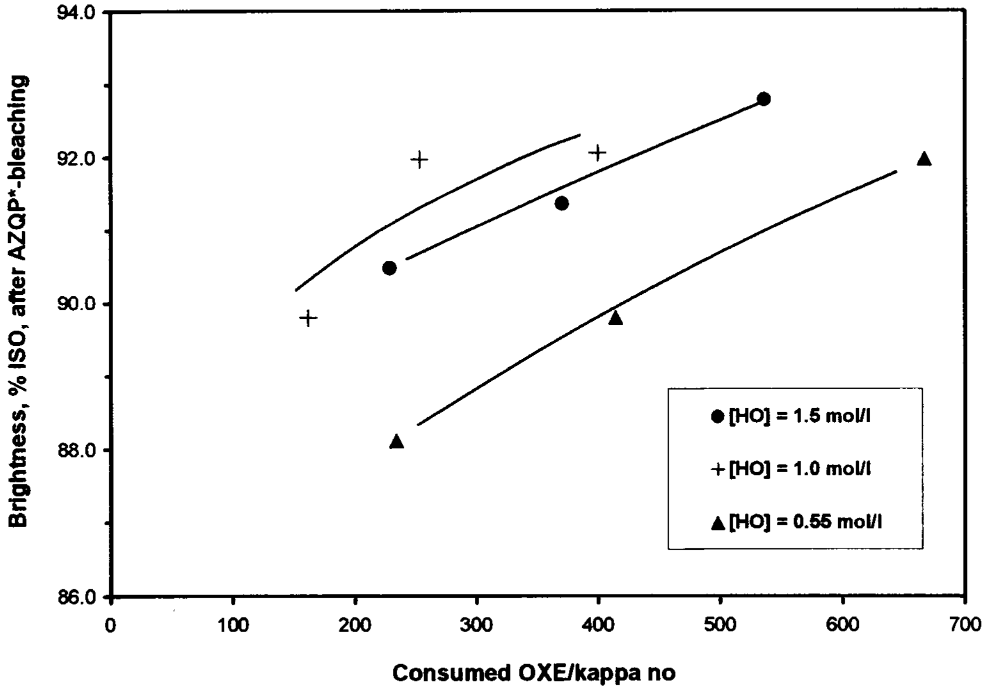


Figure 2.33. Brightness versus consumed OXE/kappa no AZQP-bleached pulps produced at $[SH^-]$=0.5 mol/l and at different $[OH^-]$ (Gustavsson, 1999).

2.3.3. Effect of Sulfidity ($[HS^-]$ Concentration)

Gustavsson et al. (1999) reported that increasing the $[SH^-]$ concentration could improve the bleachability and selectivity of softwood Kraft pulp when bleached using the QPQP (with Mg^{++}) sequence. This was especially true when the cooking was carried out at lower alkali concentration. However, varying the $[SH^-]$ concentration did not affect the bleachability in an AZQP (with Mg^{++}) sequence.

Lai and Yang (1997) also found that high-sulfidity cooking resulted in considerably higher delignification selectivity and provided beneficial effects on pulp viscosity.

2.3.4. Effect of Delignification Degree of Cooking

Poukka and co-workers (1999) showed that the degree of delignification during oxygen delignification of softwood Kraft pulp increased as the kappa number from the cook increased, even when the alkali dosage per kappa unit was lowered. Higher yield and viscosity could also be achieved, but the amount of rejects, washing capacity, and bleach plant emissions were predicted to increase, and refining energy would be decreased.

Sjostrom and Teder (1999) suggest that extending oxygen delignification instead of extending the cook to reach a low kappa number before bleaching will improve pulp bleachability, process selectivity, and pulp yield.

Paz and Melo (1996) also showed that prolonging Kraft cooking to a low final kappa number in the digester will significantly reduced pulp bleachability.

2.3.5. Effect of Kraft Pulping Profile

Hortling and Tamminen, et al. (2000) compared the effect of the alkaline cooking method--conventional Kraft pulping (CK), polysulfide/anthraquinone (PSAQ) and soda/anthraquinone(SoAQ), on the subsequent oxygen delignification. They reported that the CK pulp had the best bleachability in the DEDED, ODEDED and OQPPP bleaching sequences.

Chang and co-workers (1995) studied various North American hardwoods that were pulped using the Kraft process in a RDH digester and found that these pulps have higher bleachability than conventional Kraft pulps. Kumar (1996) also reported that for both hardwood and softwoods, RDH pulps exhibited better bleachability than did conventional Kraft-oxygen pulps in ECF bleaching sequences.

Sjostrom and Teder (1999) found that modified Kraft pulping processes resulted in improved selectivity during ECF and TCF bleaching compared to conventional pulping. They pointed out that presulphonation and postsulphonation treatments improved process selectivity in a TCF sequence based on ozone and peroxide.

Gilbert and Hsieh (1997) showed that ECF bleachability of Southern pine Kraft-AQ pulp was similar to that for conventional Kraft pulp, but the selectivity of the Kraft-AQ pulp was better than for conventional Kraft pulp.

2.3.6. Correlation between Bleachability and Chemical Structure

Froass et al. (1996) reported that the higher the content of aryl ether linkages and the lower the amount of condensed structures in the residual lignin, the more reactive it is towards ClO_2. These same phenomena were also observed in a study by Heuts (1998), who showed that β-aryl ether structures react with hydrogen peroxide in such a way that lignin dissolution is promoted through cleavage of side chains and the formation of aliphatic carboxylic acids.

Free phenolic structures are believed to be the main site of attack by several bleaching agents, such as oxygen and chlorine dioxide (Kumer, 1996). However, research by Gustavsson (1999) and Lai (1997)) did not confirm these results.

2.4. INITIAL WORK ON DELIGNIFICATION OF NORTHEASTERN HARDWOOD

In initial work on this dissertation, the effect of the alkali concentration during conventional Kraft pulping on medium consistency oxygen delignification was determined for Northeastern hardwood (Zou, 2000). Data were presented for kappa number, viscosity, COD, residual alkali and final pH following oxygen delignification.

2.4.1. Kraft Pulping Data

Conventional Kraft pulping was performed on mixed northeastern hardwood chips in a laboratory rocking digester. Four Kraft pulps of kappa number 15 to 16 ml $KMnO_4$ were produced by varying the effective alkali charge and H-factor while holding the sulfidity constant (Table 2.1).

Table 2.1. Results of Kraft pulping experiments.

Effective Alkaline	Cooking Time, m	H-factor	Kappa Number	Viscosity Cp	Bright. ISO, %	Screened Yield, %	Reject %	Black Liquor	
								pH	R. AA g/l
12%	180	3051	16.3	44.6	27.0	48.50	0.36	11.3	4.1
15%	62	1100	16.2	34.1	32.2	46.75	0.50	12.9	10.2
18%	35	654	15.5	29.6	34.4	45.05	0.66	13.1	18.2
21%	18	409	15.0	29.5	34.7	44.69	0.52	13.3	27.4

The pulp yield following pulping was systematically lowered from 49% to 45% as the effective alkali charge was systematically increased from 12% to 21% EA and the H-factor was reduced from 3000 to 400 hours. The H-factor was decreased because the effective alkali was increased. The increase in yield was thought to result from the lower effective alkali content in the digester.

2.4.2. Pulp Carbohydrate Analysis

Chemical analysis of the carbohydrates in the pulp indicated that the loss in pulp yield was caused by a reduction in the hemicellulose polymers in the pulps as additional effective alkali was added to the digester (Table 2.2).

Table 2.2. Results of carbohydrate analysis.

Sample (EA)	Glucan (%)	Xylan (%)	Mannan (%)	Arabinan (%)	Galactan (%)	(%) Total Carbohydrates
B.S						
12%	72.4	21.1	0.45	0.10	0.07	94
15%	74.0	20.6	0.35	0.00	0.00	95
18%	76.4	20.0	0.47	0.03	0.07	97
21%	78.3	17.9	0.72	0.10	0.10	97
O_2 Stage						
12%	74.9	21.5	0.37	0.05	0.05	97
15%	76.9	20.9	0.41	0.00	0.00	98
18%	78.5	19.3	0.42	0.09	0.06	98
21%	80.1	17.4	0.48	0.05	0.05	98
QC History: Aspen Wood Quality Control (QC) standard						
Mean	45.2	15.9	1.75	0.40	0.54	64%
SD	0.75	0.30	0.08	0.03	0.04	NA

The xylan hemicelluloses constituted 18 to 21% of the mass of the brownstock pulp depending upon the effective alkali used in the digester, with the highest content occurring when the lowest effective alkali was used in the digester (12% EA). The xylan polymers are quite stable and resist dissolution during Kraft pulping.

2.4.3. Kappa Number

All of these response variables following oxygen delignification were found to depend upon the effective alkali used in the digester. This is seen in Figure 2.34 for the change in kappa number with time. There was a systematic increase in the oxygen

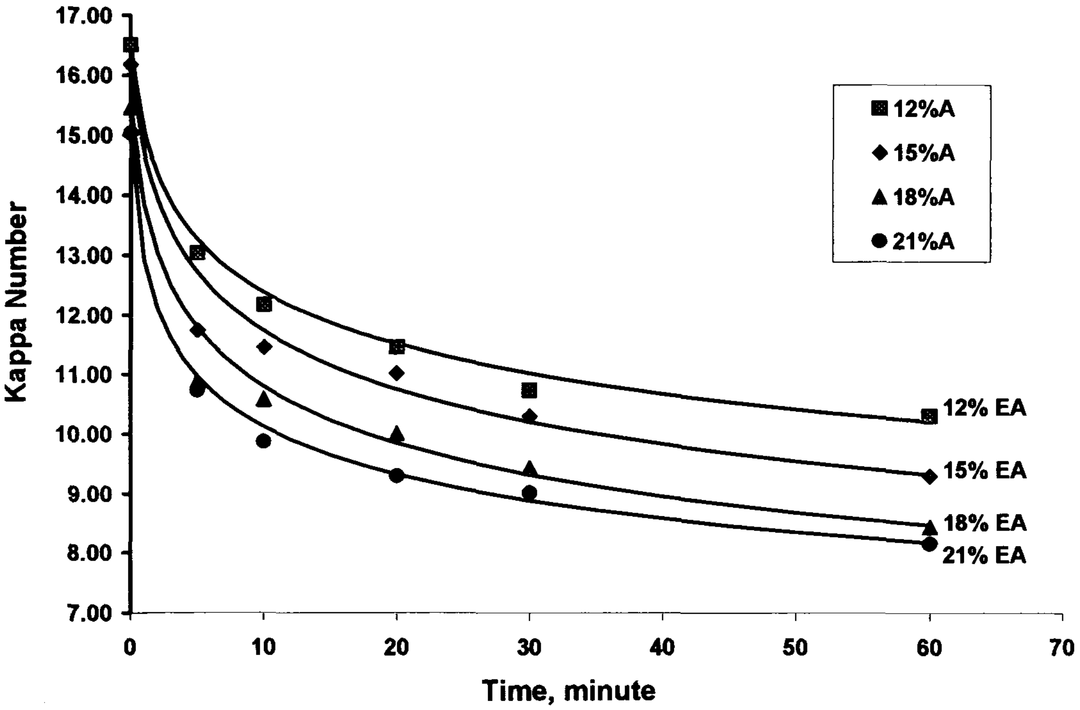


Figure 2.34. Pulp kappa number versus oxygen delignification time.

delignification rate, measured by a reduction in the kappa number, with decreasing brownstock pulp yield in the digester. The kappa number versus time data could be fit to a classical power law model (Table 2.3) indicative of lignin fragmentation occurring by an infinite number of parallel first order reactions proposed by Schoon (1982).

Table 2.3. Kinetic parameters for Schoon's model showing the effect of digester EA.

Sample	q	R^2	k
12%EA	7.7	0.8900	4.416E-10
15%EA	7.7	0.9728	7.873E-10
18%EA	7.7	0.9823	1.496E-09
21%EA	7.7	0.9720	1.970E-09

The apparent order of the reaction (q) coincided very closely with the value of 7.7 published by this laboratory for mixed southern hardwood Kraft pulps (Agarwal et al., 1996).

2.4.4. Oxygen Delignification Selectivity

The pulp viscosity (Figure 2.35) and selectivity (Figure 2.36) in the oxygen stage all had the same shape and followed closely the initial viscosity coming from the digester. Low values for the EA in the digester had the highest viscosity following oxygen delignification, but the dilignification could not be pushed to low kappa numbers. Pulps produced in the digester with high EA resulted in lower values for the kappa number exiting the oxygen reactor but had the lowest pulp viscosity.

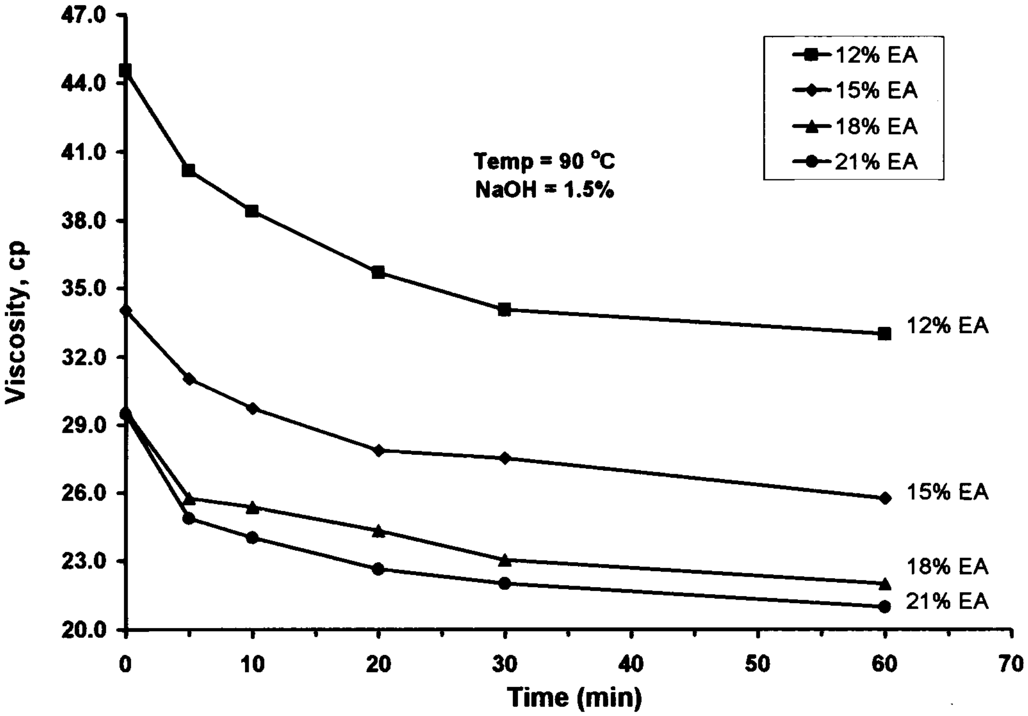


Figure 2.35. Pulp viscosity versus oxygen delignification time.

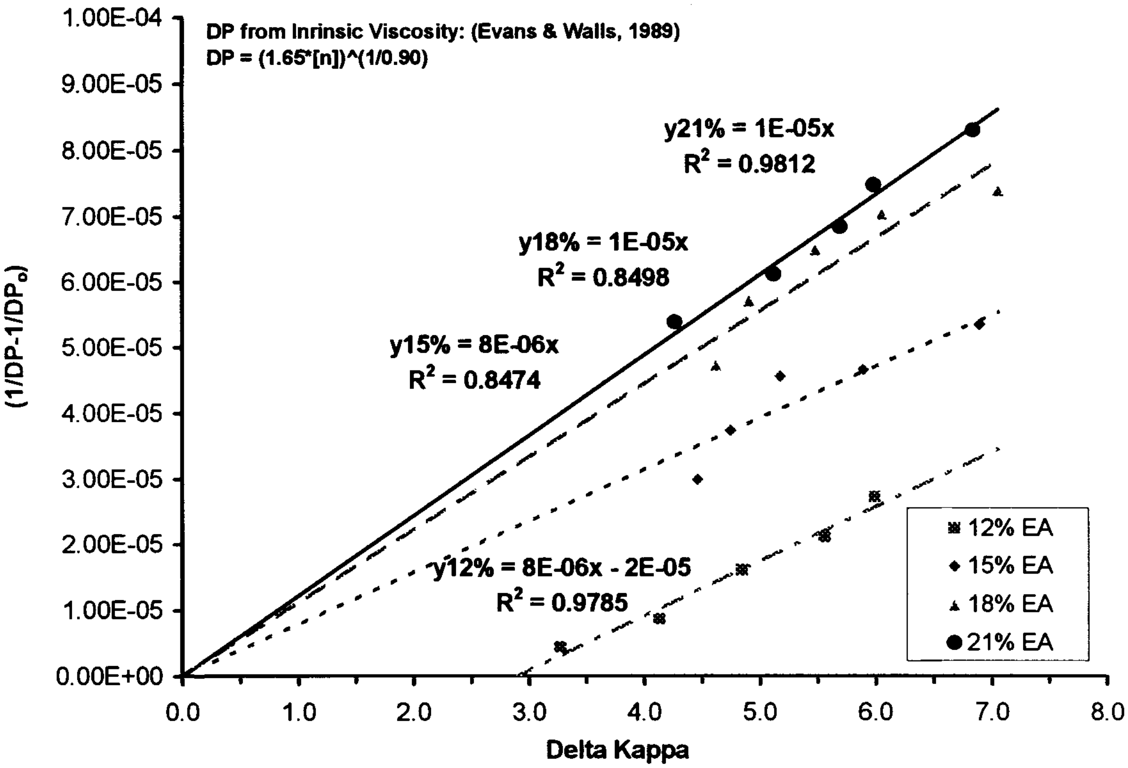


Figure 2.36. Selectivity curve when plotted as [1/DPv-1/DPvo] versus delta kappa number.

Two separate hypotheses were put forward to explain the data. The delignification results could be explained if one assumes that delignification is hindered by lignin condensation reactions that occur during pulping (Argyropoulos and Liu, 1998) or by the high xylan content as suggested by Buchert and co-workers (1996). Such effects would give rise to more refractory lignin groups that are less sensitive to the conditions present in the oxygen stage. An alternative explanation is that differences in kappa number may result partially from a difference in hexenuronic acid content in the pulp following oxygen delignification.

2.4.5. Brightness

The final brightness exiting the oxygen stage was found to follow the initial brightness of the pulp entering the oxygen stage (see Figure 2.37). These results suggest that a higher level of chromophoric groups result from longer exposure times at the maximum cooking temperature. The 12% EA pulp had the lowest brightness when compared to the three other brownstock pulps before exposure to the oxygen stage for 20 minutes. The additional chromophoric groups then must be removed in the oxygen and subsequent bleaching stages. These results further suggest that the brightness that can be expected exiting a commercial oxygen stage will track the incoming kappa number and the exposure time in the digester once the conditions in the oxygen stage are fixed.

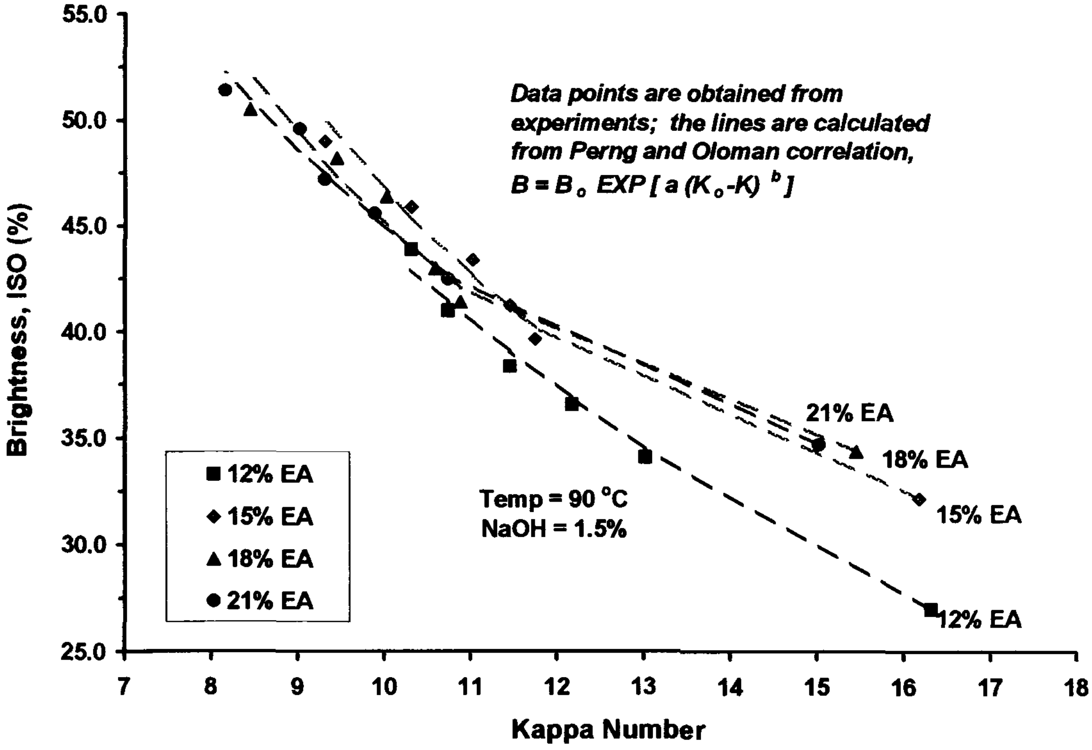


Figure 2.37. Pulp brightness versus kappa number.

2.4.6. Chemical Oxygen Demand (COD)

The data shown at time zero in Figure 2.38 are the COD values contained in liquor squeezed out of the pulp after the caustic and magnesium sulfate were mixed, prior to heating the reaction mass or adding oxygen. These data indicate that the pulp with higher yield in the digester, that is the pulp produced at 12% EA, lost more low molecular weight material than the pulps produced at the higher EA values. Consequently, the low EA pulp had higher COD in the squeezed liquor. The slopes of the curves shown in Figure 2.38 are approximately the same for the change in COD with decreasing kappa number. Oxygen and caustic will react with either the organic material removed from the cell wall and /or black liquor solids carried over from the digester. Although competitive reactions are involved, the COD curves will increase with time. This is illustrated in Figures 2.38. For well-washed pulps such as those shown in Figure 2.38, the reaction with dissolved cell wall material will be low. For high amounts of carry-over, the COD curves actually decrease with time (Miller et al., 1995; 1998) because of the reaction of the COD carried over from the digester with caustic and oxygen added to the reactor.

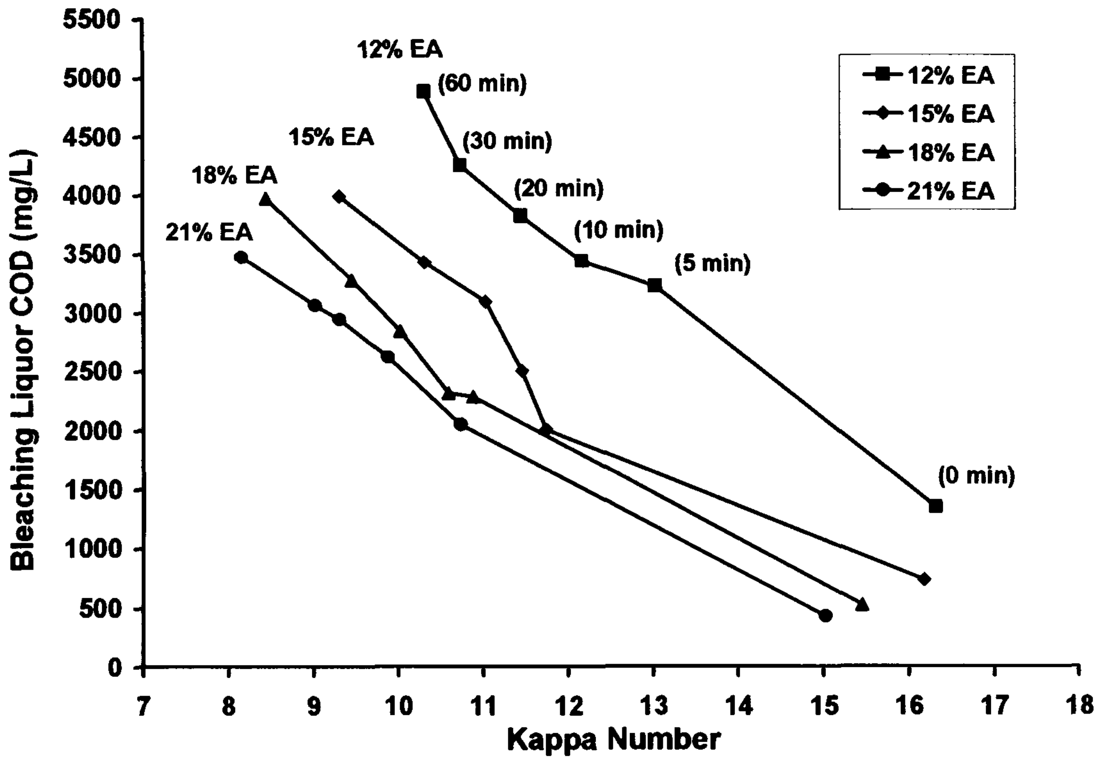


Figure 2.38. Bleaching liquor COD versus pulp kappa number.

2.4.7. Pulp Wet Zero-span Breaking Length

The results for the wet zero-span breaking length are plotted versus the number average degree of polymerization in Figure 2.39. Iribarne and Schroeder (1997) postulated that a strong relationship exists between the degree of polymerization and the wet zero-span breaking length. This was true in the present study, but not to the same degree seen by Iribarne and Schroeder (1997). For a given pulp, the higher the DP_n value the higher was the wet zero-span breaking length. However, this pattern did not hold between the four groups of data points reported in the preliminary work. In Figure 2.39, higher wet zero-span values were found with lower DP_n values for the pulp prepared at 21% EA compared to the pulp prepared at 12% EA. The reason for this behavior is may be related to the load and to fiber kink and curl in the same pulp. In the present work, no attempt was made to remove fiber kink and curl prior to measuring the wet zero-span breaking length.

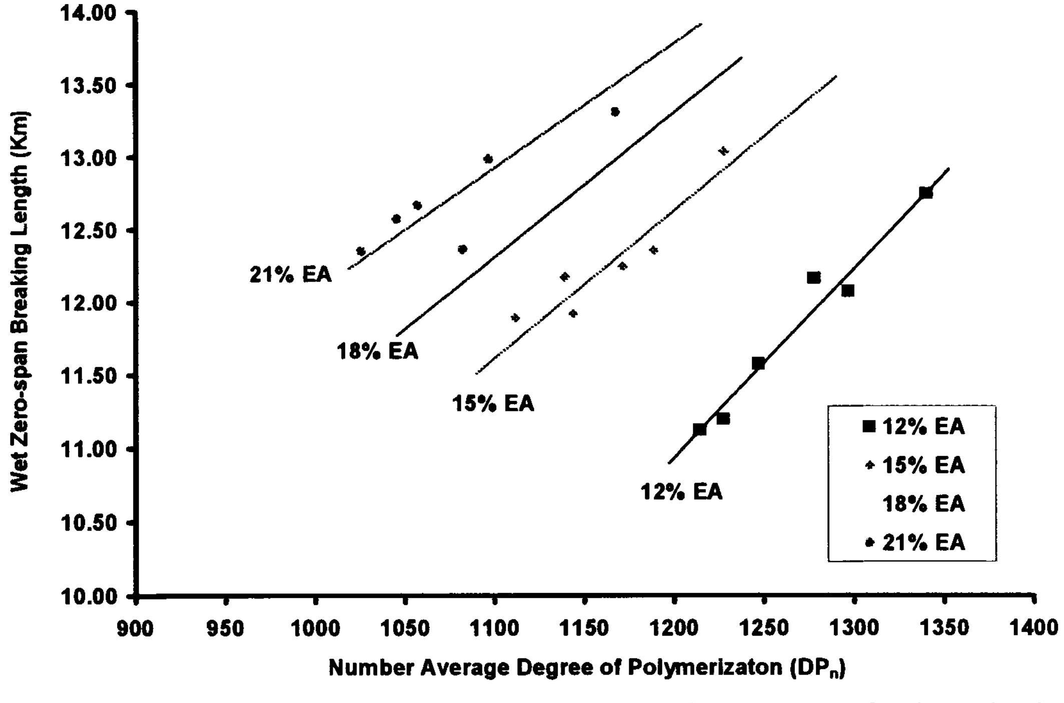


Figure 2.39. Wet zero-span breaking length versus number average of polymerization.

Chapter 3

EXPERIMENTAL PRODEDURES

Methods similar to those used in the preliminary study (Zou, 2000) were used in this dissertation.

3.1. KRAFT PULPING EXPERIMENTS

Mixed northeastern hardwood was obtained from the same commercial pulp mill used in the preliminary experiments. The chips were screened with a Weyerhauser chip classifier and the 5/8'' and 7/8'' fractions were saved for pulping. The wood chips were dried in the air and the moisture content determined. The chips were separated in batches of 2-kg mass (oven dry basis) and stored prior to pulping in a laboratory rocking digester (Figure 3.1).

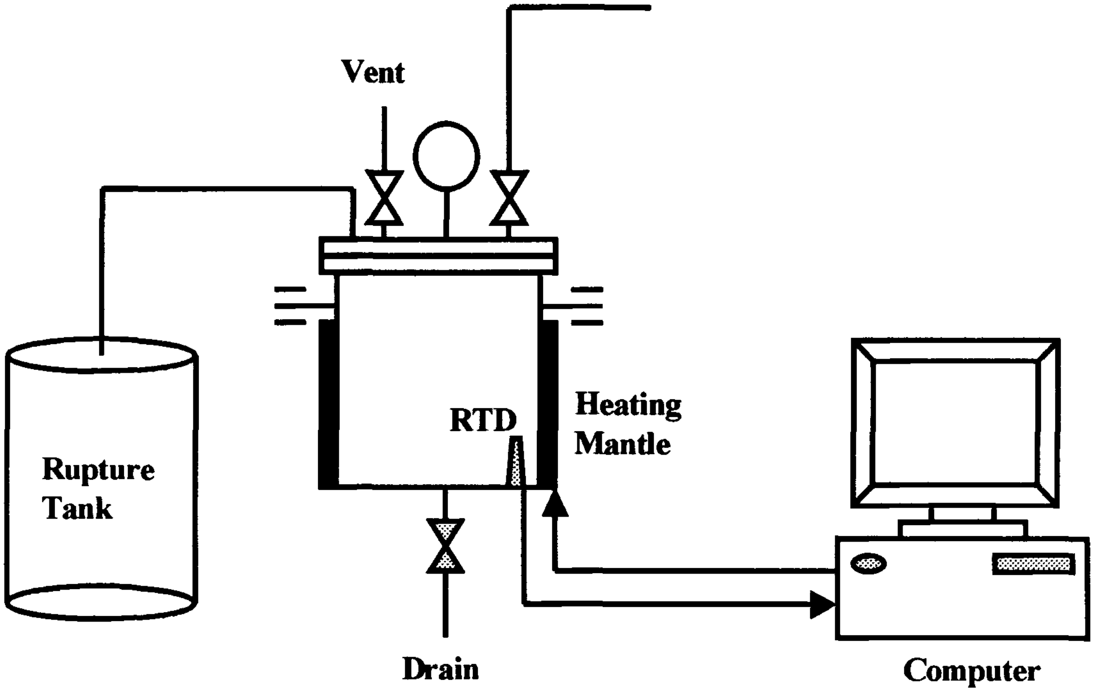


Figure 3.1. Schematic diagram of the rocking digester.

3.1.1. Effect of Kraft Pulping Temperature

The Kraft pulping conditions for the research of the effect of cooking temperature on oxygen delignification are summarized in Table 3.1. Two different kappa number values were investigated. The target kappa numbers were approximately 16 and 20. The target kappa numbers were obtained by using two different cooking temperatures (160 and 180 °C) at two different alkali levels (12 and 21%) at a fixed value of the sulfidity (30%), as shown in Table3.1.

Table 3.1.
Kraft pulping conditions that varied cooking temperature and effective alkali.

	Conditions
Northeastern Hardwood Chips (g)	2000
Effective Alkali (%)	12, 21
Sulfidity (%)	30
Temperature (°C)	160, 180
Liquor to Wood Ratio	4
Target Kappa Number	16 and 20

3.1.2. Effect of Pulp Yield (Sulfidity and Additive) on Oxygen Delignification

Alkaline Leaching Experiments. Alkaline leaching methods, suggested by Li and Macleod (1992), were investigated to remove hemicelluloses at constant kappa number. Unfortunately, these methods did not prove to be fruitful (see Appendix C). The leaching experiments lowered the pulp yield but also lowered the kappa number, and consequently were not successful.

Polysulfide Pulping. The polysulfide process was investigated similarly as an alternative cooking method to produce pulps of high yield with low kappa number and high hemicellulose content. Using the polysulfide process, the desired kappa number of

15 to 16 at 12% EA could not be obtained. The residual alkali was completely exhausted before the target kappa number was reached. High pulp yield was obtained but the kappa numbers were very high. Thus, this method did not appear promising.

Anthraquinone Pulping Experiments. By contrast, preliminary pulping experiments using anthraquinone as a pulping additive proved to be quite successful (see Appendix A). High yield pulps were readily produced by using elevated amounts of AQ. Brownstock pulps with high and low pulp yield were produced that give high and low hemicellulose contents. The Kraft pulping conditions used in the pulping experiments to produce pulps with high hemicellulose are summarized in Table 3.2. Here again, a sulfidity of 30% was used.

Table 3.2.
Kraft pulping conditions that varied AQ to give high hemicellulose pulps.

	Conditions
Northeastern Hardwood Chips (g)	2000
Effective Alkali (%)	12
AQ (%)	0, 0.1, 1, 4%
Sulfidity (%)	30
Temperature (°C)	160
Liquor to Wood Ratio	4
Target Kappa Number	16-17

Effect of Sulfidity (Highly Condensed Lignin). In an attempt to produce low hemicellulose pulps with highly condensed lignin, it was suggested that we produce pulps at very low sulfidity. The limit would be to produce a soda cook without AQ. This type of pulp would allow for investigation of oxygen delignification with highly condensed lignin. Conditions for this set of experiments are summarized in Table 3.3.

Table 3.3.
Kraft pulping conditions at low sulfidity to produce pulps with highly condensed lignin.

	Conditions
Northeastern Hardwood Chips (g)	2000
Effective Alkali (%)	21
Sulfidity (%)	0
Temperature (°C)	160
Liquor to Wood Ratio	4
Target Kappa Number	16

3.1.3. Kraft Pulping Procedure

Kraft pulping experiments were performed in a 2-liter, indirect, electrically heated, batch digester (Figure 4.1). The liquor-to-wood ratio was maintained at four to one (4:1). Wood charge added to the digester was 2 kg mass (oven dry basis) for each cook. The effective alkali (EA) values used in the experiments were calculated on a Na_2O basis. No sodium carbonate (Na_2CO_3) or black liquor was added to the digester. Water was added to achieve a liquor-to-wood ratio of 4 to 1. The cooking time was adjusted to obtain a target kappa number of 16. Heat-up time for the digester was held constant at one hour. To obtain a high level of mixing in the digester, the vessel was rocked through an arc of 135° at a rate of about four (4) revolutions per minute. This rate of moving has been previously determined to minimize mass transfer effects.

Following cooking, each pulp was washed thoroughly, and then screened in a 6-mil vibratory Bird screen, and dewatered using a vacuum screen. The total pulp yield was determined following the cooking and washing of the pulp. Samples were taken and the kappa number, viscosity and brightness determined. The pulp was stored in a refrigerator prior to use in the oxygen delignification experiments.

3.2. OXYGEN DELIGNIFICATION EXPERIMENTS

3.2.1. Medium Consistency Reactor

The oxygen delignification reactor and experimental techniques have been described previously by Guven et al. (1996) and Agarwal (1996). The oxygen delignification experiments were performed in a 20-liter, medium-consistency oxygen reactor that was equipped with a mixer designed to approximate the low level of mixing in an oxygen up-flow tower (Figure 3.2). The speed of the mixer was set at 23 RPM and held constant for all of the experiments to be performed using the oxygen delignification reactor. The reactor had previously been shown to simulate the kappa number reduction seen in mill trials (Guluen et al., 1996). The weight of the pulp to be used in these experiments was 100 grams (oven dry basis). Pulp consistency was set at 12% in all experiments.

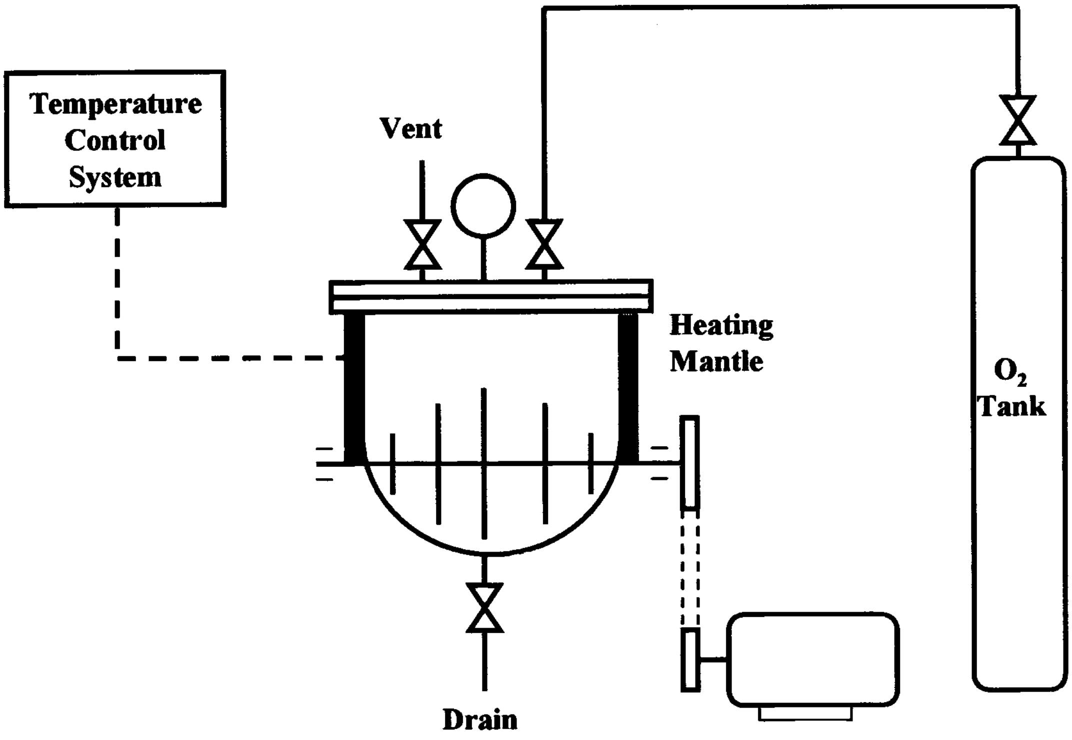


Figure 3.2. Schematic diagram of the medium consistency oxygen delignification reactor.

3.2.2. Oxygen Delignification Experimental Conditions

The conditions used in the oxygen delignification experiments are summarized in Table 3.3. All experiments were performed in a single stage process at 90 °C, caustic addition charge of 1.5% NaOH and 100 psig (0.69 MPa). In the experiments, the reaction time was varied between 5 and 60 minutes.

Table 3.4.
Oxygen delignification conditions.

	Conditions
Temperature (°C)	90
Caustic addition (%)	1.5
Oxygen pressure (psig)	100
Pressure in Argon Experiments (psig)	100
Reaction time (minute)	0, 5, 15, 30, and 60
Amount of $MgSO_4$ used (%)	0.1

Argon Experiments. Experiments were performed to determine the effect of caustic extraction. In these experiments, argon was substituted for oxygen (see Table 4.4). By comparing the two sets of experiments, in which oxygen and argon were used separately, it was possible to separate the change in kappa number and yield attributable to the oxygen delignification reactions from the effect of lignin leaching with caustic, which occurs during the period the pulp is being heated in the reactor.

3.2.3. Oxygen Delignification Experimental Procedure

For each run, 100 grams of pulp was placed into a polyethylene mixing bag. Then, the water to be used to dilute the pulp sample to 12% consistency was measured and $MgSO_4$ was dissolved into the water. The solution was then added to the pulp sample and mixed. Next the NaOH solution was added to the pulp sample and mixed. After sealing the sample bag, both sides of the bag were heated for totally about 7 minutes before the oxygen delignification experiments. Then, the pulp was placed into the reactor, and pre-heated to the experimental reaction temperature. The reactor was covered very quickly and heated to the desired temperature. During the preheat period some delignification occurred due to reaction with the caustic presented in the pulp. When the reactor reached the desired temperature, oxygen or argon was added to the reactor at the desired pressure. The oxygen pressure was held constant by an outlet flow valve located on top of the reactor. For the zero-minute experiments, the reactor was shut down immediately following reaching the reaction temperature; all subsequent procedures were the same for handling the pulp.

At the end of the delignification experiments, the oxygen or argon pressure inside the reactor was released to the atmosphere by completely opening the outlet flow valve. A sample of the residual liquor was taken and stored in a refrigerator for chemical analysis. Water was added into the reactor and the pulp slurry taken out through a bottom valve. The pulp was washed thoroughly and handsheets prepared. The kappa number, viscosity, and brightness were measured on the solid samples. The residual liquor was used to measure the residual alkali, pH, and COD value for each sample. Samples of pulp were raved for chemical analyses.

3.3. PULP AND LIQUOR ANALYSES

3.3.1. White Liquor and Black Liquor

The response variables were determined using appropriate Tappi standard methods. The white liquor titration was performed according to T-624 and the black liquor titration according to T-625.

3.3.2. Kappa Number and Permanganate Number

The kappa and permanganate numbers were determined by following Tappi Standards T-236 and UM-251 respectively.

3.3.3. Viscosity

Tappi 0.5% CED viscosity was measured by following Tappi Standard T-230. The intrinsic viscosity $[\eta]$ was estimated according to ASTM standard D1795-62 and SCAN-C 15:62. The equation of Evans and Wallis (1989) relating the degree of polymerization (DP) to the intrinsic viscosity [η] was used to estimate the degree of polymerization of the carbohydrates.

$$DP_V^{0.9} = 1.65 * [\eta] \tag{3.1}$$

3.3.4. Chemical Oxygen Demand (COD)

The chemical oxygen demand (COD) was determined using a HACH spectrophotometric method. The HACH procedure is similar to the CSAN-CM-103X technique for determining COD content in pulp.

3.3.5. Residual Alkali and pH

The residual alkali in the black liquor sample was measured following Tappi Standard T-625. The pH of the liquor samples was measured at room temperature using a high quality pH meter.

3.3.6. Pulp Yield

The kraft pulping yield was determined gravimetrically.

3.3.7. Brightness and Wet Zero-span Tensile Strength

ISO brightness was determined using a Technibrite Micro TB-1C brightness meter. The wet zero-span tensile strength was estimated using a Pulmac tester.

3.3.8. Carbohydrate and Lignin Content

The component carbohydrate content of the pulps, as well as the extractives and soluble and insoluble lignin was estimated by following the procedures summarized by Genco et al. (1990). Sugar analyses were performed using the Dionex DX 500 ion chromatograph (Figure 3.3).

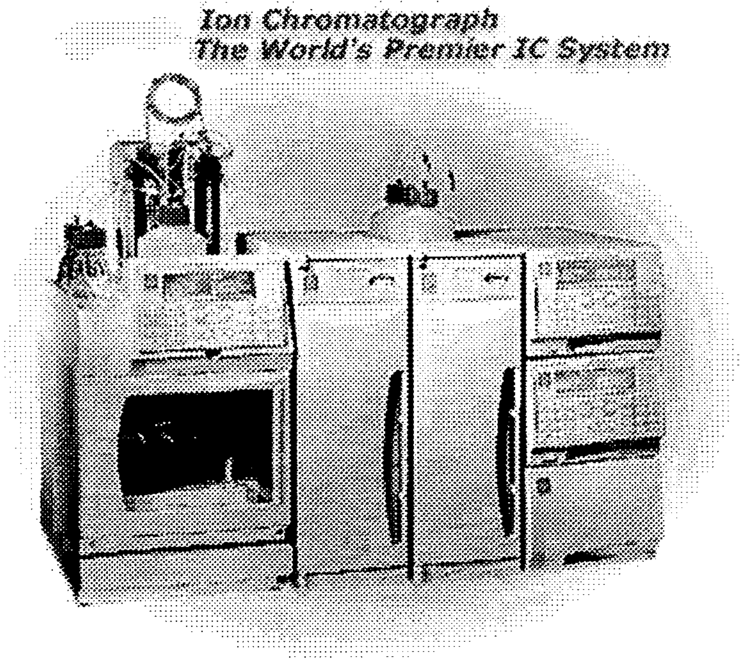


Figure 3.3. Dionex DX-500 ion chromatography.

The extractives were determined gravimetrically following extraction with dichloromethane (DCMC). Soluble and insoluble lignin was estimated following hydrolysis of the carbohydrates with concentrated sulfuric acid. Carbohydrate analyses were estimated using ion chromatography. The calculational procedure for estimating the carbohydrates is summarized in Table 3.5 following the method suggested by Genco et al. (1990) and the molecular ratios for glucuronoxylan and glucomannan given by Sjostrom (1993).

Table 3.5.

Equations were used in estimating the polymeric composition of the samples.

ID	Description
1	Extractives = E
2	Ash = A
3	Total Lignin = KL + SL
4	Uronic Acid = UA
5	4-O-MPG = %4-O-me-α-P-glycopyranose = UA*(190/176)
6	G = % glucan = Gluco * (162/180)
7	M = % mannan = Manoe * (162/180)
8	AR = % arabiman = Arabin * (132/150)
9	GA = % galactan = GA * (162/180)
10	X = % xylan = X * (132/150) + UA*0.6*(190/176)
11	Carbohydrate = AR + GA +G + X + M +4-O-MPG
12	Cellulose = G – M/1.7
13	Hemicelluloses = Carbohydrate – Cellulose
14	Glucuronoxylan = X + UA
15	Glucomannan = M* (1+ 1/1.7)

Chapter 4

RESULTS AND DISCUSSION

The experimental data are summarized in Appendix A, B, C, and D. Appendix A shows the experimental data for the pulping experiments. Data are presented for Kraft pulping cooking at various temperatures, effective alkali addition rates, H-factors, and AQ concentrations. The results for the oxygen delignification experiments are shown in Table B for reaction times of 5, 15, 30 and 60 minutes. Appendix C shows the results for the caustic leaching experiments at both low (1 to 3% caustic) and high (3 to 13%) addition rates. Lastly, Appendix D summarizes the results of chemical composition data for selected pulps. Not all of samples of pulp following oxygen delignification were analyzed. Rather, for nine (9) of the most important pulps, the brownstock and the sixty (60) minutes exposure samples were analyzed for extractives, lignin and carbohydrate composition.

4.1. RESULTS OF KRAFT PULPING EXPERIMENTS

Tables A.2 and A.4 summarizes the results of the Kraft pulping experiments that were conducted to investigate the effect of cooking temperature, effective alkali and the addition of anthraquinone as a pulping catalyst. Also a soda pulp was performed to give a pulp with low yield and highly condensed lignin. Two effective alkali levels (12% and 21%) were used at two different cooking temperatures (160 and 180 °C). Both the temperature and alkali levels bracket the range on variables used commercially.

4.1.1. Kraft Pulping without Anthraquinone (AQ)

It can be seen from the data in Table A.2 that at a constant value for the EA level (either 12% or 21%), the higher cooking temperature resulted in lower pulp yield and lower viscosity, but higher pulp brightness. These conclusions are shown graphically in Figures 4.1 (screened yield), Figure 4.2 (intrinsic viscosity) and Figure 4.3 (pulp brightness). The data suggest that lower selectivity was obtained by pulping (cooking) at high temperature and high EA.

