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Improving Degree of Delignification and Selectivity of Oxygen Delignification of Southern Pine Kraft Pulp

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IMPROVING DEGREE OF DELIGNIFICATION AND SELECTIVITY OF OXYGEN DELIGNIFICATION OF SOUTHERN PINE KRAFT PULP

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A DISSERTATION

Submitted in Partial Fulfillment of the

Requirements for the Degree of

Doctor of Philosophy

(in Chemical Engineering)

The Graduate School

The University of Maine

May 2022

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IMPROVING DEGREE OF DELIGNIFICATION AND SELECTIVITY OF OXYGEN DELIGNIFICATION OF SOUTHERN PINE KRAFT PULP

By Azadeh Pahlevanzadeh

Dissertation Advisor: Professor Adriaan van Heiningen

An Abstract of the Dissertation Presented
in Partial Fulfillment of the Requirements for the
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Oxygen delignification is a pre-bleaching stage that provides environmental benefits for bleached pulp production by replacing about 50% of the chlorine-based bleaching chemicals with oxygen. The resulting reduction in chlorine-based chemicals leads to a significantly lower release of chlorinated organics in the pulp bleaching effluent. However, the main disadvantage of applying oxygen delignification is the low delignification/cellulose degradation selectivity compared to chlorine dioxide bleaching. Modern conventional oxygen delignification is limited at level 60% delignification to maintain an acceptable cellulose Degree of Polymerization (DP) and thus fiber strength as indicated by the pulp intrinsic viscosity. The increase in the degree of delignification from 60 to 80% leads to a reduction by a factor 2 of the required bleaching chemicals and also reduces the environmental impact of the bleach plant effluent by at least a factor of two. However, to achieve this increase in the degree of delignification the delignification/cellulose degradation selectivity must be improved, and therefore the objective of the present research is to understand and improve the selectivity especially at high degrees of delignification.

The technical objective of the present PhD project was to perform extended oxygen delignification up to 80% of conventional Southern Pine kraft pulp (about 24 kappa) while maintaining acceptable cellulose DP as calculated from the measured pulp intrinsic viscosity. More importantly, the fundamental objective of the research is to understand how to increase the delignification/cellulose degradation selectivity during oxygen delignification of conventional softwood kraft pulp (about 24 kappa) in particular at very high degrees of delignification.

In the present study we found that the oxygen delignification of industrial softwood pulp consists of two contributions; phenolic delignification and alkaline leaching delignification.

In addition, we could extend the oxygen delignification up to 80% of conventional Southern Pine kraft pulp (about 24.4 kappa number) while maintaining acceptable intrinsic viscosity (>700 mL/g) in the presence of 2.186 g/L Na_2CO_3 at 100 ^{o}C for 90 minutes of oxygen delignification. But, for the conventional kraft pulp, the selectivity is not affected by the addition of 100 ppm $NaBH_4$ because of the absence of carbonyl groups on cellulose in the kraft pulp, and no improvement in pulp viscosity and selectivity is seen.

DEDICATION

My appreciation goes out to my parents Nasrin Attaran and Prof. Hassan Pahlevanzadeh and my sister Prof. Hoda and her lovely family always offer support and love.

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CHAPTER 1

INTRODUCTION

1.1 Oxygen Delignification Process

Oxygen delignification is a pre-bleaching stage that provides environmental benefits for bleached pulp production by replacing about 50% of the chlorine-based bleaching chemicals with oxygen (Ni, van Heiningen, et al. 2001), (Forslund, et al. 2001). The resulting reduction in chlorine-based chemicals leads to a significantly lower release of chlorinated organics in the pulp bleaching effluent (Solomon 1996). The decrease in the content of chlorinated organics, Chemical Oxygen Demand (COD), and Biological Oxygen Demand (BOD) in effluents and/or the color of bleach plant effluent is related to the degree of oxygen delignification. Thus, oxygen delignification is presently the standard technology placed between pulping and bleaching (see Figure 1.1) so as to achieve substantial environmental benefits and a significant reduction in bleaching chemical costs.

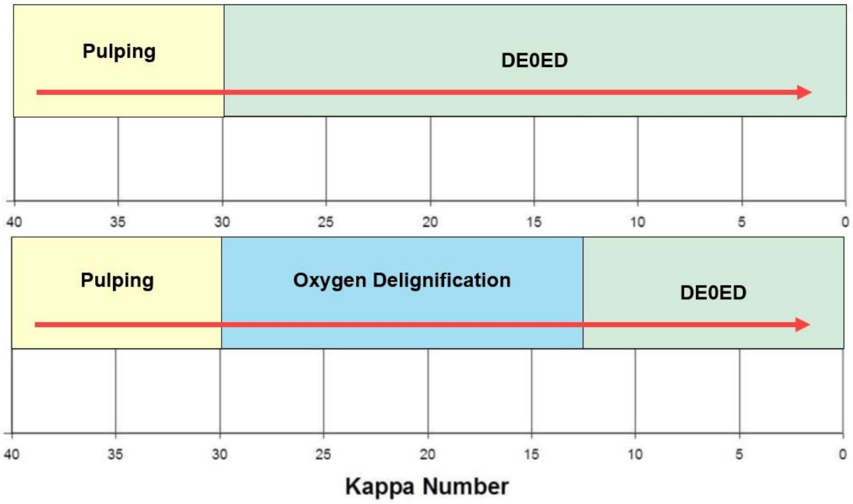


Figure 1.1. Effect on bleaching softwood kraft pulp by introducing oxygen delignification

The other advantage of oxygen delignification is improving yield selectivity of the pulp compared to extending delignification by cooking. In Figure 1.2, the cooking yield curve drops significantly by extending the kraft pulping process, while the oxygen delignification curve (indicated as O/Alkali) has a better yield at lower kappa numbers, i.e. when the kraft pulping process enters the residual delignification phase.

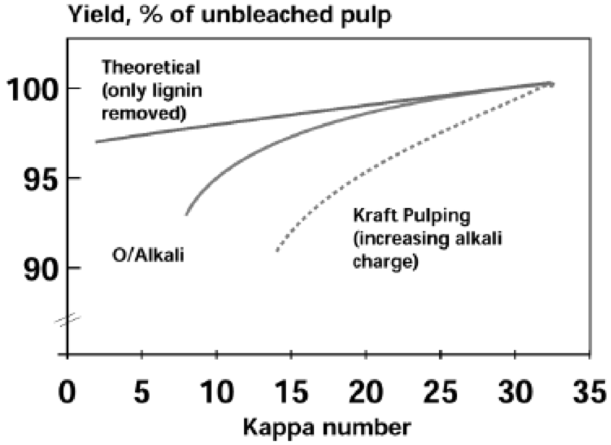


Figure 1.2. Yield selectivity of extended cooking and O_2 delignification

(Sunds Defibrator, 1999)

The disadvantages of applying oxygen delignification are the low delignification/cellulose degradation selectivity compared to chlorine dioxide (T. J. McDonough 1996), and the high capital cost of installing an oxygen delignification system (Genco, van Heiningen and Miller 2012). However, despite the low delignification/cellulose degradation selectivity, the carbohydrate loss per kappa unit removed is similar for oxygen delignification and chlorine dioxide bleaching. This may be explained by the reaction of oxygen with carbohydrate reducing end groups to form stable carboxylic groups (Samuelson and Stolpe 1969).

1.2 Softwood Structure

Softwoods come from conifer trees or evergreen plants with needle-shaped leaves such as pine, spruce, cedar, larch hemlock, and redwood. These types of woods are mostly used in the lumber and pulp and paper industries. Conifers called gymnosperms contain mostly softwood trees (>95%) and have a much simpler structure and more uniform cell types than hardwoods. The fiber length of softwood fibers is about 3.5 mm compared to about 1 mm for hardwoods, and the fiber width of hardwoods of 10-18 µm is about halve of that of softwoods of 28-35 µm (A. van Heiningen in print 2020). Also, softwoods contain about 30% lignin compared to about 25% for hardwoods, therefore more alkali is needed using the kraft pulping process to remove lignin from softwoods. The longer length of softwood fibers leads to stronger paper and board products than those made of hardwood fibers, because after paper drying individual fibers are hydrogen bonded by cellulose hydroxyl groups to a much larger number of fibers inside the paper, thus spreading out the tensile forces over a larger area. However, hardwood kraft pulps produce smoother paper with good printing and writing properties (A. van Heiningen in print 2020).

1.3 Lignin

Lignin is a hydrophobic and mostly aromatic biopolymer protecting wood against microbial degradation. This biopolymer works as a glue bonding the cellulose microfibrils and hemicelluloses together. The composite fiber structure provides a tree with its high compressive strength and bending stiffness required for growth to great heights and withstanding nature's wind forces (Salmen 2006). Lignin has a complex structure with a mixture of aliphatic and aromatic moieties. The structure of lignin is not linear like cellulose nor branched like hemicellulose. Lignin has a three-dimensional amorphous structure with the monomers randomly connected to each other by ether (C-O-C) and carbon-carbon (C-C) bonds. The three main monomers forming the lignin structure known as monolignols, are ρ-Coumaryl alcohol (H), Coniferyl alcohol (G), and Sinapyl alcohol (S) (Figure 1.3).

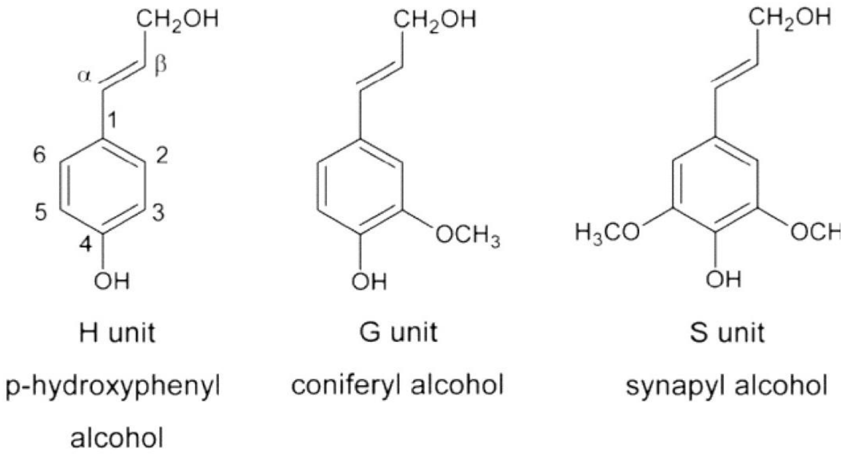


Figure 1.3. The three main monolignols (Duval and Lawoko 2014)

Lignin in softwood contains mostly coniferyl alcohol (>95%) and a small amount of ρ-coumaryl alcohol (<5%) and hardly any synapyl alcohol. Hardwood lignin contains both coniferyl alcohol (25-50) and sinapyl alcohol (46-75%).

1.4 Cellulose

Cellulose is the most common organic polymer on earth since 40 to 50% of wood is cellulose. This homo-polymer has a linear structure made from D-glucose connected by β-1,4-glycosidic bonds. Native cellulose consists of crystalline and amorphous regions. The crystalline region makes the cellulose strong, rigid, and resistant to dissolution in most solvents. The amorphous region is more accessible and can be chemically attacked which could lead to cleavage of the polymer chain. Examples of this are alkaline hydrolysis during kraft cooking and direct hydroxyl radical attack on the glycosidic bond during oxygen delignification.

1.5 Kraft Pulping

The kraft pulping process, also known as sulfate pulping process, is a technology for the conversion of wood chips into pulp which is mostly cellulose. In this pulping process, an aqueous solution of sodium hydroxide and sodium sulfide are added to a pressure vessel known as digester at 140 to 180 ℃ for several hours. Under these conditions, most of the lignin and a significant amount of the hemicelluloses degrade and dissolve in the strong alkali. The spent liquor (black liquor) is discharged from the digester and the remaining solid pulp (brown stock) is collected and washed to separate the pulp from the dissolved wood and waste pulping chemicals. Kraft pulping is a low yield process with a yield of about 50% of the tree, so the rest ends up in black liquor which after concentration in multiple effect evaporators is combusted for energy generation and recovery of the inorganic pulping chemicals.

In the conventional kraft pulping process, 90-95% of the lignin from softwoods is removed and 5-10% remains in the pulp. Since this more condensed residual lignin is darker in color, the pulp has a brown color and is called brown stock. Therefore, further delignification is needed to remove the rest of the lignin in order to increase the brightness. Oxygen delignification and bleaching stages are two chemical processing steps that are needed to remove the residual lignin and increase the brightness of the pulp.

1.6 Sulfite pulping

In the sulfite pulping process, sulphurous acid (H_2SO_3) and bisulphite ions (HSO_3^-) are the cooking chemicals used to degrade and dissolve lignin. Sulfite pulping can be conducted under acidic (pH 1-2) or neutral (pH 7-9) conditions. The conditions of sulfite pulping lead lignin to react with the sulfur dioxide and/or bisulfite ions to produce sulfonated lignin which can be easily degraded by acid hydrolysis reactions. However, besides delignification, cellulose and hemicellulose will also be hydrolyzed and degraded. The recovery cycle in sulfite pulping is longer and more complicated than for kraft pulp or even impractical. That is because of the counter ions such as calcium, sodium, magnesium and ammonium which are more complex to recover together with SO_2. In the case of calcium, recovery is impractical because $CaSO_4$ is very stable at normal combustion temperature (Biermann 1996) (Gellerstedt 2006). Only magnesium can be relatively easy recovered because $MgSO_3$ decomposes into MgO and SO_2 during combustion of the dissolved wood. On the other hand, sulfite pulps are bright and contain lower amounts of lignin than kraft pulps, so fewer bleaching chemicals are required (Biermann 1996). The relatively high reactivity of the residual sulfite lignin also makes sulfite pulp more bleachable. (Hintz 2001).

CHAPTER 2

DESCRIPTION OF PROBLEM AND OBJECTIVES

2.1 Description of Problem

Modern conventional oxygen delignification of softwood is carried out in two sequential stages at 85 and 100°C with all NaOH added in the first stage to obtain about 60% delignification. Delignification is limited at this level to maintain an acceptable pulp intrinsic viscosity (Bokström and Nordén 1998). It is generally accepted that delignification proceeds by attack of oxygen on dissociated phenolic lignin. However certain phenolic structures, such as p-hydroxyphenyl structures and condensed phenolics, are less reactive (Akim, Colodette and Argyropoulo 2001), (Argyropoulos 2003) and therefore accumulate in residual lignin in brownstock after kraft pulping. The degradation rate of these structures may be increased by raising the temperature to 110-115°C, and by using a flow-through mode of operation at low but relatively constant alkali concentration. Unfortunately, the increased temperature also leads to increased cellulose degradation in particular when the delignification is extended beyond 60%. The main reason for cellulose degradation is attack by oxygen-based radicals generated during phenolic delignification by dissolved oxygen in the alkali solution. Another minor pathway is initial alkaline attack of labile groups on cellulose, most likely carbonyls, which have survived Kraft pulping. Nevertheless, it would be very beneficial if the degree of delignification could be increased for a standard softwood kraft pulp of 30 kappa number from 60% to 80% leading to a kappa of 6 for the pulp entering the bleaching stage. The increase of the degree of delignification from 60 to 80% leads to a reduction by a factor 2 of the required bleaching chemicals, and also reduces the environmental impact of the bleach plant effluent by at least a factor of two. So the problem which is tackled in the present thesis is to obtain a fundamental understanding of the delignification/cellulose degradation selectivity during oxygen delignification of conventional softwood kraft pulp (about 30 kappa) at very high degrees of delignification. Based on this understanding, the study aims to identify the operational conditions which will allow production of an 80% delignified conventional Southern Pine kraft pulp while maintaining an acceptable cellulose Degree of Polymerization, DP, as calculated from the measured pulp intrinsic viscosity.

2.2 Objectives of this study

The technical objective of the present Ph.D. project is to perform extended oxygen delignification up to 80% of conventional Southern Pine kraft pulp (about 30 kappa) while maintaining acceptable cellulose DP. The pulp properties are characterized by measuring the kappa number, lignin content, intrinsic viscosity, pulp chemical composition, cellulose DP and pulp yield. More importantly, the fundamental objective of the research is to understand how to increase the delignification/cellulose degradation selectivity during oxygen delignification of conventional softwood kraft pulp (about 30 kappa) in particular at very high degrees of delignification.

Initially, the research is focused on improving the oxygen delignification selectivity by applying small amounts of $NaBH_4$ during or before alkali-oxygen treatment of conventional kraft pulp in a through-flow reactor set-up (Berty reactor). Since this approach was successfully used for conventional sulfite pulp and high kappa softwood kraft pulp but not for conventional kraft pulp, the oxygen delignification selectivity of Southern Pine kraft pulp of two different kappa numbers (30 and 100) and conventional sulfite pulp are studied. Also, the amount of labile carbonyl groups in these three pulps are quantified. The high degree of delignification is obtained by using increased times and higher temperatures (up to 120 ℃). To minimize the attack on cellulose by oxygen-based radicals the approach is to add radical scavengers (such as carbonate, methanol, and glycerol) and to reduce the effect of transition metals (Cu, Fe, Mn) on peroxide decomposition by addition of $MgSO_4$ and reducing chemicals. Finally, to evaluate industrial implementation oxygen delignification of kraft pulp a number of experiments will be performed in a horizontal stirred batch reactor at a few optimal operating conditions.

CHAPTER 3

LITERATURE REVIEW

3.1 Introduction

Oxygen delignification is a proven technology to remove the residual lignin by using alkali and oxygen. This process is very flexible and is performed at moderate temperatures and pressures in a single or several stages between the cooking and bleaching stages. The delignification for a single-stage softwood kraft pulp is in the range of 30-50%, while in the second oxygen delignification stage, this range can be extended up to 50-60% with preserving the pulp quality. Oxygen delignification can also minimize the usage of bleaching chemicals which are much more expensive than oxygen. That is why oxygen delignification is environmentally and economically attractive. On the other hand, there are two major disadvantages of oxygen delignification; First, the high capital cost; Second, the low delignification/cellulose degradation selectivity. Generally, when the lignin content decreases and thus the delignification rate decreases, the cellulose degradation by oxygen-based radicals continues at a relatively higher rate because less of the radicals are captured by lignin. This decreases the pulp viscosity at higher degrees of delignification, and ultimately paper strength properties. Therefore, understanding of the chemistry of oxygen, lignin, cellulose, and the free radicals generated during the oxygen delignification could help to discover conditions which would lead to improved oxygen delignification (T. J. McDonough 1996).

3.2 Autoxidation of lignin Model Compounds

The driving force in oxygen delignification is the reduction of molecular oxygen to water (Gierer, Reitberger, et al. 2001). This reaction is a strong exothermic process, and may be able to oxidize all the lignin compounds in the pulp. However, oxygen in its normal configuration (triplet ground state, $\cdot O - O \cdot$) has the lowest energy level. So, initial energy is needed to raise the energy level of the triplet oxygen to the higher energy level of singlet oxygen state, $O - O$: (van Heiningen, Ji and Jafari 2019). The singlet oxygen can react selectively with electron-rich sites such as the phenolate group on lignin which ultimately leads to the opening of the aromatic ring and the formation of carboxylic groups which makes the lignin hydrophilic leading to its dissolution and removal from the pulp (Gierer, Reitberger, et al. 2001).

The four-electron reduction of oxygen is seen in reaction (3.1).

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \qquad (3.1)$$

The uptake of electrons by oxygen can be represented into the following 4 steps:

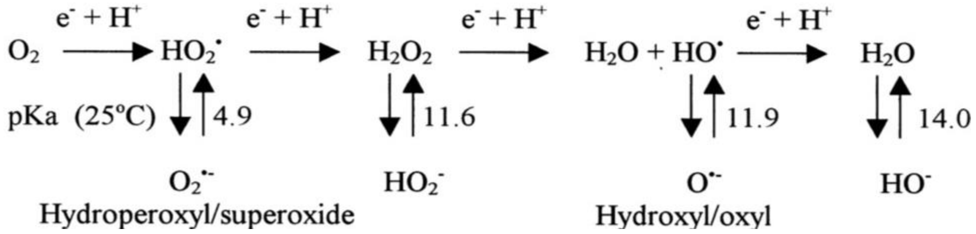


Figure 3.1. Four steps of 1-electron reduction of oxygen

The initial step of uncatalyzed oxygen delignification starts by the abstraction of an electron from phenolic lignin to generate a superoxide anion radical, $O_{\dot{2}}^{-}$, while abstraction of a proton from wood organics leads to the formation of a hydroperoxy radical, $HO_{\dot{2}}$.

$$RO^- + O_2 \rightarrow RO^{\cdot} + O_2^{\cdot -} \tag{3.2}$$

$$RH + O_2 \rightarrow R^{\cdot} + HO_2^{\cdot} \tag{3.3}$$

The superoxide anion radical, $O_2^{\cdot -}$, is a mild oxidizing agent under alkaline conditions and is not believed to attack carbohydrates and degrade them. Also, at the alkaline conditions of oxygen delignification, superoxide anion radicals are difficult to protonate to hydroperoxyl radicals, $HO_2^{\cdot}$, due to the low pKa (4.9) of this equilibrium, except when catalyzed by transition metal as:

$$O_2^{\cdot -} + HO_2^{\cdot} \rightarrow O_2 + HO_2^{-\cdot} \tag{3.4}$$

Under the alkaline condition, the rate of protonation of superoxide is negligible. At pH higher than 6, the rate constant of this reaction can be expressed as $k = 6 \times 10^{(12-pH)}\ M^{-1}s^{-1}$; which shows that at alkaline conditions (pH 12 or higher) the life-time for superoxide increases, and can diffuse and penetrate further into the fibers (Gierer, Reitberger, et al. 2001).

The superoxide radical also plays a key role in opening aromatic rings and the cleavage of carbon-carbon linkages of lignin in the presence of hydroxyl radicals. Oxygen and hydroxyl radicals cannot directly cause carbon-carbon cleavage (Gierer, Reitberger, et al. 2001). The final products of these reactions can be muconic acid, oxirane and $C_\alpha - C_\beta$ cleavage products (Gierer, Yang and Reitberger 1994). Superoxide can be the source of unselective radicals such as hydroxyl radicals (Gierer, Reitberger, et al. 2001). The superoxide anion radical reacts with resonance-stabilized phenolic lignin and generates the hydroperoxyl radical, $HO_2^{\cdot}$, since the reduction potential of hydroperoxyl radical is 0.75 V and the oxidation potential of phenolate lignin is 0.55 V. This occurs in the second electron transfer step, and a hydroperoxy anion, HO_2^-, will be generated (Gierer, Reitberger, et al. 2001) (Asgari and Argyropoulos 1998). On the other hand, since the phenols have already been deprotonated under alkaline conditions the reaction below does not play an important role in oxygen delignification.

$$O_2^{\cdot -} + AOH \leftrightarrow \{HO_2^{\cdot} + AO^-\} \rightarrow HO_2^- + AO^{\cdot} \qquad (3.5)$$

The hydroperoxy anion, $\mathrm{HO_2^-}$, is in equilibrium with hydrogen peroxide, $\mathrm{H_2O_2}$, at a $\mathrm{pK_a}$ of 11.6

As the product of the third reduction step, the hydroxyl radical, $\mathrm{HO^{\cdot}}$, is generated by the reduction of hydrogen peroxide (Gierer, Reitberger, et al. 2001):

$$H_2O_2 + e \ \rightarrow \ HO^{\cdot} + HO^- \qquad (3.6)$$

The hydroxyl radical is an unselective radical which is responsible for degrading cellulose by random cellulose chain scission. There have been two mechanisms described for the random cellulose scission; First, hydroxyl radicals cause the scission of glycosidic bonds by β-elimination under alkaline conditions. In this mechanism, an hydroxyl radical abstracts the hydrogen of carbon 2 on the glucose unit and forms a carbonyl group (J. Gierer 1997). Second, the hydroxyl radical directly attacks the glycoside linkage (carbon 1) which leads to scission of the cellulose chain (Guay, et al. 2001).

