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**PULP PRETREATMENTS FOR IMPROVED SELECTIVITY AND
EXTENDED OXYGEN DELIGNIFICATION**

By

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B.S. Nanjing University of Science and Technology, 1995

A THESIS

Submitted in Partial Fulfillment of the

Requirements for the Degree of

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(in Chemical Engineering)

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The University of Maine

August, 2002

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PULP PRETREATMENTS FOR IMPROVED SELECTIVITY AND EXTENDED OXYGEN DELIGNIFICATION

By Zheng Dang

Thesis Advisor: Dr. Joseph M. Genco

An Abstract of the Thesis Presented
in Partial Fulfillment of Requirements for the
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Oxygen delignification has developed steadily since it was introduced commercially in 1970 in South Africa and virtually all new fiber lines incorporate an oxygen delignification system following the digester prior to the bleach plant. Currently, the degradation of cellulose and consequently the loss of pulp strength limit the drop in kappa number that can be obtained using an oxygen process. Pulp selectivity, given by the selectivity coefficient (α), relates the reduction in the molecular weight of cellulose to the reduction in the lignin content of the pulp when measured by the kappa number.

$$\alpha = \frac{d\left[\frac{1}{DP} - \frac{1}{DP_o}\right]}{dK} \cong \frac{\Delta\left[\frac{1}{DP} - \frac{1}{DP_o}\right]}{\Delta K}$$

An evaluation of selectivity of delignification data published by Agarwal (1998) for mixed southern hardwood treated in a single stage oxygen process showed that temperature has little effect on pulp selectivity within the temperature range of 90 to 110 °C. Rather, pulp selectivity is determined primarily by the addition rate of caustic and thus, the caustic concentration present in the reactor during the oxygen process.

The objective of this thesis was to investigate three pulp pretreatment techniques known to improve pulp selectivity by removing metal ions that enhance the formation of hydroxyl free radicals that degrade cellulose by random hydrolysis reactions. The techniques investigated were pretreatment of the pulp using DTPA, termed a Q-stage, pretreatment by washing the pulp with acid (A-stage), and acid washing the pulp with a small amount of ClO_2 present (A_D -stage). In addition to removing metals prior to oxygen delignification, the use of ClO_2 in an A_D -stage is thought to activate the lignin in the pulp to promote a high level of delignification. The three pretreatment techniques investigated were compared to control experiments that were conducted with no pulp pretreatment. Each of the four delignification conditions was investigated in both a stainless steel reactor and in glass to test the hypothesis that metals are leached from the stainless steel reactor and influence the results. All of the experiments were performed in quadruplicate with and without H_2O_2 reinforcement in the oxygen stage. Response variables in this investigation were the kappa number, intrinsic viscosity, degree of delignification, and the selectivity coefficient (α). The effectiveness of the various conditions on the response variables was determined using the student t -test. This thesis was limited to the study of northeastern brownstock kraft pulp.

The results of the experimental investigation showed that all of the pretreatment techniques improved the selectivity of oxygen delignification. Metals present in the stainless reaction vessel contributed little to the reduction in kappa number except for the case of the A_D stage where the stainless steel reactor improved the delignification. Also, use of the stainless steel reactor decreased the selectivity only in the DTPA pretreatment case. Use of the A_D pretreatment stage led to additional delignification compared to the

no pretreatment case and also when compared to the Q- and A-stage pretreatment techniques. Lastly the use of H_2O_2 to reinforce an oxygen stage resulted in an improvement in the level of delignification but a loss in selectivity. This was true for all of the cases evaluated except for the oxygen stage with A_D pretreatment where no difference was detected in delignification when the reaction was conducted in stainless steel. DTPA was extremely effective in controlling metals and no drop in selectivity was observed even for the case of using H_2O_2 reinforced oxygen delignification.

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CHAPTER 1

INTRODUCTION

1.1 OXYGEN DELIGNIFICATION

Lignin is the main contributor to pulp color in chemical pulp. During the production of fully bleached chemical pulp, residual lignin is removed in bleaching. Traditionally, bleaching effluents arising from bleaching with chlorine and chlorine dioxide cannot be easily incorporated in a mill's chemical recovery system. Therefore, it is important for cost and for environmental protection that the lignin content of the pulp be minimized before bleaching (Gullichsen and Fogelholm, 2000).

Carbohydrate losses increase considerably near the end of kraft cooking, so there is a practical limit as to how far delignification can be continued without a serious loss in pulp yield (Hook, 2000). It would be highly desirable economically if more selective delignification methods, preferably without negative environmental consequences, could be developed to reduce the lignin content of pulp before bleaching. One such method that has this attribute is alkaline oxygen delignification. It fits particularly well with kraft pulping because it can use oxidized white liquor as an alkaline source and the spent solids and chemicals can be recovered through counter-current washing and combustion with the spent kraft liquor. For economic reasons, chlorine-free bleaching is the most attractive bleaching process at the present time. Currently, oxygen-reinforced extraction is a low cost, popular, extended delignification process (Gullichsen and Fogelholm, 2000). Unfortunately, the effluent from a conventional E_O stage cannot be returned to the recovery cycle.

There has been a steady increase in the use of oxygen delignification worldwide since the first commercial installation in South Africa in 1970. Oxygen delignification is now an established process in pulping and bleaching plants. In mill operations, in a single vessel process, the degree of delignification for hardwood kraft pulp is around 40% to 45%, while that of softwood kraft pulp is between 50% and 60% when measured by a reduction in the Kappa number (Miller, 1992). The primary reason limiting the degree of delignification is degradation of cellulose, and therefore a decrease in pulp strength. This is especially true if the delignification is carried beyond 50% for hardwood and about 60% for softwood (Al Van Tran, 2000).

Van Lierop (1999) summarized the advantages and the disadvantages of oxygen delignification. The principal advantages of installing the oxygen delignification process are (1) improving bleaching process efficiency, allowing for shorter bleaching sequences, (2) proven technology, (3) the spent liquor is free of chlorine ions, (4) the effluent can be handled by the kraft recovery system, (5) decreased consumption of bleaching chemicals used in subsequent stages, (6) oxygen is considerably cheaper than chlorine dioxide or hydrogen peroxide, and (7) the compatibility of oxygen delignification with chlorine compound-free technology. Three principal disadvantages to oxygen delignification listed by van Lierop (1999) are (1) limited lignin-removal capabilities for high-strength pulps, (2) high capital costs from use of high pressure oxygen, and (3) the kraft recovery boiler may have to be upgraded.

Increasing delignification in the oxygen stage reduces the impact on the environment since the spent liquor is evaporated and burned in the recovery furnace. The potential for system closure of the final bleaching stage is also increased. In addition,

there is a potential for increasing the yield if the cooking is terminated earlier and the oxygen delignification is extended (Hook, 2000).

One way to increase the degree of delignification is to install a two-stage, or multi-stage oxygen delignification system. An alternative way is to use additives to enhance the degree of delignification. Methods for improving delignification include surfactants, chelating agents, and lignin activators. Another way is to extend oxygen delignification to very high level, by means of pretreatment followed by conventional oxygen delignification or alternatively, reinforcing the oxygen stage with hydrogen peroxide. Recent developments in the area of pretreatment have made it possible to achieve a high level of delignification (60%) while maintaining acceptable pulp viscosity in one oxygen stage (Ku, Hsieh, and co-workers, 1992). Pulp treatment methods include acid washing, acid washing with ClO_2 , nitrosation pretreatment, DTPA (chelating agents), and various biological treatments. The objective of virtually all pretreatment methods, including chelation (DTPA), use of a hot acidic stage (A), and a hot acid reinforced stage with ClO_2 (A_D stage) is to remove the transition metals inside the pulp, since it has been known for many years that transition metals induce the attack of hydroxyl radicals on the carbohydrates, and thus reduce the pulp viscosity. The addition of a small amount of hydrogen peroxide to an oxygen alkali system increases the rate of degradation (Johansson and Ljunggren, 1994).

1.2 THE BASIC PROCESS

Oxygen delignification uses oxygen and alkali to remove a substantial fraction of the lignin remaining after cooking and can be applied to all pulp types. The process is

very flexible, and is best viewed as a bridging strategy - between cooking and final bleaching.

Figure 1.1 shows the basic oxygen delignification process. The brownstock pulp following washing is pumped through one or more mixers, where alkali, oxygen, steam and a carbohydrate protector for protecting against carbohydrates decomposition are dispersed under pressure into a medium-consistency upflow reactor. Pulp screening can be done either before or after the oxygen delignification process. Robert et al. discovered that magnesium ion such as MgSO_4 can protect against carbohydrates decomposition. MgSO_4 added under appropriate pH can deactivate transition metals and stabilize hydrogen peroxide to such an extent that high rates of delignification can be achieved without excessively degrading and depolymerizing cellulose by hydroxyl radicals (Gratzl and co-workers, 1990). Following addition of the caustic oxygen and magnesium sulfate, the pulp passes through an up-flow reactor and is discharged from the top of the reactor to a blow tank where gases are separated out from the pulp. From the blow tank, the pulp is pumped to a set of washers for the recovery of spent liquor. The spent liquor from the post-oxygen washers is used as the wash medium in brown stock washing (Gullichsen and Fogelholm, 2000).

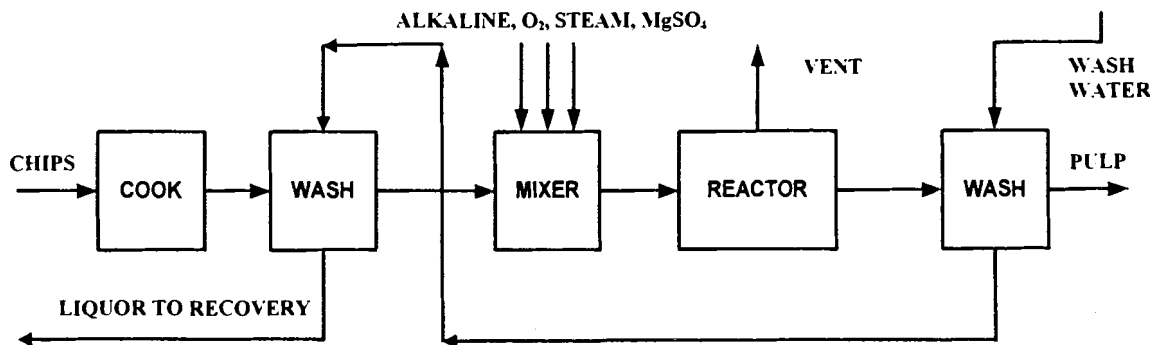


Figure 1.1 The Basic Process of Oxygen Delignification

The transition metals and the metals in the reactor like copper (Cu^{2+}), manganese (Mn^{2+}), and iron (Fe^{2+}) induce detrimental effects on the viscosity (Johansson and Ljunggren). Transition metals decompose peroxides, which are intermediates in the reduction sequence of oxygen. The catalytic decomposition forms hydroxyl radicals which can attack cellulose with detrimental results. Hydroxyl free radicals are formed through reaction of peroxide with hydroxyl ion following Fenton's chemistry (Walling, 1975). Consequently, the management of transition metals is very important for the selectivity of oxygen delignification (Gullichsen and Fogelholm, 2000). The decomposition of peroxide can be controlled (1) by removing transition metals by prior acid washing and/or chelation and (2) by stabilizing the transition metals by adding magnesium salts and silicates.

1.3 OBJECTIVE

During the research reported here, Northeast hardwood kraft pulp was used as the pulp of interest. Hardwood pulp was selected because the lignin in hardwood is more difficult to remove than softwood lignin. The objective of this work was to investigate the effects of three different pretreatment techniques on the oxygen delignification process. The three techniques investigated were (1) pretreatment using DTPA as a chelating agent, (2) pretreatment of hardwood kraft brownstock with a hot acidic stage (A), and (3) use of an acidic stage combined with chlorine dioxide as a lignin activation (A_D) stage. Also, conventional oxygen delignification was compared to a reinforced oxygen delignification by adding H_2O_2 . Oxygen delignification, when reinforced with H_2O_2 , is termed a pressurized peroxide stage. To evaluate the effect of the metals in the

reactor on the oxygen delignification stage, delignification experiments were performed in a stainless steel reactor as well as in glass and the results are compared.

CHAPTER 2

LITERATURE REVIEW

2.1 CHEMISTRY OF OXYGEN DELIGNIFICATION

Oxygen in alkaline medium reacts through complex radical chain reactions with both lignin and carbohydrates. Oxygen is reduced to water in reactions with the organic components in the pulp, while the organic components in the pulp are oxidized. Dence and Reeve (1996) identified three distinct types of chemical reactions as shown in Figure 2.1.

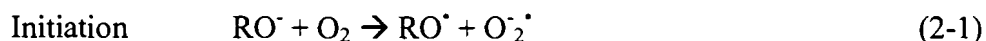


Figure 2.1 Steps in the Mechanism of Oxygen Delignification (Dence and Reeve, 1996)

Oxygen in its normal state is a weak oxidizing agent, and is as such in delignification. The oxidizing power of oxygen can be promoted by raising the temperature and pressure of the reaction mixture. This is achieved in alkaline conditions which ionize free phenolic hydroxyl groups remaining in the residual lignin structures. These conditions will result in the formation of a superoxide anion and a phenoxy radical (Reaction 2-1). It is also possible that a hydrogen atom is abstracted from a non-ionized phenolic group to give the corresponding organic radical (Reaction 2-2). The chain reaction is propagated by reactions between oxygen and the organic radical to form a

peroxy radical, which in turn may abstract a hydrogen atom to generate a new organic radical. (Reactions 2-3 and 2-4). Finally, the chain reaction may be terminated by coupling reactions, which are termed lignin condensation reactions (Reaction 2-5).

Lignin reacts mainly via free phenolic hydroxyl groups. When ionized by the addition of alkali, lignin provides high electron density which is needed to initiate reactions with oxygen. This, together with the weakly acidic nature of phenolic hydroxyl groups, explains why strongly alkaline conditions are required to achieve appreciable delignification rates.

Carbohydrates are readily attacked during alkaline oxygen delignification, more so than in many bleaching chemistries. Carbohydrate degradation increases as delignification proceeds, so oxygen delignification has to be stopped when about half of the residual lignin had been dissolved. Reactions that degrade cellulose are of two categories: random chain cleavage, which may occur anywhere along the polymer chain, and endwise peeling, which removes monomers one-by-one from the terminal sugars in the carbohydrate polymers. Random chain cleavage is evidently the dominating reaction during oxygen delignification. Hydroxyl radicals ($\text{HO}\cdot$), the strongest one-electron oxidant in aqueous media, have been suggested to be the actual species responsible for cellulose degradation (McGrouther and co-workers, 2000).

Selectivity, expressed as the ratio of attack on lignin to attack on carbohydrates, is affected by process conditions and pulp contaminants. Selectivity also depends on factors related to the wood species being delignified, the pulping history, and other factors. Reasons for this may be related to the multiplicity of reactive oxygen-containing compounds present in the reaction mixture (Gullichsen and Fogelholm, 2000).

Transition metals, and certain organic compounds originated from pulping may initiate carbohydrate degradation.

2.2 TRANSITION METALS

Transition metal ions are frequently present in wood and pulp. Earlier studies have shown that metal ions like manganese (Mn), copper (Cu), and iron (Fe) play an important role during the lignin oxidation process. The metal ions can act as catalyzing agents during oxygen delignification (Johansson and Ljunggren, 1994).

The random chain cleavage reactions that occur during carbohydrate degradation reactions are catalyzed by the presence of metal ions. In the presence of these metals, reactive oxygen based radicals, such as hydroxy radicals, are formed that randomly attack links in the cellulose chain, resulting in chain breakage at the point of attack. This reduces the molecular weight of the carbohydrate, measured as a decrease in pulp viscosity, and results in a loss of pulp strength (Agarwal, 1998).

The order of selectivity decrease for oxygen delignification when conducted in the presence of ruthenium (Ru), manganese (Mn), iron (Fe), and cobalt (Co) corresponds to the ability of these metal ions to catalyze hydrogen peroxide decomposition. At the high pH values present in the oxygen delignification process, metal ions will catalyze hydrogen peroxide decomposition to generate hydroxyl radicals ($\cdot\text{OH}$) and superoxide anion radicals (O_2^-). This is illustrated in Figure 2.2. The hydroxyl radical initiates reactions which lead to both lignin and carbohydrate degradation. Increased generation of hydroxyl radicals are thought to account for decreased pulp selectivity observed when the above metals are present during oxygen delignification (Hall, Suckling, and Wright, 1996).

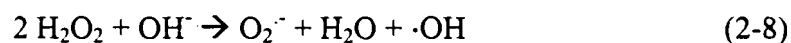
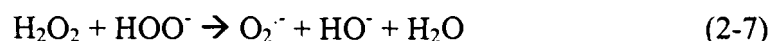


Figure 2.2 Hydrogen Peroxide Decomposition in Alkaline Solution

Hall and co-workers found that Nickel (Ni) was the one metal that when present during oxygen delignification was found to enhance the selectivity of oxygen delignification, brought about by increasing delignification while suppressing carbohydrate degradation (Hall, Suckling, and Wright, 1996).

Van Tran (2000) suggested that there exists a difference in the lignin present in hardwood and softwood kraft pulp in terms of the inorganic composition. Table 2.1 shows the inorganic content in hardwood and softwood (Van Tran, 2000). Comparing the data shown in Table 2.1, there is no iron present in the softwood sample, while the magnesium content in both hardwood and softwood pulps is similar. Moreover, compared to hardwood pulp, softwood pulp contains a lower amount of manganese. The detrimental effects of transition metals on oxygen delignification can be reduced by removing them by acid pretreatment/chelation prior to oxygen delignification or by adding compounds which protect carbohydrates from decomposition.

Table 2.1

Inorganic Composition of Hardwood and Softwood Kraft Pulps

(Van Tran, 2000)

| Inorganics | Hardwood kraft pulp | Softwood kraft pulp |
|------------|---------------------|---------------------|
| Fe | 0.001 | 0.000 |
| Mn | 0.005 | 0.002 |
| Na | 0.350 | 0.051 |
| Mg | 0.124 | 0.127 |
| Al | 0.024 | 0.012 |
| Si | 0.013 | 0.037 |
| P | 0.000 | 0.007 |
| S | 0.050 | 0.047 |
| Cl | 0.004 | 0.001 |
| K | 0.012 | 0.000 |
| Ca | 0.334 | 0.450 |

2.3 PRETREATMENTS

During the alkaline kraft pulping process, transition metals are reduced and converted to their sulfides and oxides (Eul, Helmling, and Suss, 1989). For example:



Neither of these compounds is soluble under the alkaline conditions of brown stock washing. They remain in the pulp and cause side reactions in the oxygen stage. The selectivity of oxygen delignification is affected by high amounts of organic compounds present in the pulp and the transition metal content. To avoid detrimental side reactions, both types of compounds have to be removed in order to achieve the maximum benefit from an oxygen stage (Eul, Helmling, and Suss, 1989). To boost the efficiency and degree of delignification that can be achieved in an oxygen stage, pulp pretreatment is the subject of this research study. The three pretreatment methods investigated in the current

study, that is DTPA pretreatment, acid washing, and the use of A_D stage, will be discussed briefly in the following narration.

2.3.1 Acid Washing

The transition metals cannot be removed by washing, because they are insoluble. An acidification treatment of the pulp converts the insoluble sulfides, oxides, and hydroxides into soluble salts. All the transition metals reduced by the kraft pulping process become soluble under acidic conditions. For example, Fe²⁺, Mn²⁺, Co²⁺, and Ni²⁺ are all soluble as sulfates.

Figure 2.3 shows the effect on delignification and viscosity reduction for softwood kraft pulp and Figure 2.4 shows the oxygen delignification system with acid prewashing (Eul, Helmling, and Suss, 1989). In Figure 2.3, adding Mg⁺⁺ ion raises the pulp viscosity at a given exit kappa number leaving the oxygen stage. Similarly, the best result occurred when acid prewashing preceded oxygen delignification. The most frequently applied method of acid washing is to wash the pulp using sulfuric acid at a pH value less than about 3.

In Figure 2.4, the acid washing step is achieved by adding sulfuric acid in a tower prior to the oxygen stage. Note that the metal ion are sent to the sewer and not recycled back to the recovery boiler. Also please note that in conventional oxygen delignification without the acid prewashing step, the pulp is normally at a high pH, about 9 or 10, leaving the brownstock washer. This is the acid washing process; the user not only incurs the cost of the sulfuric acid required to lower the pH to less than three (3), but then has to pay for additional caustic to raise the pH back up to the pH value of the pulp leaving the

brownstock washers, that is, about 9 to 10. So in essence, the user must pay twice; once for lowering the pH and then a second time for raising the pH.

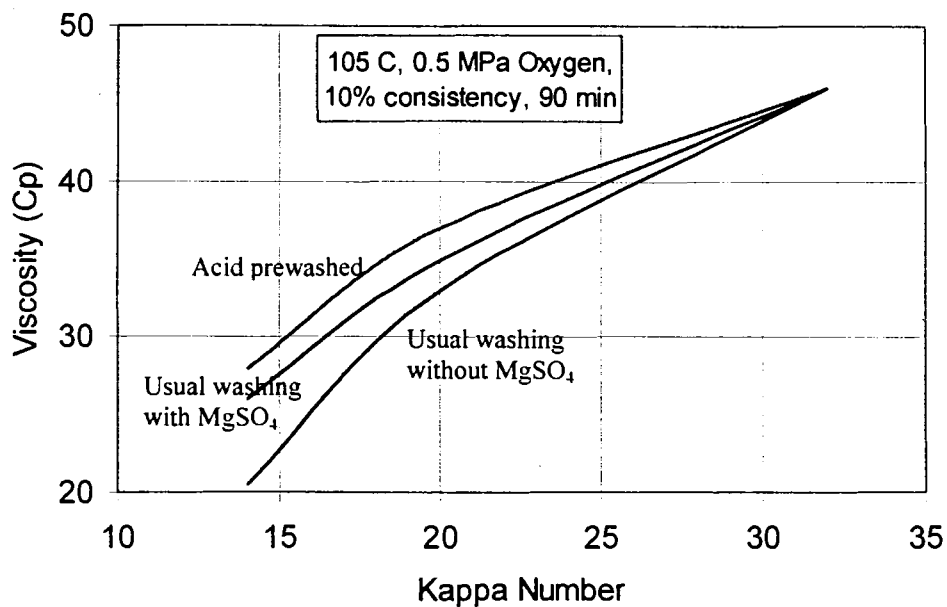


Figure 2.3 Effects of Acid Prewashing and Mg Addition on Delignification and Viscosity in Oxygen Treatment (Eul, Helmling, and Suss, 1989)

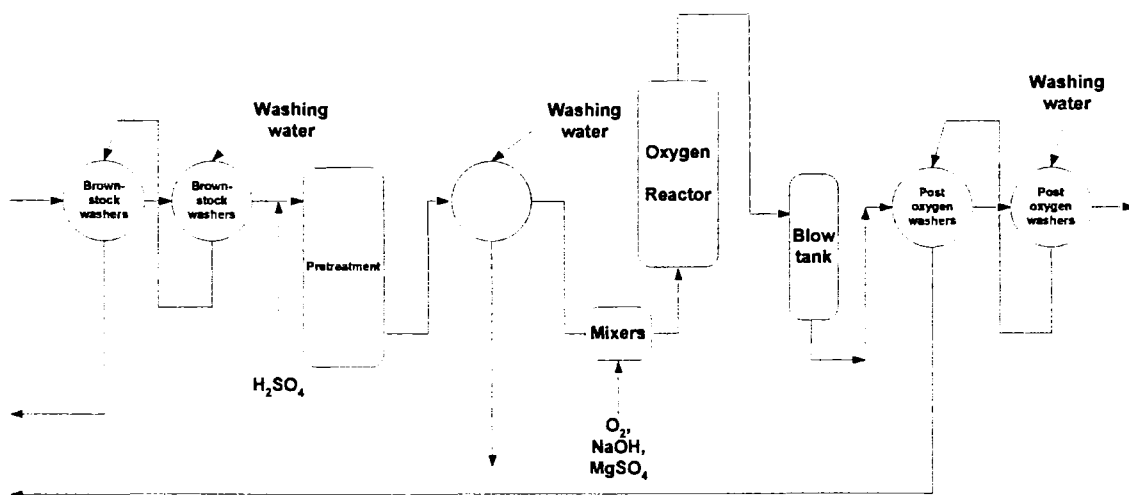


Figure 2.4 Water Circuits of Oxygen Delignification with Acid Prewashing (Eul, Helmling, and Suss, 1989)

2.3.2 DTPA Pretreatment

Chelating agent such as DTPA (diethylenetriamine pentaacetate) and EDTA (ethylenediamine tetraacetic acid) are able to deactivate and remove transition metal ions present in pulps. The most effective of the commercially available chelating agents is the penta-sodium salt of diethylenetriamine pentaacetic acid (Na₅DTPA) (Bambrick, 1985). The Na₅DTPA is a negatively charged compound that can form a ringed structure that alters the reactivity of a positively charged ion. For example, the positive charge from manganese (Mn²⁺) reacts with and become neutralized by the negatively charged acetate groups. This new complex, Na₃MnDTPA, is now stabilized by an overall negative charge. Covalent bonds from the nitrogens and ionic bonds from the acetate groups are the stabilizing forces holding the manganese ion within the DTPA structure. The heavy metal is now inhibited from entering into undesirable reactions, and the perhydroxyl ion is adequately protected (Bambrick, 1985).