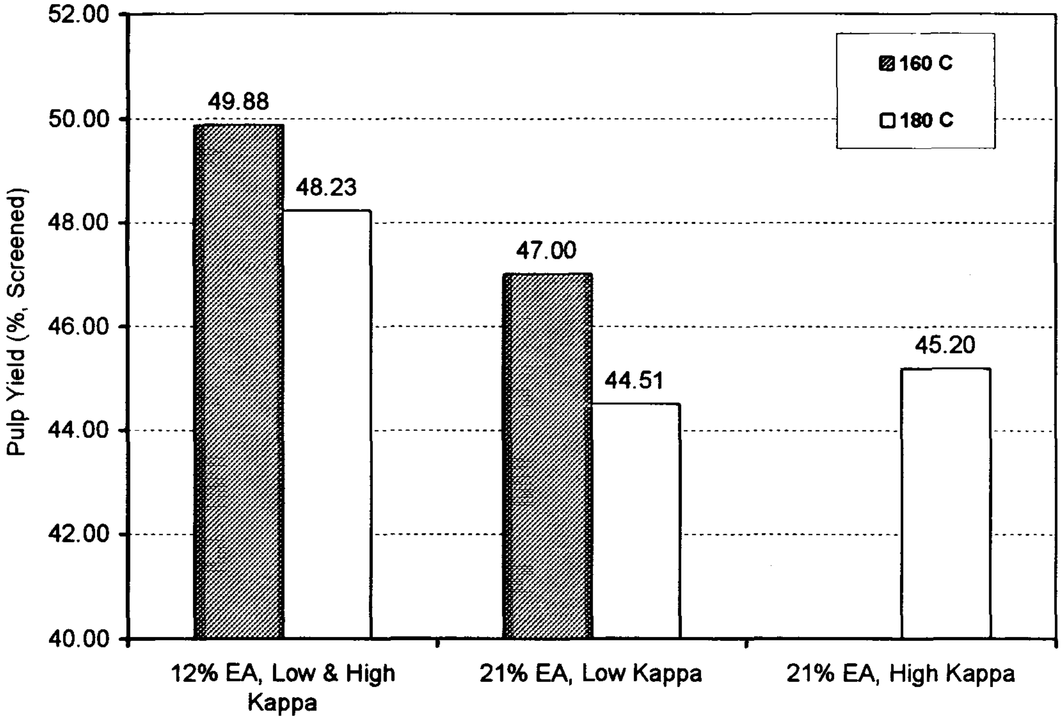


Figure 4.1. Effect of EA and cooking temperature on pulp yield.

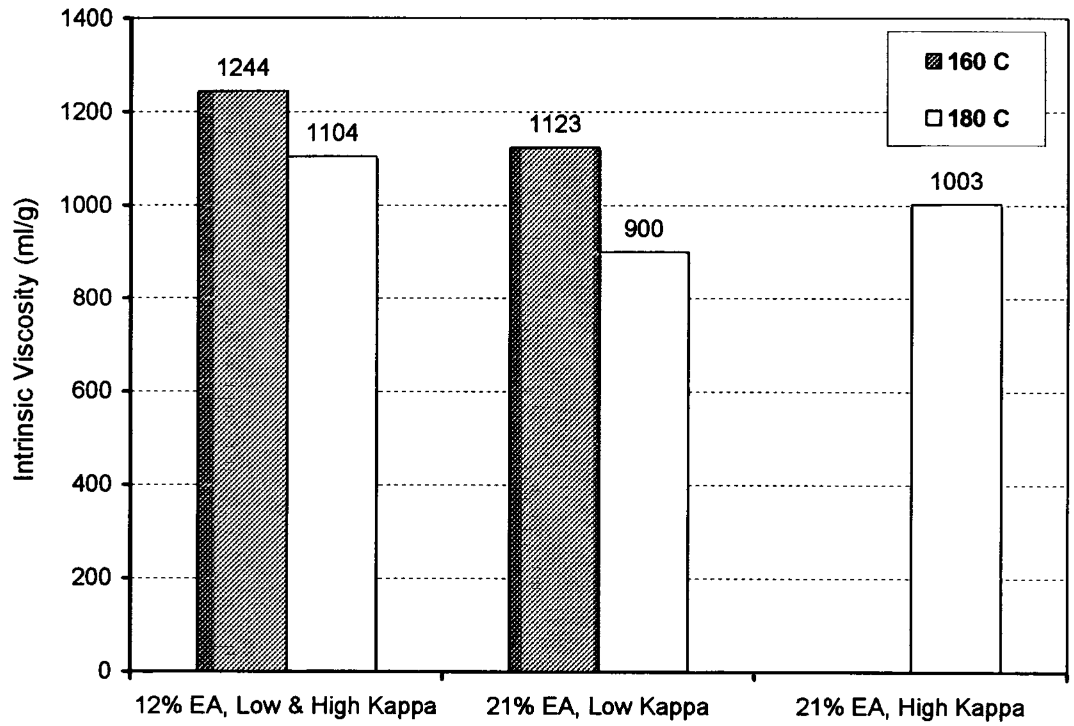


Figure 4.2. Effect of EA and cooking temperature on pulp intrinsic viscosity.

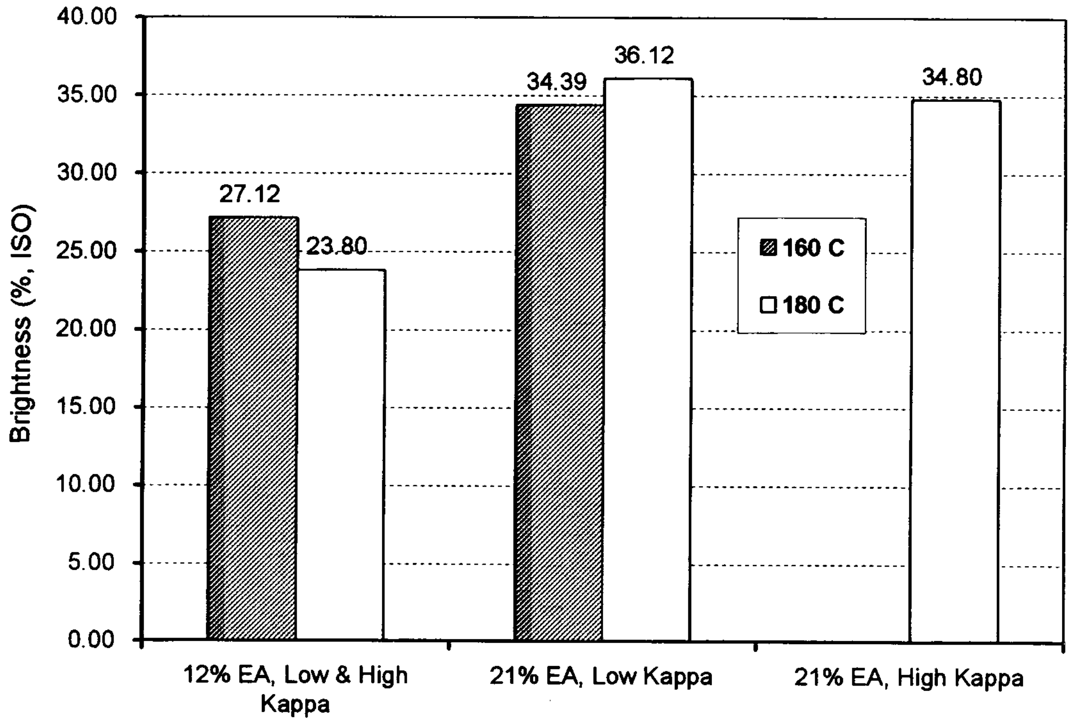


Figure 4.3. Effect of EA and cooking temperature on pulp brightness.

A kappa number value of 16 could not be obtained by cooking at an effective alkali level of 12% and 180 °C (see Table A.5). Rather, an equilibrium value or "floor" in the kappa number was reached at about 21 under these conditions. A constant value for the lignin content is reached when cooking for prolonged periods of time. This floor in the lignin content is recognized in several of the kinetic models used to describe Kraft pulping (Edwards and Norberg, 1973). At low selectivity the alkali in the pulping liquor has a greater chance of attacking carbohydrates and is unavailable for further lignin reduction. For experiments B1 thru B4, when the kappa number in the pulp reached approximately 21, the alkali in the cooking liquor was essentially exhausted and the kappa number reached an equilibrium value, but the viscosity and pulp yield kept decreasing. These results suggest that the peeling reaction is still going on even though the residual alkali is low.

The results in Tables A.2 and Figure 4.3 further suggest that high brightness pulps were obtained when cooking at high temperature or high effective alkali (compare B2/B4 and D-3). This means that at the same temperature, cooking at high effective alkali will lead to high brightness pulps. Also, cooking at the same effective alkali, high temperature will also lead to high brightness pulps. Either condition shortens the cooking time and thus reduces the number of chromophoric groups, or light absorption centers, that form in the pulp.

4.1.2. Kraft Pulping with Anthraquinone (AQ) Additive

Anthraquinone was added during Kraft pulping. The objective of these experiments was to produce brownstock pulps with high pulp yield with the same kappa number under the same cooking conditions. It is well known that cooking with AQ leads to pulps with higher hemicellulose content and thus higher pulp yield. In this set of experiments, four levels of anthraquinone (0, 0.1%, 1%, and 4%) were added to the digester during the Kraft pulping process. In each case a target kappa number of 16 was achieved. Commercially, AQ levels typically added to the digester are between 0.05 to 0.1% because of economic reasons. These experiments are summarized in Table A.4 and in Figures 4.4 and 4.5.

Pulp Yield. The pulp yield increased from approximately 50% for the cook in which no AQ was added to the digester (control) to 56% yield when 4% anthraquinone was added (see Figure 4.5). The high pulp yield was attributed to the increasing amount of anthraquinone used as a pulping catalyst. Applying AQ is a promising method for producing pulps with widely different carbohydrate contents with the same kappa number. Above about 1% AQ, the yield improvement was still increasing but slowed considerably.

H-Factor. By adding anthraquinone to the digester, the cooking time in the digester to achieve the target kappa number (H-factor) was significantly decreased (Figure 4.4). The cooking time was shortened from 464 minutes for the control (A-1) to 171 minutes for 4% AQ additive (AQ 4.0%). The H-factor decreased from 3065 hours for the control (A-1) to 1247 hours for 4% AQ charge (AQ 4.0%), approximately a 60% decrease in cooking time.

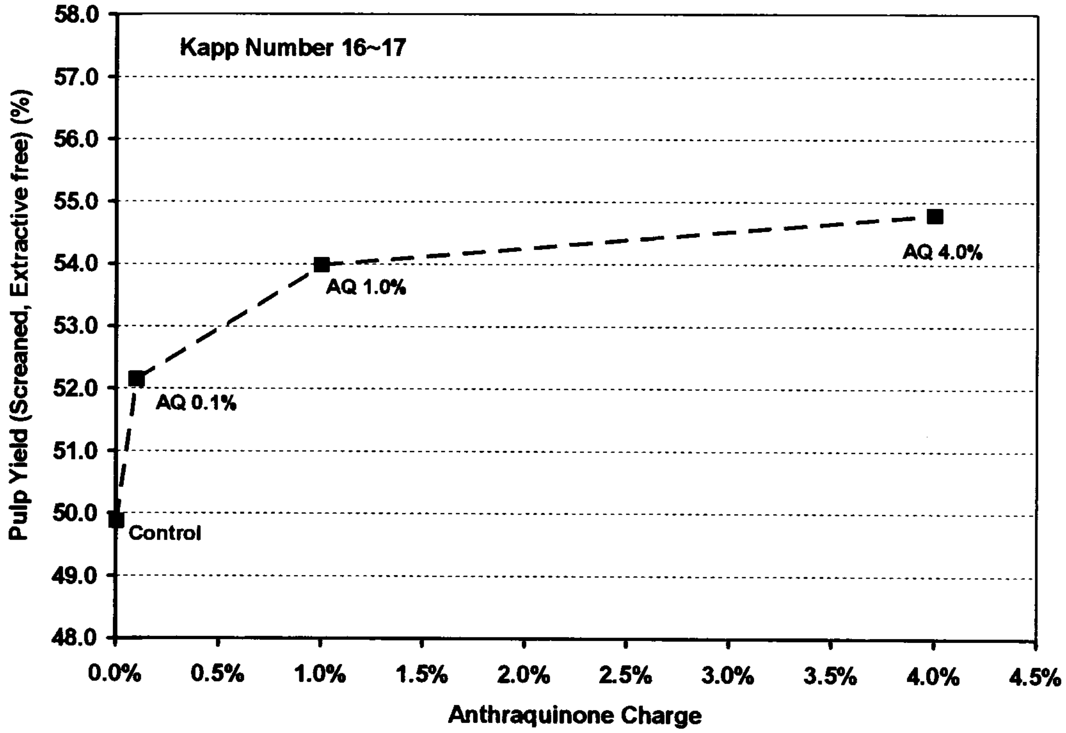


Figure 4.4. Pulp yield versus AQ charge in the digester.

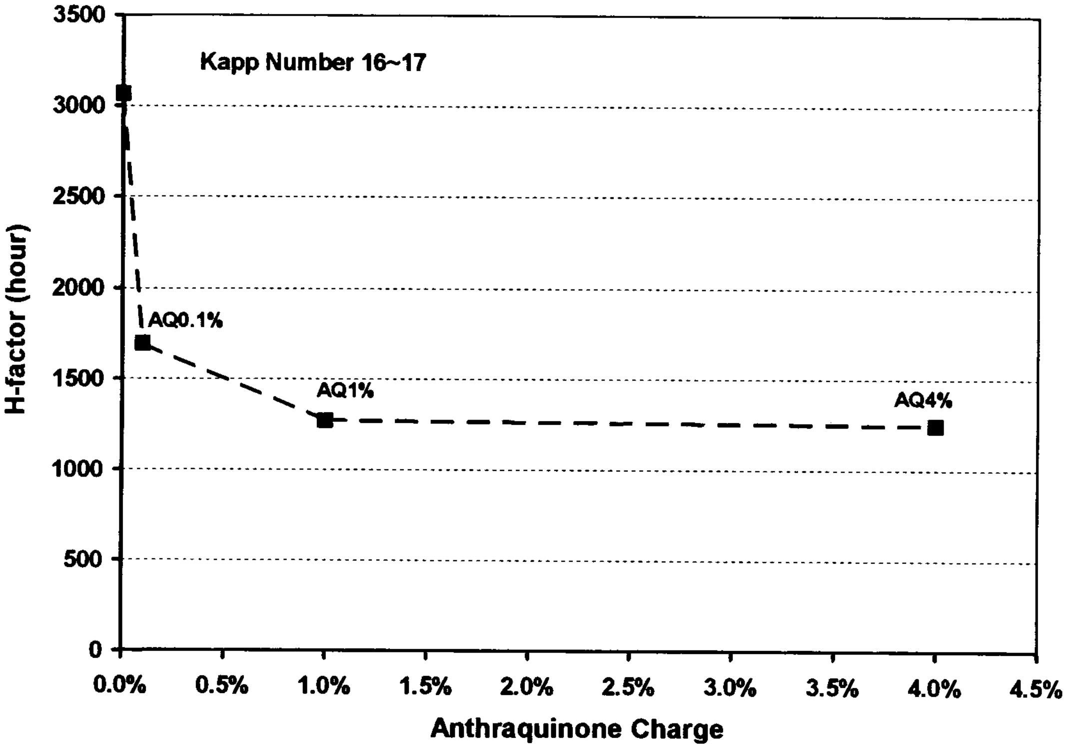


Figure 4.5. H-factor versus anthraquinone charge in the digester to achieve a kappa number of 16-17.

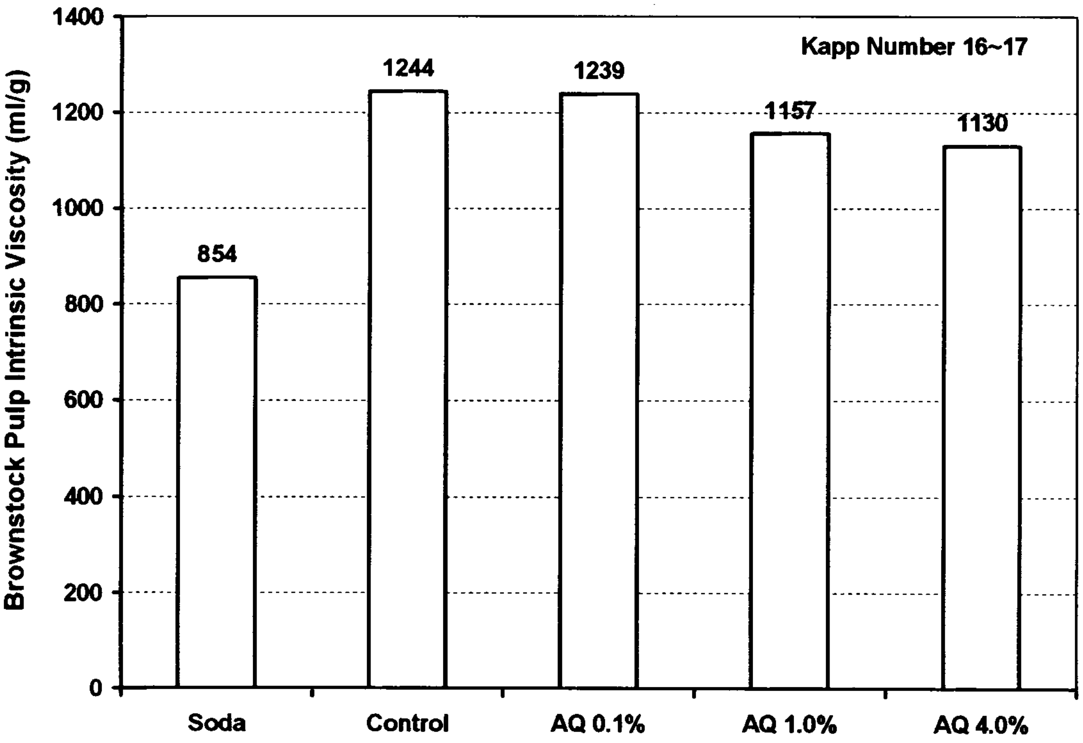


Figure 4.6. Intrinsic viscosity versus anthraquinone charge in the digester to achieve a kappa number of 16-17.

Viscosity and Brightness. The data of intrinsic viscosity versus AQ charge are plotted in Figure 4.6. In this figure, the pulp produced with soda showed a very low intrinsic viscosity (854 ml/g). Increasing the AQ charge not only increased the pulp yield but also decreased the pulp viscosity. Although pulping with AQ in the digester reduced the cooking time to achieve a target kappa number (see Figure 4.5), no improvement could be measured for the brightness of the brownstock pulp. These results are shown summarized in Figure 4.7 for pulping experiments performed using of AQ as a catalyst.

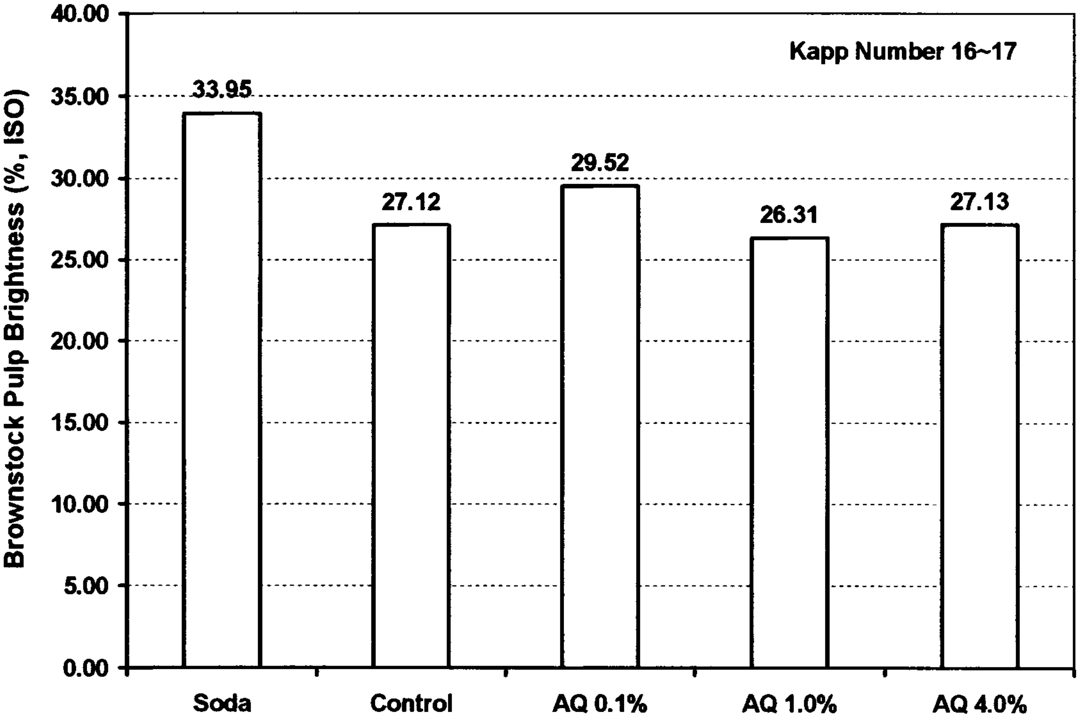


Figure 4.7. Brightness versus anthraquinone charge in the digester to achieve a kappa number of 16-17.

4.2. EFFECT OF CAUSTIC EXTRACTION ON OXYGEN DELIGNIFICATION

Caustic extraction contributes to removal of lignin during the oxygen delignification process. Figure 4.8 shows typical results for experiments conducted with argon substituted for oxygen in the delignification experiments. Data like that shown in Figure 4.8 permits the kinetic data to be corrected for the caustic extraction that takes place when the pulp sample is raised to the reaction temperature. These results are applicable for a condition of 1.5% caustic and 90 °C and a kappa number of 20. Under these conditions, caustic extraction during the reactor preheating period contributes to a reduction in the kappa number of approximately 25% prior to the addition of oxygen.

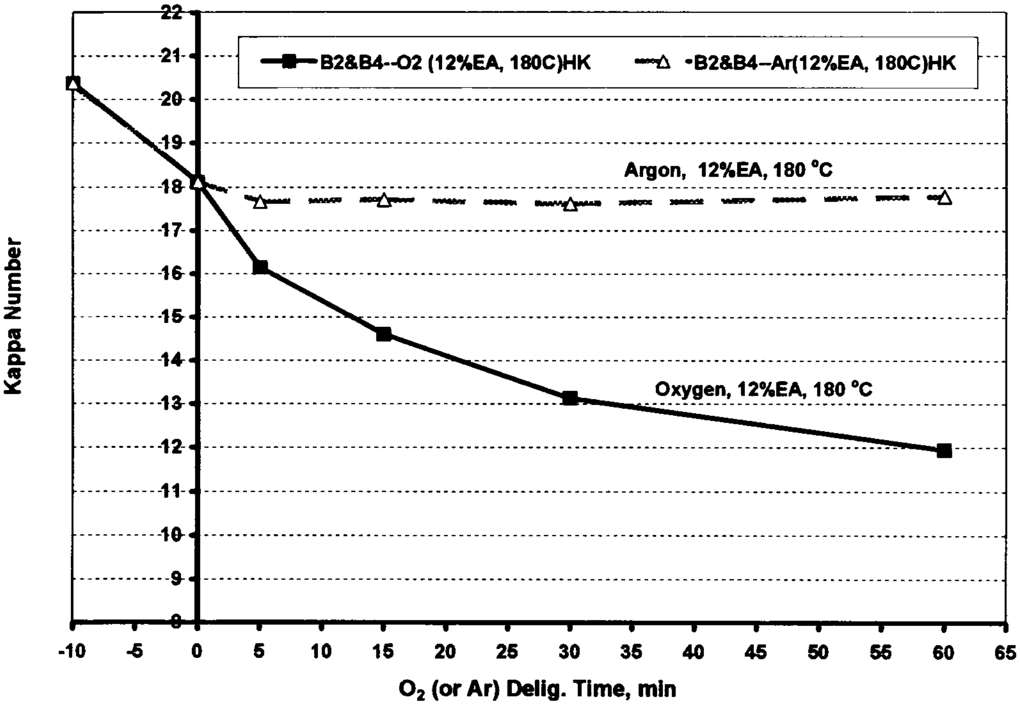


Figure 4.8. Effect of argon versus oxygen for pulp cooked at 180 °C and 12% EA.

The data clearly show that oxygen is necessary for further lignin removal. As seen in the argon experiments, without the presence of oxygen, the kappa number reaches a constant value. But there is little loss in pulp viscosity (Figure 4.9) and pulp yield (Figure 4.10); this may resulted from the peeling reactions.

The oxygen delignification data presented in Appendix B have been corrected for the effect of the heat up period in the reactor.

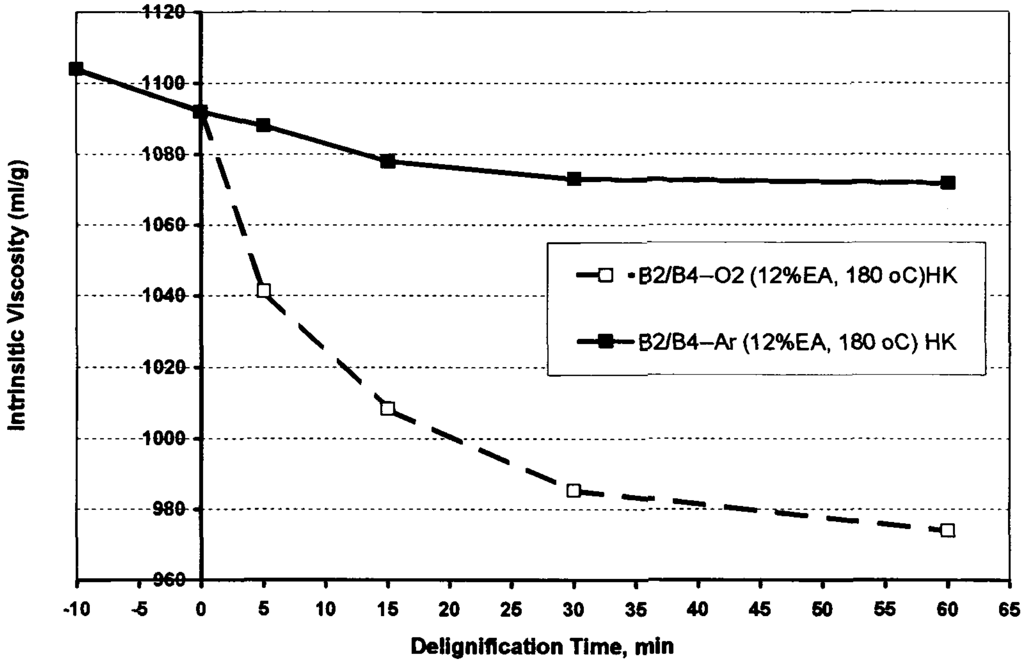


Figure 4.9. Viscosity trend during delignification with argon versus oxygen.

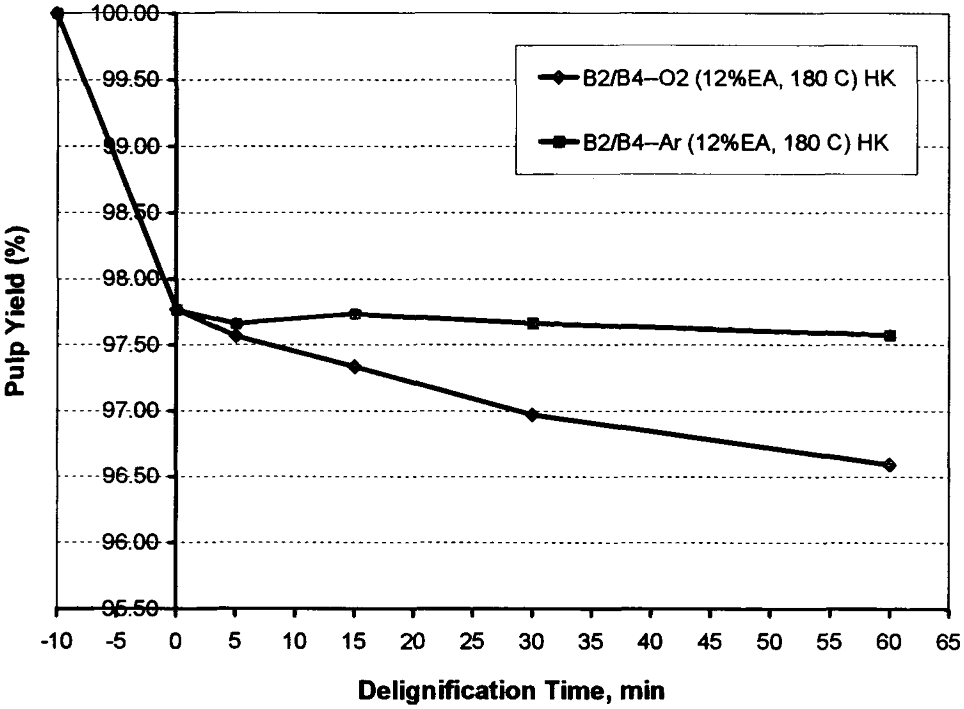


Figure 4.10. Pulp yield versus time.

4.3. RESULTS OF OXYGEN DELIGNIFICATION EXPERIMENTS

4.3.1. Analysis of Kinetics Data

Schoon's (1983) method was used to analyze the data for the oxygen delignifcation kinetics as described previously. The objective of this exercise was to develop data for the kinetic rate constant (k') and order of the reaction (q). This permitted a direct comparison of the kinetics for the reaction. The results of this analysis are shown in Table 4.1 and Table 4.2.

$$\frac{K^{(1-q)} - K_0^{1-q}}{q-1} = k' \cdot t \qquad (2.23)$$

Table 4.1.
Results for the integral method of analysis – non-AQ pulps.

ID	q	R^2	k'
A-1, 12%EA, 160 °C	7.7	0.9990	4.246E-10
C-2, 21%EA, 160 °C	7.7	0.9994	8.801E-10
D-2, 21%EA, 180 °C	7.7	0.9982	8.154E-10
B2/B4, 12%EA, 180 °C, HK	7.7	0.9980	1.394E-10
D-3, 21%EA, 180 °C, HK	7.7	0.9987	1.903E-10

Table 4.2.
Results for the integral method of analysis – Pulps produced using AQ.

ID	q	R^2	k'
SODA	7.7	0.9928	1.004E-09
A-1, 12%EA, 160 °C	7.7	0.9990	4.246E-10
AQ0.1%	7.7	0.9878	2.639E-10
AQ1.0%	7.7	0.9956	2.602E-10
AQ4.0%	7.7	0.9977	1.702E-10

The experimental data fit Shoon's model very well as seen by the high values for the coefficient of regression (R^2). The reaction rate order for oxygen delignification "q" is 7.7 when the kappa number data are corrected for the reduction that takes place during the caustic extraction in the preheating stage. The value for the reaction order (q) of 7.7 perfectly matches the results reported by Agarwal (2000) for mixed southern hardwoods having a kappa number of 13. Hence, the "q" value in the oxygen delignifcation for northern mixed hardwood appears to be close to 7.7.

Figures 4.11 and 4.12 show the kappa number trend during delignification. The dots in these figures are the experiment data points, while the curves are the points calculated from Schoon's model (equation 2.11).

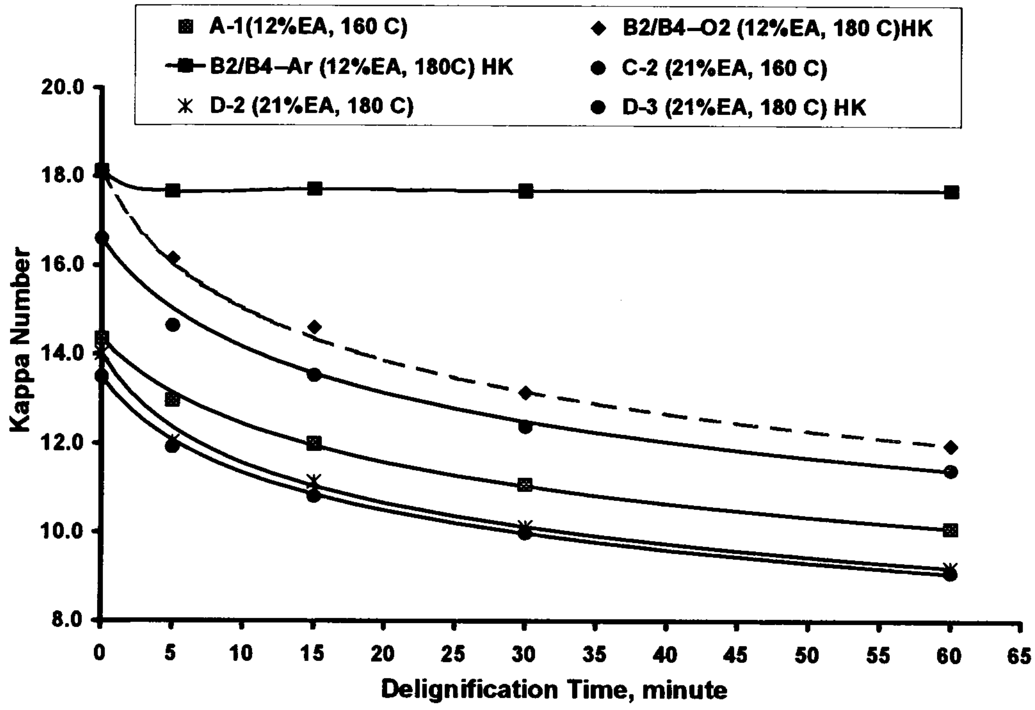


Figure 4.11. Kappa number trend during delignification – non-AQ results.

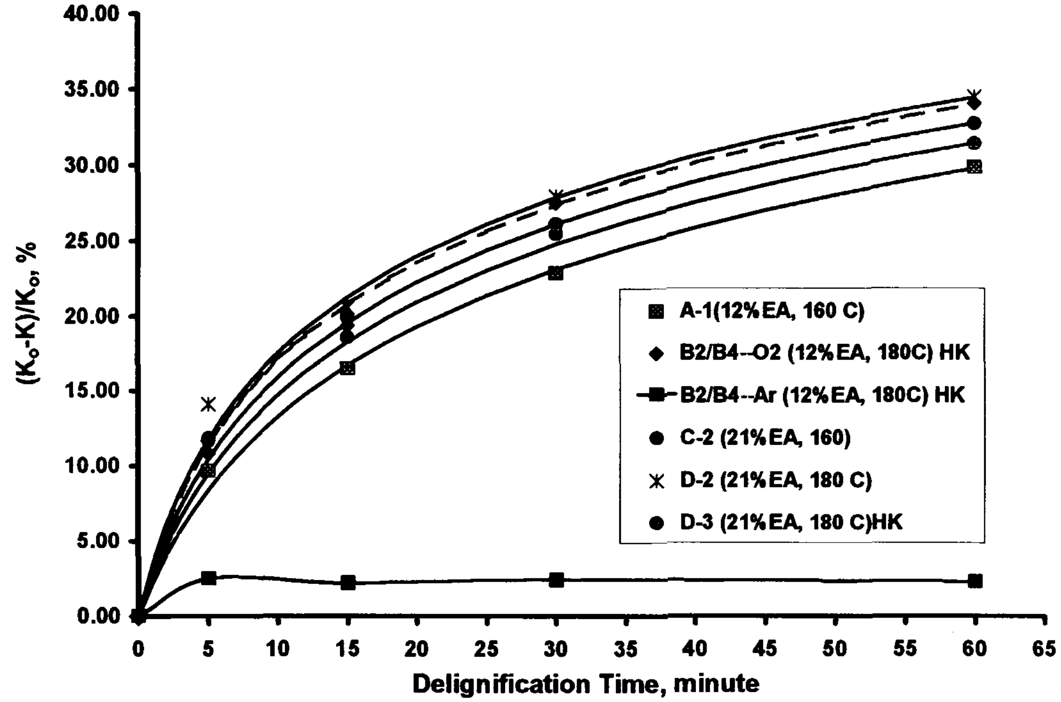


Figure 4.12. Kappa number trend (%) during delignification – non-AQ results.

4.3.2. Comparison of Effective Alkali and Temperature for Non AQ Data

4.3.2.1. Effect of Digester Effective Alkali at Low Kappa Number and 160 °C

Figure 4.13 is a summary of the effect of alkali at a kappa number 16. Two pulps were produced by using a cooking temperature of 160 °C, and by varying the effective alkali (12 EA and 21% EA). The data show that cooking at high EA in the digester (21%) resulted in a pulp that gave a high O_2 delignification rate (high k' value). These results match Zou's (2000) previous work.

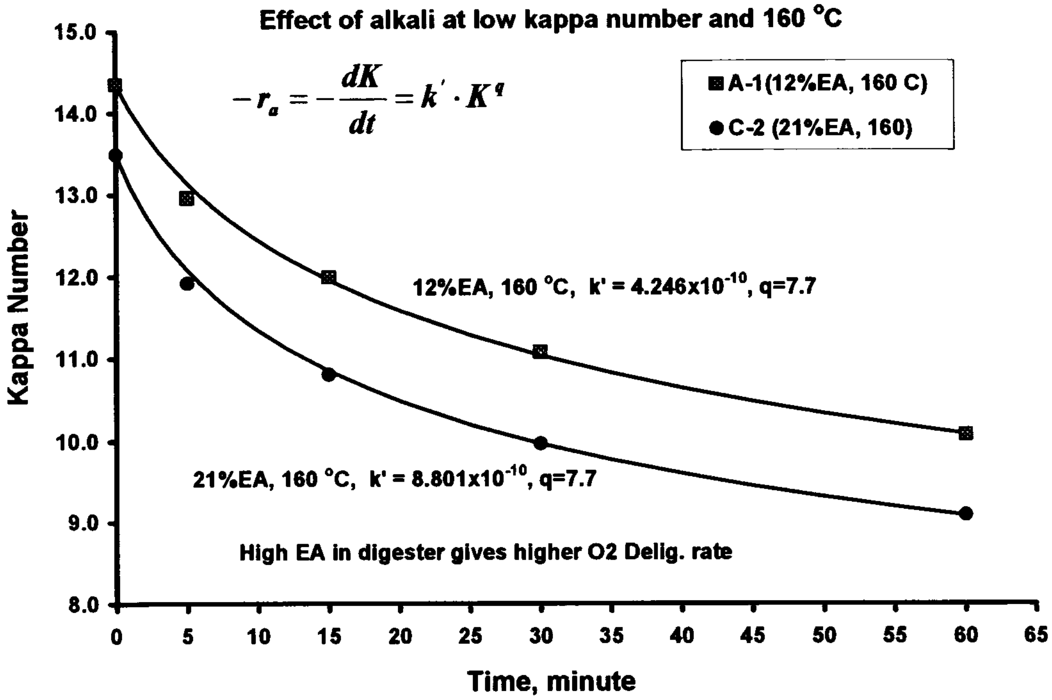


Figure 4.13. Effect of cooking EA on oxygen delignification rate. Kappa number of 15 to 16 and cooking temperature of 160 °C.

4.3.2.2. Effect of Digester Effective Alkali at High Kappa Number and 180 °C

Figure 4.14 compares the data for brownstock pulps produced in the digester at high kappa number (20) at both high (21%) and low (12%) alkali when the cooking temperature was fixed at 180 °C. At high kappa number (20), high effective alkali in the digester gives a slightly higher oxygen delignification rate (Figure 4.14), but not nearly as significant as that seen when the digester cooking temperature (160 °C) and kappa number (16) were both low. By contrast, Figure 4.15 compares similar data at low kappa number (16).

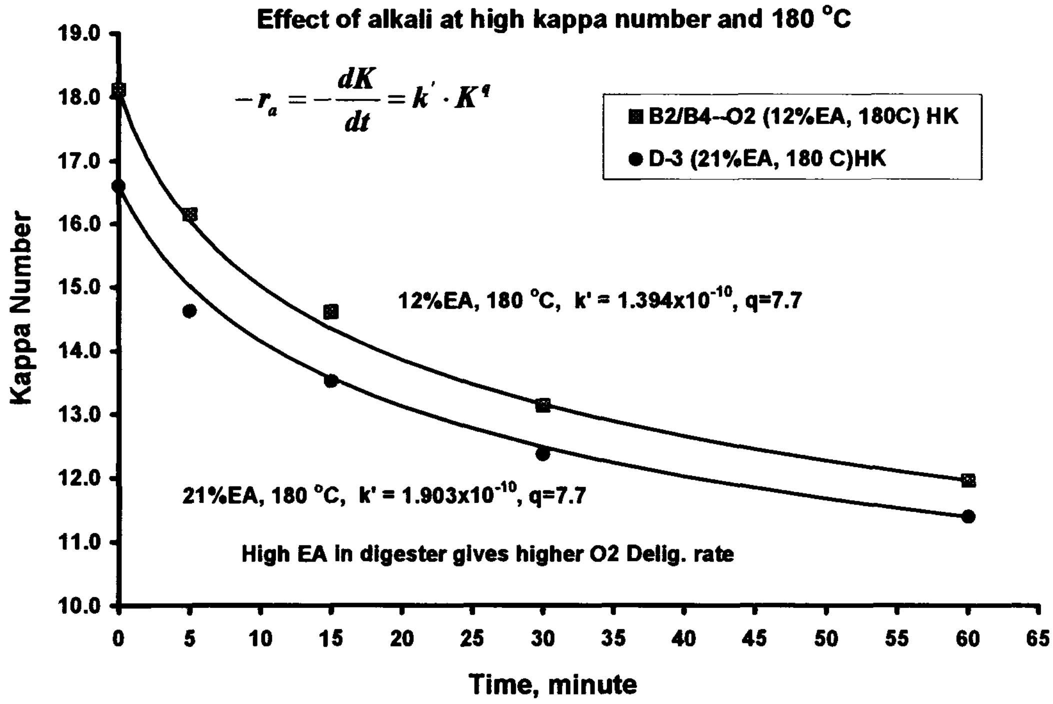


Figure 4.14. Effect of digester effective alkali at high kappa number and 180 °C.

4.3.2.3. Effect of Digester Cooking Temperature at High Effective Alkali

Figure 4.15 present data for the difference in cooking temperature at high effective alkali (21%) on the oxygen delignification rate. These data (Figure 4.15) show clearly that there was no difference in the oxygen delignification kinetics when low kappa pulp (16) was produced at 21% EA at either 160 or 180 °C. This result suggests that if the effective alkali in the digester is high, and the target kappa number is relatively low, then the cooking temperature in the digester will not affect the oxygen delignification rate.

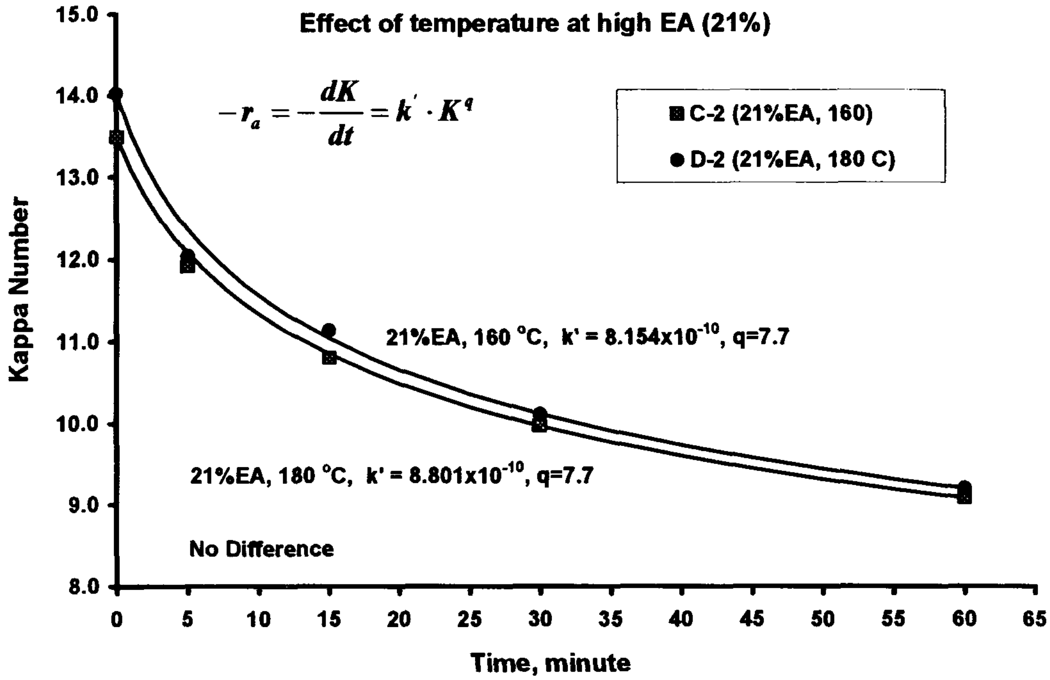


Figure 4.15. Effect of digester cooking temperature at high EA (21%) on oxygen delignification rate.

4.3.2.4. Effect of Digester Effective Alkali When Cooking to High Kappa Number and 180 °C

Figure 4.16 compares the oxygen delignification kinetics for brownstock pulps produced at high (20) and low (16) kappa numbers. Both brownstock pulps were produced with a digester cooking temperature of 180 °C and an effective alkali of 21%. Predicated on the results of Agarwal (1999), one would expect that brownstock with higher initial kappa number would give higher delignification kinetics. However, the data of Figure 4.16 show that for pulping at 21% EA the opposite results occurred, that is-- the lower kappa number pulp showed a slightly higher delignification result. It should be pointed out that Agarwal (1999) produced his higher kappa number pulps at 15% EA. Consequently, there is a major difference in these results where very high EA

(21%) was used in the digester. The hypothesis is that at high level EA in the digester, the longer the cooking time, the easier will be the oxygen delignification (higher rate constant) for the similar initial kappa number brownstock.

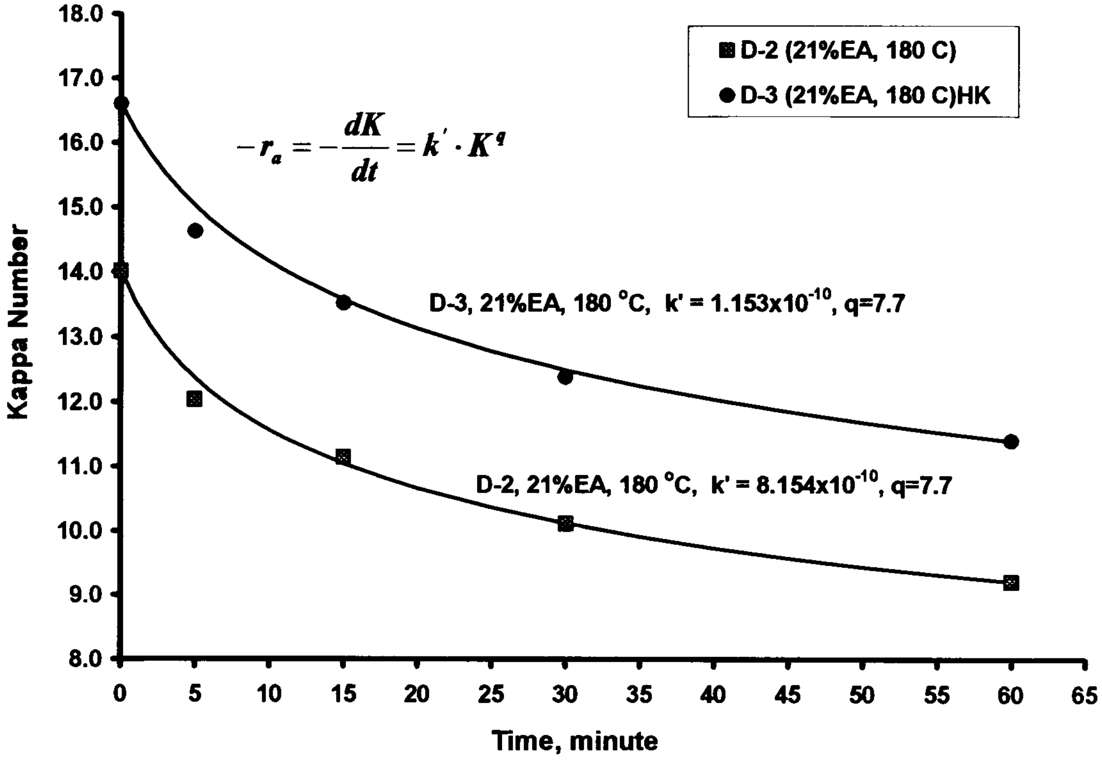


Figure 4.16. Effect of initial Kappa number on oxygen delignification rate for pulp produced at 21% and temperatures of 160 °C and 180 ° C.

4.3.3. Effect of Hemicellulose Content on Oxygen Delignification Kinetics – Pulping With AQ

The effect of the hemicellulose content on oxygen delignification is shown in Figure 4.17. As we expected in our previous work, higher hemicellulose content in the brownstock will hinder oxygen delignification and result in lower oxygen delignification efficiency. This was confirmed again in this investigation. The reaction rate constants for oxygen delignification are summarized in Table 4.4 and the kappa number versus time curves are shown graphically in Figure 4.17. In Figure 4.17, the initial kappa number has been shifted slightly or modified so that all of experiments start at an initial kappa number value of 15.5. For purposes of comparison, the curve for the soda pulp, which had very low hemicellulose content, is also shown. No matter what basis is chosen, either lignin content, kappa number, or corrected kappa number, it can be found that with an increase in the hemicellulose content of the brownstock, the kinetics and efficiency for oxygen delignification was decreased (Figure 4.18).