The oxyl radical, $\mathrm{O^{\cdot -}}$, is in equilibrium with the hydroxyl radical under alkaline conditions ($\mathrm{pK_a}$ 11.9). This radical, $\mathrm{O^{\cdot -}}$, is even more unselective and reacts faster with carbohydrates than a hydroxyl radical. Above $\mathrm{pK_a}$ 11.9, the oxyl radical dominates, and more cellulose degradation takes place, and consequently, the pulp viscosity decreases faster in oxygen delignification when the pH is higher, i.e. when the alkali charge is higher. Thus to improve delignification/ cellulose degradation selectivity, the pH should be kept below pH 12 to minimize the concentration of oxyl radicals, and above $\mathrm{pK_a}$ 10.5 so that phenolic lignin is dissociated (Norgren and Lindstrom 2000).

3.3 Lignin Chemistry

Many investigations have been done using lignin model compounds at oxygen delignification conditions in order to increase the delignification rate without loss of strength properties of pulp. Under alkaline conditions, the first delignification step is the dissociation of phenolic lignin to create a phenolate ion by reaction with alkali (Figure 3.2).

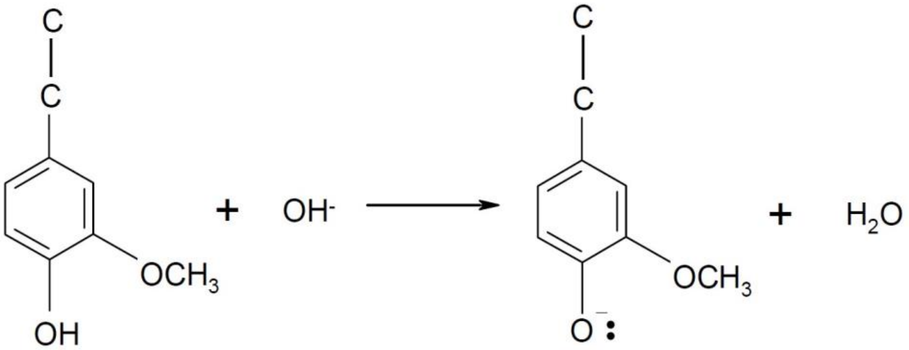


Figure 3.2. Initial dissociation of phenolic lignin under alkaline condition

As shown in Figure 3.3, the oxidation potentials of different phenolic lignin model compounds are plotted versus pH. The oxidation potentials for creosol and vanillin as models for phenolic lignin are low at pH above 10.5, while veratrylglycol and veratraldehyde representing non-phenolic and ether phenolic lignin respectively, remain high even at strong alkaline conditions. For this reason, non-phenolic lignin is unreactive during oxygen delignification and only can be removed if a hydroxyl group is introduced into the aromatic ring by reaction with oxygen-based radicals.

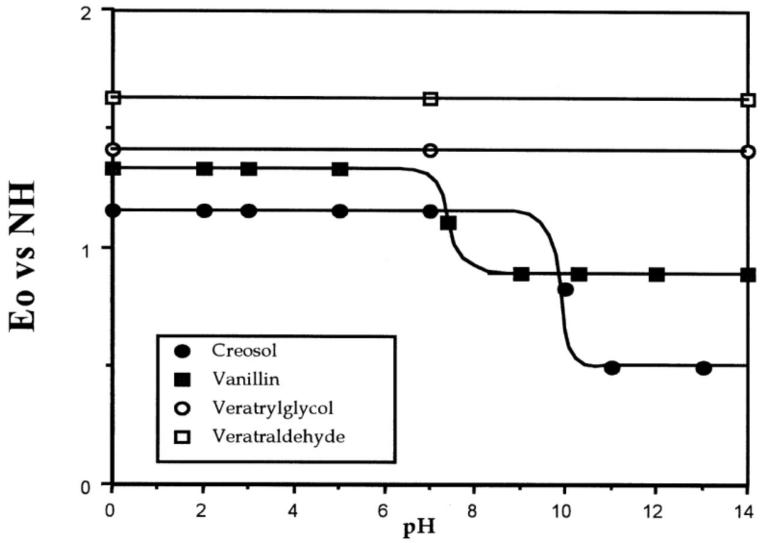


Figure 3.3. Oxidation potentials for four lignin model compounds plotted versus pH (Gierer, Reitberger, et al. 2001)

After the formation of dissociated phenolic lignin, the primary reaction between oxygen and the phenolate anion takes place. Oxygen abstracts an electron from the phenolate anion and the resonance stabilized phenoxy radical and the superoxide anion radical is formed.

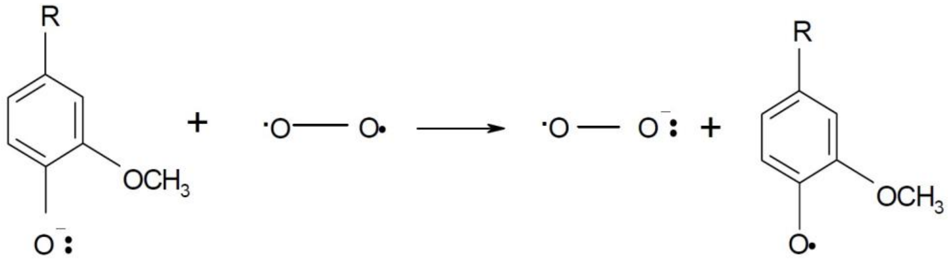


Figure 3.4. The initial attack of oxygen on phenolic lignin

The phenoxy radical then undergoes reactions with other oxygen radicals such as superoxide, $O_2^{\cdot -}$, hydroperoxy $HOO^{\cdot}$, and hydroxyl, $HO^{\cdot}$, radicals, and lignin condensation and degradation take place (Figure 3.5). These radicals are responsible for lignin and carbohydrate degradation. As previously mentioned, the hydroxyl radical is a strong oxidizer, $E_0\ (HO^{\cdot}, H^+/H_2O) = +2.8\ V$, and plays an essential role in removing phenolic and even non-phenolic lignins by generating substrate radicals, opening $C_\alpha - C_\beta$ linkages. It is interesting to know that hydroxyl radicals can cleave the

$C_\alpha - C_\beta$ linkage of non-phenolic bonds directly, but are not able to open the $C_\alpha - C_\beta$ linkage of the phenolic lignin without the presence of oxygen (J. Gierer 1997). In contrast to hydroxyl radical, superoxide radical, $O_2^{\cdot -}$, is a weak oxidizer agent, $E_0\,(O_2^{\cdot -}, H^+/HO_2^-) = +0.2$ V, and it is not able to oxidize carbohydrates, non-phenolic and phenolic lignins, $E_0\,(PhO^\cdot/PhO^-) = +.50$ V, directly. But, this radical, $O_2^{\cdot -}$, in co-operation with hydroxyl radicals can attack phenolic lignin and degrade it. In other words, superoxide radicals cannot oxidize and degrade phenolic lignin, unless in the presence of hydroxyl radical (J. Gierer 1997).

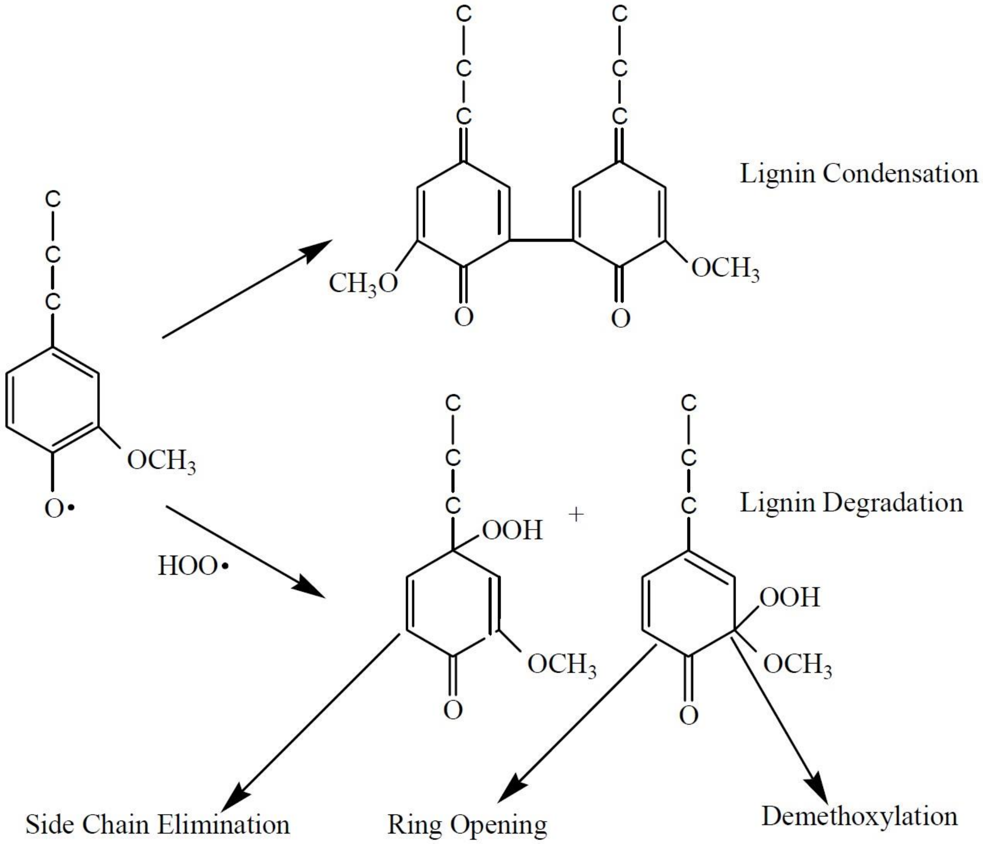


Figure 3.5. Possible reaction of lignin via phenoxyradical

(Johansson and Ljunggren 1994)

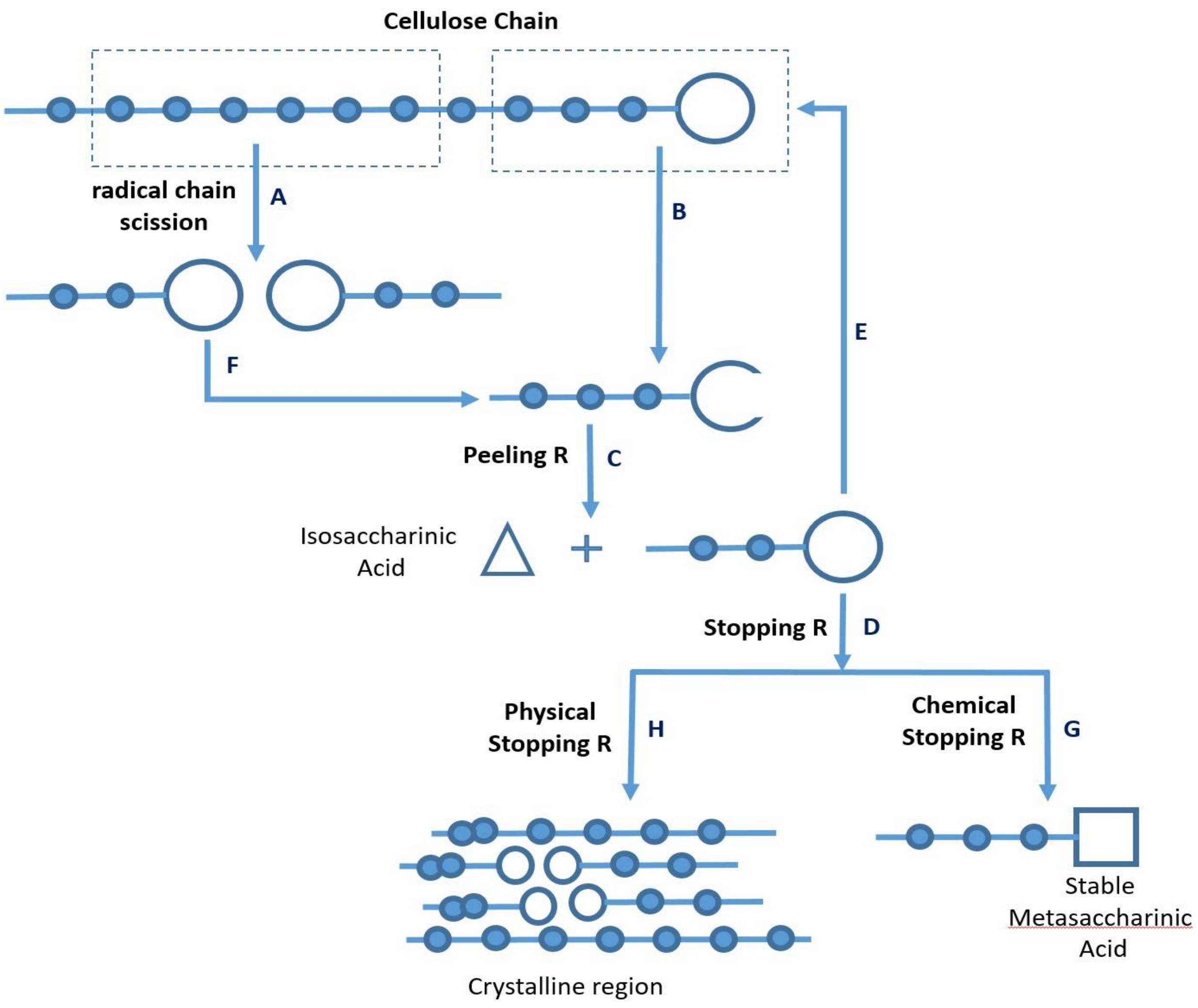
Johansson and Ljunggren (1994) found that during oxygen delignification, the fraction of residual phenolic lignin decreases, while the diphenylmethane-type, which is a condensed structure such as 5,5’-biphenolic moieties, and p-hydroxylphenyl structures accumulate because they are quite stable and particularly resistant to degradation at standard oxygen delignification conditions (Haixuan 2002). It seems that the phenolic compounds especially with a conjugated side chain like stilbene and enol ethers are very reactive and easy to degrade during oxygen delignification.

3.4 Carbohydrate Chemistry

Cellulose degradation under alkaline conditions at oxygen delignification temperatures takes place along four main pathways: (I) Cleavage of cellulose by oxygen-based radicals such as the hydroxyl radical (Pathway A in Scheme 1); (II) Alkaline attack on carbonyl groups at C2 and C3 glucose positions on the chains followed by glucosidic bond cleavage through β-alkoxy elimination; (III) Cellulose cleavage by radicals formed by metal (Cu, Mn, and Fe) catalyzed decomposition of peroxides formed as part of the oxygen-lignin reaction (Pathway A in Scheme 1); (IV) The alkaline peeling reaction, which occurs at the reducing end of the cellulose chain, leads to the endwise scission of one glucose unit at a time. The result of the peeling reaction is yield loss of carbohydrates especially when the reaction temperature is above 100 ℃ (da Silva Perez and van Heiningen 2015). For cellulose, the degree of dissolution by the peeling reaction is small since the starting degree of polymerization (DP) of cellulose is around 10,000 - 5,000, while the peeling reaction removes an order of magnitude less sugar units during alkaline pulping (Gellerstedt 2006) while during oxygen delignification the peeling chain length is expected to be much shorter due to oxidation of the reducing end group by oxygen. On the other hand, for hemicelluloses like glucomannans with a smaller DP around 100, the peeling reaction can be very destructive (Gellerstedt 2006).

In general, there can identify two types of peeling reactions during alkaline pulping and at oxygen delignification; primary and secondary peeling. Primary peeling occurs when cellulose contains a reducing end group at the end of its chain and the carbohydrate degradation continues until the competing stopping reaction takes place (Pathway BC in Scheme 1). The stopping reaction occurs by chemical or physical pathways (Pathways DG and DH in scheme 1 respectively); In the chemical stopping reaction, reducing end-groups are converted into a non-reacting end-groups such as metasaccharinic acid which is stable in alkali and is able to stop the peeling reaction. It is interesting to know that with the high dissolved oxygen concentration the peeling reaction can be stopped by oxidation of the reducing end and less so by the stopping reaction. The other way that can stop cellulose from degradation is the physical stopping reaction. In this pathway, the end groups reach the crystalline region which cannot be accessed by alkali, therefore cellulose degradation is not able to proceed further.

The secondary peeling reaction occurs when the cellulose chain has already cleaved and new reducing end groups are formed. At this point, the new reducing ends are subject to peeling (Pathway FC in Scheme 1).



Scheme 1

Structural Elements:

○ - Reducing end-group (Aldehyde functional group)

C - Activated end-group (Enolate functional group)

△ - Intermediate product (Isosaccharinic acid)

□ - Chemically stopped end-group (Metasaccharinic acid)

Reactions:

- Peeling R Peeling Reaction
- Stopping R Stopping Reaction

In oxygen delignification, the decreasing pulp yield is mostly caused by the dissolution of lignin. The dissolution of hemicellulose occurs after they are cleaved by a radical attack, and the hemicellulose fragments become small enough that they become soluble in alkali and then are subjected to peeling reactions and attack by oxygen. The importance of carbohydrate dissolution during oxygen delignification has been studied by Salmela (Salmela 2007). Because the degree of polymerization of cellulose is high (about 5000), and the alkaline peeling reaction is suppressed by the parallel reaction with oxygen, it is expected that essentially all cellulose is retained during oxygen delignification.

They found that the degree of swelling of the pulp fibers correlates with the extent of carbohydrate degradation in NaOH solutions up to 6 N because of the increasing peeling reaction rate, and then sharply decreases at higher alkalinity because the stopping reaction increases further while the peeling reaction does not (Lai and Ontto 1979)

3.5 Selectivity and Cellulose DP of the Oxygen Delignification Process

The progress of the delignification/cellulose degradation selectivity is normally monitored by plotting the intrinsic viscosity versus Kappa number. However, the cellulose degree of polymerization (DP) provides a better insight into the degree of cellulose degradation because the change in 1/DP directly quantifies the number of cellulose chain scissions (van Heiningen, Ji and Jafari 2019). The relationship between pulp intrinsic viscosity and the degree of polymerization of cellulose is given by Equation 3.7 (da Silva Perez and van Heiningen 2015). This formula also takes into account the effect of hemicellulose content of regular pulp on the calculation of the degree of cellulose polymerization.

$$DP = \left(\frac{1.65[\eta]-116H}{G}\right)^{1.111} \qquad (3.7)$$

where, DP is the degree of polymerization of cellulose, [η] is the intrinsic viscosity, and H and G are the hemicellulose and cellulose weight fractions respectively.

The delignification/cellulose degradation selectivity, S, may then be defined as the ratio of kappa decrease, $(\mathrm{K_0} - \mathrm{K_t})$, and the number of cellulose chain scissions, $(\frac{1}{\mathrm{DP_t}} - \frac{1}{\mathrm{DP_0}})$, Equation (3.8).

$$S = \frac{K_0 - K_t}{\frac{1}{DP_t} - \frac{1}{DP_0}} \tag{3.8}$$

where $(\frac{1}{\mathrm{DP_t}} - \frac{1}{\mathrm{DP_0}})$ is the number of cellulose chain scissions (Miller 2011), $\mathrm{DP_0}$ and $\mathrm{DP_t}$ are the average degree of cellulose polymerization at time 0 and t, $\mathrm{K_0}$ and $\mathrm{K_t}$ are the Kappa number at time 0 and t. Another delignification/cellulose degradation selectivity ratio called S_{LC} will be introduced in section 3.7.2 which takes into account that the capture of oxygen-based radicals decreases proportionally with the amount of lignin remaining in the pulp.

3.6 Mass Transfer of Oxygen

In oxygen delignification, the oxygen mass transport occurs through three phases consisting of the gas phase (oxygen gas), the liquid phase (caustic solution), and the solid phase (fiber walls) (van Heiningen, Krothapalli, et al. 2003). The physical transport of oxygen takes place in three steps; First, oxygen passes through the gas-liquid interface, then diffuses through the caustic solution surrounding the pulp fibers, and finally penetrates into the fiber walls. The rate of oxygen mass transfer in the three phases is different (Ljunggren and Johansson 1990), and the slowest pathway controls the rate of the overall process of oxygen delignification. The oxygen transport through the liquid phase is the rate-determining step during oxygen delignification (van Heiningen, Krothapalli, et al. 2003). In order to eliminate the liquid phase mass transfer resistance, oxygen gas can be dissolved in the liquid phase before commencement of oxygen delignification (Ji, Wheeler and van Heiningen 2007). This approach is taken in the present study when using the Berty reactor.

3.7 Kinetics of Oxygen Delignification

The intrinsic kinetics of oxygen delignification are best studied in a Berty reactor which operates as a Continuous Stirred Tank Reactor (CSTR). In the Berty basket reactor, the delignification rate is measured continuously by monitoring the dissolved lignin concentration in the reactor effluent by UV-VIS absorption. The oxygenated caustic solution is rapidly circulated through a pad of pulp fibers contained in a basket inside the Berty reactor, so that the dissolved lignin concentration inside the reactor is the same as that in the effluent.

The kinetics of oxygen delignification is influenced by the alkali and dissolved oxygen concentration and reaction temperature, while the delignification rate should not be affected by the amount of pulp, circulation rate in the reactor, and type and pressure of driving gas to provide the hydraulic pressure to feed the liquor to the reactor (Pahlevanzadeh and van Heiningen 2018). The indirect way of measuring degree of delignification is by determining the kappa number of the pulp after oxygen delignification. However, recent studies show that the kappa number represents other structures than just the residual lignin in the pulp. The non-lignin structures that have double bonds can also contribute to the kappa number. Hexenuronic acid (HexA) is a non-lignin structure with double bonds that also consumes potassium permanganate ($KMnO_4$) in the test used for measuring kappa number (Ragauskas 2000). Thus the HexA content of pulp should be determined and expressed in kappa number units and then subtracted from the pulp kappa number in order to determine the real lignin content of the pulp.

3.7.1 Kinetics of Delignification During Oxygen Delignification

3.7.1.1 Single Equation Power Law Model

The kinetics of delignification during oxygen delignification has mostly been expressed by the single equation power law (Irabarne and Schroder 1997).

$$-r(t) = -\frac{dK}{dt} = k[OH^-]^m[P_{O2}]^n K^q \tag{3.9}$$

where K is the kappa number, $[OH]$ is the concentration of sodium hydroxide, and P_{O2} is the oxygen pressure. The reaction rate coefficient (k) which depends on reaction temperature is defined by the Arrhenius equation:

$$k = A\, exp(-\frac{E_A}{RT}) \tag{3.10}$$

where E_A represents the activation energy, R is the gas constant, T is the absolute temperature, and A is the pre-exponential constant.