The effect of chelation on the content of various metal components is illustrated in Table 2.2.

Table 2.2

Effect of Chelation on Metal Content of Softwood Kraft Pulps

(Gullichsen and Fogelholm, 2000)

| Metal Content, ppm | | | | | |
|--------------------------------|----------|---------|-----|----|---------|
| | Ca | Mg | Fe | Mn | Cu |
| Before chelation | 1400 | 300 | 11 | 47 | 0.6 |
| After chelation ⁽¹⁾ | 500-1000 | 120-580 | 6-8 | <5 | 0.1-0.2 |

(1) Chelation (Q) conditions: 0.2% EDTA, 90°C, 1 hour, pH 5-7

Kraft pulps function as ion exchange materials due to their content of weakly acidic groups. Neither chelation nor an acid wash are capable of eliminating all transition

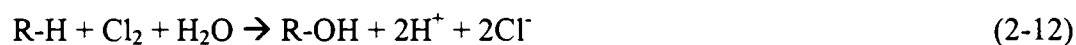
metals from kraft pulp. Iron is especially difficult to remove. Fortunately, iron is the least active in decomposing peroxide. Gullichsen and Fogelholm (2000) list the transition metals in the order based on their aggressivity to peroxide. They are given as Mn>Cu>Fe.

2.3.3 A_D Stage

The A_D stage is called an activation stage prior to oxygen delignification. In this stage sulfuric acid is used to lower the pH value of the pulp along with a small amount of chlorine dioxide or chlorine. The objectives for incorporating this stage into the oxygen delignification process are metals removal, partial treatment for hexenuronic acids, washing, and activation of lignin prior to the oxygen stage (Boniface, 2000).

Chlorine and chlorine dioxide have been, and still are, the most common delignifying chemicals used in chemical pulp bleaching. Chlorine reacts with lignin not only oxidatively but also by addition and substitution. Substitution and oxidation, which are the dominating chemical reactions, are not independent of each other.

Substitution (2-11) and oxidation reactions (2-12) are



Reactions (2-11) and (2-12) can happen simultaneously to form chlorinated chinons or dicarboxylic acids. Lignin is depolymerized and hydrophilic groups (OH⁻ and -COOH) are formed. Lignin solubility is improved in both acidic and alkaline media. Chlorine dioxide reacts differently from chlorine, but is capable of performing a delignification in a similar fashion. Chlorine dioxide is reduced through a series of steps involving several intermediates including chlorite ion (ClO₂⁻), hypochlorous acid (HOCl), chlorine (Cl₂), chlorate, and chloride ion (Cl⁻). Hypochlorous acid and chlorine are capable of forming

organochlorine compounds just as molecular chlorine. Chlorolignin is further hydrolysed by sodium hydroxide to form new phenols which immediately ionize, increasing lignin solubility further. Reaction between chlorine and lignin are extremely fast, and are almost complete in less than a minute. Reactions with carbohydrates are much slower (Gullichsen and Fogelholm, 2000). The important point in both the Cl_2 and ClO_2 chemistries is that adding either material prior to the oxygen stage leads to additional free phenolic groups which are important in causing oxygen delignification to occur.

2.4 ADDITIVES

The addition of Mg-salts reduces the attack of hydroxyl radicals on the carbohydrates, and thus raises the pulp viscosity. According to Liden's work, transition metals are inactivated by redox stabilization when they are incorporated in magnesium precipitates (Liden, 1997). Magnesium should be present in a certain excess over the amount required to tie up the transition metals in bleaching with oxygen or hydrogen peroxide.

There are also other additives such as the chelating agents, which can enhance the degree of delignification and protect the degree of polymerization of the carbohydrates (Van Tran, 2000). Sjogren and Hook (2000) state that DTPA pretreatment prior to oxygen delignification is more efficient than addition of DTPA directly into oxygen delignification in terms of preservation of pulp viscosity (Sjogren and Hook, 2000).

2.5 HYDROGEN PEROXIDE REINFORCEMENT

Hydrogen peroxide has been used in wood pulp bleaching and brightening since 1940. It is increasingly being used during the bleaching of chemical pulps, and plays a key role in bleaching sequences that are totally free of chlorine chemicals. Hydrogen

peroxide under alkaline conditions, as it is normally used, reacts with the hydroxyl ion (OH^-) to yield a perhydroxyl anion (HOO^-):

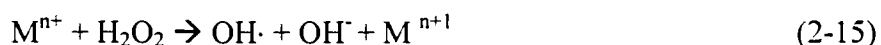


The perhydroxyl anion is a strong nucleophile and is thought to be responsible for most of the bleaching effect under alkaline conditions. Peroxide may also decompose to form oxygen via the simplified reaction (Gullichsen and Fogelholm, 2000):



Also, during oxygen delignification, a small amount of peroxide is formed (Johansson and Ljunggren, 1994).

The general transition metal induced decomposition can be written as:



where M^{n+} is a transition metal in the reduced state and M^{n+1} is the transition metal in the oxidized state. The unstable hydroxy radicals ($\text{OH}\cdot$) are a very powerful one-electron oxidant. They were found to be responsible for the delignification and oxidation degradation of cellulose during oxygen bleaching (Johansson and Ljunggren, 1994).

Reinforcing the oxygen delignification reaction with hydrogen peroxide is another option to raise the level (%) of delignification compared to conventional oxygen delignification. In the model system without metal ions, hydrogen peroxide decreases the formation of biphenols during oxygen delignification (Johansson and Ljunggren, 1994). Biphenols are quite stable against further attack by oxygen. In practice, reinforcement of the oxygen delignification process with hydrogen peroxide encounters some difficulties, since the manganese content in the pulp at this point is often quite high, and also because of dissolved solids carried over to the oxygen reactor. To realize the potential of the

hydrogen peroxide fully, the washing must be efficient and the content of transition metals in the pulp must be lowered in some manner (Sjogren and Hook, 2000). The benefit realized or achieved through addition of hydrogen peroxide to the oxygen stage depends on the mode of addition. Addition of less than 0.5% H_2O_2 improved the properties of oxygen-bleached pulp. Higher charges of hydrogen peroxide lowered the viscosity, compared to a conventional oxygen stage (Gratzl and co-workers, 1990).

2.6 CARBOHYDRATE DEGRADATION

Gierer (1997) proposed one possible reaction mechanism for the degradation of carbohydrates by hydroxyl free radicals. This mechanism is summarized in Figure 2.5.

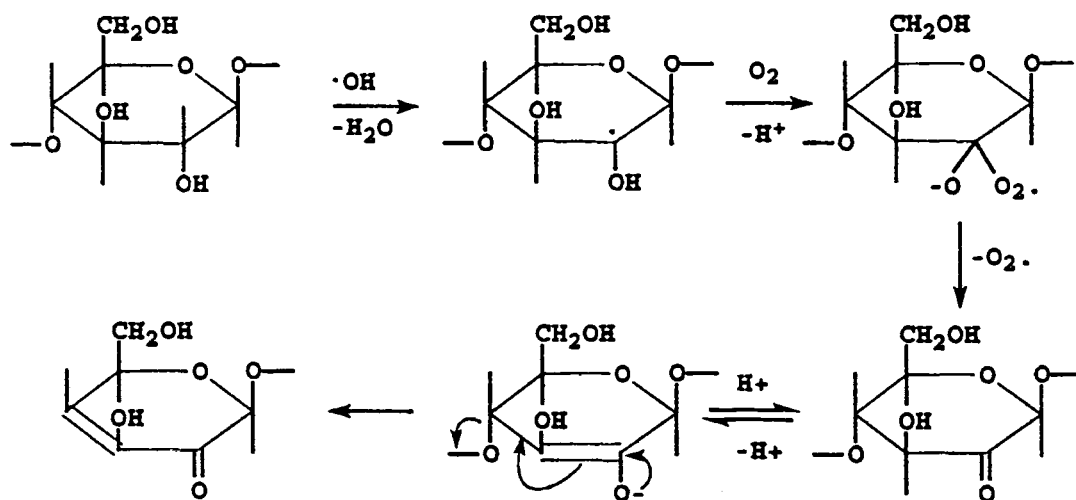


Figure 2.5 Reactions of Hydroxyl Radicals with Carbohydrates (Gierer, 1997).

An alternative mechanism for the oxidative degradation of carbohydrates during oxygen delignification has been suggested by Guay (1999). By means oxygen delignification of model compounds, Guay stated that hydroxyl free radical ($\text{OH}\cdot$) induced the significant degradation to carbohydrate model compounds. Quay (1999) also found that molecular oxygen, superoxide anions, hydrogen peroxide, and hydroxyl anions

did not show the degradation to carbohydrate model compounds directly. He reported that no experimental evidence was found to support the mechanism proposed by Gierer (1997) that is shown in Figure 2.5. Rather, Guay (1999) proposed an alternative degradation mechanism based upon studies with methyl- β -D-cellobioside as a model compound. Guay's mechanism for carbohydrate degradation is shown in Figure 2.6.

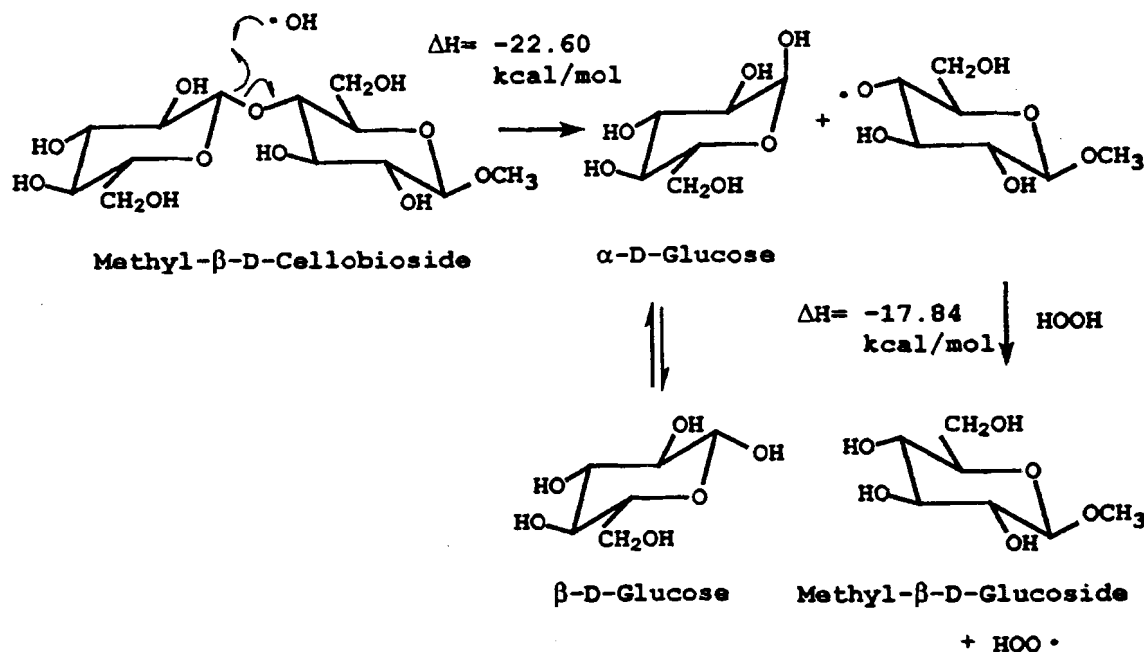


Figure 2.6 Methyl- β -D-glucoside and D-glucose Formation (Guay, 1999).

2.7 SELECTIVITY DURING OXYGEN DELIGNIFICATION

Selectivity is defined as the level of carbohydrate degradation, measured as the decrease in viscosity, per unit drop in lignin content when measured by a reduction in kappa number. Industrially, selectivity data are often plotted as the viscosity versus the kappa number (Gullichsen and Fogelholm, 2000). Figure 2.7 is a schematic diagram presenting perfect selectivity, commonly observed selectivity, and poor selectivity. Perfect selectivity would occur if there is no change in pulp viscosity as delignification occurs. Perfect selectivity would be represented as a horizontal line on the plot of pulp

viscosity versus kappa number. By contrast, infinitely poor selectivity would be represented by a vertical line on the viscosity versus kappa number diagram. For infinitely poor selectivity, there would be a very large drop in pulp viscosity with a small change in kappa number. Commercially, plots of pulp viscosity versus kappa number typically fall between these two limits and is illustrated as “Selectivity Observed Commonly” in Figure 2.7.

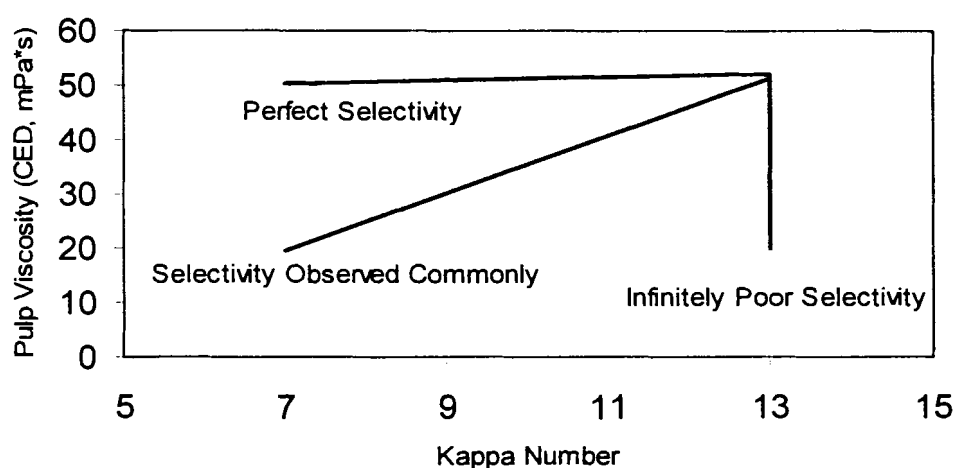


Figure 2.7 Schematic Diagram Showing Perfect Selectivity Compared to Common and Infinitely Poor Selectivity

Selectivity Data of Agarwal (1998). Agarwal (1998) presented a very detailed data base for the oxygen delignification of mixed southern hardwood kraft pulp. These data are described in appendix A. In the current study, the data of Agarwal were analyzed to estimate the selectivity coefficient (α) for a wide variety of temperature conditions and caustic addition rate.

In this exercise, the data were treated by plotting the change in kappa number (ΔK) against the reciprocal change in the degree of polymerization ($\Delta(1/DP)$) of the cellulose in the pulp. This method of treating selectivity data was suggested by Bubniak

(1999) and Zou (2002). The results of these analyses are presented by Figures 2.8, 2.9, and 2.10.

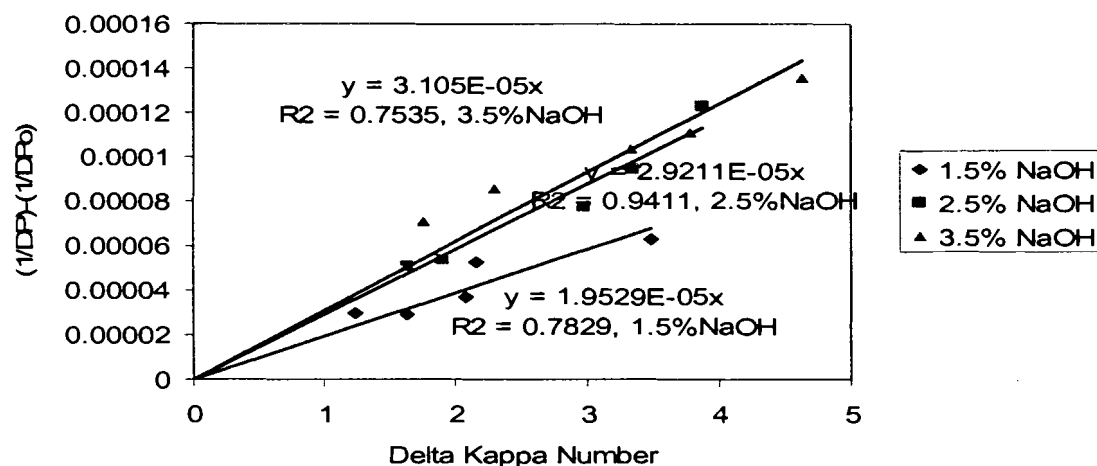


Figure 2.8 Selectivity Plot for Southern Hardwood Kraft Pulp during Oxygen

Delignification – Effect of Caustic Addition at 90 °C, 100 psi

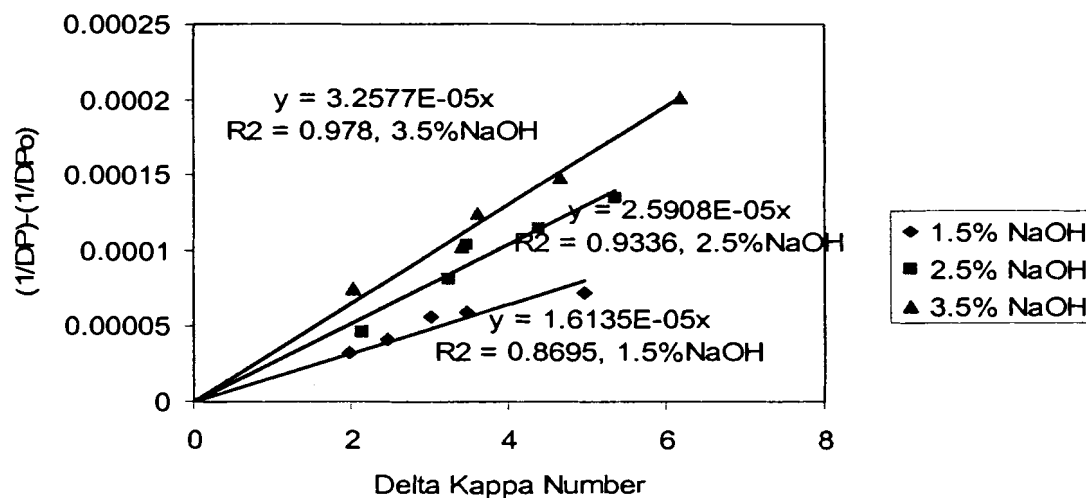


Figure 2.9 Selectivity Plot for Southern Hardwood Kraft Pulp during Oxygen

Delignification – Effect of Caustic Addition at 100 °C, 100 psi

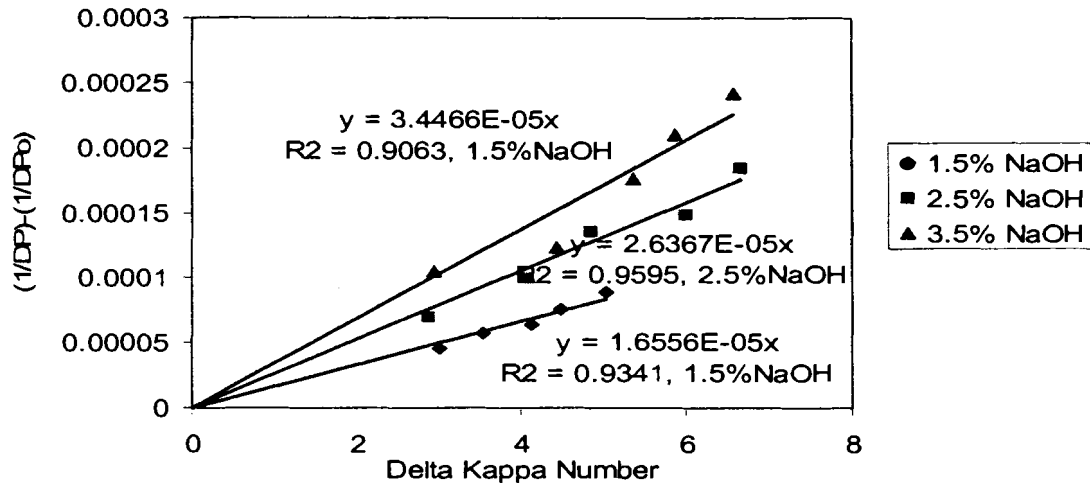


Figure 2.10 Selectivity Plot for Southern Hardwood Kraft Pulp during Oxygen Delignification – Effect of Caustic Addition at 110 °C, 100 psi

From Figures 2.8, 2.9, and 2.10, the trend line for each set data shows that there is a strongly linear relationship between $\Delta(1/DP)$ and ΔK , which is a measure of the rate of carbohydrate degradation as delignification proceeds. In the Bubniak (1999) representation, the selectivity coefficient (α) is taken to be the slopes shown in Figures 2.8, 2.9, 2.10.

$$\alpha = \frac{d[1/DP - 1/DP_0]}{dK} \cong \frac{\Delta[1/DP - 1/DP_0]}{\Delta K} \quad (2-16)$$

The data for the selectivity coefficient (α) are summarized in Table 2.3 as a function of the caustic addition rate and the conditions in the oxygen reactor. The units on the selectivity coefficient (α) are given in terms of (ml⁻¹).

Table 2.3

Selectivity Coefficient (α) for Oxygen Delignification of Mixed Southern Hardwood

Brownstock

| Conditions | Caustic Charge (NaOH) | Selectivity Coefficient (α) | R ² Value |
|------------------------------|-----------------------|--------------------------------------|----------------------|
| 90 ⁰ C 100psi | 1.50% | 1.95 | 0.7929 |
| | 2.50% | 2.92 | 0.9411 |
| | 3.50% | 3.11 | 0.7535 |
| 100 ⁰ C 100psi | 1.50% | 1.61 | 0.8695 |
| | 2.50% | 2.59 | 0.9336 |
| | 3.50% | 3.26 | 0.9780 |
| 110 ⁰ C 100psi | 1.50% | 1.66 | 0.9341 |
| | 2.50% | 2.64 | 0.9595 |
| | 3.50% | 3.45 | 0.9063 |

The selectivity coefficient (α) for southern hardwood is plotted versus the caustic addition rate for temperatures of 90 ⁰C, 100 ⁰C and 110 ⁰C in Figure 2.11. The data for the selectivity coefficient (α) have been replotted in Figure 2.12 as a function of temperature using the caustic addition rate as a parameter. Based upon the definition of the selectivity coefficient (α), the higher the value for the selectivity coefficient, the lower or poorer will be the selectivity during oxygen delignification. In other words, the lower the value of the selectivity coefficient (α), the lower the number of carbohydrate chains that have been cleaved during oxygen delignification by random hydrolysis reactions (See Figures 2.5 and 2.6). From the data plotted in Figures 2.11 and 2.12, it is abundantly clear that for mixed southern hardwood, temperature has very little effect on pulp selectivity; rather pulp selectivity is being influenced primarily by the caustic addition rate. Thus, the industrial significance of the data in Figures 2.11 and 2.12 is clear. Industrially, in a one stage oxygen delignification system, to maximize the percent

delignification and drive the oxygen delignification reactions to the lowest possible kappa number with the least carbohydrate degradation, the temperature should be raised to as high a level as possible and the system operated with the lowest level of caustic addition.