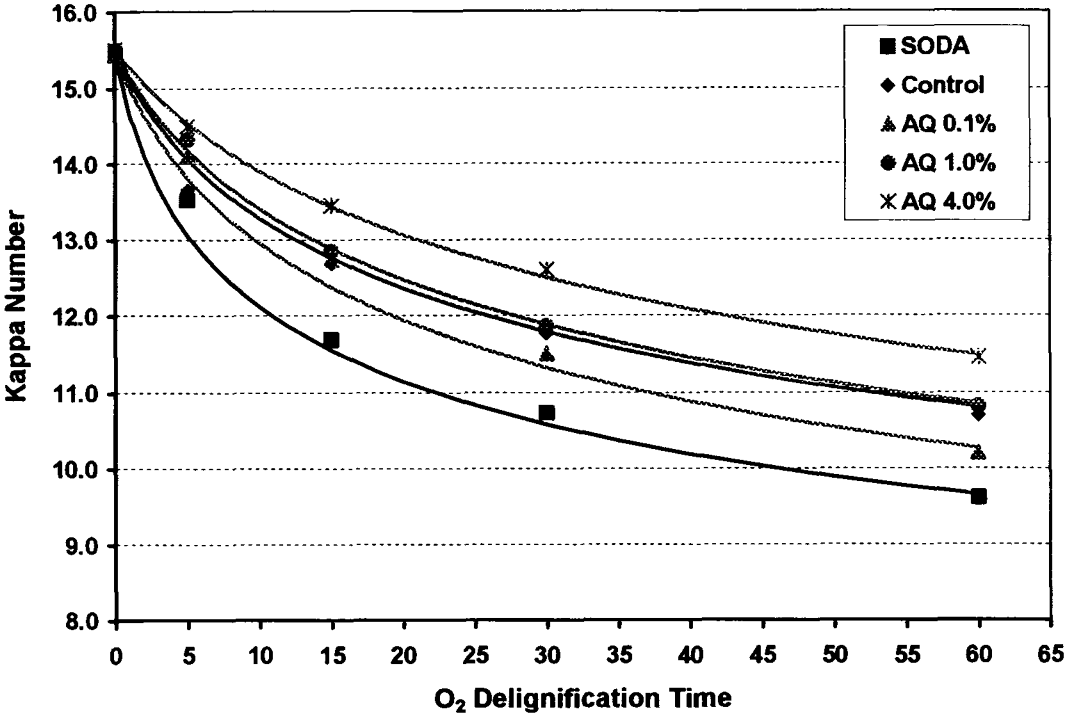


Figure 4.17. Effect of hemicellulose content on oxygen delignification.

Pulp cooked with 4% AQ additive had the highest hemicellulose content (highest pulp yield); it also presented the lowest oxygen delignification efficiency. Contrarily, pulp cooked with no AQ additive (control) presented the highest oxygen delignification efficiency. These results can be seen in Figure 4.18.

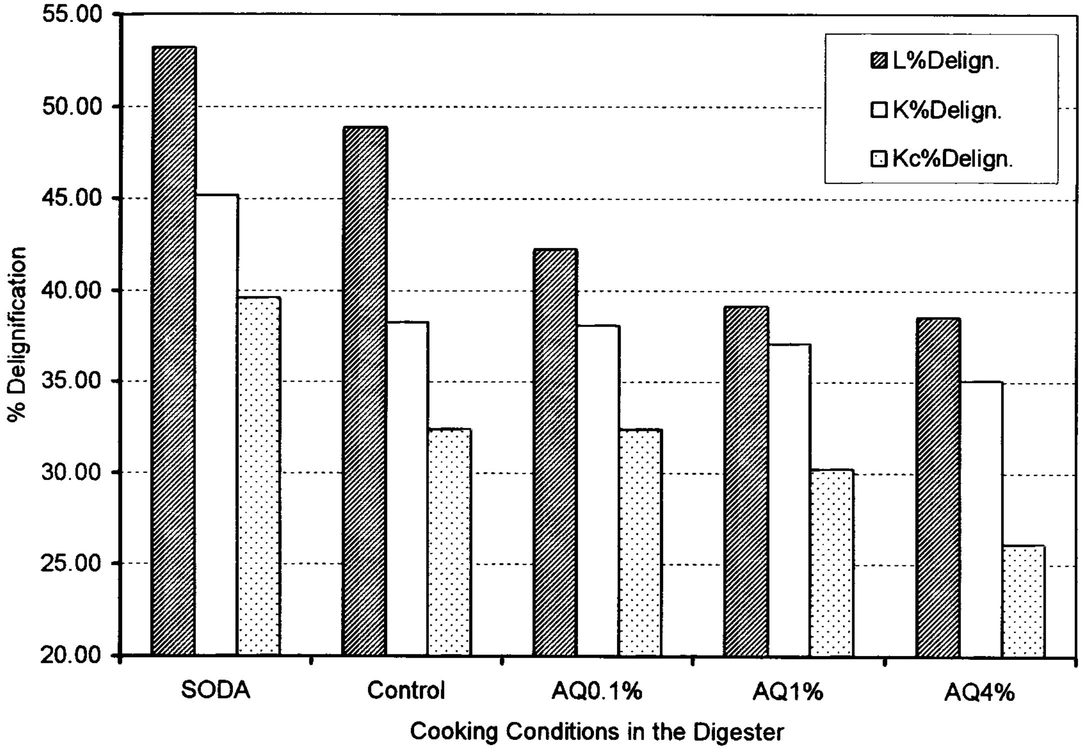


Figure 4.18. Delignification rate versus cooking conditions in the digester.

The oxygen delignification rate decreased significantly with an increase in the hemicellulose content which resulted from an increase in pulp yield in the brownstock. This is illustrated in Figures 4.19 and 4.20 which show the Schoon rate constants plotted versus the pulp yield (Figure 4.19) and also the hemicellulose contents in the brownstocks (Figure 4.20). The data for the AQ pulps are more regular and have less scatter than the pulps produced under the widely different cooking conditions represented by the soda, the control and the low and high EA Kraft cooks.

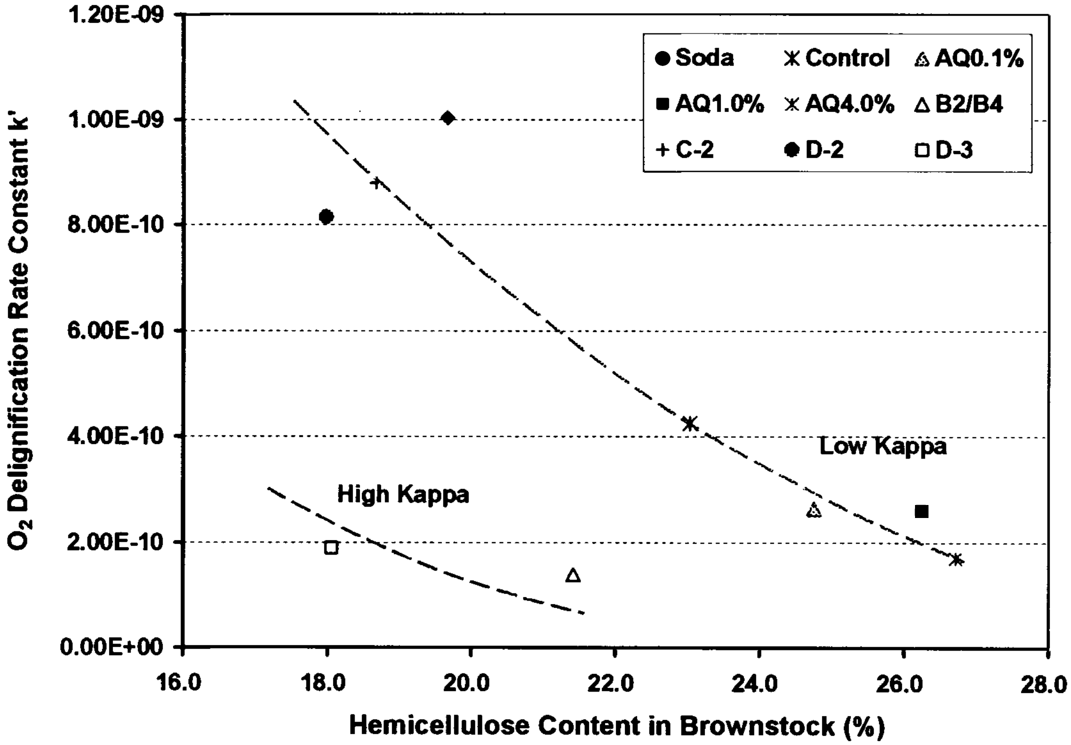


Figure 4.19. Effect of hemicellulose content on oxygen delignification kinetics.

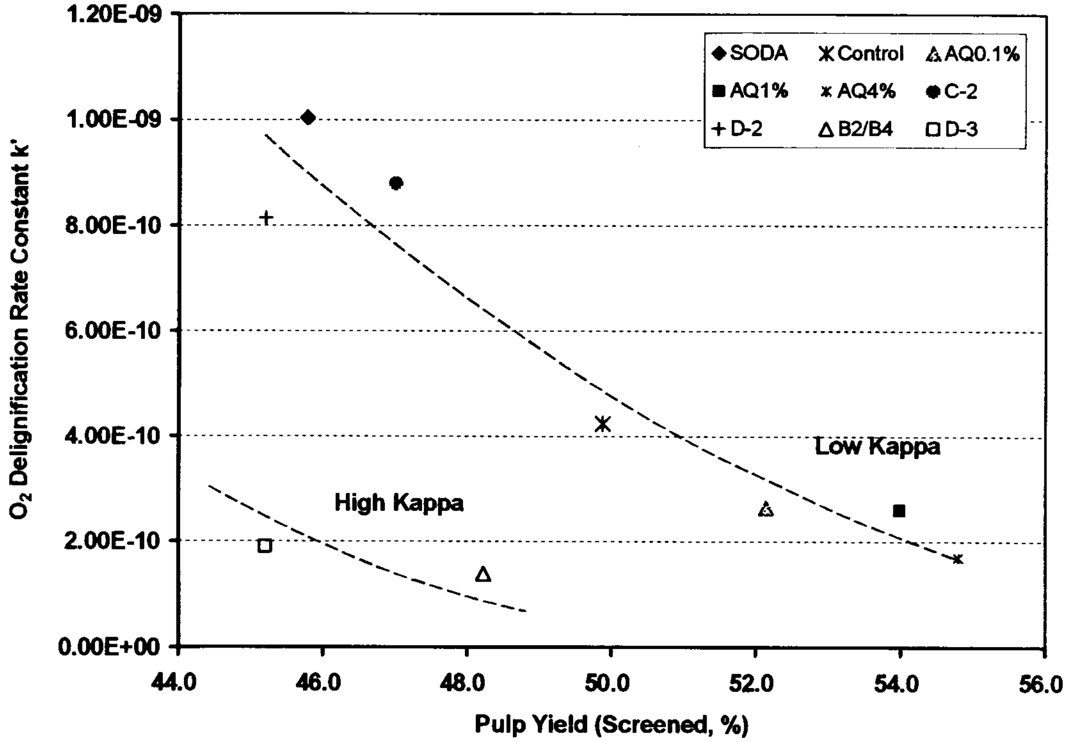


Figure 4.20. Effect of pulp yield on oxygen delignification kinetics.

4.3.4. Viscosity and Selectivity

4.3.4.1. Selectivity or Intrinsic Viscosity versus Kappa Number for Non-AQ Pulps

Figures 4.21 summarize the selectivity curves for brownstock pulps produced under various cooking conditions. From these curves, it is difficult to estimate pulp selectivity. Consequently, the data were re-plotted in terms of the degree of polymerization [DP] suggested by Bubniak (1999).

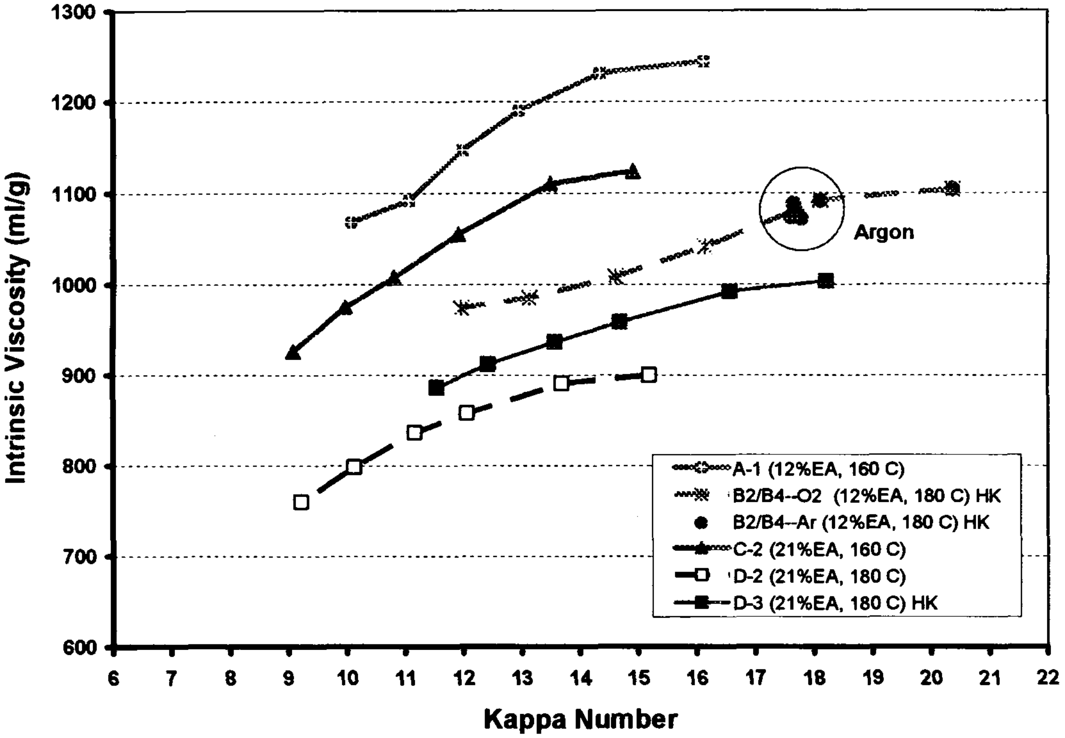


Figure 4.21. Selectivity data plotted as intrinsic viscosity versus kappa number.

4.3.4.2. Selectivity Estimated from the Degree of Polymerization

The degree of polymerization was estimated from the intrinsic viscosity [η] by using the Evans and Wallis (1989) equation,

$$DP_V^{0.90} = 1.65 \cdot [\eta] \qquad (4.1)$$

Bubniak (1999) showed that there is a relationship between the degree of polymerization and the change in kappa number during oxygen delignification.

$$\frac{d[1/DP_V]}{dt} = -\alpha \cdot \frac{dK}{dt} \qquad (4.2)$$

Equation (4.2) can be readily integrated to give an expression for the selectivity coefficient (α).

$$(\frac{1}{DP_V}) - (\frac{1}{DP_{V0}}) = -\alpha \cdot (K - K_0) \qquad (4.3)$$

Equation (4.3) predicts that the change in the degree of polymerization taken as the reciprocal and estimated from intrinsic viscosity will be linearly related to the change in kappa number. Values for the selectivity coefficient (α) are summarized in Table 4.5. By comparing values for (α), the selectivity can be determined for the brownstock pulps produced under the various digester conditions. Such a plot is shown in Figure 4.22 for the five pulps produced by varying the digester cooking conditions without AQ. As seen in Figure 4.22, very good agreement is obtained using this method for treating the five sets of data.

4.3.3.3. Improved Selectivity

In Figure 4.22, the lower the value for the slope (α) the better or the higher will be the pulp selectivity. The best selectivity was obtained by cooking at low EA (12%) and temperature (180 °C) and maintaining a high kappa number. When comparing the results for the high and low initial kappa numbers, maintaining a high kappa number will give higher selectivity in oxygen delignifcation (compare D-2 and D-3). This was true even when the pulping was conducted at high effective alkali (21%) and high temperature (180 °C), see experiment D-3. Furthermore, when cooking at the same temperature, low EA in the digester will give high selectivity in oxygen delignification (compare A-1 and D-2).

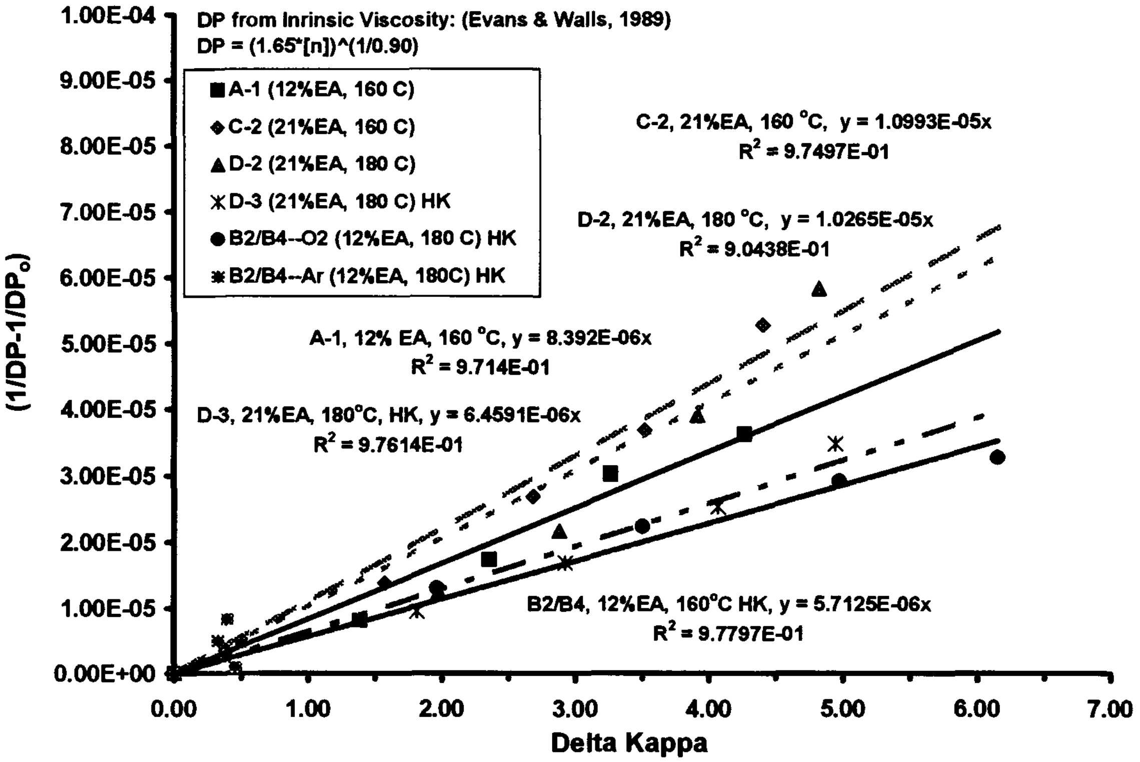


Figure 4.22. Selectivity curve when plotted as [1/DP-1/DPo] versus delta kappa number – non-AQ pulps.

These data tend to suggest that pulps high in hemicellulose content give improved selectivity.

Table 4.3.
Summary of selectivity data in terms of coefficient (α) – non AQ pulps.

Sample ID	Effective Alkali	Temp. (°C)	Kappa Number	Pulp Yield (%)	α
C-2 (Worst selectivity)	21%	160	15	47.5	1.099×10^{-5}
D-2	21%	180	16	46.9	1.027×10^{-5}
A-1	12%	160	16	50.1	0.839×10^{-5}
D-3 (HK)	21%	180	21	49.5	0.646×10^{-5}
B2/B4 (Best selectivity) (HK)	12%	180	21	50.2	0.571×10^{-5}

4.3.4.4. Effect of Hemicellulose Content on Oxygen Delignification Selectivity

Pulp viscosity is expected to be a strong function of the carbohydrate composition in the pulp and also the degree of polymerization (DP) of the constituents. This would involve the relative abundance of the cellulose and hemicellulose polymers comprising.

$$MW_{Ave} = x_1 * MW_{Cellulose} + (1-x_1)*MW_{Hemicelluloses} \qquad (4.4)$$

The DP of the cellulose is considerably greater than that of the hemicellullose polymers. During pulping and bleaching processes, the DP of the hemicellulose polymers does not change appreciably because the DP is low. By contrast, the DP of the cellulose changes appreciably primarily because of cellulose degradation. Consequently, if cellulose degradation occurs at a faster rate than the increase in the cellulose content, the DP of the pulp and hence, the viscosity of the pulp, will decrease. This situation occurs in most pulping and bleaching processes-- pulp viscosity generally decreases with an increase in cellulose content. This phenomenon is illustrated in Figure 4.23 where the intrinsic viscosity is plotted versus the glucan content of mixed hardwood pulps that have undergone oxygen delignification for 60 minutes (Zou, 2000). The brownstock pulps were prepared at constant temperature but variable H-factor and EA contents.

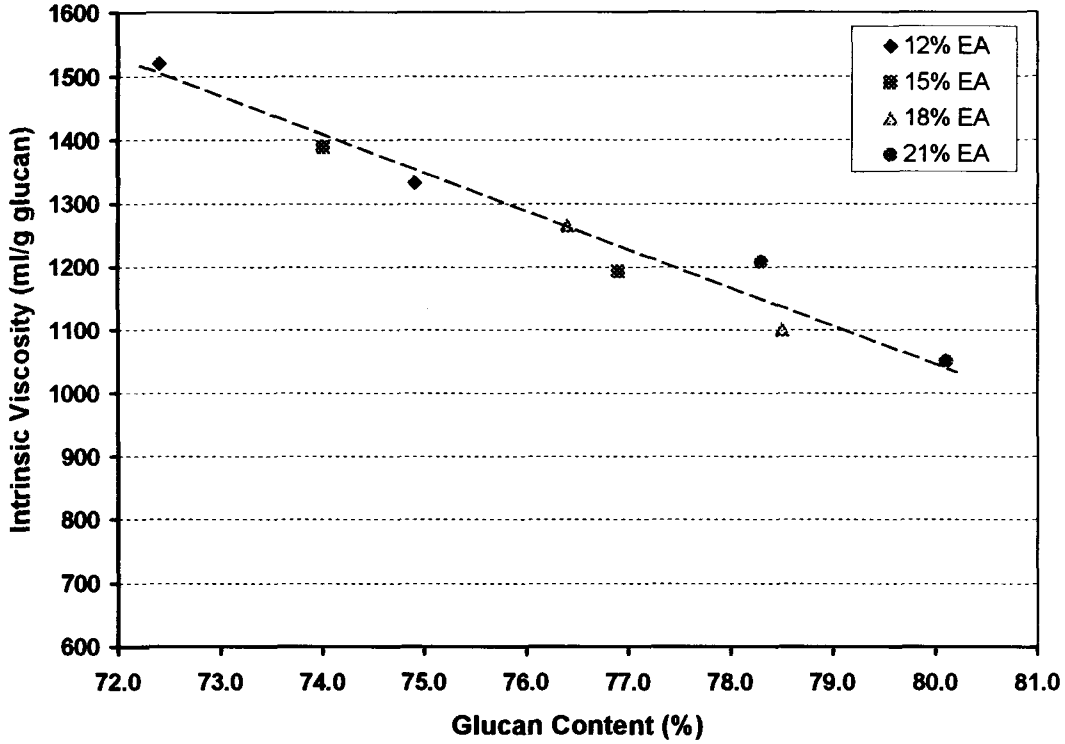


Figure 4.23. Intrinsic viscosity versus glucan content.

If the pulp was cooked under the best possible conditions, that is, under low EA and low cooking temperature, the cellulose would not be significantly degraded; and since the pulp had a high content of low molecular weight hemicelluloses, the pulp would exhibit lower viscosity. This is shown in Figure 4.24. The pulp with the highest viscosity was the control that was cooked at 12% EA, 160 °C, and 30% sulfidity without AQ. Under these conditions the cellulose would not be degraded significantly and the DP of the cellulose would be high. As the cooking time was decreased with addition of AQ at constant EA (12%) while cooking under conditions similar to the control, pulps with progressively greater hemicellulose content (greater pulp yield) would be produced without degrading the cellulose. This would give rise to pulps with progressively lower viscosity at constant kappa number. Cooking with 4% AQ that is cooking with the shortest time at 160 C resulted in the highest hemicellulose content (greatest yield) and the lowest viscosity at constant kappa number. The lowest viscosity pulps were obtained when cooking with the soda pulp. The soda pulp was prepared by cooking at 160 C but very high EA (21%). Under these conditions the hemicellulose content would be expected to be low (poor yield) and the cellulose degraded.

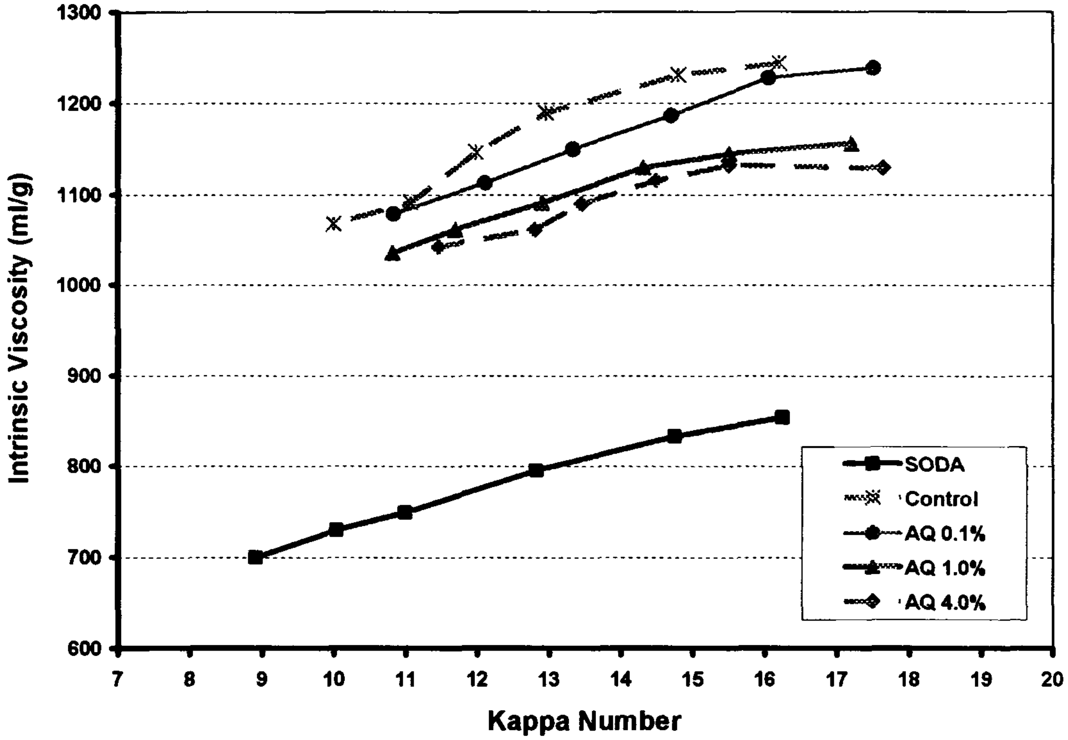


Figure 4.24. Effect of hemicellulose content on oxygen delignification selectivity.

The intrinsic viscosity of the pulp [η] will depend upon both the cellulose and hemicellulose contents in the pulp (x_1 and x_2=1-x_2) and the degree of polymerization (DP) of each (DP_1 and DP_2), but primarily upon the cellulose content.

$$[\eta] = \alpha \cdot f(x_1, DP_1, DP_2) \tag{4.5}$$

where α is a constant.

In equation (4.5), if DP is held constant, and the cellulose contents increased in the pulp, this will give rise to a higher viscosity [η]. This is confirmed for the brownstock in Figure 4.25 where the intrinsic viscosity is shown plotted versus the cellulose content of the pulp.

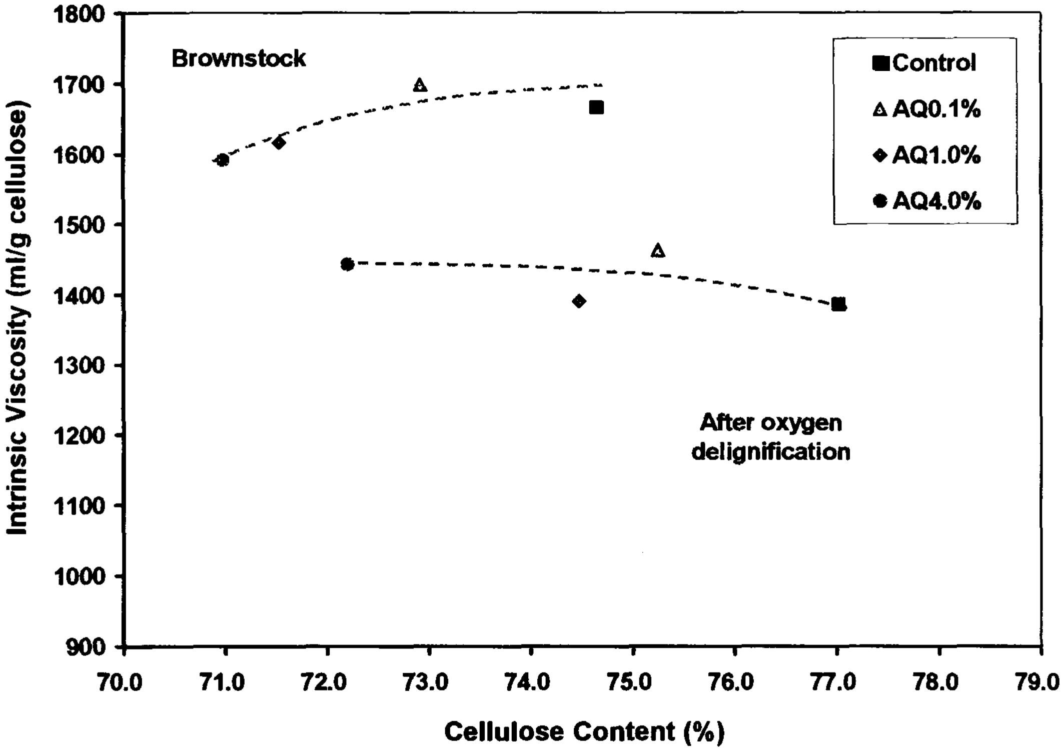


Figure 4.25. Intrinsic viscosity versus pulp cellulose content for brownstock pulp and following oxygen delignification at 60 minutes.

The selectivity is a function of the changes of intrinsic viscosity (Δη) and the change of kappa number (ΔK), that is, it is a function of the change in the cellulose content (Δx_1), the change in the degree of polymerization (ΔDP) and the change in the kappa number (ΔK) since as the kappa number changes the DP of the cellulose will change. If β is a constant, this may be expressed as

$$S = \beta \cdot f(\Delta\eta, \Delta K) \qquad (4.5)$$

Then, since the intrinsic viscosity [η] is a function of the cellulose content (x_1) and the DP, we get

$$S = \beta \cdot f(\Delta x_1, \Delta DP, \Delta K) \qquad (4.6)$$

If we neglect the effect of cellulose content (x_1), the selectivity can be defined from G-factor according to Kubes and co-workers (1981) as shown in equation (2.30), and at a simple form of Bubniak equation will result (see equation 4.3),

$$\frac{1}{DP_t} - \frac{1}{DP_0} = \frac{k \cdot t}{[Gly]} \qquad (2.30)$$

$$(\frac{1}{DP}) - (\frac{1}{DP_o}) = -\alpha \cdot (K - K_0) \qquad (4.3)$$

From (4.3), if we set

$$\Delta(\frac{1}{DP}) = (\frac{1}{DP_t}) - (\frac{1}{DP_0}) \qquad (4.7)$$

and

$$\Delta K = (K - K_0) \qquad (4.8)$$

then we will obtain,

$$\alpha = -\frac{\Delta(\frac{1}{DP})}{\Delta K} = \frac{(\frac{1}{DP_t} - \frac{1}{DP_0})}{(K_0 - K)} \qquad (4.9)$$

For this dissertation, we will define (α) as the selectivity parameter. By this definition, the higher the value of the selectivity factor (α) the poorer will be the pulp selectivity.

By contrast lower values for the selectivity parameter (α) the better will be the pulp selectivity.

The effect of hemicellulose content on the selectivity of oxygen delignification is shown in Figure 4.26. Table 4.4 shows the selectivity parameter for the pulps produced using AQ.

Table 4.4.

Summary of selectivity data in terms of coefficient (α) –AQ pulps.

ID	Effective Alkali %	Temp. (oC)	Sulfidity (%)	Additives %	Pulp Yield (%)	α
SODA	21	160	0		45.78	1.128E-5
Control	12	160	30		49.88	7.258E-6
AQ 0.1%	12	160	30	0.1% AQ	52.14	5.631E-6
AQ 1.0%	12	160	30	1.0% AQ	53.98	5.421E-6
AQ 4.0%	12	160	30	4.0% AQ	54.79	5.592E-6

The data for the selectivity parameters shown in Table 4.6 are plotted versus the hemicellulose content and pulp yield in Figures 4.27 and 4.28 respectively. Generally, during oxygen delignification, the pulp selectivity will increase with an increase in the hemicellulose content in brownstock pulp. Rather than increasing continuously, a shallow minimum occurred in both the selectivity versus yield and selectivity versus hemicellulose contents curves. These minima occurred at approximately 53.5% pulp yield and 25.6% in the total hemicellulose content.

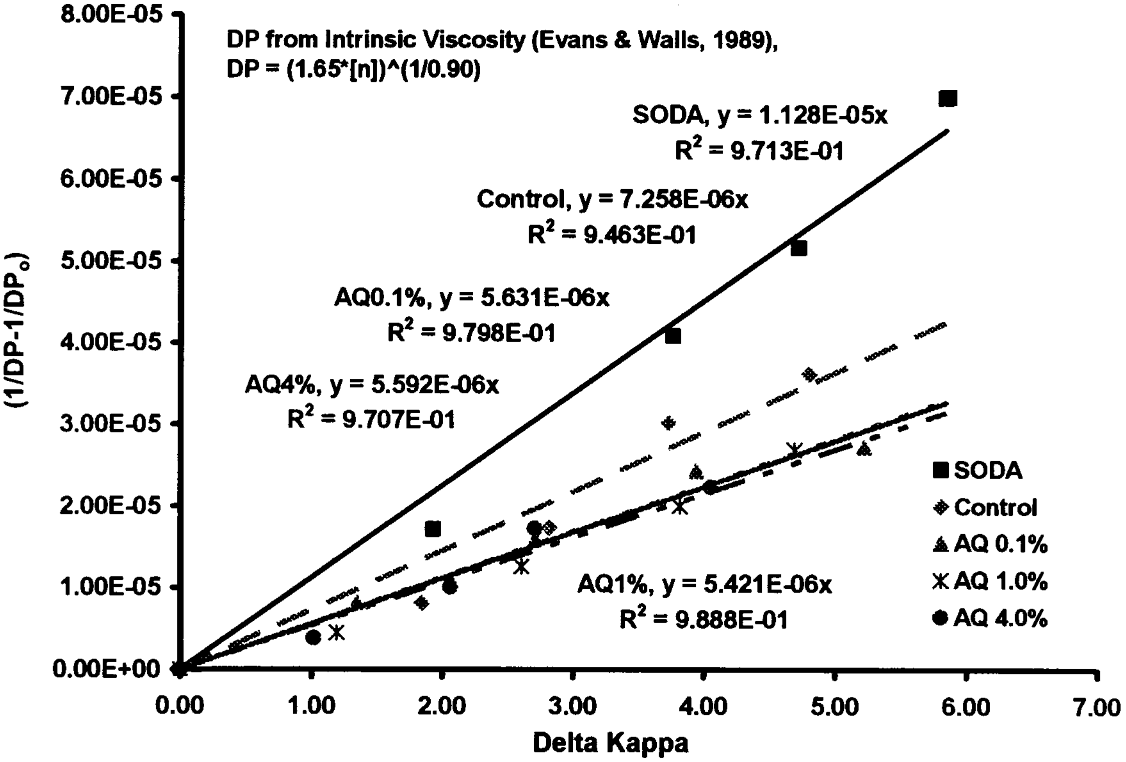
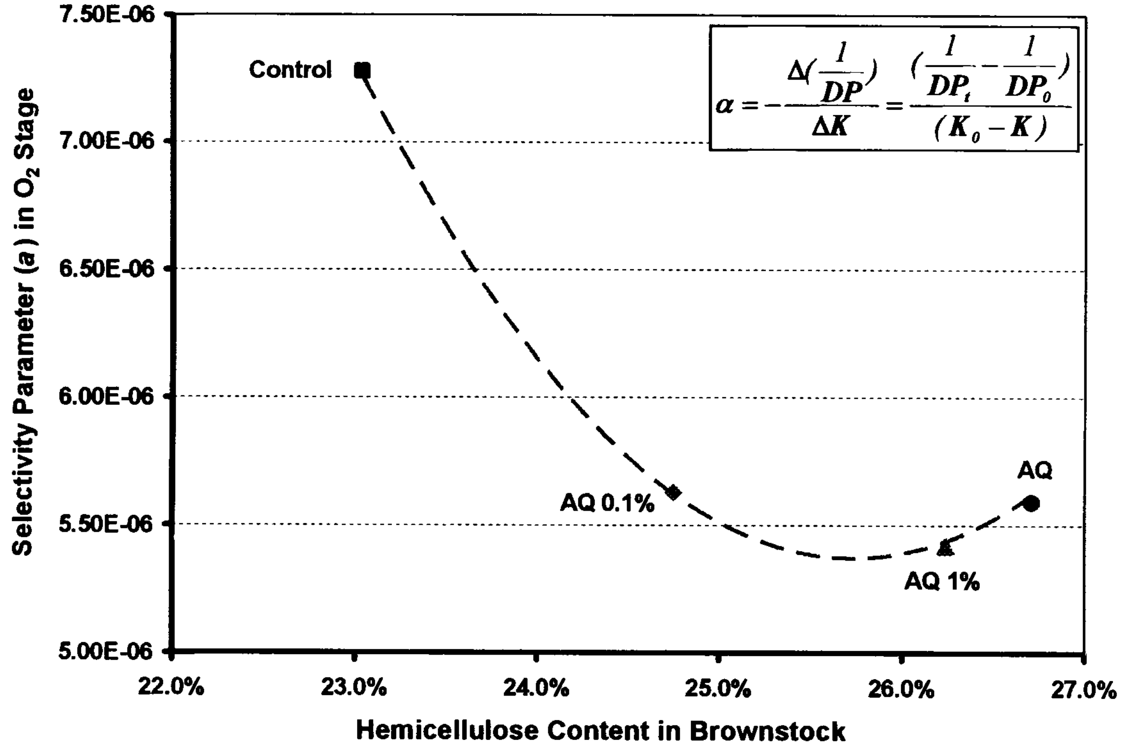


Figure 4.26. Effect of hemicellulose content on oxygen delignification selectivity.



$$\alpha = -\frac{\Delta(\frac{1}{DP})}{\Delta K} = \frac{(\frac{1}{DP_t} - \frac{1}{DP_0})}{(K_0 - K)}$$

Figure 4.27. Effect of hemicellulose content on oxygen delignification selectivity.

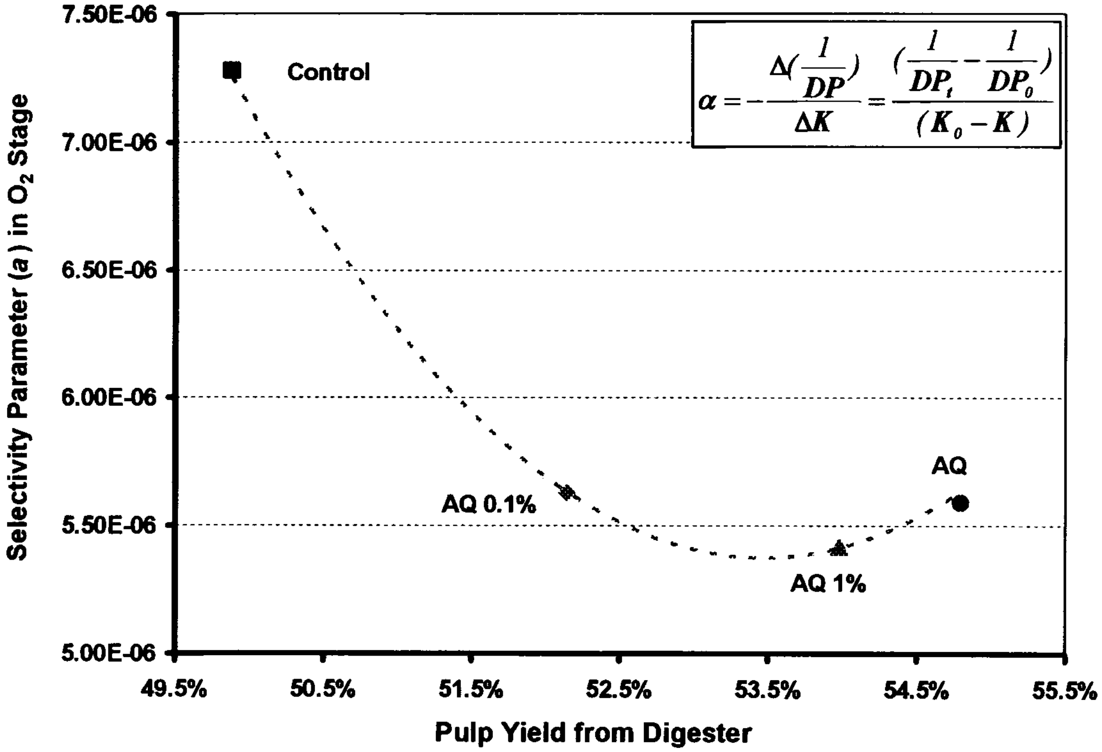


Figure 4.28. Effect of pulp yield on oxygen delignification selectivity.

4.3.4.5. Correction of the Early Data Reported by Zou (2000)

According to equations (4.2) and (4.3), a plot of [(1/DP)-(1/DP$_0$)] versus the change in kappa number (K-K$_0$) should go through zero. In the previous experiments for pulping at an effective alkali of 12% reported by Zou (2000), the selectivity line was straight but did not go through zero. This line differed from lines for pulps produced under conditions of high EA in the digester (15%. 18%, and 21%). The results for the non-zero intercept could be explained by low residual alkali in the digester, which then led to the re-precipitated of lignin on the pulp. This pulp would be expected to undergo high dissolution of re-precipitation lignin in the early stages of the oxygen delignification experiments. In other words, lignin dissolution from the surface of the fiber was being mistaken for lignin dissolution from the interiors of the fiber. The new experimental data were corrected for the loss in the kappa number because of the caustic extraction that takes place during the preheating before oxygen is added to the reactor (Figure 4.23). In this figure, please notice that all of the straight lines go through zero including the pulp produced at 12% EA.

4.3.5. Brightness

Brightness data are presented in Figures 4.29 and 4.30. Generally, the final brightness exiting the oxygen stage follows the initial brightness of the pulp entering the oxygen stage. This is seen in Figures 4.29 and 4.30 where the brightness data are plotted versus the oxygen delignification time, and in Figure 4.31 and 4.32 where the brightness data are plotted versus the kappa number following oxygen delignification.

Pulp Brightness after Oxygen Delignification. The final pulp brightness following oxygen delignification will always increase with decreasing kappa number. This behavior has been seen by many investigators (Agarwal, 1999, Guven, 1996). Additionally, the brightness data in Figures 4.31 and 4.32 are tending toward the same line as the kappa number is reduced. These figures also show that the pulp brightness following oxygen delignification will depend on the brightness of the brownstock (Figures 4.31 and 4.32).

Brightness of Brownstock. Data for the brownstock brightness are summarized in Tables A.1 and A.2 in Appendix A. The pulp brightness of the brownstock would be expected to be related to the conditions in the digester, the initial lignin content in the wood, and its initial brightness which would be governed by the chromophoric groups present in the lignin. The lowest initial brightness for the brownstock occurred for Pulp B2/B4 (23.8 ISO), which had a kappa number of 21 ml, and was produced under high

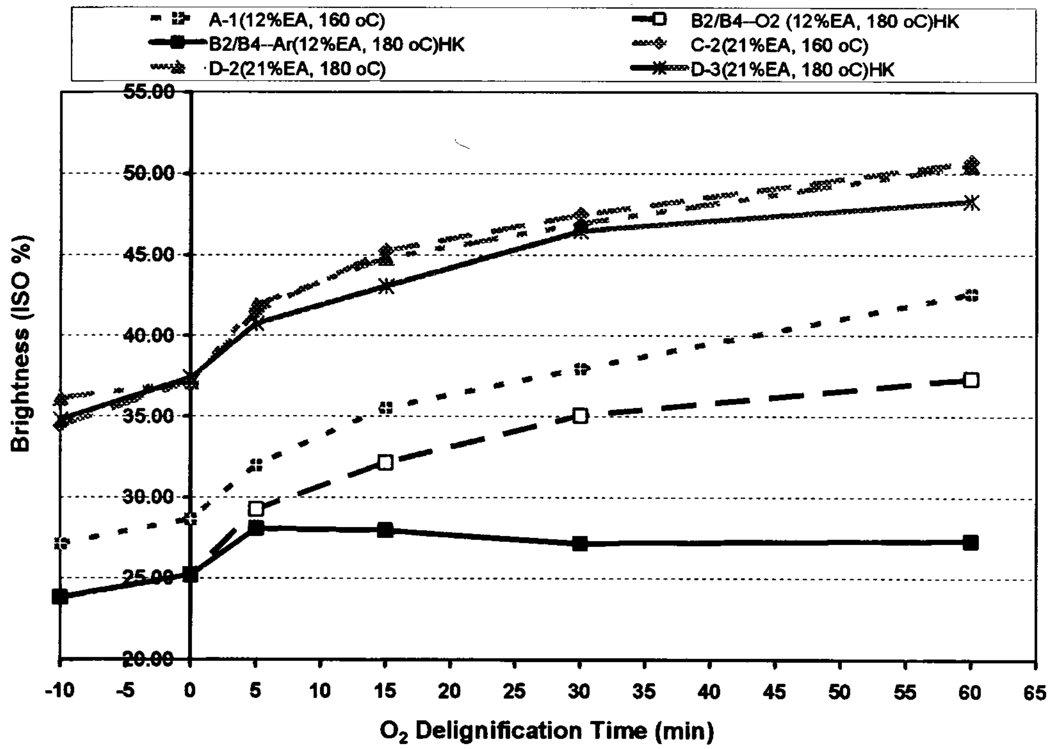


Figure 4.29. Brightness versus oxygen delignification time for pulps produced without AQ.

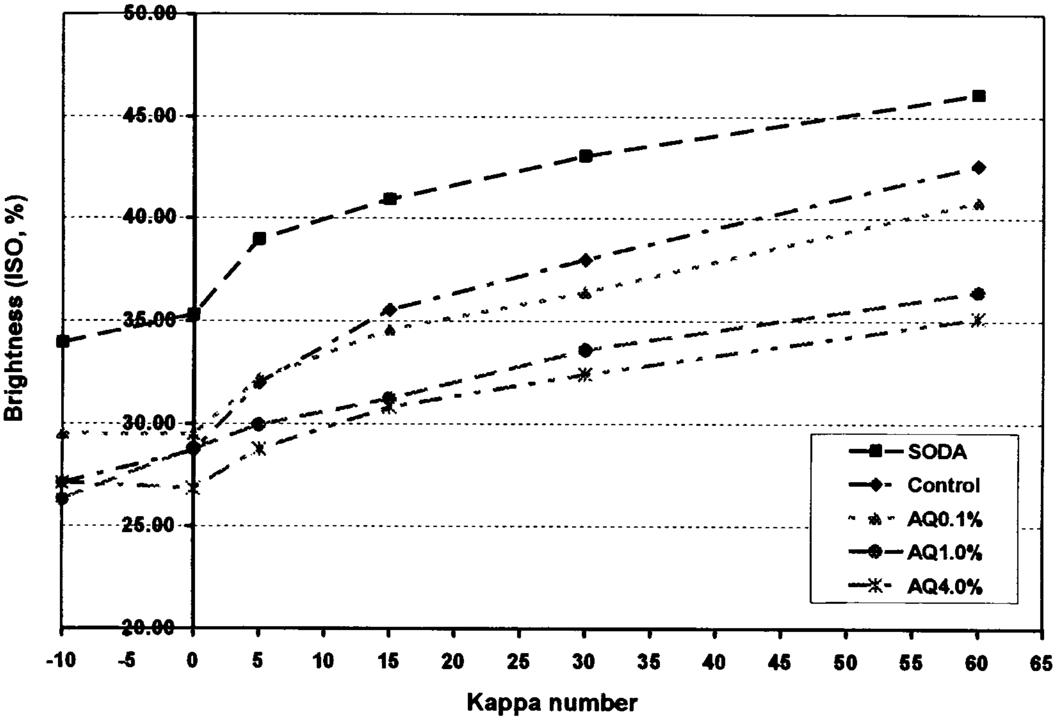


Figure 4.30. Brightness versus oxygen delignification time for pulps produced with AQ.

temperature (180 °C) and low EA (12%) conditions in the digester for an extended period of time (72 minutes) By contrast, the highest initial brightness of the brownstock occurred for Pulp D2 (36.1% ISO), which had low kappa number (16 mL) and was produced under high temperature (180 °C) and high EA (21%) condition but low reaction time (4 minutes). Comparing Pulp D2 (highest initial brightness) to B2/B4 (lowest initial brightness), the exposure time to the alkali was considerably shorter for Pulp D2 (4 minutes at 180 C) versus B2/B4 (72 minutes at 180 °C). For the pulps produced using AQ under 12% EA cooking conditions at 160 C and 30% sulfidity, the brightness values were between 26.3 and 29.5 ISO all were all quite similar. The reaction time at 160 C varied between 464 and 175 minutes depending upon the amount of AQ charged to the digester. The exposure times are long and an equilibrium condition for the number of chromophoric groups in the pulp may have occurred. Also, the hemicellulose content was high (22 to 24%) in all of these pulps (see Appendix D, Table D.1). By contrast, the soda pulp produced at 0% sulfidity and 21% EA and 160 °C had the highest brightness value (34% ISO). The reaction time in the soda cook was 218 minutes which is also long. It is interesting to note that the xylan content in the soda pulp was low (17.8%, see Table D). These results suggest that the hemicellulose content in the pulp is affecting the brightness of the brownstock. The hemicellulose polymers themselves should not have chromophoric groups that give rise to color. More, likely it is the chromophoric groups associated with the lignin or the lignin carbohydrate linkage is influencing the brightness of the brownstock.