3.7.1.2 Two Equation Power Law Model

The kinetics of oxygen delignification can also be described by using two power-law contributions (Olm and Teder 1979). In the initial phase, more reactive lignin moieties are degraded and dissolved, leading to rapid delignification. The less reactive lignin is also degraded simultaneously but at a slower rate and continues over a longer period of time (Figure 3.6).

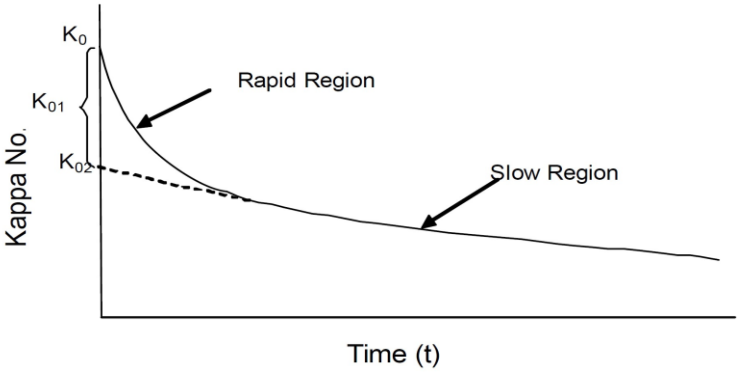


Figure 3.6. Two Region Model (Olm and Teder 1979)

Therefore, this kinetic model consists of two power-law kinetic contributions; one for the fast-reacting lignin (Kappa K_1) and one for the slow-reacting lignin (K_2) expressed as:

$$-r = -\frac{dK}{dt} = k_1[OH^-]^{m1}[P_{O2}]^{n1}K_1^{q1} + k_2[OH^-]^{m2}[P_{O2}]^{n2}K_2^{q2} \qquad (3.11)$$

where the measured kappa number, K, is

$$K = K_1 + K_2 \qquad (3.12)$$

3.7.2 Kinetics of Cellulose Degradation during Oxygen Delignification

It has been proposed that the rate of cellulose degradation is proportional to the rate of delignification and alkaline hydrolysis (Ji, Wheeler and van Heiningen 2007). In this model, two pathways of cellulose degradation are proposed, radical attack and alkaline hydrolysis.

$$\frac{dm_n}{dt} = -k_c\frac{dK}{dt} + k_h[OH^-] \qquad (3.13)$$

where $\mathrm{m_n}$ is the average number of moles of cellulose per metric ton of pulp ($\mathrm{m_n} = \frac{10^6}{(162\,DP_n+18)}$), $\mathrm{k_c}$ is the radical attack rate constant, $\mathrm{k_h}$ is the rate constant for alkaline hydrolysis, and $[\mathrm{OH^-}]$ is the alkaline concentration in mol/l.

The basis for the model is that the amount of oxygen-based radicals generated is proportional to the amount of lignin degraded by oxygen via the phenolic lignin pathway. However, the amount of generated radicals that can reach and attack cellulose is inversely proportional to the amount of residual lignin since lignin functions also as a radical scavenger. Alkaline hydrolysis is unlikely to take place under oxygen delignification conditions since this random reaction occurs at higher temperatures (>140℃) (Gellerstedt 2006), while oxygen delignification is performed at lower temperatures (up to 120 °C). Therefore, it can be assumed that cellulose degradation by alkaline hydrolysis is negligible ($\mathrm{k_h}[\mathrm{OH^-}]\sim 0$). Therefore, equation (13) becomes:

$$S_{LC}\frac{d(\frac{1}{DP})}{dt} = -\frac{1}{L_c}\frac{dL_c}{dt} = -\frac{d\ln L_c}{dt} \tag{3.14}$$

Integration of Equation (3.14) gives:

$$S_{LC}(\frac{1}{DP} - \frac{1}{DP_0}) = ln\ \frac{L_{c0}}{L_c} \tag{3.15}$$

where L_{c0} and L_c are the residual lignin content of the pulp at time = 0 and t respectively, and S_{LC} is a new measure of the delignification/cellulose degradation selectivity ratio which should be independent of the lignin content L. S_{LC} can be determined as:

$$S_{LC} = \frac{ln\frac{L_{c0}}{L_c}}{\frac{1}{DP} - \frac{1}{DP_0}} \tag{3.16}$$

This relationship was previously presented by Jafari et al (Jafari, Nieminen, et al. 2015).

3.8 Protection of Carbohydrates During Oxygen Delignification

In order to protect carbohydrates from degradation during oxygen delignification, the effect of adding chemicals that scavenge harmful radicals and those which remove or block the effect of transition metals on radical generation will be studied in this research.

3.8.1 Scavenging Hydroxyl Radical During Oxygen Delignification

As previously discussed, the hydroxyl radical is known as an unselective radical which is generated in the stepwise reduction of oxygen to water during oxygen delignification. Hydroxyl radicals can be scavenged by organic compounds in different pathways such as hydrogen atom abstractions, and electron abstractions. Hydroxyl radical scavenging via the hydrogen atom abstraction takes place with amines, alkanes, carboxylic acids, aldehydes, ketones, esters, ethers, alcohols. etc. (Atkinson 1987). Hydrogen atom abstraction by hydroxyl radicals depends on the reactivity and strength of C-H bond. For instance, the dissociation energy of the C-H bond in methane (the primary alcohol (1°)), propane C-2 (the secondary alcohol (2°)), and 2-methyl-2-

propanol C-2 (tert-butanol) (the tertiary alcohol (3°)) are 438, 401, and 390 kJ/mol. Thus, the C-H bond in a tertiary alcohol has the highest reactivity among these alcohols to react with hydroxyl radicals during oxygen delignification (McMurry 1996).

In order to scavenge hydroxyl radicals by electron abstraction, the carbonate ion is used in this study. Hydroxyl radicals can be scavenged by carbonate anions (CO_3^{2-}) to form the carbonate ion radical ($CO_3^{\cdot\,-}$) which is more reactive toward lignin than carbohydrates (Carlsson, et al. 2003). The carbonate ion radical formation reaction is:

$$CO_3^{-2} + HO^{\cdot} \rightarrow CO_3^{\cdot\,-} + OH^{-} \tag{3.17}$$

- #### 3.8.1.1 Sodium Carbonate as Radical Scavenger

Under oxygen delignification conditions, the addition of sodium carbonate as a base can improve the oxidation of phenolic lignin (Mih and Thompson 1983), and extend the delignification (Allison, Suckling and Sun 2000). Sodium carbonate can also be used as a replacement for NaOH.

$$Na_2CO_3 + 2H_2O \rightarrow 2NaOH + H_2CO_3 \tag{3.18}$$

Carbonate is known as a radical scavenger and can react with hydroxyl radicals to generate carbonate radicals (Equation 17). Furthermore, the carbonate radical is much more selective than the hydroxyl radical. This is clear when the reactivities of these radicals towards lignin and carbohydrates are compared. The second-order reaction rate constant of the carbonate radical ($\mathrm{CO}_3^{\cdot\,-}$) with carbohydrate and lignin model compounds are in the range of 10^5 - 10^6 ($M^{-1}s^{-1}$) and 10^8 - 10^9 ($M^{-1}s^{-1}$) respectively at pH of around 12. On the other hand, the rate constant of hydroxyl radicals with lignin and cellulose model compounds are both in the range of 10^9 - 10^{10} ($M^{-1}s^{-1}$) (Carlsson, et al. 2003). So, the selectivity ratio of the rate constants of the carbonate and hydroxyl radicals with lignin and cellulose model compounds as ($\frac{k_{Lignin}}{k_{Cellulose}}$) at pH 12.5 are approximately 10^3 and 1 $(M^{-1}s^{-1})$ which confirms that the carbonate radical is significantly more selective than the hydroxyl radical (Carlsson, et al. 2003).

The carbonate radical has a maximum selectivity at pH 10.5, i.e. at the pH of a 1:1 HCO_3^-/CO_3^{2-} buffer solution (Carlsson, et al. 2003). At higher pHs, the carbonate radical can behave unselectively towards carbohydrates since at higher alkalinity the carbohydrate itself is activated toward oxidation because of increased deprotonation of the hydroxyl groups, which leads to a lower delignification/cellulose degradation selectivity (Carlsson, et al. 2003). At lower pHs (around pH 10), the reaction rate constants of carbonate radical with carbohydrates decrease from the range of 10^5 - 10^6 to 10^4 - 10^5 $(M^{-1}s^{-1})$.

▪ 3.8.1.2 Methanol as Radical Scavenger

As mentioned earlier, tertiary alcohols have higher activity in scavenging radicals compared to primary and secondary alcohols. However, methanol, a primary alcohol, is still preferred as a radical scavenger because methanol is already produced as a byproduct in the pulping process. Therefore, using methanol can minimize pulp mill raw material costs when it is used as an additive in the oxygen delignification stage (Hu, et al. 2015).

3.8.2 Removing Transition Metals

3.8.2.1 Magnesium Sulfate

The presence of magnesium sulfate ($MgSO_4$) can improve the delignification/cellulose degradation selectivity during oxygen delignification (Bouchard, Wang and Berry 2011). Magnesium sulfate under alkaline condition is converted to magnesium hydroxide, $Mg(OH)_2$, which can physically encapsulate the transition metals in the 2+ redox state such as Fe^{2+}, Cu^{2+}, Mn^{2+} (Liden and Ohman, 1997).

$$MgSO_4 + NaOH \rightarrow Mg(OH)_2 + NaSO_4 \tag{3.19}$$

As previously mentioned, transition metals increase the generation of unwanted radicals such as hydroxyl and oxyl, by catalytically accelerating the decomposition of hydrogen peroxide, H_2O_2, formed during oxygen delignification (Figure 3.1) (Equation (3.6). These unselective radicals randomly oxidize the cellulose chain by forming carbonyl groups, which then undergo the β-elimination reaction leading to cleavage of the chain. Because transition metals can form complexes with lignin and cellulose, metals located near or on cellulose chains can lead to cleavage of cellulose chains through to the Fenton reaction mechanism to produce hydroxyl radicals on or near the cellulose chains (D. Cardona-Barrau 1998). Cardona-Barrau have also shown that $NaBH_4$ not only reduces carbonyl groups on cellulose, but more importantly reduces the transition metals into the lower valency state that are not capable of further catalyzing the formation of hydroxyl radicals (Cardona-Barrau and Lachenal 2001).

3.8.2.2 Sodium Carbonate

Sodium carbonate can react with transition metals and form insoluble metal carbonates in aqueous solutions at standard state conditions (25 ^oC, 1 atm).

$$M^{2+}(aq) + CO_3^{2-} \leftrightarrow MCO_3(s) \tag{3.20}$$

The metal carbonates at higher temperature and pressure like oxygen delignification condition (100 ^oC, 120 psi) are still stable and solid (Robie, Hemingway and Fisher 1978).

3.8.3 Glycerol

The other solvent for extending the delignification is glycerol. This chemical has three groups of alcohol which can break down at higher temperatures. Therefore they can more penetrate the pulp fibers and easier the delignification (Küçük 2003). The other reason might be because of cleaving the intermolecular ether in the lignin matrix which eases the delignification (Küçük 2003). The other advantage of using glycerol is that glycerol is a byproduct of biodiesel mills, so using the glycerin would be beneficial.

3.9 The half-life of Sodium Borohydride Decomposition

In an aqueous solution, $NaBH_4$ is hydrolyzed at low pH and high temperature according to the reaction:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \quad (3.21)$$

Pozio and his colleagues presented the following equation for the $NaBH_4$ half-life (Pozio, et al. 2008).

$$Log\, t_{1/2} = pH - (0.034T - 1.92) \quad (3.22)$$

where $t_{1/2}$ is the half-life of $NaBH_4$ mass in minutes, and T is the absolute temperature. Based on this equation, the rate of $NaBH_4$ hydrolysis slows down by increasing pH and decreasing the temperature (Table 3.1).

Table 3.1. The half-life of $NaBH_4$ decomposition at various temperatures and two different caustic concentrations (3.3 and 1.1 g/LNaOH)

	NaBH$_4$ Half-Life Decomposition			
T (°C)	3.3 g/LNaOH pH=12.92		1.1 g/LNaOH pH=12.44	
25	35.5	Day	12	Day
30	24	Day	8	Day
50	5	Day	1.5	Day
70	1	Day	8	Hour
75	17	Hour	5.5	Hour
80	11.5	Hour	4	Hour
100	2	Hour	48	min
120	30	min	10	min
150	3	min	1	min

Based on the results in this table it can be concluded that most $NaBH_4$ will remain stable during the initial phase of oxygen delignification (90°C, 3.3 g/LNaOH), but that near the end of oxygen delignification (90-100 °C, pH about 12.3) a significant fraction of $NaBH_4$ will decompose.

CHAPTER 4

EXPERIMENTAL; EQUIPMENT, PROCEDURES, DATA COLLECTION AND TREATMENT, VALIDATION OF RESULTS

4.1 Testing Standards

- Kappa number: T236 cm-85 (or SCAN-C 1:77)
- Intrinsic viscosity: D1795-62 (re-approved 1985)
- Copper number: TAPPI standard method T 430

4.2 Raw Materials

A commercial unbleached Southern Pine kraft pulp, a laboratory high kappa Southern Pine kraft pulp, and an unbleached Black Spruce Magnesium bisulfite pulps were used in this study. The sulfite pulp has a kappa number of 20.15, and intrinsic viscosity of 914 mL/g. The high kappa (98) kraft pulp has an intrinsic viscosity of 1157 mL/g, and the conventional kraft pulp has a kappa number of 24.42 and an intrinsic viscosity of 996 mL/g. The HexA contents for the conventional kraft pulp, high kappa kraft pulp, and sulfite pulp were equivalent to 3, 5.5, and 3 kappa units respectively. The standard deviations of the intrinsic viscosity, kappa number, and HexA analysis are less than 25 mL/g, 0.35, and 0.1 kappa units respectively.

4.3 Equipment

- Parr Reactor

The Parr reactor is a 2-liter Continuously Stirred Horizontal Batch Reactor obtained from Parr Instrument.

- Berty Basket Reactor

The Berty Basket reactor is a Continuous Stirred Tank Reactor (CSTR) manufactured by Autoclave Engineers. The reactor has a nominal volume of 280 ml and contains a 100 ml basket with a rotor underneath to provide a well-mixed environment (Figure 4.1). The basket holds a pulp pad through which a constant composition oxygenated caustic solution is circulated at a high rate. The oxygenated caustic composition inside the reactor is close to that of the feed because the supply rate of caustic and oxygen to the reactor are significantly larger than the consumption rates by the pulp. The oxygenated caustic solution was obtained by bubbling pressurized oxygen through the 3.3 g/LNaOH solution to obtain a saturated oxygen concentration at room temperature.

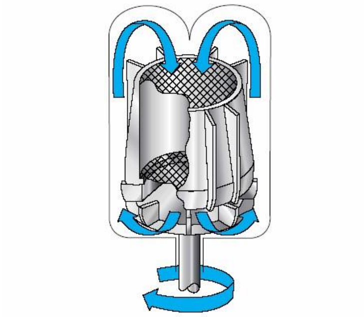


Figure 4.1. Berty Stationary Basket Inside the Reactor

The flow diagram of the Berty setup is shown in Figure 4.2.

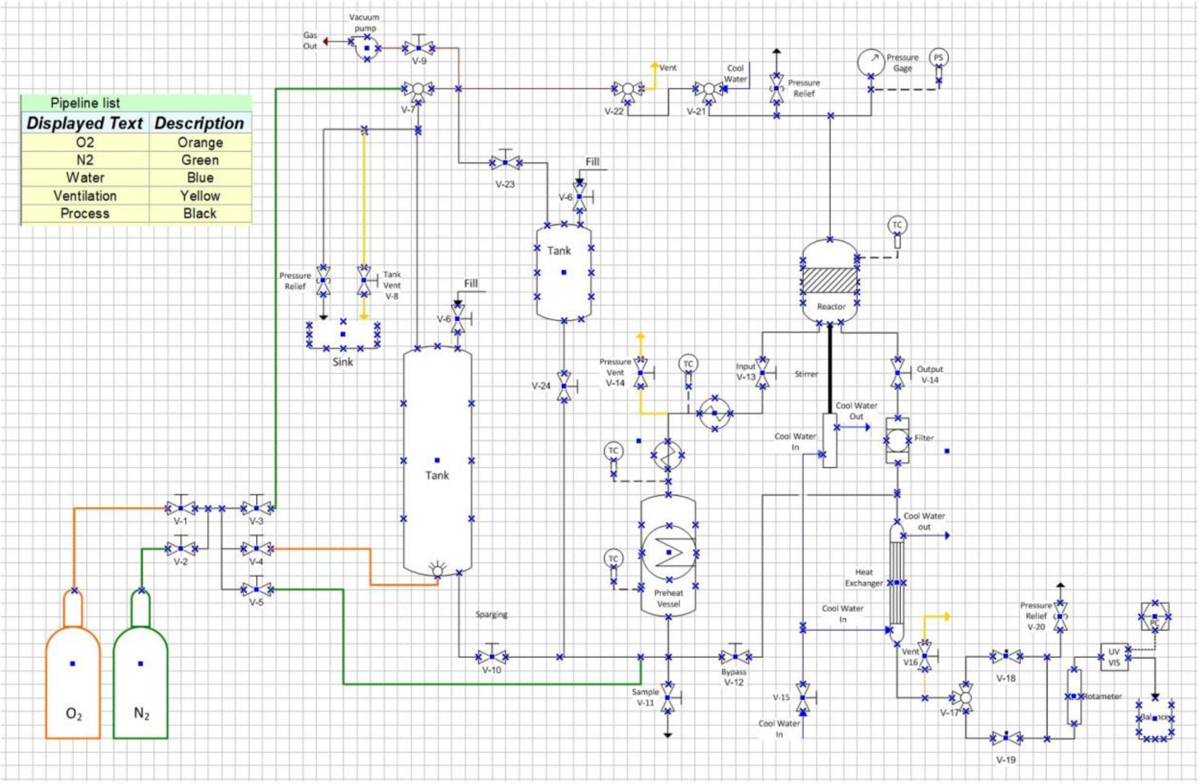


Figure 4.2. Diagram of Berty Basket Setup

4.4 Experimental Conditions

- Alkali Concentration (3.3 g/liter NaOH)
- Oxygen Saturation Pressure at room temperature (65 psig)
- Nitrogen Pressure as the driving gas (120 psig)
- Pretreatment Time (5, 20 min)
- Pretreatment Temperature (25, 80, 100, 120 °C)
- Reaction Temperature (90, 100 and 120 °C)
- Reaction Time (0, 20, 40, 60, 90 min)

4.4.1 Pretreatment Procedure

1. Place the pulp inside the Berty basket and close the reactor;

2. Heat the reactor to reach the temperature of 80 °C;
3. Let the caustic (in the absence of oxygen) into the reactor at 120 psig for 4 min to obtain stable operation (the caustic flows underneath the pulp basket and would not touch the pulp);
4. Release the nitrogen in the reactor from the top sothat the caustic fills up the entire reactor and basket; allow 15 min to get a stable reactor temperature (temperature, pressure, and flow rate data collected every 30 seconds);
5. Then start mixing by starting the stirrer, and allow 5 min mixing;
6. Stop the mixing by turning off the stirrer, release the pressure, close the inflow valve, and flush the reactor with room temperature tap water;
7. Turn on the stirrer again to force the water into the pulp pad to remove all caustic inside the pulp pad.

4.4.2 Reaction Procedure

1. Pressurize the reactor at 120 psi; heat the reactor, and preheat the oxygenated caustic;
2. Use the by-pass flow to measure the fresh caustic UV as the blank.
3. Let the oxygenated caustic into the reactor at 120 psig for 4 min to get stable operation(the caustic flows underneath the pulp basket and would not touch the pulp);
4. Release the nitrogen in the reactor and let the caustic fill up the reactor; leave it for 15 min to get a stable temperature (temperature, pressure, and flow rate data collected every 30 seconds);
5. Start the UV-VIS (UV data collected every 30 seconds) measurement.
6. After 15 min stabilization, the pulp oxygen delignification is reaction begins by starting the stirrer.

7. During the reaction, the temperature and pressure are monitored every 5 seconds and the flow rate is calculated by weighing the collected effluent flow every 30 seconds;
8. Stop the reaction by turning off the stirrer, release the pressure, close the inflow valve, flush the reactor with room temperature water;
9. Open the Berty basket reactor, and wash the pulp and let it dry for future analysis.

4.5 Measurements

- Modified Kappa Number Measurement

The kappa number was determined by a modification of the TAPPI standard T236-cm-85. Due to the small amount of pulp, all amounts were reduced to one-fourth (Table 4.1).

Table 4.1. Modified Method for Kappa Number Measurement

Chemical Dosages	TAPPI Method	Modified Method
Oven-dried pulp (g)	2-10	0.5-0.7
Volume of 0.1N $KMnO_4$ (ml)	100	25
Volume of 4N H_2SO_4 (ml)	100	25
Total Volume (ml)	1000	200
Volume of 1.0N KI (ml)	20	5
Total reaction Time (min)	10	10

- Hexenuronic Acid (HexA)

Hexenuronic acid (HexA) is a non-lignin structure with double bonds that also consumes potassium permanganate ($KMnO_4$) in the test used for measuring kappa number (Ragauskas 2000). Thus the HexA content of pulp should be determined and expressed in kappa number units and then subtracted from the pulp kappa number in order to determine the real lignin content of the pulp. One kappa unit is equivalent to 10 μmol/g pulp HexA content. Thus the corrected kappa number for HexA can be written as Kappa-HexA/10. HexA is inert during oxygen delignification. As can be seen in Table 4.2, HexA content is measured after oxygen delignification at different reaction conditions. It clearly shows that HexA content barely changes during oxygen delignification. Ji in 2007 also pointed out that HexA content would not change during oxygen delignification (Y. Ji 2007).

Table 4.2. HexA Content at Different Reaction Conditions (Conventional Kraft Pulp)

Samples	HexA Content in Kappa unite (HexA/10)
Initial Conventional Kraft Pulp	2.9 ± 0.1
5.5 g/LNaOH- 30 ppm $NaBH_4$- 100 ^oC- 60 min	3.0 ± 0.1
3.3 g/LNaOH- 90 ^oC- 60 min	2.9 ± 0.1
6.6 g/LNaOH- 30 ppm $NaBH_4$-100 ^oC- 60 min	3.1 ± 0.1
3.3 g/LNaOH- 120 ^oC- 90 min	2.8 ± 0.1

- Intrinsic Viscosity

The intrinsic viscosity of the pulp was measured according to the A.S.T.M. designation D1795-62 (re-approved 1985).