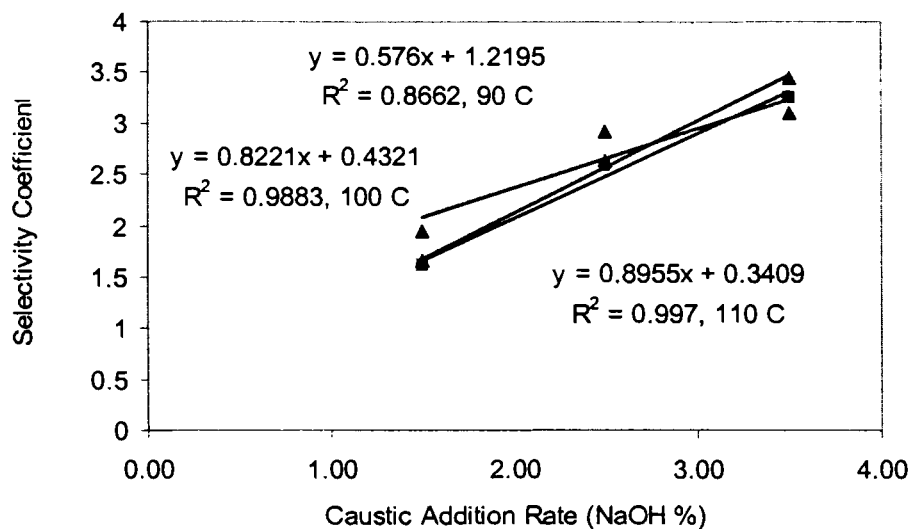


Figure 2.11 Selectivity Coefficient (α) for Southern Hardwood Brownstock versus Caustic Addition Rate

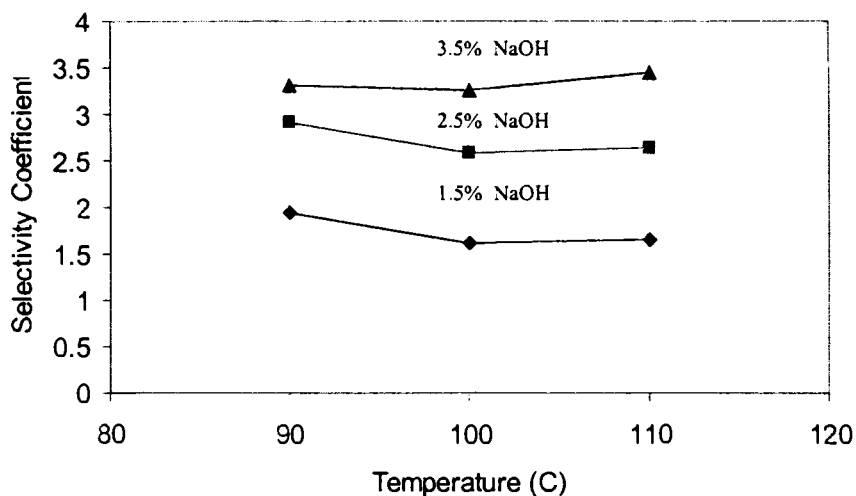


Figure 2.12 Selectivity Coefficient (α) for Southern Hardwood Plotted versus Temperature

CHAPTER 3

EXPERIMENTAL CONDITIONS

3.1 CONVENTIONAL OXYGEN DELIGNIFICATION

3.1.1 Samples

Northeast hardwood kraft brownstock pulp was obtained from a kraft pulp mill located in Old Town, Maine. It was thereafter washed and screened on a Bird flat screen in the Pilot Plant in the Department of Chemical Engineering at the University of Maine. The brownstock pulp after it was cleaned and screened pulp was mixed thoroughly and stored in a refrigerator. The pulp was used without further washing before oxygen delignification. The moisture content was determined prior to use in the oxygen stage. The initial Kappa Number was 13.7, and the initial Intrinsic Viscosity was 1196 cc/g. On all occasions, de-ionized water was used, i.e. for the dilution of pulp, washing, and the preparation of bleaching chemicals.

3.1.2 Chemicals

A variety of chemicals were used in the oxygen delignification experiments.

1. Sodium hydroxide (0.5mol/l). Sodium hydroxide was used at a concentration of 0.5 mole/l.
2. Hydrogen Peroxide. The concentration of hydrogen peroxide was determined every month due to the decomposition of hydrogen peroxide.
3. DTPA (diethylenetriamine pentaacetate). The DTPA was prepared to a concentration of 0.005g/ml.
4. MgSO_4 . Magnesium sulfate was prepared to a concentration of 0.02g/ml.

5. Sulfuric acid. 10% sulfuric acid was prepared for the use of adjusting pH value during pretreatment.
6. Chlorine Dioxide (ClO_2). The solution was prepared by Seong Kyung Park in the Pilot Plant, at a concentration of 8 to 10 g/l. The concentration of ClO_2 was measured prior to use.

3.1.3 Oxygen Delignification Experiments

Oxygen delignification experiments were carried out in a stainless steel 20-liter autoclave equipped with a mixer and temperature controller. The experiments were performed using two methods. Pulp was distributed on a glass plate and compared to identical experiments performed in the stainless steel reactor. These experiments were performed to evaluate the effect of pickup of metal from the reactor surface on oxygen delignification. The speed of the mixer was set at 23 RPM and was constant for all the experiments during the oxygen delignification reactions performed in the stainless steel reactor. For the experiments performed in glass, the glass plate was surrounded by water in the metal reactor and was set on the shaft of the mixer. When the experiments in glass were performed, the speed of the mixer was set at 0 RPM. Unless otherwise stated, the following conditions were used: temperature, 90 °C; reaction time, 1 hour; pulp stock consistency, 12%; oxygen pressure, 100 psig; sodium hydroxide charge, 2%; MgSO_4 charge, 0.2%. These conditions are tabulated in Table 3.1.

The quantity of pulp used in the metal reactor was 100 g, based on the oven dried weight. Because of the poor mixing during the oxygen delignification experiments performed in glassware, the oven-dried weight of pulp used in the glassware was reduced to 50 g. The oxygen delignification experiments were initially performed in the glassware

at the same conditions as those performed in the metal reactor (Table 3.1) except that the O.D. weight of pulp was raised between 25g, 50g, and 100g. The results showed that the final kappa number and the final intrinsic viscosity were virtually identical when the experiments were conducted with 25g pulp and 50g pulp. The experiments that were performed with 100g pulp (Figure 3.1 and Figure 3.2) indicated that the reactions were controlled by mass transfer effects. These results are tabulated in Table 3.2.

Table 3.1

Conventional Oxygen Delignification Conditions

| Pulp | Northeast Hardwood Kraft |
|-----------------------------|--------------------------|
| Consistency | 12% |
| Initial Kappa Number | 13.7 |
| Initial Intrinsic Viscosity | 1196ml/g |
| Temperature | 90 ⁰ C |
| NaOH charge | 2% on O.D. pulp |
| Oxygen pressure | 100 psig |
| Reactions Time | 60 minutes |
| MgSO ₄ charge | 0.2% on O.D. pulp |

Table 3.2

Effect of Mass of Pulp on Oxygen Delignification

| Mass (g) | Final Kappa Number | Final Intrinsic Viscosity (ml/g) |
|----------|--------------------|----------------------------------|
| 100 | 10 | 1038 |
| 50 | 9.8 | 1096 |
| 25 | 9.8 | 1110 |

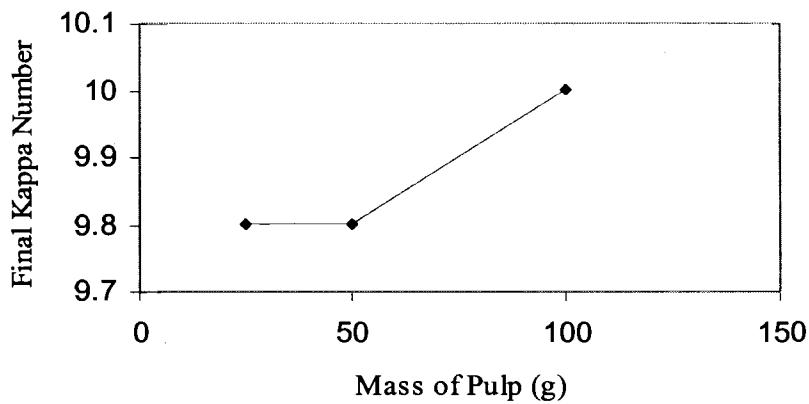


Figure 3.1 Mass of Pulp versus the Final Kappa Number

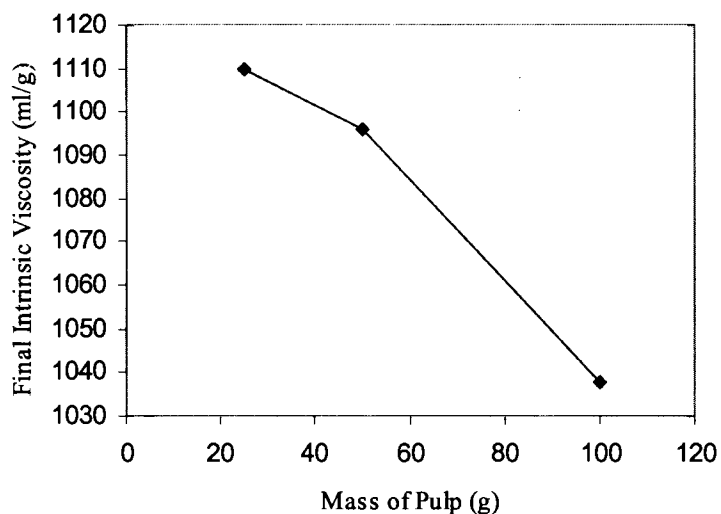


Figure 3.2 Mass of Pulp versus the Final Intrinsic Viscosity

3.1.4 Delignification Procedure

3.1.4.1 Oxygen Delignification in the Stainless Steel Reactor

The stainless steel reactor was filled with water and preheated generally to a target temperature of 92 °C, which was slightly higher than the reaction temperature. The kraft brownstock pulp (100 g) was mixed with MgSO_4 and NaOH successively in a polyethylene bag. If H_2O_2 was required, it was the last chemical to be added. After the

chemicals were added, the stock was diluted to 12% consistency. The polyethylene sample bag was then sealed and placed into a microwave oven and preheated for 8 minutes.

The hot water in the reactor was drained, and the pulp was placed into the reactor and covered. The reactor was covered quickly but removing the cover caused a decrease in the temperature of the reactor. The mixer was turned on and the speed adjusted to 23 RPM. When the reactor was heated to the desired reaction temperature (90 °C), oxygen was added to the reactor and pressurized to 100 psig. Once the temperature and pressure were set, the stopwatch was started.

After 1-hour reaction, the oxygen pressure was released to the atmosphere. The delignified pulp was taken out and washed in a Buchner funnel with de-ionized water. The pulp pad was air dried in the laboratory and stored for the later evaluation of kappa number and intrinsic viscosity.

3.1.4.2 Oxygen Delignification in Glass

The reactor was filled with water and preheated generally to the reaction temperature (90 °C). The glass plate was laid on the mixer in the reactor and surrounded by the water. The kraft brownstock pulp (50 g) was mixed with MgSO_4 and NaOH successively in a polyethylene bag. If H_2O_2 was required, it was the last chemical to be added. The stock was diluted to 12% consistency. After the sample bag was sealed, it was placed into the microwave oven and preheated for 7 minutes.

The heated pulp was placed into the glass plate and the reactor was covered quickly. The temperature of the reactor did not decrease because the hot water was not drained. Oxygen was added to the reactor and pressurized to 100 psig, and the stopwatch started. After 1-hour reaction, the oxygen pressure was released to the atmosphere. The

delignified pulp was taken out and washed in a Buchner funnel with de-ionized water. The pad was air dried in the laboratory and stored for the later evaluation of kappa number and intrinsic viscosity.

3.2 THE PRETREATMENT CONDITION AND RESULTS

3.2.1 DTPA Pretreatment

The water bath was set at 60 °C. The desired weight of pulp was placed into a beaker. The pulp was diluted to 3% consistency by adding de-ionized water which contained DTPA. The DTPA addition rate was 0.3% based on the pulp. The pH value of the slurry was adjusted to a pH of 6.0 by adding 10% H₂SO₄. The slurry was placed into a polyethylene bag and sealed. Following that, the slurry was put into the water bath for 30 minutes.

After the DTPA pretreatment, the slurry was squeezed by hand and washed in a Buchner funnel using de-ionized water. The pad was weighed for the next oxygen delignification stage.

Table 3.3 shows the metals profile of the pulp with and without DTPA pretreatment. The metal content in pulp was measured by using Induction Coupled Plasma spectroscopy (ICP) in the Analytical Lab in the Department of Plant, Soil, and Environmental Sciences.

Table 3.3

Results of the Metal Analysis of the Chelated Pulp by DTPA

| Sample | Metal (PPM for all nutrients in dry sample) | | | | | |
|------------------------------|---|-----|------|-------|------|------|
| | Ca | Mg | Al | Cu | Fe | Mn |
| Original Pulp | 3900 | 430 | 14.3 | 6.66 | 8.02 | 73.7 |
| Pulp after DTPA pretreatment | 2240 | 225 | 8.89 | 0.751 | 7.46 | 7.01 |

The results showed that DTPA pretreatment was capable of removing the transition metals in the pulp, especially copper and manganese.

3.2.2 Acid Washing

Two conditions for acid washing were compared. Acid washing techniques are described by Hook (2000) and Boniface (2000). The acid washing conditions described by Boniface (2000) are being applied in the Lincoln pulp mill operated by Eastern Fine Paper Company. The conditions given by both Hook (2000) and Boniface (2000) are summarized in Table 3.4. Initial work showed that there was a large decrease in the intrinsic viscosity of the pulp when Hook's conditions were used.

Table 3.4

The Conditions Used by Hook (2000) and Boniface (2000)

| Condition Item | Hook | Boniface |
|----------------|-------------------|-------------------|
| Temperature | 90 ⁰ C | 60 ⁰ C |
| pH value | 3.0 | 2.8-3.2 |
| Time | 180 min | 30 min |

3.2.2.1 Condition Used by Hook (2000)

The water bath was set at 90 ⁰C. The desired weight of pulp was placed into a beaker. The pulp was diluted to 3% consistency by de-ionized water. To evaluate the effect of the pH on the acid pretreatment, the pH of the pulp was systematically adjusted between neutral condition and a pH value of 1.5. The pH value of the slurry was adjusted by adding 10% H₂SO₄. The slurry was then placed into a polyethylene bag and sealed. Following that, the slurry was put into the water bath for 180 minutes. After the acid pretreatment, the slurry was squeezed by hand and washed in a Buchner funnel by using

de-ionized water. Table 3.5 shows the metal profile of the pulp before and after application of Hook's condition.

It is clear from the data shown in Table 3.5 that systematically decreasing the pH of the acid stage leads to increased removal of metals.

Table 3.5

Results of the Metal Analysis of the Pulp before and after Acid Pretreatment Using Hook's Condition

| Sample | | Metal (PPM for all nutrients in dry sample) | | | | | |
|------------------|---------------|---|------|-------|-------|-------|-------|
| | | Ca | Mg | Al | Cu | Fe | Mn |
| Original | | 3900 | 430 | 14.3 | 6.66 | 8.02 | 73.7 |
| Hook's Condition | pH=1.5 | 10.3 | 1.94 | <4.97 | <.199 | <4.62 | 0.199 |
| | pH=2.0 | 43.9 | 6.79 | <5.03 | 0.704 | 2.87 | 0.805 |
| | pH=3.0 | 142 | 18 | <5.41 | 4 | 10 | 3.19 |
| | pH=3.5 | 291 | 37.3 | <4.95 | 5.34 | 9.79 | 7.67 |
| | pH=4.0 | 933 | 93.4 | 9.78 | 5.76 | 8.89 | 21.7 |
| | no acid added | 3020 | 297 | <4.97 | 6.36 | 8.7 | 68.8 |

The kappa number and the intrinsic viscosity were checked to determine whether acid pretreatment affected the results. Table 3.6 shows that the acid pretreatment conditions published by Hook (2000) decreased the kappa number and the intrinsic viscosity simultaneously. The decrease in the kappa number was attributed to the removal of lignin and also the removal of hexenuronic acid in the pulp. The intrinsic viscosity was lowered probably because of acidic hydrolysis of the cellulose.

Table 3.6

Results of Kappa Number and Intrinsic Viscosity after Acid Pretreatment Using Hook's Condition

| pH value of the acid washing | Kappa Number | Intrinsic Viscosity (ml/g) |
|------------------------------|--------------|----------------------------|
| 1.5 | 9.3 | 734 |
| 2.0 | 9.4 | 913 |
| 3.0 | 9.7 | 1092 |
| 4.0 | 12.7 | 1158 |
| No acid added | 13.7 | 1196 |

3.2.2.2 Condition Used at Eastern Fine Paper Co. (Boniface, 2000)

In the investigation of the A stage conditions published by Boniface (2000), the water bath was set at 60 °C. The desired weight of pulp was placed into a beaker. The pulp was diluted to 3% consistency by de-ionized water. The pH value of the slurry was adjusted to three (3) by adding 10% sulfuric acid (H₂SO₄). The slurry was placed into a polyethylene bag and sealed. Following that, the slurry was placed in the water bath. Time periods of 30, 60, 120, and 180 minutes were applied to the acid pretreatment stage to evaluate the effectiveness of this technique.

After the acid pretreatment process was applied, the slurry was squeezed by hand and washed in a Buchner funnel by using de-ionized water.

Table 3.7 shows the metal profile of the pulp before and after application of an A-stage using the conditions reported by Boniface (2000).

Table 3.7

Results of the Metal Analysis for Pulp Samples with and without Boniface's Condition

| Sample | | Metal (PPM for all nutrients in dry sample) | | | | | |
|-----------|-------|---|------|-------|------|------|------|
| | | Ca | Mg | Al | Cu | Fe | Mn |
| Original | | 3900 | 430 | 14.3 | 6.66 | 8.02 | 73.7 |
| Lincoln's | 0.5hr | 246 | 31.7 | <4.92 | 3.25 | 7.78 | 6.15 |
| | 1.0hr | 172 | 22.2 | <4.93 | 2.17 | 8.78 | 4.14 |
| | 2.0hr | 201 | 26 | <4.96 | 3.37 | 6.75 | 4.91 |
| | 3.0hr | 255 | 33.5 | <4.98 | 2.79 | 7.66 | 6.47 |

The results shown in Table 3.7 illustrate that the acid pretreatment summarized by Boniface (2000) readily removes the metal contents of the pulp and that the metal contents following treatment are not strongly dependent upon the time period.

The kappa number and the intrinsic viscosity were measured to determine the effect of the acid pretreatment. Table 3.8 shows that the Boniface pretreatment decreases the kappa number slightly, but does not materially affect the intrinsic viscosity of the pulp.

Table 3.8

Results of Kappa Number and Intrinsic Viscosity Using Acid Pretreatment Condition
Given by Boniface (2000)

| Time (hour) | Kappa Number | Intrinsic Viscosity (ml/g) |
|-------------|--------------|----------------------------|
| 0.5 | 13.7 | 1196 |
| 1.0 | 13.6 | 1196 |
| 2.0 | 13.4 | 1194 |
| 3.0 | 13.3 | 1193 |

Finally, the time period for the acid treatment was selected as 0.5 hour based on the results for the metal content, the final kappa number, and the final intrinsic viscosity shown in Tables 3.7 and 3.8.

3.2.3 A_D Stage

In evaluating the effectiveness of an A_D pretreatment stage, the water bath was set at 60 °C. The desired weight of pulp was placed into a beaker. The pulp was diluted to 3% consistency by using de-ionized water with 0.4% ClO₂ added based on the pulp. The pH value of the slurry was then adjusted to three (3) by adding 10% H₂SO₄. The slurry was placed into a polyethylene bag and sealed. Following that, the slurry was put into the water bath for 30 minutes.

After the A_D pretreatment had been completed, the slurry was squeezed by hand and washed in a Buchner funnel using de-ionized water. Table 3.9 shows the metal profile of the pulp before and after application of an A_D stage using conditions similar to those reported by Boniface (2000).

Table 3.9

Results of the Metal Analysis of the Pulp after an A_D Stage

| Sample | Metal (PPM for all nutrients in dry sample) | | | | | |
|------------------------------|---|-----|-------|------|------|------|
| | Ca | Mg | Al | Cu | Fe | Mn |
| Original Pulp | 3900 | 430 | 14.3 | 6.66 | 8.02 | 73.7 |
| Pulp after DTPA pretreatment | 302 | 28 | <4.96 | 3.80 | 6.40 | 5.62 |

Table 3.10 shows the results for the kappa number and intrinsic viscosity after the A_D stage. These preliminary experiments showed that the A_D stage decreases the kappa number from 13.7 to 10.5, and decreases the intrinsic viscosity.

Table 3.10

Results of Kappa Number and Intrinsic Viscosity after an A_D Stage Using Condition
Given by Boniface (2000)

| Condition of A _D | Kappa Number | Intrinsic Viscosity (ml/g) |
|--|--------------|----------------------------|
| 0.5 hr, pH=3.0, 0.4% ClO ₂ , 60°C | 10.5 | 1154 |

3.3 ANALYSIS OF THE PULP

3.3.1 Kappa Number

The kappa number is defined as the number of ml of 0.1N KMnO₄ that reacts with one gram of the pulp under specified conditions following the TAPPI standard method. It is proportional to the lignin content of the pulp. The kappa number of the pulp was measured according to TAPPI standard method T236 os-76.

3.3.2 Intrinsic Viscosity

The intrinsic viscosity of the pulp is representative of the degree of polymerization of the cellulose chains in the pulp. The intrinsic viscosity $[\eta]$ was estimated according to ASTM standard D1795-62 which is similar to SCAN-C 15:62. The degree of polymerization of the cellulose was estimated using equation (A-2) in Appendix A.

3.3.3 Hydrogen Peroxide (H₂O₂) Content

The strength of the H₂O₂ was analyzed by the procedure in the Pilot Plant in the Department of Chemical Engineering. In this method, 5 ml of peroxide solution was pipetted into a flask. The sample was acidified by adding 10 ml 20% H₂SO₄. The mixture was then titrated with 0.1N potassium permanganate until a pink end point. The volume

(V, ml) of 0.1N potassium permanganate added to the sample was recorded for calculating the peroxide content by equation (3-1).

$$\text{H}_2\text{O}_2 \text{ (g/l)} = 0.3402 \times V \quad (3-1)$$

3.3.4 ClO₂ Content

The strength of the ClO₂ solution was analyzed by the procedure in the Pilot Plant in the Department of Chemical Engineering. First, 50 ml of distilled water was mixed with 15 ml 1N KI and 5 ml 20% H₂SO₄. Second, 5 ml of ClO₂ of liquor was added using a pipette into the mixture below the liquid level. The mixture was then titrated with 0.1N Na₂S₂O₃ using a starch indicator near the end point. The consumption volume (V, ml) of 0.1N Na₂S₂O₃ was recorded for calculating the ClO₂ content by equation (3-2).

$$\text{ClO}_2 \text{ (g/l)} = 0.2698 \times V \quad (3-2)$$

3.3.5 Metal Analysis

Metals in the pulp were analyzed using Induction Coupled Plasma (ICP) spectroscopy. This ICP technique is described in Appendix D.

CHAPTER 4

EXPERIMENTAL RESULTS

The experimental design is summarized in Figure 4.1. The experimental matrix was distinguished by performing oxygen delignification experiments with four (4) different pretreatments. These were characterized as (1) no pretreatment, (2) pretreatment with DPTA (Q-stage), (3) pretreatment in an acid washing (A-stage), and (4) pretreatment in an acid stage fortified with a small amount of chlorine dioxide (A_D -stage). Each of the four (4) delignification conditions was investigated in both (5) glass and (6) in a 316 stainless steel reactor. Experiments in the metal reactor were conducted to investigate the effect of metals contaminating the reaction mixture. Lastly, all of the above experiments were performed (7) with and (8) without using hydrogen peroxide to reinforce the oxygen stage. Altogether sixteen (16) different experimental conditions were investigated in the experimental design. Four (4) replicate oxygen delignification experiments were performed for each of the sixteen (16) conditions. Thus the data base consisted of sixty (64) actual experiments.