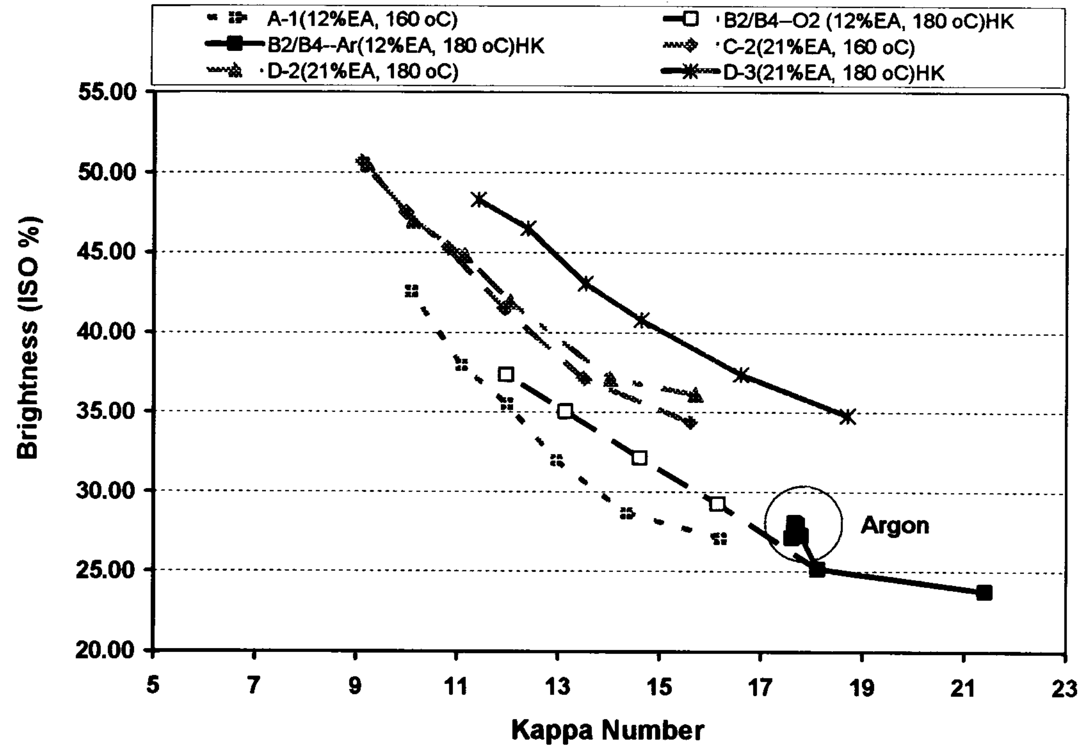


Figure 4.31. Brightness versus kappa number for pulps produced without AQ.

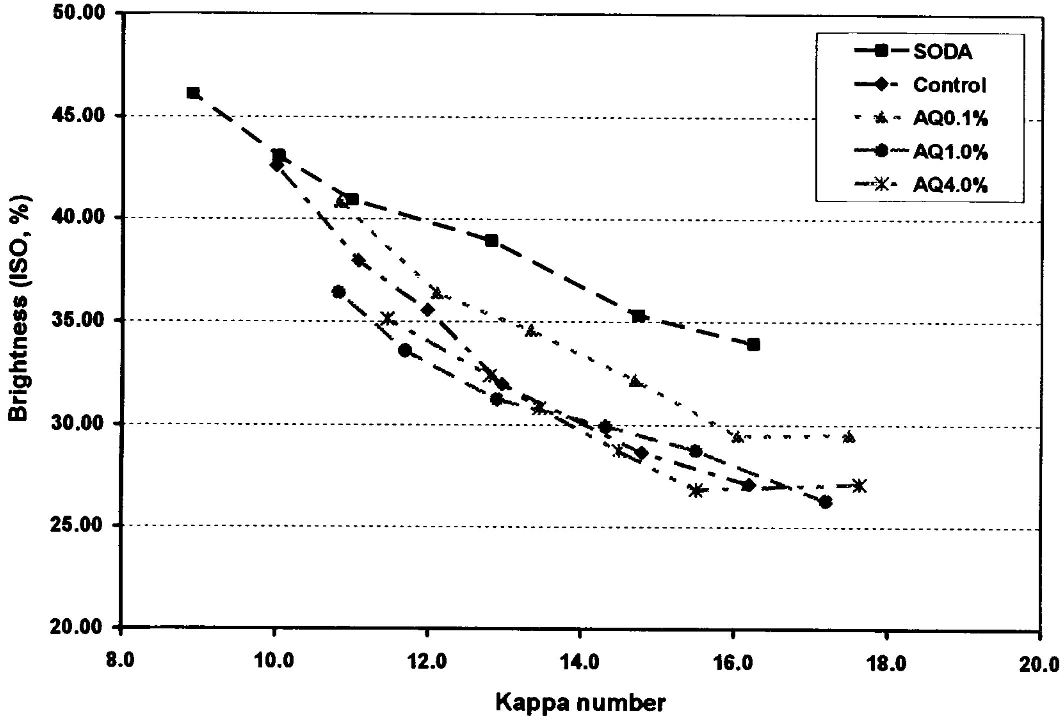


Figure 4.32. Brightness versus kappa number for pulps produced using AQ.

4.3.6. Alkali Consumption

Alkali would be expected to be consumed during oxygen delignification by reacting with the phenolic hydroxide groups on the lignin, see Figure 2.15. Alkali would also be consumed during primary and secondary peeling reactions that take place with carbohydrates, both cellulose and hemicellulose polymers (see Figure 2.1).

Figures 4.33 and 4.34 illustrate the values obtained for the residual alkali contained in the liquor squeezed from the pulp samples following exposure to oxygen. For the brownstock pulps produced without AQ in the digester, the data in Figure 4.33 shows that at equivalent kappa number drop, similar alkali was consumed during oxygen delignification. For the pulps produced with AQ shown in Figure 4.34, there was no systematic variation in the alkali consumption versus kappa number drop. The alkali consumption data for the AQ pulps may be affected by the presence of residual AQ which possibly could react with HCL to titrate the residual alkali.

The pulp with the lowest consumption of alkali was the soda pulp which had the lowest xylan content (17%) and would be expected to undergo the lowest levels of peeling. The soda pulp also did not contain residual AQ which could consume HCl during the titration.

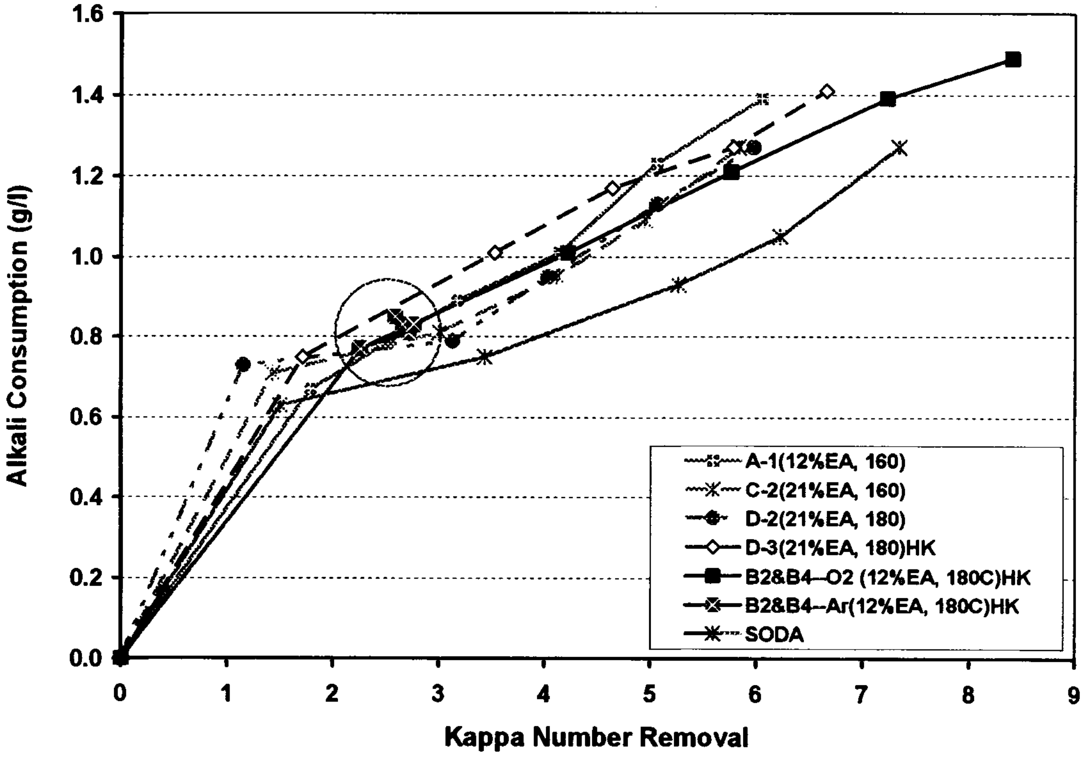


Figure 4.33. Alkali consumption versus kappa number removal for pulps produced without AQ.

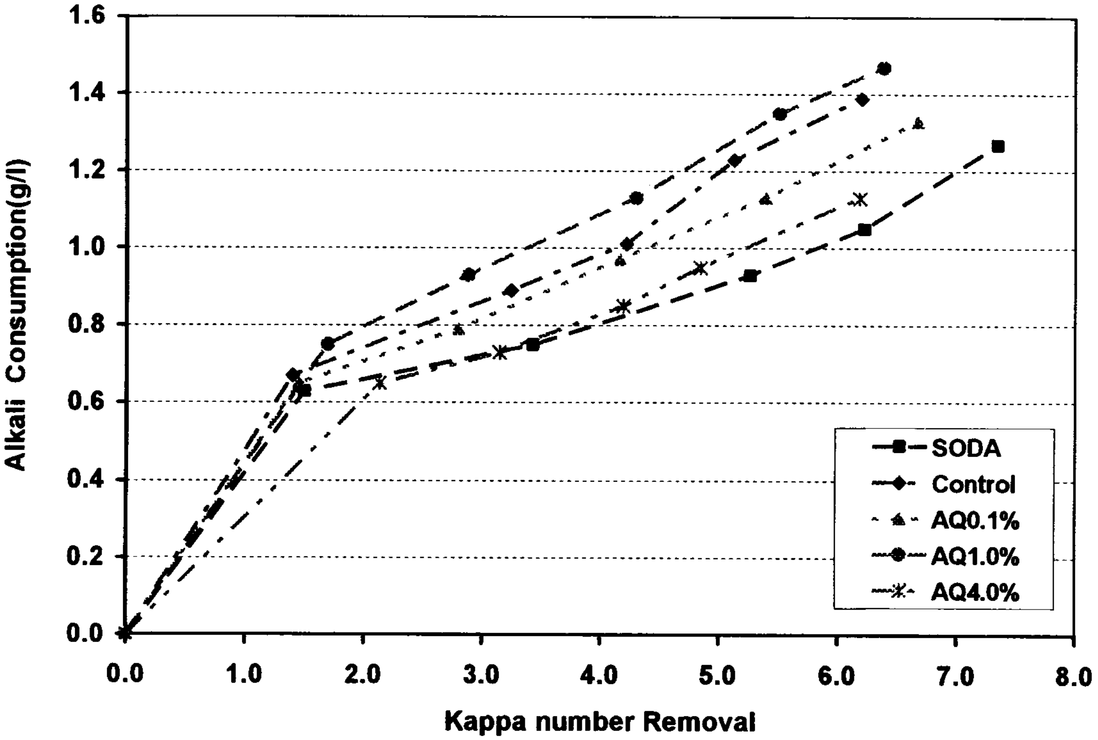


Figure 4.34. Alkali consumption versus kappa number removal for pulps produced with AQ.

4.3.7. Pulp Yield Following Oxygen Delignification

4.3.7.1. Experimental Results

Pulps Produced Without AQ. The data for pulp yield following oxygen delignification are shown plotted in Figures 4.35 and 4.36 as a function of the delta kappa number following oxygen delignification and (1/DP – 1/DP$_o$) respectively. These data have been corrected for caustic extraction during the heat up period in the oxygen reactor and for fines losses during washing. The pulp yield after oxygen delignification varied between 99.8% and 98% or between 0.2% and 2% yield loss (see Figures 4.35 and 4.36).

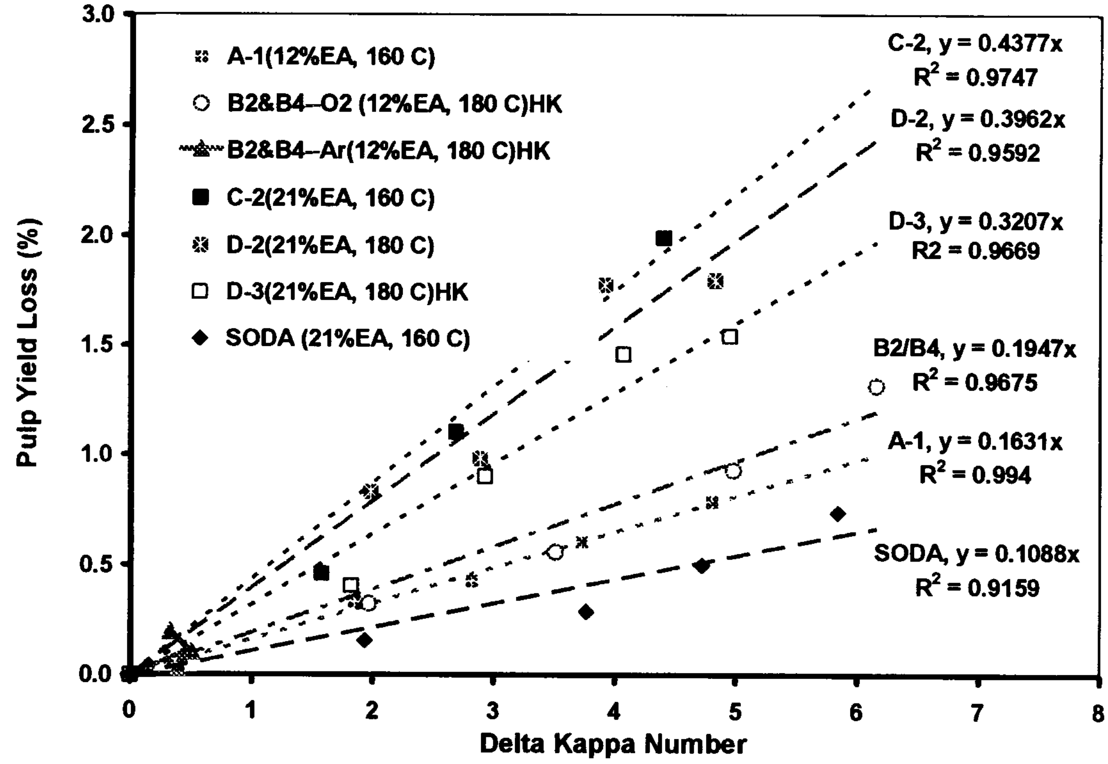


Figure 4.35. Pulp yield loss versus delta kappa number for pulps produced without AQ.

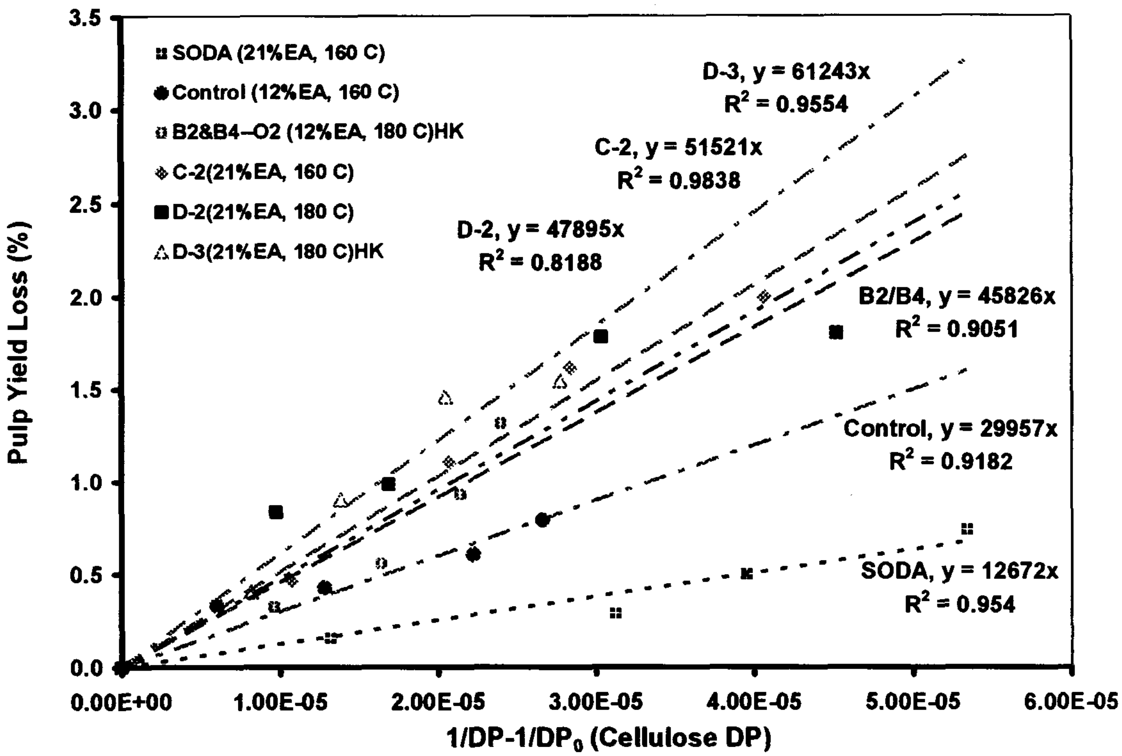


Figure 4.36. Pulp yield versus (1/DP – 1/DP$_o$) with pulps produced without AQ.

The yield loss is a linear function of drop in kappa number (see Figure 4.35) and (1/DP-1/DP$_o$), see Figure 4.36. For experiments in which oxygen was used in the experiments, including those pulps in which AQ was used and also pulps that were prepared under conventional cooking conditions, the soda pulp had the highest yield following oxygen delignification (see Figures 4.35 and 4.36) and the lowest slope versus kappa number drop or change in DP. By contrast, the pulp with the highest yield loss and greatest slope versus kappa number drop (Figure 4.35) was pulp C-2, which was prepared at 21% EA and 160 °C. When plotted versus the change in DP (Figure 4.36), pulp D-3 was the pulp with the highest yield loss. Except for the soda cook, pulps produced with high EA in the digester exhibit greater losses in pulp yield during oxygen delignification compared to pulps produced with low EA when measured by the drop in kappa number and $(1/DP - 1/DP_0)$ (Figures 4.35 and 4.36). These results may be explained in two ways. Please note the yield data have been corrected for loss of pulp mass by both extraction in the caustic extraction phase of the oxygen delignification experiments and also for the loss of fines. First, compared to pulps produced under high EA conditions in the digester, pulps produced under low EA conditions lose a greater mass during the heat up period or caustic extraction phase of the oxygen experiments. In treating the data, the loss of fine particles during the heat up period was eliminated from the yield data. By contrast, pulps produced under high EA conditions in the digester lost less fine material during the heat up period but lost more material during the phase of the experiments in which oxygen was present in the reactor (see Figure 4.37). Secondly, pulp produced with high EA in the digester had much lower DP values. Consequently there would be more aldehyde end groups which should undergo a greater level of peeling reactions with a lose in yield. Also since there is a lower content of hemicellulose polymers present in the high EA pulps, there would be less protection for the cellulose and therefore greater cellulose attack. Greater random hydrolysis reactions would lead to higher levels of cellulose peeling for the pulps produced with low EA.

There did not seem to be a correlation between pulp composition of the brownstock and the yield loss in oxygen delignification. Both pulp C-2 and the soda pulp had about the same kappa number and lignin content in the brownstock. The hemicellulose content in the brownstock for the soda pulp (19.66%) was somewhat higher in hemicellulose content than that of pulp C-2 (18.67%). The hemicellulose content following delignification for the soda pulp was 18.67% while that of C-2 was 18.93% which are essentially the same. The total yield for the two pulps was different with pulp C-2 having a brownstock yield of 47.07% compared to the soda pulp which had the lowest yield of 45.85%.

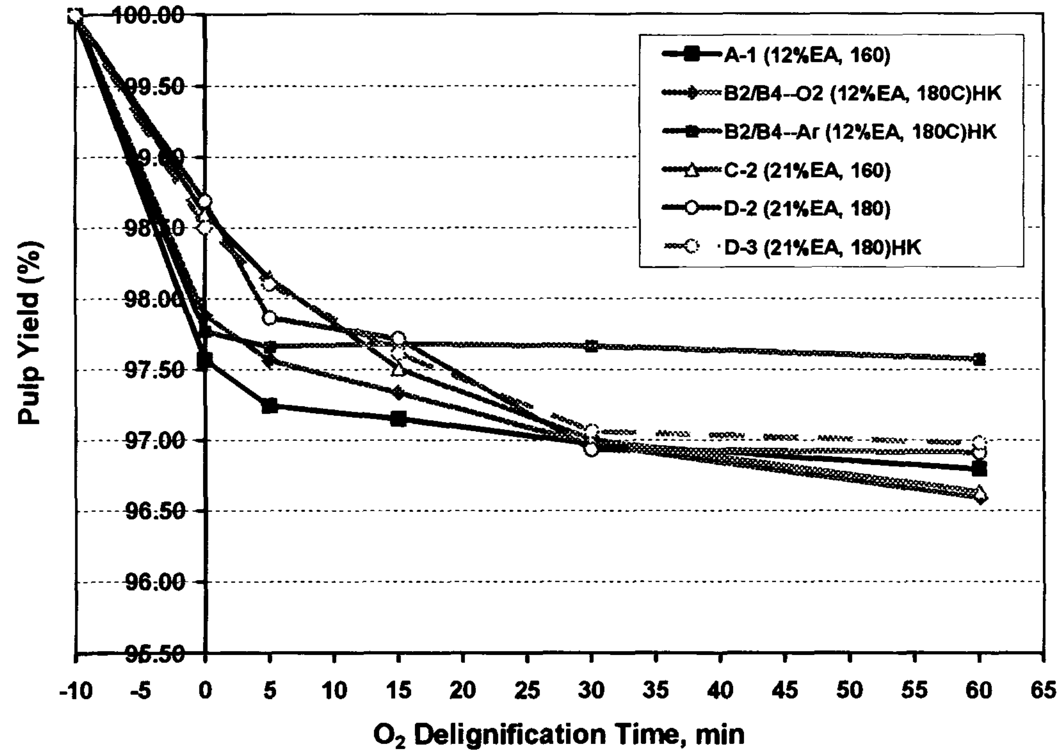


Figure 4.37. Pulp yield loss versus O2 delignification time.

Pulps Produced Using AQ. The results for the pulp yield during oxygen delignification are summarized in Figures 4.38 and 4.39 for pulps produced using AQ. Data are presented for pulp yield loss versus delta kappa number (Figure 4.38) and also for pulp yield loss versus the change in DP (Figure 4.39). The pulp yield loss data at the 4% AQ addition rate are suspect because the pulp may contain residual AQ. The soda pulp is again shown in both figures for comparison, and had the lowest yield loss and lowest slope of yield loss versus change in kappa number. The pulp with highest absolute yield loss and the greatest slopes was the pulp produced using 4% AQ during cooking (see Figure 4.38 and 4.39). It was also the pulp with the highest pulp yield following cooking. As a general rule, pulps with high yield in the digester resulting from the use of AQ exhibited high yield loss in the oxygen reactor. This was thought to result from dissolution of carbohydrates in the caustic because of the high xylan content. Similar results such as these were observed for Kraft pulps by Aurell and Hartler (1965).

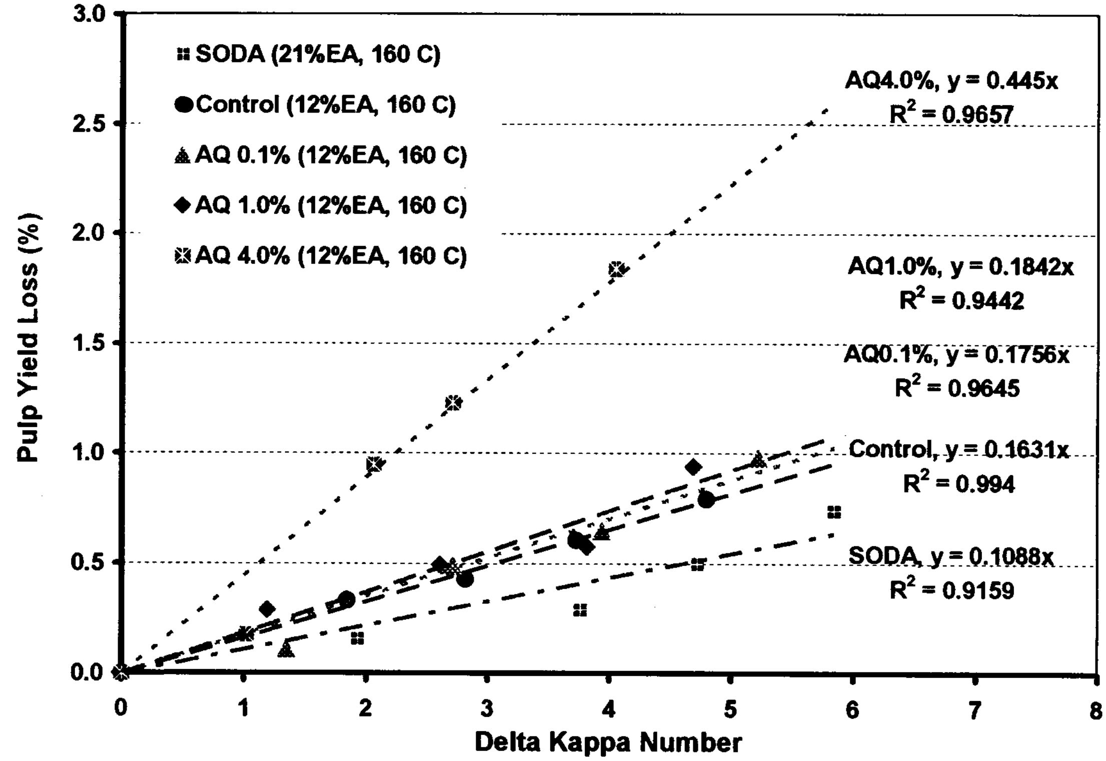


Figure 4.38. Pulp yield loss versus delta kappa number for pulps produced with AQ.

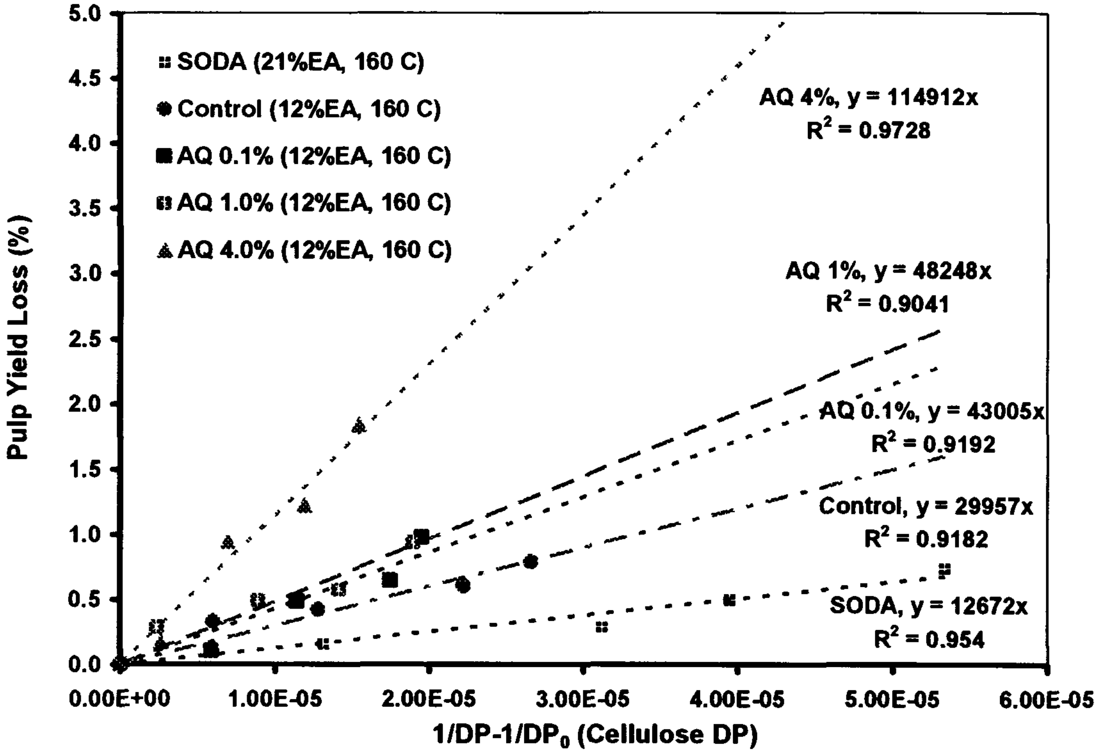


Figure 4.39. Pulp yield loss versus (1/DP-1/DP$_0$) for pulps produced with AQ.

4.3.7.2. Correlation of Pulp Yield Loss Following Oxygen Delignification with COD

Data are presented for the total pulp yield loss following oxygen delignification versus the total COD in the spent liquor (see Figures 4.40). The pulp yield data shown in Figure 4.40 have been correlated to the COD in the spent liquor. Although the data are noisy, there appears to be a linear relationship. The pulp yield data shown in Figure 4.40 have not been corrected for the loss of fine particles and caustic extraction during the heat up period. From the linear correlation of the data, the value for the intercept is 14.065 Kg pulp loss per metric ton of pulp. Theoretically the curve of pulp yield loss versus COD should go through zero. From Figure 4.40 the value of 14.1 Kg loss per ton pulp gives an estimate for the average loss of fine particles during the heat up period in the oxygen delignification experiments.

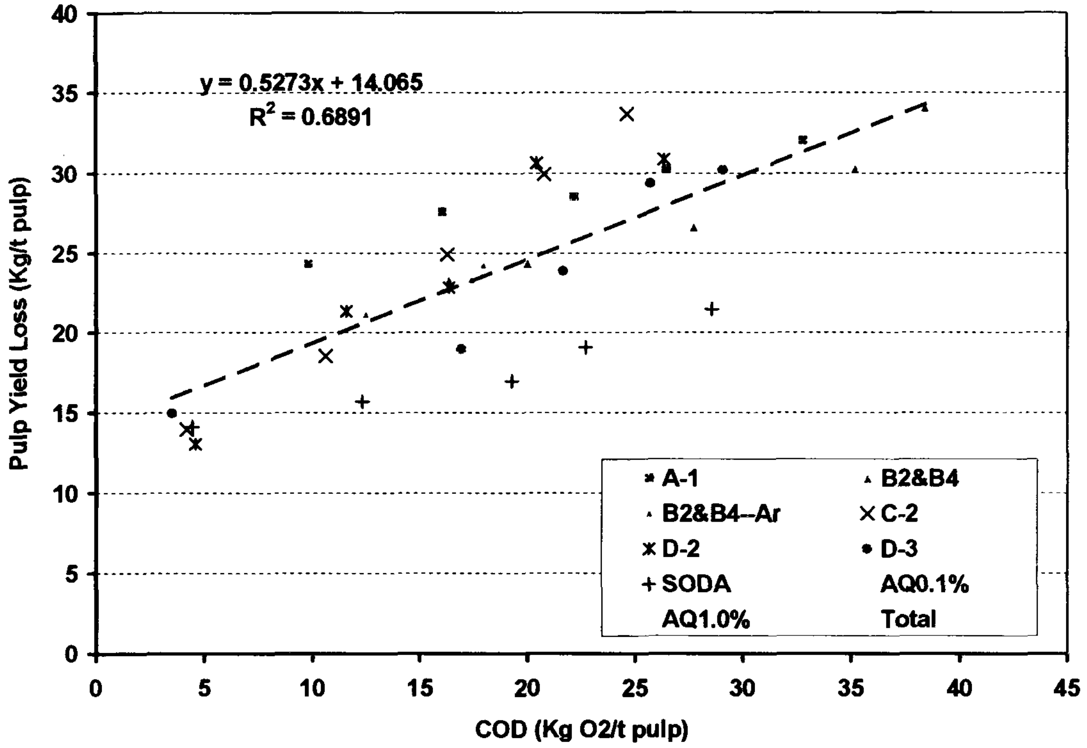


Figure 4.40. Pulp yield loss versus COD for all pulps.

Rayleigh COD Model. Genco, Zorn and Cole (2000) developed a simple model that relates the pulp yield loss ($\delta = 1 - Y$) to the chemical oxygen demand (COD) of the spent liquor. This model is predicated on the Rayleigh equation for dissolution of a solute from a solvent (Foust, 1960). In the model, pulp in the oxygen stage is assumed to consist of two components, lignin and carbohydrates (Appendix E). The oxygen demand in the spent liquor increases because of the removal of lignin from the lignin-carbohydrate matrix together with degradation of the carbohydrates as the pulp passes through the oxygen stage. The model relates the pulp yield (Y) to the initial (x_1^o) and final (x_1) weight fraction of lignin in the pulp.

$$Y = \frac{M}{M_0} = \left(\frac{x_l}{x_0}\right)^{\left(\frac{1}{k-1}\right)} = (1-\delta) = \textit{Unitless} \qquad (4.10)$$

The parameter (k) in equation (4.10) is a distribution coefficient that relates the lignin content in the dissolved liquor (y) to the lignin content in the pulp (x) and was assumed to be a linear function. Similarly, the chemical oxygen demand (COD) of the dissolved solids was assumed to be characterized by a stochiometric coefficient (R_{DS}) that is representative of the lignin and carbohydrate molecules in solution. The units on R_{DS} are given in terms of grams O_2 per gram pulp. For well-washed pulp the COD of the spent liquor is given by the equation

$$COD = R_{DS}\,\delta = g\ O_2 / g\ Pulp \qquad (4.11)$$

In deriving equation (4.11), it was assumed that none of the black liquor solids are carried over into the reactor from the washers. The chemical oxygen demand in the liquor (COD) can be further related to the lignin content in the pulp through the pulp yield.

$$COD = R_{DS}[1-(\frac{x_1}{x_1^o})^{1/(k-1)}] \qquad (4.12)$$

The simple model predicts that the COD resulting from oxygen delignification is a function of the initial (x^o_1) and final (x_1) lignin fraction in the pulp, the stochiometric coefficient R_{DS} and the distribution coefficient (k). The above model treats the problem of predicting yield as a non-reactive system and assumes no loss of carbon dioxide or no uptake of oxygen, both of which are shortcomings to the model. Fortunately, the errors introduced by these assumptions are compensating since they are in opposite directions. Genco, Zorn and Cole (2001) published the following relationship between the lignin content in the pulp (x_1) and the loss in pulp yield (δ) for mixed hardwood Kraft pulp assuming no carryover of black liquor solids.

$$\delta(Kg/M\,Ton) = 0.46 * COD(Kg\,O_2/M\,Ton\,Pulp) \qquad (4.13)$$

4.3.7.3. Comparison to COD Model

A linear line was put through the pulp yield loss versus COD data according to the model given by equation 4.12. The data have a slope of 0.5273 and represent an estimate for the stochiometric coefficient (R_{DS}).

$$slope = \frac{1}{R_{DS}} \qquad (4.14)$$

This estimate for the stoichiometric coefficient compares favorably with that published by Genco, Zorn and Cole (2000).

However, the model predicts that the line should go through zero. The model is predicated on using well-washed pulp and oxygen delignification occurring at time zero. Part of the discrepancy between the model and the data in Figure 4.40 could be due to loss in fines and also the caustic extraction during the heat up period. Consequently, the data shown in Figure 4.40 were corrected for fines loss and dissolution in caustic during the heat up period. The corrected data are summarized in Figures 4.41 and 4.42 for the pulps prepared using conventional pulping and AQ respectively. The data shown in Figures 4.41 and 4.42 are indeed linear and pass through zero but indicate a variety of slopes that depend upon the pulping conditions (Figure 4.41) and the amount of AQ added to the digester (Figure 4.42). Here again the soda pulp (Figure 4.41) had the lowest slope (0.268 kg pulp per kg oxygen) or the highest value for the stoichiometric coefficient (R_{DS}, 3.73 kg oxygen per kg pulp). By contrast pulp C-2 had the lowest value for the slope (0.939 kg pulp per kg oxygen) and the highest value for the stoichiometric coefficient (R_{DS}, 1.06 kg oxygen per kg pulp). The slopes and the coefficient for the rest of the pulps are shown summarized in Table 4.5.

Table 4.5.
Summary of Slope and Stoichiometric (R_{DS}).

ID	Conditions in Digester	Slope	R_{DS} (kg O_2 / kg Pulp)
A-1	12% EA, 160 °C, 30% Sulfidity	0.358	2.795
B2/B4	12% EA, 180 °C, 30% Sulfidity	0.439	2.276
C-2	21% EA, 160 °C, 30% Sulfidity	0.939	1.065
D-2	21% EA, 180 °C, 30% Sulfidity	0.917	1.090
D-3	21% EA, 160 °C, 30% Sulfidity	0.558	1.793
SODA	21% EA, 160 °C, 0% Sulfidity	0.268	3.734
AQ0.1%	12% EA, 160 °C, 30% S., 0.1% AQ	0.400	2.498
AQ1.0%	12% EA, 160 °C, 30% S., 1.0% AQ	0.450	2.225
AQ4.0%	12% EA, 160 °C, 30% S., 4.0% AQ	0.982	1.018
Average		*0.590*	*2.055*

Suss and Kronis (1998) used the formulas for cellulose $(C_6H_{10}O_5)_n$ to estimate the oxygen demand for one kilogram of carbohydrates. They calculated that one kg. of cellulose requires 1.185 kg. of oxygen for complete oxidation. Furthermore Suss and Kronis (1998) estimated that a COD value of 11 kg/t is equivalent to a 1% yield loss. Similarly, using the chemical composition of Kraft lignin of $(C_9H_{9.7}O_{3.3})_n$, they estimated that the corresponding COD is 1.850 kg of O_2 per kg Kraft lignin. The COD for lignin was significantly higher than the COD for cellulose and other carbohydrates. They reported that for different oxygen delignified pulps a similar ratio of the COD to the yield loss was determined. For softwood, the ratio of COD to the yield loss was reported as 0.9 Kg O_2 per Kg yield loss. For soda pulp one would expect very condensed lignin to be dissolved with low oxygen content which would give rise to high value for the stoiciometric coefficient (low slope). As higher amounts of carbohydrates are dissolved (greater hemicelluloses content) in the during oxygen delignification, then the slope would be higher and the stoichiometric coefficient (R_{DS}) lower. The data of Table 4.7 and Figure 4.40 suggest that as the pulp yield increases, grater amounts of the hemicelluloses are retained, some of which are removed in the oxygen stage which raise the slope and lower the stoicihiometric coefficient.

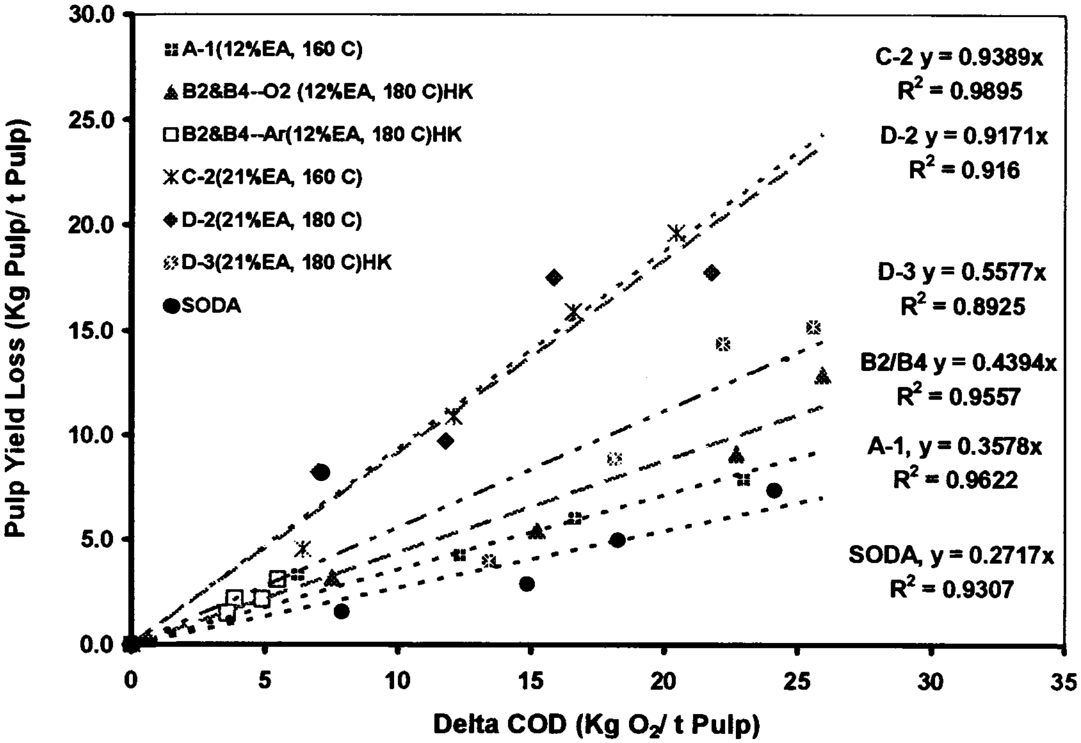


Figure 4.41. Pulp yield loss versus COD for pulps produced without AQ.

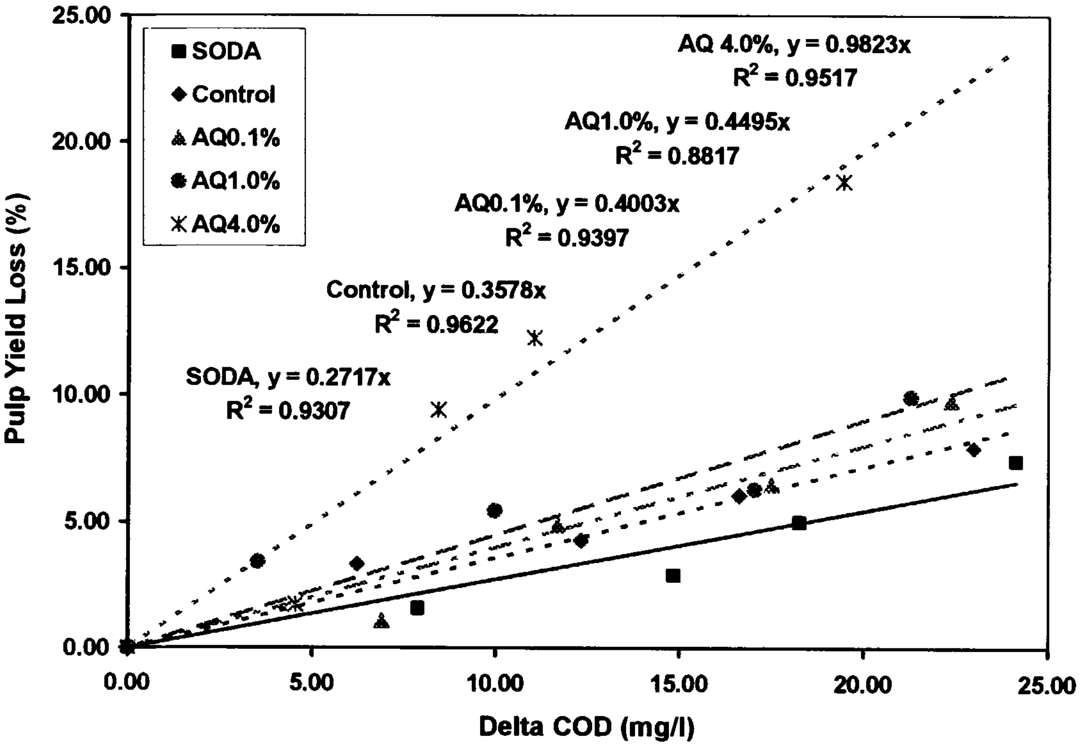


Figure 4.42. Pulp yield loss versus COD for pulps produced with AQ.

Dependence of Kappa Number on COD. The COD content of the spent liquor will depend upon the change in the lignin content of the pulp as suggested by equation (4.15).

$$COD = R_{DS}[1-(\frac{x_1}{x_1^o})^{1/(k-1)}] \qquad (4.15)$$

Consequently the uncorrected COD data are plotted versus the kappa number in Figures 4.43 and 4.44. A series of parallel lines are obtained that have the same slope which is proportional to R_{DS}. Also the intercept along the kappa number axis will depend upon the initial kappa number. Equation (4.15) predicts dependence upon the initial lignin content (x^o_1).

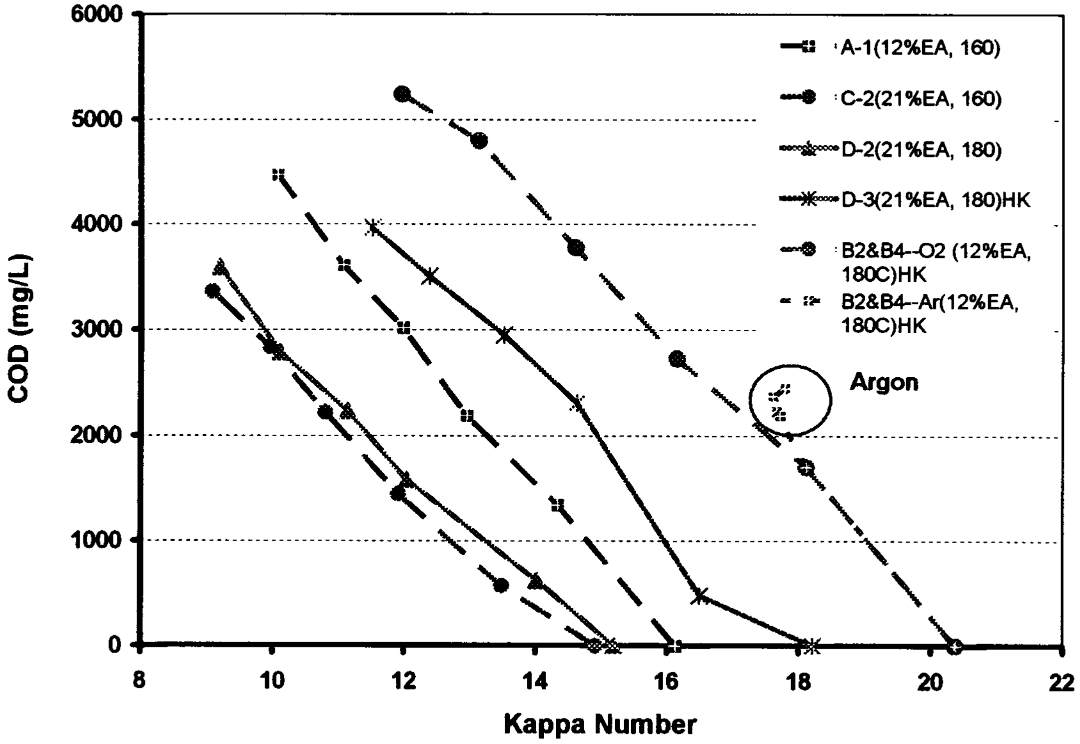


Figure 4.43. COD versus kappa number for pulps produced without AQ.