As mentioned earlier, cellulose degree of polymerization (DP) (Equation (4.1) provides a better insight into the selectivity (Da Silva Perez and van Heiningen 2015). Because the number of cellulose chain scissions ($\frac{1}{DP_t} - \frac{1}{DP_0}$) can be calculated by the change in 1/DP (van Heiningen, Ji and Jafari 2019).

$$DP = (\frac{1.65[\eta] - 116H}{G})^{1.111} \tag{4.1}$$

- Oxygen Delignification/Cellulose Degradation Selectivity

The most common definition of oxygen delignification/cellulose degradation selectivity, S, is the ratio of kappa decrease, $(K_0 - K_t)$, and the number of cellulose chain scissions, $(\frac{1}{DP_t} - \frac{1}{DP_0})$ (Equation (4.2)).

$$S = \frac{K_0 - K_t}{\frac{1}{DP_t} - \frac{1}{DP_0}} \tag{4.2}$$

Recently, van Heiningen et al. in 2019 derived a new expression for the oxygen delignification/ cellulose degradation selectivity, S_{LC}, by assuming that the rate of cellulose chain scission, d(1/DP)/dt, is proportional to the rate of delignification, based on the phenoxy radical oxygen delignification mechanism (see Figure 3.4) (van Heiningen, Ji and Jafari 2019). The rate of delignification is defined as, -d(LY)/dt, where L is the pulp lignin content and Y is the fractional oxygen delignification pulp yield. The oxygen-based radicals are created from lignin, and because of their high reactivity, they react mostly with lignin rather than with cellulose and hemicellulose. As the lignin content in pulp decreases during oxygen delignification, more radicals will attack cellulose. Thus it is assumed that the rate of cellulose chain scissions per mole of cellulose is inversely proportional to the residual lignin content based on the original pulp weight, LY (van Heiningen, Ji and Jafari 2019), or :

$$\frac{d\frac{1}{DP}}{dt} = -\frac{1}{S_{LC}L}\frac{dLY}{dt} \qquad (4.3))$$

Integration of Equation (4.3 gives:

$$S_{LC} = \frac{ln\frac{L_0}{LY}}{\frac{1}{DP} - \frac{1}{DP_0}} \tag{4.4}$$

where DP_0 is the degree of polymerization of cellulose in the initial pulp and DP is the degree of polymerization of cellulose in the pulp after time t of oxygen delignification. In this thesis, we will use Equation (4.4) to determine the selectivity, and when the pulp yield is unknown or cannot be estimated, we will set Y equal to 1.0 as was done earlier by Jafari (Jafari, Nieminen, et al. 2015). It should be mentioned that the pulp yield from CSTR data could not be estimated accurately because of the low amount of pulp that could be loaded in the Berty basket reactor (up to 6-gram pulp with 12% consistency). Since calculating the pulp yield with this small amount of pulp causes a high standard deviation therefore we ignored the pulp yield data and set Y equal to 1.0.

- Flow Rate

The liquid flow rate was determined based on the measurement of the mass of liquid collected over a certain period of time and recorded by OHAUS Navigator XL Capacity Portable Scale.

- Dissolved Lignin Concentration

The dissolved lignin concentration is measured online by a HP 8453 UV-VIS from Agilent Technology. The soluble degradation products in the effluent of oxygen delignification liquor can be measured by UV absorption at 205 or 280 nm to quantify the lignin concentration using different calibration curves for the three different pulps. The dissolved kraft lignin concentration is obtained by the UV absorption at 280 nm using an absorptivity of 0.043 g/L based Ji (Y. Ji 2007). More details will be provided in the next chapter.

- Mono Sugar Analysis

Mono Sugars are measured by HPAEC (High-Performance Anion Exchange Chromatography) in the Chemical and Biological Engineering Department at the University of Maine. The pulp after oxygen delignification is converted into mono sugars using a two steps acid hydrolysis (Davis 1998). The sugar monomers are then analyzed by HPAEC. Fucose is used as an internal standard.

- Carbonyl Group Content of Pulp

The carbonyl group content of pulp was determined with TAPPI standard method T 430 using the so-called copper number. The copper number ($Cu^{\#}$) expresses the number of grams of copper (Cu_2O) as resulting from the reduction of $CuSO_4$ per 100 g of pulp fibers (TAAPI). Carbonyl group content is directly proportional to copper number and can be calculated with Equation (4.5 (Röhrling, et al. 2002).

$$Carbonyl\ Group\ Content\ (mmol/100g\ o.d\ pulp) = (Cu^{\#} - 0.07)/0.6 \tag{4.5}$$

- Transition Metal Content of Pulp

Transition metals (Cu^{+2}, Fe^{+2}, and Mn^{+2}) were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) at MAFES Analytical lab and Maine Soil Testing Service at the University of Maine.

- Chelation

The high kappa kraft pulp is going to be chelated with ethylenediaminetetraacetic acid (EDTA) at a charge of 0.2% based on the oven-dried pulp, at 50°C and 5% consistency for 30 min. The pH of the stirred pulp suspension will be maintained at 5.5 by adding sulphuric acid. Then the pulp will be centrifuged and homogenized for later experiments.

- Residual Effective Alkali in Black liquor

The residual effective alkali (REA) in black liquor is needed to be measured to determine how much effective alkali is left in the black liquor. In this study, REA is measured according to SCAN-N 33:94. In this method, the pH of the black liquor determines the amount of alkali in the black liquor. If the pH value is at or below 11.3, then no effective alkali is left in the black liquor, otherwise, the black liquor does contain alkali and can be determined by following the SCAN-N 33:94 procedure.

4.6 Data Reduction Procedure

The delignification rate can be calculated from the dissolved lignin mass balance over the reactor:

$$inflow - Outflow + Dissolved\ by\ Reaction = Accumulated\ in\ Reactor$$

$$0 - \phi_v C(t) + r(t) m_p d_t = V_r C(t) \tag{4.6}$$

$$r(t) = [\phi_v C(t) + V_r \frac{dC(t)}{dt}] \frac{1}{m_p} \tag{4.7}$$

where

r(t) is the delignification rate (mg lignin/g o.d pulp/min)

ϕ_v is the flow rate of liquid (mL/min)

C(t) is the dissolved lignin concentration (mg lignin/ml)

V_r is the reactor volume (ml)

m_p is the pulp weight (g o.d pulp)

4.7 Oxygen Saturation Pressure

Figure 4.3 shows the Henry coefficient of dissolved oxygen in NaOH solution at different concentrations and different temperatures. Based on this information the saturated oxygen concentration obtained with 66 psig O_2 in 3.3 g/LNaOH at room temperature is equivalent to the saturated oxygen concentration at 100 °C obtained with 100 psig O_2 pressure.

Using the information in Figure 4.3:

At $T = 298\ {}^0K$ $\frac{C_{aq}}{P_{O2}} = 0.0012$

At $T = 373\ {}^0K$ $\frac{C_{aq}}{P_{O2}} = 0.0008$

$$C_{aq\ 298} = C_{aq\ 373}$$

$$(0.0012).P_{O2\ 298} = (0.0008).P_{O2\ 373}$$

So,

$$P_{O2\ 373} = 100\,psig$$

$$P_{O2\ 298} = 66\ psig$$

where

$P_{O2\ 373}$ is the pressure inside the reactor at 373 ^{o}K

$P_{O2\ 298}$ is the saturation pressure at room temperature (298 ^{o}K)

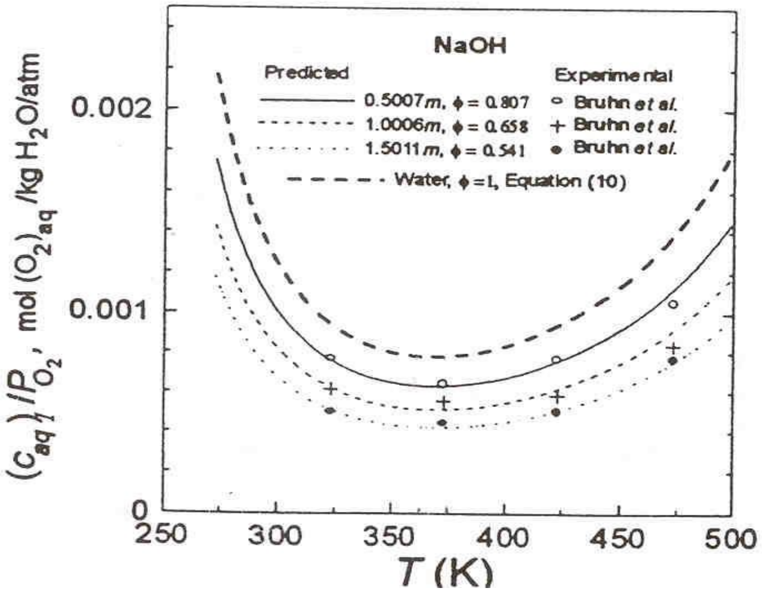


Figure 4.3. Predicted and Experimental Oxygen Solubility Behavior in NaOH Solution (Tromans D. 1998)

4.8 UV-VIS Absorption Calibration by Indulin AT

In this study, indulin AT was obtained from MeadWestvaco. Indulin AT is a purified form of Kraft Pine lignin. The chemical name of Indulin AT is the protonated form of sodium lignate (Indulin C). The chemical formula is $\{(CH3O)(OH)Ar(C3H4O)\}x$. Indulin AT is not soluble in water, but soluble in caustic solutions. Indulin AT is completely free of hemicellulose and it contains a very low amount of inorganic materials (the average ash content of Indulin AT is 3.3%), thus Indulin is almost pure kraft lignin.

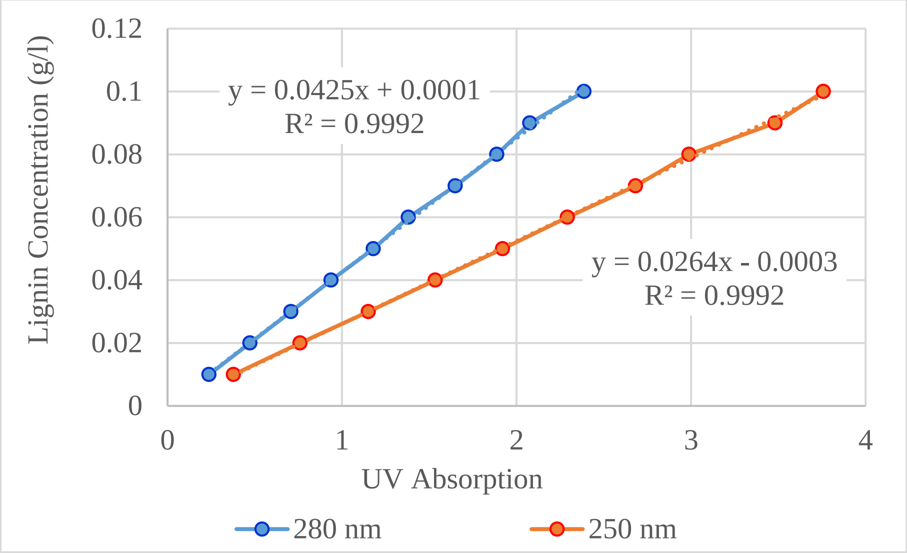


Figure 4.4. Calibration Curve of Indulin AT

In Figure 4.4, the comparison of the calibration curves of Indulin AT for 280 and 250 nm is shown. From this figure, it is obvious that at 280 nm the absorptivity of lignin is greater than at 250 nm. Therefore, the lignin concentration by UV absorption is measured at 280 nm.

According to Beer-Lambert Law (Equation (4.8)), the calibration coefficient, k, at 280 nm was determined to be 0.043 g/L (The path length is 1 cm). Ji obtained a calibration coefficient at 0.040 (g.cm/l) at the same wavelength (280 nm) and 3% NaOH (Y. V. Ji 2009).

$$k = \frac{Lignin\ concentration\ (g/l)}{Absorbance} \tag{4.8}$$

Figure 4.5 shows that the UV absorption of Indulin AT is almost the same when different reference blank samples (NaOH and NaOH+$NaBH_4$ (10 ppm)) are used.

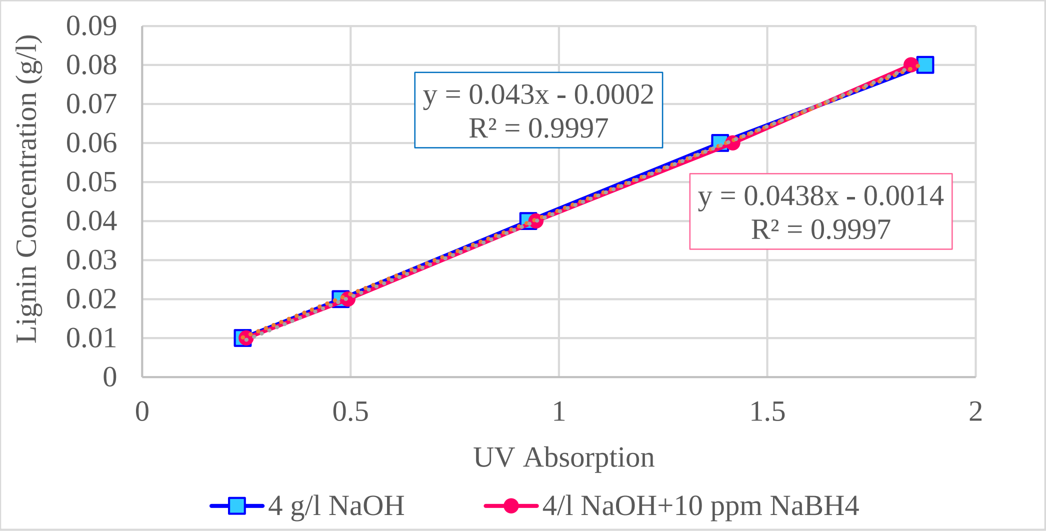


Figure 4.5. UV Absorption of Indulin AT with

NaOH (4g/L) and NaOH+NaBH$_4$ (10 ppm) as Blank

4.9 Transition Metals

Transition metals (Cu^{+2}, Fe^{+2}, and Mn^{+2}) were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) at MAFES Analytical Lab and Maine Soil Testing Service at the University of Maine.

The transition metal ion contents of the mill unbleached Black Spruce Magnesium bisulfite and the Southern Pine kraft pulps before and after pulp washing are presented in Table 4.3.

Phenolic and carbonyl groups of lignin have a great affinity to adsorb heavy metals. These two sites are responsible for the replacement of H^{+} and/or other cations respectively by heavier and higher valence metal ions (Lalvani, et al. 1997), (Lebow and Morrell 1995). Thus by washing pulps with transition metal containing water, metal cation exchange might take place on lignin, and as a result the heavy metals contents in pulp increase. As shown in Table 4.3, Cu^{+2} and Fe^{+2} contents increase by 61% and 8% in conventional kraft pulp and 76% and 30% in the sulfite pulp respectively.

Compared to conventional kraft pulp, the sulfite pulp adsorbed more Cu^{+2} ion because of the presence of both phenolic sites and carbonyl groups (Guo, Zhag and Shan 2008), while the conventional kraft pulp contains just phenolic groups and no carbonyl group (Table 4.3 and Table 6.1 in next chapter).

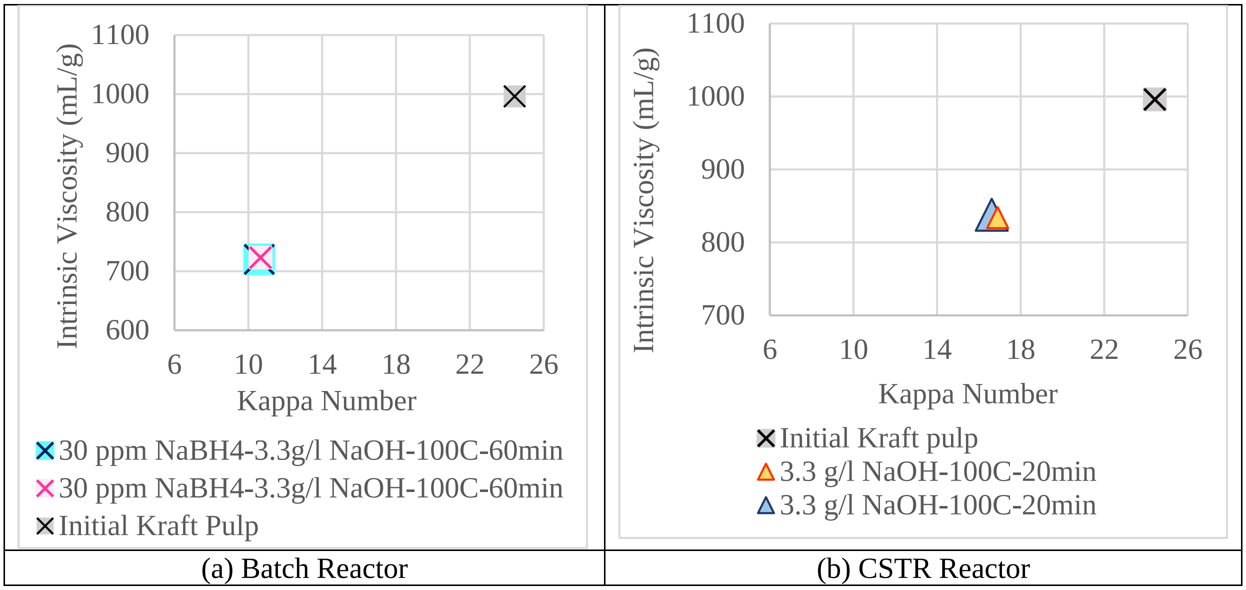
The data in Table 6.1 shows that the sulfite pulp contains 2 mmol/100 g oven dried (o.d.) pulp carbonyl groups which may explain the higher adsorption of Fe^{+2} than the conventional kraft pulp with no carbonyl groups. The high copper content may be caused by the copper containing screening and washing equipment in the PDC pilot plant.

Table 4.3. Heavy Metal Contents of Sulfite Pulp and Conventional Kraft Pulp Before and After Washing at 25 °C

Sample	Cu^{+2}	Fe^{+2}	Mn^{+2}	Kappa Number	Intrinsic Viscosity mL/g
	mg/kg dry weight basis				
Washed High Kappa Pulp	428	30.6	4.34	98	1157
Unwashed Conventional Kraft Pulp	7.54	66.5	70.2	24.42	996
Washed Conventional Kraft Pulp	19.5	72.4	52.4		
Unwashed Sulfite Pulp	2.95	65.0	28.0	20.15	914
Washed Sulfite Pulp	12.5	92.7	15.8		

4.10 Repeatability of Experiments in Berty Reactor

To test the repeatability of the experiments in the Batch (Parr) and CSTR (Berty) reactors, duplicate tests were performed in each system (Figure 4.6). Both reactors show reproducible results. In the Parr reactor, the experiments done at the same operation conditions fall almost on top of each other, while the kappa number differences for the Berty reactor system are still lower than the standard deviation of the kappa number analysis. Thus the reproducibility of both systems is acceptable.

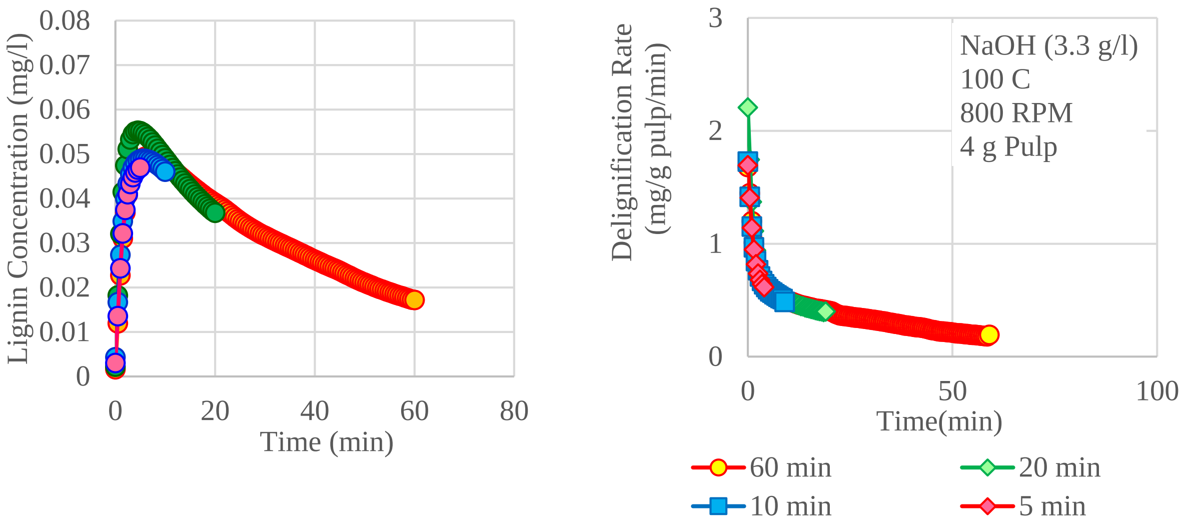


(a) Batch Reactor

(b) CSTR Reactor

Figure 4.6. Experimental Reproducibility

In the CSTR reactor, experimental reproducibility was also investigated during oxygen delignification. Four different reaction times (5, 10, 20, 60 min) were used at 100 ^{o}C, 65 psig O_2 (at room temperature), 3.3 g/LNaOH, 800 rpm, and 4 g pulp, and overnight oxygen saturation. The results are presented in Figure 4.7. The close agreement of the lignin concentration (Figure 4.7a) and delignification rates (Figure 4.7b) curves confirms the experimental repeatability.

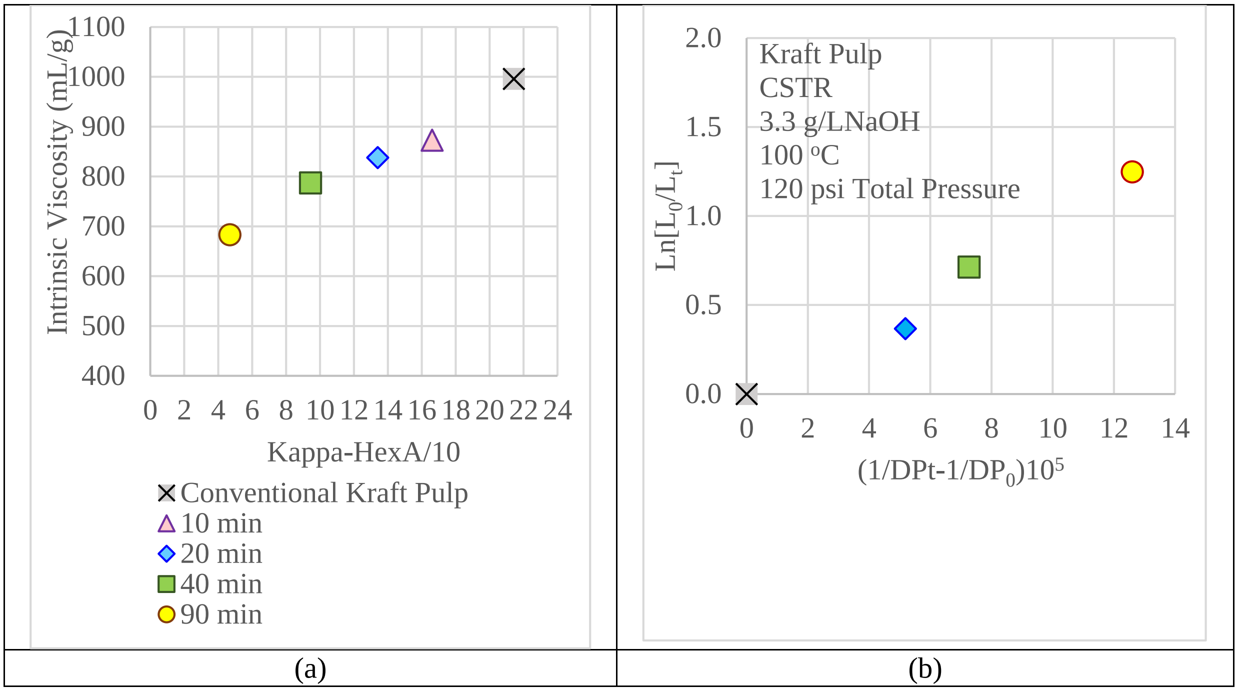


(a) (b)

Figure 4.7. Repeatability of Experiments

(a) Lignin Concentration, (b) Delignification Rate versus Time

Figure 4.8 a shows the effect of reaction time on selectivity. It can be seen that the decrease in intrinsic viscosity increases as more reactive lignin (estimated as kappa-HexA/10) is removed. This was also found by Violette in 2003 and many other studies that used a Batch reactor rather than the present Berty reactor (Violette 2003). van Heiningen in 2019 explains this by reduced capture of oxygen radicals by the smaller amount of lignin remaining at larger delignification (van Heiningen, Ji and Jafari 2019). However when the same data is plotted according to Equation (4.4), i,e. Ln[$\text{Kappa}_{\text{initial}}$-HexA/10)/(($\text{Kappa}_{\text{time}}$-HexA/10)Yield] or in short Ln[L0/L_tY] versus 1/DP - 1/DP_0 then a straight line is obtained. The yield is set equal to 1 since the CSTR yield data was not available because of the usage of a low amount of pulp in the Berty basket (6 g o.d). This validates the assumption underlying Equation (4.4) that proportionally fewer radicals are captured with decreasing reactive lignin.