Number of Experiments = 4 Pretreatments \times 2 Materials \times 2 H_2O_2 Treatments \times 4

Replicate Experiments = 64 Total Experiments

For each experiment, the measured response variables were the kappa number and intrinsic viscosity after oxygen delignification.

All of the oxygen delignification experiments were performed at 90 °C and 100 psig oxygen pressure (6.89 bar). The caustic and magnesium sulfate were applied at a dose rate of 2% NaOH and 0.2% $MgSO_4$ based on pulp. In those cases where hydrogen

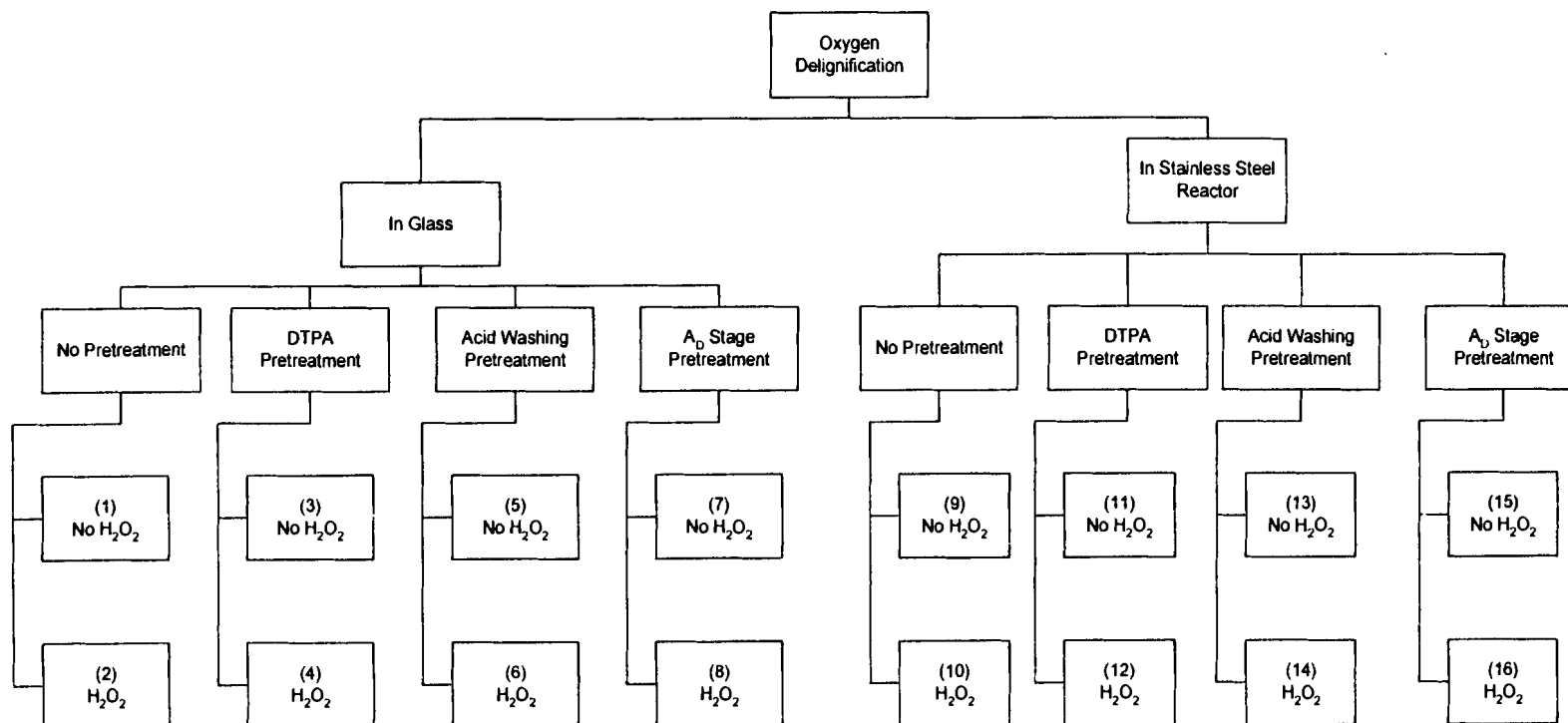


Figure 4.1 Summary of Experimental Design for Oxygen Delignification

peroxide was used to fortify the reaction mixture; the hydrogen peroxide was applied at a dose rate of 0.5% H₂O₂ based on pulp.

4.1 RESULTS OF OXYGEN DELIGNIFICATION

The experimental results are summarized in Table 4.1 through 4.4. The experiment numbers in the table are based on the experimental design shown in Figure 4.1. Detailed results include the final kappa number (K), the final intrinsic viscosity ([η]), the percent delignification (% Delig), and the selectivity coefficient (α). For each of the sixteen (16) experimental conditions shown in the tables, the mean value, the standard deviation and the 95% upper and lower confidence limits are presented. Treatment of the data to calculate the selectivity coefficient (α) is described in Appendix B. Also, the sample calculation for estimating the 95% confidence intervals is shown in Appendix B.

The percent delignification was calculated from the equation

$$\% Delignification = \frac{K_0 - K_t}{K_0} \quad (4-1)$$

where K_0 is the initial kappa number and K_t is the kappa number at the end of oxygen delignification. The selectivity coefficient (α) was estimated by the equation as follows:

$$\alpha = \frac{d[1/DP - 1/DP_0]}{dK} \cong \frac{\Delta[1/DP - 1/DP_0]}{\Delta K} \quad (4-2)$$

In the definition of the selectivity coefficient (α), a lower number represents better selectivity during oxygen delignification.

4.1.1 No Pretreatment

Table 4.1 summarizes the results of the oxygen delignification experiments that were performed without pretreatment. The best selectivity was achieved in Experiment 1, which was the oxygen delignification experiment without pretreatment, and was carried

out without hydrogen peroxide present in glass ($\alpha=0.933\text{ml}^{-1}$). Slightly lower, but similar selectivity was achieved in Experiment 9, which was performed without pretreatment in the stainless steel reactor ($\alpha=1.00\text{ml}^{-1}$).

4.1.2 DTPA Pretreatment

The results for oxygen delignification experiments with DTPA pretreatment are tabulated in Table 4.2. In terms of the selectivity ($\alpha=0.644\text{ml}^{-1}$), the best result was achieved in Experiment 4, which was the oxygen delignification experiments that were performed with hydrogen peroxide reinforcement in glass with DTPA pretreatment.

4.1.3 Acid Washing

Detailed results of the oxygen delignification experiments conducted with an acid washing pretreatment are summarized in Table 4.3. Based on the selectivity coefficient (α), the best result for the oxygen delignification experiments was achieved in Experiment 13, which was the oxygen delignification experiments conducted in the stainless steel reactor without hydrogen peroxide present ($\alpha=0.758\text{ml}^{-1}$).

4.1.4 A_D Stage

The results for the experiments performed with an A_D stage as a pretreatment are shown in Table 4.4. Similar to the previous results, the selectivity coefficient (α) in Experiment 7 had the lowest value ($\alpha=0.519\text{ml}^{-1}$). Experiment 7 was the oxygen delignification experiment performed in glass without the presence of hydrogen peroxide.

4.1.5 Metals Analysis

The results for the metals analysis are summarized in Appendix D. Table D.1 presents the data for the concentration of important metals thought to affect oxygen delignification. Transition metals of particular importance are iron (Fe), manganese (Mn)

and copper (Cu). The copper analyses are suspect since all of the samples showed elevated copper contents except for the original pulp and some samples pretreated early in the work that is the first four (4) samples in Table D.1. One possible explanation for these results is that the pulp was contaminated with copper during processing; or alternatively, there may have been a problem in the ICP analysis. The results for the analysis for iron (Fe) and Manganese (Mn) suggest that all three of the pretreatment processes were effective for control of manganese (Mn) but considerably less effective for the control of iron (Fe).

Table 4.1

Results of the Oxygen Delignification Experiments without Pretreatment Showing 95% Upper and Lower Confidence Limits

| Initial Kappa Number (K_0) = 13.7, Initial Intrinsic Viscosity ($[\eta]$) = 1196ml/g | | | | | | | | | |
|--|------------------------------|----------------------------|--|--|---|------------------------------|----------------------------|--|--|
| Performed in Glass | Final Kappa number (K_t) | Intrinsic Viscosity (ml/g) | Percent Delignification (% Delig = $(K_0 - K_t)/K_0$) | Selectivity $[(1/DP) - (1/DPO)] * 10^5 / \Delta K = \alpha$ (1/ml) | Performed in Stainless steel reactor | Final Kappa number (K_t) | Intrinsic Viscosity (ml/g) | Percent Delignification (% Delig = $(K_0 - K_t)/K_0$) | Selectivity $[(1/DP) - (1/DPO)] * 10^5 / \Delta K = \alpha$ (1/ml) |
| Experiment 1 (No Pretreatment No H_2O_2) | 9.2 | 1021 | 32.8% | 0.931 | Experiment 9 (No Pretreatment No H_2O_2) | 8.8 | 1001 | 35.8% | 0.973 |
| | 9.2 | 1022 | 32.8% | 0.925 | | 9.2 | 993 | 32.8% | 1.113 |
| | 9.4 | 1024 | 31.4% | 0.955 | | 8.8 | 1012 | 35.8% | 0.908 |
| | 9.3 | 1026 | 32.1% | 0.921 | | 8.9 | 999 | 35.0% | 1.006 |
| Mean | 9.3 | 1023 | 32.3% | 0.933 | Mean | 8.9 | 1001 | 34.9% | 1.000 |
| Stand Dev | 0.096 | 2.217 | 0.00699 | 0.015 | Stand Dev | 0.189 | 7.932 | 0.01382 | 0.086 |
| Upper Limit | 9.4 | 1027 | 33.4% | 0.957 | Upper Limit | 9.23 | 1013.87 | 37.1% | 1.136 |
| Lower Limit | 9.1 | 1020 | 31.2% | 0.909 | Lower Limit | 8.62 | 988.63 | 32.7% | 0.864 |
| Experiment 2 (No Pretreatment with H_2O_2) | 9.0 | 992 | 34.3% | 1.072 | Experiment 10 (No Pretreatment with H_2O_2) | 8.5 | 965 | 38.0% | 1.129 |
| | 8.9 | 981 | 35.0% | 1.119 | | 8.6 | 945 | 37.2% | 1.279 |
| | 8.7 | 962 | 36.5% | 1.194 | | 8.8 | 937 | 35.8% | 1.386 |
| | 8.6 | 965 | 37.2% | 1.152 | | 8.6 | 944 | 37.2% | 1.286 |
| Mean | 8.8 | 975 | 35.8% | 1.134 | Mean | 8.6 | 948 | 37.0% | 1.270 |
| Stand Dev | 0.183 | 14.07 | 0.01333 | 0.052 | Stand Dev | 0.13 | 12.04 | 0.00918 | 0.106 |
| Upper Limit | 9.1 | 997 | 37.9% | 1.216 | Upper Limit | 8.8 | 967 | 38.5% | 1.439 |
| Lower Limit | 8.5 | 953 | 33.6% | 1.052 | Lower Limit | 8.4 | 929 | 35.6% | 1.102 |

Table 4.2

Results of the Oxygen Delignification Experiments with DTPA Pretreatment Showing 95% Upper and Lower Confidence Limits

| Initial Kappa Number (K_0) = 13.7, Initial Intrinsic Viscosity ($[\eta]$) = 1196 ml/g | | | | | | | | | |
|---|------------------------------|----------------------------|--|--|--|------------------------------|----------------------------|--|--|
| Performed in Glass | Final Kappa number (K_t) | Intrinsic Viscosity (ml/g) | Percent Delignification (% Delig = $(K_0 - K_t)/K_0$) | Selectivity $[(1/DP) - (1/DPO)] \cdot 10^5 / \Delta K = \alpha$ (1/ml) | Performed in Stainless steel reactor | Final Kappa number (K_t) | Intrinsic Viscosity (ml/g) | Percent Delignification (% Delig = $(K_0 - K_t)/K_0$) | Selectivity $[(1/DP) - (1/DPO)] \cdot 10^5 / \Delta K = \alpha$ (1/ml) |
| Experiment 3 (DTPA Pretreatment No H_2O_2) | 8.9 | 1058 | 35.0% | 0.663 | Experiment 11 (DTPA Pretreatment No H_2O_2) | 9 | 1004 | 34.3% | 0.996 |
| | 9.3 | 1043 | 32.1% | 0.814 | | 9 | 1026 | 34.3% | 0.862 |
| | 8.7 | 1042 | 36.5% | 0.722 | | 9.2 | 1024 | 32.8% | 0.913 |
| | 9.1 | 1067 | 33.6% | 0.641 | | 9.3 | 1029 | 32.1% | 0.902 |
| Mean | 9.0 | 1053 | 34.3% | 0.710 | Mean | 9.1 | 1021 | 33.4% | 0.918 |
| Stand Dev | 0.26 | 12.12 | 0.01885 | 0.077 | Stand Dev | 0.150 | 11.35 | 0.01095 | 0.056 |
| Upper Limit | 9.4 | 1072 | 37.3% | 0.833 | Upper Limit | 9.4 | 1039 | 35.1% | 1.008 |
| Lower Limit | 8.6 | 1033 | 31.3% | 0.587 | Lower Limit | 8.9 | 1003 | 31.7% | 0.828 |
| Experiment 4 (DTPA Pretreatment with H_2O_2) | 8.5 | 1063 | 38.0% | 0.587 | Experiment 12 (DTPA Pretreatment with H_2O_2) | 8.8 | 1012 | 35.8% | 0.908 |
| | 8.2 | 1039 | 40.1% | 0.671 | | 8.9 | 1009 | 35.0% | 0.945 |
| | 8.4 | 1045 | 38.7% | 0.666 | | 8.8 | 1028 | 35.8% | 0.815 |
| | 8.3 | 1045 | 39.4% | 0.653 | | 8.9 | 1011 | 35.0% | 0.933 |
| Mean | 8.4 | 1048 | 39.1% | 0.644 | Mean | 8.9 | 1015 | 35.4% | 0.900 |
| Stand Dev | 0.13 | 10.39 | 0.00942 | 0.039 | Stand Dev | 0.058 | 8.756 | 0.00421 | 0.059 |
| Upper Limit | 8.6 | 1065 | 40.6% | 0.706 | Upper Limit | 8.9 | 1029 | 36.1% | 0.993 |
| Lower Limit | 8.1 | 1031 | 37.6% | 0.582 | Lower Limit | 8.8 | 1001 | 34.7% | 0.807 |

Table 4.3

Results of the Oxygen Delignification Experiments with Acid Washing Pretreatment Showing 95% Upper and Lower Confidence

Limits

| Initial Kappa Number (K_0) = 13.7, Initial Intrinsic Viscosity ($[\eta]$) = 1196 ml/g | | | | | | | | | |
|---|------------------------------|----------------------------|--|--|--|------------------------------|----------------------------|--|--|
| Performed in Glass | Final Kappa number (K_f) | Intrinsic Viscosity (ml/g) | Percent Delignification (% Delig = $(K_0 - K_f)/K_0$) | Selectivity $[(1/DP)-(1/DPO)] \cdot 10^5 / \Delta K = \alpha$ (1/ml) | Performed in Stainless steel reactor | Final Kappa number (K_f) | Intrinsic Viscosity (ml/g) | Percent Delignification (% Delig = $(K_0 - K_f)/K_0$) | Selectivity $[(1/DP)-(1/DPO)] \cdot 10^5 / \Delta K = \alpha$ (1/ml) |
| Experiment 5 (Acid washing No H_2O_2) | 9.4 | 1058 | 31.4% | 0.740 | Experiment 13 (Acid washing No H_2O_2) | 9.0 | 1043 | 34.3% | 0.762 |
| | 9.3 | 1048 | 32.1% | 0.784 | | 9.0 | 1042 | 34.3% | 0.768 |
| | 9.0 | 1037 | 34.3% | 0.797 | | 9.0 | 1051 | 34.3% | 0.717 |
| | 9.4 | 1056 | 31.4% | 0.752 | | 9.2 | 1045 | 32.8% | 0.784 |
| Mean | 9.3 | 1050 | 32.3% | 0.768 | Mean | 9.1 | 1045 | 33.9% | 0.758 |
| Stand Dev | 0.19 | 9.535 | 0.01382 | 0.026 | Stand Dev | 0.100 | 4.031 | 0.00730 | 0.029 |
| Upper Limit | 9.6 | 1065 | 34.5% | 0.810 | Upper Limit | 9.2 | 1052 | 35.1% | 0.804 |
| Lower Limit | 9.0 | 1035 | 30.1% | 0.726 | Lower Limit | 8.9 | 1039 | 32.8% | 0.712 |
| Experiment 6 (Acid washing with H_2O_2) | 8.5 | 1012 | 38.0% | 0.855 | Experiment 14 (Acid washing with H_2O_2) | 8.5 | 1024 | 38.0% | 0.790 |
| | 8.5 | 995 | 38.0% | 0.951 | | 8.7 | 1013 | 36.5% | 0.884 |
| | 8.5 | 988 | 38.0% | 0.992 | | 8.6 | 1013 | 37.2% | 0.867 |
| | 8.8 | 1014 | 35.8% | 0.896 | | 8.6 | 1001 | 37.2% | 0.935 |
| Mean | 8.6 | 1002 | 37.4% | 0.924 | Mean | 8.6 | 1013 | 37.2% | 0.869 |
| Stand Dev | 0.15 | 12.76 | 0.0109 | 0.060 | Stand Dev | 0.082 | 9.394 | 0.00596 | 0.060 |
| Upper Limit | 8.8 | 1023 | 39.2% | 1.019 | Upper Limit | 8.7 | 1028 | 38.2% | 0.965 |
| Lower Limit | 8.3 | 982 | 35.7% | 0.828 | Lower Limit | 8.5 | 998 | 36.3% | 0.773 |

Table 4.4

Results of the Oxygen Delignification Experiments with A_D Stage Pretreatment Showing 95% Upper and Lower Confidence Limits

| Initial Kappa Number (K_0) = 13.7, Initial Intrinsic Viscosity ($[\eta]$) = 1196 ml/g | | | | | | | | | |
|---|------------------------------|----------------------------|--|---|--|------------------------------|----------------------------|--|---|
| Performed in Glass | Final Kappa number (K_1) | Intrinsic Viscosity (ml/g) | Percent Delignification (% Delig = $(K_0 - K_1)/K_0$) | Selectivity $[(1/DP) - (1/DP_0)] \cdot 10^5 / \Delta K = \alpha$ (1/ml) | Performed in Stainless steel reactor | Final Kappa number (K_1) | Intrinsic Viscosity (ml/g) | Percent Delignification (% Delig = $(K_0 - K_1)/K_0$) | Selectivity $[(1/DP) - (1/DP_0)] \cdot 10^5 / \Delta K = \alpha$ (1/ml) |
| Experiment 7 (Ad stage no H ₂ O ₂) | 7.0 | 1043 | 48.9% | 0.535 | Experiment 15 (Ad stage no H ₂ O ₂) | 6.7 | 1035 | 51.1% | 0.543 |
| | 7.2 | 1058 | 47.4% | 0.490 | | 6.8 | 1040 | 50.4% | 0.531 |
| | 7.1 | 1044 | 48.2% | 0.539 | | 6.8 | 1038 | 50.4% | 0.539 |
| | 7.1 | 1050 | 48.2% | 0.514 | | 6.8 | 1030 | 50.4% | 0.571 |
| Mean | 7.1 | 1049 | 48.2% | 0.519 | Mean | 6.8 | 1036 | 50.5% | 0.546 |
| Stand Dev | 0.082 | 6.898 | 0.00596 | 0.022 | Stand Dev | 0.050 | 4.349 | 0.00365 | 0.017 |
| Upper Limit | 7.2 | 1060 | 49.1% | 0.555 | Upper Limit | 6.9 | 1043 | 51.1% | 0.574 |
| Lower Limit | 7.0 | 1038 | 47.2% | 0.484 | Lower Limit | 6.7 | 1029 | 50.0% | 0.518 |
| Experiment 8 (Ad stage with H ₂ O ₂) | 6.9 | 996 | 49.6% | 0.723 | Experiment 16 (Ad stage with H ₂ O ₂) | 6.8 | 1010 | 50.4% | 0.653 |
| | 6.9 | 994 | 49.6% | 0.732 | | 6.8 | 1017 | 50.4% | 0.624 |
| | 6.8 | 1005 | 50.4% | 0.674 | | 6.7 | 998 | 51.1% | 0.694 |
| | 6.9 | 1008 | 49.6% | 0.671 | | 6.7 | 1005 | 51.1% | 0.665 |
| Mean | 6.9 | 1001 | 49.8% | 0.700 | Mean | 6.8 | 1008 | 50.7% | 0.659 |
| Stand Dev | 0.050 | 6.801 | 0.00365 | 0.032 | Stand Dev | 0.058 | 8.021 | 0.00421 | 0.029 |
| Upper Limit | 7.0 | 1012 | 50.4% | 0.751 | Upper Limit | 6.8 | 1020 | 51.4% | 0.705 |
| Lower Limit | 6.8 | 990 | 49.2% | 0.649 | Lower Limit | 6.7 | 995 | 50.1% | 0.613 |

4.2 SUMMARY OF RESULTS

The experimental data are summarized in Figures 4.2 through 4.8. The average value for each of the sixteen (16) conditions is shown plotted against the oxygen delignification condition. For purposes of comparison, the upper and lower control limits are also shown in selected graphs.

4.2.1 Kappa Number Reduction.

The results for the kappa number data showing the 95% confidence limits are plotted in Figure 4.2. For purpose of clarity, the kappa number data have been re-plotted as percent delignification in Figure 4.3.

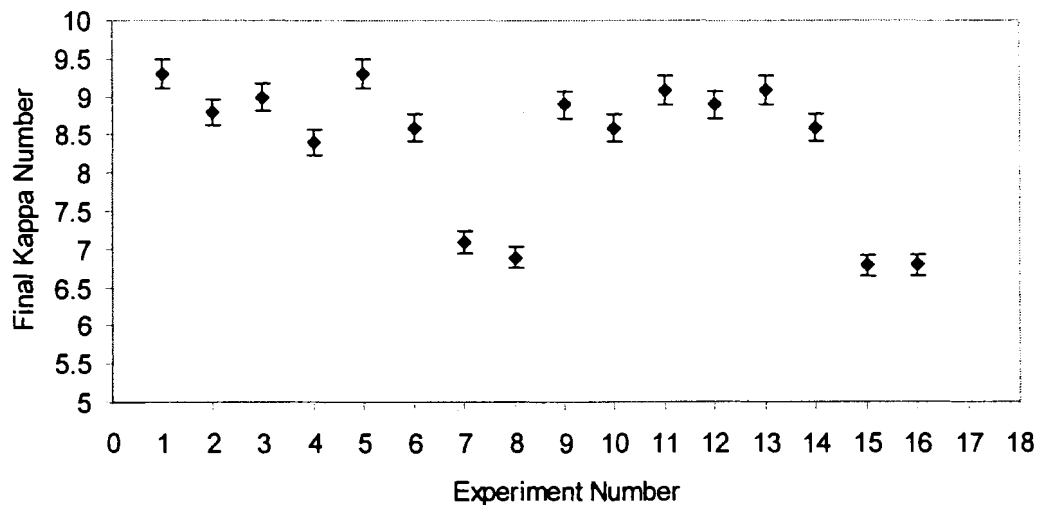


Figure 4.2 The Final Kappa Number (K) for Oxygen Delignification Experiments

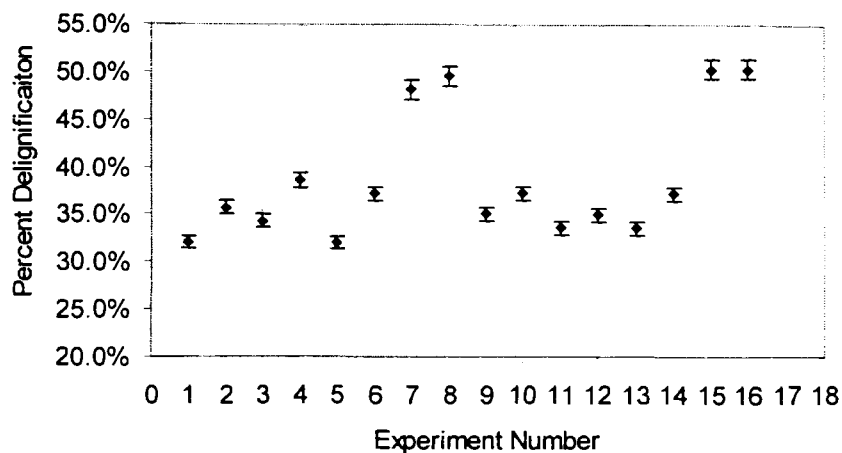


Figure 4.3 Percent Delignification for Oxygen Delignification Experiments

It is clear from Figures 4.2 and 4.3 that the data fall into two groups. High levels of delignification were achieved in experiments conducted with the A_D treatment. Secondly, the other pretreatment conditions gave rise to results that were closely grouped together. It is apparent from the data shown in Figures 4.2 and 4.3 that a statistical analysis is required to determine differences between the various conditions.