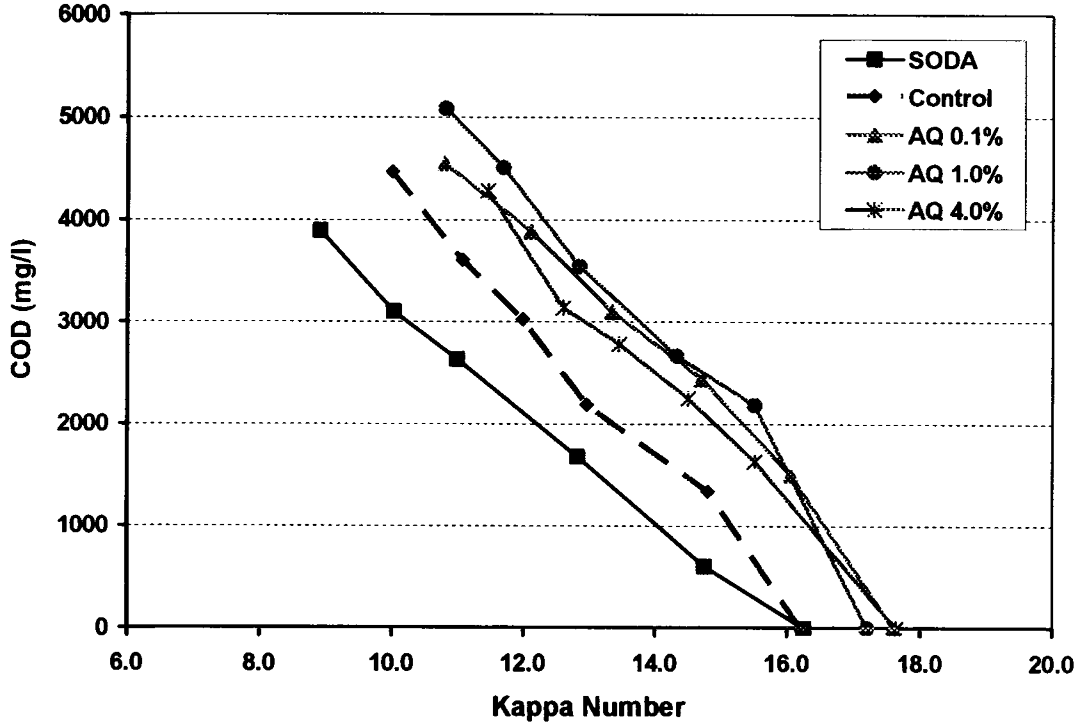


Figure 4.44. COD versus kappa number for pulps produced with AQ.

4.3.8. Carbohydrate Degradation

4.3.8.1. Effect of Argon versus Oxygen at 180 °C and 12% EA

Simoes and Castro (2001) method of analysis was used to estimate the rate of carbohydrate scissions during oxygen delignification (equation (4.16)). Figure 4.45 represents the rate of scissions that take place as a function of time for oxygen delignification experiments conducted for brownstock pulp produced at 180 °C at 12% EA. For comparison the data are also shown for the experiments in which argon was substituted for oxygen. The data show that little degradation occurs in the presence of argon. By contrast, serious carbohydrate degradation takes place at the beginning of the oxygen delignification experiments. This is especially true when the initial pulp viscosity is high. When argon is substituted for oxygen, carbohydrate degradation also occurs, but at a much lower level when compared to oxygen delignification experiments. For the argon experiments, the carbohydrate degradation data may be explained in terms of residual oxygen present in the pulp sample when the sample was transferred to the oxygen reactor. Alternatively, even without oxygen present, caustic extraction will continue to degrade carbohydrates but at a very low rate.

$$\Psi = \left(\frac{1}{DP} - \frac{1}{DP_0}\right) \cdot \frac{6.023 \times 10^{23}}{162} \times \frac{1}{reaction \quad time} \qquad (4.16)$$

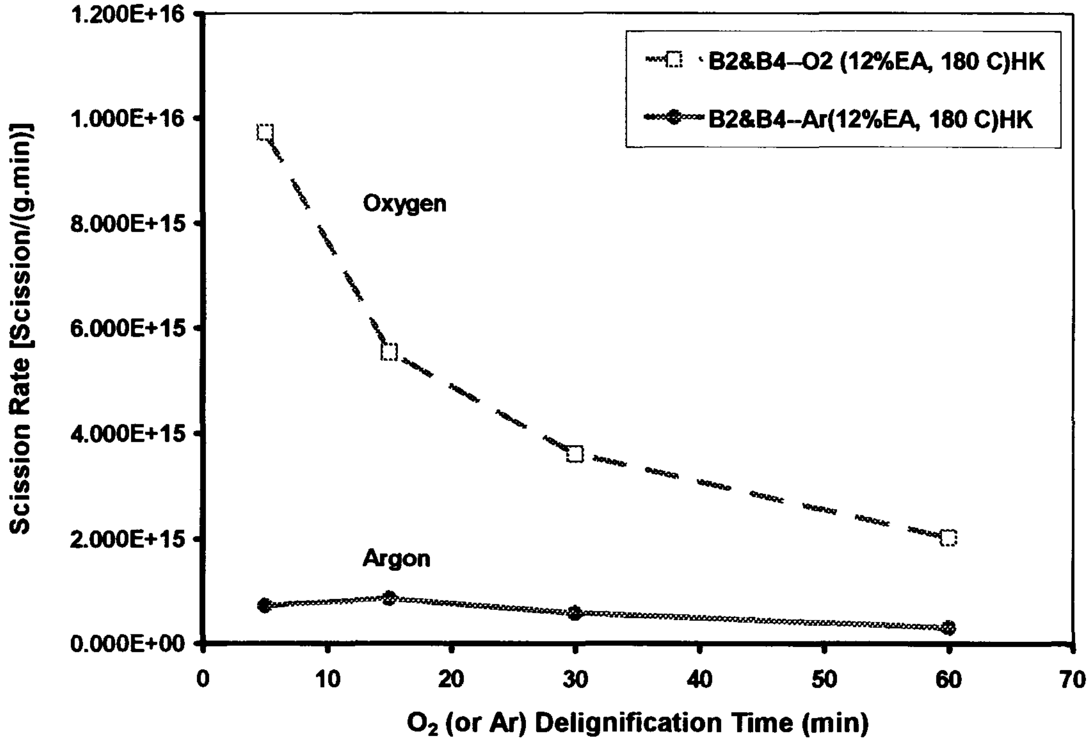


Figure 4.45. Carbohydrate degradation for brownstock pulp produced at 180 °C and 12% EA.

4.3.8.2. Effect of Alkali at Low Kappa Number and 160 °C

Carbohydrate degradation occurred at a much higher rate for the pulp cooked at a higher effective alkali level at low cooking temperature. This effect is shown in Figure 4.46 for pulp produced at low kappa number at 160 ° C and at effective alkali values of 21% EA and 12% EA. Even though pulp sample (C-2) cooked at higher EA (21%) had lower initial viscosity (1123 ml/g), it still had a higher scission rate than did the pulp sample (A-1) produced at an EA value of 12% (1244 ml/g).

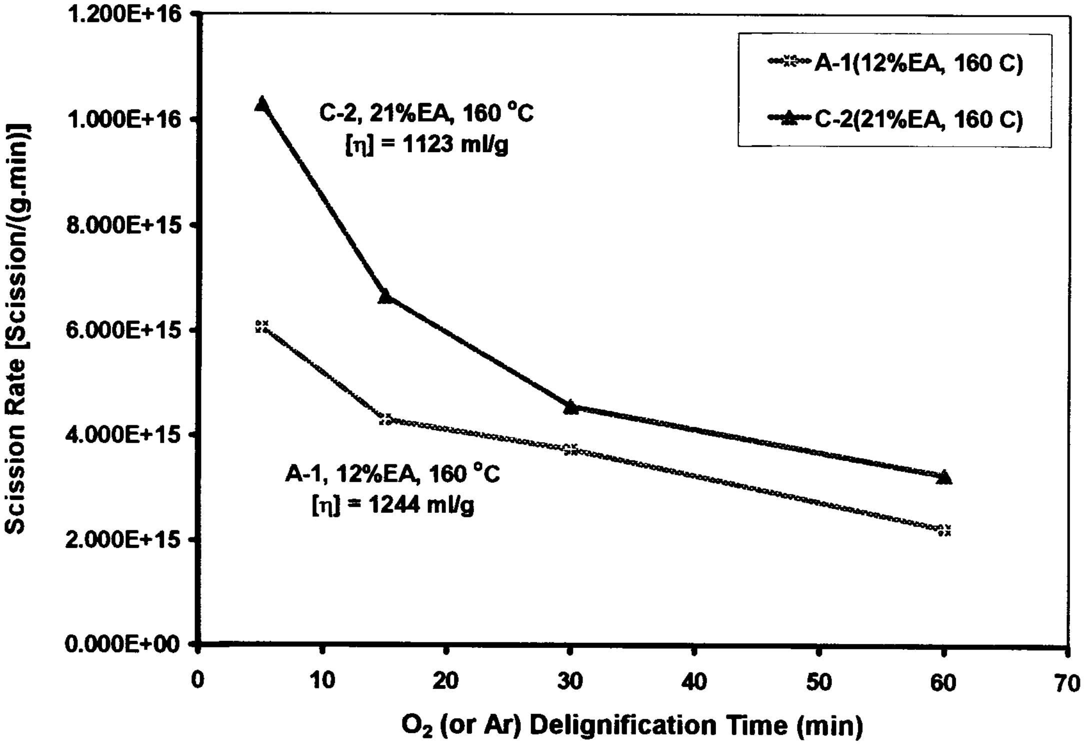


Figure 4.46. Effect of alkali at low kappa number and 160 °C.

4.3.8.3. Effect of Alkali at High kappa Number and 180 °C

Figure 4.47 compares the data for experiments B2/B4 and D-3. Data are shown for the carbohydrate scission rate for pulps produced at high kappa number using high temperature in the digester. Here again the effect of alkali is shown (see Figure 4.43). At the beginning of the oxygen delignification, carbohydrate degradation took place at a slightly faster rate for the pulp with higher initial viscosity pulp (1104 ml/g), which was produced using the EA value in the digester. It is interesting to note that the final scission rate was about the same regardless of the EA used in the digester at long reaction times.

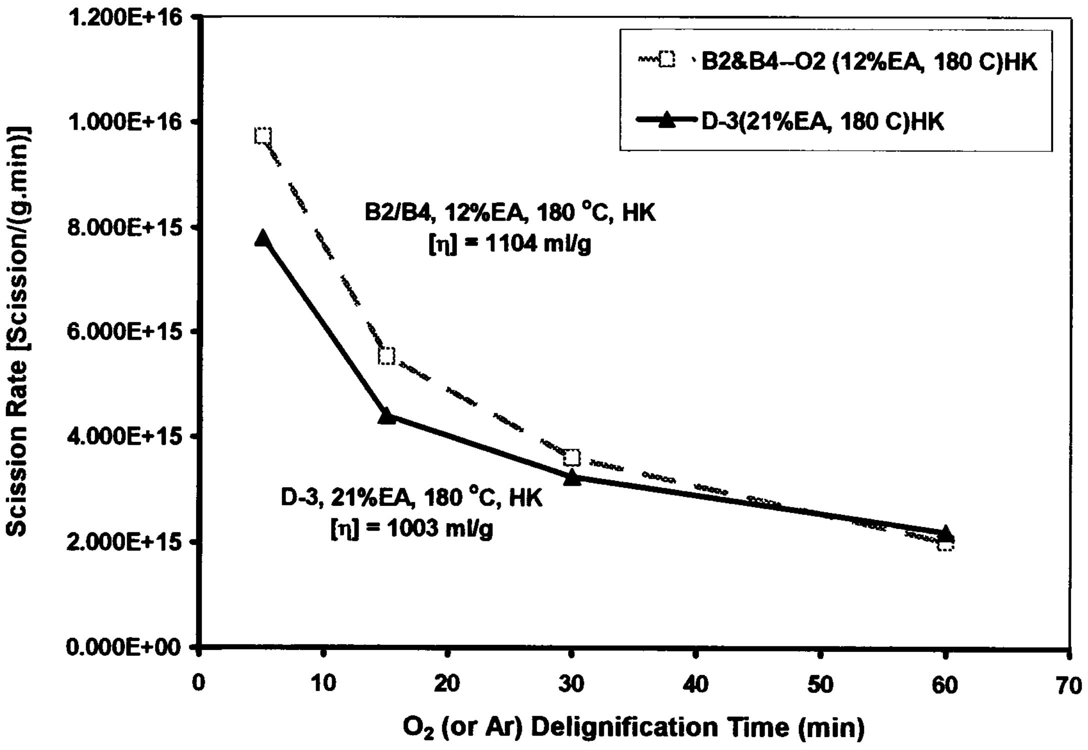


Figure 4.47. Effect of alkali at high kappa number and 180 °C.

4.3.8.4. Effect of Temperature at High EA (21%)

Figure 4.48 compares the carbohydrate scission rate for pulps produced at 160 and 180 °C for the same effective alkali content in the digester (21%). The samples that were compared were C-2 (160 °C) and D-2 (180 °C). The carbohydrate scission rate for the 160 °C sample (C-2) degraded at a slightly faster rate at the beginning of the oxygen delignification experiments than the 180 °C sample (D-2). These results were thought to occur because the 160 °C sample had a higher initial viscosity (DP). However, the scission rate slowed down as the reaction time in the oxygen reactor increased.

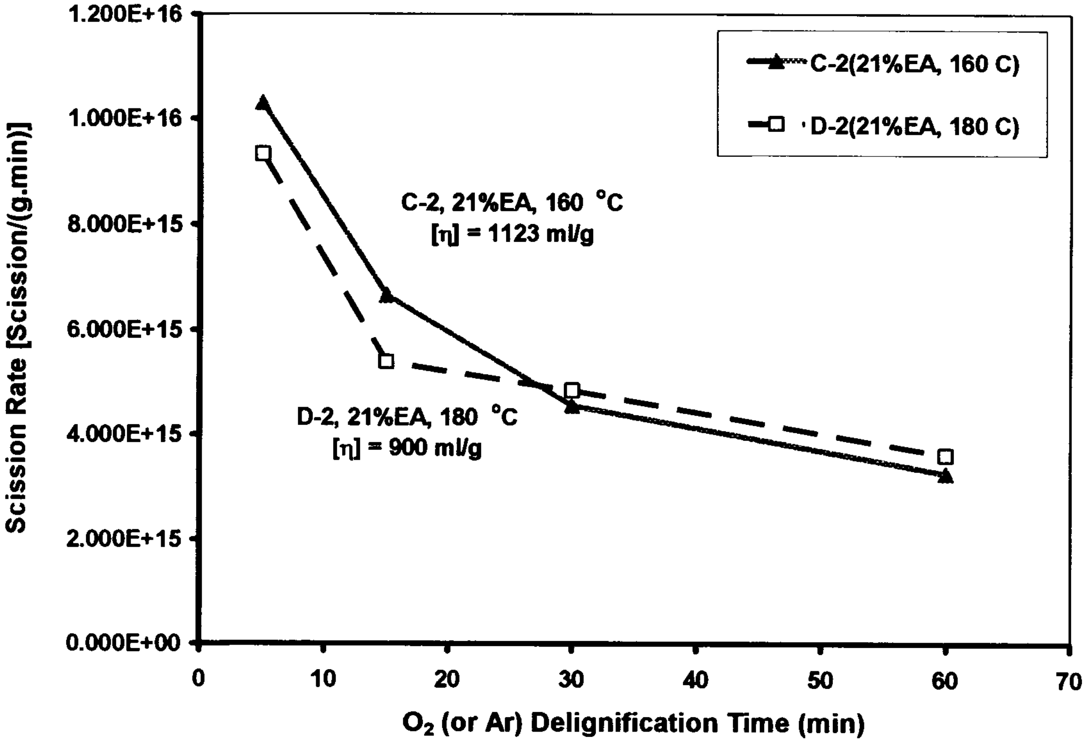


Figure 4.48. Effect of temperature at high EA (21%).

4.3.8.5. Effect of Kappa Number at 180 °C

Figure 4.49 illustrates the data for both high (20) and low (16) kappa number pulp produced at 180 °C and the same EA value (21%). The only variable changed in the cooking process was the time at maximum temperature (H-Factor). The high kappa number pulp (20) resulted from cook D-3 (intrinsic viscosity = 1003 ml/g) while the low kappa number pulp (16) resulted from cook D-2 (intrinsic viscosity = 900 ml/g). For the pulp cooked to kappa number 16 (D-2), the carbohydrate scission rate during the oxygen delignification stage was higher even though it was cooked for a longer period of time in the digester. What is surprising about these results is that the lower kappa pulp actually had a lower initial viscosity (900 ml/g).

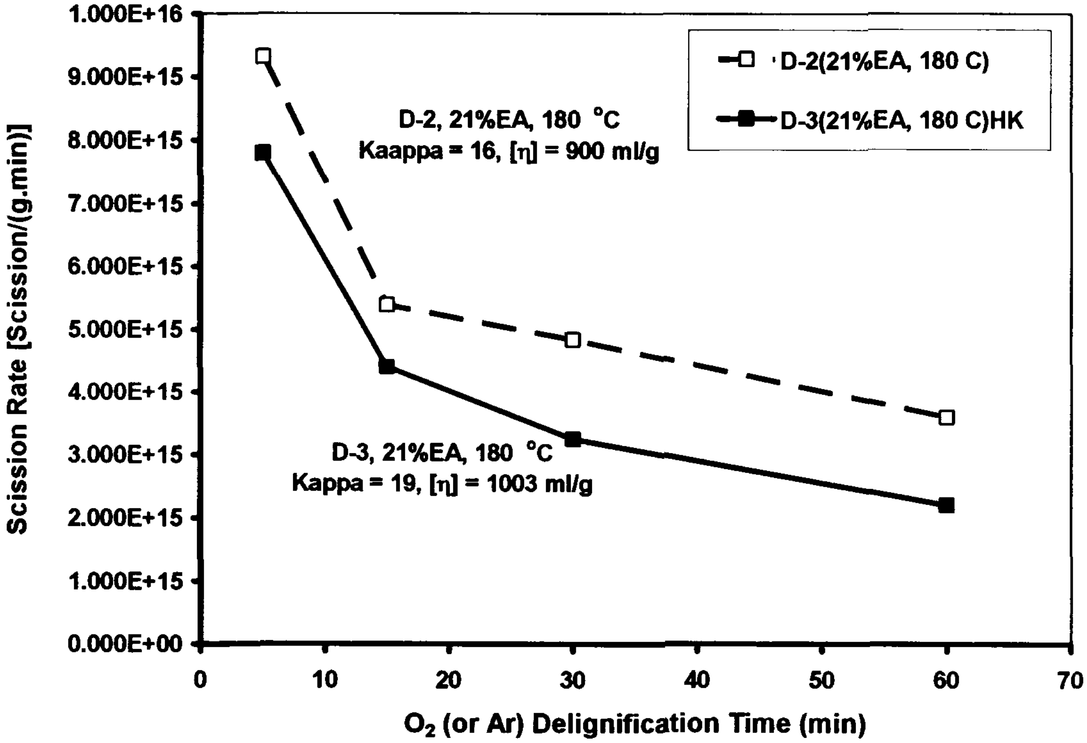


Figure 4.49. Effect of kappa number in the digester on carbohydrate scission rate in the oxygen delignification stage.

4.3.8.6. Effect of Hemicellulose Content

Pulps with high brownstock yield invariable have hemicellulose contents that would be expected to affect the carbohydrate scission rate. This effect of pulp yield and hemicellulose content is shown in Figure 4.50. The higher the hemicellulose content in pulp, the lower was the carbohydrate scission rate in the oxygen delignification. The brownstock pulp produced using 4% AQ had the highest hemicellulose content, and also the highest pulp yield, and had the lowest cellulose degradation rate. The pulps with the highest carbohydrate degradation rates were the soda pulp and the control. These two pulps also had the lowest hemicellulose content. These results suggest that the hemicellulose polymers present in the pulp are protecting the cellulose from degradation by hydroxyl free radicals (OH•) present during oxygen delignification (Guay, 2000). The hemicellulose polymers compete with the cellulose for hydroxyl free radicals and thus avoid undue lowering of the molecular weight of the cellulose.

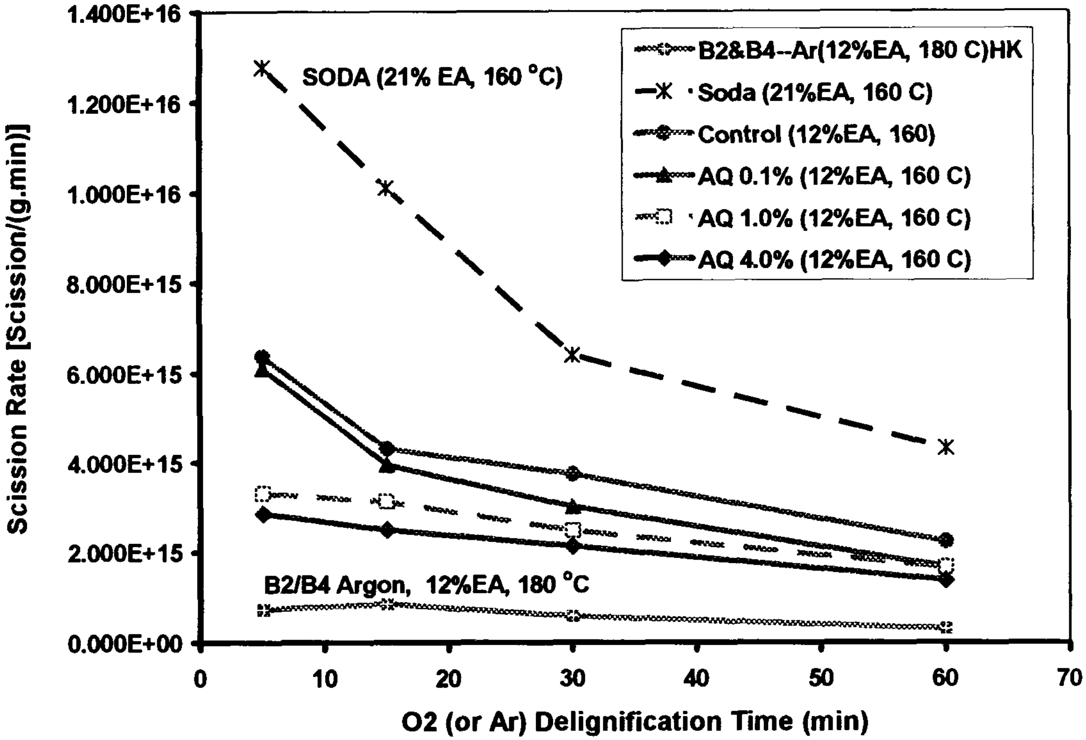


Figure 4.50. Effect of hemicellulose content on carbohydrate scission rate in the oxygen delignification stage.

4.3.9. Pulp Composition During Oxygen Delignification

Pulp composition data were determined by following the method described by Genco and co-workers (1990). The procedure is described in the experimental section. Individual components in the pulps are summarized in Table 3.5. Notable in this analysis was the determination of component sugars that were performed by using the Dionex DX 500 ion chromatograph (Figure 3.3). These data are summarized in Appendix D.1.

4.3.9.1. Effect of Cooking Conditions on the Relationship of Kappa Number to Lignin Content

The total lignin content for all of the brownstock pulps varied between 2.2 and 3.5%. The total lignin content in the pulp following oxygen delignification was found to be approximately 1.2 to 1.5% after 60 minutes exposure time. Furthermore, the data for the total lignin content were found to be linearly dependent upon the kappa number.

$$L\,(\%\,Total\,Ligni) = a * Kappa\,No. + b \qquad (4.17)$$

These correlations are shown in Figure 4.51 and the regression constants summarized in Table 4.6. The normal linear relationship was found to exist between total lignin content and kappa number except that the lines were parallel and dependent upon the effective alkali used in the digester. The pulps produced at 12% EA had higher pulp yield and higher hemicellulose contents compared to the pulps produced at 21% EA. This apparent dependence upon the EA content in the digester may be related to the hexenuronic acid content of the pulps. Li and Gellerstedt (1997) found that hexenuronic acid in a pulp will lead to elevated values of the kappa number. It may be possible that in the current study, pulps produced with low EA in the digester had higher hexenuronic acids contents that artificially raise the kappa number. It has also been suggested by Gellerstedt and Li (2000) that other groups in the hemicellulose polymers are also capable of consuming potassium permanganate and thus raising the kappa number of the pulp.

Table 4.6.
Regression constants for total lignin versus kappa number content.

Conditions	a	b	R^2
AQ Pulp (12% EA and 160 °C)	0.151	-0.2895	0.9840
High EA or High Temperature (21% EA or 180 °C)	0.155	0.1781	0.9556

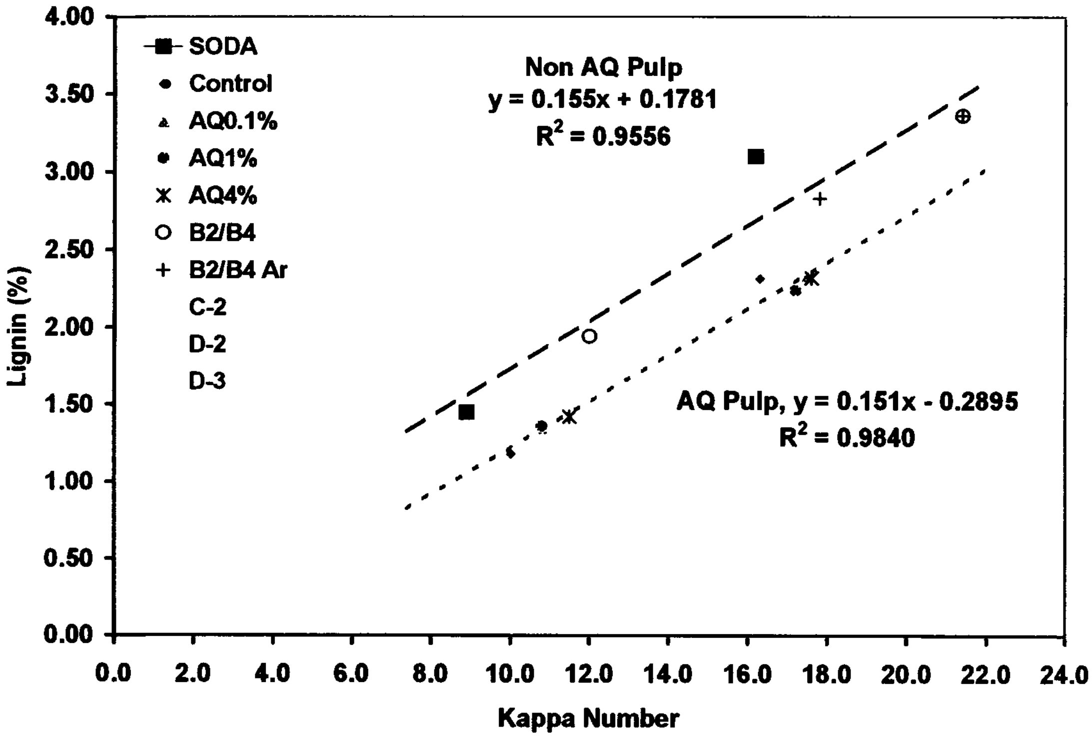


Figure 4.51. Lignin content versus kappa number.

4.3.9.2. Effect of Carbohydrate Content on Pulp Yield

Carbohydrate Contents for AQ Pulp. The data for the carbohydrate composition for the brownstock pulps produced using AQ in the digester are summarized in Appendix D.1 and are plotted in Figure 4.52. The chemical analysis showed that these four (4) pulps had the same lignin contents, which was about 2.3%. On an absolute basis (x_i^P), the hemicellulose contents of the four (4) pulps were found to increase while the cellulose contents were found to decrease. By contrast the retention of both the hemicellulose and cellulose polymers was found to increase when cooking with anthraquinone. This can be seen if the carbohydrate contents of the pulps are expressed on the basis of wood going to the digester (x_i^W).

$$x_i^W = \frac{y_{Pulp} * x_i^P}{100} \qquad (4.18)$$

where y_{Pulp} is the pulp yield following Kraft pulping and x_i^P is the weight fraction of the carbohydrates in the pulp on an absolute basis. These data are shown in Figures 4.53. The data of Figure 4.53 clearly show that both the cellulose and hemicellulose polymers are retained as the AQ to the digester is increases. Although both the cellulose and hemicellulose contents of the pulp increase, the greatest yield gain originated from the retention of the hemicellulose (xylan) polymers. This increase in the hemicellulose contents results because the AQ reduces aldehyde end groups on the carbohydrates and increase the rate of delignification. Also, the hemicellulose polymers are more accessible to the alkali in the pulping liquor and more prone to undergo peeling reactions compared to cellulose because of their amorphous structure.

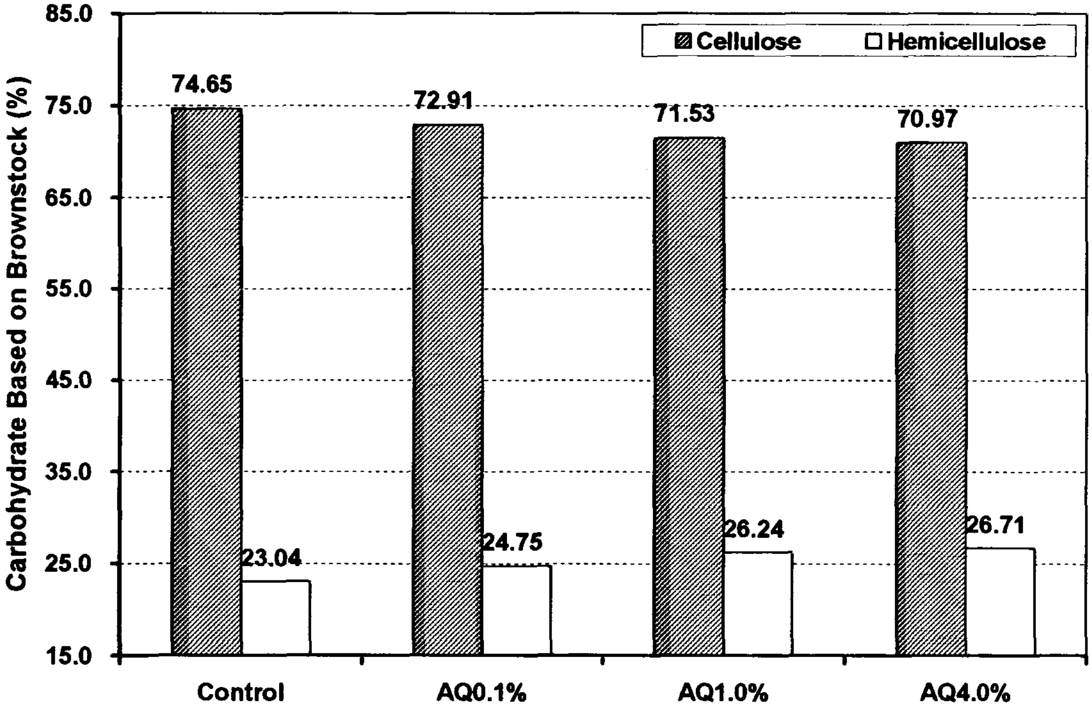


Figure 4.52. Carbohydrate content based upon brownstock.

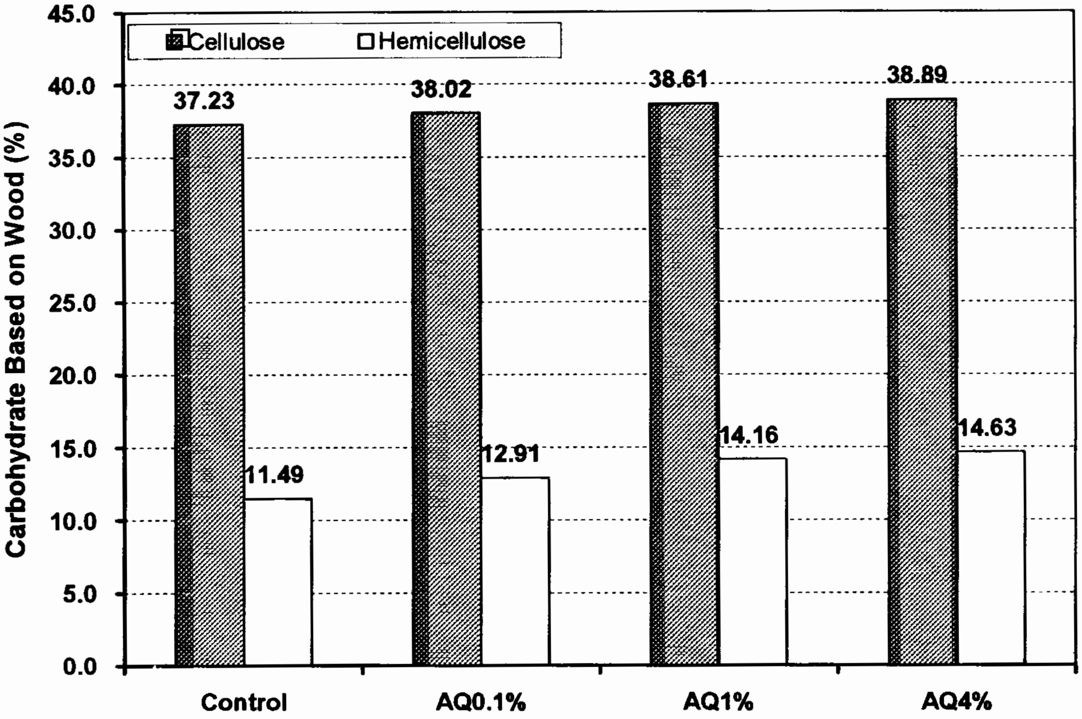


Figure 4.53. Carbohydrate content based upon wood versus AQ charge in the digester.

Dependence of Pulp Yield on Hemicellulose Content. For the brownstock pulps produced using AQ, there was an excellent linear relationship between pulp yield and the hemicellulose content in the pulp (Figure 4.54). For pulps produced at the same kappa number, invariably, pulps with higher yield contained greater amounts of the hemicellulose polymers and less cellulose (Figure 4.54). Approximately 70% of the increase in pulp yield can be attributed to the increase in the hemicellulose polymers and only 30% resulted from improved cellulose retention. Xylan is a dominion component in the hemicellulose polymers comprising northeastern hardwoods. Invariable, the retention of xylan increased with increasing pulp yield (Figure 4.55).

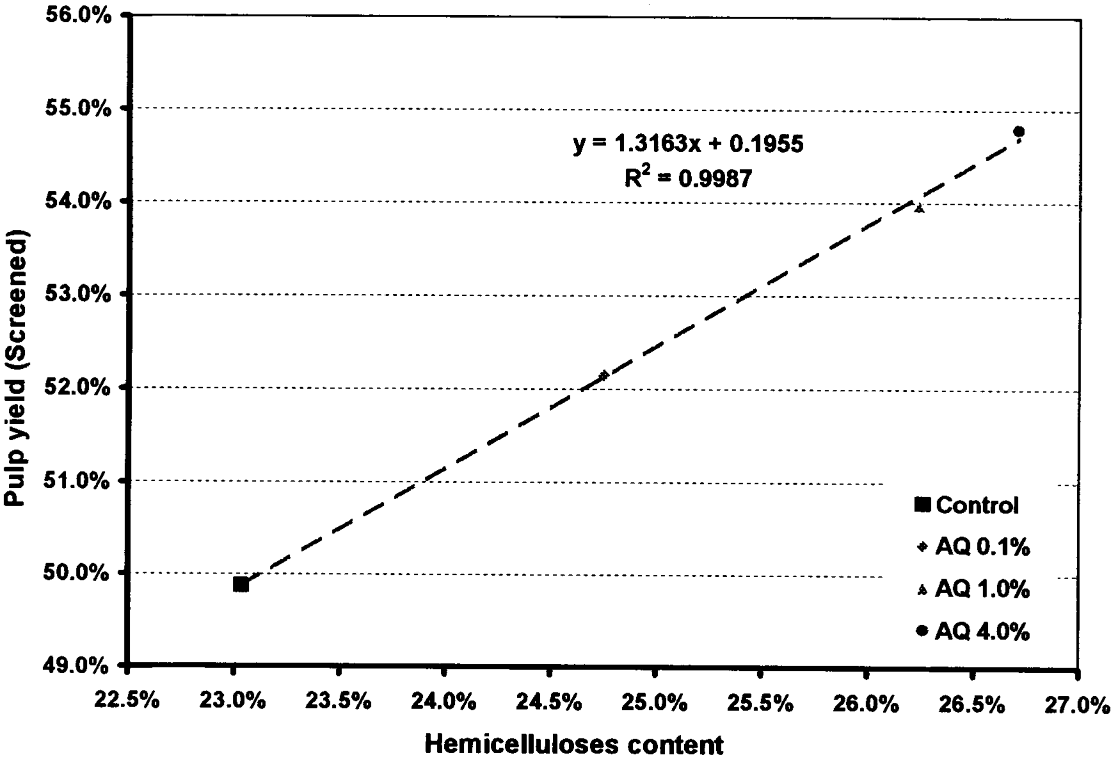


Figure 4.54. Kraft Screened yield versus hemicellulose content in the brownstock pulps produced using AQ.

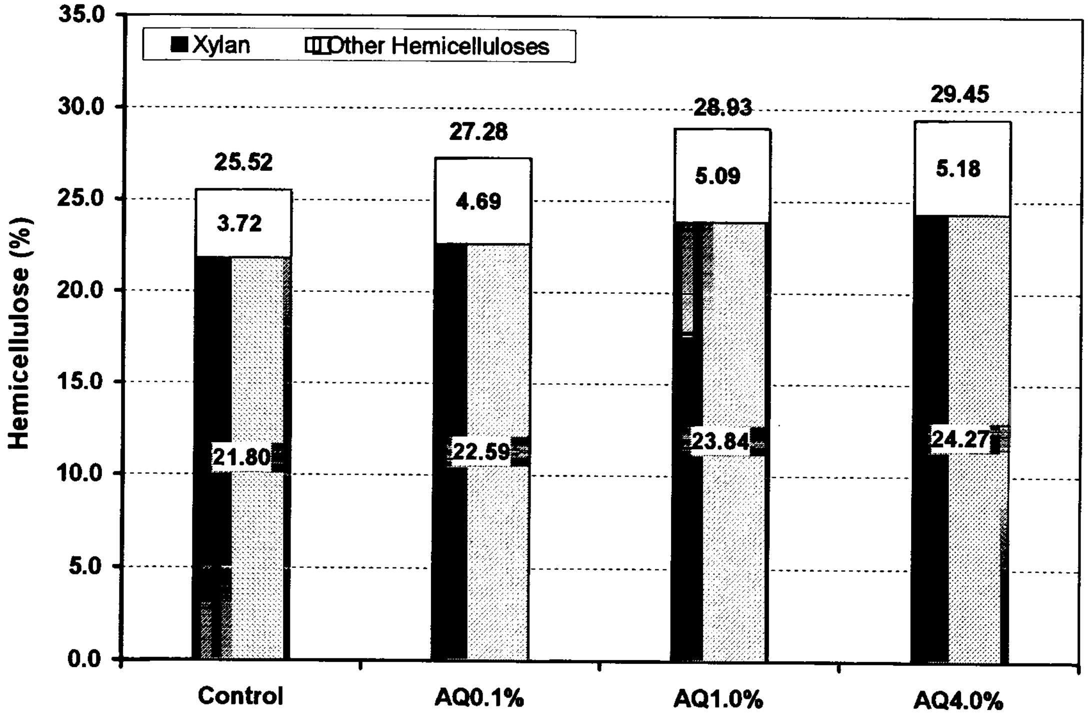


Figure 4.55. Xylan and other hemicellulose contents in brownstock pulps produced using AQ.

Extractive Content. At high rates of anthraquinone addition to the digester, it was difficult to remove residual AQ through the regular washing process, and therefore extra anthraquinone remained in the pulp after the cooking process. To remove AQ from the washed pulp and correct the pulp yield, samples of the brownstock pulp were extracted with dichloromethane (Figure 4.56). The pulp yield data shown in Appendix A have been corrected for removal of residual AQ. For all of the brownstock pulps except the pulp produced using 4% AQ, this correction was less than about 0.2%. However, for the pulp produced using 4% AQ addition to the digester, the residual AQ was greater than 2% (see Figure 4.56).

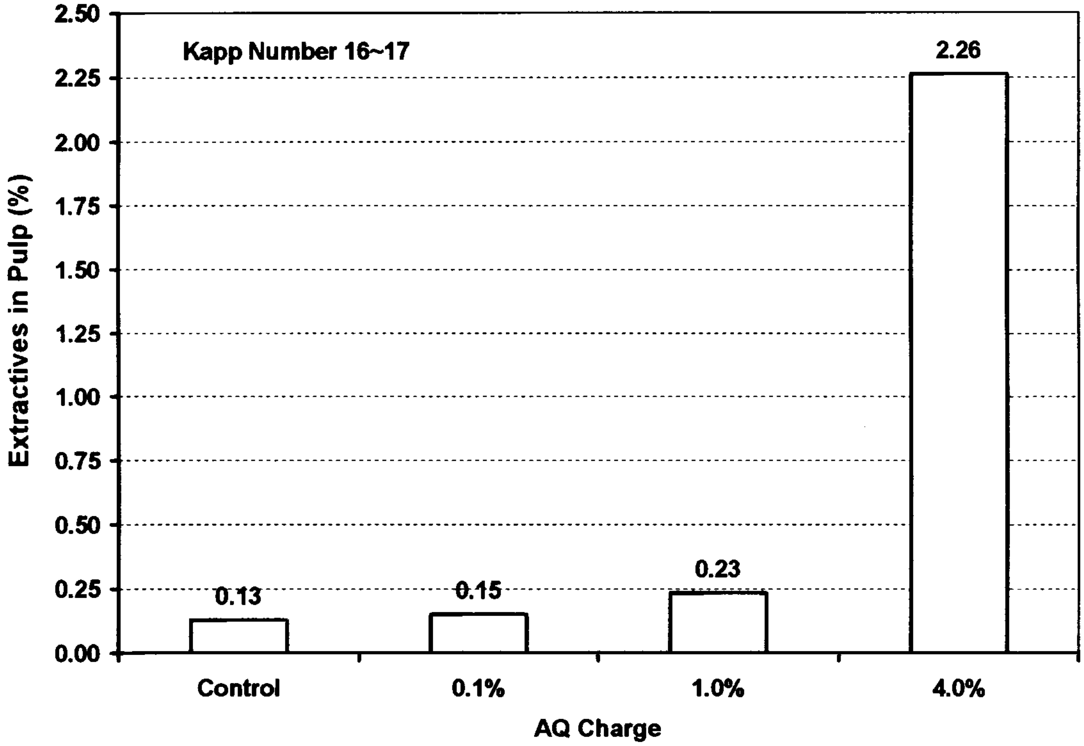


Figure 4.56. Extractives versus AQ charge in the digester.

Correlation of Carbohydrate Contents to Brownstock Pulp Yield. It has previously been shown that the brownstock pulp yield depends to a great extent on the cooking conditions in the digester. The carbohydrate contents is plotted versus the screened pulp yield in Figures 4.57 and 4.58 for all of the brownstock pulps produced in this study, both conventional pulps and those produced using AQ.. Excellent linear correlations were obtained between the screened pulp yield and the cellulose (Figure 4.57) and hemicellulose (Figure 4.58) composition in the pulp. The slopes of the two lines are approximately the same (0.8 to 0.9) except that the cellulose curve has a negative slope while the hemicellulose content is positive. Neglecting any extractives and inorganic components present in the pulp, the composition (fraction) of the brownstock can be represented by a three component system, cellulose (x_1^P), hemicellulose (x_2^P) and lignin (x_3^P) that must total 1.0. If the lignin content is low and held constant than approximately

$$x_1^P + x_2^P \cong 1 \qquad (4.19)$$

and the change in composition with a change in pulp yield (Y) would by definition be:

$$\frac{dx_1^P}{dY} \cong -\frac{dx_2^P}{dY} \qquad (4.20)$$

Thus it is concluded that the composition data shown in Figures 4.57 and 4.58 are consistent.

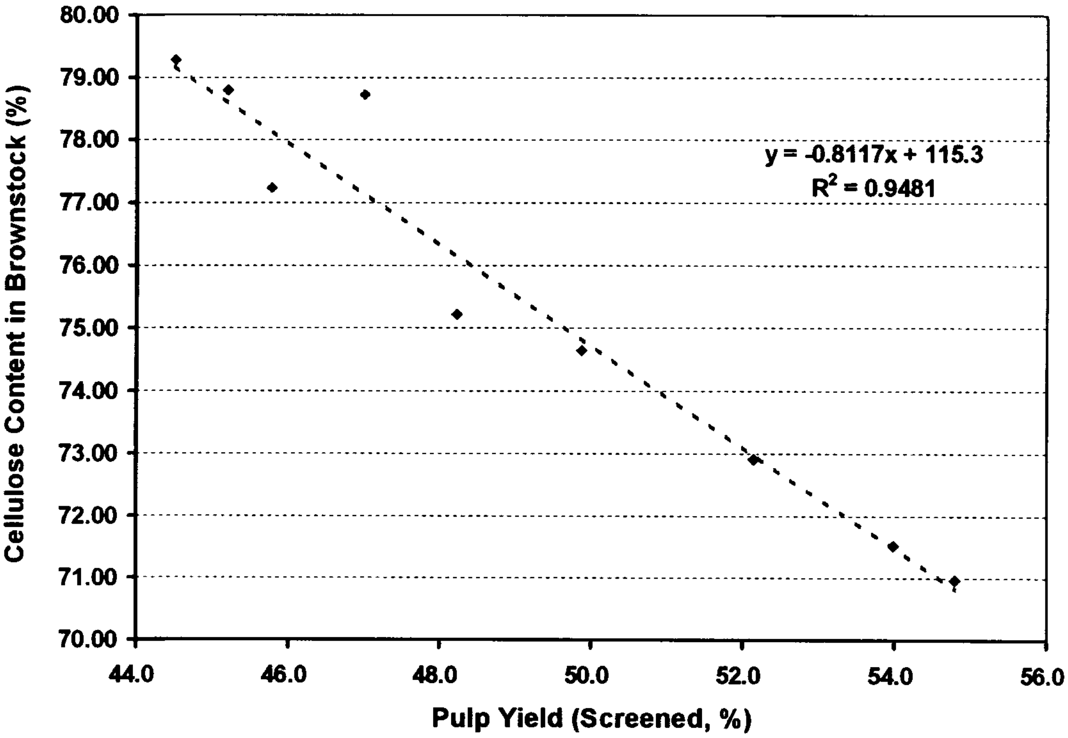


Figure 4.57. Cellulose content in brownstock versus pulp yield.

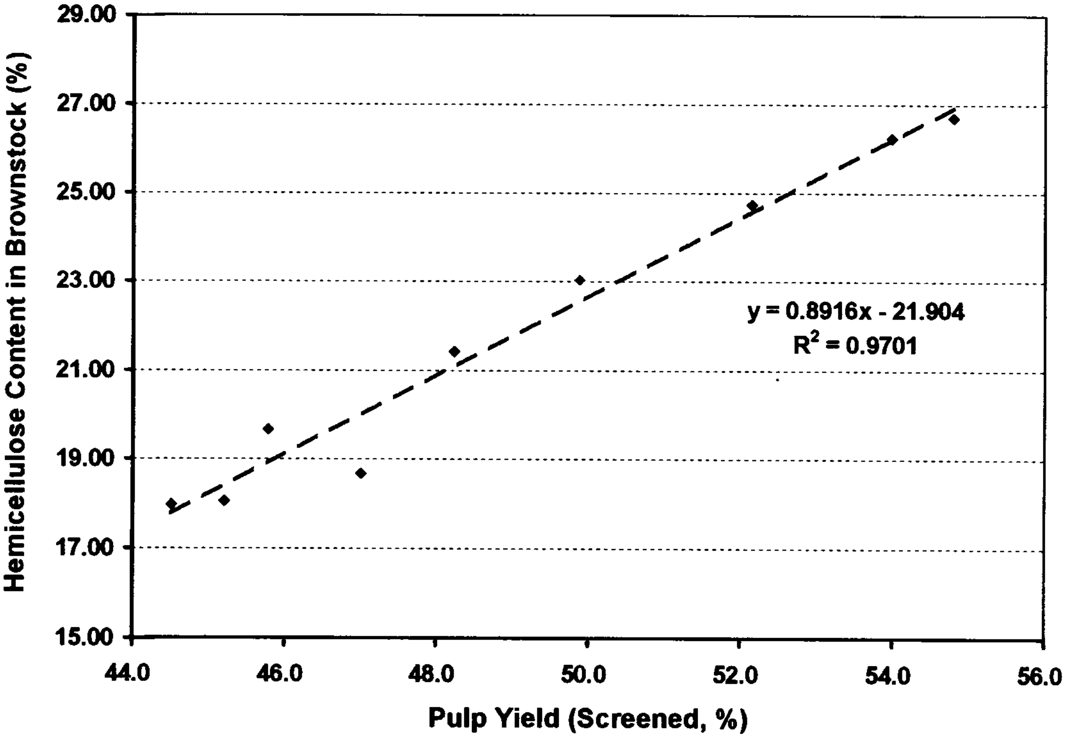


Figure 4.58. Hemicellulose content in brownstock versus pulp yield.