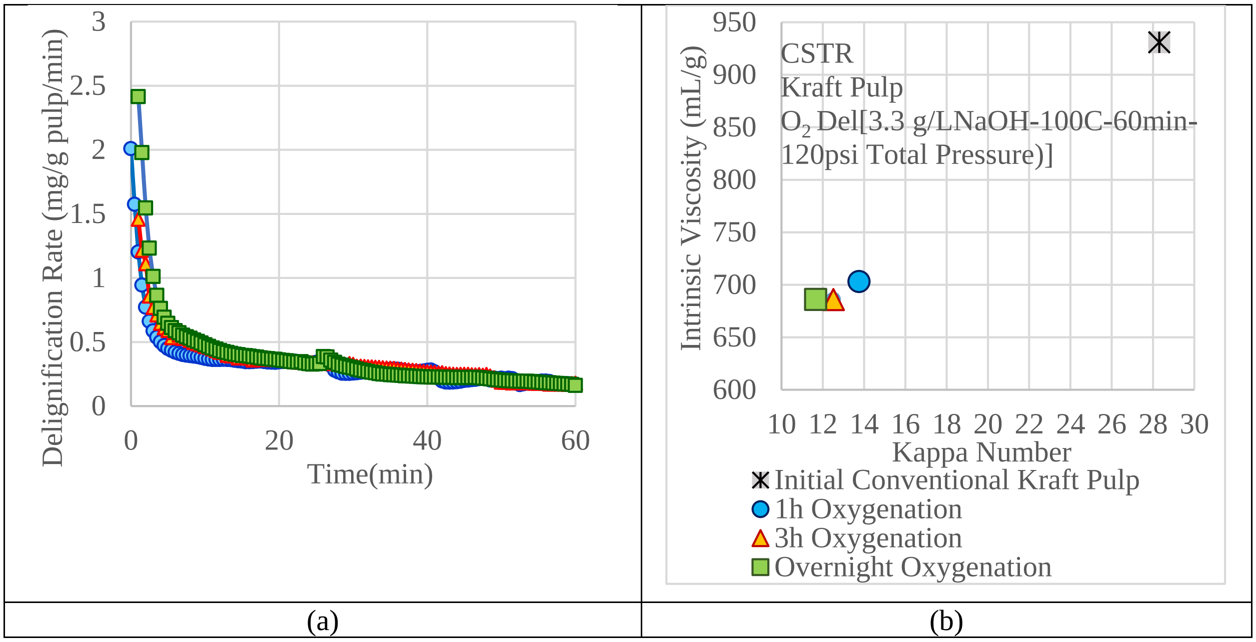
(a) (b)

Figure 4.8. Intrinsic Viscosity versus Kappa Number

4.11 Validation of Berty System

4.11.1 Effect of Oxygen Saturation Time on Lignin Concentration and Delignification Rate

The influence of oxygen saturation time on delignification rate and viscosity-kappa selectivity was studied to determine how long oxygen needs to be bubbled through the supply reservoir of a caustic solution to obtain a saturated oxygen concentration at the set oxygen pressure of 65 psi and flow rate of 10 mL/min. Figure 4.9 (a) shows that the delignification rate after overnight saturation was somewhat higher during the first 20 minutes of oxygen delignification than after 1 and 3 h saturation times. In Figure 4.9 (b), it is shown that by increasing the oxygenation time from 1 hour to overnight, further delignification takes place, while the intrinsic viscosity hardly changed. It seems at 3 hours' oxygenation or more the caustic gets very close to its saturation condition since the kappa and viscosity changes are very small. As the result, the overnight saturation was chosen for most experiments to make sure that the caustic gets fully oxygenated.



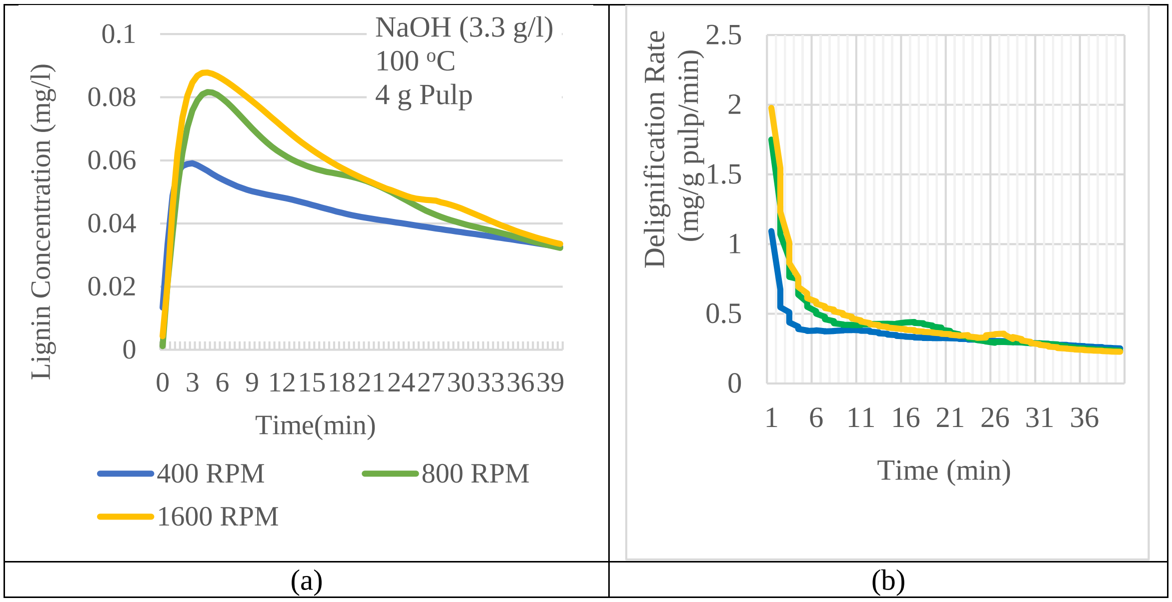
(a) (b)

Figure 4.9. Effect of Oxygen Saturation Time on

(a) Delignification Rate and (b) Viscosity-Kappa Selectivity

4.11.2 Effect of Liquor Circulation Rate in the Reactor

Figure 4.10 shows the effect of rotor stirring rate on the dissolved lignin concentration and delignification rate. It can be seen that by increasing the stirring speed from 400 to 800 rpm, both the lignin concentration and delignification rate increase. However, the lignin concentration is not much further increased when the stirring speed is from 800 to 1600 rpm. Therefore, 800 rpm was chosen as the optimum speed for obtaining uniform conditions in the reactor and (most importantly) the pulp pad, and used in further experiments.



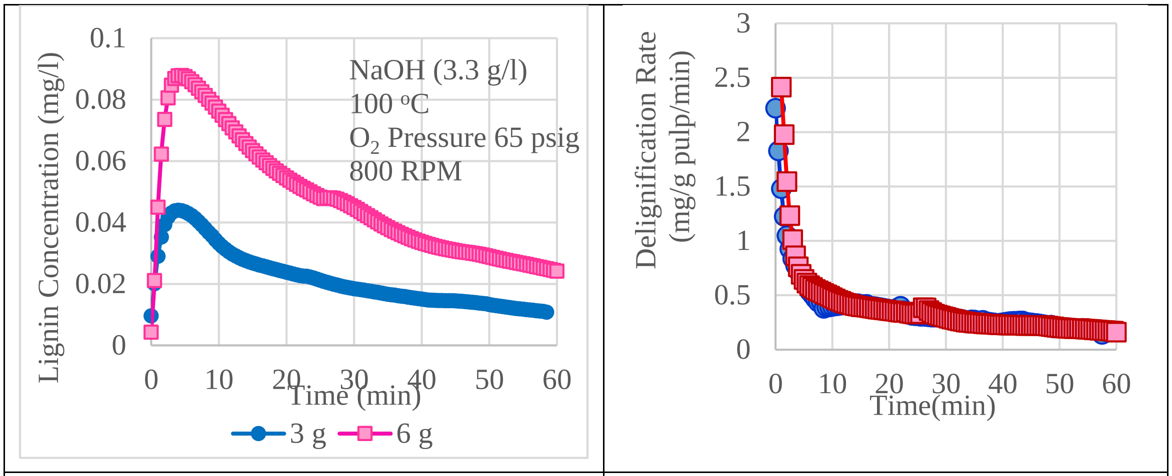
(a) (b)

Figure 4.10. Effect of Stirring Speeds on Berty Basket Reactor

(a) Delignification Rate vs. Time (b) Lignin Concentration vs. Time

4.11.3 Effect of Different Amount of Pulp Sample in Berty Basket

The impact of pulp weight on lignin concentration and delignification rate are represented in Figure 4.11a and 4.11b respectively. As can be seen, the lignin concentration approximately doubles when the pulp weight is increased from 3 to 6 grams. However, the delignification rate is not affected by the different pulp sample weights, which is clear evidence that the delignification rate obtained with the Berty reactor produces intrinsic kinetics.



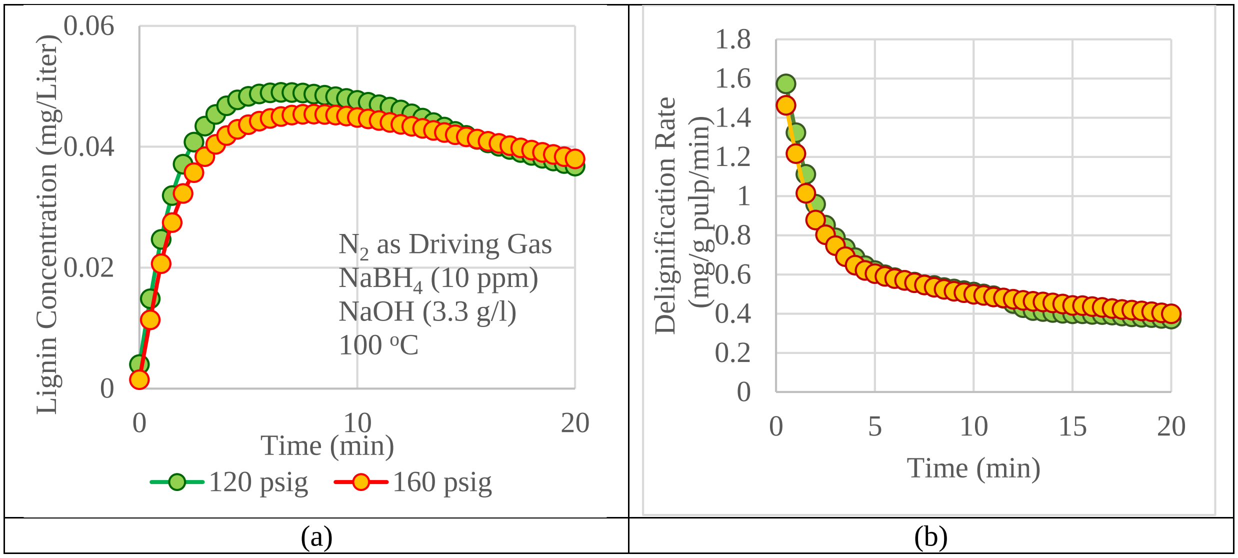
(a) (b)

Figure 4.11. Effect of Pulp Weight on

(a) Lignin Concentration and (b) Delignification Rate

4.11.4 Effect of Driving Gas (N_2) Pressure on Lignin Concentration and Delignification Rate

Figure 4.12 shows that the lignin concentration and delignification rate are not affected by the pressure of the driving gas which provides the hydraulic pressure at the top of the solution feed tank to transport the oxygenated caustic liquor into the reactor. At both 120 and 160 psig driving pressure, the conditions are such that oxygen remains dissolved when the feed liquor is heated to 100 °C because the hydraulic pressure is greater than the equilibrium oxygen pressure of 100 psig at 100 °C.



(a) (b)

Figure 4.12. Effect of Driving Gas (N_2) Pressure on

(a) Lignin Concentration and (b) Delignification Rate

CHAPTER 5

KINETICS OF OXYGEN DELIGNIFICATION

Oxygen delignification is complicated due to the complexity of the pulp matrix and the presence of solid, liquid, and gas phases in the process. To obtain a profound understanding of the mechanism of oxygen delignification, it is essential to have an accurate description of the chemical kinetics of lignin dissolution. The kinetic equations can also be used for controlling oxygen delignification plants and designing oxygen delignification reactors.

In this chapter, the kinetics of oxygen delignification is studied for a commercial unbleached Southern Pine kraft pulp. The power-law model was adopted to describe the delignification kinetics. The delignification data determined in the Berty/CSTR reactor were analyzed according to the differential method. The effect of the major process variables on delignification kinetics such as alkali and oxygen concentrations and temperature are quantified.

5.1 Differential Method Based on CSTR Data (Power-Law Model)

One way to obtain delignification kinetics is to fit a kinetic equation to the pair of data sets of delignification rate and the corresponding residual reactive lignin concentration in the pulp at different delignification times. In the CSTR, the delignification rate at time t, $r_{(t)}$, can be directly calculated from the dissolved lignin concentration in the CSTR effluent, C(t), as:

$$r(t) = [\phi_v C(t) + V_r \frac{dC(t)}{dt}] \frac{1}{m_p} \tag{5.1}$$

where,

ϕ_v is the flow rate (mL/min)

V_r is the reactor volume (mL)

m_p is the pulp weight (gram of o.d pulp)

The concentration C(t) is measured in the flowthrough UV-VIS cuvet where the CSTR effluent arrives after t_d seconds flowing through the connecting tubes. t_d (dead-time) is the residence time between the CSTR reactor and the UV-VIS cuvet. The value of t_d can be calculated by dividing the piping volume between the CSTR reactor and the UV-VIS (89 ml) flowthrough cell by the flowrate (ϕ_v) in ml/s; i.e. ($t_d = 89/\phi_v$).

The residual reactive lignin content in the pulp, L_C, is calculated by subtracting the amount of lignin removed from the pulp pad at time t from the HexA corrected lignin content of the original pulp, as:

$$L_C = \left(K_0 - \frac{HexA}{10}\right) \times 1.5 - \frac{\phi_v \int_{t_d}^{t+t_d} C(t)dt + V_r C(t+t_d)}{m_p} \tag{5.2}$$

where,

L_c is the residual reactive (or HexA corrected) lignin ($\frac{mg}{g\ pulp}$)

K_0 is the initial kappa number

HexA is the hexenuronic acid content of pulp (µmol/g pulp)

10 is the conversion of HexA content of pulp to kappa number (µmol/g pulp)

1.5 is the conversion of kappa number to % lignin on pulp (% lignin/kappa)

t_d is the residence (or dead) time in the piping between the CSTR exit and the UV cell used for the lignin concentration measurement (min)

$C(t)$ is the dissolved lignin concentration (mg lignin/ml) at the exit of the CSTR

The power-law model (Equation (5.3)) is used to fit the pair of data sets. The residual lignin was corrected for the hexenuroric acid (HexA) because HexA is inert during oxygen delignification (Table 4.2) but is oxidized during the Kappa test (Roost, Lawoko and Gellerstedt 2003).

$$r(t) = -\frac{dL_C}{dt} = k[OH^-]^n[O2]^m L_C^q \tag{5.3}$$

where, $r_{(t)}$ is the delignification rate (lignin reduction/min), L_C is the residual lignin corrected for HexA (mg/g pulp), t is reaction time (min), [OH] is the caustic concentration (mol/l), $[O_2]$ is the oxygen concentration in the solution (mol/l), m, n, and q are reaction orders obtained by fitting the experimental data, and k is the reaction rate constant which depends only on temperature.

Inside the CSTR, the caustic concentration and oxygen pressure are constant over time. Therefore, at a fixed temperature the term $k[OH]^n[O_2]^m$ in Equation (5.3) can be considered as constant (k_α):

$$k_\alpha = k[OH^-]^n[O_2]^m \tag{5.4}$$

Thus Equation (5.3) can be written as:

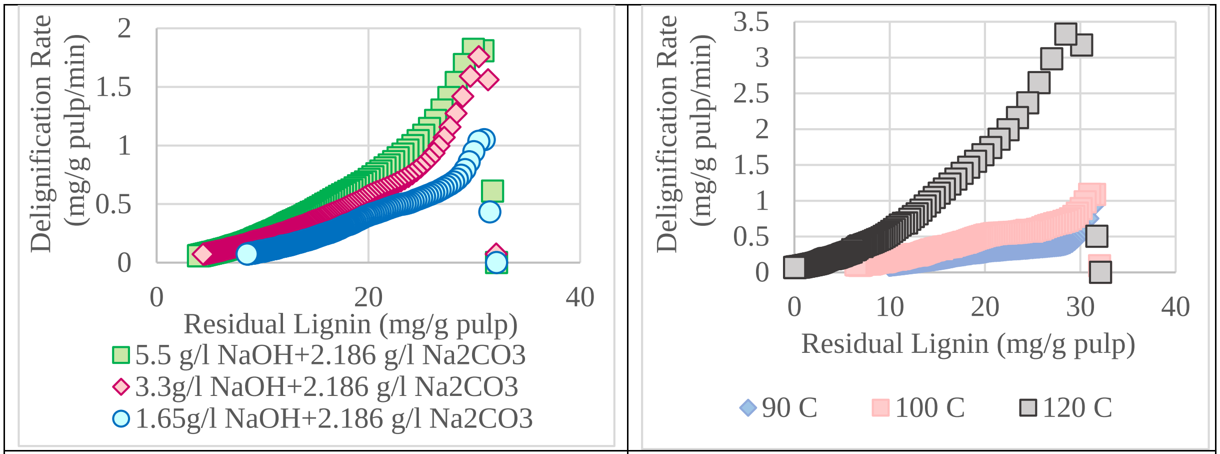
$$r(t) = -\frac{dL_C}{dt} = k_\alpha L_C^q \tag{5.5}$$

The differential kinetic analysis was performed at the different reaction conditions listed in Table 5.1.

Table 5.1, Different Reaction Conditions

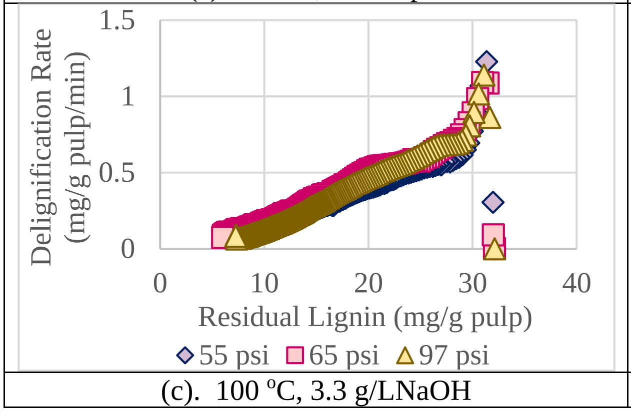
Temperature °C	NaOH (g/L)		P_{O2} (psig)
100	3.3		55
100	3.3		65
100	3.3		97
90	3.3		65
120	3.3		65
Temperature °C	NaOH (g/L)	Na_2CO_3 (g/l)	P_{O2} (psig)
100	1.65	2.186	65
100	3.3	2.186	65
100	5.5	2.186	65

The reaction order in reactive residual lignin can be obtained by inspection of the data in Figure 5.1, which shows the delignification rate, $r_{(t)}$, plotted against the residual reactive lignin, L_C, for different reaction conditions.



(a). 100 °C, P_{O2} 65 psi

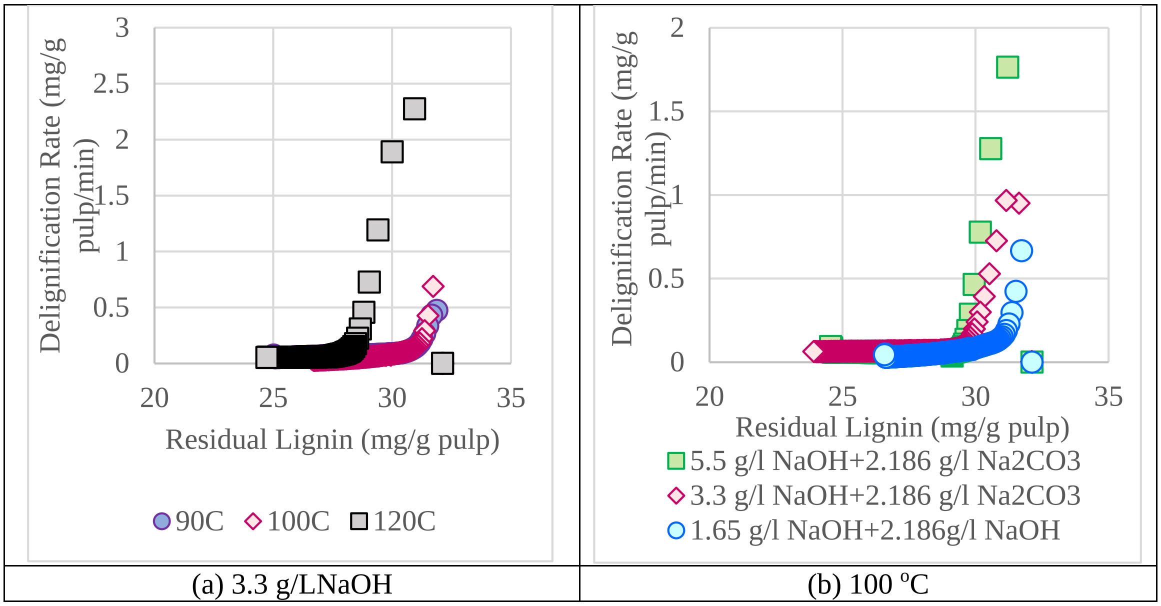
(b). 3.3 g/LNaOH, P_{O2} 65 psi



(c). 100 °C, 3.3 g/LNaOH

Figure 5.1. Delignification Rate versus Residual Lignin Corrected for HexA

As can be seen in Figure 5.1, there is a clear peak at the beginning of each reaction kinetic curve. The calculated delignification rate increases rapidly in the first few minutes from the start of inflow (and outflow) of the oxygenated caustic solution into (and out of) the Berty basket reactor after equilibration of the pulp pad in the basket at 80 °C for 15 minutes without any mixing. During this equilibration time, some alkali-extractable lignin will be released from the pulp fibers and contribute to additional oxygen delignification in our calculation procedure. In addition, it takes time to establish a steady-state operation after the stirring at time zero. Therefore, the analysis of the oxygen delignification rate data must account for the removal of alkali-extractable lignin which was still trapped inside the pores of the fiber cell wall matrix of the original kraft pulp obtained after industrial (and thus incomplete) pulp washing. The correction is done by determining the rate of removal of alkali extractable lignin, $r(t)_{NaOH}$, in separate experiments using a caustic solution that has not been oxygenated, see Figure 5.2.