The results for the reduction in kappa number have been re-plotted in Figures 4.4 and 4.5. The experiments have been grouped according to the pretreatment used and whether the experiments were performed in glass (Figure 4.4) or in the stainless steel reactor (Figure 4.5). It is apparent, that not all of the treatments lead to the same kappa number drop or percent delignification. Experiments 7, 8, 15 and 16 gave lower final kappa number values at the end of the oxygen delignification experiments and high percent delignification; approximately 50% with only 2% caustic addition. All of these experiments had the A_D stage pretreatment. Experiments 7 and 15 were performed without peroxide while Experiments 8 and 16 were performed by reinforcement with hydrogen peroxide. The results clearly demonstrate that use of an A_D stage leads to high

levels of delignification. One possible explanation for the behavior is that use of chlorine dioxide in the pretreatment process activates the lignin so that additional oxidation reactions can take place.

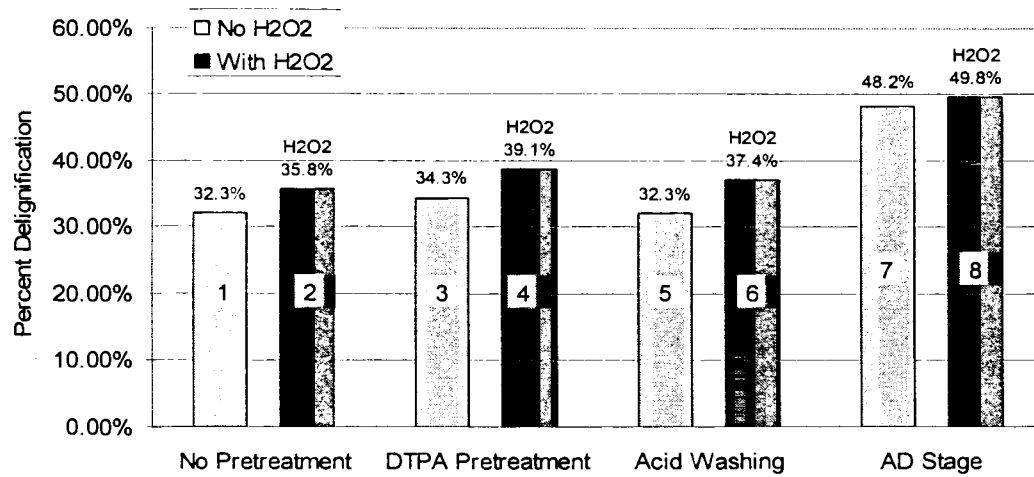


Figure 4.4 Results for Percent Delignification for Experiments Performed in Glass

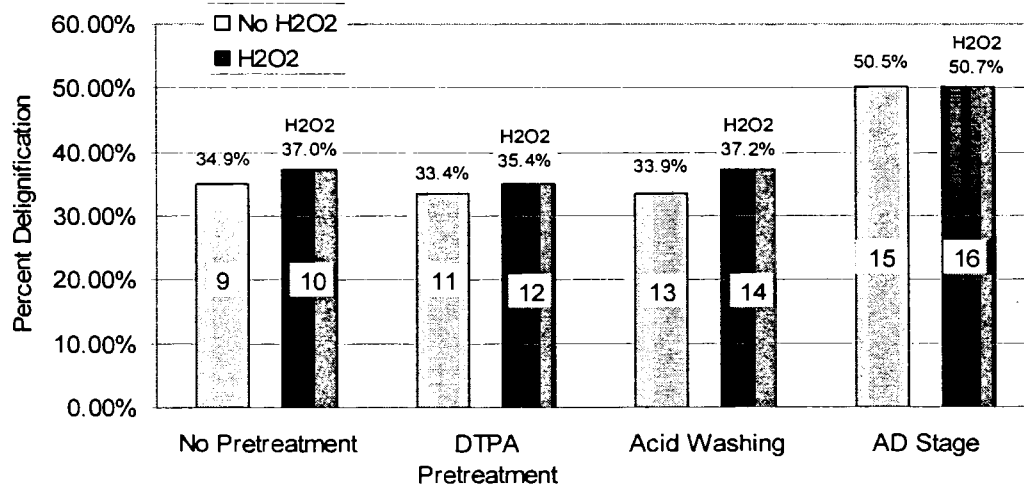


Figure 4.5 Results for Percent Delignification for Experiments Performed in the Stainless Steel Reactor

4.2.2 Intrinsic Viscosity and Selectivity

The results for the final intrinsic viscosity are plotted in Figure 4.6. The experiments with the lowest viscosity were obtained in Experiments 2 and 10 which had intrinsic viscosities of 975 cc/g and 948 cc/g, respectively. Both Experiment 2 and 10 were performed with hydrogen peroxide present in the oxygen stage with no pretreatment to control metals. The experiments with the highest viscosity were achieved in Experiments 3, 4, 5, 7, 13 and 15. All of these experiments are distinguished by having a pretreatment stage of some type.

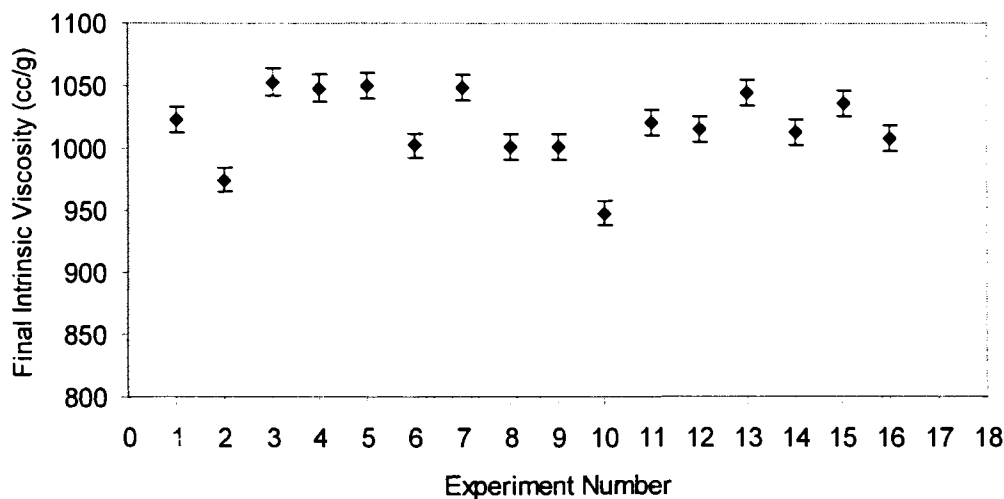


Figure 4.6 Final Intrinsic Viscosity $[\eta]$ for Oxygen Delignification Experiments

The selectivity coefficient (α) for each of the sixteen (16) conditions is summarized in Figure 4.7. The data in Figure 4.7 indicate that there is a wide range in selectivity possible depending upon the pretreatment conditions.

The ranges in the selectivity coefficient (α) occurred between the limits of approximately 0.52 and 1.27. For ease in comparing the various conditions, the data for the selectivity coefficient (α) are shown replotted in Figures 4.8 and 4.9. Here again the

data have been categorized according to the four pretreatment conditions and whether the experiments were performed in glass (Figure 4.8) or in the stainless steel reactor (Figure 4.9). The best selectivity was obtained in Experiments 7 and 15, which were both performed using the A_D stage pretreated without peroxide reinforcement. One notable difference between the two experiments is that Experiment 7 was performed in glass while Experiment 15 was performed in the stainless steel reaction vessel. Thus, it would appear possible to obtain high selectivity in the metal reactor provided an A_D stage pretreatment is used.

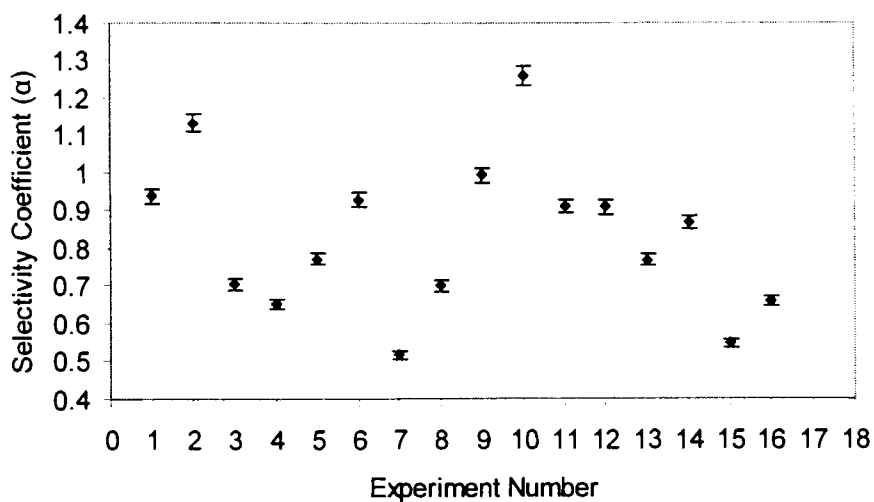


Figure 4.7 The Selectivity Coefficient (α) for Oxygen Delignification Experiments

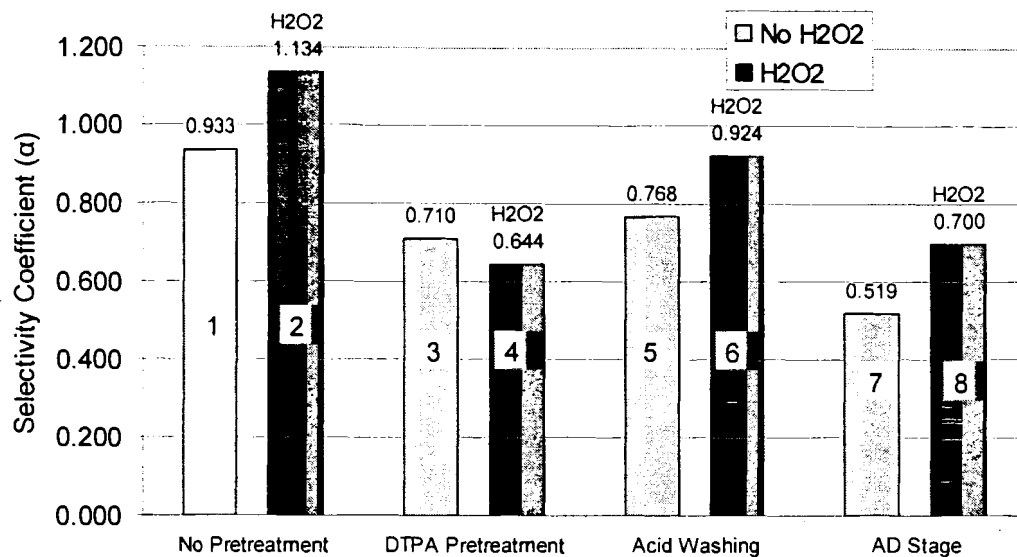


Figure 4.8 Results for Selectivity Coefficient (α) for Experiments Performed in Glass

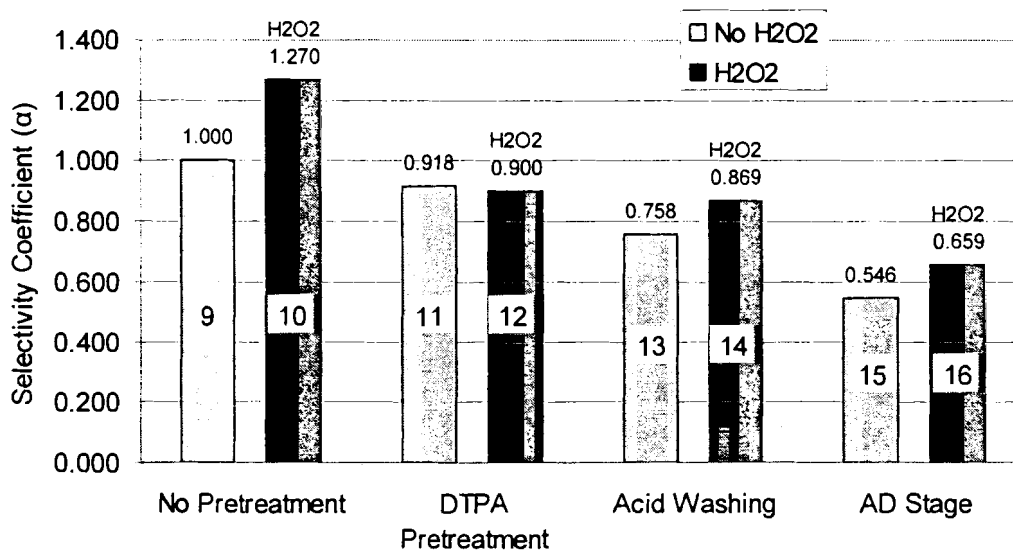


Figure 4.9 Results for Selectivity Coefficient (α) for Experiments Performed in the Stainless Steel Reactor

CHAPTER 5

DISCUSSION OF RESULTS

In this chapter, comparisons are made for the various delignification conditions. In this analysis, the effect of metals associated with the stainless steel reactor, the effect of the various pretreatment options, and the effect of fortifying the reaction mixture with hydrogen peroxide have been considered. The percent delignification (% Delig) and the selectivity coefficient (α) were the dependent variables used in this comparative analysis. The five (5) cases considered were:

Case 1. The effect of conducting the reaction in glass versus stainless steel reactor,

Case 2. The effect of pretreatment with DTPA in a Q-Stage,

Case 3. The effect of pretreatment with acid washing in an A-Stage,

Case 4. The effect of pretreatment in an acid washing stage fortified by the addition of a small amount of ClO_2 (A_D -Stage), and lastly,

Case 5. The use of hydrogen peroxide to fortify the delignification reaction.

To evaluate these differences statistically, the student t -test was applied to determine if the differences in the mean values (\bar{x}) measured for the percent delignification (% Delig) and the selectivity coefficient (α) for the various cases were truly independent or simply the result of random variations in the experimental data. Details of the student t -test and sample calculations are summarized in Appendix C.

5.1 THE EFFECT OF THE STAINLESS STEEL REACTOR

Because the concentration of H_2O_2 affects the final kappa number and intrinsic viscosity of the pulp, the experiments were divided into two groups to make the

comparison clear. The first group was the oxygen delignification experiments conducted without H_2O_2 presence, while the second group was the oxygen delignification experiments reinforced by adding H_2O_2 .

For the first group, which was carried out without the presence of H_2O_2 , four pairs of experiments were compared respectively. They were the oxygen delignification experiments performed without pretreatment that were carried out in glass (Experiment 1) versus those that were carried out in the stainless steel reactor (Experiment 9), the experiments with DTPA pretreatment carried out in glass (Experiment 3) versus the stainless steel reactor (Experiment 11), the experiments with an acid washing as a pretreatment carried out in glass (Experiment 5) versus the stainless steel reactor (Experiment 13), and the experiments with an A_D stage as a pretreatment carried out in glass (Experiment 7) versus the stainless steel reactor (Experiment 15).

In the second set of experiments that were compared, the pairings were identical as those described above except that the pairs compared were for experiments that were reinforced with hydrogen peroxide. Thus, the pairs compared were for Experiments 2 versus 10 (without pretreatment), Experiments 4 versus 12 (Q-stage), Experiments 6 and 14 (A-stage), and lastly Experiments 8 versus 16 (A_D -stage).

The results of the student t -test for these eight (8) pairs of experiments are presented in Table 5.1. If the calculated value of the t -statistic was greater than 2.447, this indicated that statistically there was a difference in the measured mean value for the percent delignification or the selectivity coefficient (α) at the 95% confidence level. In the above analysis the t value of 2.447 arises for a two-tail t -test with six degrees of freedom. These calculations are explained in detail in Appendix C.

Comparisons for the experiments performed in glass versus those performed in the stainless steel reactor are presented in Figures 5.1 and 5.2 for percent delignification; and also for the selectivity coefficient (α) in Figures 5.3 and 5.4.

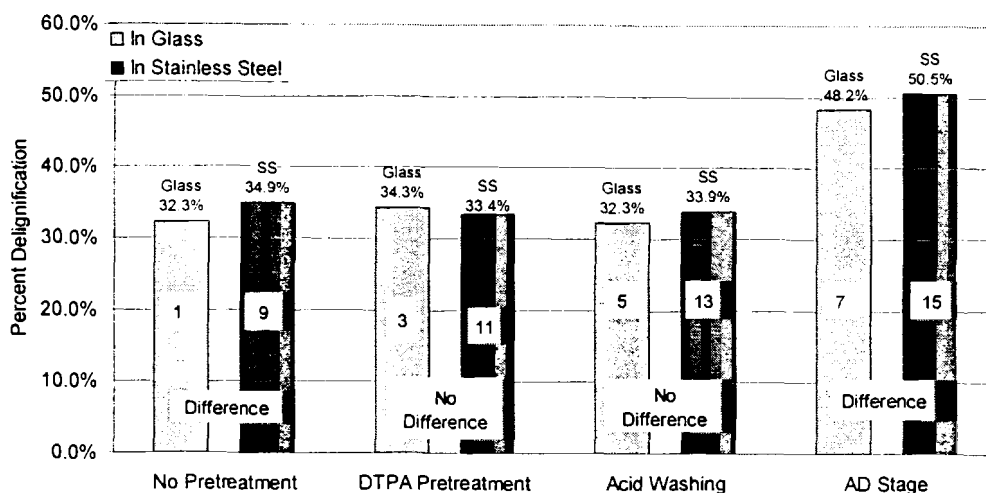


Figure 5.1 Comparisons for Percent Delignification when Experiments were Conducted in Glass and Stainless Steel – Without H_2O_2 Presence

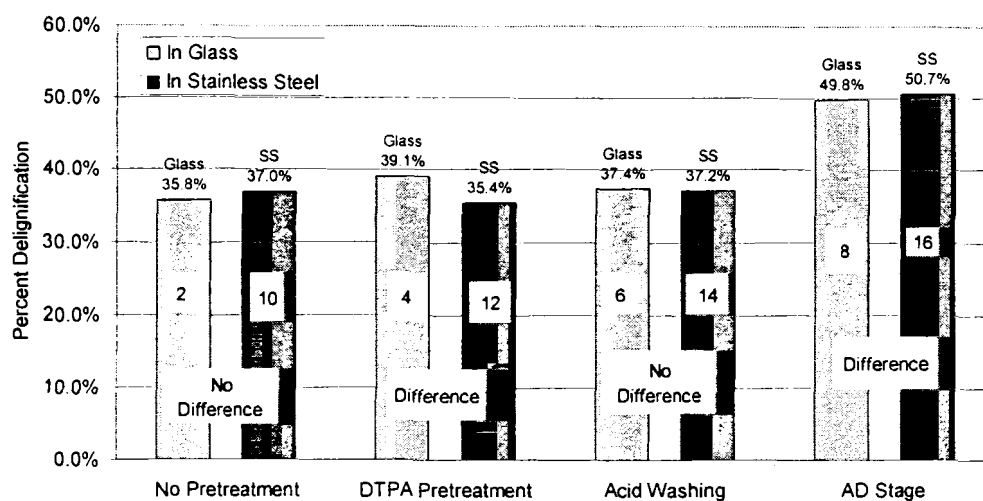


Figure 5.2 Comparisons for Percent Delignification when Experiments were Conducted in Glass and Stainless Steel – With H_2O_2 Presence

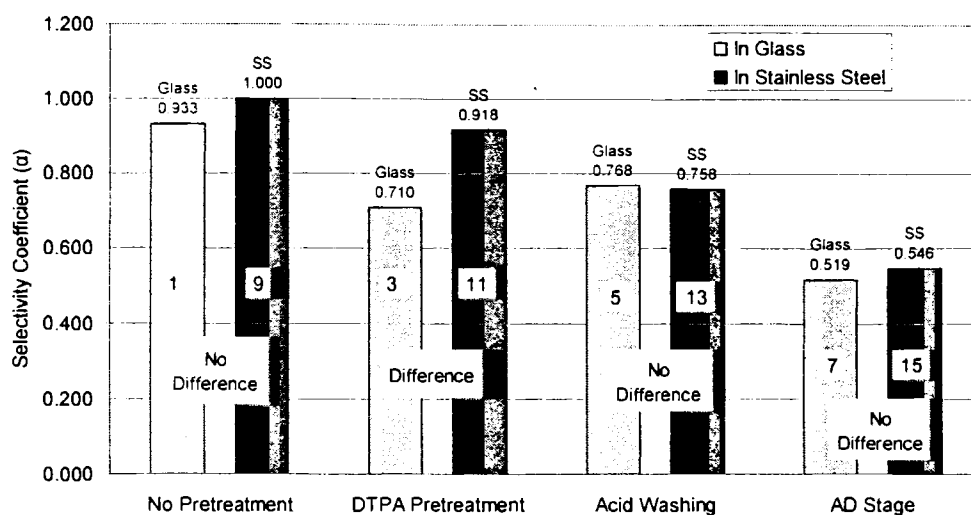


Figure 5.3 Comparisons for Selectivity Coefficient (α) when Experiments were Conducted in Glass and Stainless Steel – Without H_2O_2 Presence

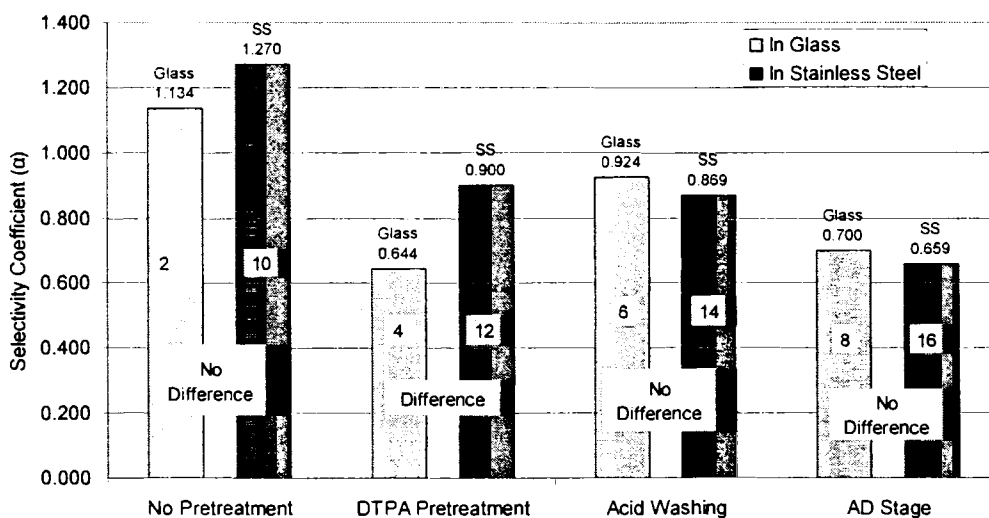


Figure 5.4 Comparisons for Selectivity Coefficient (α) when Experiments were Conducted in Glass and Stainless Steel – With H_2O_2 Presence

Table 5-1
Results of the *t*-test Showing the Effect of Glass versus Stainless Steel Reactor

| Experiment Item | Mean of Percent Delig. (% Delig. = $(K_0 - K_1)/K_0$) | SD of % Delig | <i>t</i> | Diff. | Mean of Selectivity Coefficient $[(1/DP)-(1-DPo)] \cdot 10^5 / \Delta K = \alpha$ (1/ml) | SD of Selectivity | <i>t</i> | Diff. |
|----------------------------------|--|---------------|----------|-------|--|-------------------|----------|-------|
| No H ₂ O ₂ | 1 (In glass, no Pretreatment) | 32.3% | 0.00699 | Yes | 0.933 | 0.015 | 1.535 | No |
| | 9 (In reactor, no Pretreatment) | 34.9% | 0.01382 | | 1.000 | 0.086 | | |
| | 3 (In glass, DTPA) | 34.3% | 0.01885 | No | 0.710 | 0.077 | 4.369 | Yes |
| | 11 (In reactor, DTPA) | 33.4% | 0.01095 | | 0.918 | 0.056 | | |
| | 5 (In glass, A) | 32.3% | 0.01382 | No | 0.768 | 0.026 | 0.513 | No |
| | 13 (In reactor, A) | 33.9% | 0.00730 | | 0.758 | 0.029 | | |
| | 7 (In glass, A _p) | 48.2% | 0.00596 | Yes | 0.519 | 0.022 | 1.942 | No |
| | 15 (In reactor, A _p) | 50.5% | 0.00365 | | 0.546 | 0.017 | | |
| | 2 (In glass, no Pretreatment) | 35.8% | 0.01333 | No | 1.134 | 0.052 | 2.304 | No |
| | 10 (In reactor, no Pretreatment) | 37.0% | 0.00918 | | 1.270 | 0.106 | | |
| H ₂ O ₂ | 4 (In glass, DTPA) | 39.1% | 0.00942 | Yes | 0.644 | 0.039 | 7.239 | Yes |
| | 12 (In reactor, DTPA) | 35.4% | 0.00421 | | 0.900 | 0.059 | | |
| | 6 (In glass, A) | 37.4% | 0.01090 | No | 0.924 | 0.060 | 1.296 | No |
| | 14 (In reactor, A) | 37.2% | 0.00596 | | 0.869 | 0.060 | | |
| | 8 (In glass, A _p) | 49.8% | 0.00365 | Yes | 0.700 | 0.032 | 1.899 | No |
| | 16 (In reactor, A _p) | 50.7% | 0.00421 | | 0.659 | 0.029 | | |

5.1.1 Percent Delignification (% Delig)

In Figures 5.1 and Figure 5.2 and in Table 5.1, four *t*-test values show that there exists a difference in the percent delignification for the experiments performed in glass compared to those in the stainless steel reactor. These comparisons were Experiments 1 versus 9, which were experiments performed without pretreatment and without H₂O₂ presence; Experiments 7 versus 15, which were experiments performed with the A_D stage pretreatment and without H₂O₂ presence; Experiments 4 versus 12, which were both performed with the Q-stage pretreatment and with H₂O₂ presence; and Experiments 8 versus 16, which were both performed with the A_D stage pretreatment with H₂O₂ presence. The other four (4) comparisons show that no difference existed in the results for the percent delignification when the reaction was carried out in glass or stainless steel. The conclusion drawn from this analysis is that in most cases the metals present in the reaction vessel contributed little to the reduction in kappa number except for the case of the A_D stage where both sets of experiments with and without H₂O₂ showed a difference. The reactor improved the delignification in the experiments with the A_D stage pretreatment, but even this small improvement may be attributed to the improved mixing in the stainless steel reactor.