4.3.9.3. Relationship Between Pulp Viscosity and the Carbohydrate Composition of the Pulp

The data for intrinsic pulp viscosity were plotted versus cellulose and hemicellulose composition of various pulps. This was done for all of the brownstock pulps and for those same pulps following exposure to oxygen for 60 minutes. These correlations are summarized in Figures 4.59 and 4.60. Pulp viscosity would be expected to be determined by the cellulose content and its degree of polymerization (DP). This has previously been discussed in Section 4.3.4.4. During the pulping and bleaching processes, the cellulose contents of the pulp will be increased but simultaneously the molecular weight and DP of the cellulose will be degraded. As previously described cellulose degradation normally plays a more important role than the improvement in cellulose content. Consequently, the pulp viscosity will decreases with an increase in the cellulose content (Figure 4.59). Similarly, the intrinsic viscosity of the pulp for either brownstock or that following oxygen delignification will increase with an increase in the hemicellulose content. It has previously been shown in Figure 4.25 that for both oxygen delignified pulps and for their brownstock pulps that the intrinsic viscosity will increase with the cellulose content only if the cellulose has not been degraded.

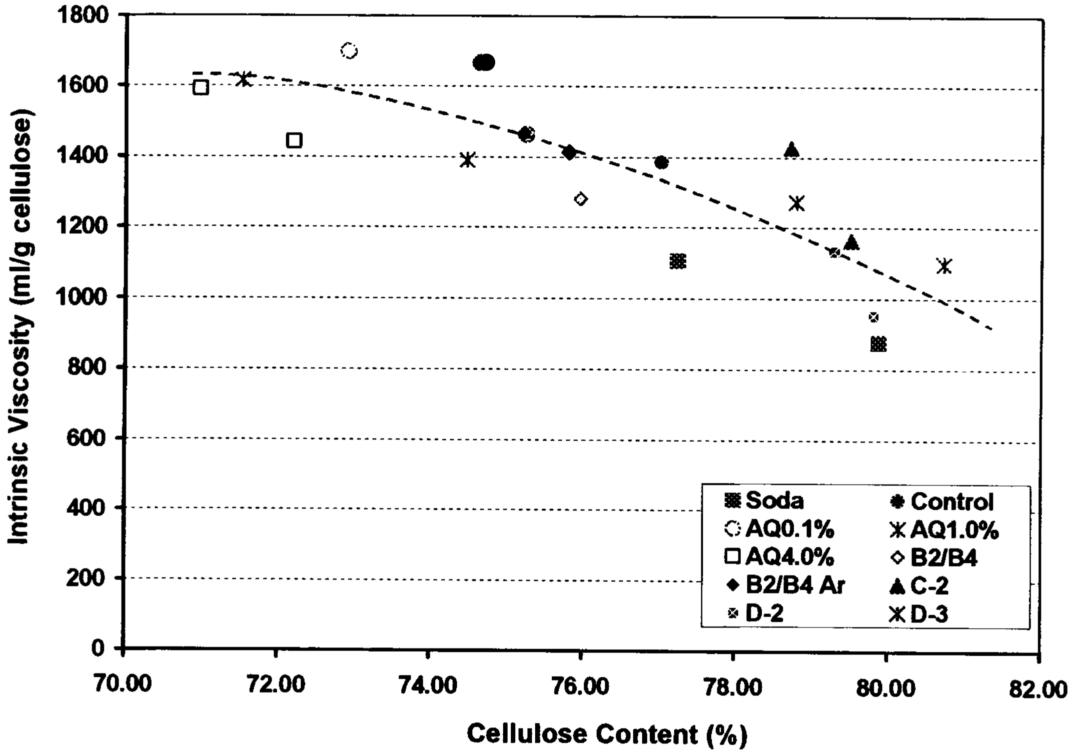


Figure 4.59. Intrinsic viscosity versus cellulose content for brownstock and oxygen delignified pulps at 60 minutes.

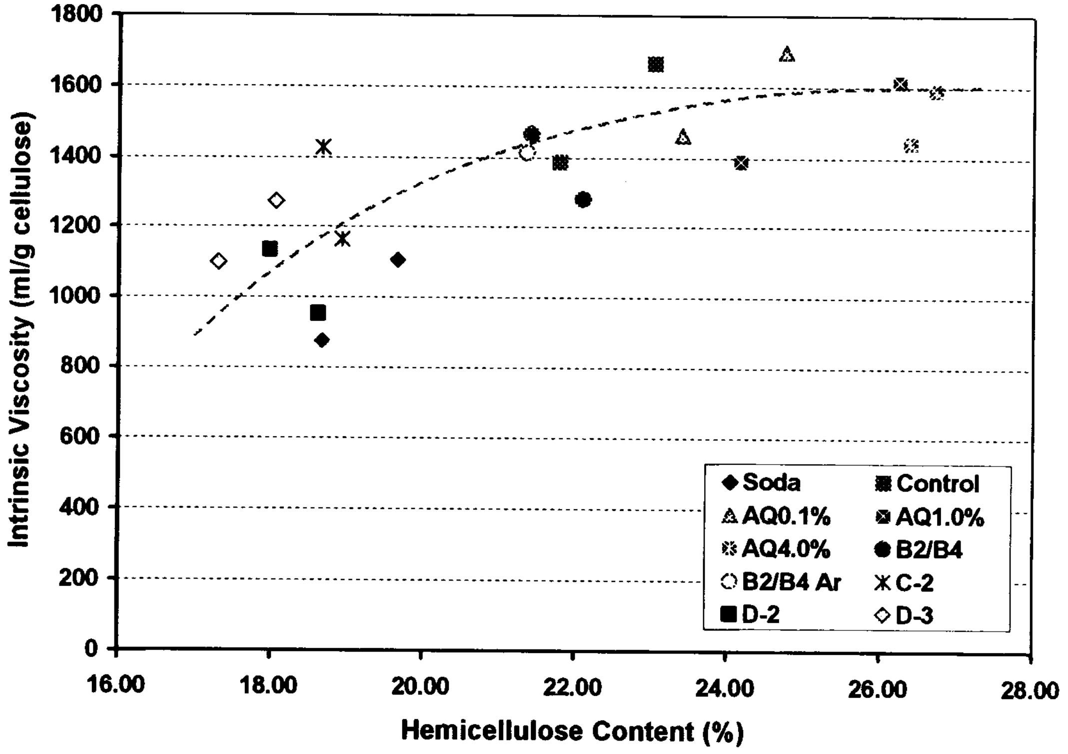


Figure 4.60. Intrinsic viscosity versus hemicellulose content for brownstock and oxygen delignified pulps at 60 minutes.

4.3.9.4. Effect of Oxygen Delignification on Carbohydrate Content

Cellulose Content after Oxygen Delignification. The cellulose and glucan contents of the pulp before and after oxygen delignification are shown in Figures 4.61 and 4.62. Together with the removal of lignin during pulping and bleaching processes, the hemicellulose and cellulose polymers will be partially removed. Generally, the quantity of the lignin and the hemicellulose polymers that are removed during processing will be greater than the amount of cellulose that is simultaneously removed. Invariably, a higher cellulose content will be observed after oxygen delignification than in the brownstock. These are essentially the results that were observed in this study.

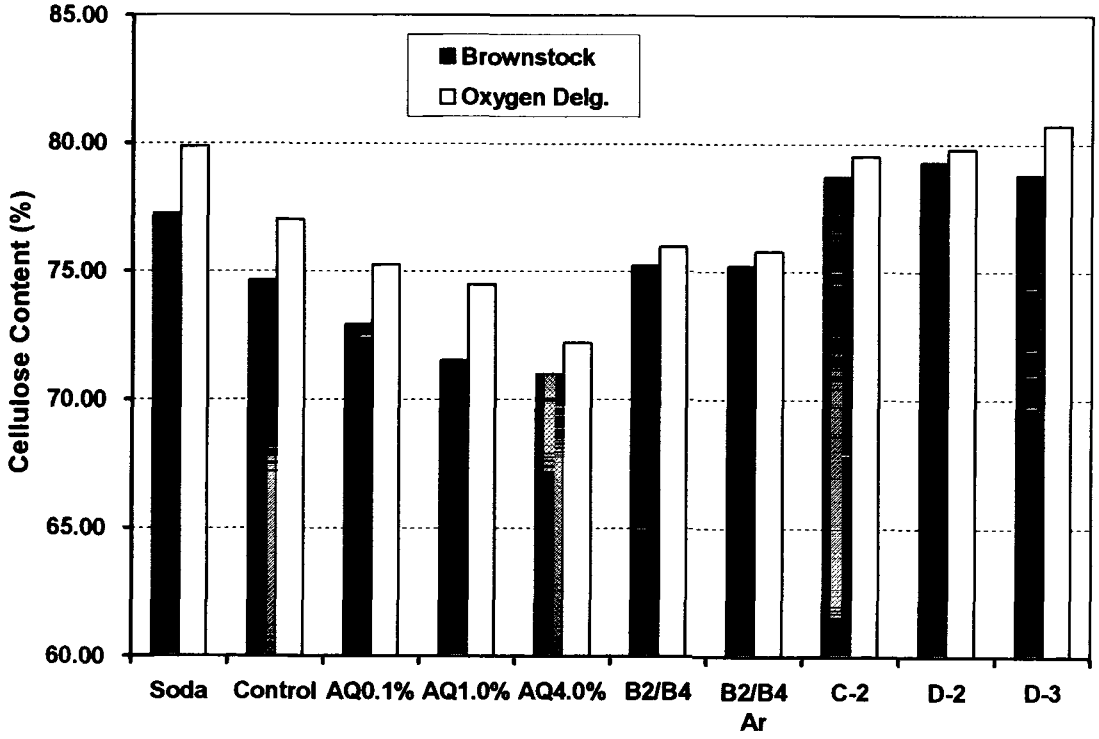


Figure 4.61. Cellulose content change before and after oxygen delignification.

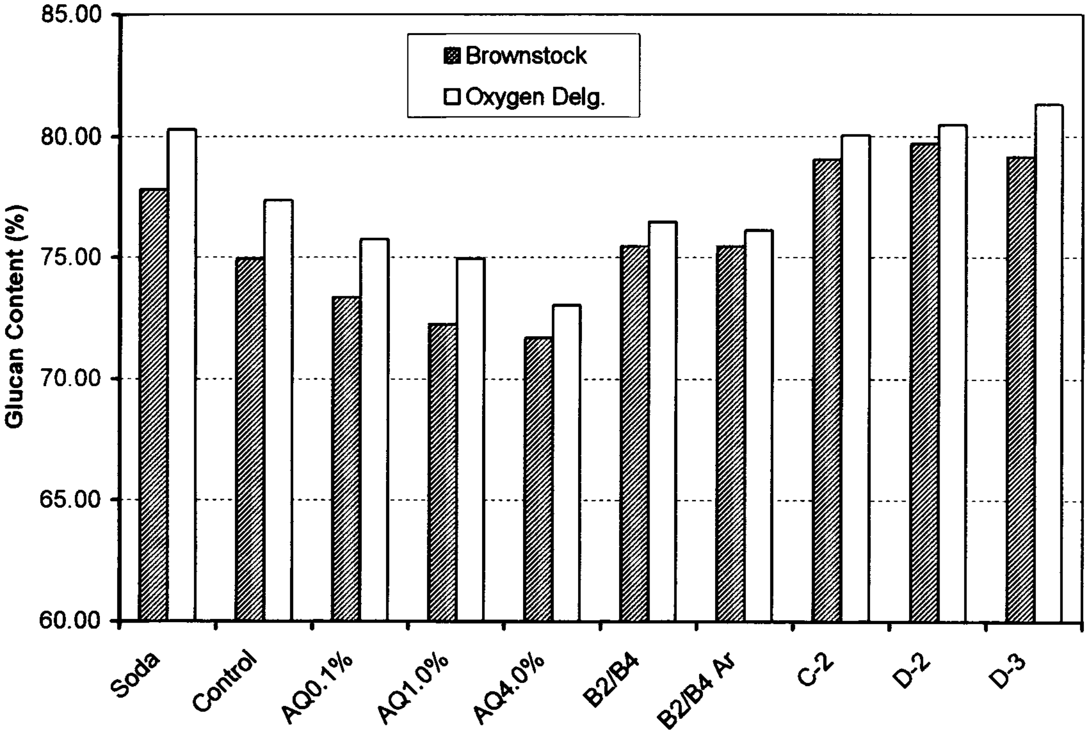


Figure 4.62. Glucan content change before and after oxygen delignification.

Hemicellulose Contents after Oxygen Delignification. The change in the hemicellulose content is more complicated than the change in glucan contents in the pulp following oxygen delignification. The data for pulp composition are shown in Figure 4.63. Some of the pulps showed an increase in the hemicellulose content following oxygen delignification while some showed a decrease. Whether the composition of the hemicellulose polymers in the pulp shows an increase or a decrease will depend upon the relative dissolution rates for the cellulose and hemicellulose polymers or more specifically for the glucan and xylan polymers. This will depend predominately upon the conditions used during cooking process and to a lesser extent upon the conditions used in the oxygen stage. In this investigation, it appears that the hemicellulose content in the high yield pulps produced using AQ in the digester, that there occurred predominately a decrease following the oxygen delignification stage.

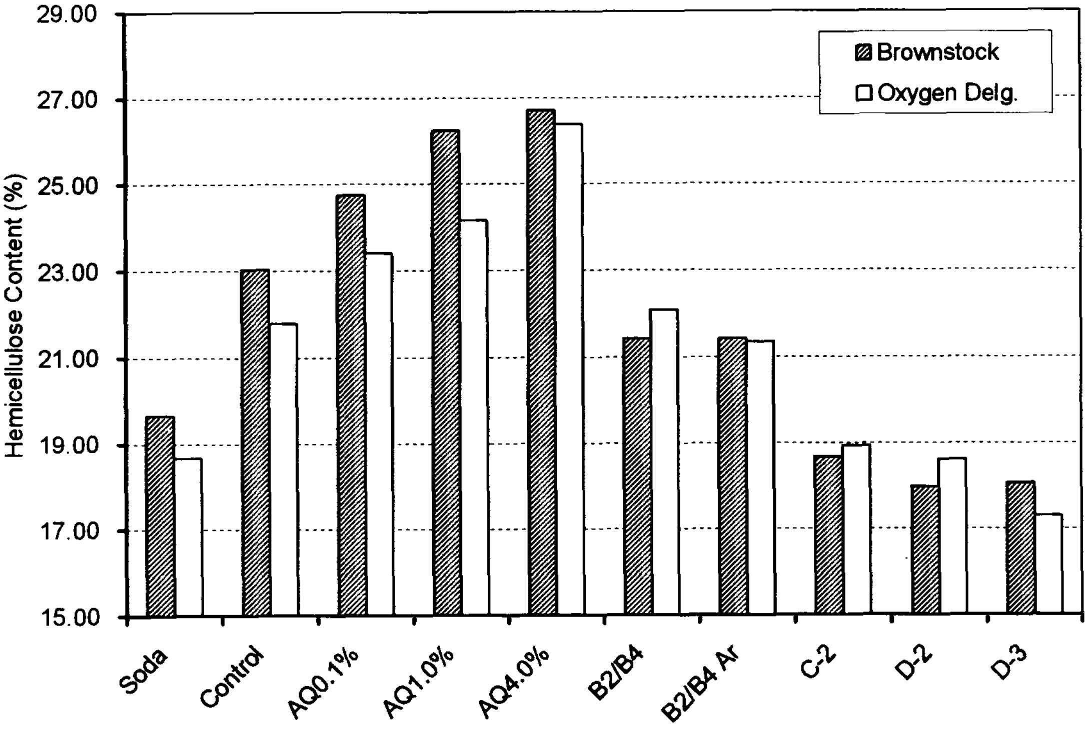


Figure 4.63. Hemicellulose content change before and after oxygen delignification.

Linkage of the Hemicellulose. The xylan and mannan contents in the pulps before and after oxygen delignification are shown in Figures 4.64 and 4.65. From these figures it can be seen that xylan content in the pulp always decreased, that is the weight fraction xylan in the pulp after exposure to oxygen delignification was less than that of the brownstock. In general this decrease was less than 2%. The decrease in the xylan fraction was greatest in the pulps prepared using AQ and for the soda pulp. By contrast the weight fraction mannan in the pulps invariable increased. This was true for all of the pulps except two; the soda pulp and the pulp produced using AQ at 1%. The 1% AQ data may be in error because both the 0.1% and 4% AQ pulps both showed and increase in the mannan content. From these results, one possible explanation is that the xylan polymer is most likely linked to lignin while the mannan polymer is most likely to link to cellulose. Various studies have shown that xylan is linked to lignin (Fengel and Wegener, 1984). Another possibility is that the mannan is also linked to lignin, but that the lignin-mannan complex is stable and the lignin moieties are not removed by oxygen. Tamminen and Hortling (2001) made a comparison of the lignin structure before and after oxygen delignification and concluded that structural differences between the isolated lignin were small. Rather they concluded that lignin-carbohydrate linkages plan the dominant role in hindering delignification. More specifically, the conditions present during oxygen delignification are insufficient to break lignin-carbohydrate linkages.

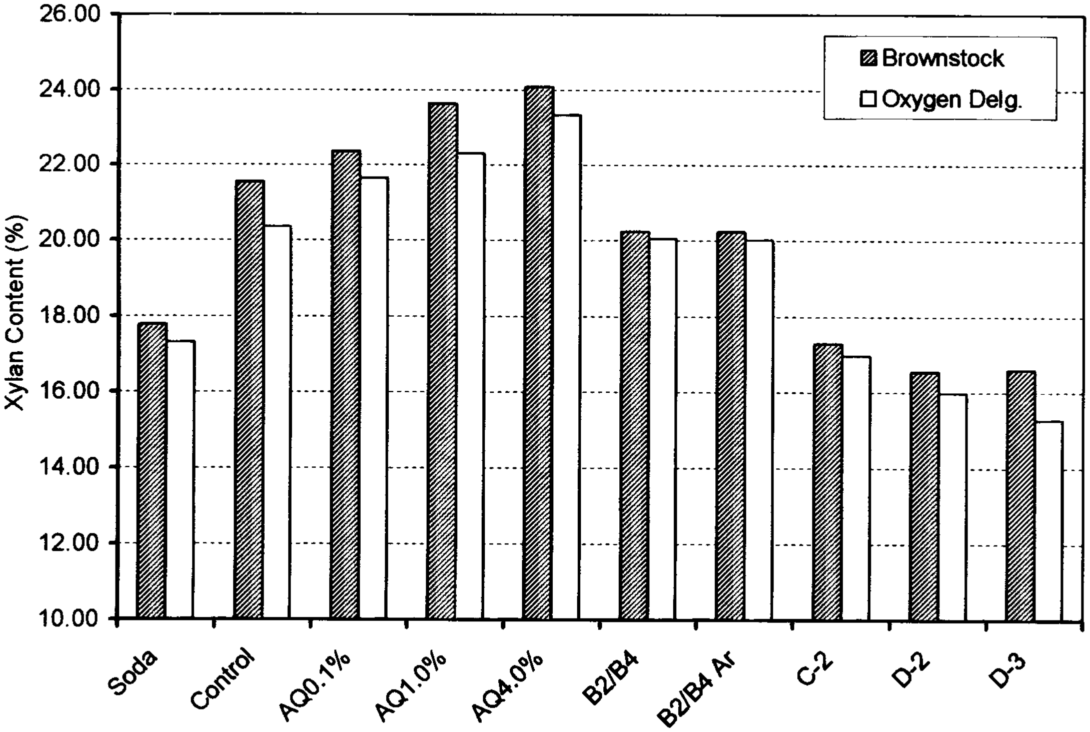


Figure 4.64. Change in the xylan content of the pulp before and after oxygen delignification – All data.

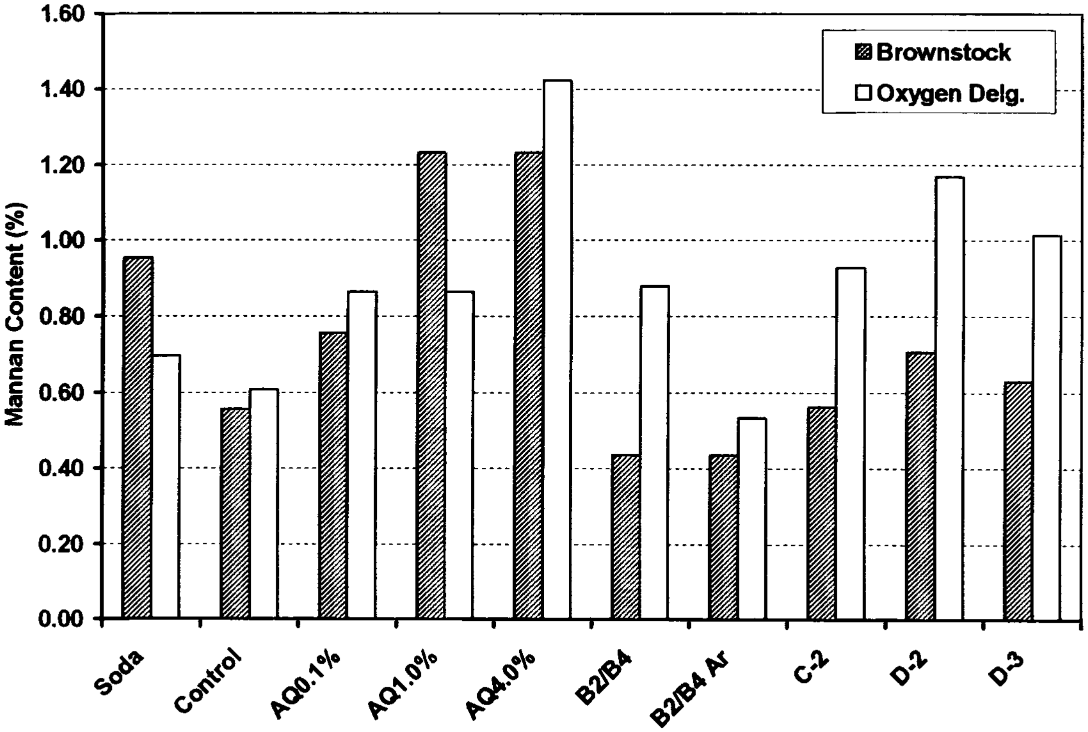


Figure 4.65. Change in the mannan content of the pulp before and after oxygen delignification – All data.

Chapter 5

CONCLUSIONS AND RECOMMENDATIONS

5.1. CONCLUSIONS

In the laboratory experiments reported here, the EA, sulfidity, H-factor (time and temperature) and liquor-to-wood ratio (L/W) were carefully controlled. The effective alkali (EA), sulfidity (S) and liquor to wood ratio determine the concentration of the S=, OH- and SH- ions while the time at temperature determines the H-factor and thus, greatly influences reaction kinetics. In the mill situation, many other variables are involved in determining the quality of the final pulp; notable among these variables are the chip thickness and distribution, moisture content, level of air removal through steaming, the degree of chemical penetration, liquor profiling, and black liquor re-circulation. These variables together with the primary process variables would be expected to affect the final lignin content and carbohydrate composition of the pulp leaving the digester. In mill practice, there is, of course, more variability in the wood, changes to the cooking liquor, and numerous secondary variables that affect the quality of the pulp leaving the digester.

5.1.1. Effect of Effective Alkali During Kraft Pulping

Because of resistance to alkaline pulping, the xylan content was high in the resulting hardwood brownstock pulp. Cooking at high effective alkali, for example 21% EA, resulted in low hemicellulose content in the brownstock, hence the pulp yield was low. By contrast, cooking at high effective alkali shortened the cooking time when pulping to the same target kappa number when compared to cooking at the low effective alkali conditions. To achieve brownstock pulps with high hemicellulose content and high pulp yield, low effective alkali should be used. This will of course lengthen the reaction time.

5.1.2. Effect of Cooking Temperature During Kraft Pulping

Cooking at high temperature resulted in brownstock pulps with low hemicellulose content and low pulp yield. By contrast, cooking at high temperature can shorten the cooking time when pulping to the same target kappa number when compared to cooking at low temperature. To achieve pulps with high hemicellulose content and high pulp yield, low cooking temperature should be used. Here again, this will lengthen the cooking time.

5.1.3. Effect of Anthraquinone During Kraft Pulping

Adding anthraquinone to the digester increased the pulp yield, but also shorten the cooking time. Very high pulp yields can be obtained by using high levels of AQ. At high AQ levels, it is very difficult to wash the AQ from the residual pulp using water. Rather AQ had to be removed from the pulp by using dichloromethane and a correction made to the pulp yield.

5.1.4. Oxygen Delignification

Delignification Kinetics. Cooking mixed northeastern hardwood chips with high and low EA to the same brown stock kappa number greatly affected the rate of oxygen delignification for well-washed pulps when the change in kappa number was used as the indicator of delignification. The power law model, suggested by Schoon (1982) for hindered chemical reactions, can adequately describe the kinetic rate data for oxygen delignification. For oxygen delignification, the observations in this and other studies suggest that the high reaction order can be explained by assuming that delignification proceeds through a great number of parallel, first-order reactions taking place simultaneous with the different lignin moieties reacting at different rates as suggested by Schoon (1982).

Effect of Pulping on the Schoon Rate Constant. Conventional Kraft pulps produced using low EA in the digester and also pulps produced using AQ both proved to be difficult to delignify in the oxygen stage, that is they had low rate constants in the Schoon delignification model. For the pulps prepared using AQ, the difficulty in oxygen delignification followed the addition level (concentration) of AQ in the digester. As the yield and hemicellulose content in the pulps increased, the reaction rate coefficient (k) in the Schoon delignification model decreases in regular manner. Those pulps that proved to be readily delignified in the oxygen stage were produced using low H-factor and high effective alkali concentrations in the digester. Pulps produced under these conditions tended to have lower yield and lower hemicellulose contents but high rate constants for the Schoon delignification model. When cooking at high effective (21%) alkali, the temperature did not seem to affect the kinetics of oxygen delignification.

Pulp Selectivity. Those pulps that had low yield and low hemicellulose content, which were produced using the high EA and/or high temperature in the digester showed poorer selectivity during the oxygen delignification. Improved pulp selectivity was obtained for those pulps produced with high yield and high hemicellulose content, that is, for conventional pulps produced under low EA and low temperature conditions in the digester, and also for pulps produced using AQ.

Yield and Hemicellulose Content. Based upon these results it is concluded that the hemicellulose polymers, specifically xylan, function as a viscosity protector for cellulose, that is, there was less cellulose degradation and higher pulp viscosity when the hemicellulose content in the pulp was high. It was also concluded that no matter what the conditions in the digester that lead to pulps with elevated levels of hemicellulose, the selectivity would be high and the rate constant would be low.

Possible Linkages. The carbohydrate components analyses show that during delignification in the pulping and oxygen bleaching process, mannan content always increases while xylan always decreases. Thus it was concluded that the xylan polymer is most likely linked to lignin while the mannan may possibly be linked to cellulose. An alternative explanation is that the mannan polymer is unreactive with the superoxide anion which seems unlikely.

Proposed Mechanism. In addition to the observations reported here on the effect of the hemicellulose content on oxygen delignification, Buchert, et al. (1996) have observed that pulps with high xylan content inhibit delignification. The mechanism for the observed results in both Buchert's work and in the present study is unclear, but several mechanisms suggest themselves. First, the hemicellulose polymers function as an encrustation substance and surrounds elementary crystallites of cellulose (Fengel and Wegener, 1984). The hemicelluloses are also know to be bound to the lignin and are amorous. Consequently, the reagents are physically present in higher concentration than in cellulose crystallites. The hydroxyl free radicals (OH•) are formed in situ from dissociation of oxygen and as products of reaction of the superoxide anion with lignin. Metal ions are known to influence the production of hydroxyl free radicals. Thus physically, the hemicellulose polymers would act to protect the cellulose. Hydroxy free radicals are produced in situ and would be free to react with the hemicelluloses preferentially to the cellulose. Also, since the molecular weights of the hemicellulose polymers are low, perhaps DP 100 to 200 or lower compared to 1000 to 2000 for cellulose in unbleached pulp, the overall viscosity will not be greatly lowered. There will of course be some decrease in yield.

Secondly, the hemicellulose polymer present in the pulp will undergo competitive reactions with alkali present. The peeling reaction will consume caustic and thus will lower the alkalinity in the oxygen stage. There would be less alkali available locally to react with the cellulose. This would result in less cellulose degradation and lead to a higher selectivity, but the oxygen delignification would also be low.

Other possibilities for explaining the experimental results have been suggested by Argyropoulos (1998) and also Tamminen and Hortling (2001). Argyropoulos et al. (1998) believe that delignification in the oxygen stage is hindered by refractory lignin moieties formed in the pulping process. The work by Tamminen and Hortling (2001) suggest that it is the lignin to carbohydrate linkages that inhibit delignification, that is the superoxide free radicals present under the conditions of oxygen delignification do not react with the lignin to carbohydrate linkages. Obviously, considerable fundamental study is required to elucidate the exact mechanism.

5.1.5. Pulp Yield and COD in Spent Liquor

The COD content in the spent liquor following oxygen delignification could be correlated to the pulp yield. With decreasing pulp yield following the oxygen stage the COD in the spent liquor increased and could be roughly correlated using a model predicated upon the Raleigh equation as suggested by Genco, Zorn and Cole (2000). Pulps produced at low EA, low cooking temperature and by using AQ as a pulping catalyst had higher levels of COD in the spent liquor following oxygen delignification. It has been shown that the elevated COD levels in the spend liquor resulted primarily from dissolution of hemicellulose carbohydrates. For pulps with high hemicellulose content, these results raise questions regarding the preservation of pulp yield in the bleach plant.

5.2. RECOMMENDATIONS

The current work suggests several other studies that should be conducted to further elucidate the effects of kraft pulping on oxygen delignification.

5.2.1. Effect of Lignin Structure and Carbohydrate Lignin Linkages on Delignification

Based upon the present study it is strongly recommended that fundamental studies be conducted on lignin structure in the brownstock pulp and the lignin carbohydrate linkages to determine what role they play in affecting oxygen delignification.

5.2.2. Delignification Kinetics, Hemicellulose Content and Selectivity of Softwood on Oxygen Delignification

The current study should be extended to softwood pulps. Specifically selectivity and retention of hemicelluloses should be studied since softwood contains less hemicelluloses, higher lignin and the residual lignin in softwood brownstock pulps tend to be more condensed than hardwood pulps. Consequently, the hemicellulose content in softwood brownstock may play a very important role in oxygen delignification kinetics. Viollette and van Heiningen (2001) have reported that carbohydrate polymers that are added to the pulp can increase softwood pulp selectivity during oxygen delignification. The question is "Can this improvement in selectivity be realized by varying the cooking conditions and thus avoid having to add external carbohydrate polymers such as guar gum and other low molecular polymers that function as free radical scavengers"?

5.2.3. Effect of Alkali Profiling During Kraft Pulping on Oxygen Delignification Kinetics

Modern pulp mills are rapidly phasing out conventional cooking and are being converted to pulping systems that utilize alkali profiling. In conventional cooking, all of the alkali is added at the beginning of the cook prior to the heat up period and the wood is cooked at some maximum temperature. This leads to high dissolution of carbohydrates, especially the hemicellulose polymers, which dissolve in the high caustic concentration during the heat-up period. By contrast, in the new alkali profiling technology, the alkali addition is staged and the wood chips are brought up to the cooking temperature in the presence of low alkali, thus avoiding carbohydrate dissolution during the heat up phase.

Additionally, schemes have been designed to conserve energy during the cooking process by recycling black liquor and both weak and strong white liquor. Such schemes often lead to pulping at high levels of sulfidity and low alkali. Thus, pulps produced using the alkali profiling schemes often have much higher yield and higher hemicellulose contents. This is especially important if one considers that the pulps produced at low EA content in the present work showed greater selectivity. Using conventional cooking methods in the present work limited the range on the pulp yield between the high and the low EA data and proved to be a shortcoming in this thesis. Clearly, the present work would have been more relevant had it been conducted using alkali-profiling technology. Future work should be done to correct this deficiency.

5.2.4. Effect of Pretreatments on Oxygen Delignification Kinetics

Recent work by Sjogren and Hook (2000) has shown that oxygen delignification is greatly affected by pretreatment and removal of metal ions. The abilities of different pre-treatments on pulp selectivity were studied in single- and two-stage oxygen delignification. Very high levels of delignification, 65 to 70%, could be achieved by using various pretreatment methods. Oxygen delignification was improved by hydrogen peroxide reinforcement, pretreatment with DTPA to remove and sequester metal ions, and the addition of Mg^{+2} during hydrogen peroxide reinforcement. The selectivity was improved further in two-stage delignification when intermediate washing was conducted between stages. Further work could be done to extend the work of Sjogren and Hook and investigate oxygen pre-treatments and lignin activation. Boniface (2000) reports a commercial installation that uses an acid pretreatment and pulp activation by the use of

ClO_2 prior to a two-stage oxygen delignification process. Work of this type holds the promise of raising the level of oxygen delignification to 65 or 70% while improving selectivity. If successful, it would shrink the bleach plant and save capital and operating expenses because oxygen would be substituted for ClO_2 as the oxidizing agent.

5.2.5. Bleachability Factor

Since many parameters affect the bleachability (or selectivity) of brownstock pulps during delignification processes, it would be helpful if a general bleachability factor can be developed to predict the bleachability of Kraft brownstock pulp. The bleachability factor of the brownstock should be set up thru the measurements of the properties of the brownstock (such as its compositions) and the cooking conditions. Based on the brownstock bleachability factor, it should be possible to predict the quantity chemical equivalents and thus amounts of bleaching chemicals required to achieve a target brightness. Bleachability factor may be evaluated thru the combination of brightness, kappa number, viscosity, and carbohydrate components (especially, hemicellulose content.

REFERENCES

Agarwal, S., Cole, B. J. W., Kwon, H., Miller, W., and Genco, J. M., "Oxygen Delignification of Southern Hardwoods", *AIChE sessions, Tappi Pulping Conference,* Nashville, (1996).

Agarwal, S.B., Genco, J.M., Cole, B. and Miller, W., "Kinetics of Oxygen Delignification", *Journal of Pulp and Paper Science,* 25(10): 361-366 (1999).

Argyropoulos, D. and Liu Y., "The Role and Fate of Lignin's Condensed Structures During Oxygen Delignification", *Tappi Pulping Conference Proceedings,* (1998).

Akim, L., Colodette, J. and Argyropoulos, D., "Factors Limiting Oxygen delignification of Kraft Pulp", 2000 *International Pulping and Bleaching Conference* (2000).

Asgari, F. and Argyropoulos D., "Kinetics of Function Group Formation/Elimination in Residual Kraft Lignin During Oxygen Delignification", *Tappi Pulping Conference Proceedings,* pp. 951-961 (1997).

Aurell, R. and Hartler, N., "Kraft Pulping of Pine – Part 1", *Svensk Papperstidng,* 3: 59 (1965); Part 2, *Svensk Papperstidng,* 4: 97 (1965).

Axegard, P., Moldenius, S., and Olm, L., *Svensk Papperstidng,* 82: 13 (1979).

Backstrom, M., Hagglund M. and Olm, L., "Effect of cooking temperature during extended delignification—selectivity, strength properties and TCF-bleachability", *PAPERI JA PUU- PAPER AND TIMBER* VOL. 78/NO. 6-7/1996, pp 392-397 (1997).

Berry, R.M. and Fleming, B.I., "Why Do Chlorination and Extraction Fail to Delignify Unbleached Kraft Pulp Completely?", *Holzforschung,* 41(3);177 (1987).

Boniface, A., "Lincoln Pulp & Paper Starts New Bleaching Process", *Tappil,* 83(8): 47-50 (2000).

Brunow, G., Sipilä, J., and Karhunen, P., "Lignin Chemistry", (1998) [http://www.helsinki.fi/~orgkm_ww/lignin_structure.html]

Bubniak, G., M.S. thesis, The University of Maine (1999).

Buchert, J., Tenkanen, M., Ek, M., Teleman, A., Viikari, L., and Vuorinen, T., "Effects of Pulping and Bleaching on Pulp Carbohydrates and Technical Properties", *International Pulp Bleaching Conference, Tappi Proceedings,* pp. 39-42 (1996).

Chang, H., Jameel, H. and Kumar, K., "Effect of Pulping Conditions on the Bleachability of Hardwoods", *Tappi Pulping Conference Proceedings* (1995).

Chen, J., Hayashi, J., Shimizu, Y., and Takai, M., "Effect of Cooking Conditions on Efficiency of Oxygen Delignification; Structural Characteristics of Residual Lignin in Oxygen-Delignified Pulp", *Journal of the Japan Wood Research Society*, 42(5): 497-505 (1996).

Cole, B.J., <u>Wood Chemistry, A Course in Introductory Wood Chemistry</u>, the University of Maine, 1999.

Edwards, L., and Norberg, S. E., "Alakline Delignification: A General Model Applied To Oxygen Bleaching And Kraft Pulping", *Tappi,* 56 (11): 108-111(1973).

Evans, R. and Wallis, A., "Cellulose Molecular Weights Determined by Viscometry", *Journal of Polymer Science*, Vol.37, pp2331-2340 (1989).

Fengel, D., and Wegener, G., <u>Wood, Chemistry, Ultrastructure, Reactions</u>, Walter de Gruyter, Berlin, Chapters 5 and Chapter 6, pp. 106-181 (1984).

Foust, A. S., Wenzel, L. A., Clump, C. W., Maus, L., and Andersen, L. B., <u>Principles of Unit Operations</u>, p81, John Wiley & Sons, Inc., New York (1960).

Froass, P., Ragauskas, A., McDonough, T., and Jiang J., "Relationship between residual lignin structure and pulp bleachability", *International Pulping and Bleaching Conference*, pp:163-169 (1996).

Gellerstedt, G., Li, J. and Sevastyanova, O., "The Relationship Between Kappa Number and Oxidizable Structures in Bleached Kraft Pulps", *International Pulping and Bleaching Conference* (2000).

Genco, J., Busayasakul, N., Medhora, H. K., and Robbins, W., "Hemicellulose Retention During Kraft Pulping", *Tappi*, 73(4): 223-233 (1990).

Genco, J., Zorn, K. and Cole, B., "Estimation of Pulp Yield Loss in Oxygen Delignification Using COD Measurements," *Tappi Pulping Conference Proceedings,* (2000).

Gierer, J., "The Reaction of Lignin during Pulping, a Description and Comparison of Conventional Pulping Process", *Svensk Papperstion.* 73, 571-596.

Gierer, J. and Imsgard, F., "The Reaction of Lignin with Oxygen and Hydrogen Peroxide in Alkaline Media", *Svensk Papperstidng*, 80(16): 510(1977).

Gierer, J., "Chemistry of delignification", *Wood Science and Technology, 19*: 289-312(1985).

Gierer, J., "Chemistry of delignification", *Wood Science and Technology, 20*: 1-33(1986).

Gilbert, C., and Hsieh J., "ECF bleachability comparison between conventional kraft and kraft-AQ softwood pulp", *Tappi Pulping Conference Proceedings,* pp.921-930 (1997).

Godsay, M.P. and Pearce, E.M., "Physico-Chemical Properties of Ozone Oxidized Kraft Pulps" in Oxygen Delignification Symp. Tappi Press, Atlanta, pp 55-70 (1984).

Grace, T.M. and Malcolm, E.W., Alkaline Pulping. Published by the Technology Section Canadian Pulp & Paper Association (1989).

Guay, D., Ph.D. thesis, The University of Maine (1999).

Gustafson, R. R., Ricker, N. L., "Use of Simulation in the Optimization of the Kraft Pulping Process", *Tappi,* 65 (11): 115-118 (1982).

Gustavsson, C., Sjostrom, K., and Wafa Aldajani, W., "Influence of Cooking Conditions on the Bleachability and Chemical Structure of Kraft Pulps", *Nordic Pulp and Paper Research Journal* 14, No. 1:71-81(1999).

Guven, E., Genco, J. M., Miller, W., and Hart, P., "Medium Consistency Oxygen Delignification of Southern Hardwoods", *AICHE Symposium Series,* 92: 10-28 (1996).

Hatton, J. V., "Development of Yield Prediction Equations in Kraft Pulping", *Tappi* 56(7): 97-100 (1973).

Hatton, J. V., "The Potential of Process Control in Kraft Pulping of Hardwoods Relative to Softwoods", *Tappi* 59(8): 48-50 (1976).

Holton, H.H., U.S. paten, 4,012280 (March 15, 1977).

Hsu, C. L., and Hsieh, J. S., "Effects of Mass Transfer on Medium-Consistency Oxygen Bleaching Kinetics", *Tappi,* 68(11): 126-130 (1985).

Iribarne, J. and Schroeder, L., "High-pressure Oxygen Delignification of Kraft Pulps, Part I: Kinetics", *Tappi,* 80(10): 241-250 (1997).

Jiang, Z. and Argyropoulos, D., "Isolation and Characterization of Residual Lignins in Kraft Pulps", *Journal of Pulp and Paper Science,* 25(1), (1999).

Johansson, E. and Ljunggren, S., "The Kinetics of Lignin Reaction during Oxygen Delignification, Part 4. The Reactivates of Different Lignin Model Compounds and the Influence of Metal ions on the Rate of Degradation", *Journal of Wood Chemistry and Technology* 14(4): 507 (1994).

Johnsson, L., "Mathematics Model of The Kraft Cooking Process", ACTA Polytechnica Scandinavica Math. Comp. Mach. Ser. No. 22 ST'M (1971).

Kerr, A.J., "The Kinetics of Kraft Pulping: Process in the Development of a Mathematics Model", APPITA 24(3):180 (1970).

Kettunen, A., Ramark, H., Harsia, K., and Henricson, K., "Effect of cooking stage EA concentration profiles on softwood kraft pulping", *PAPERI JA PUU- PAPER AND TIMBER* V. 79(4): 232-239 (1994).

Kubes, G.J., Fleming, B.I., Macleod, J.M., and Bolker, H.I., "Viscosities of Unbleached Alkaline Pulps. II. The G-Factor", *Pulp and Paper Reports*, March, 1981.

Kumar, K., et al., "Bleachability difference between RDH and kraf-O2 pulp-role of phenolic hydroxyl groups in the residual lignin", *1996 International Pulp Bleaching Conference, Tappi Proceedings*, pp. 147 - 162 (1996).

Lachenal, D., and Chirat, C., "About the Efficiency of the Most Common Bleaching Agents", *1999 Tappi Pulping Conference*, pp: 623-630, Orlando, Florida, (1999).

Lai, Y. and Yang, R., "Influence of Sulfidity in Kraft pulping on Nature of Residual Lignin", *Journal of Wood Chemistry and Technology*, 17 (4): 383-390 (1997).

Levenspiel, O., Chemical Reaction Engineering, John Wiley & Sons, Inc., 1972.

Li, J. and Gellerstedt, G., "The Contribution to Kappa Number from Hexenuronic Acid Groups in Pulp Xylan", *Carbohydrate Research*, 302, pp. 213-218 (1997).

Liebergott, N., van Lierop, B., Teodorescu, G., Kubes, G. J., "Comparison Between Low- and High-Consistency Oxygen Delignification of Kraft Pulps", *Tappi Pulping Conference*, pp. 213-232 (1985).

Lin, C. P., Mao, W. Y., and Jane, C. Y., "Development of a Kappa-Number prediction Equation in Kraft Pulping for All Types of Hardwood", *Tappi*, 61 (2): 72 (1978).

Ljunggren, S.C.H. and Johansson, E.C., "Reaction Kinetics of Lignin Structures during Oxygen Bleaching - Effects of Solvent, Oxygen Pressure and pH", *1987 International Oxygen Delignification Conference, Tappi Proceedings*, p.125 (1987).

Matthews, C., "Carbohydrate Losses at High Temperature in Kraft Pulping", *Svensk Papperstidng*, 17: 629 (1974).

McDonough, T. J., "Oxygen Bleaching", contained in Dence, C. W. and Reeve, D. W., Pulp Bleaching, Principles and Practice, Tappi Press, pp. 213-239 (1996).

Miller, W., Kwon, H., Liukkonen, A., and Genco, J. M., "Medium Consistency Oxygen Delignification Design Utilizing a Two Phase Concept – Part 1", *Tappi Pulping Conference Proceedings*, pp. 393-403 (1995).

Mimms, A., Koucurek, M., Pyatte; J., and Wright, E., Kraft Pulping—A compilation of Notes, Tappi press (1993).

Olm, L., and Teder, A., "The Kinetics of Oxygen Bleaching", *Tappi* 62(12):43(1979).

Parthasarathy, V. R., "Conversion of (D, C+D)*(EO)DED Sequence to O_{2P}(D,C+D)(EO)DD Sequence for Chemical Savings and Pollution Abatement, *TAPPI Pulping Conference Proceedings*, p. 185 (1992).

Pazz, J. and Solis, A., "Effect of Cooking Conditions on the Bleachability of Pinus Radiata Prolonged Kraft Pulp", *Tappi Pulping Conference Proceedings,* p.33 (1996).

Poukka, O., Isotalo, I., and Gullichsen, J., "Optimal Delignification Degrees of Cooking and Oxygen /Alkali Stage in Production of ECF Bleached Softwood Kraft", *PAPERI JA PUU- PAPER AND TIMBER,* 81(4): 316-324 (1999).

Rawat, N. and Madoungh, J., "Effects of Pulping Conditions on the Bleachability of Hardwood Kraft Pulps: 1. Effect of Effective Alkali Charge in the Pulping of Birth and Maple", *Tappi Pulping Conference Proceedings,* pp. 883-891 (1998).

Schoon, N. H., "Interpretation of Rate Equations from Kinetic Studies of Wood Pulping and Bleaching", *Svensk Papperstidng*, R185–R193 (1982).

Sing, R., P. and Dilner, B., C., The Bleaching of Pulp, Tappi Press, pp. 159-206 (1979).

Sjogren, B. and Hook, J., "Extended Oxygen Delignification—The Effect of Pretreatments and Process Conditions", *International Pulping and Bleaching Conference*, (2000).

Sjöström, E., Wood Chemistry, Fundamentals and Applications, Academic Press, New York, p. 208 (1993).

Sjöström, K., "Kraft Cooking with Varying Alkali Concentration—Influence on TCF Bleachability", *Nordic Pulp & Paper Journal,* 13 (1): 57-63 (1998).

Sjöström, K. and Teder, A., "Changes within the Modified Kraft Process Aiming to Improve TCF Bleachability", *Journal of Pulp and Paper Science,* 25 (5): 176-182 (1999).

Smook, G.A., Handbook for Pulp & Paper Technology. Angus Wilde Publications, second edition, pp. 74-83 (1992).

Suss, H., and Kronis, J., "The Correlation of COD and Yield in Chemical Pulp Bleaching", *1998 Tappi Breaking the Pulp Yield Barrier Symposium,* Atlanta, Georgia, pp.153-162 (1998).

Tamminen, T. L. and Hortling, B. R., "Lignin Reactions during Oxygen Delignification of Various Alkaline Pulps", Oxidative Delignification Chemistry : Fundamentals and Catalysis, Argyropoulos (Washington, DC, American Chemical Society : Distributed by Oxford University), pp. 73-91 (2001).

Tasman, J. E., "Kraft Delignification Models", *Tappi,* 64 (3): 175-176 (1981).

Vincent, A., Nguyen, K., and Mathews, J., "Kinetics of Oxygen Delignification of Eucalypt Kraft Pulp", *Appita,* 47 (3): 217-220 (1994).

Violette, S. and van Heiningen, A., "Selectivity Improvement during Oxygen Delignification by Adsorption of Polymeric Additives," *88th Annual Meeting, PAPTAC 88e Congres Annuel* (2001).