(a) 3.3 g/LNaOH

(b) 100 °C

Figure 5.2. Delignification Rate versus Residual Lignin at Different

(a) Reaction Temperatures and (b) Alkali Concentrations

in the Absence of Oxygen

Using the data presented in Figure 5.1 and Figure 5.2, the calculation procedure for determining the oxygen delignification rate corrected for the rate of removal of alkali extractable lignin, $r(t)_{C,O2}$, becomes:

$$r(t)_{C,O2} = r(t)_{O2} - r(t)_{NaOH} \tag{5.6}$$

or

$$r(t)_{C,O2} = \{\left[\phi_v c(t) + V_r \frac{dC(t)}{dt}\right]\frac{1}{m_p}\}_{O2} - \{\left[\phi_v c(t) + V_r \frac{dC(t)}{dt}\right]\frac{1}{m_p}\}_{NaOH} \qquad (5.7)$$

where,

$r(t)_{C,O2}$: Oxygen delignification rate corrected for alkali extractable lignin

$r(t)_{O2}$: Experimental oxygen delignification rate

$r(t)_{NaOH}$: Experimental NaOH delignification

$$L_C = \left(K_0 - \frac{HexA}{10}\right) \times 1.5 - \frac{\phi_v \int_{t_d}^{t+t_d} C_L(t)dt + V_r C_L(t+t_d)}{m_p} \qquad ((5.2))$$

The oxygen delignification rates calculated without or with accounting for the removal of alkali extractable lignin using Equations 5.1 and 5.7 respectively are shown in Figure 5.3. It can be seen that when the oxygen delignification rate is corrected for the removal of alkali extractable lignin, the peak at the beginning of the oxygen delignification process has been eliminated. Also, at the end of 90 min reaction, the corrected reaction rate approaches zero at a residual lignin content close to 4 mg/g pulp. This suggests that 4 mg of lignin per one gram of oven-dried (o.d) pulp cannot be removed by oxygen and will remain in the pulp matrix even by infinitely extending the reaction time. This unreactive lignin may be nonphenolic or p-hydroxyphenyl and condensed phenolic structures such as 5,5 biphenyls and diphenyl methane which have been shown to be relatively inert during oxygen delignification (Akim, Colodette and Argyropoulo 2001), (Lai, Funaoka and Chen 1994), and (Argyropoulos 2003). In addition, unreactive lignin may be lignin fragments covalently bound to glucomannan, i.e. a lignin-carbohydrate complex (LCC) which is relatively resistant to removal during oxygen delignification (Lawoko, Henriksson and Gellerstedt 2005). On the other hand, when no alkali extractable lignin correction is applied to the oxygen delignification rate, the reaction kinetic curve approaches the origin (see Figure 5.3). This suggests that alkali extraction may remove most of the unreactive lignin if the reaction time is extended and that these lignin fragments have a larger hydrodynamic size similar to that of the cell wall pores which limit their removal from the fiber wall controlled by the slow process of activated diffusion (Favis and Goring 1984). The above analysis implies that the lignin removed by oxygen delignification is different from that removed by alkali extraction and that the two processes proceed independently from each other.

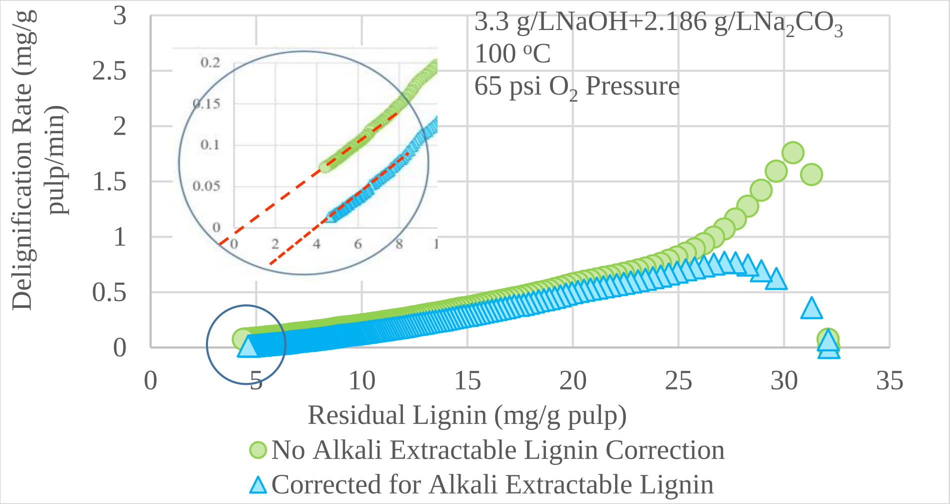


Figure 5.3. Effect of Alkali Extractable Lignin Correction on Oxygen Delignification Rate

In order to make sure that no measurable oxygen delignification takes place during alkali extraction, the alkali extraction experiment was repeated using alkaline liquor which was fully deaerated by bubbling nitrogen through the caustic at a flow rate of 10 mL/min at room temperature for 4 hours. In Figure 5.4, the delignification rate is plotted versus time for both the regular caustic solution and the deaerated caustic solution. As can be seen, there is no significant difference between the two cases, confirming that no significant oxygen delignification occurs when the extraction is performed with caustic which was in contact with atmospheric air containing 3 psi oxygen.

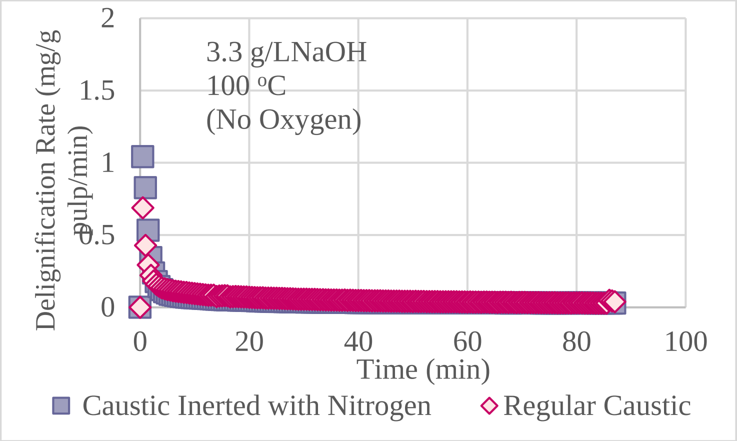
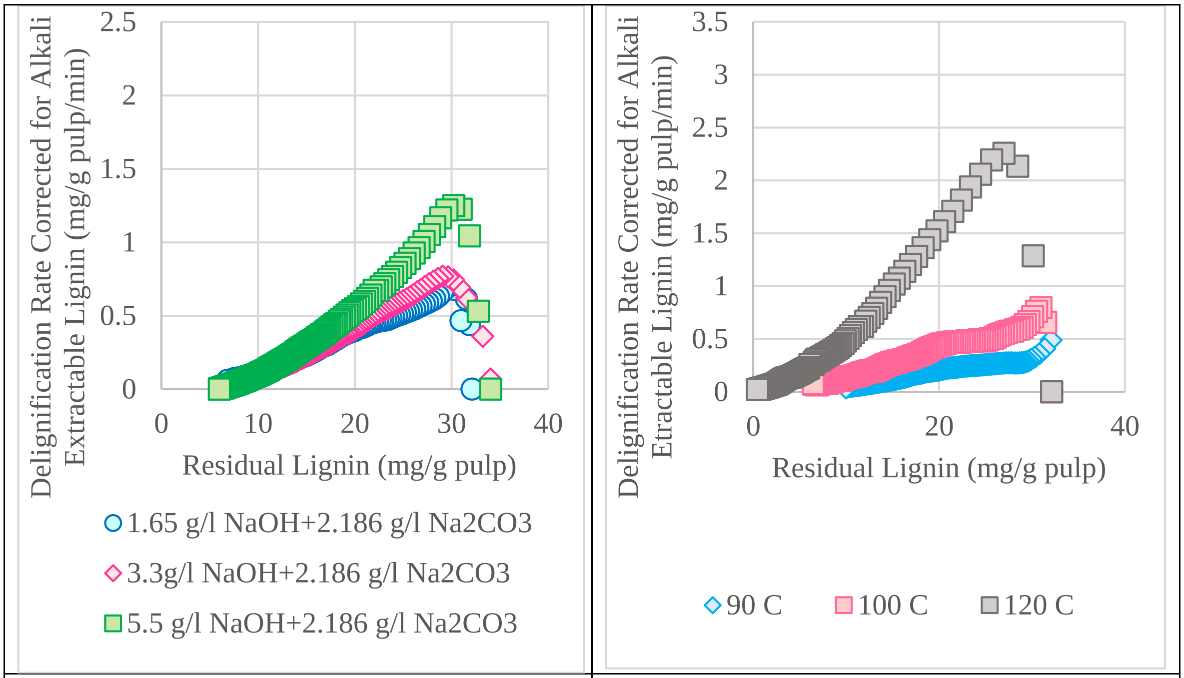


Figure 5.4 Delignification Rate versus Time for Both Regular Caustic Solution and Deaerated Caustic Solution

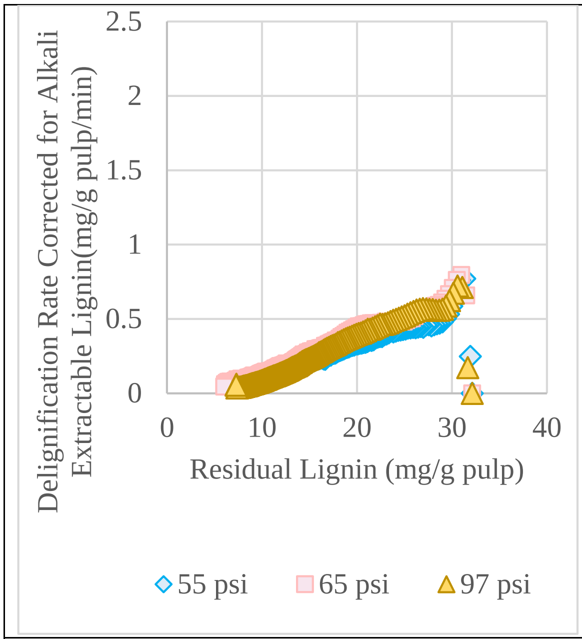
In Figure 5.5, the oxygen delignification rate is corrected for alkali extractable lignin at all reaction conditions.



(a). 100 ºC, P_{O2} 65 psi

(b). 3.3 g/LNaOH, P_{O2} 65 psi

Figure 5.5 Continued.



(c). 100 °C, 3.3 g/LNaOH

Figure 5.5 Delignification Rate Corrected for Alkali Extractable Lignin versus Residual Lignin

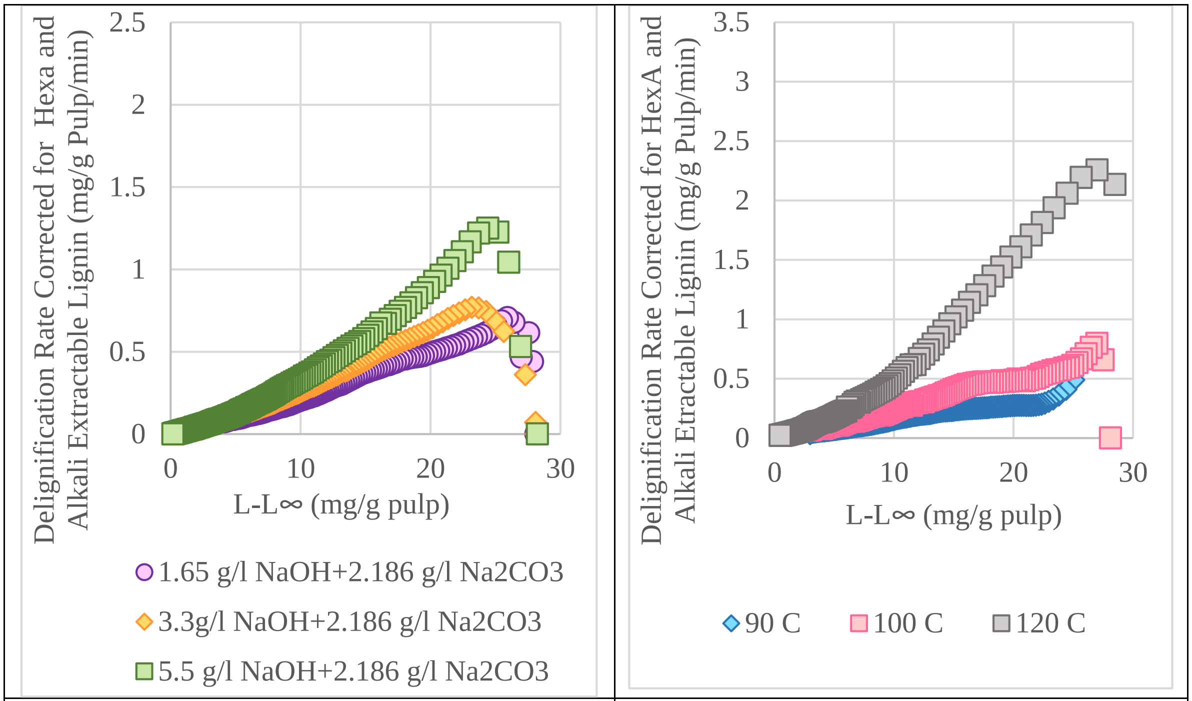
As can be seen in Figure 5.5, for all experimental conditions except T=120 °C, the kinetics show that there is some “unreactive” lignin which is quantified by extending a straight line through the reaction rate (Corrected for HexA and alkali extraction) for the last 45 minutes at each reaction condition versus residual lignin to zero delignification rate. The values of this “unreactive” lignin, L_∞, for the different reaction conditions are listed in Table 5.2. The value of L_∞ at 120 °C could not be determined using this procedure because at the high temperature (T=120 °C) other dissolved UV-absorbing substances originating from degraded hemicelluloses lead to an overestimation of the amount of lignin removed. In other words, at 120 °C the UV-VIS calibration curve is not strictly valid anymore as was earlier suggested by Ji (Y. Ji 2007). This is confirmed by the HexA corrected kappa number of 1.4 or lignin content of 1.4x1.5 = 2.1 mg/g pulp for the final pulp after 90 minutes of oxygen delignification at 120 °C while the UV data suggest there is no lignin left.

Table 5.2. “Unreactive” Lignin Content, L_∞, at Different Reaction Conditions

Temperature (^{o}C)	NaOH (g/L)		P_{O2} (psi)	Kappa Number After 90 min	HexA Free Lignin Content (mg/g pulp)	L_∞ (mg/g pulp)
100	3.3		55	7.2	6.3	5
100	3.3		65	7.5	6.7	4
100	3.3		97	6.5	5.3	5
90	3.3		65	11.2	12.3	7
120	3.3		65	4.4	2.1	-
Temperature (^{o}C)	NaOH (g/l)	Na_2CO_3 (g/l)	P_{O2} (psi)	Kappa Number After 90 min	HexA Free Lignin Content (mg/g pulp)	L_∞ (mg/g pulp)
100	1.65	2.186	65	7.5	6.7	4
100	3.3	2.186	65	6.7	5.5	4
100	5.5	2.186	65	6.1	4.6	4

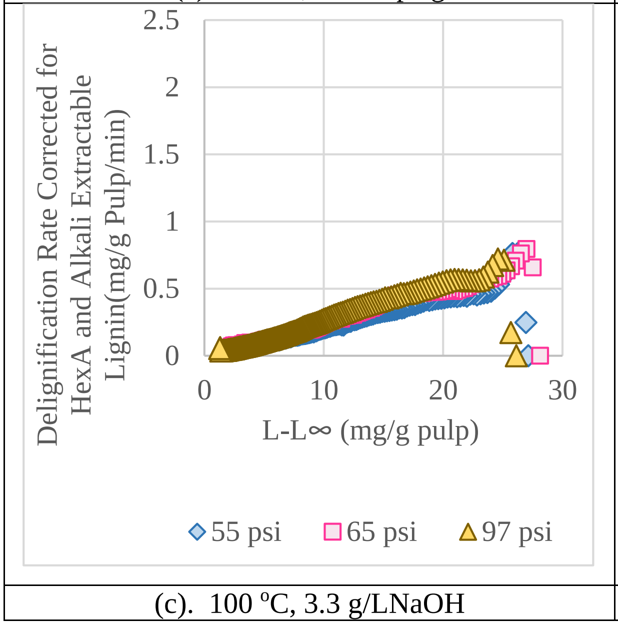
The data in Table 5.2 shows the HexA free lignin content remaining in one g o.d pulp after 90 min and the amount of unreactive lignin, L_∞. As can be seen, at 100 ^{o}C the measured HexA free lignin after 90 minutes of reaction is only slightly larger than the amount of unreactive lignin, meaning that very little further delignification can be accomplished by increasing the reaction time. At the low reaction temperature of 90 ^{o}C, the amount of removable lignin is still significant at 5.3 (12.3-7=5.3) (mg/g o.d pulp) after 90 min of oxygen delignification, i.e. at this temperature it would make sense to further increase the oxygen delignification time. It also be seen that at 90 ^{o}C a higher amount of lignin is unreactive (7 mg/g o.d pulp) in comparison with that at 100 ^{o}C (about 4-5 mg/g o.d pulp). This would be expected since at higher temperature some of the unreactive lignin structures (nonphenolic, p-hydroxyphenyl, phenolic 5,5 biphenyls and diphenyl methane) would become amenable to reaction with oxygen.

In Figure 5.6, the oxygen delignification rate corrected for HexA and alkali extractable lignin is plotted residual lignin minus the 'unreactive" lignin, L∞, for all reaction conditions.



(a). 100 °C, P_{O2} 65 psig

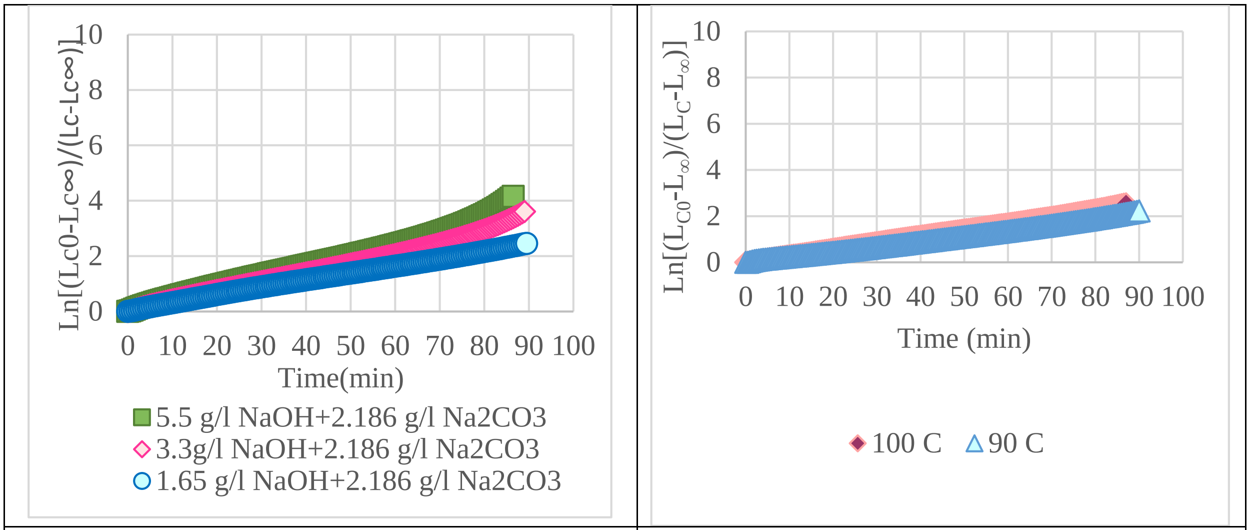
(b). 3.3 g/LNaOH, P_{O2} 65 psig



(c). 100 °C, 3.3 g/LNaOH

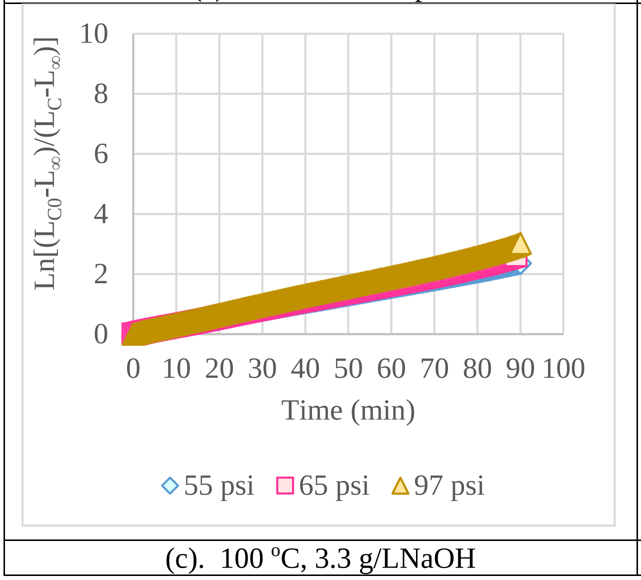
Figure 5.6. Delignification Rate Corrected for HexA and Alkali Extractable Lignin versus Residual Lignin Corrected for Unreactive Lignin

It can be seen from these plots (except for the 120 °C data) that the delignification rate is first order in reactive lignin. This was tested by replotting the data as the natural logarithm of the ratio of the “reactive” lignin content at time zero and t, ($Ln\frac{L_{C,0}-L_{\infty}}{L_{C,t}-L_{\infty}}$), versus time in Figure 5.7.



(a). 100 °C, P_{O2} 65 psi

(b). 3.3 g/LNaOH, P_{O2} 65 psi



(c). 100 °C, 3.3 g/LNaOH

Figure 5.7. Ln[($L_{C,0}$-L_{∞})/($L_{C,t}$-L_{∞})] versus Time

Since straight lines are obtained the delignification rate is indeed first-order in “reactive lignin, and the rate constant, kα, can be obtained from the straight lines through the plotted data (Equations (5.8) and (5.9)).

$$r(t) = -\frac{d(L_{C,t} - L_{\infty})}{dt} = k_{\alpha}\,(L_{C,t} - L_{\infty})^{q=1} \tag{5.8}$$

$$Ln\left(\frac{L_{C,0} - L_{\infty}}{L_{C,t} - L_{\infty}}\right) = k_{\alpha} t \tag{5.9}$$

5.1.1 Reaction Rate Constant, k_{α}

In Table 5.3, the values for the reaction rate constant, k_{α}, are listed for the different reaction conditions studied.