5.1.2 Selectivity Coefficient (α)

The two sample *t*-test showed differences in the mean value for the selectivity coefficient (α) only for the conduction of experiments that were pretreated with DTPA. Positive results for the *t*-test were obtained for Experiment 3 versus Experiment 11 that were performed without H₂O₂ reinforcement (see Figure 5.3) and Experiment 4 versus Experiment 12 that were performed with H₂O₂ reinforcement (see Figure 5.4). In the

other six (6) cases, there was no difference in the selectivity coefficient (α) between the experiments performed in glass and in the stainless steel reactor. Lastly, it was concluded that only in the experiments with DTPA pretreatment the reaction vessel affected the selectivity results. Specifically, better selectivity was obtained when the reaction was conducted in glass.

5.2 THE EFFECT OF PULP PRETREATMENT

Three types of comparisons were made for the oxygen delignification experiments conducted with pulp pretreatment. Comparisons were made for the (1) no pretreatment case compared to DTPA pretreatment (Q-stage) case, (2) no pretreatment compared to the acid washing the pulp (A-stage), and (3) no pretreatment compared to acid washing fortified by chlorine dioxide (A_D -stage).

5.2.1 Effect of DTPA Pretreatment (Q-Stage)

The no pretreatment case was considered the control and the experiments were divided into two groups depending upon whether hydrogen peroxide was added or not and the experiments were performed in glass or stainless steel.

For the first group of experiments, which were carried out without H_2O_2 presence, two pairs of experiments were compared. These were the oxygen delignification experiments carried out in glass with no pretreatment (Experiment 1) versus DTPA pretreatment (Experiment 3); and the experiments carried in the stainless steel reactor with no pretreatment (Experiment 9) versus DTPA pretreatment (Experiment 11). For the second group of experiments, which were carried out with H_2O_2 reinforcement, two pairs of experiments were compared. These were the oxygen delignification experiments carried out in glass with no pretreatment (Experiment 2) versus DTPA pretreatment

(Experiment 4); and the experiments carried in the stainless steel reactor with no pretreatment (Experiment 10) versus DTPA pretreatment (Experiment 12). The results of student *t*-test evaluation for these four (4) pairs of experiments are summarized numerically in Table 5.2 and graphically in Figure 5.5 for percent delignification and for the selectivity coefficient (α) in Figure 5.6.

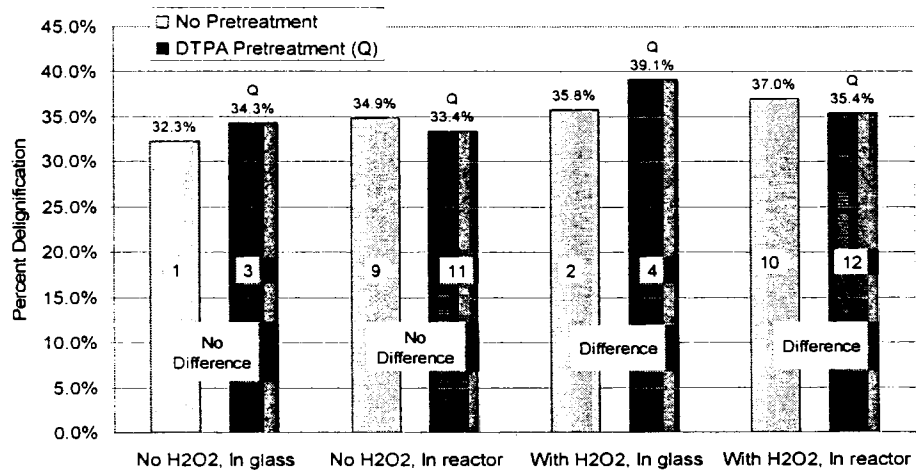


Figure 5.5 Comparisons of the Results for Percent Delignification for the Case of DTPA Pretreatment

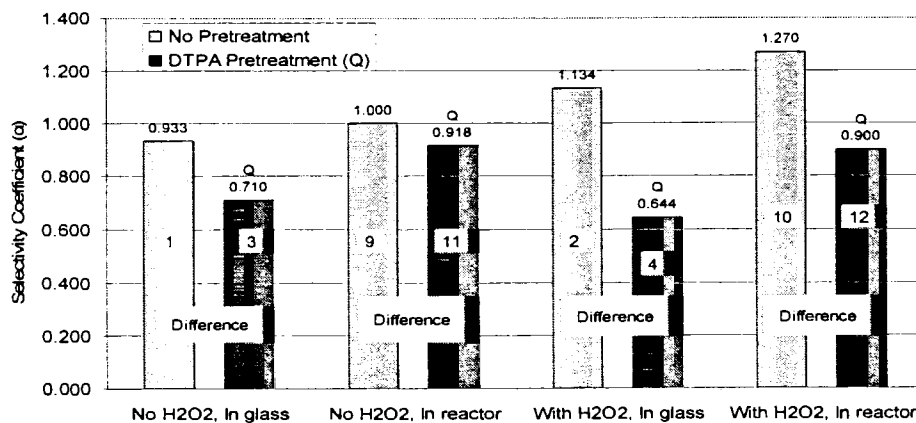


Figure 5.6 Comparisons of the Results for the Selectivity Coefficient (α) for the Case of DTPA Pretreatment

Table 5-2
Results of the *t*-test Showing the Effect of No Pretreatment Compared to DTPA Pretreatment (Q-Stage)

| Experiment Item | | Mean of Percent Delig. (% Delig= (K ₀ -K _d)/K ₀) | SD of % Delig | t | Diff. | Mean of Selectivity Coefficient [(1/DP)-(1- DP ₀)] *10 ^{^5} /Δ K = α (1/ml) | SD of Selectivity | t | Diff. |
|-------------------------------------|----------------------------------|--|------------------|-------|-------|--|----------------------|--------|-------|
| No H ₂ O ₂ | 1 (In glass, no Pretreatment) | 32.3% | 0.00699 | 1.990 | No | 0.933 | 0.015 | 5.685 | Yes |
| | 3 (In glass, DTPA) | 34.3% | 0.01885 | | | 0.710 | 0.077 | | |
| | 9 (In reactor, no Pretreatment) | 34.9% | 0.01382 | 1.701 | No | 1.000 | 0.086 | 2.598 | Yes |
| | 11 (In reactor, DTPA) | 33.4% | 0.01095 | | | 0.918 | 0.056 | | |
| H ₂ O ₂ | 2 (In glass, no Pretreatment) | 35.8% | 0.01333 | 4.043 | Yes | 1.134 | 0.052 | 15.077 | Yes |
| | 4 (In glass, DTPA) | 39.1% | 0.00942 | | | 0.644 | 0.039 | | |
| | 10 (In reactor, no Pretreatment) | 37.0% | 0.00918 | 3.169 | Yes | 1.270 | 0.106 | 6.100 | Yes |
| | 12 (In reactor, DTPA) | 35.4% | 0.00421 | | | 0.900 | 0.059 | | |

5.2.1.1 Percent Delignification (% Delig)

From Table 5.2 and Figure 5.5, the *t*-test values show that there exists a difference in the percent delignification for the experiments with DTPA pretreatment in two of the four cases evaluated. These were Experiment 2 versus Experiment 4, and also in Experiment 10 versus Experiment 12. Both sets of experiments that showed positive results were performed with H₂O₂ reinforcement. Experiments 2 and 4 were performed in glass while Experiments 10 and 12 were performed in the stainless steel reactor. However, the percent delignification in the experiments with the DTPA pretreatment (Experiments 4 and 12) were not always higher than those conducted without pretreatment (Experiments 2 and 10). Thus, it was concluded that DTPA pretreatment most likely did not improve the level of delignification.

5.2.1.2 Selectivity Coefficient (α)

From the data in Table 5.2 and Figure 5.6, it is clear that the use of DTPA as a pretreatment improved selectivity. All four of the cases showed positive results for the *t*-test. This included both the no peroxide and peroxide reinforcement cases. Also, this conclusion was true no matter whether the experiments were performed in glass or in the stainless steel reactor. Also, please note that the selectivity coefficients (α) for the experiments with no pretreatment (Experiment 1, 2, 9, and 10) were all higher than those for experiments with DTPA pretreatment (Experiment 3, 4, 11, and 12).

It can be concluded that DTPA pretreatment improves the selectivity during the oxygen delignification compared to the no pretreatment case.

5.2.2 Effect of Acid Washing (A-Stage)

Similar to previous results, the evaluation of the effectiveness of an acid washing stage was made by performing the *t*-test for four cases. The comparisons were divided into groups predicated on whether hydrogen peroxide was present and whether the experiments were performed in glass or in the stainless steel reactor. For the first group of experiments, which were carried out without H₂O₂ reinforcement, two pairs of experiments were compared. These were the oxygen delignification experiments carried out in glass with no pretreatment (Experiment 1) versus acid washing pretreatment (Experiment 5); and the experiments carried out in the stainless steel reactor with no pretreatment (Experiment 9) versus acid washing pretreatment (Experiment 13). For the second group which was carried out with H₂O₂ reinforcement, two pairs of experiments were compared, they were the oxygen delignification experiments carried out in glass with no pretreatment (Experiment 2) versus acid washing pretreatment (Experiment 6); and also the experiments carried out in stainless steel reactor with no pretreatment (Experiment 10) versus acid washing pretreatment (Experiment 14). The results of student *t*-test for the four (4) pairs of experiments are presented numerically in Table 5.3 and graphically in Figures 5.7 and 5.8.

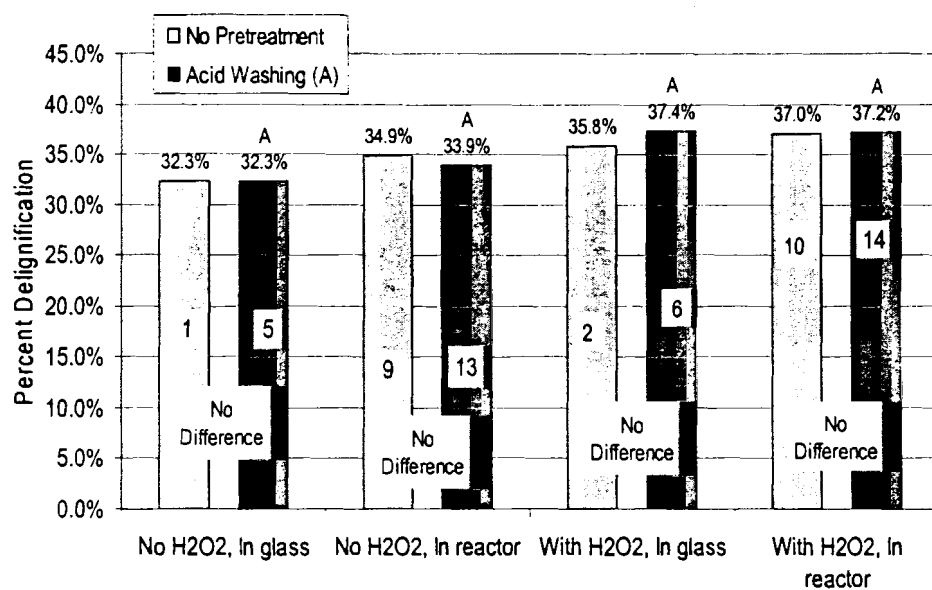


Figure 5.7 Comparisons of the Results for Percent Delignification for Pretreatment by
Acid Washing

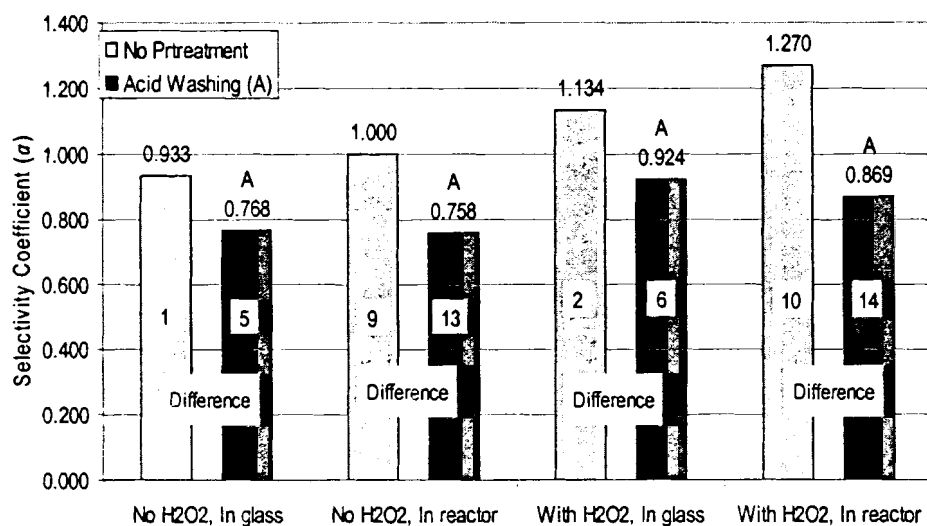


Figure 5.8 Comparisons of the Results for Selectivity Coefficient (α) for Pretreatment by
Acid Washing

Table 5-3
Results of the *t*-test Showing the Effect of No Pretreatment Compared to Acid Washing (A-Stage)

| Experiment Item | Mean of Percent Delig. (% Delig. = $(K_0 - K_i)/K_0$) | SD of % Delig | <i>t</i> | Diff. | Mean of Selectivity Coefficient $[(1/DP)-(1-DPo)] * 10^5 / \Delta K = \alpha$ (1/ml) | SD of Selectivity | <i>t</i> | Diff. |
|-----------------|--|---------------|----------|-------|--|-------------------|----------|-------|
| No H_2O_2 | 1 (In glass, no Pretreatment) | 32.3% | 0.00699 | No | 0.933 | 0.015 | 10.994 | Yes |
| | 5 (In glass, Acid washing) | 32.3% | 0.01382 | | 0.768 | 0.026 | | |
| | 9 (In reactor, no Pretreatment) | 34.9% | 0.01382 | No | 1.000 | 0.086 | 5.333 | Yes |
| | 13 (In reactor, Acid washing) | 33.9% | 0.00730 | | 0.758 | 0.029 | | |
| H_2O_2 | 2 (In glass, no Pretreatment) | 35.8% | 0.01333 | No | 1.134 | 0.052 | 5.290 | Yes |
| | 6 (In glass, Acid washing) | 37.4% | 0.01090 | | 0.924 | 0.060 | | |
| | 10 (In reactor, no Pretreatment) | 37.0% | 0.00918 | No | 1.270 | 0.106 | 6.584 | Yes |
| | 14 (In reactor, Acid washing) | 37.2% | 0.00596 | | 0.869 | 0.060 | | |

5.2.2.1 Percent Delignification (% Delig)

Analysis of the data using the t -test clearly shows that there is no difference in the degree of delignification achieved by acid washing. All four of the cases that are compared in Table 5.3 and shown graphically in Figure 5.7 gave negative results for the t -test. This was true for the experiments conducted with hydrogen peroxide reinforcement and also for the experiments conducted in glass or in the stainless steel reactor. This can be seen by comparing experiments 1 and 5, 9 and 13, 2 and 6 and 10 and 14. The conclusion drawn from this analysis is that acid washing as a pretreatment did not affect the level of delignification.

5.2.2.2 Selectivity Coefficient (α)

The results of the t -test clearly show that the acid washing improves the selectivity. Also, the selectivity coefficient (α) of the experiments with no pretreatment (Experiments 1, 2, 9, and 10) are greater than those for the experiments with acid washing pretreatment (Experiments 5, 6, 13, and 14).

Thus, it can be concluded that acid washing pretreatment improves the selectivity during the oxygen delignification compared to no pretreatment.

5.2.3 Effect of Acid Washing Fortified with Chlorine Dioxide (A_D -stage)

In considering the effect of an A_D stage prior to oxygen delignification, the comparisons were divided into two groups based upon whether H_2O_2 was present or not. For the first group of experiments, which were carried out without H_2O_2 reinforcement, two pairs of experiments were compared. These were the oxygen delignification experiments carried out in glass with no pretreatment (Experiment 1) versus A_D stage pretreatment (Experiment 7); and the experiments carried out in the stainless steel reactor

with no pretreatment (Experiment 9) versus an A_D stage pretreatment (Experiment 15). For the second group of experiments, which were carried out with H₂O₂ reinforcement, two pairs of experiments were compared. They were the oxygen delignification experiments carried out in glass with no pretreatment (Experiment 2) versus the A_D stage pretreatment (Experiment 8); and also the experiments carried out in the stainless steel reactor with no pretreatment (Experiment 10) versus an A_D stage pretreatment (Experiment 16). The results of the student *t*-test for these four (4) pairs of experiments are presented numerically in Table 5.4 and graphically in Figures 5.9 and 5.10.

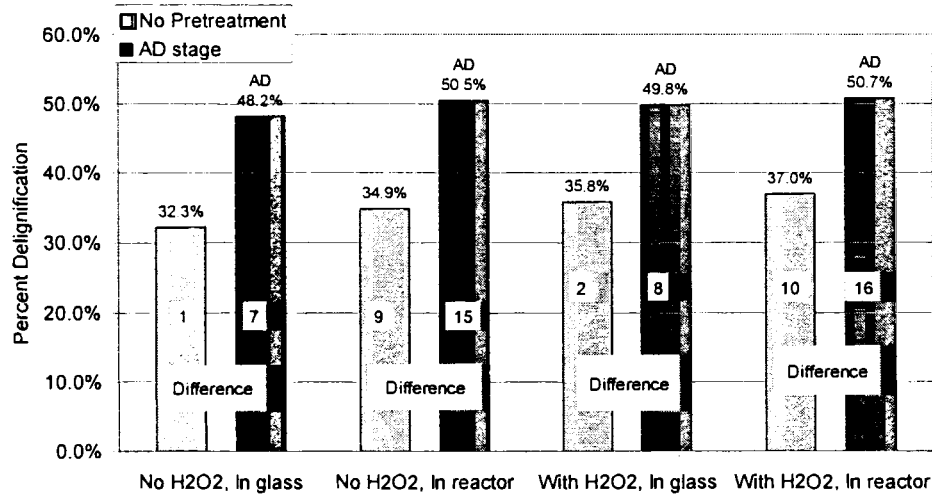


Figure 5.9 Comparisons of the Results for Percent Delignification for Pretreatment in an A_D Stage

Table 5-4
Results of the *t*-test Showing the Effect of No Pretreatment Compared to A_D-Stage

| Experiment Item | | Mean of Percent Delig. (% Delig = $(K_0 - K_i)/K_0$) | SD of % Delig | t | Diff. | Mean of Selectivity Coefficient [(1/DP)-(1-DP ₀)] * 10 ⁵ /Δ K = α (1/ml) | SD of Selectivity | t | Diff. |
|----------------------------------|---------------------------------------|--|---------------|--------|-------|--|-------------------|--------|-------|
| No H ₂ O ₂ | 1 (In glass, no Pretreatment) | 32.3% | 0.00699 | 34.618 | Yes | 0.933 | 0.015 | 31.096 | Yes |
| | 7 (In glass, A _D stage) | 48.2% | 0.00596 | | | 0.519 | 0.022 | | |
| | 9 (In reactor, no Pretreatment) | 34.9% | 0.01382 | 21.828 | Yes | 1.000 | 0.086 | 10.358 | Yes |
| | 15 (In reactor, A _D stage) | 50.5% | 0.00365 | | | 0.546 | 0.017 | | |
| H ₂ O ₂ | 2 (In glass, no Pretreatment) | 35.8% | 0.01333 | 20.259 | Yes | 1.134 | 0.052 | 14.216 | Yes |
| | 8 (In glass, A _D stage) | 49.8% | 0.00365 | | | 0.700 | 0.032 | | |
| | 10 (In reactor, no Pretreatment) | 37.0% | 0.00918 | 27.131 | Yes | 1.270 | 0.106 | 11.519 | Yes |
| | 16 (In reactor, A _D stage) | 50.7% | 0.00421 | | | 0.659 | 0.004 | | |

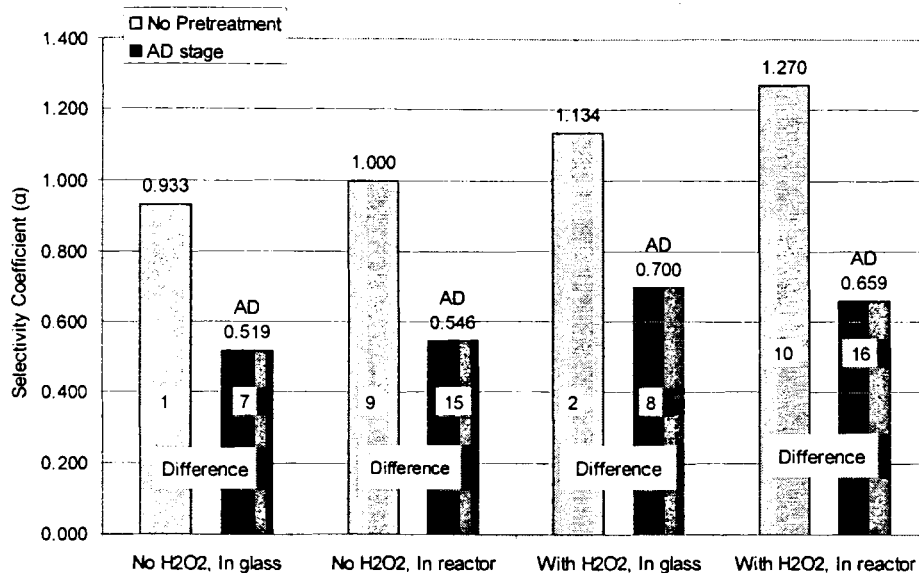


Figure 5.10 Comparisons of the Results for Selectivity Coefficient (α) for Pretreatment in an A_D Stage

5.2.3.1 Percent Delignification (% Delig)

The results summarized in Table 5.4 and Figure 5.9 strongly suggest that there is a difference in the percent delignification in the experiments with no pretreatment (Experiment 1, 2, 9, and 10) compared to the ones conducted with A_D stage pretreatment (Experiment 7, 8, 15, and 16). All four of the cases that are compared in Table 5.4 and presented graphically in Figure 5.9 gave positive results for the t -test. This conclusion was true for the experiments performed in glass or in the stainless steel reactor and for the experiments with or without peroxide reinforcement. Also the percent delignification for the experiments conducted with no pretreatment (Experiments 1, 2, 9, and 10) are less than those observed for the experiments with the A_D stage pretreatment (Experiments 7, 8, 15, and 16). The conclusion that can be drawn from these experiments is that pretreating the pulp with an A_D stage pretreatment leads to additional delignification compared to the no pretreatment case.