Vroom, K.E., *Pulp and Paper Mag. Canada,* 58:228-31 (1957).

Wilder, H.D. and Daleski, E.J., *Tappi* 47 (5):270 (1964).

Yan, J. F., "Delignification: A Molecular Approach", *Science*, 215 (4538): 1390-1392 (1982).

Zou, H., M.S. thesis, The University of Maine, 2000.

Zou, H., Liukkonen, A., Cole, B., Genco, J., and Miller, W., "Influence of Kraft Pulping on the Kinetics of Oxygen Delignification", *Tappi*, 83(2), pp 65-71 (2000).

APPENDIX A

SUMMARY OF KRAFT PULPING DATA

APPENDIX A

SUMMARY OF EXPERIMENTAL DATA

A.1. KRAFT COOKING DATA

Table A.1.
Kraft pulping conditions that varied cooking temperature and effective alkali

	Conditions
Northeastern Hardwood Chips (g)	2000
Effective Alkali (%)	12, 21
Sulfidity (%)	30
Temperature (°C)	160, 180
Liquor to Wood Ratio	4
Target Kappa Number	16 and 20

Table A.2.
Summary of kraft pulping results - effect of temperature and effective alkali

ID	Effective Alkali %	Temperature (°C)	Sulfidity (%)	Time at Temperature (Minute)	H-factor	Screened Yield (%)	Reject (%)	Total Yield (%)	Kappa Number	Intrinsic V. (ml/g)	Brightness (%, ISO)
A-1	12	160	30	464	3065	49.94	0.151	50.10	16.3	1244	27.12
B2/B4	12	180	30	72	2621	48.30	2.303	50.61	20.6	1104	23.80
C-2	21	160	30	42	333	47.07	0.410	47.48	15.7	1123	34.39
D-2	21	180	30	4	388	44.56	2.315	46.88	16.1	900	36.12
D-3	21	180	30	1	281	45.26	2.905	48.17	19.1	1003	34.80

Table A.3.
Kraft pulping conditions that varied AQ to give high hemicellulose pulps

	Conditions
Northeastern Hardwood Chips (g)	2000
Effective Alkali (%)	12
AQ (%)	0.1, 1, 4%
Sulfidity (%)	30
Temperature (°C)	160
Liquor to Wood Ratio	4
Target Kappa Number	15-16

Table A.4.
Summary of kraft pulping results - effect of pulp yield caused by addition of AQ

ID	Effective Alkali %	Temp. (°C)	Sulfidity (%)	Additives AQ %	Time at temp. min	H-factor	Screened Yield (%)	Reject (%)	Total Yield (%)	Kappa Number	Intrinsic V. (ml/g)	Brightness (%, ISO)
SODA#4	21	160	0		218	1517	45.84	0.117	45.96	16.2	854	33.95
Control	12	160	30		464	3065	49.94	0.151	50.10	16.3	1244	27.10
AQ 0.1%	12	160	30	0.1	246	1694	52.22	0.285	52.50	17.5	1239	29.52
AQ 1.0%	12	160	30	1.0	185	1271	54.11	0.200	54.31	17.2	1157	26.31
AQ 4.0%	12	160	30	4.0	171	1247	56.06	0.250	56.31	17.6	1130	27.13

Table A.5.
Summary of kraft pulping results - low effective alkali and high tempearture

ID	Effective Alkali %	Temp. (°C)	Sulfidity (%)	Time at temp. min	H-factor	Screened Yield (%)	Reject (%)	Total Yield (%)	Kappa Number	Brightness % ISO	Residual pH	Residual AA (g/l)	Intrinsic Viscosity
B1	12	160	30	59	2119	48.64	2.468	51.11	*20.9*	24.33	11.03	4.65	1127
B2	12	160	30	85	3122	47.96	2.138	50.10	*20.3*	23.61	10.82	4.34	1080
B3	12	160	30	102	3713	47.58	1.570	49.15	*21.8*	23.15	10.74	3.32	1050
B4	12	160	30	139	5011	47.48	1.225	48.71	*21.7*	22.80	10.56	3.10	1041

Table A.6.

Summary of kraft pulping results – effect of high AQ addition on kappa number

ID	Effective Alkali (%)	Temperature. (°C)	Sulfidity (%)	Additives (% AQ)	Time at temp. (min)	H-factor (hour)	Screened Yield (%)	Reject (%)	Total Yield (%)	Kappa Number
AQ#3	12	160	30	4.0	108	819	55.88	0.593	56.47	17.95
AQ#4	12	160	30	4.0	121	901	56.45	0.605	57.06	18.87
AQ#5	12	160	30	4.0	144	1018	56.50	0.285	56.78	18.53
AQ#6	12	160	30	4.0	171	1247	56.06	0.250	56.31	17.64

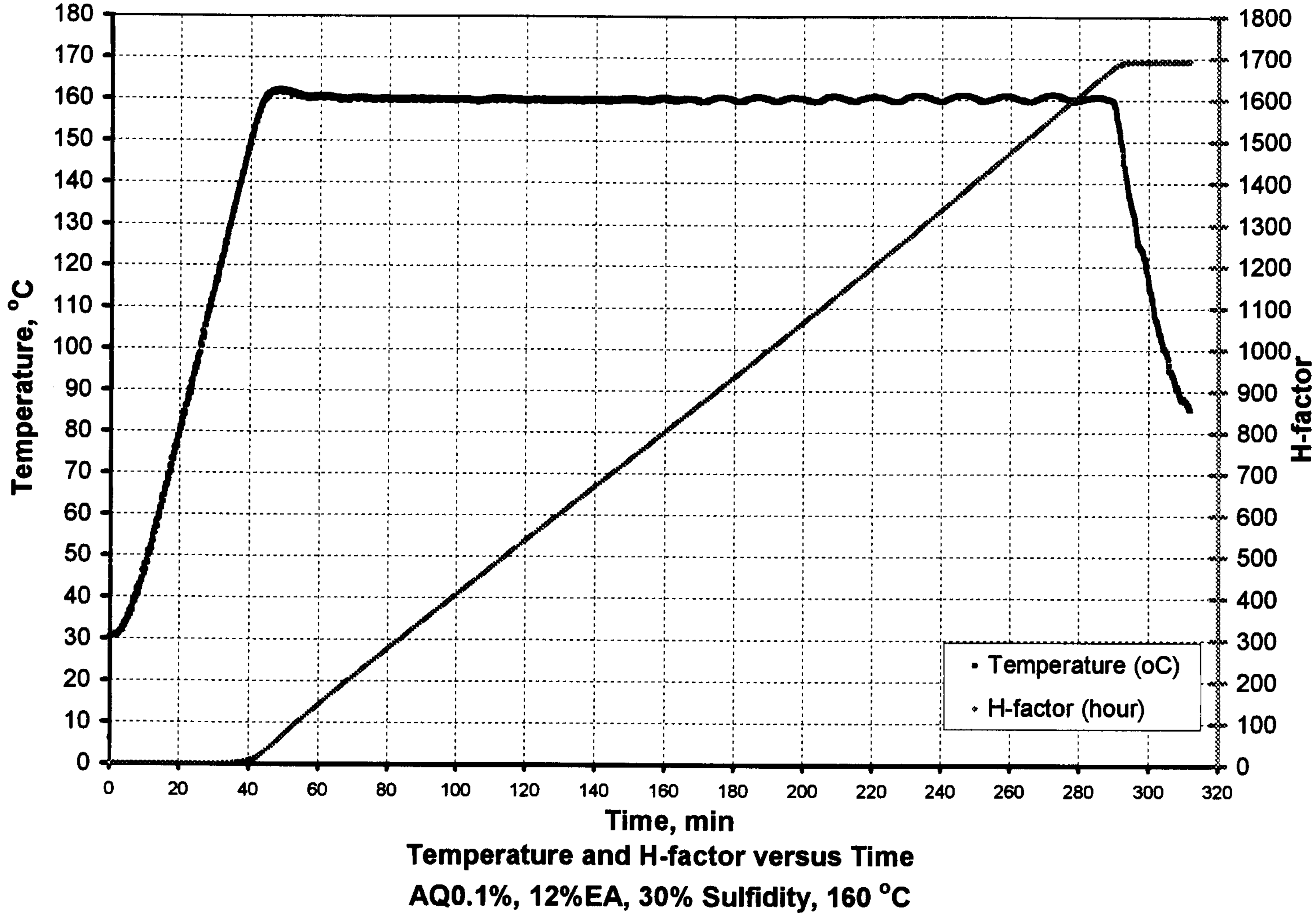


Figure A.1. Typical Kraft pulping heat up curve – Kraft pulping with 0.1% anthraquinone additive.

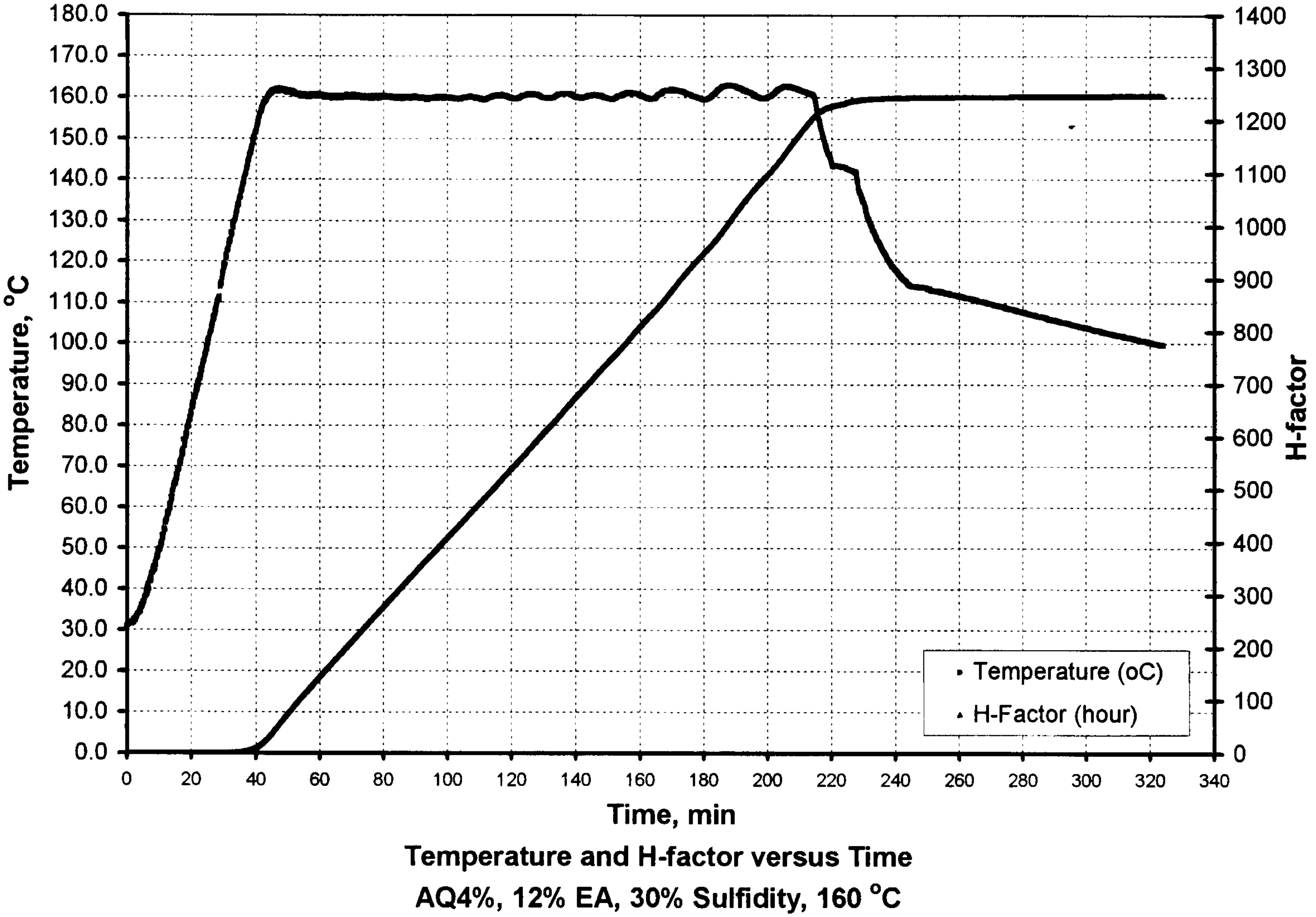
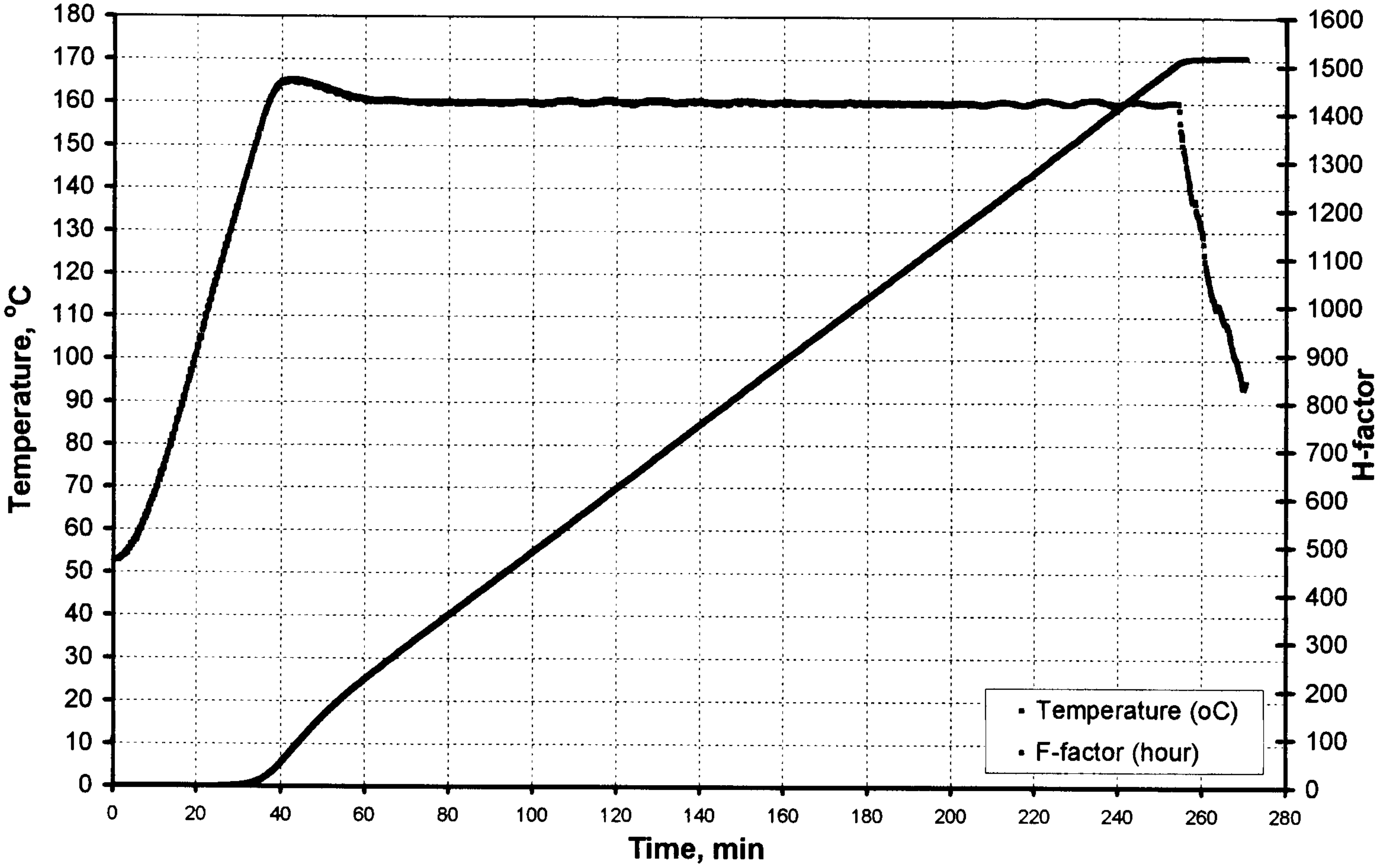


Figure A.2. Typical Kraft pulping heat up curve – Kraft pulping with 4% anthraquinone additive.



Temperature and H-factor versus Time

SODA Pulping, 21%EA, 0% Sulfidity, 160 °C

Figure A.3. Typical Soda pulping heat up curve – Soda pulping with 21% EA at 160 °C.

APPENDIX B

SUMMARY OF OXYGEN DELIGNIFICATION DATA

APPENDIX B

SUMMARY OF OXYGEN DELIGNIFICATION DATA

Table B.1.
Oxygen delignification conditions.

	Conditions
Temperature (°C)	90
Caustic addition (%)	1.5
Oxygen pressure (psig)	100
Pressure in Argon Experiments (psig)	100
Reaction time (minute)	0, 5, 15, 30, and 60
Amount of $MgSO_4$ used (%)	0.1

Table B.2.
Summary of oxygen delignification data for sample A-1 [12% EA, 160 °C (16 Kappa)].

O_2 minute	End pH	R. NaOH g/l	Kappa Number	$(K_0-K)/K_0$ %	$(K_0-K)/K_0$ Zero Time	Brightness % ISO	COD mg/L	Yield %	Intrinsic V. ml/g	Tappi V. cp	DP from Intrinsic V.
BS	11.00	4.65	16.2	0	A1	27.12		100.00	1244	58.5	4790
0 min	12.44	1.38	14.3	11.46	0.00	28.67	1341	97.57	1231	56.9	4736
5 min	12.40	1.16	13.0	20.02	9.68	31.99	2189	97.24	1190	51.9	4560
15 min	12.33	1.04	12.0	26.03	16.46	35.54	3021	97.15	1147	47.0	4375
30 min	12.18	0.82	11.1	31.65	22.81	37.97	3609	96.98	1092	41.2	4143
60 min	12.02	0.66	10.1	37.80	29.76	42.61	4473	96.80	1068	38.8	4043

Table B.3.
Summary of oxygen delignification data for sample B2/B4 [12% EA, 180 °C (20 Kappa)].

O_2 minute	End pH	R. NaOH g/l	Kappa Number	$(K_0\text{-}K)/K_0$ %	$(K_0\text{-}K)/K_0$ Zero Time	Brightness % ISO	COD mg/L	Yield %	Intrinsic V. ml/g	Tappi V. cp	DP from Intrinsic V.
BS			21.4	0	D3	23.8		100.00	1104	42.5	4195
0 min	12.43	1.28	18.1	15.34	0.00	25.2	1703	97.88	1092	41.2	4144
5 min	12.34	1.04	16.2	24.53	10.85	29.3	2729	97.57	1041	36.3	3931
15 min	12.03	0.84	14.6	31.73	19.36	32.2	3779	97.34	1008	33.3	3793
30 min	11.36	0.66	13.1	38.61	27.48	35.1	4800	96.97	985	31.3	3697
60 min	10.16	0.56	12.0	44.11	33.98	37.4	5240	96.59	974	30.3	3650

Table B.4.
Summary of argon delignification data for sample B2/B4 [12% EA, 160 °C (20 Kappa)].

Ar minute	End pH	R. NaOH g/l	Kappa Number	$(K_0\text{-}K)/K_0$ %	$(K_0\text{-}K)/K_0$ Zero Time	Brightness % ISO	COD mg/L	Yield %	Intrinsic V. ml/g	Tappi V. cp	DP from Intrinsic V.
BS			21.4	0		23.8		100.00	1104	42.5	4195
0 min	12.43	1.28	18.1	15.34	0.00	25.2	1703	97.88	1092	41.2	4144
5 min	12.43	1.24	17.7	17.47	2.51	28.1	2231	97.66	1088	40.8	4127
15 min	12.44	1.22	17.7	17.21	2.21	28.0	2192	97.74	1078	39.8	4085
30 min	12.42	1.22	17.6	17.70	2.78	27.1	2371	97.67	1073	39.3	4064
60 min	12.43	1.20	17.8	16.88	1.81	27.3	2448	97.58	1072	39.2	4059

Table B.5.
Summary of oxygen delignification data for sample C-2 [21% EA, 160 °C (16 Kappa)].

O_2 minute	End pH	R. NaOH g/l	Kappa Number	$(K_0\text{-}K)/K_0$ %	$(K_0\text{-}K)/K_0$ Zero Time	Brightness % ISO	COD mg/L	Yield %	Intrinsic V. ml/g	Tappi V. cp	DP from Intrinsic V.
BS	12.38	28.83	15.6	0	C2	34.4		100.00	1123	44.5	4277
0 min	12.60	1.34	13.5	13.54	0.00	37.1	572	98.60	1110	43.1	4220
5 min	12.55	1.24	11.9	23.64	11.69	41.5	1447	98.15	1055	37.6	3987
15 min	12.42	1.10	10.8	30.75	19.91	45.3	2221	97.51	1008	33.2	3790
30 min	12.25	0.96	10.0	36.10	26.10	47.5	2836	97.01	975	30.4	3653
60 min	11.96	0.78	9.1	41.76	32.64	50.7	3360	96.63	926	26.5	3452

Table B.6.
Summary of oxygen delignification data for sample D-2 [21% EA, 180 °C (16 Kappa)].

O_2 minute	End pH	R. NaOH g/l	Kappa Number	$(K_0\text{-}K)/K_0$ %	$(K_0\text{-}K)/K_0$ Zero Time	Brightness % ISO	COD mg/L	Yield %	Intrinsic V. ml/g	Tappi V. cp	DP from Intrinsic V.
BS	12.36	28.06	15.7	0	D2	36.1		100.00	900	24.6	3343
0 min	12.52	1.32	14.0	10.70	0.00	37.1	625	98.69	891	23.9	3306
5 min	12.44	1.26	12.0	23.31	14.12	41.9	1579	97.87	859	21.7	3174
15 min	12.38	1.10	11.1	29.04	20.54	44.8	2231	97.72	837	20.2	3084
30 min	12.14	0.92	10.1	35.61	27.89	47.0	2788	96.94	799	17.8	2928
60 min	11.44	0.78	9.2	41.40	34.38	50.5	3593	96.91	760	15.6	2772

Table B.7.
Summary of oxygen delignification data for sample D-3 [12% EA, 160 °C (20 Kappa)].

O_2 minute	End pH	R. NaOH g/l	Kappa Number	$(K_0\text{-}K)/K_0$ %	$(K_0\text{-}K)/K_0$ Zero Time	Brightness % ISO	COD mg/L	Yield %	Intrinsic V. ml/g	Tappi V. cp	DP from Intrinsic V.
BS	13.16	29.61	18.7	0	D3	34.8		100.00	1003	32.8	3771
0 min	12.51	1.30	16.6	11.23	0.00	37.4	479	98.50	992	31.9	3725
5 min	12.30	1.04	14.6	21.76	11.87	40.8	2308	98.10	958	29.1	3585
15 min	12.08	0.88	13.5	27.70	18.55	43.1	2952	97.61	936	27.3	3493
30 min	11.82	0.78	12.4	33.80	25.42	46.5	3508	97.06	912	25.4	3393
60 min	10.68	0.64	11.4	39.04	31.33	48.3	3968	96.98	887	23.6	3288

Table B.8.
Summary of oxygen delignification data for sample SODA [21% EA, 160 °C (16 Kappa)].

O_2 minute	End pH	R. NaOH g/l	Kappa Number	$(K_0\text{-}K)/K_0$ %	$(K_0\text{-}K)/K_0$ Zero Time	Brightness % ISO	COD mg/L	Yield %	Intrinsic V. ml/g	Tappi V. cp	DP from Intrinsic V.
BS			16.2	0		33.95		100.00	854	21.4	3155
0 min	12.63	1.42	14.8	9.22	0.00	35.31	605	98.58	833	20.0	3069
5 min	12.47	1.30	12.8	21.11	13.09	38.95	1680	98.43	796	17.6	2915
15 min	12.15	1.12	11.0	32.38	25.51	40.93	2630	98.30	749	15.0	2727
30 min	11.95	1.00	10.0	38.28	32.01	43.06	3095	98.09	730	14.0	2649
60 min	10.50	0.78	8.9	45.16	39.59	46.12	3895	97.85	700	12.5	2528
Xylose 60	8.95	0.24	11.8	27.38	20.01	40.29		98.12	748	15.0	2723
Xylan 60	9.95	0.70	8.7	46.46	41.02	44.38		98.17	688	12.0	2480

Table B.9.

Summary of oxygen delignification data for sample AQ 0.1% [12% EA, 160 °C (16 Kappa)].

O_2 minute	End pH	R. NaOH g/l	Kappa Number	$(K_0\text{-}K)/K_0$ %	$(K_0\text{-}K)/K_0$ Zero Time	Brightness % ISO	COD mg/L	Yield %	Intrinsic V. ml/g	Tappi V. cp	DP from Intrinsic V.
BS			17.5	0		29.52		100.00	1239	57.8	4767
0 min	12.60	1.40	16.1	8.29	0.00	29.48	1500	97.82	1228	56.5	4722
5 min	12.48	1.26	14.7	15.98	8.39	32.19	2440	97.72	1187	51.5	4545
15 min	12.40	1.08	13.3	23.78	16.90	34.58	3095	97.34	1150	47.4	4391
30 min	12.28	0.92	12.1	30.81	24.55	36.39	3885	97.19	1113	43.4	4234
60 min	11.87	0.72	10.8	38.11	32.52	40.83	4550	96.86	1101	42.2	4184

Table B.10.

Summary of oxygen delignification data for sample AQ 1.0% [12% EA, 160 °C (16 Kappa)].

O_2 minute	End pH	R. NaOH g/l	Kappa Number	$(K_0\text{-}K)/K_0$ %	$(K_0\text{-}K)/K_0$ Zero Time	Brightness % ISO	COD mg/L	Yield %	Intrinsic V. ml/g	Tappi V. cp	DP from Intrinsic V.
BS			17.2	0		26.31		100.00	1157	48.1	4418
0 min	12.60	1.30	15.5	9.84	0.00	28.78	2185	97.65	1145	46.8	4368
5 min	12.55	1.12	14.3	16.76	7.67	29.95	2665	97.32	1130	45.2	4305
15 min	12.48	0.92	12.9	25.00	16.81	31.24	3545	97.12	1091	41.1	4140
30 min	12.15	0.70	11.7	32.03	24.61	33.58	4510	97.04	1062	38.2	4017
60 min	11.71	0.58	10.8	37.11	30.25	36.41	5085	96.68	1036	35.8	3909

Table B.11.
Summary of oxygen delignification data for sample AQ 4.0% [12% EA, 160 °C (16 Kappa)].

O_2 minute	End pH	R. NaOH g/l	Kappa Number	$(K_0\text{-}K)/K_0$ %	$(K_0\text{-}K)/K_0$ Zero Time	Brightness % ISO	COD mg/L	Yield %	Intrinsic V. ml/g	Tappi V. cp	DP from Intrinsic V.
BS			17.6	0		27.13		100.00	1130	45.2	4305
0 min	12.62	1.40	15.5	12.09	0.00	26.85	1630	96.78	1133	45.5	4316
5 min	12.55	1.32	14.5	17.85	6.55	28.76	2250	96.61	1116	43.7	4246
15 min	12.51	1.20	13.4	23.77	13.30	30.83	2780	95.87	1090	41.0	4136
30 min	12.47	1.10	12.8	27.44	17.47	32.41	3135	95.59	1062	38.2	4017
60 min	12.28	0.92	11.5	35.05	26.12	35.12	4280	95.00	1042	36.4	3935

APPENDIX C

SUMMARY OF CAUSTIC LEACHING DATA

APPENDIX C

CAUSTIC LEACHING DATA

Initial experiments were conducted on caustic leaching. The objective of this work was to partially remove hemicelluloses from the pulp sample without changing the kappa number, which is decrease the pulp yield without appreciably changing the kappa number. Unfortunately, this work was not successful. The experiments showed that the alkali leaching significantly removed lignin and resulted in a lower kappa number without significantly removing the hemicellulose polymers. These data are shown in Figure C.1. In this figure, the COD content of the residual liquor was almost constant after an initial increase.

Table C.1.
Summary of leaching data for low caustic addition rates.

Sample ID	NaOH %	Consistency %	Temperature °C	Time (min)	Kappa Number	Brightness (% ISO)	Intrinsic V. (ml/g)	Tappi V. (c.p.)
BS					21.4	23.8	1104	42.5
B2/B4-CE1	0.50	3.0	***12~15***	60.0	18.4	23.1	1088	40.8
B2/B4-CE2	1.00	3.0	***12~15***	60.0	18.1	23.1	1080	40.0
B2/B4-CE3	1.50	3.0	***12~15***	60.0	18.0	23.5	1098	41.8

Table C.2.
Summary of leaching data at elevated caustic addition rates.

Sample ID	NaOH (%)	Consistency (%)	Temperature (°C)	Time (min)	Kappa Number	Brightness % ISO	Intrinsic V. (ml/g)	Tappi V. (c.p.)	COD mg/g.pulp
BS					21.4	23.80		42.5	
B2/B4-CE4	0.00	3.0	***25***	60.0	18.4	25.15	1094	41.5	12.3
B2/B4-CE5	1.00	3.0	***25***	60.0	17.7	25.62	1080	40.1	13.3
B2/B4-CE6	2.00	3.0	***25***	60.0	17.6	25.76	1097	41.7	13.4
B2/B4-CE7	3.50	3.0	***25***	60.0	17.5	25.82	1084	40.4	13.5
B2/B4-CE8	7.50	3.0	***25***	60.0	17.6	26.27	1075	39.6	13.6
B2/B4-CE9	13.00	3.0	***25***	60.0	17.2	26.64	1072	39.2	15.4

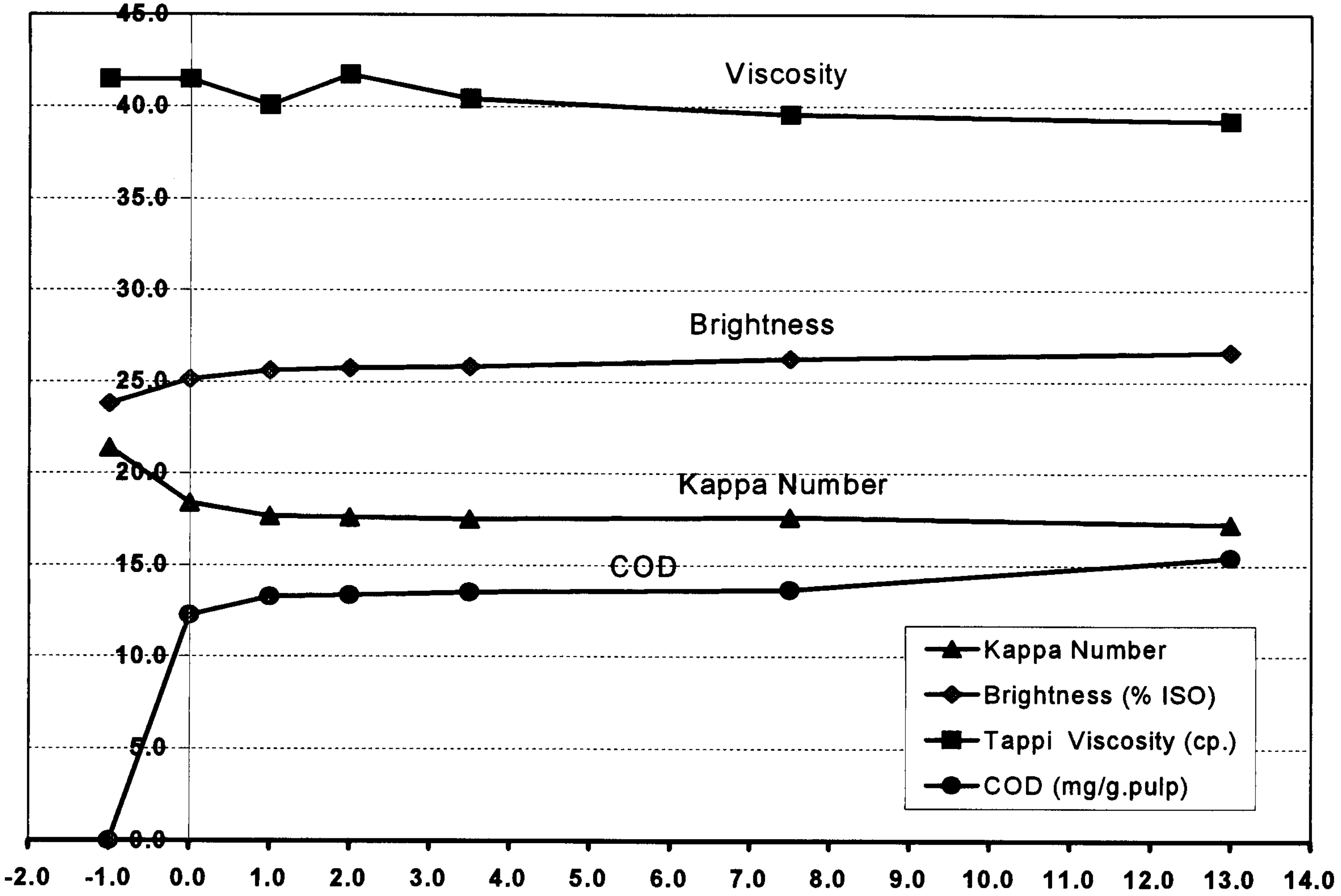


Figure C.1. Alkali leaching study results for elevated caustic addition rates.

APPENDIX D

SUMMARY OF CHEMICAL COMPOSITION DATA

Table D.1.

Summary of chemical composition data.

Sample ID	Ash (%)	Extractives (%)	Total Lignin (%)	Uronic Anhydride (%)	Arabinan (%)	Galatan (%)	Glucan (%)	Xylan (%)	Mannan (%)	Cellulose (%)	Hemi-cellulose (%)
SODA BS	0.11	0.14	3.10	0.14	0.18	0.04	77.80	17.77	0.95	77.24	19.66
A-1 BS	0.12	0.12	2.31	0.24	0.10	0.23	74.98	21.56	0.56	74.65	23.04
AQ0.1% BS	0.17	0.14	2.33	0.24	0.46	0.47	73.36	22.37	0.76	72.91	24.75
AQ1.0% BS	0.16	0.23	2.24	0.18	0.13	0.31	72.25	23.64	1.23	71.53	26.24
AQ4.0% BS	0.18	2.26	2.32	0.17	0.22	0.27	71.70	24.09	1.23	70.97	26.71
B2/B4 BS	0.16	0.16	3.36	0.18	0.11	0.19	75.48	20.24	0.44	75.22	21.42
B2/B4 Ar	0.14	0.12	2.83	0.19	0.10	0.19	76.12	20.02	0.54	75.81	21.36
C-2 BS	0.13	0.14	2.60	0.10	0.10	0.29	79.06	17.29	0.56	78.72	18.67
D-2 BS	0.11	0.12	2.74	0.11	0.07	0.12	79.70	16.54	0.71	79.28	17.98
D-3 BS	0.13	0.13	3.15	0.10	0.11	0.26	79.17	16.58	0.63	78.79	18.06
SODA O_2 60 min	0.10	0.12	1.45	0.04	0.09	0.14	80.29	17.30	0.70	79.88	18.67
A-1 O_2 60 min	0.11	0.12	1.18	0.09	0.13	0.24	77.38	20.36	0.61	77.02	21.80

Table D.1. (continued)

Sample ID	Ash (%)	Extractives (%)	Total Lignin (%)	Uronic Anhydride (%)	Arabinan (%)	Galatan (%)	Glucan (%)	Xylan (%)	Mannan (%)	Cellulose (%)	Hemi-cellulose (%)
AQ0.1% O_2 60 min	0.12	0.12	1.35	0.14	0.07	0.15	75.76	21.65	0.86	75.25	23.40
AQ1.0% O_2 60 min	0.11	0.14	1.36	0.13	0.12	0.24	74.98	22.31	0.86	74.48	24.16
AQ4.0% O_2 60 min	0.13	0.64	1.42	0.18	0.28	0.30	73.04	23.34	1.42	72.20	26.38
B2/B4 O_2 60 min	0.12	0.12	1.94	0.18	0.19	0.26	76.48	20.05	0.88	75.96	22.10
C-2 O_2 60 min	0.11	0.14	1.56	0.15	0.12	0.22	80.06	16.96	0.93	79.51	18.93
D-2 O_2 60 min	0.12	0.12	1.58	0.12	0.31	0.34	80.49	15.98	1.17	79.80	18.62
D-3 O_2 60 min	0.11	0.14	1.97	0.11	0.13	0.18	81.32	15.27	1.02	80.72	17.31

APPENDIX E

RAYLEIGH DISSOLUTION MODEL

APPENDIX E

RAYLEIGH DISSOLUTION MODEL

If the original mass of pulp in the oxygen reactor is (M_o), then at any time the initial mass of pulp must equal the total mass dissolved in the liquid phase (D) and mass of pulp remaining as pulp in the reactor (M).

$$M_o = D + M \tag{E.1}$$

The yield is simply the ratio (M/M_o) which is related to the mass fraction of material that was dissolved (δ).

$$\frac{M}{M_o} + \frac{D}{M_o} = 1 \tag{E.2}$$

$$Y + \delta = 1 \tag{E.3}$$

The loss in mass of the pulp (-dM) is equal to the change in mass of dissolved solids (dD). This equation assumes that no lignin is converted to carbon dioxide CO_2 or oxygen is incorporated into the dissolved solids.

$$-dM = +dD \tag{E.4}$$

Similarly, at any time during the oxygen delignification process, the mass of lignin that exists in the oxygen reactor is (M^*x_l), where x_l is the weight fraction lignin. If (dM) kilograms of composition x_l are removed from the pulp, then the lignin from the wood pulp goes into the liquid phase at lignin fraction (y_l). Thus, a lignin balance will become:

(Lignin in the pulp at any time) = (Lignin dissolved in liquid phase) +

(Lignin remaining in the pulp) (E.5)

$$M\,x_1 = (d\,M) * y_1 + (M - dM) * (x_1 - d\,x_1) \tag{E.6}$$

Expanding equation (E.6) and neglecting 2nd order differentials yields:

$$\frac{dM}{M} = \frac{d\,x_1}{(y_1 - x_1)} = d\ln M \tag{E.7}$$

A fundamental question relates to how the weight fraction of lignin in the dissolve solids (y_1) relates to the weight fraction lignin in the pulp being dissolved. The change in lignin entering the liquid phase as dissolved solids (dy_1) is assumed to be proportional to the mass of lignin in the pulp

$$dy_1 = k\,dx_1 \tag{E.8}$$

where k is a distribution coefficient. The simplest possible function relating the lignin content in the liquid (y_1) to that in the solid (x_1) phase can be obtained by integrating equation (E.8) between (0,0) and any point (x_1, y_1) (Figure E.1):

$$\int_0^{y_1} dy_1 = k\int_0^{x_1} dx_1 \quad or \quad y_1 = k\,x_1 \tag{E.9}$$

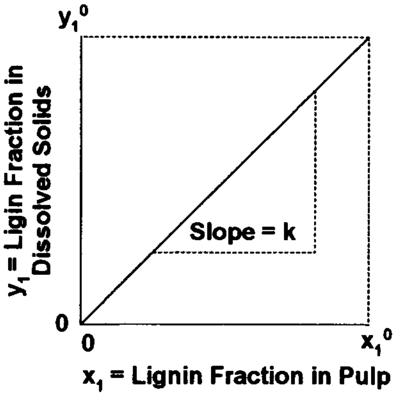


Figure E.1. Relation between lignin fraction in solid phase and liquid phase

If equation (E.9) is substituted into equation (E.7) and integrated, the results will be equation (6) given in the text for the pulp yield (Y) following oxygen delignification.

$$\int_{M_o}^{M}\frac{dM}{M}=\int_{x_1^o}^{x_1}\frac{dx_1}{(k-1)\,x_1}=\int_{y=1}^{y}d\ln(Y) \tag{E.10}$$

$$\ln Y=[\frac{1}{(k-1)}]\ln(\frac{x_1}{x_1^o}) \tag{E.11}$$

$$Y=(\frac{x_1}{x_1^o})^{\frac{1}{(k-1)}} \tag{E.12}$$

Many other functions are possible for the relationship between (y_1) and (x_1), but the function $y_1=k^*x_1$ gives appropriate boundary conditions. For example, at $x_1 = x_1^0$, at the initial lignin concentration in the pulp, equation (E.12) gives Y= 1, while at $x_1 = 0$ when no more lignin remains in the pulp, the yield will be Y = 0.

Similarly the relationship between the dissolved solids (δ) and the COD follows from the definitions of the dissolved solids and the definition COD. From equation (E.3), the dissolved solids (δ) in terms of grams solids per gram of pulp is:

$$\delta=(1-Y)=[1-(\frac{x_1}{x_1^o})^{\frac{1}{(k-1)}}] \tag{E.13}$$

For the dissolution of solids (dD), the oxygen demand ($dCOD^*$) will increase according to the stochiometric coefficient (R_{DS})

$$d\,COD^*=grams\,O_2=R_{DS}dD=-R_{DS}\,dM \tag{E.14}$$

Rearranging and dividing by the mass of pulp in the oxygen reactor gives

$$\frac{d\,COD^*}{R_{DS}\,M_o}=\frac{d\,COD}{R_{DS}}=-\frac{dM}{M_o}=-d\,Y \tag{E.15}$$

In equation (E.15), the COD is defined as the oxygen demand per unit mass ($COD = COD^*/M_o$). Consequently, equation (E.15) may be integrated assuming that the stochiometric coefficient R_{DS} is a constant and the pulp is well washed.

$$\int_0^{COD} d\,COD = -R_{DS} \int_1^{Y} d\,Y \qquad \text{(E.16)}$$

This gives the relationship for the COD in terms of the grams O_2 per unit mass of pulp in the reactor.

$$COD = R_{DS}\,(1-Y) = R_{DS}\,\delta = grams\,O_2\,/\,gram\ \ Pulp \qquad \text{(E.17)}$$

Lastly, substituting the relationship for the dissolved solids (δ) from equation (E.13) into equation (E.17) gives the model equation.

$$COD = R_{DS}\,[1-(\frac{x_1}{x_1^o})^{\frac{1}{(k-1)}}] \qquad \text{(E.18)}$$

APPENDIX F

SAMPLE CALCULATION

APPENDIX F

SAMPLE CALCULATION

F.1. ESTIMATION OF RATE ORDER (q) AND RATE CONSTANT (k)

The delignification data were fit to the general model

$$-\frac{dK}{dt} = k \cdot K^{q} \qquad \text{(F.1)}$$

where

$$k = k' \cdot [OH]^{m}[P_{O_2}]^{n} = A \cdot e^{E/RT} \cdot [OH]^{m}[P_{O_2}]^{n} \qquad \text{(F.2)}$$

K = Kappa number,

[OH] = sodium hydroxide concentration (g/l),

P_{O2} = oxygen partial pressure (psig),

t = time (minute).

A trial-and-error method was used to find the reaction order (q), since it cannot be obtained explicitly from equation (F.1). Both the integral and differential methods were used to calculate q. The differential method was used to estimate the initial value of q. Then the integral method was used to more accurately estimate q based on the correlation coefficient (R^2) obtained by plotting the kappa number versus time data.

F.1.1. Differential Method

The differential method is predicated on plotting the logarithm of the reaction rate (-dK/dt) versus the logarithm of the kappa number. Sample calculations are presented in Figure F.1 through F.9 and Table F.1 through F.9.

$$log(-dK/dt) = q \cdot log(K) + log(k) \qquad \text{(F.3)}$$

Table F.1. Differential method applied to A-1 sample data.

Kappa Number	O_2 (minute)	Ln(K)	Ln(-dK/dt)
16.2	-10		
14.3	0	0	0
13.0	5	2.5616	-1.2815
12.0	15	2.4835	-2.3304
11.1	30	2.4044	-2.8010
10.1	60	2.3102	-3.4050

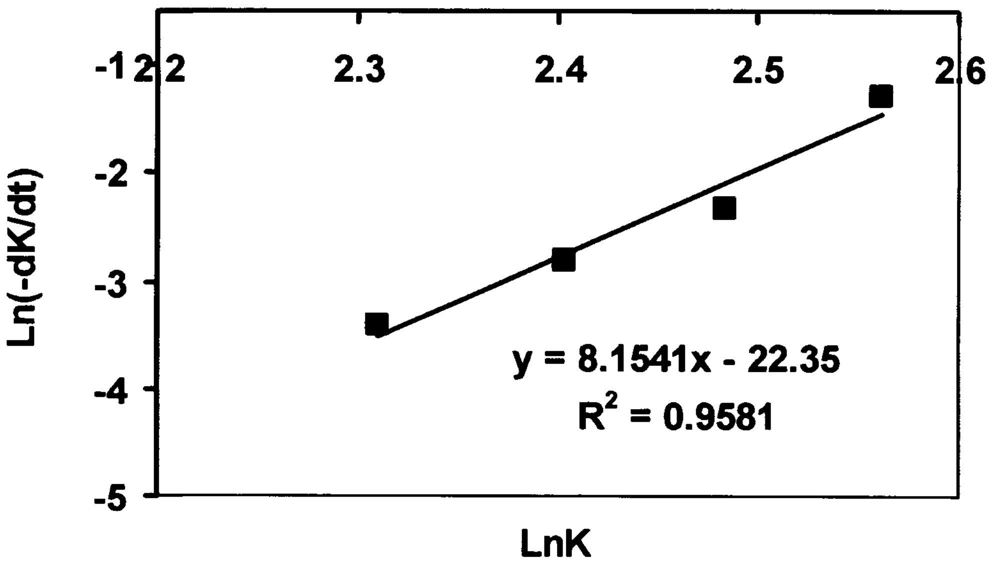


Figure F.1. Estimation of q for A-1 sample using the differential method.

Table F.2. Differential method applied to the B2/B4 sample data.

Kappa Number	O_2 (minute)	Ln(K)	Ln(-dK/dt)
21.4	-10		
18.1	0	0	0
16.2	5	2.7820	-0.9337
14.6	15	2.6816	-1.8694
13.1	30	2.5755	-2.3225
12.0	60	2.4817	-3.2379

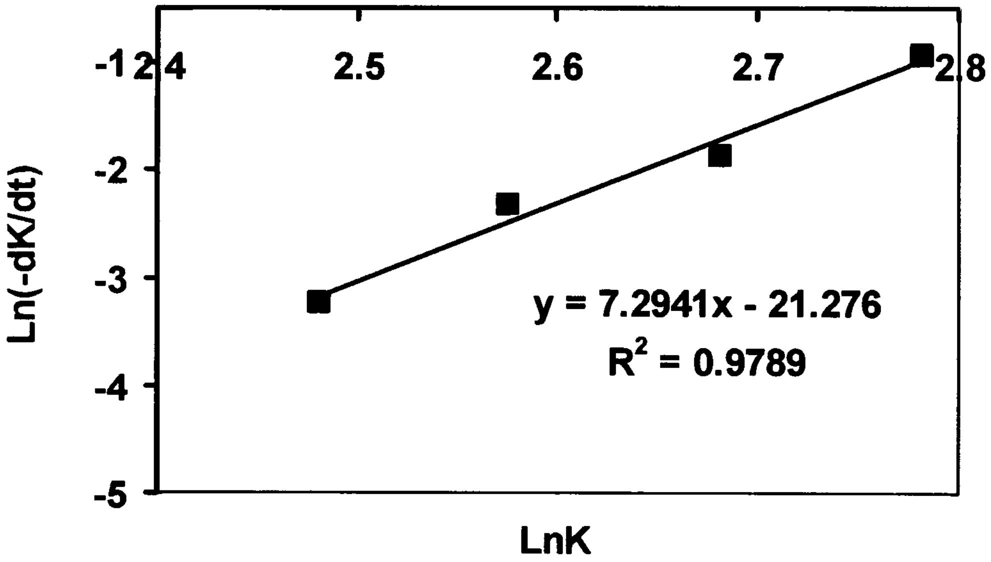


Figure F.2. Estimation of q for B2/B4 data using the differential method.

Table F.3. Differential method applied to C-2 sample data.