Table 5.3. Value of Reaction Rate Constant, k_{α}, at Different Reaction Conditions After Corrections for HexA, Alkali Extractable Lignin, and Unreactive Lignin

Temperature (°C)	NaOH (g/L)		[OH] (mol/l)	P_{O2} (psig)	$[O_2]$ (mol/l)	Rate Constant, k_{α}, (1/min) Corrected for HexA, Alkali Extractable Lignin, and Unreactive Lignin
100	3.3		0.082	55	0.0056	0.023
100	3.3		0.082	65	0.0064	0.023
100	3.3		0.082	97	0.0090	0.029
90	3.3		0.082	65	0.0064	0.017
120	3.3		0.082	65	0.0064	0.078
Temperature (°C)	NaOH (g/l)	Na_2CO_3 (g/l)	[OH] (mol/l)	P_{O2} (psig)	$[O_2]$ (mol/l)	Rate Constant, k_{α}, (1/min) Corrected for HexA, Alkali Extractable Lignin, and Unreactive Lignin
100	1.65	2.186	0.041	65	0.0064	0.026
100	3.3	2.186	0.082	65	0.0064	0.027
100	5.5	2.186	0.137	65	0.0064	0.046

Since the reaction order in “reactive” lignin using the differential kinetic approach is first-order, Equation (5.4) can be written as:

$$Ln(k_\alpha) = Ln(k) + n\ Ln[OH^-] + m\ Ln[O_2] \tag{5.10}$$

5.1.2 Reaction Order in Caustic Concentration, n

The reaction order in caustic concentration, n, can be calculated by using Equation (5.10) at constant reaction temperature and oxygen pressure. Therefore, Equation (5.10) simplifies to:

$$Ln[k_\alpha] = C_1 + nLn[OH^-] \tag{5.11}$$

where, $C_1 = Ln(k[O_2]^m)$ is constant for constant oxygen concentration and temperature.

The logarithm of the rate constant, k_α, is plotted versus alkali concentration, [OH] mol/L, for three different caustic conditions but at the same oxygen pressure and temperature. The plot presented in Figure 5.8 shows that the reaction order in caustic concentration, n, is 0.4.

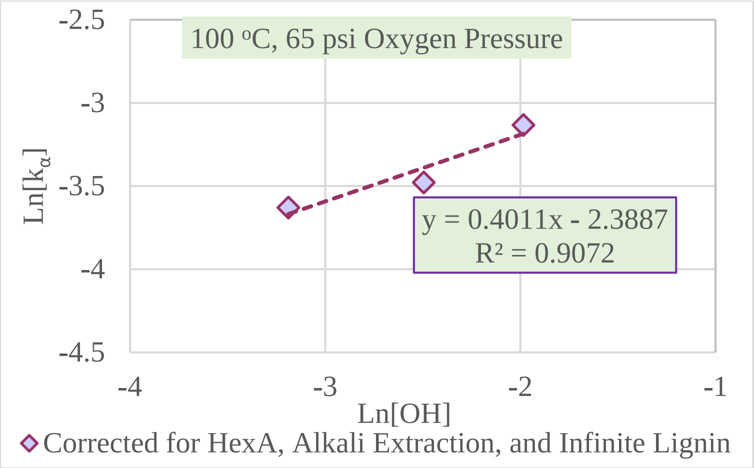


Figure 5.8, Ln(k_α) versus Ln[OH] at 100 °C, P_{O2} 65 psi

5.1.3 Reaction Order in Dissolved Oxygen Concentration, m

To calculate the reaction order in oxygen concentration, m, Equation (5.10) can be written as;

$$Ln[k_\alpha] = C_2 + mLn[O_2] \tag{5.12}$$

where $C_2 = Ln\ (k[OH]^n)$ is constant at constant temperature and alkali concentration. In Table 5.3, the dissolved oxygen concentration (mol/L) is represented at different oxygen pressures. The dissolved oxygen concentration is obtained using the Henry coefficient of dissolved oxygen in a

NaOH solution (see Figure 4.3). Because in this study oxygenation of the caustic solution was done at room temperature for many hours, the oxygen concentration is at saturation, and $\frac{[O_2]_{Dissolved}}{P_{O2}}$ = 0.0012 mol/L atm can be obtained from Figure 4.3 at 25 °C, where $[O_2]_{Dissolved}$ is the dissolved oxygen concentration in 3.3 g/L NaOH solution (mol/L) and P_{O2} is the absolute oxygen pressure used for oxygenating the caustic (atm), thus,

$$[O_2]_{Dissolved} = 0.0012\left(\frac{P_{O2} + 14.7}{14.7}\right)$$

where P_{O2} is the gauge oxygen pressure used for caustic saturation in psi.

By plotting the logarithm of reaction rate constant against oxygen concentration for three oxygen pressures, the reaction order in oxygen concentration, m, would be obtained as the slope of the straight line passes through the three plots. As can be seen in Figure 5.9, the reaction order in oxygen concentration, m, is 0.51.

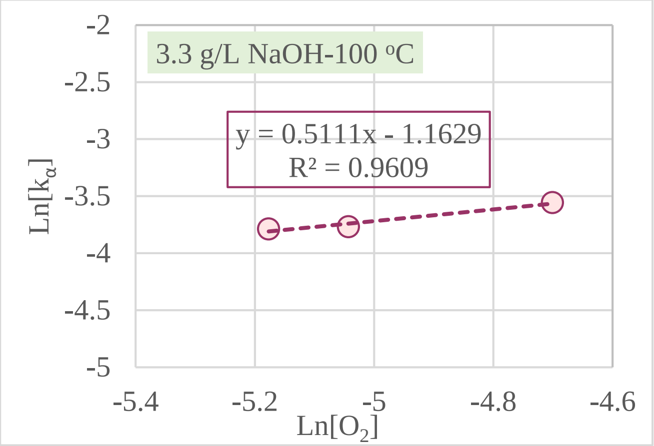


Figure 5.9. $Ln[k_\alpha]$ versus $Ln[O_2]$ at 100 °C, 65 psi

5.1.4 Activation Energy and Arrhenius Factor

To estimate the activation energy, E_A, and frequency factor, A, the Arrhenius equation is applied:

$$k = A\, exp(\frac{-E_A}{RT}) \qquad 5.13$$

In the Arrhenius equation, A is the Arrhenius constant (frequency factor), E_A is the activation energy (J/mol), R is the gas constant (8.314 J/mol.K), and T is the absolute temperature (°K). Thus, Equation (5.4) can be written as:

$$k_\alpha = A\exp\left(\frac{-E_A}{RT}\right)[OH^-]^n[O_2]^m \tag{5.14}$$

At constant caustic and oxygen concentrations, at variable temperatures, Equation (5.10) reduces to:

$$Ln[k_\alpha] = C_3 - \frac{E_A}{RT} \tag{5.15}$$

where, $C_3 = Ln[A] + nLn[OH] + mLn[O_2]$ is constant under constant alkali and oxygen concentration.

The value of the activation energy, E_A, can be estimated from the slope of $Ln[k_\alpha]$ versus (1/T) for different reaction temperatures and constant caustic and oxygen concentrations (Figure 5.10).

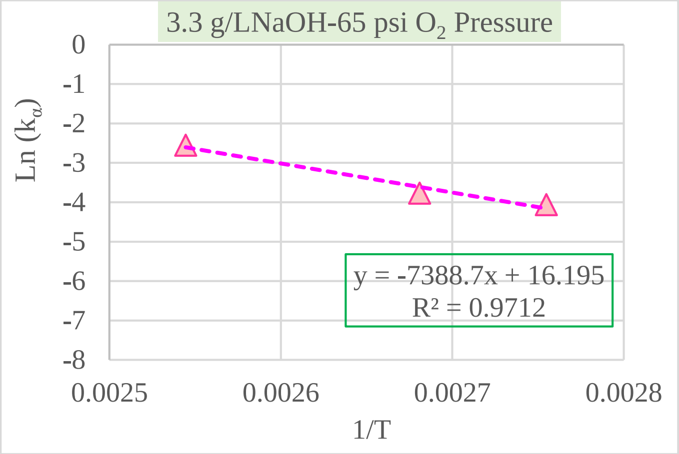


Figure 5.10. Ln[k_α] versus 1/T

As represented in Equation (5.15), the slope of the straight line shown in Figure 5.10 is equal to –E/R (R=8.314 J/mol °K). Thus, the activation energy, E_A, with Alkali extractable lignin correction is 61.429 kJ/mol.

Knowing k_α, m, n, and E_A, the Arrhenius coefficient, A, can be obtained by plotting Ln[k_α] versus $\{\mathrm{mLn}[\mathrm{O_2}] + \mathrm{nLn}[\mathrm{OH}] - \frac{\mathrm{E_A}}{\mathrm{RT}}\}$ (Equation (5.16) for all reaction conditions (see Table 5.1).

$$Ln[k_\alpha] = Ln[A] + \{mLn[O_2] + nLn[OH] - \frac{E_A}{RT}\} \tag{5.16}$$

As shown in Figure 5.11, the straight-line fits the plots for all the reaction conditions studied with an R-squared of 0.89 with the HexA, alkali extraction, and unreactive lignin corrections and the slope is one. This shows that the reaction parameters (k_α, m, n, and E_A) have been correctly predicted since the slope in Equation (5.16) and Figure 5.11 is one. Based on Equation (5.16), the natural logarithm of Arrhenius factors is the intercept, i.e. 3.8×10^8 $(mol_{OH}/l)^{-n}$ $(mol_{O2}/l)^{-m}$ min^{-1}.

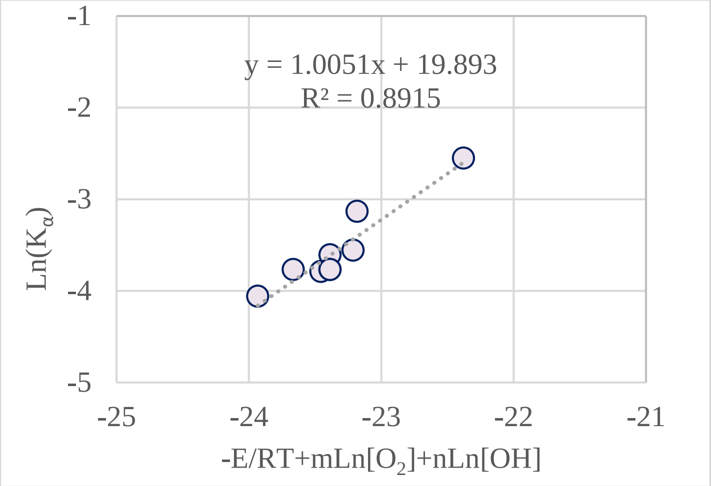


Figure 5.11. Ln[k_α] versus mLn[O_2]+nLn[OH]-E/RT

at Different Reaction Conditions

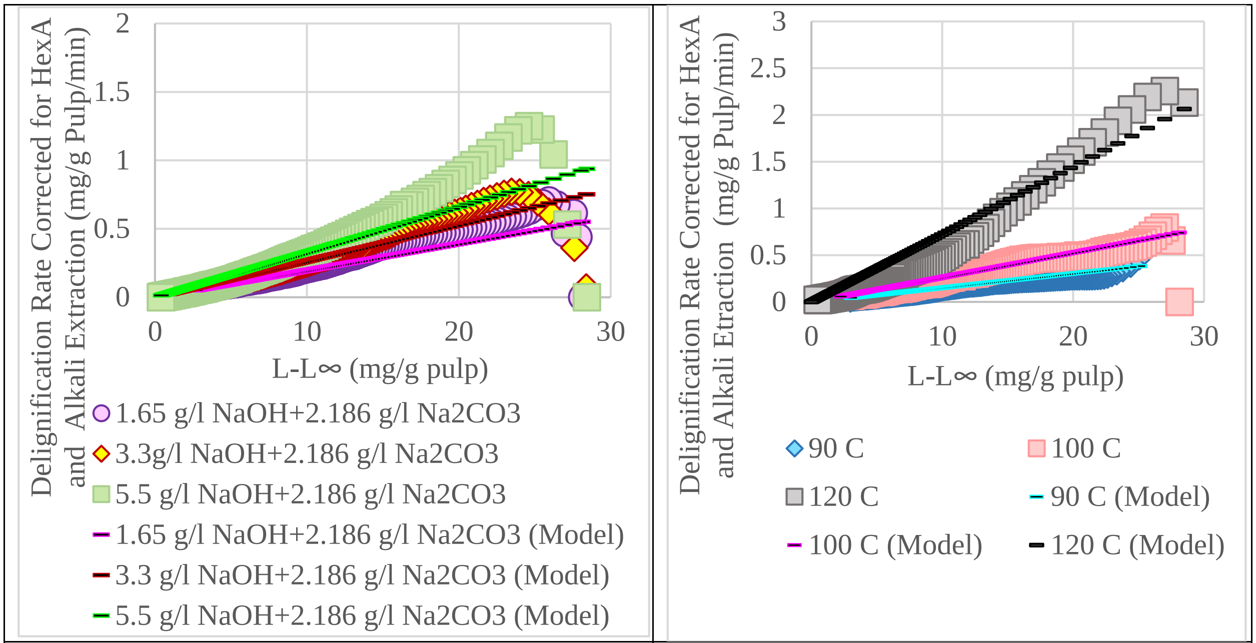
Based on the above differential method of analysis of the kinetic data, the oxygen delignification rate becomes:

$$r(t)_{C,O2} = -\frac{d(L_C - L_\infty)}{dt} = 3.8 \times 10^8 \, exp\left(\frac{-61429}{RT}\right) [OH^-]^{0.40} [O_2]^{0.51} (L_C - L_\infty)^1 \tag{5.17}$$

As shown in the equation above, the reaction order in dissolved oxygen concentration, m, is slightly higher than the reaction order in alkali concentration, n. Essentially the same results were obtained by Ji (2007) for a commercial Southern Pine pulp of Kappa 26 and intrinsic viscosity 1,189 mL/g with values for m and n of 0.44 and 0.42 respectively. This is not unexpected since the pulps and the range of operating conditions studied are very similar, except that the present pulp was not well-washed. The activation energy determined by Ji of 53 kJ/mol is smaller than the present 61 kJ/mol and the oxygen delignification rate is described by Ji as ($-\frac{dL_C}{dt} = 5 \times 10^4 e^{\frac{5.32\times10^4}{RT}}[OH]^{0.423}[P_{O2}]^{0.443}L_c$) (Y. Ji 2007) which also shows a first-order dependence on the HexA-free lignin content. Thus the most important difference between these two studies is that the present kinetics are for pure oxygen delignification, i.e. eliminates the contribution of alkali leaching of lignin, and that there is a small amount of lignin that does not react with oxygen resulting in dissolution. The present activation energy for oxygen delignification of 61 kJ/mol is similar to that reported by Hartler, Teder, and Perng for softwood kraft pulp of E_A=69, 70 and 60, kJ/mol respectively (Hartler, Norrström and Rydin 1970), (Teder and Olm 1981), and (Perng and Oloman 1994).

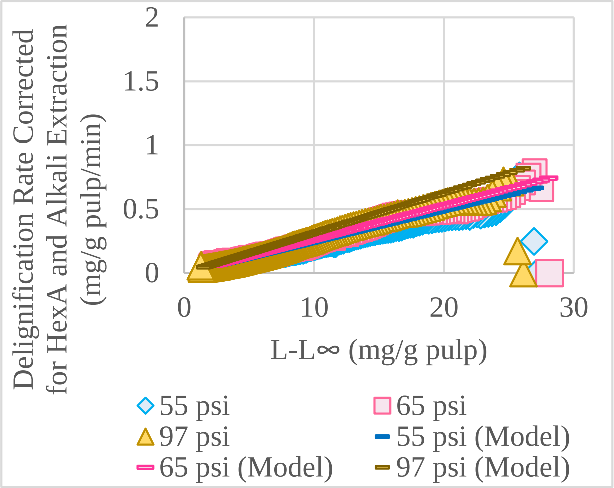
5.1.5 Power-Law Model Verification on Differential Approach

In Figure 5.12, the predictions of the power-law kinetic model for oxygen delignification (Equation (5.17)) are compared to the CSTR's experimental data. It can be seen that the predicted model is representing the data very well at all conditions studied (Table 5.1) except for the highest temperature (120 ^oC) and alkali concentration (5.5 g/L NaOH+2.186 g/L Na_2CO_3).



(a). 100 °C, P_{O2} 65 psi

(b). 3.3 g/LNaOH, P_{O2} 65 psi



(c). 100 °C, 3.3 g/LNaOH

Figure 5.12. Model Verification at Different Reaction Conditions

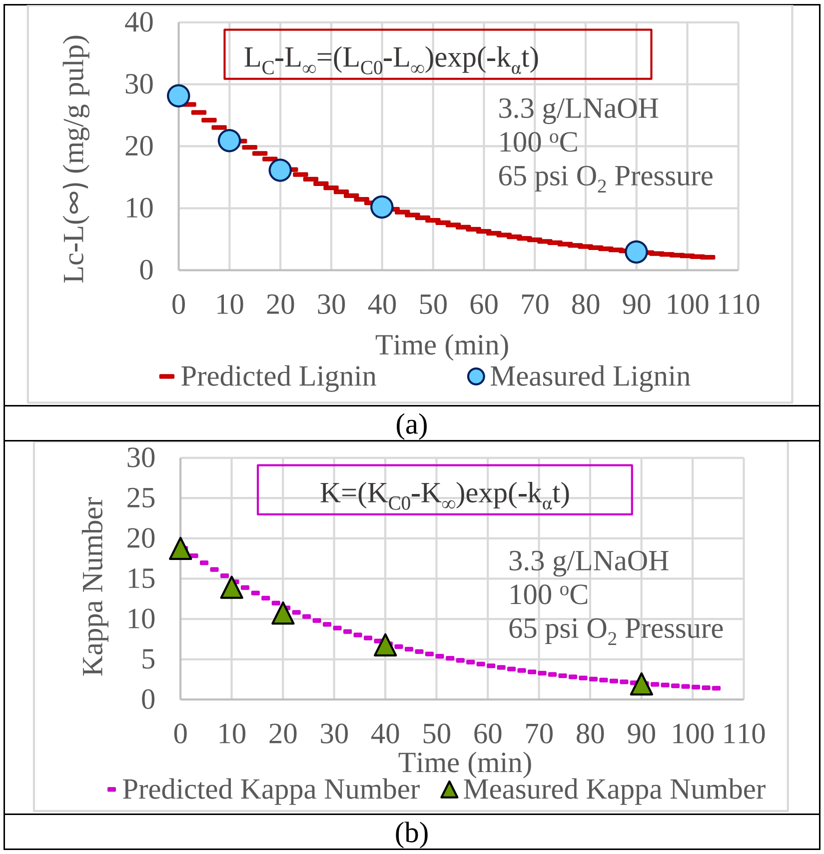
(The Reaction Rate is Corrected for HexA and Alkali Extractable Lignin and Lignin is Corrected for Unreactive Lignin)

5.1.6 Validation of Kinetic Model for Measured and Predicted Lignin Content

Based on the power-law parameters obtained above, the kinetic equation with respect to residual lignin (corrected for unreactive lignin) in CSTR for oxygen delignification at 100 °C with 3.3 g/L NaOH can be written as:

$$r(t)_{C,O2} = 0.023(L_C - L_\infty)^1 \tag{5.18}$$

In Figure 5.13 (a), the measured and predicted lignin contents are plotted against time, and in Figure 5.13 (b), the predicted and measured kappa numbers versus time are represented. It can be seen that the kinetic model describes both the measured lignin content and kappa number in the CSTR very well.



(a)

(b)

Figure 5.13. Validation of Kinetic Models for Measured and Predicted Lignin Content and Kappa Number, (CSTR)

In Figure 5.14, the model prediction is plotted against the measured lignin (corrected for unreactive lignin) at the reaction conditions of 3.3 g/L NaOH at 100 ºC and 65 psi oxygen pressure. It can be seen that there is a linear relationship between the predicted and measured lignin with a slope of one which shows the model is representing the data very well.

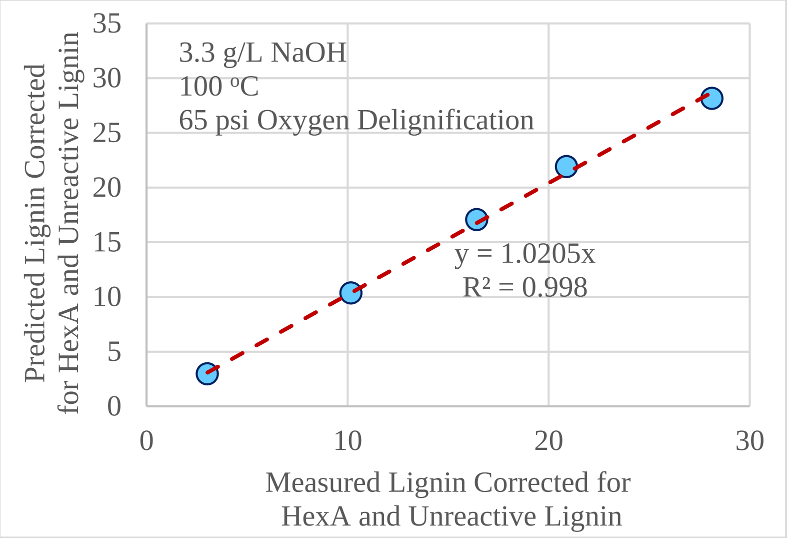


Figure 5.14 Predicted Lignin versus Measured Lignin

5.2 Delignification Kinetics with Additives

The effect of the additives sodium carbonate and methanol on the delignification kinetics was investigated. Sodium carbonate and methanol can scavenge hydroxyl radicals generated during oxygen delignification with the objective to improve the delignification/cellulose degradation selectivity (to be presented in Chapter 7). Because the radicals can also react with lignin and lead to further delignification, these two additives may also slightly change the delignification kinetics.

Oxygen delignification was done at 100 ºC and 65 psig oxygen pressure for 90 min without and with addition of 2.186 g/L Na_2CO_3 or 2 g/L Methanol to a 3.3 g/L NaOH caustic solution. The reaction rates were corrected for HexA and alkali extractable lignin, $r(t)_{O2}$-$r(t)_{NaOH}$, and the residual lignin was corrected for unreactive lignin, L-L∞. As shown in Figure 5.15, the three curves of 2.186 g/L Na_2CO_3+3.3 g/L NaOH, 2 g/L methanol+3.3 g/L NaOH and the control (3.3 g/L NaOH) are almost superimposed on each other, showing that the delignification kinetics are not affected by these radical scavenging additives at these concentration levels.