5.2.3.2 Selectivity Coefficient (α)

Based on Table 5.4, the t -test values show that a difference exists between the mean values for the selectivity coefficient (α) measured in the experiments with no pretreatment compared to the ones with the A_D stage pretreatment. Also, the selectivity coefficient (α) of the experiments with no pretreatment (Experiments 1, 2, 9, and 10) were all greater than those of the experiments with the A_D stage pretreatment (Experiments 7, 8, 15, and 16). Clearly, pretreatment of the pulp in an A_D stage decreases the selectivity coefficient (α), and thus, improves the selectivity during the oxygen delignification. This was true for all four of the cases examined.

Therefore, it can be concluded that pretreatment of the pulp in an A_D stage improves both the selectivity and the level of delignification during the oxygen delignification compared to the case of no pretreatment.

5.3 THE EFFECT OF HYDROGEN PEROXIDE REINFORCEMENT

In considering the effect of H₂O₂ reinforcement in an oxygen stage, comparisons were divided into four (4) groups based on whether the experiments were performed in glass or in the stainless steel reactor, and also whether H₂O₂ was present or not. This gave rise to eight (8) separate combinations of results for which the t -test was used to compare the mean values for the percent delignification and the selectivity coefficient (α). This analysis is summarized in Table 5.5. The results are shown graphically for percent delignification in Figures 5.11 and 5.12 when the experiments were performed in glass (Figure 5.11) and in the stainless steel reactor (Figure 5.12). Similarly, the results for the selectivity coefficient (α) are shown graphically in Figures 5.13 and 5.14, again

segregated depending whether the experiments were performed in glass (Figure 5.13) and in the stainless steel reactor (Figure 5.14).

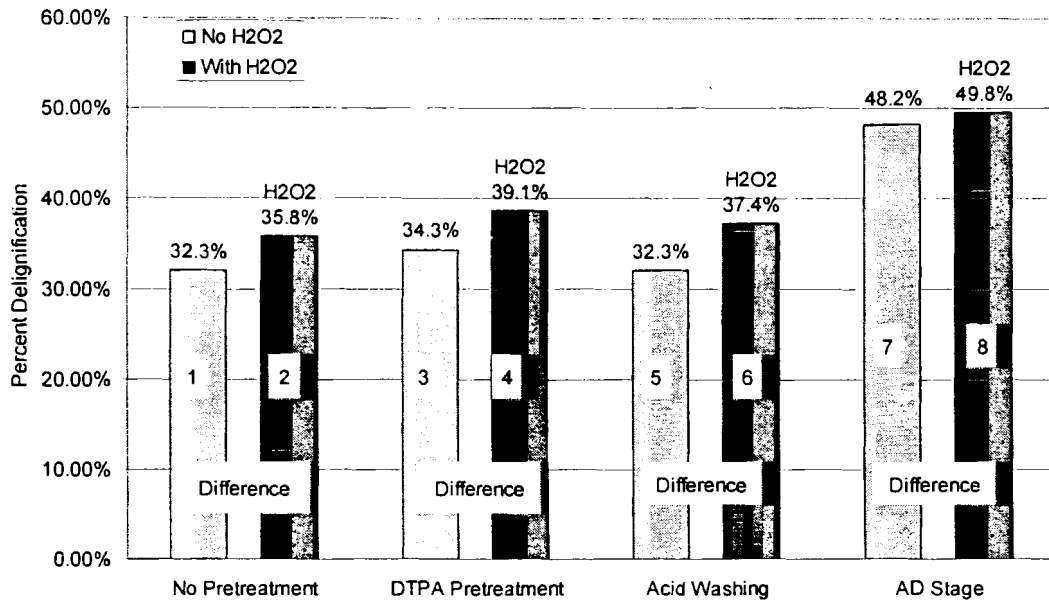


Figure 5.11 Comparisons of the Results for Percent Delignification for Experiments Conducted in Glass with and without H₂O₂ Reinforcement

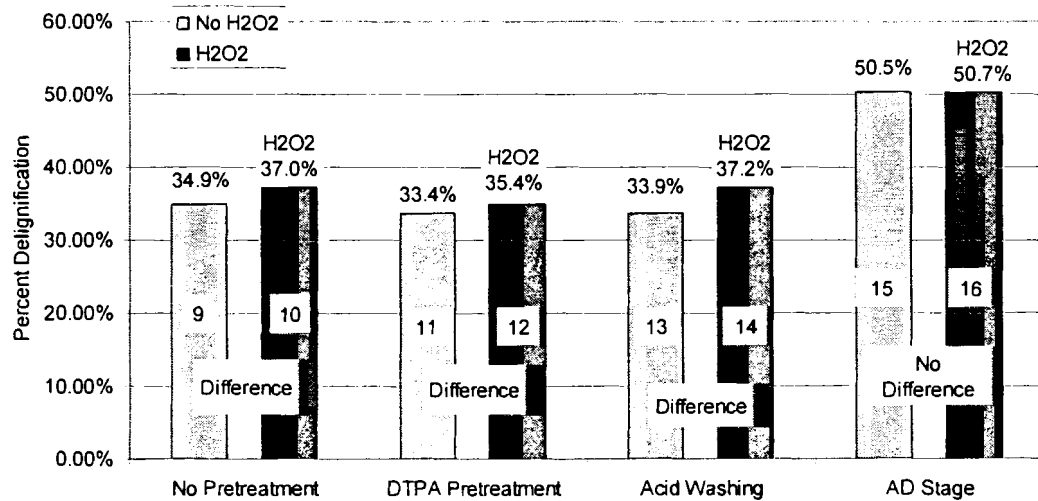


Figure 5.12 Comparisons of the Results for Percent Delignification for Experiments Conducted in the Stainless Steel Reactor with and without H₂O₂ Reinforcement

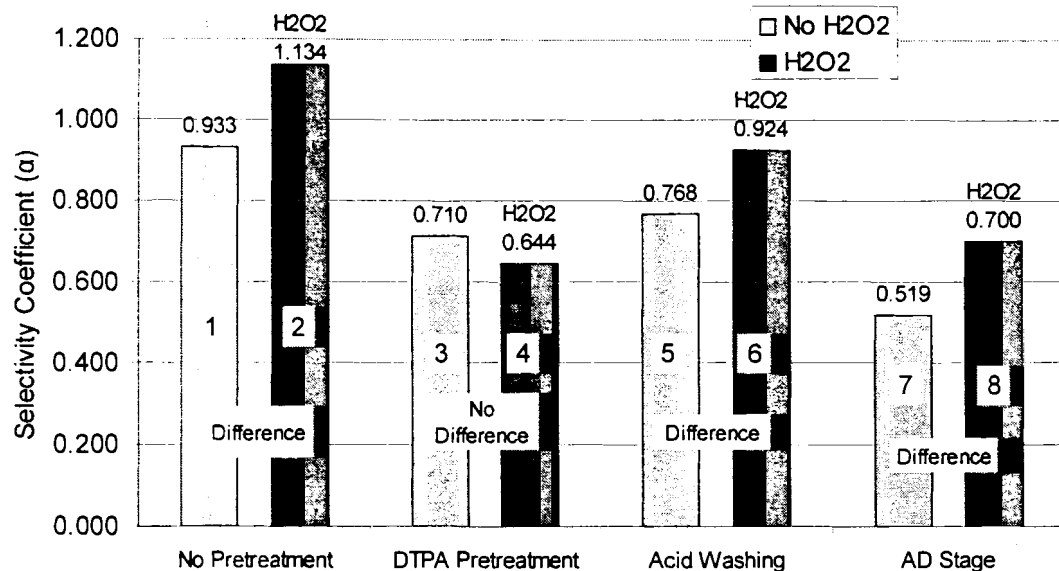


Figure 5.13 Comparisons of the Results for Selectivity Coefficient (α) for Experiments Conducted in Glass with and without H₂O₂ Reinforcement

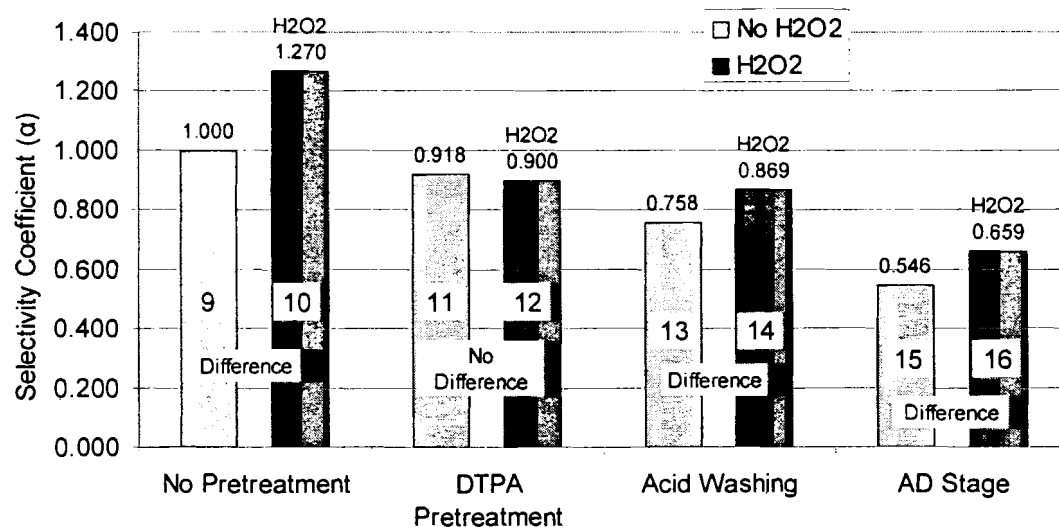


Figure 5.14 Comparisons of the Results for Selectivity Coefficient (α) for Experiments Conducted in the Stainless Steel Reactor with and without H₂O₂ Reinforcement

Table 5-5
Results of the *t*-test Showing the Effect of Hydrogen Peroxide (H₂O₂)

| Experiment Item | | Mean of Percent Delig. (% Delig= (K ₀ -K _i)/K ₀) | SD of % Delig | t | Diff. | Mean of Selectivity Coefficient [(1/DP)-(1-DP ₀)] • 10 ⁵ /Δ K = α (1/ml) | SD of Selectivity | t | Diff. |
|----------------------------|--|---|---------------|-------|-------|--|-------------------|-------|-------|
| In Glass | 1 (no H ₂ O ₂ , no Pretreatment) | 32.3% | 0.00699 | 4.651 | Yes | 0.933 | 0.015 | 7.428 | Yes |
| | 2 (H ₂ O ₂ , No Pretreatment) | 35.8% | 0.01333 | | | 1.134 | 0.052 | | |
| | 3 (no H ₂ O ₂ , DTPA) | 34.3% | 0.01885 | 4.556 | Yes | 0.710 | 0.077 | 1.529 | No |
| | 4 (H ₂ O ₂ , DTPA) | 39.1% | 0.00942 | | | 0.644 | 0.039 | | |
| | 5 (no H ₂ O ₂ , A) | 32.3% | 0.01382 | 5.795 | Yes | 0.768 | 0.026 | 4.771 | Yes |
| | 6 (H ₂ O ₂ , A) | 37.4% | 0.01090 | | | 0.924 | 0.060 | | |
| | 7 (No H ₂ O ₂ , AD) | 48.2% | 0.00596 | 4.579 | Yes | 0.519 | 0.022 | 9.322 | Yes |
| | 8 (H ₂ O ₂ , AD) | 49.8% | 0.00365 | | | 0.700 | 0.032 | | |
| In Stainless Steel Reactor | 9 (no H ₂ O ₂ , no Pretreatment) | 34.9% | 0.01382 | 2.531 | Yes | 1.000 | 0.086 | 3.956 | Yes |
| | 10 (H ₂ O ₂ , No Pretreatment) | 37.0% | 0.00918 | | | 1.270 | 0.106 | | |
| | 11 (no H ₂ O ₂ , DTPA) | 33.4% | 0.01095 | 3.410 | Yes | 0.918 | 0.056 | 0.443 | No |
| | 12 (H ₂ O ₂ , DTPA) | 35.4% | 0.00421 | | | 0.900 | 0.059 | | |
| | 13 (no H ₂ O ₂ , A) | 33.9% | 0.00730 | 7.003 | Yes | 0.758 | 0.029 | 3.331 | Yes |
| | 14 (H ₂ O ₂ , A) | 37.2% | 0.00596 | | | 0.869 | 0.060 | | |
| | 15 (No H ₂ O ₂ , AD) | 50.5% | 0.00365 | 0.718 | No | 0.546 | 0.017 | 6.723 | Yes |
| | 16 (H ₂ O ₂ , AD) | 50.7% | 0.00421 | | | 0.659 | 0.029 | | |

5.3.1 Percent Delignification (% Delig)

From Table 5.5, it can be seen that seven (7) out of eight (8) comparisons made for conditions with H_2O_2 reinforcement showed positive results for the t -test. This was true for the control and for the three pretreatment conditions in which the experiments were performed in glass (see Figure 5.11). For all conditions where the experiments were performed in glass, the introduction of H_2O_2 into the oxygen stage led to a reduction in the kappa number and thus, an increase in the percent delignification. Similar results were obtained for the experiments performed in the stainless steel reactor. The one exception to this pattern was the experiments performed with the A_D stage in the stainless steel reactor, Experiments 15 and 16. The experiments in the stainless steel reactor showed that there was no difference in percent delignification for the A_D stage when H_2O_2 is used in the oxygen process. Use of the A_D stage significantly raised the level of delignification, no matter whether peroxide was used as an oxidizing reinforcement agent or not.

The primary conclusion drawn from these experiments is that use of H_2O_2 in an oxygen stage leads to an improved level of delignification for well washed pulp. The only condition for which this was not true was for the case of pretreatment with the A_D stage where the percent delignification was high in any case. It should be stressed that this conclusion is only true for well washed pulp. In industrial situations where black liquor solids are covered over into the oxygen stage, this conclusion may not be valid.

5.3.2 Selectivity Coefficient (α)

The results of the t -test analysis performed for the selectivity coefficient (α) summarized numerically in Table 5.5 and graphically in Figures 5.13 and 5.14, strongly

suggest that use of H_2O_2 as a reinforcement agent leads to poor or lower selectivity. Six (6) out of the eight (8) possible combinations showed positive for the t -test results (see Figures 5.13 and 5.14). The only conditions that led to a negative result, or the conclusion that there was no difference in the selectivity coefficient (α) when H_2O_2 was introduced into the reactor, were in Experiments 3 and 4, and also in Experiments 11 and 12. These experiments compared the condition of pretreatment of the pulp with DTPA prior to exposure to oxygen delignification to the no pretreatment base case. It should be noted that Experiments 3 and 4 were performed in glass (see Figure 5.13), while Experiments 11 and 12 were performed in the stainless steel reactor (see Figure 5.14). From these results, it would appear that use of DTPA is a particularly effective pretreatment for preserving carbohydrates from degradation reactions with oxygen delignification. For all of the other cases, the conclusion is drawn that use of hydrogen peroxide during oxygen delignification leads to lower selectivity and increased carbohydrate degradation.

CHAPTER 6

CONCLUSION

Oxygen delignification can be regarded as an oxygen-reinforced extraction stage. During oxygen delignification, carbohydrate degradation reactions occur that reduce the strength of the pulp. Carbohydrate degradation reactions are monitored by measuring the intrinsic viscosity, which is related to the molecular weight and degree of polymerization of cellulose. The use of the selectivity parameter (α), originally published by Bubniak (1997) and later used by Zou (2002), can be readily estimated from intrinsic viscosity data.

$$\alpha = \frac{d\left[\frac{1}{DP} - \frac{1}{DP_o}\right]}{dK} \cong \frac{\Delta\left[\frac{1}{DP} - \frac{1}{DP_o}\right]}{\Delta K}$$

In the current work, the selectivity coefficient (α) proved to be a convenient tool for comparing various pulp treatments for preserving pulp viscosity during oxygen delignification.

Agarwal (1999) has published oxygen delignification data for the delignification of mixed southern hardwood treated in a single stage oxygen process. Evaluation of these data using the selectivity coefficient (α) showed that there is a linear relationship between the rate of carbohydrate degradation and the decrease in the lignin content of the pulp. It was concluded from this analysis that for mixed southern hardwood pulp, temperature has little effect on pulp selectivity within the temperature range of 90 to 110 °C. Rather, pulp selectivity is determined primarily by the addition rate of caustic and thus, the caustic concentration present in the reactor during the oxygen process. This

conclusion suggests that, commercially, one possible method for optimizing oxygen delignification systems is to raise the temperature in the oxygen delignification reactor and carefully control the caustic concentration. This strategy would increase the level of delignification and preserve pulp strength through improved selectivity.

To evaluate differences between the response variables for the various pulp treatments studied in this work, specifically the degree or level of delignification and the pulp selectivity, a statistical analysis was required. The statistic test used in this evaluation was the student *t*-test. Although tedious, the use of the *t*-test permitted a differentiation between the measured response variables for the various pretreatment processes.

Use of the stainless steel reactor did not materially change the experimental results for most of the pretreatment conditions evaluated in this thesis relative to the ideal case of conducting the delignification reactions in a glass reactor. Only in the case of the DTPA pretreatment did use of the stainless steel reactor material alter the results. Thus, it is concluded that for most purposes, evaluation of delignification experiments in stainless steel is an acceptable practice.

It was concluded that, as a general rule, use of a pretreatment process did not significantly reduce the final kappa number of the pulp relative to the case of no pretreatment. This was true for both the Q-state and A-stage pretreatment processes. Rather, in the Q- and A-stage processes, the primary effect of pulp pretreatment is to improve the selectivity of the oxygen delignification process. Analysis on the metal ions present in the pulp samples, before and after exposure to the pretreatment process, indicated that the improvement in pulp selectivity resulted primarily from a reduction in

the transition metals content of the pulp before oxygen delignification. The lower metals content most likely resulted in a reduction in the concentration of hydroxyl free radicals ($\text{OH}\cdot$) generated during oxygen delignification, that are known to react detrimentally with the pulp carbohydrates.

The use of an A_D -stage to treat the pulp prior to oxygen delignification was particularly effective in raising the level of delignification and also in improving pulp selectivity. These results confirm the information published by Boniface (2000) and use of an A_D stage prior to oxygen delignification at the Lincoln mill of Eastern Fine Paper Company. The use of chlorine dioxide (ClO_2) in the acid stage pretreatment was thought to function in two ways. The presence of the low pH was thought to remove metal ions while the addition of the chlorine dioxide functions to activate the pulp for additional delignification by promoting the formation of free phenolic groups in the pulp. This is speculation however since the free phenolic contents of the pulps was not measured. Use of an A_D stage commercially has a drawback because the effluent from the oxygen process could be contaminated with chloride ion. Thus, it is unlikely that the effluent from the oxygen stage would be recycled back to the recovery boiler because of fears of corrosion and boiler tube failure. Rather it would most likely be sent to the sewer and to the waste treatment plant.

Lastly, it was concluded that the use of hydrogen peroxide to reinforce the oxygen stage raises the level of delignification, but lowered the pulp selectivity. This conclusion did not seem to be dependent upon the pretreatment process used to remove metal ions from the pulp. The only exception was the A_D stage where the level of delignification was improved even without the addition of hydrogen peroxide. In a commercial sense it

is doubtful that reinforcing an oxygen stage with hydrogen peroxide will prove to be attractive because of the loss of pulp quality and the modest gains achieved by the increase in delignification.

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APPENDICES

APPENDIX A
TREATMENT OF AGARWAL'S KINETIC DATA (1998)
FOR ESTIMATION OF SELECTIVITY

The oxygen delignification data of Agarwal (1998) were used to estimate the selectivity for mixed southern hardwood kraft pulp. This was done by comparing the selectivity coefficient(α) for the various experiments reported by Agarwal. Agarwal's data are summarized in Table A.1 for oxygen delignification experiments performed with mixed southern hardwood kraft pulp. Data are presented for temperatures of 90 °C, 100 °C, and 110 °C at caustic addition rates of 1.5%, 2.5%, and 3.5%. All data are presented for delignification at 100 psig (6.89 bar) in the oxygen reactor. The selectivity coefficient (α) was estimated using the method described by Zou (2002). The change in kappa number was calculated from the equation

$$\Delta K = K_0 - K_t \quad (A-1)$$

where K_t represents the kappa number at time (t) and K_0 represents the initial kappa number. The degree of polymerization (DP) was obtained the equation

$$DP = 961.38 \cdot \log_{10}(V) - 245.3 \quad (A-2)$$

where V is the CED Tappi viscosity (T230), cps. Equation (A-2) was taken from the work of Iribarne and Schroeder (1997).

The change in the reciprocal of the degree of polymerization ($1/DP$) was taken as a measure of the change in number of moles of cellulose per gram of pulp. This parameter was estimated from the equation

$$\Delta(1/DP) = [1/DP_t - 1/DP_0] \quad (A-3)$$

where DP_t is the degree of polymerization at time (t). Lastly, the selectivity coefficient (α) was estimated from the slope of a plot of $\Delta(1/DP)$ versus ΔK as

$$[1/DP_t - 1/DP_0] = -\alpha (K_t - K_0) \quad (A-4)$$

Data for the parameter $(1/DP)$ are shown in Table A.1. A sample plot is shown in Figure A.1 where the selectivity coefficient (α) was estimated from the equation

$$\alpha = \Delta(1/DP) * 10^5 / \Delta K \quad (A-5)$$

Note that the value of selectivity coefficient (α) given in equation (A-5) was multiplied by a factor of 10^5 . For 90 °C, the selectivity coefficient (α) was estimated to be 3.105, 2.921, or 1.953 ml^{-1} depending upon the caustic addition rate.