Kappa Number	O_2 (minute)	Ln(K)	Ln(-dK/dt)
15.6	-10		
13.5	0	0	0
11.9	5	2.4775	-1.1544
10.8	15	2.3797	-2.1986
10.0	30	2.2993	-2.8892
9.1	60	2.2067	-3.5267

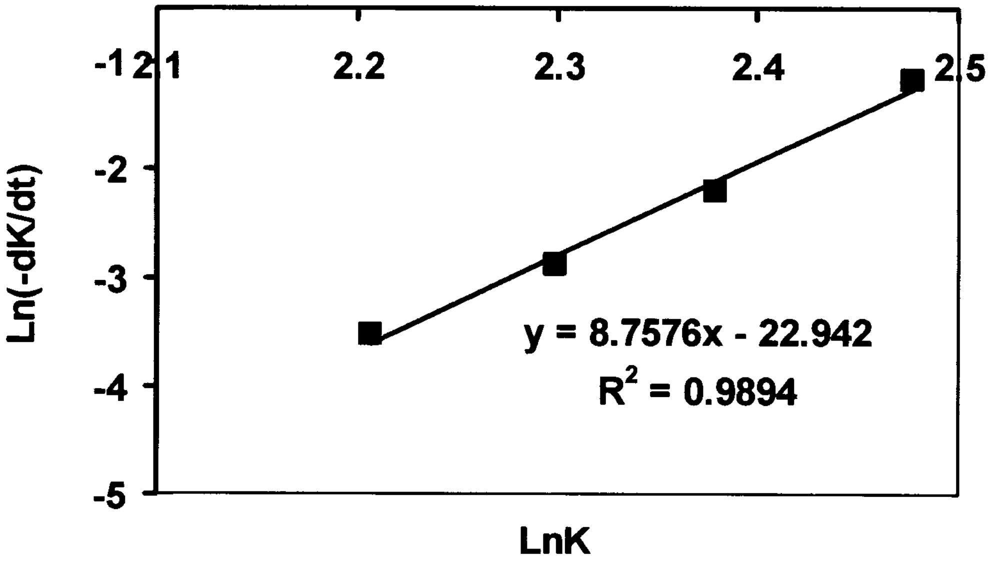


Figure F.3. Estimation of q for 18% EA data using the differential method.

Table F.4. Differential method applied to D-2 sample data.

Kappa Number	O_2 (minute)	Ln(K)	Ln(-dK/dt)
15.7	-10		
14.0	0		
12.0	5	2.4882	-0.9263
11.1	15	2.4105	-2.4079
10.1	30	2.3135	-2.6785
9.2	60	2.2192	-3.4955

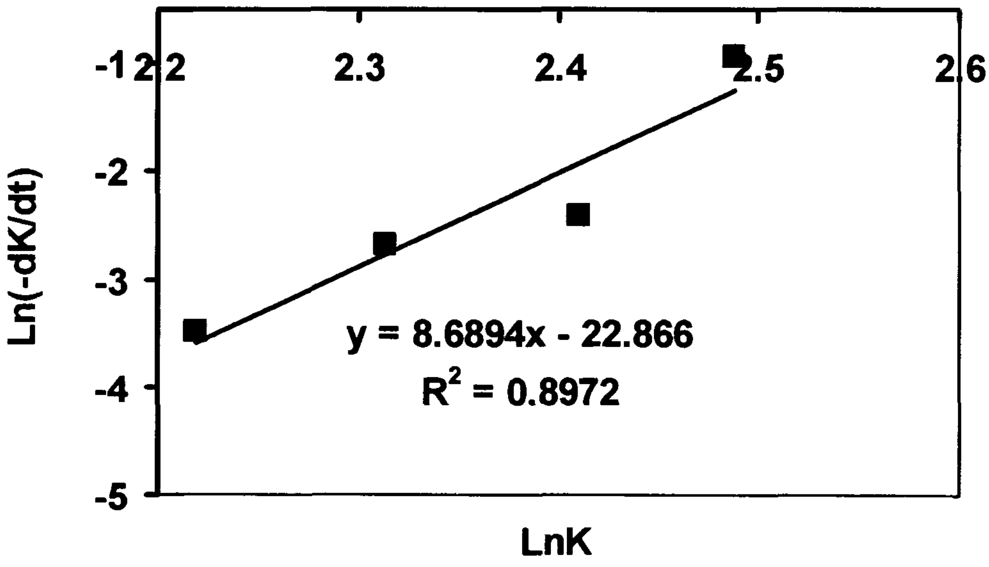


Figure F.4. Estimation of q for D-2 sample data using the differential method.

Table F.5. Differential method applied to D-3 sample data.

Kappa Number	O_2 (minute)	Ln(K)	Ln(-dK/dt)
18.7	-10		
16.6	0		
14.7	5	2.68785	-0.96758
13.5	15	2.60417	-2.13707
12.5	30	2.52573	-2.68825
11.4	60	2.43361	-3.30589

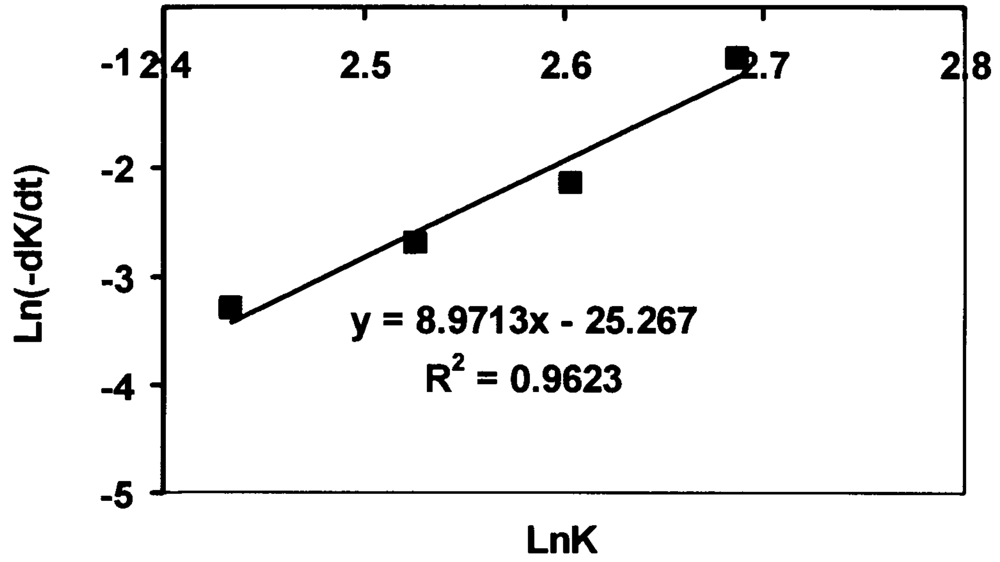


Figure F.5. Estimation of q for D-3 sample data using the differential method.

Table F.6. Differential method applied to SODA pulp sample data.

Kappa Number	O_2 (minute)	Ln(K)	Ln(-dK/dt)
16.2	-10		
14.8	0	0	0
12.8	5	2.5510	-0.9514
11.0	15	2.3967	-1.6968
10.0	30	2.3055	-2.7511
8.9	60	2.1873	-3.2892

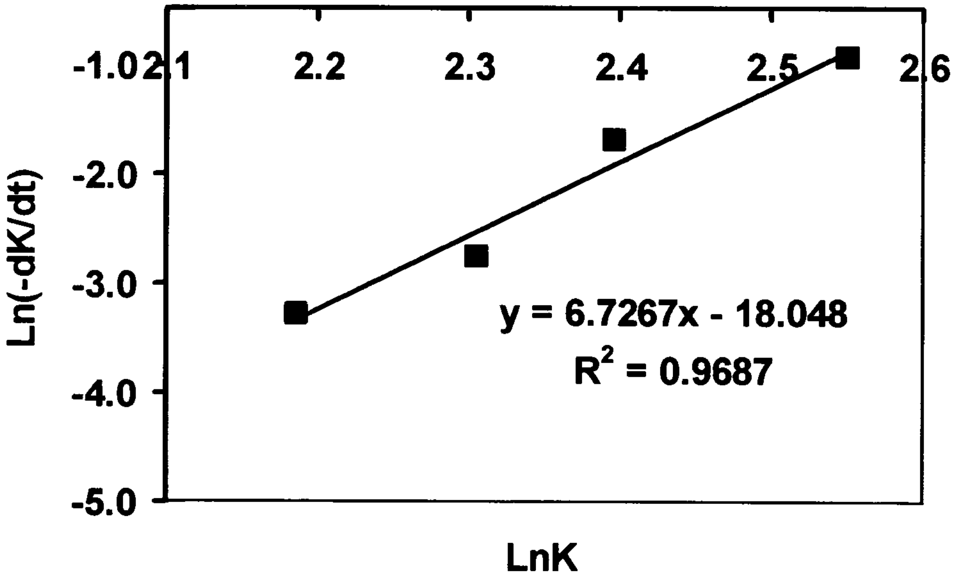


Figure F.6. Estimation of q for SODA sample data using the differential method.

Table F.7 Differential method applied to AQ 0.1% sample data.

Kappa Number	O_2 (minute)	Ln(K)	Ln(-dK/dt)
16.2	-10		
14.8	0	0	0
12.8	5	2.5510	-0.9514
11.0	15	2.3967	-1.6968
10.0	30	2.3055	-2.7511
8.9	60	2.1873	-3.2892

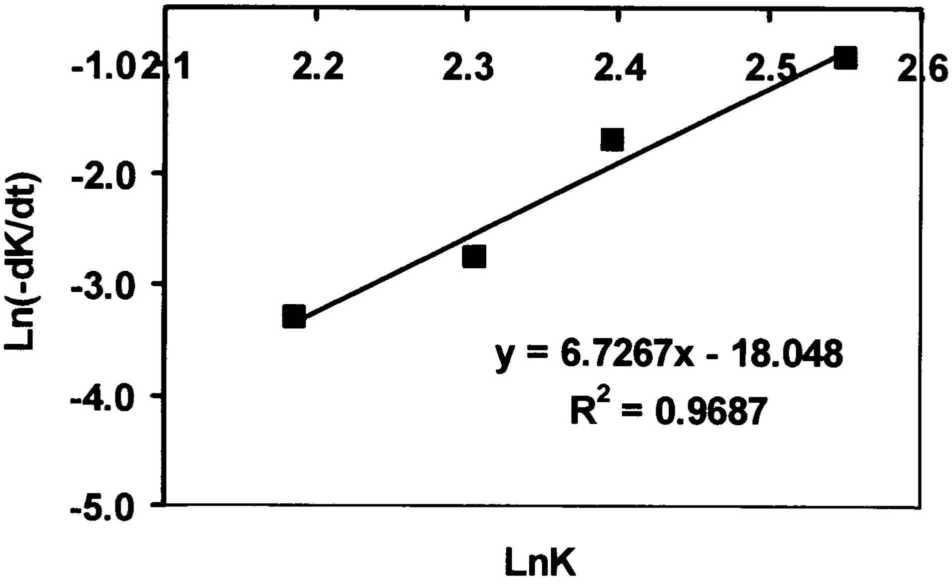


Figure F.7. Estimation of q for AQ 0.1% sample data using the differential method.

Table F.8. Differential method applied to AQ 1.0% sample data.

Kappa Number	O_2 (minute)	Ln(K)	Ln(-dK/dt)
17.2	-10		
15.5	0	0	0
14.4	5	2.6672	-1.5080
13.0	15	2.5649	-1.9661
12.0	30	2.4849	-2.7081
10.8	60	2.3811	-3.2330

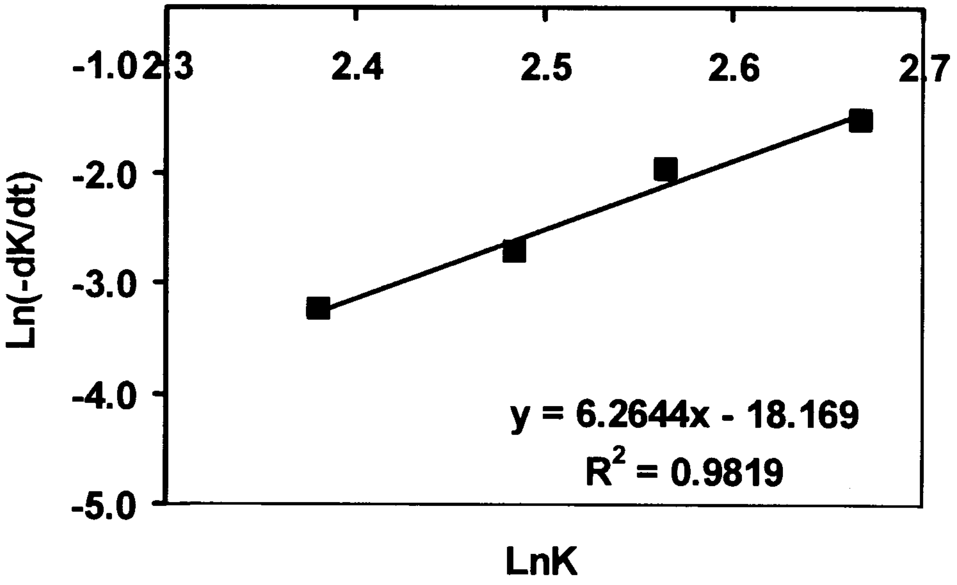


Figure F.8. Estimation of q for AQ 1.0% sample data using the differential method.

Table F.9. Differential method applied to AQ 4.0% sample data.

Kappa Number	O_2 (minute)	Ln(K)	Ln(-dK/dt)
17.6	-10		
15.5	0	0	0
14.5	5	2.6736	-1.5931
13.4	15	2.5987	-2.2581
12.6	30	2.5337	-2.8743
11.5	60	2.4387	-3.2686

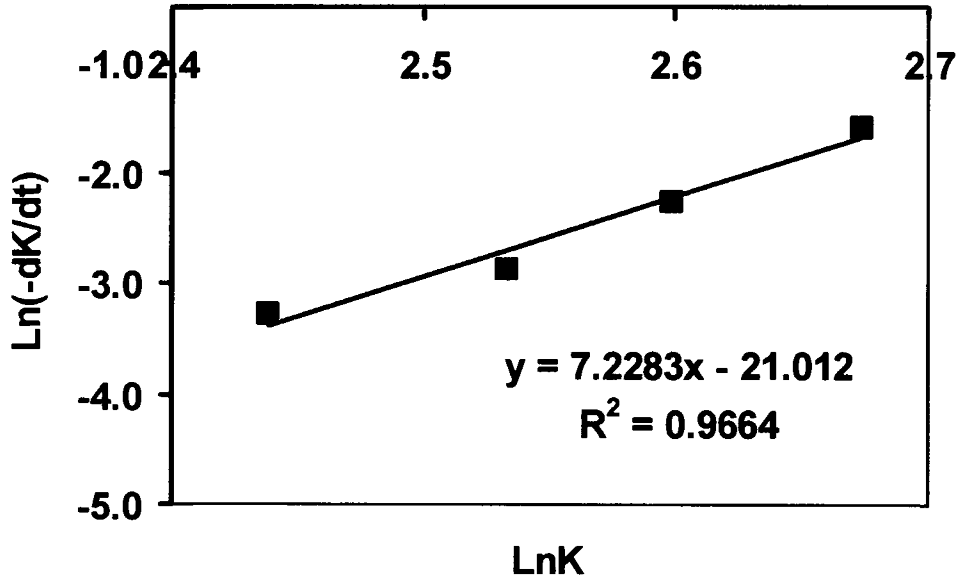


Figure F.9. Estimation of q for AQ 4.0% sample data using the differential method.

The parameters k and q found for each data set obtained by plotting log(-dK/dt) versus log(K) are shown in Table F.10.

Table F.10. Values for q and k value calculated from the differential method.

Sample	q	k	R^2
A-1 (Control)	8.1541	1.966E-10	0.9581
B2/B4	7.2940	5.754E-10	0.9789
C-2	8.7576	1.087E-10	0.9894
D-2	8.6894	1.173E-10	0.8972
D-3	8.9713	1.063E-10	0.9623
AQ0.1%	6.7267	1.452E-08	0.9687
AQ1.0%	6.2644	1.286E-08	0.9819
AQ4.0%	7.2283	7.492E-10	0.9664
Average	7.7607	3.654E-09	0.9629

The results for the reaction order (q) reported here are about 7.76 constant and the values for correlation coefficient (R^2) are pretty high.

F.1.2. Integral Method

Integration of equation (F.1) gives:

$$y = \frac{K^{1-q} - K_0^{-q}}{(q-1)} = k \cdot t \qquad \text{(F.4)}$$

where K_0 is the initial kappa number and q is the reaction order. Equation (F.4) is the equation for a linear line passing through zero with slope k. To evaluate reaction order (q) requires a trial and error solution. In the integral method, the value of (q) is assumed and the left hand side of equation (F.4) evaluated. The value of (y) is then plotted versus time (t). The correct value will be obtained when the regression coefficient (R^2) reach a maximum. The calculations are shown in Tables F.11 through F.21. Figures F.10 through F.27 plot the data graphically. Lastly, Table F.21 summarizes the best value for (k) assuming (q) values of 7.7. This assumes the same (q) value for all four pulps. The last entry in Table F.20 gives the best value for q and k at the maximum R^2 for each pulp.

Table F.11. Value for (q) and (k) estimated from the integral method for A-1 data.

Kappa Number	O_2 (minute)	$(K^{(1-q)} - K_o^{(1-q)})/(q-1)$
14.3	0	0
13.0	5	2.221E-09
12.0	15	5.322E-09
11.1	30	1.067E-08
10.1	60	2.218E-08

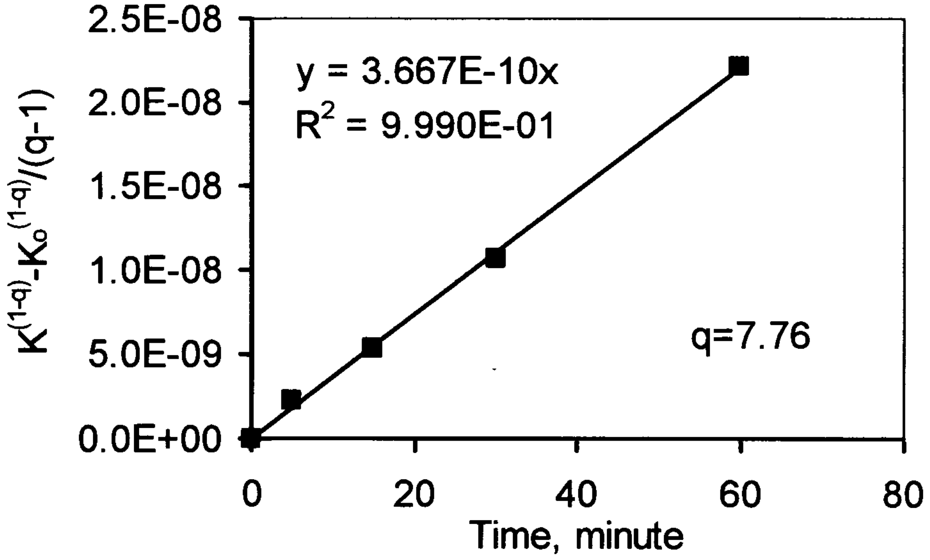


Figure F.10. Estimation of q and k for A-1 data using the integral method.

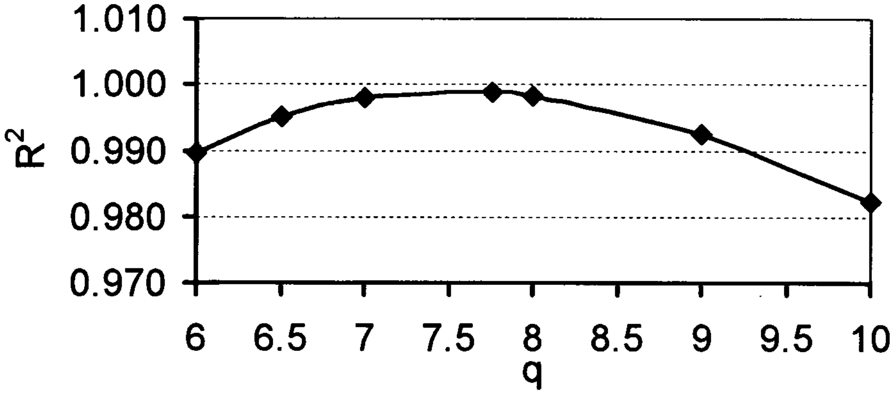


Figure F.11. Value of R^2 plotted versus q for A-1 data.

Table F.12. Value for (q) and (k) estimated from the integral method for B2/B4 data.

Kappa Number	O_2 (minute)	$(K^{(1-q)} - K_o^{(1-q)})/(q-1)$
18.1	0	0
16.2	5	5.432E-10
14.6	15	1.52E-09
13.1	30	3.599E-09
12.0	60	7.199E-09

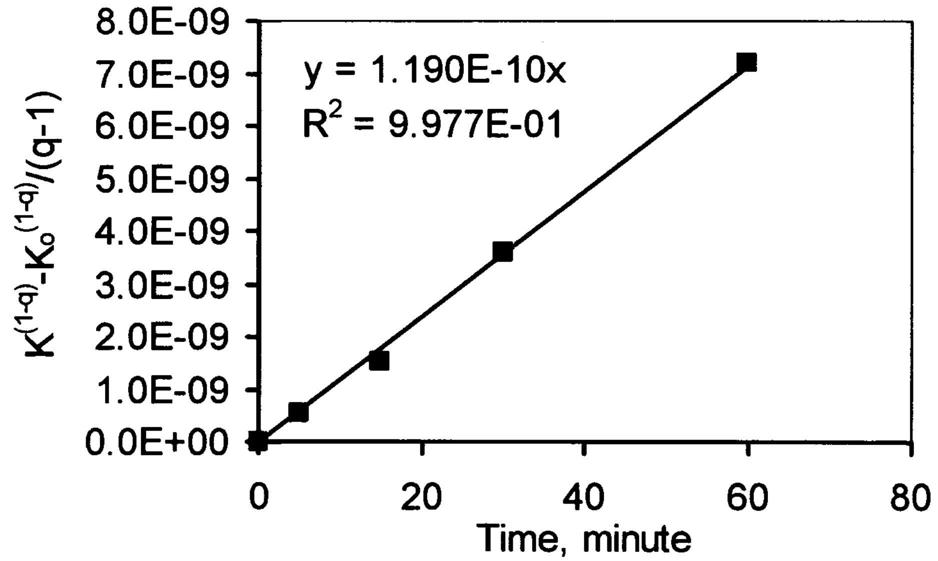


Figure F.12. Estimation of q and k for B2/B4 data using the integral method.

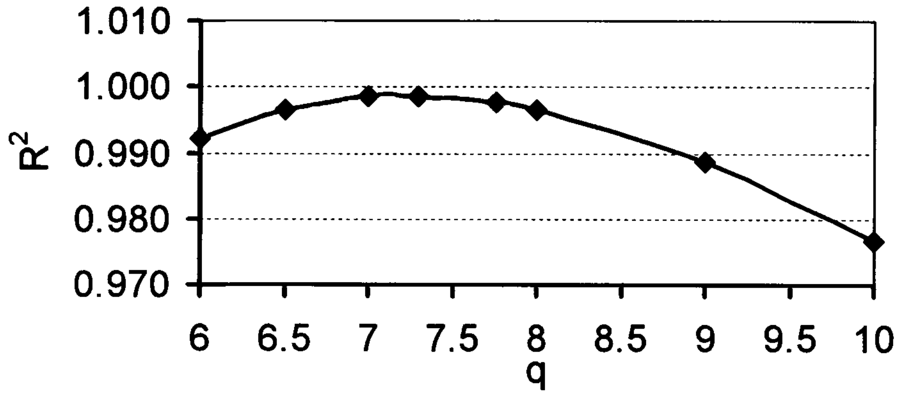


Figure F.13. Value of R^2 plotted versus q for B2/B4 data.

Table F.13. Value for (q) and (k) estimated from the integral method for C-2 data.

Kappa Number	O_2 (minute)	$(K^{(1-q)} - K_o^{(1-q)})/(q-1)$
13.5	0	0
11.9	5	4.477E-09
10.8	15	1.186E-08
10.0	30	2.287E-08
9.1	60	4.575E-08

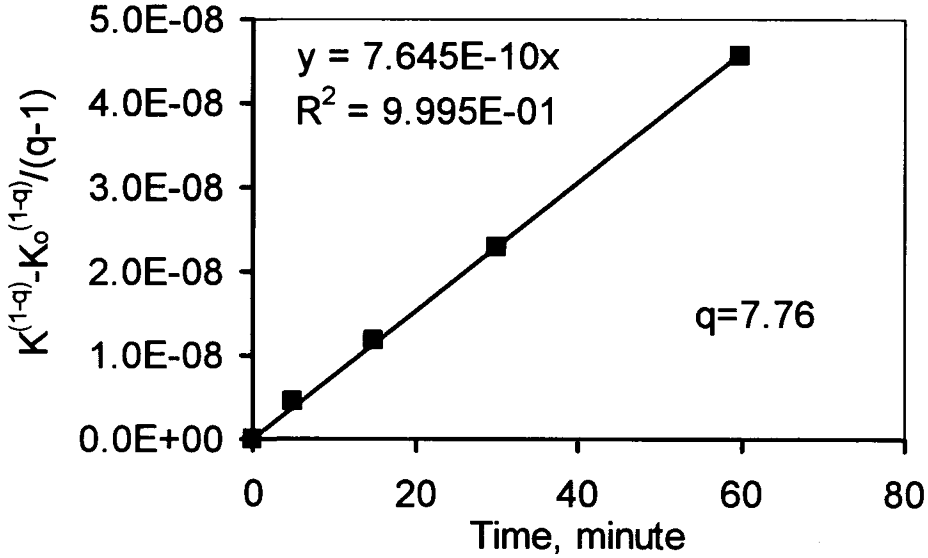


Figure F.14. Estimation of q and k for C-2 data using the integral method.

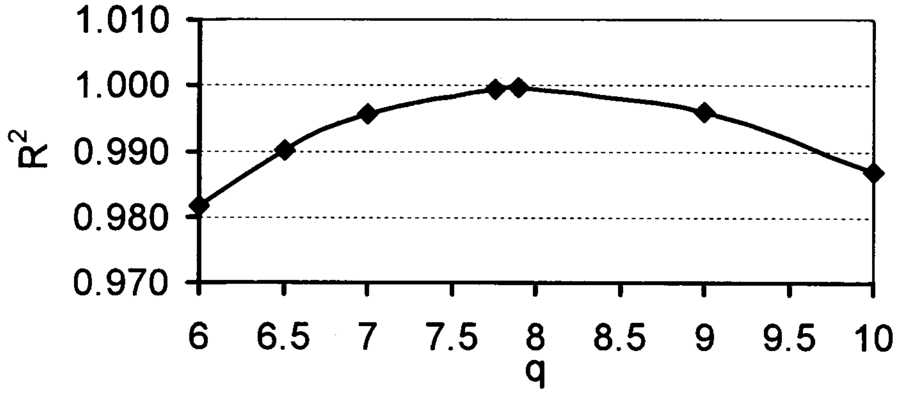


Figure F.15. Value of R^2 plotted versus q for C-2 data.

Table F.14. Value for (q) and (k) estimated from the integral method for D-2 data.

Kappa Number	O_2 (minute)	$(K^{(1-q)} - K_o^{(1-q)})/(q-1)$
14.0	0	0
12.0	5	4.710E-09
11.1	15	9.773E-09
10.1	30	2.126E-08
9.2	60	4.255E-08

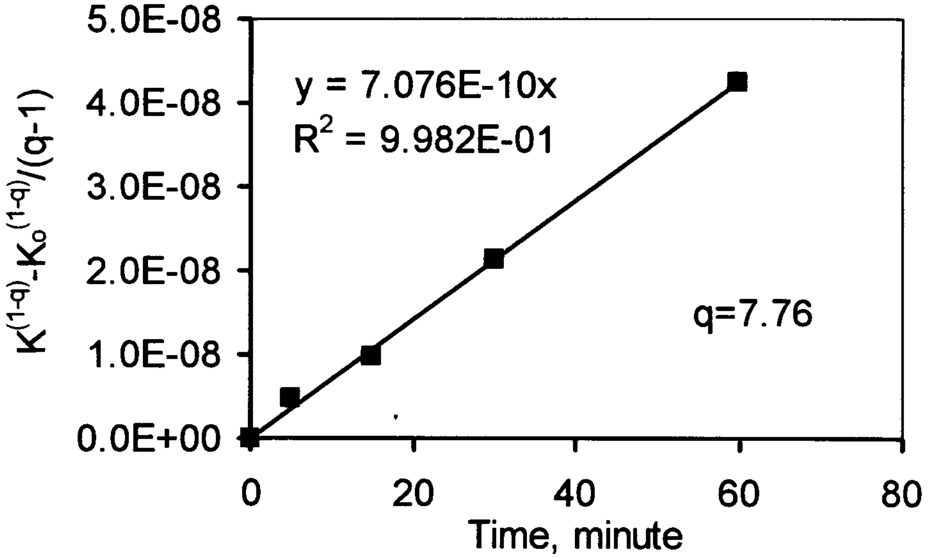


Figure F.16. Estimation of q and k for D-2 data using the integral method.

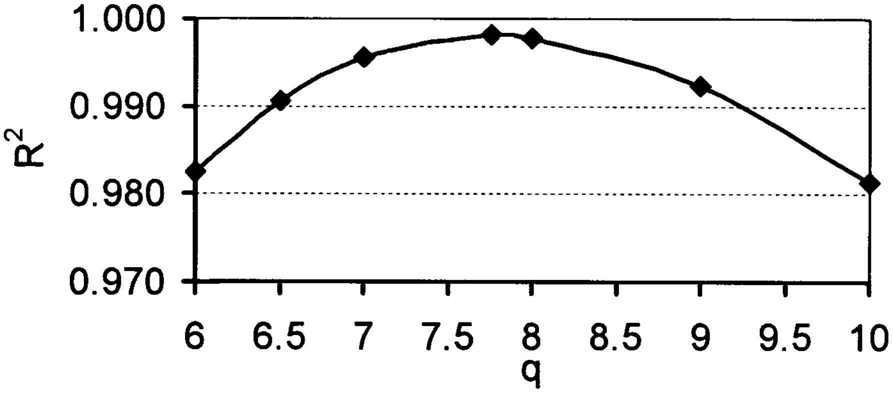


Figure F.17. Value of R^2 plotted versus q for D-2 data.

Table F.15. Value for (q) and (k) estimated from the integral method for D-3 data.

Kappa Number	O_2 (minute)	$(K^{(1-q)} - K_o^{(1-q)})/(q-1)$
16.6	0	0
14.7	5	1.065E-09
13.5	15	2.511E-09
12.5	30	4.852E-09
11.4	60	9.766E-09

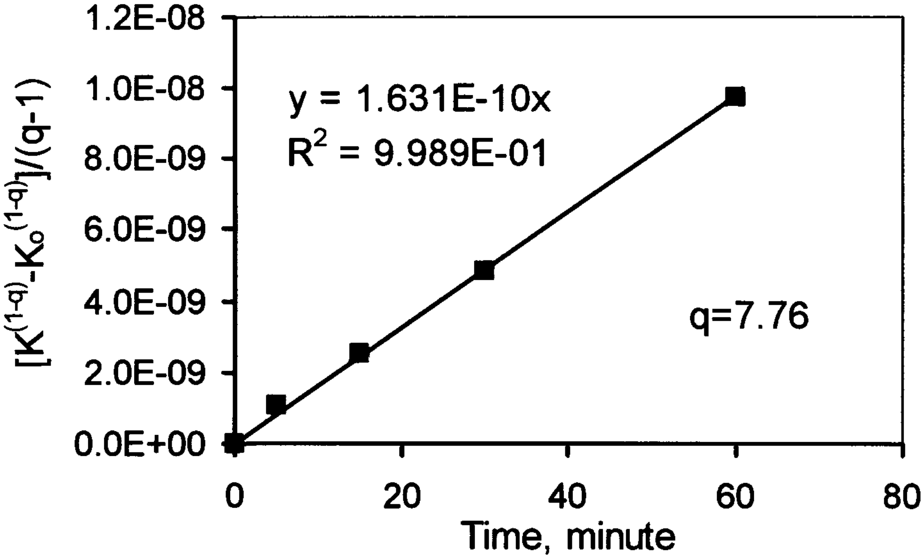


Figure F.18. Estimation of q and k for D-3 data using the integral method.

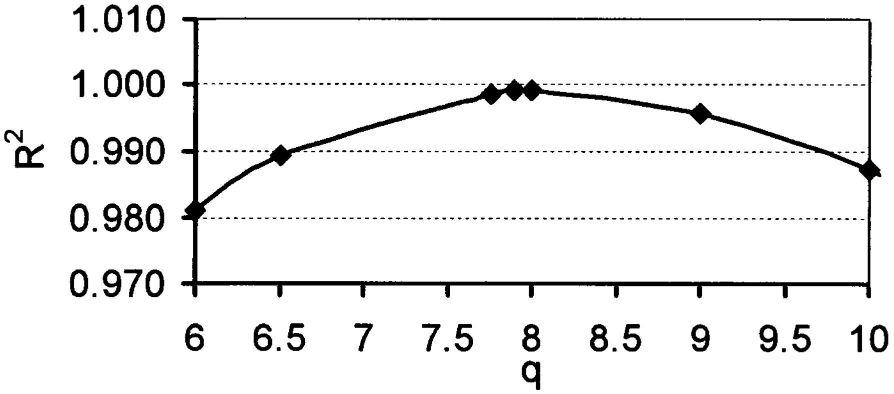


Figure F.19. Value of R^2 plotted versus q for D-3 data.

Table F.16. Value for (q) and (k) estimated from the integral method for SODA pulp data.

Kappa Number	O_2 (minute)	$(K^{(1-q)} - K_o^{(1-q)})/(q-1)$
14.8	0	0
12.8	5	2.937E-09
11.0	15	1.174E-08
10.0	30	2.334E-08
8.9	60	5.419E-08

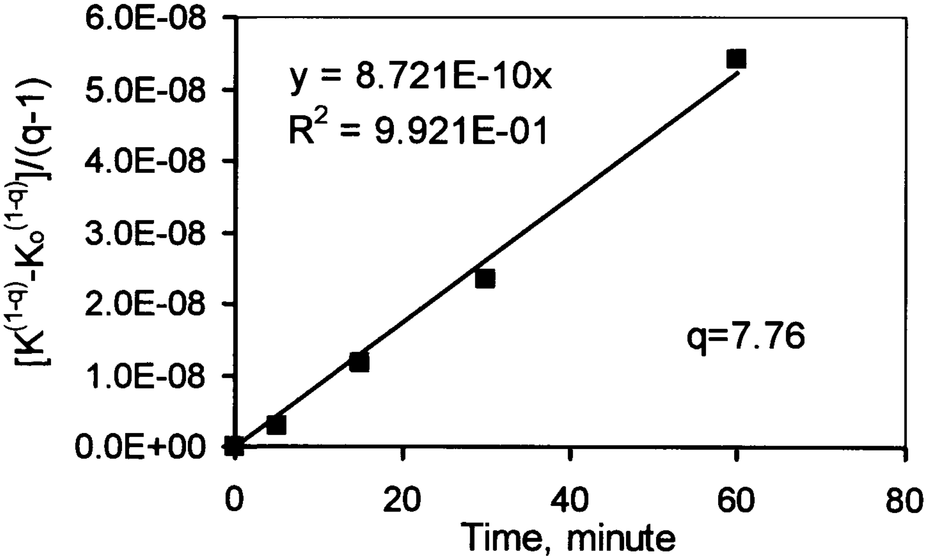


Figure F.20. Estimation of q and k for SODA data using the integral method.

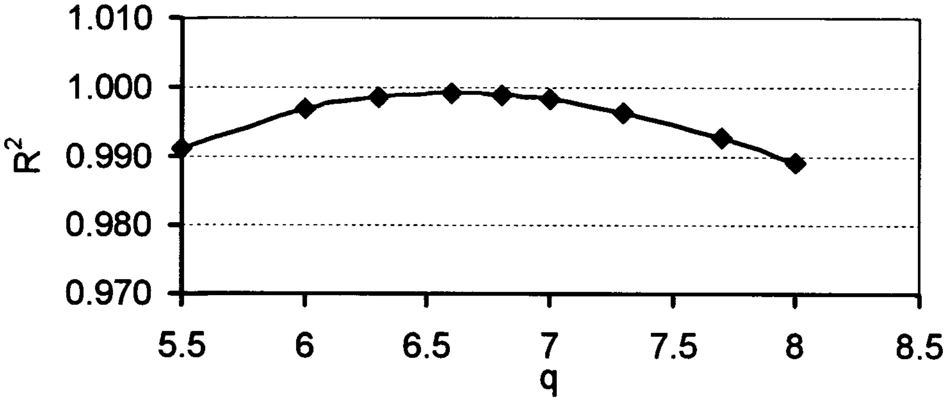


Figure F.21. Value of R^2 plotted versus q for SODA data.

Table F.17. Value for (q) and (k) estimated from the integral method for AQ0.1% data.

Kappa Number	O_2 (minute)	$(K^{(1-q)} - K_o^{(1-q)})/(q-1)$
16.1	0	0
14.7	5	1.000E-09
13.3	15	3.073E-09
12.1	30	7.012E-09
10.8	60	1.653E-08

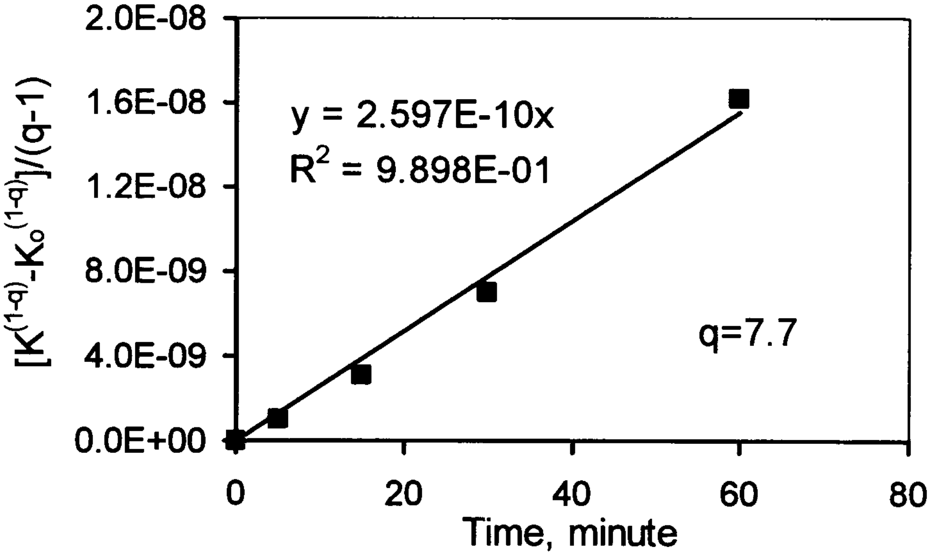


Figure F.22. Estimation of q and k for AQ0.1% data using the integral method.

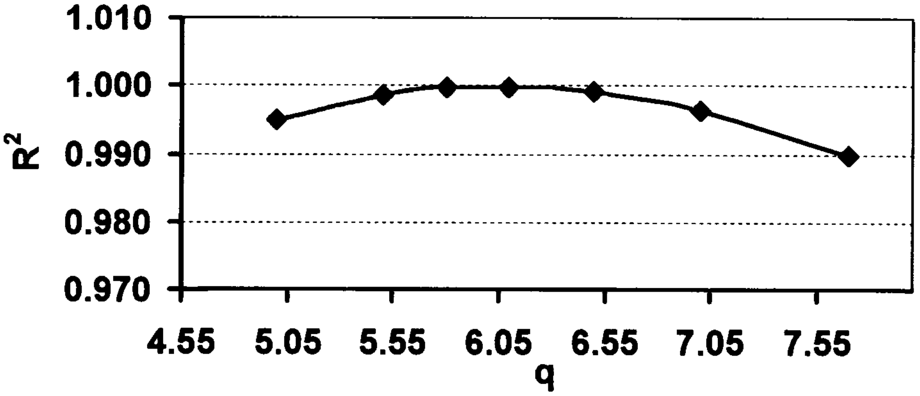


Figure F.23. Value of R^2 plotted versus q for AQ0.1% data.

Table F.18. Value for (q) and (k) estimated from the integral method for AQ1.0% data.

Kappa Number	O_2 (minute)	$(K^{(1-q)} - K_o^{(1-q)})/(q-1)$
15.5	0	0
14.4	5	1.012E-09
13.0	15	3.559E-09
12.0	30	7.203E-09
10.8	60	1.602E-08

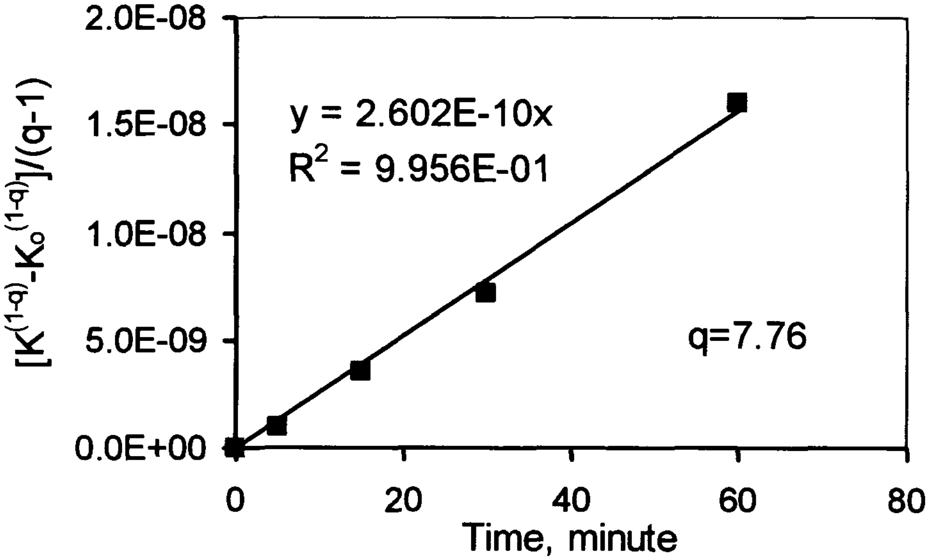


Figure F.24. Estimation of q and k for AQ1.0% data using the integral method.

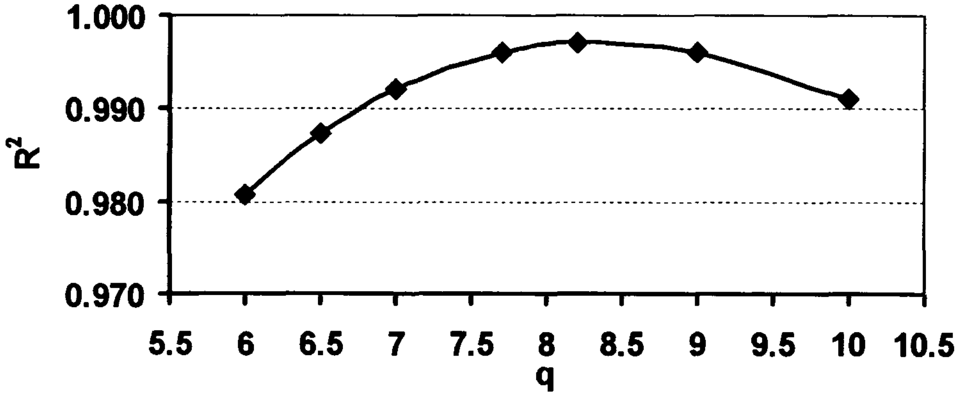


Figure F.25. Value of R^2 plotted versus q for AQ1.0% data.

Table F.19. Value for (q) and (k) estimated from the integral method for AQ 4.0% data.

Kappa Number	O_2 (minute)	$(K^{(1-q)} - K_o^{(1-q)})/(q-1)$
15.5	0	0
14.5	5	7.694E-10
13.4	15	2.148E-09
12.6	30	4.066E-09
11.5	60	8.920E-09

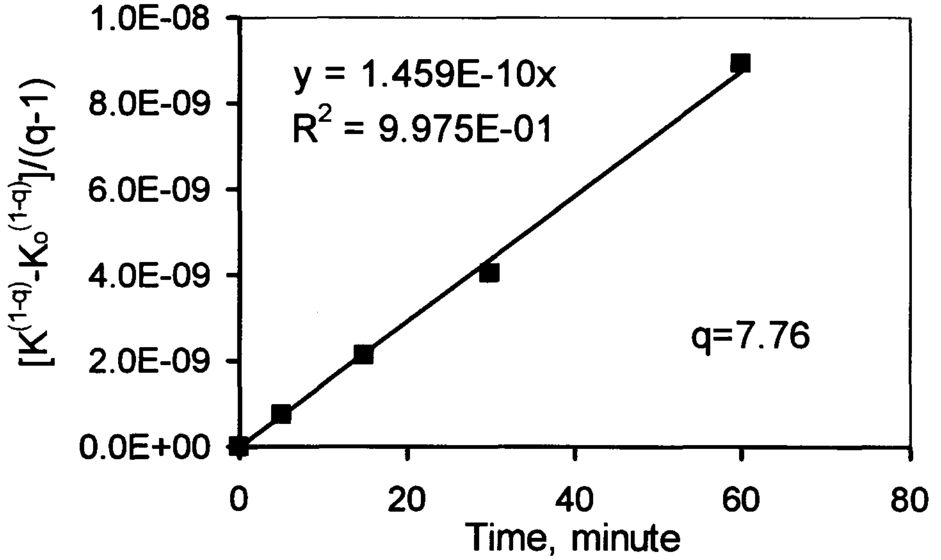


Figure F.26. Estimation of q and k for AQ4.0% data using the integral method.

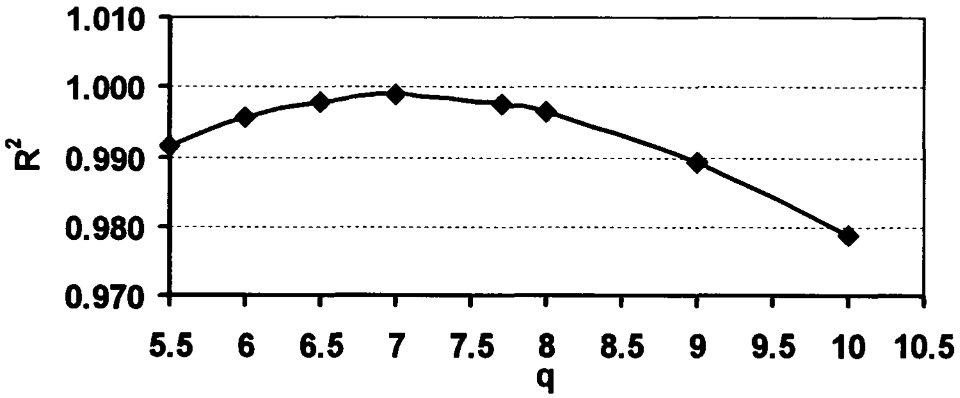


Figure F.27. Value of R^2 plotted versus q for AQ4.0% data.

Table F.20. Values for q and k value calculated from the integral method.

Sample	q	k	R^2
A-1 (Control)	7.7	4.25E-10	0.999
B2/B4	7.3	3.99E-10	0.9987
C-2	7.9	4.35E-10	0.9997
D-2	7.7	8.15E-10	0.9982
D-3	7.9	1.14E-10	0.9991
SODA	6.7	1.13E-08	0.9992
AQ0.1%	6.4	4.35E-10	0.9991
AQ1.0%	8.2	6.82E-09	0.9998
AQ4.0%	7.0	7.75E-11	0.9971
Average	7.4	2.55E-09	0.9989

Table F.21. Best Values for q and k value calculated from the integral method.

ID	q	R^2	k'
A-1(Control), 12%EA, 160 °C	7.7	0.9990	4.246E-10
C-2, 21%EA, 160 °C	7.7	0.9994	8.801E-10
D-2, 21%EA, 180 °C	7.7	0.9982	8.154E-10
B2/B4, 12%EA, 180 °C, HK	7.7	0.9980	1.394E-10
D-3, 21%EA, 180 °C, HK	7.7	0.9987	1.903E-10
SODA	7.7	0.9928	1.004E-09
AQ0.1%	7.7	0.9878	2.639E-10
AQ1.0%	7.7	0.9956	2.602E-10
AQ4.0%	7.7	0.9977	1.702E-10

BIOGRAPHY OF THE AUTHOR

Haixuan Zou was born in Guangdong, China on April 21, 1964. He received his high school education in Meizhou City, China.

He attended South China University of Technology, Department of Chemical Machinery Engineering and graduate with a Bachelor of Science degree in 1985. He was enrolled for graduate study in Light Chemical Engineering at South China University of Technology in 1985 and obtained his M.S. degree in 1988. Then he worked two years as an assistant professor in the Department of Light Chemical Engineering and six years as a lecturer/engineer in Pulp and Paper State Key Laboratory, South China University of Technology.

In 1996, Haixuan came to the University of Maine as a visiting scholar. He was enrolled in the Ph.D. program in Chemical Engineering at the University of Maine in 1997 and obtained the M.S. degree in Chemical Engineering from the University of Maine in 2000.

Haixuan is a candidate for the Doctor of Philosophy degree in Chemical Engineering from The University of Maine in May, 2002.