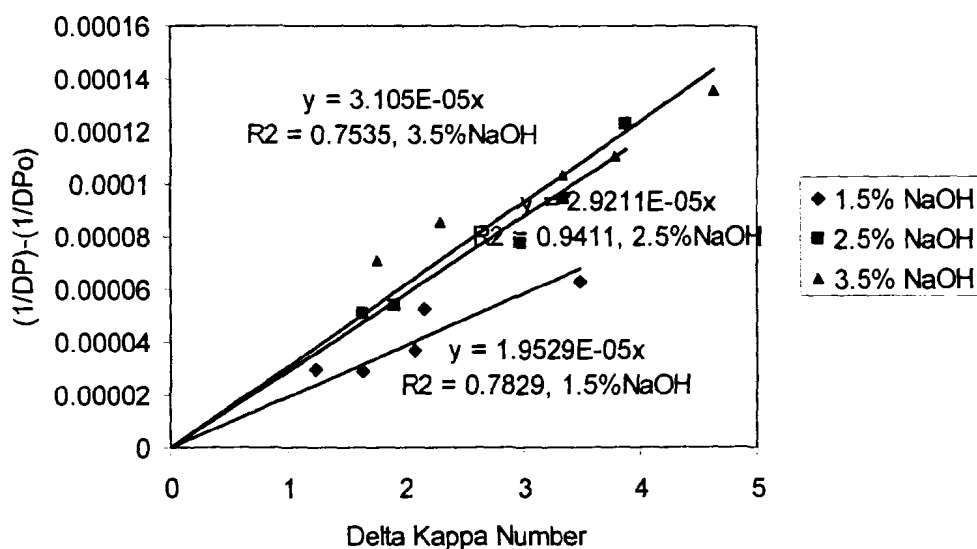


Figure A.1 Selectivity during Oxygen Delignification (90 °C 100 psi)

Table A.1

Medium Consistency Oxygen Delignification Data of Agarwal

Conditions: 90 °C, 100 psi, and 1.5% NaOH

| Time,min | Kappa number | Tappi Viscosity,cps | Δ Kappa | $(1/DP-1/DP_0) * 10^5$ |
|----------|--------------|---------------------|----------------|------------------------|
| 0 | 13.17 | 53.64 | 0 | 0.00 |
| 5 | 11.94 | 46.8 | 1.23 | 2.95 |
| 10 | 11.54 | 46.9 | 1.63 | 2.91 |
| 20 | 11.09 | 45.3 | 2.08 | 3.70 |
| 30 | 11.01 | 42.3 | 2.16 | 5.31 |
| 60 | 9.69 | 40.6 | 3.48 | 6.31 |

Conditions: 90 °C, 100 psi, and 2.5% NaOH

| Time,min | Kappa number | Tappi Viscosity,cps | Δ Kappa | $(1/DP-1/DP_0) * 10^5$ |
|----------|--------------|---------------------|----------------|------------------------|
| 0 | 13.18 | 56.13 | 0 | 0.00 |
| 5 | 11.55 | 44.4 | 1.63 | 5.09 |
| 10 | 11.28 | 43.8 | 1.9 | 5.41 |
| 20 | 10.2 | 39.8 | 2.98 | 7.73 |
| 30 | 9.83 | 37.2 | 3.35 | 9.46 |
| 60 | 9.3 | 33.5 | 3.88 | 12.29 |

Conditions: 90 °C, 100 psi, and 3.5% NaOH

| Time,min | Kappa number | Tappi Viscosity,cps | Δ Kappa | $(1/DP-1/DP_0) * 10^5$ |
|----------|--------------|---------------------|----------------|------------------------|
| 0 | 13.01 | 54.8 | 0 | 0.00 |
| 5 | 11.26 | 40 | 1.75 | 7.12 |
| 10 | 10.72 | 37.8 | 2.29 | 8.55 |
| 20 | 9.68 | 35.3 | 3.33 | 10.36 |
| 30 | 9.23 | 34.4 | 3.78 | 11.06 |
| 60 | 8.38 | 31.5 | 4.63 | 13.56 |

Table A.1
(Continued)

Conditions: 100 °C 100 psi, and 1.5% NaOH

| Time,min | Kappa number | Tappi Viscosity,cps | Δ Kappa | $(1/DP-1/DP_0) * 10^5$ |
|----------|--------------|---------------------|----------------|------------------------|
| 0 | 13.17 | 53.64 | 0 | 0.00 |
| 5 | 11.19 | 46.23 | 1.98 | 3.23 |
| 10 | 10.7 | 44.43 | 2.47 | 4.15 |
| 20 | 10.16 | 41.75 | 3.01 | 5.62 |
| 30 | 9.7 | 41.3 | 3.47 | 5.89 |
| 60 | 8.21 | 39.11 | 4.96 | 7.24 |

Conditions: 100 °C 100 psi, and 2.5% NaOH

| Time,min | Kappa number | Tappi Viscosity,cps | Δ Kappa | $(1/DP-1/DP_0) * 10^5$ |
|----------|--------------|---------------------|----------------|------------------------|
| 0 | 13.18 | 56.13 | 0 | 0.00 |
| 5 | 11.05 | 45.31 | 2.13 | 4.62 |
| 10 | 9.95 | 39.22 | 3.23 | 8.10 |
| 20 | 9.72 | 35.95 | 3.46 | 10.36 |
| 30 | 8.78 | 34.48 | 4.4 | 11.49 |
| 60 | 7.82 | 32.18 | 5.36 | 13.43 |

Conditions: 100 °C 100 psi, and 3.5% NaOH

| Time,min | Kappa number | Tappi Viscosity,cps | Δ Kappa | $(1/DP-1/DP_0) * 10^5$ |
|----------|--------------|---------------------|----------------|------------------------|
| 0 | 13.01 | 54.8 | 0 | 0.00 |
| 5 | 10.99 | 39.36 | 2.02 | 7.52 |
| 10 | 9.6 | 35.39 | 3.41 | 10.29 |
| 20 | 9.39 | 32.79 | 3.62 | 12.40 |
| 30 | 8.35 | 30.14 | 4.66 | 14.87 |
| 60 | 6.83 | 25.56 | 6.18 | 20.15 |

Table A.1
(Continued)

Conditions: 110 °C, 100 psi, and 1.5% NaOH

| Time,min | Kappa number | Tappi Viscosity,cps | Δ Kappa | $(1/DP-1/DP_0) * 10^5$ |
|----------|--------------|---------------------|----------------|------------------------|
| 0 | 13.17 | 53.64 | 0 | 0.00 |
| 5 | 10.15 | 43.63 | 3.02 | 4.57 |
| 10 | 9.63 | 41.53 | 3.54 | 5.75 |
| 20 | 9.03 | 40.41 | 4.14 | 6.42 |
| 30 | 8.68 | 38.6 | 4.49 | 7.57 |
| 60 | 8.14 | 36.67 | 5.03 | 8.90 |

Conditions: 110 °C, 100 psi, and 2.5% NaOH

| Time,min | Kappa number | Tappi Viscosity,cps | Δ Kappa | $(1/DP-1/DP_0) * 10^5$ |
|----------|--------------|---------------------|----------------|------------------------|
| 0 | 13.18 | 56.13 | 0 | 0.00 |
| 5 | 10.29 | 41.01 | 2.89 | 6.99 |
| 10 | 9.09 | 36.4 | 4.09 | 10.03 |
| 20 | 8.33 | 32.03 | 4.85 | 13.57 |
| 30 | 7.19 | 30.58 | 5.99 | 14.93 |
| 60 | 6.51 | 27.24 | 6.67 | 18.52 |

Conditions: 110 °C, 100 psi, and 3.5% NaOH

| Time,min | Kappa number | Tappi Viscosity,cps | Δ Kappa | $(1/DP-1/DP_0) * 10^5$ |
|----------|--------------|---------------------|----------------|------------------------|
| 0 | 13.01 | 54.8 | 0 | 0.00 |
| 5 | 10.06 | 35.13 | 2.95 | 10.49 |
| 10 | 8.56 | 32.75 | 4.45 | 12.44 |
| 20 | 7.64 | 27.47 | 5.37 | 17.76 |
| 30 | 7.15 | 24.86 | 5.86 | 21.11 |
| 60 | 6.44 | 22.77 | 6.57 | 24.26 |

APPENDIX B

SUMMARY OF EXPERIMENTAL DATA AND CONFIDENCE INTERVAL CALCULATION

Tables 4.1, 4.2, 4.3 and 4.4 in the main text summarize the mean values of the experimental data. Detailed results are presented for the final kappa number (K), the final intrinsic viscosity ($[\eta]$), the percent delignification (% Delig), and the selectivity coefficient (α). For each value shown in the table, the mean value (\bar{x}), the standard deviation (S_d) and the 95% upper and lower confidence limits are presented. The treatment of the data for selectivity coefficient (α) has been described in Appendix A.

The percent delignification was calculated from the equation

$$\%Delignification = \frac{K_0 - K_t}{K_0} \quad (B-1)$$

where K_0 is the initial kappa number and K_t is the kappa number at the end of oxygen delignification.

The selectivity coefficient (α) was estimated by the equation as follows

$$\alpha = \frac{d[1/DP - 1/DP_0]}{dK} \cong \frac{\Delta[1/DP - 1/DP_0]}{\Delta K} \quad (B-2)$$

where, the degree of polymerization ($[DP]$) was calculated from the intrinsic viscosity ($[\eta]$).

$$DP^{0.90} = 1.65 \cdot [\eta] \quad (B-3)$$

In equation (B-3), the intrinsic viscosity ($[\eta]$) has the units of cc/g.

Based on the definition of selectivity coefficient, the lower the values for selectivity coefficient (α) the higher will be the selectivity during oxygen delignification.

As a result, the best selectivity was obtained under Experiment seven (7) performed in glass and Experiment fifteen (15) performed in the stainless steel reactor, respectively.

Four experiments were performed for each condition. The mean (\bar{x}), the standard deviation (S_d), and upper limit and lower limit were estimated by following the methods presented by Pazer and Awanson (1972). The data were treated to give the mean (\bar{x}), and standard deviation (S_d).

$$\bar{x} = \sum_{i=1}^n \frac{x_i}{n} \quad (\text{B-4})$$

$$S_d = \sqrt{\frac{\sum_{i=1}^n (\bar{x} - x_i)^2}{n-1}} \quad (\text{B-5})$$

The estimate for the standard error is

$$S_x = S_d / \sqrt{n} \quad (\text{B-6})$$

Assuming $n-1$ degrees of freedom (d_f), the confidence interval (μ) can be obtained by using equation (B-7). Similarly, the upper and lower confidence levels were estimated from this equation.

$$\bar{x} - t_{\alpha/2}(n-1) \cdot S_x < \mu < \bar{x} + t_{\alpha/2}(n-1) \cdot S_x \quad (\text{B-7})$$

Where the term (α) is the error associated with the measurement (5% or 0.05).

A sample calculation is shown for treating the kappa number and the intrinsic viscosity data for Experiment No. 1, the no-pretreatment case with no peroxide added to the reactor. The sample calculation for the kappa number is summarized in Table B.1.

Table B.1

Sample Calculation of Kappa Number of Experiment No. 1 for Confidence Interval

| The Confidence Interval Calculation of Kappa Number of Experiment No. 1: | | |
|--|--|---------------|
| $K := \begin{pmatrix} 9.2 \\ 9.2 \\ 9.4 \\ 9.3 \end{pmatrix}$ | $n := 4$ | ORIGIN := 1 |
| Mean of the four numbers | $\chi := \frac{\sum_{i=1}^n K_i}{n}$ | $\chi = 9.3$ |
| Standard deviation | $Sd := \sqrt{\frac{\sum_{i=1}^n (\chi - K_i)^2}{n - 1}}$ | $Sd = 0.096$ |
| Estimate S_x | $S_x := \frac{Sd}{\sqrt{n}}$ | $S_x = 0.048$ |
| For 95% confidence level, | $t := 3.182$ | |
| Upper limit | $\mu_1 := \chi + t \cdot S_x$ | $\mu_1 = 9.4$ |
| Lower limit | $\mu_2 := \chi - t \cdot S_x$ | $\mu_2 = 9.1$ |
| As a result, the experiment can say that the probability is approximately 95% that the true value of K is covered by an interval such as that between 9.1 and 9.4. | | |

The mean value is calculated from equation (B-4) as 9.3.

$$K_{\text{exp } 1} = (K_1 + K_2 + K_3 + K_4) / 4 = (9.2 + 9.2 + 9.4 + 9.3) / 4 = 9.3 \quad (\text{B-8})$$

The standard deviation was estimated from equation (B-5) as 0.096, while the value for the standard error (S_x) is estimated from equation (B-6) to be 0.048. Assuming a two tail t -test at the 95% confidence limit ($\alpha/2=0.025$), the t -statistic with 3 degrees of freedom is obtained from the standard table

$$t_{0.025}(3) = 3.182 \quad (\text{B-9})$$

Using equation (B-7), the upper and lower confidence limits are

$$9.1 < K < 9.4 \quad \text{ml} \quad (\text{B-10})$$

Similar results were obtained for the intrinsic viscosity (see Table B.2).

Thus, it is concluded that the true intrinsic viscosity lies between

$$1020 < V < 1027 \text{ cc/g} \quad (\text{B-11})$$

At the 95% confidence level, the true kappa number lies between 9.1 and 9.4 and the true intrinsic viscosity lies between 1020 and 1027 ml/g. Similar calculations were performed for the other fifteen experiments.

Table B.2

Sample Calculation for the Intrinsic Viscosity for Experiment No. 1 for Confidence
Interval

The Confidence Interval Calculation of Intrinsic Viscosity of Experiment No. 1:

$$V := \begin{pmatrix} 1021 \\ 1022 \\ 1024 \\ 1026 \end{pmatrix}$$

$$n := 4$$

$$\text{ORIGIN} := 1$$

Mean of the four numbers

$$\chi := \frac{\sum_{i=1}^n v_i}{n}$$

$$\chi = 1023$$

Standard deviation

$$Sd := \sqrt{\frac{\sum_{i=1}^n (\chi - v_i)^2}{n - 1}}$$

$$Sd = 2.217$$

Estimate S_x

$$S_x := \frac{Sd}{\sqrt{n}}$$

$$S_x = 1.109$$

For 95% confidence level,

$$t := 3.182$$

Upper limit

$$\mu_1 := \chi + t \cdot S_x$$

$$\mu_1 = 1027$$

Lower limit

$$\mu_2 := \chi - t \cdot S_x$$

$$\mu_2 = 1020$$

As a result, the experiment can say that the probability is approximately 95% that the true value of V is covered by an interval such as that between 1020 and 1027.

APPENDIX C
DATA ANALYSIS USING
TWO SAMPLE STUDENT *t*-TEST

The *t*-test was estimated by following the methods presented in John A. Rice (1995). The student *t*-test was used to test the hypothesis that the kappa number (K) and the intrinsic viscosity ($[\eta]$) were different for the sixteen (16) oxygen delignification cases studied experimentally. Since the difference between two means was of interest, a two-sample *t*-test was used. The two-sample test is used when the numbers of sample points, four (4) in this case, is small. The following nomenclature is used to test the basic hypothesis that the mean (μ_1) for case (1) is the same as the mean (μ_2) for case (2).

μ_1 = true mean kappa number or intrinsic viscosity after oxygen delignification
for case (1)

μ_2 = true mean kappa number or intrinsic viscosity after oxygen delignification
for case (2)

We then test the **null hypothesis** denoted by H_0

$$H_0: \quad \mu_1 = \mu_2 \quad (C-1)$$

which states that there is essentially no difference in the kappa number or the intrinsic viscosity between case (1) and case (2).

The **two-sided alternative hypothesis** denoted by H_1 is that the kappa number or intrinsic viscosity is different in case (1) compared to case (2).

$$H_1: \quad \mu_1 \neq \mu_2 \quad (C-2)$$

The number of degrees of freedom (df) that is appropriate to the two-sample t -test is calculated from the equation (C-3).

$$df = n_1 + n_2 - 2 = (n_1 - 1) + (n_2 - 1) \quad (C-3)$$

where (n_1) and (n_2) are the numbers of data points in the first and second cases. The criterion for rejection of the null hypothesis, given in equation (C-1) in favor of the two-sided alternative hypothesis (C-2), is summarized in Table C.1. In Table C.1, (α) represents the error associated with the measurement. The use of $(\alpha/2)$ assumes that a two tail t -test is used, or that the error can occur on either side of the mean. The value of the t statistic in the two sample t -test for difference of means is calculated using equation (C-4).

$$t = \frac{(\bar{x}_1 - \bar{x}_2)}{\sqrt{\frac{(n_1 - 1) \cdot Sd_1^2 + (n_2 - 1) \cdot Sd_2^2}{n_1 + n_2 - 2} \cdot \left(\frac{1}{n_1} + \frac{1}{n_2}\right)}} \quad (C-4)$$

Lastly, the criterion for rejection of the hypothesis is

$$|t| > t_{\alpha/2}(n_1 + n_2 - 2) \quad (C-5)$$

depending upon the null hypothesis (see Table C.1).

Normally, $\alpha = 0.05$ is used as the level of uncertainty. So, in this case, $t_{0.025}(6) = 2.447$. If $|t| > 2.447$, it states that there is a difference in the percent delignification or the selectivity coefficient (α) between case (1) and case (2). If $|t| < 2.447$, it states that there is no difference in the percent delignification or the selectivity coefficient (α) between cases (1) and (2).

Table C.1

Rejection Rule for Alternative Hypothesis Using Two-Sample t -Test

$$H_0: \mu_1 = \mu_2$$

| Alternative | Reject H_0 in Favor of Alternative (A) at Significance Level α |
|-------------------------|---|
| $H_1: \mu_1 \neq \mu_2$ | $ t > t_{\alpha/2}(n_1 + n_2 - 2)$ |
| $H_2: \mu_1 > \mu_2$ | $t > t_{\alpha}(n_1 + n_2 - 2)$ |
| $H_3: \mu_1 < \mu_2$ | $t < -t_{\alpha}(n_1 + n_2 - 2)$ |

Comparisons were made for the sixteen (16) oxygen delignification experiments by dividing the results into five (5) categories. These comparisons are summarized in Table 5.1 through 5.5 and correspond to the results in terms of the effect of glass versus the stainless steel reactor (Table 5.1), no pretreatment compared to DTPA pretreatment (Table 5.2), no pretreatment compared to acid washing (Table 5.3), no pretreatment compared to A_D stage (Table 5.4), and the effect of hydrogen peroxide reinforcement (Table 5.5).

APPENDIX D

RESULTS OF METALS ANALYSIS ON SELECTED SAMPLES

Selected pulp samples following pretreatment and after exposure to oxygen were analyzed for their metals content. This was done for the pulp without pretreatment and the three pretreatments investigated, that is, the DTPA pretreatment (Q stage), the acid washing stage pretreatment (A stage), and the acid washing stage pretreated with chlorine dioxide (A_D stage). The metals content of the various samples was checked in the Soil Testing and Analytical Laboratory in the Department of Plant, Soil, and Environmental Sciences at the University of Maine.

The analytical procedure used for analysis of the metals content of the samples was to place a dried sample into a clean porcelain crucible and combust the sample in a muffle furnace at 550 °C for 6 hours. The crucible with ash was cooled and wetted with deionized water. The ash was then dissolved in 50% HCl, by heating the sample on a hotplate for 30 minutes to dissolve it totally with HCl. After cooling the solution, the solution was checked by Inductively Coupled Plasma emission spectrometer (ICP-AES). The metals in the pulp sample that were determined using the ICP spectrometers were Ca, Mg, Al, Cu, Fe, Mn.

The results for the metal analysis are summarized in Table D.1. The experimental numbers correspond to Figure 4.1 which is for the experimental design for the oxygen delignification experiments.

Based on Table D.1, the three pretreatments can remove the metals including Ca, Mg, Al, Cu, Fe, and Mn, but Fe was not removed as easily as the other metals. The acid

washing pretreatment and A_D stages had almost the same effect on removing metals from pulp. The reason for the similarity in the results arises most likely because the conditions of both pretreatments were the same except that a small amount of chlorine dioxide was applied in the A_D stage. Both the acid washing and the A_D stages were more effective in removing calcium than the DTPA pretreatment. The results of the metals analysis showed that pulps exposed to oxygen delignification in a stainless steel reactor sometimes were contaminated with higher metals content. This was especially true for the iron (Fe) and manganese (Mn) content of the pulps processed in the stainless steel. The data are also very unusual in that the copper (Cu) content in the pulp was much higher in the exposed samples than in the original pulp. This was true no matter whether the pulps were pretreated or not, or whether the experiments were performed in the stainless steel reactor or not. Possible explanations for these results may be that the wash water had a high content of copper (Cu) or alternatively, the auxiliary equipment used to treat the pulp may have contaminated the samples.

Table D.1

The Results of Metal Analysis (PPM for all nutrients in dry sample)

| Sample I. D. | Metal | | | | | |
|--|-------|-------|-------|-------|------|------|
| | Ca | Mg | Al | Cu | Fe | Mn |
| Original Pulp | 3900 | 430 | 14.3 | 6.66 | 8.02 | 73.7 |
| Pulp after DTPA Pretreatment | 2240 | 225 | 8.89 | 0.751 | 7.46 | 7.01 |
| Pulp after Acid Washing Pretreatment | 246 | 31.7 | <4.92 | 3.25 | 7.78 | 6.15 |
| Pulp after A_D Stage Pretreatment | 302 | 28 | <4.96 | 3.80 | 6.40 | 5.62 |
| Experiment 1 (No Pretreatment, No H ₂ O ₂ , In Glass) | 3610 | 587 | 12.3 | 25.2 | 5.43 | 49.2 |
| Experiment 2 (No Pretreatment, H ₂ O ₂ , In Glass) | 3790 | 518 | 12.9 | 41.4 | 3.66 | 45 |
| Experiment 3 (DTPA Pretreatment, No H ₂ O ₂ , In Glass) | 2600 | 355 | 7.52 | 29.6 | 4.77 | 4.58 |
| Experiment 4 (DTPA Pretreatment, H ₂ O ₂ , In Glass) | 2940 | 327 | <4.76 | 43 | 3.59 | 4.41 |
| Experiment 5 (Acid Washing Pretreatment, No H ₂ O ₂ , In Glass) | 350 | 153 | <4.96 | 30.3 | 4.39 | 4.50 |
| Experiment 6 (Acid Washing Pretreatment, H ₂ O ₂ , In Glass) | 368 | 140 | <4.93 | 26.4 | 3.83 | 5.09 |
| Experiment 7 (A _D Stage Pretreatment, No H ₂ O ₂ , In Glass) | 370 | 160 | <4.90 | 31.5 | 4.21 | 4.67 |
| Experiment 8 (A _D Stage Pretreatment, H ₂ O ₂ , In Glass) | 346 | 159 | <4.97 | 36.2 | 4.89 | 5.16 |
| Experiment 9 (No Pretreatment, No H ₂ O ₂ , In Stainless Steel Reactor) | 3640 | 486 | 10.3 | 60.3 | 7.67 | 38.9 |
| Experiment 10 (No Pretreatment, H ₂ O ₂ , In Stainless Steel Reactor) | 3920 | 489 | 8.79 | 50.1 | 3.95 | 40.7 |
| Experiment 11 (DTPA Pretreatment, No H ₂ O ₂ , In Stainless Steel Reactor) | 2983 | 371.7 | 9 | 45.9 | 9.85 | 8.59 |
| Experiment 12 (DTPA Pretreatment, H ₂ O ₂ , In Stainless Steel Reactor) | 3080 | 361 | 8.89 | 35.2 | 5.63 | 7.27 |
| Experiment 13 (Acid Washing Pretreatment, No H ₂ O ₂ , In Stainless Steel Reactor) | 376 | 140 | <5.23 | 35.2 | 5.08 | 8.67 |
| Experiment 14 (Acid Washing Pretreatment, H ₂ O ₂ , In Stainless Steel Reactor) | 389 | 138 | <4.96 | 32.9 | 4.69 | 7.98 |
| Experiment 15 (A _D Stage Pretreatment, No H ₂ O ₂ , In Stainless Steel Reactor) | 405 | 129 | <4.98 | 38.9 | 4.99 | 9.05 |
| Experiment 16 (A _D Stage Pretreatment, H ₂ O ₂ , In Stainless Steel Reactor) | 367 | 151 | <5.26 | 36.8 | 5.81 | 8.43 |

BIOGRAPHY OF THE AUTHOR

Zheng Dang was born in Xi'an, P.R. China on November 27, 1972. He was raised in Xi'an and graduated from Qinchuan High School in 1991. He attended Nanjing University of Science and Technology in Nanjing and graduated in 1995 with a Bachelor's degree in Chemical Engineering. He returned to Xi'an and worked in the Institute of Qinchuan Factory as an Assistant Engineer for one year. He attended Northwest University in Xi'an in 1996 and obtained his Master's degree in Biochemical Engineering in 1999. He attended The University of Maine in the spring of 2000.

After receiving his degree, Zheng will be joining the Institute of Paper Science and Technology to work toward his Ph.D. degree. Zheng is a candidate for the Master of Science degree in Chemical Engineering from The University of Maine in August, 2002.