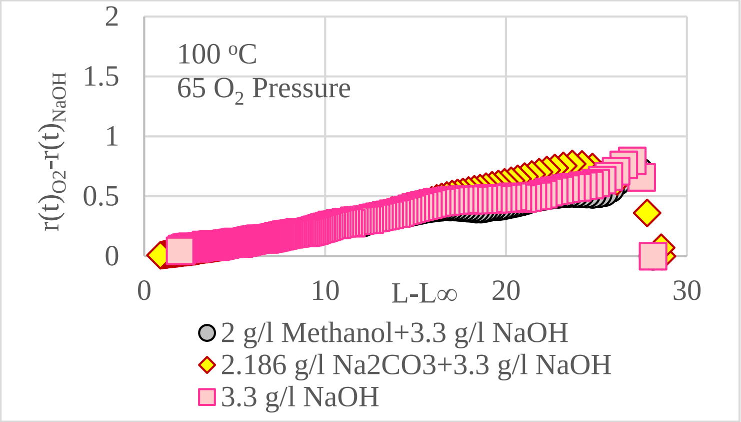


Figure 5.15. Effect of Additives on Delignificaiton Kinetics

5.3 Conclusions

- The important finding of the present study is that the oxygen delignification of industrial softwood pulp consists of two contributions; phenolic delignification and alkaline leaching delignification. In addition, the pulp contains unreactive lignin and HexA which is stable during oxygen delignification. When the kappa number is corrected for these two contributions, and the alkaline leaching delignification rate is subtracted from the total delignification rate, the rate of dissolution of the reactive lignin is obtained. The kinetics of oxygen delignification of the reactive lignin is first order in reactive lignin content and the reaction orders in alkali concentration and oxygen are 0.40 and 0.51 respectively. The present activation energy for oxygen delignification of reactive lignin is 61 kJ/mol.
- We also found that the delignification kinetics are not affected by the radical scavenging additives, Na_2CO_3 and methanol.

CHAPTER 6

EFFECT OF NABH$_4$ PRETREATMENT ON SELECTIVITY DURING OXYGEN DELIGNIFICATION OF KRAFT AND SULFITE PULPS

6.1 Introduction

In order to protect cellulose from degradation and thus improve the delignification/cellulose degradation selectivity during oxygen delignification, different degradation pathways must be addressed. One pathway is the reduction of carbonyl groups at C_2 and C_3 anhydro-glucose positions of cellulose using $NaBH_4$. In a study of oxygen delignification of a high lignin content Pine kraft pulp (kappa 65, intrinsic viscosity of 1295 mL/g), it was found that a $NaBH_4$ feed concentration of 10 ppm in a through-flow CSTR reactor operating at 115 °C, increased the intrinsic viscosity relative to the control (50 ppm $MgSO_4$) from about 750 mL/g to about 900 mL/g, both measured at a final kappa number of about 10 (Jafari 2015). Ni in 1998 also reported substantial improvements in pulp yield, pulp strength, brightness, and intrinsic viscosity for magnesium bisulfite pulp (kappa 25.2) when $NaBH_4$ was added during magnesium-based oxygen delignification at low charges of 0.02-0.05 % on pulp (Y. H. Ni 1998).

In this chapter, the carbonyl group content of pulps are estimated by the so called copper number. It is known that cellulose in sulfite pulp contains more carbonyl groups than that of kraft pulps (N. Hartler 1962). Therefore, we first focused on the effect of very low $NaBH_4$ concentrations on the oxygen delignification selectivity of sulfite pulp, and also investigated the impact of $NaBH_4$ pretreatment operating conditions on the subsequent oxygen delignification-cellulose degradation selectivity. Then, since kraft pulp is much more prevalent than sulfite pulp we set out to investigate the effect of $NaBH_4$ concentrations on reducing carbonyl groups on cellulose (by measuring the copper number) and on the oxygen delignification selectivity of conventional softwood kraft pulp (Kappa of about 24) with the ultimate objective to reach 80% delignification while keeping the intrinsic viscosity at an acceptable level (≥700 mL/g).

- Carbonyl Content of Pulps

As mentioned earlier, $NaBH_4$ reduces carbonyl groups to alditols which stabilize cellulose polymers (Browning 1967). The carbonyl group content of the three original pulps is presented in Table 6.1. It shows that the laboratory high kappa Southern Pine kraft and mill unbleached Black Spruce Magnesium bisulfite pulps contain a significant amount of carbonyl groups, while the mill unbleached Southern Pine kraft pulp has no measurable amount of carbonyl groups. In comparison, the carbonyl content reported in literature for unbleached Beech acid sulfite (kappa 8.76) and unbleached Eucalyptus kraft pulp (kappa 7.55) using the CCOA method were 3.85 and 0.26 mmol/100g pulp respectively, so also much higher values for sulfite than kraft pulps (Potthast, et al. 2004). The value for the carbonyl group content of the bisulfite pulp is very similar to the value of 2.16 mmol/100g pulp reported by Ni et al. in 1998 for a magnesium bisulfite pulp obtained from the same pulp mill as ours more than 20 years earlier (Ni, Ghosh, et al. 1998).

The absence of carbonyl groups in the mill unbleached Southern Pine kraft pulp compared to the high kappa Southern Pine kraft pulp implies that the carbonyl groups are removed during the final stage of kraft cooking. It is known that carbonyl groups are removed from cellulose chains by alkali-induced β-alkoxy elimination (Hosoya, et al. 2018) resulting in chain cleavage. Potthast and her colleagues believe that in the kraft process most of the carbonyl groups originate from the hemicellulose (Potthast, Rosenau and Kosma 2006).

Table 6.1. Carbonyl Group Content, Kappa, and Intrinsic Viscosity of the Three Original Pulps

Initial Pulp Sample	Carbonyl Contents (mmol/100g o.d. pulp)	Kappa Number	Intrinsic Viscosity (mL/g)
Conventional Kraft Pulp	0	24.42	996
High Kappa Kraft Pulp	2.32	98	1157 (After $NaClO_2$ Treatment)
Sulfite Pulp	2	20.15	914

- **Effect of Carbonyl Groups on Intrinsic Viscosity**

As mentioned earlier, the presence of carbonyl groups leads to the cleavage of cellulose chains under alkaline conditions. Since the solvent used to dissolve cellulose for the determination of the intrinsic viscosity, (Cupri Ethylene Diamine, CED), is alkaline, it potentially can depolymerize cellulose when carbonyl groups are present on the chains, thus leading to an artificial low viscosity value. Oasmaa also showed that there is a correlation between the increase in carbonyl groups and decrease in viscosity (Oasmaa, Korhonen and Kuoppala 2011). To test the effect of the presence of carbonyl groups on the intrinsic viscosity value of the original sulfite pulp, it was treated with a 0 and 100 ppm $NaBH_4$-3.3 g/LNaOH solution at 80 ^{0}C for 5 min. The results are presented in Table 6.2. They show that the pulp intrinsic viscosity values after treatment are 934 and 1041 mL/g, and the carbonyl groups are 1.78 and 1.51 (mmol/100 g o.d. pulp) respectively. In order to find the real value of the intrinsic viscosity of the pulps containing a high carbonyl group content, additional $NaBH_4$ treatment was performed on the produced pulps using 5500 ppm or 5% $NaBH_4$ (based on o.d. pulp) at room temperature for 20 min kneading (Perrin, et al. 2014). This high amount of $NaBH_4$ was used to reduce the remaining carbonyl groups on cellulose so as to prevent any cellulose degradation during viscosity determination (Perrin, et al. 2014). As shown in Table 6.2 after 5500 ppm $NaBH_4$ treatment, the carbonyl group content was reduced by 65%, while the viscosity increased only slightly for both pulps (Table 6.2). Thus, pretreatment at 100 ppm $NaBH_4$

at 80 C for 5 minutes is sufficient to eliminate most carbonyl groups on the cellulose chains, and the intrinsic viscosity measured after oxygen delignification treatment represents the DP of the cellulose chains without significant degradation occurring due to the alkaline nature of the CED solution.

Table 6.2. Effect of $NaBH_4$ Pretreatment for Sulfite Pulp

Samples	Intrinsic Viscosity (mL/g)	Carbonyl Group Content (mmol/100g o.d. pulp)	Kappa Number	After 5% $NaBH_4$ Treatment	
				Intrinsic Viscosity (mL/g)	Carbonyl Group Content (mmol/100g o.d. pulp)
Pre [0ppm $NaBH_4$-3.3g/LNaOH-80C-5 min mixing]	934±15	1.78±0.1	15.5±0.2	1056±15	0.62±0.1
Pre [100ppm $NaBH_4$-3.3g/LNaOH-80C-5 min mixing]	1041±15	1.30±0.1	15.4±0.2	1072±15	0.51±0.1

6.2 Sulfite Pulp

$NaBH_4$ was applied to the sulfite pulp at different pretreatment conditions to investigate the effect of $NaBH_4$ to find the best pretreatment condition for increasing delignification/cellulose degradation selectivity by reducing the carbonyl group content.

The CSTR reactor basket was filled with 6g pulp at 12% consistency. The caustic solution (3.3 g /L NaOH, which simulates 2.42% NaOH charge on pulp at 12% consistency) was saturated with oxygen overnight at room temperature and 65 psig O_2 pressure. The oxygen pressure of 65 psig at 25 °C was adopted because the equilibrium dissolved oxygen concentration at this condition is the same as that at 100 ^oC and 100 psig oxygen pressure using Henry's law (Tromans 1998). Earlier it was shown that the kinetics of O_2 delignification were not affected by the amount of the pulp (3-6 g), liquor circulation rate in the reactor (400-1600 rpm), flow rate, and type of gas (N_2 or O_2)

which is used to transport the liquor into the reactor (Pahlevanzadeh and van Heiningen 2018). Based on these experiments the following conditions were adopted: weight of the pulp 6 g (oven-dry basis), mixer speed 800 rpm, the flow rate for the reaction with conventional and high kappa pulp at 50 and 150 mL/min respectively, and N_2 was selected as the transport gas (Pahlevanzadeh and van Heiningen 2018).

6.2.1 Effect of Operating Conditions on Selectivity during $NaBH_4$ Pretreatment in CSTR Reactor

Figure 6.1 shows that the intrinsic viscosity of sulfite pulp increased by 100 mL/g when it was treated with 100 ppm $NaBH_4$ at 25 °C for 5 minutes in the CSTR reactor, but no significant additional increase was obtained when the pretreatment temperature was further increased to 120 °C. The decrease in kappa number seen in Figure 6.1 with increasing $NaBH_4$ treatment temperature may likely be explained by increased alkaline leaching of lignin at increasing temperatures (Favis and Goring 1984).

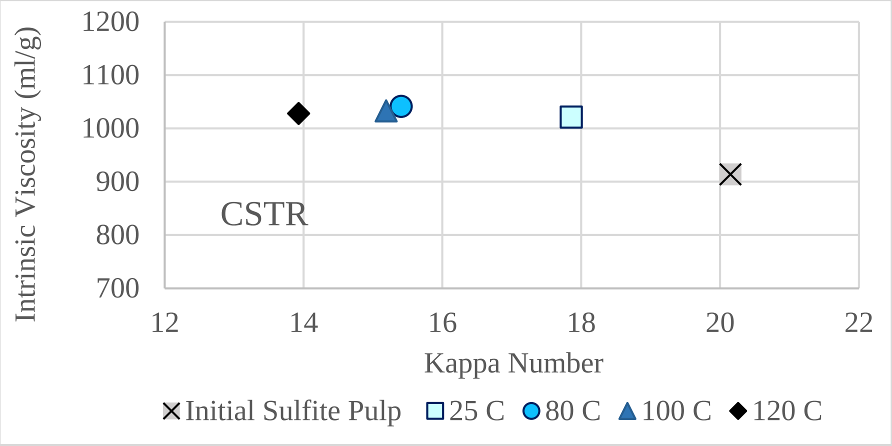


Figure 6.1. Effect of Pretreatment Temperature with 100 ppm $NaBH_4$ on Sulfite Pulp (Pretreatment[100ppm $NaBH_4$-3.3g/LNaOH-5min]-No Oxygen Delignification)

In Table 6.3, it is seen that the carbonyl group content after treatment with 100 ppm $NaBH_4$ at 25 °C for 5 minutes decreases slightly compared to that of the untreated pulp (1.75 vs 2.0 mmol/100 g o.d. pulp resp.), while there is a significant increase in intrinsic viscosity. This suggests that the carbonyl groups on cellulose, which are subject to β-alkoxy elimination and following chain cleavage, are easily reduced by $NaBH_4$, and that these carbonyl groups represent only a small fraction of the total carbonyl group content.

Alkaline treatment (3.3 g/L NaOH) with 100 ppm $NaBH_4$ at 120 °C results in a decrease of 6 kappa units, or 30%. This relatively large kappa decrease can be explained by the fact that this sulfite pulp has not previously been in contact with NaOH. The decrease in carbonyl content at temperatures above 25 °C seen in Table 6.3 is possibly due to the removal of these groups associated with hemicellulose and lignin.

Table 6.3. Effect of Temperature on Selectivity during 100 ppm $NaBH_4$ Pretreatment

	$NaBH_4$ Pretreatment Conditions				Carbonyl Contents (mmol/100g o.d. pulp)	Kappa Number	Intrinsic Viscosity (mL/g)
	Mixing Time (min)	Temp °C	NaOH (g/l)	$NaBH_4$ (ppm)			
Sulfite Pulp	—	—	—	—	2	20.15	914
	5	25	3.3	100	1.75	17.86	1021
	5	80	3.3	100	1.37	15.40	1041
	5	100	3.3	100	0.91	15.19	1033
	5	120	3.3	100	0.40	13.93	1028

Decomposition of $NaBH_4$ becomes more important at higher temperatures. However, even at the highest temperature of 120 °C only 11 % of $NaBH_4$ is decomposed after 5 minutes at 3.3 g/L NaOH (see Table 3.1). (Pozio, et al. 2008), (Rohm n.d.), (Valentina G.Minkina 2012).

Figure 6.2 shows the dissolution of lignin measured by UV during the 5-minute alkaline $NaBH_4$ treatment at different temperatures. When comparing the lignin concentration curves with the kappa reductions in Figure 6.2, it is clear that the lignin concentration at 120 °C is too high, presumably due to the removal of UV-colored material which originates from (degraded) hemicellulose rather than lignin at this high temperature as was earlier described in Chapter 5. The reduction in kappa number by 2 units at 25 °C shows that alkaline dissolution of sulfite lignin already takes place at room temperature, which was earlier found by Evstigneev (Evstigneev 2011).

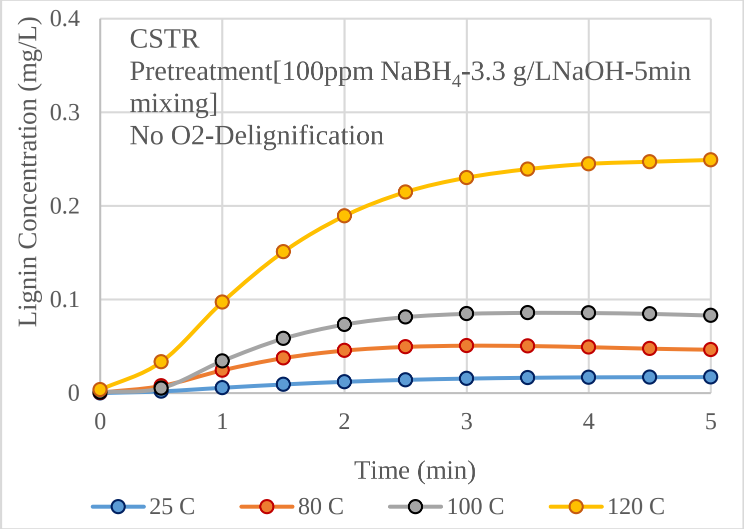


Figure 6.2. Dissolved Lignin Concentration versus Time at Different Temperatures

The effect of extending the time of 100 ppm $NaBH_4$ pretreatment beyond 5 minutes at 120°C on intrinsic viscosity-kappa selectivity is displayed in Figure 6.3 (a). It shows that the intrinsic viscosity increases by 80 mL/g while the kappa number decreases by 2.5 units when the pretreatment time is increased from 5 to 20 minutes (Figure 6.3 (c)). The carbonyl group content decreases to zero from 0.4 mmol/100 g pulp at 5 minutes after 10 and 20 minutes’ treatment. The further increase in intrinsic viscosity after 20 minutes pretreatment compared to 10 minutes when in both cases the carbonyl group content is zero may be explained by the loss of lignin and hemicellulose which increases the number of cellulose chains per gram of pulp, and thus the intrinsic viscosity if the average DP of the cellulose chains remains the same.

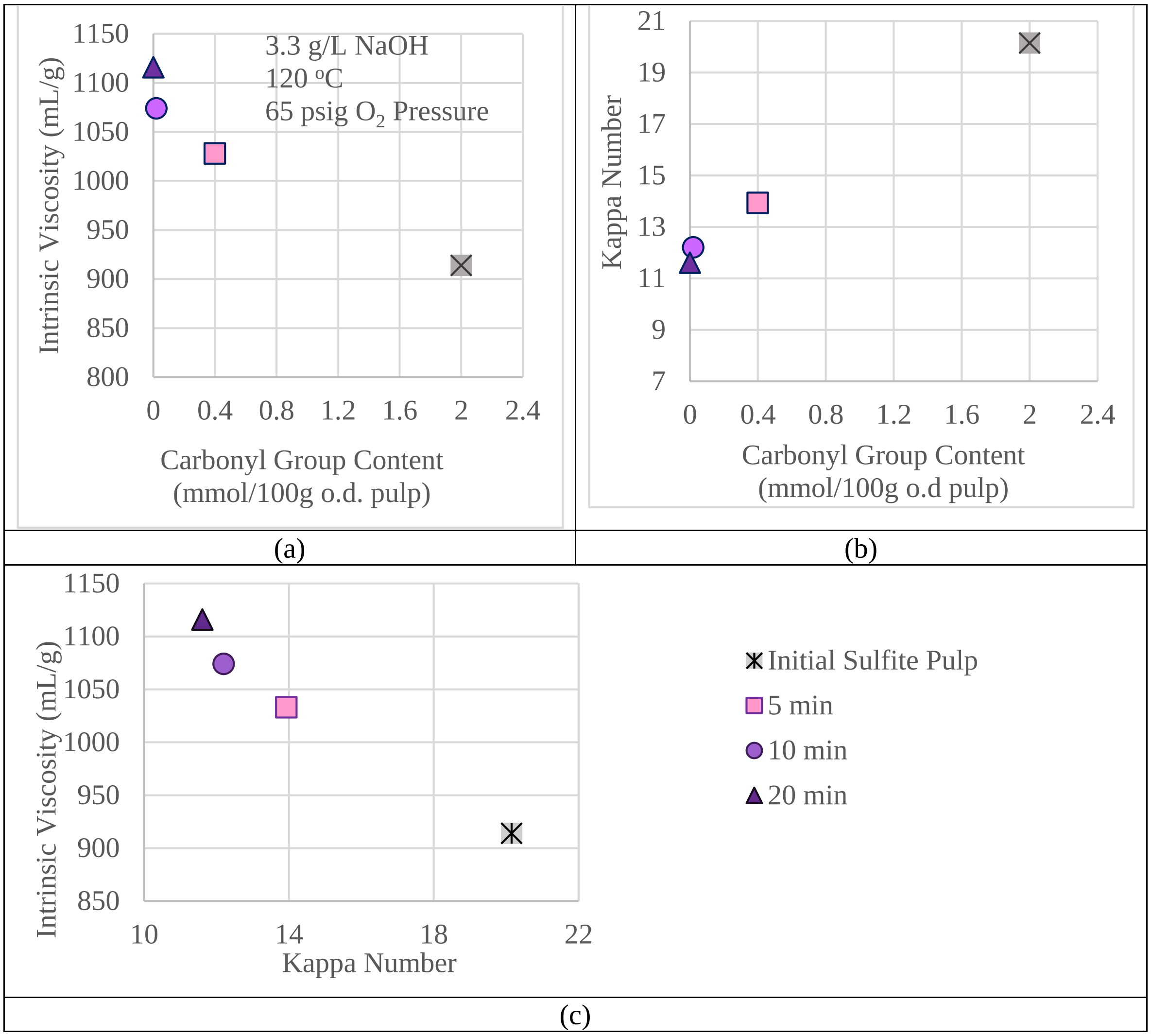


Figure 6.3. Effect of 100 ppm $NaBH_4$ Pretreatment Time on (a) Intrinsic Viscosity versus Carbonyl Group (b) Kappa Number versus Carbonyl Number (c) Viscosity-Kappa Selectivity Pretreatment[100ppm $NaBH_4$-3.3g/LNaOH-120ºC]- No O_2 Del-Sulfite Pulp-CSTR

The data in Figure 6.4 shows that the viscosity-kappa selectivity increases at a higher NaOH concentration (3.3 vs 1.1 g/L NaOH) during $NaBH_4$ pretreatment. This may be explained by the fact that more $NaBH_4$ is decomposed at lower alkalinity (Equation (3.22)). Table 3.1 shows that the $NaBH_4$ half-life at 3.3 and 1.1 g/L NaOH solution at 120 °C are 30 and 10 min respectively. Thus less $NaBH_4$ is available for carbonyl reduction at the lower alkalinity.

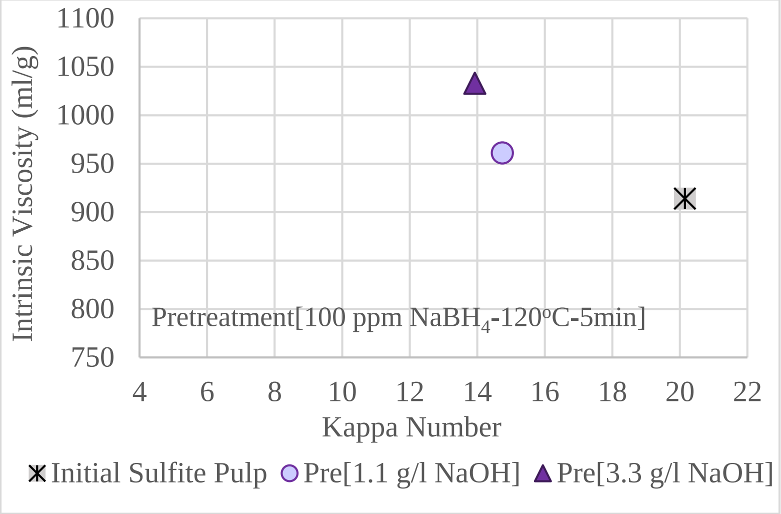


Figure 6.4. Effect of NaOH on Viscosity-Kappa Selectivity

During $NaBH_4$ Pretreatment of Sulfite Pulp at CSTR

6.2.2 Effect of $NaBH_4$ Pretreatment on Oxygen Delignification Selectivity in the CSTR

The effect of $NaBH_4$ pretreatment on the oxygen delignification selectivity of sulfite pulp was investigated in the CSTR reactor. In Figure 6.5. (a and b) the sulfite pulp is treated at different concentrations of $NaBH_4$ (0, 30, and 100 ppm) in 3.3 g/L NaOH solution at 80 °C for 5 minutes followed by oxygen delignification at 100 °C using overnight oxygenated caustic (3.3 g/L NaOH) at an oxygen pressure of 65 psig at room temperature. As expected for sulfite pulp, $NaBH_4$ has a significant impact on the selectivity since sulfite pulp contains a high amount of carbonyl groups (Table 6.1), the $NaBH_4$ converts the carbonyl groups on cellulose into alditols to protect cellulose from cleavage by β-elimination (Browning 1967). The data in Figure 6.5 (b) shows that the selectivity improves by about 50% compared to the control (0 ppm NaBH4) with 30 ppm $NaBH_4$ and by about 100% at 100 ppm $NaBH_4$.

In Figure 6.5 (a) it is also important to notice that the increase in intrinsic viscosity due to $NaBH_4$ pretreatment is essentially maintained, while the kappa numbers of the three pulps are all around 6.5. Thus, $NaBH_4$ pretreatment has a positive impact on intrinsic viscosity, but no effect on delignification of the final oxygen delignified sulfite pulp.

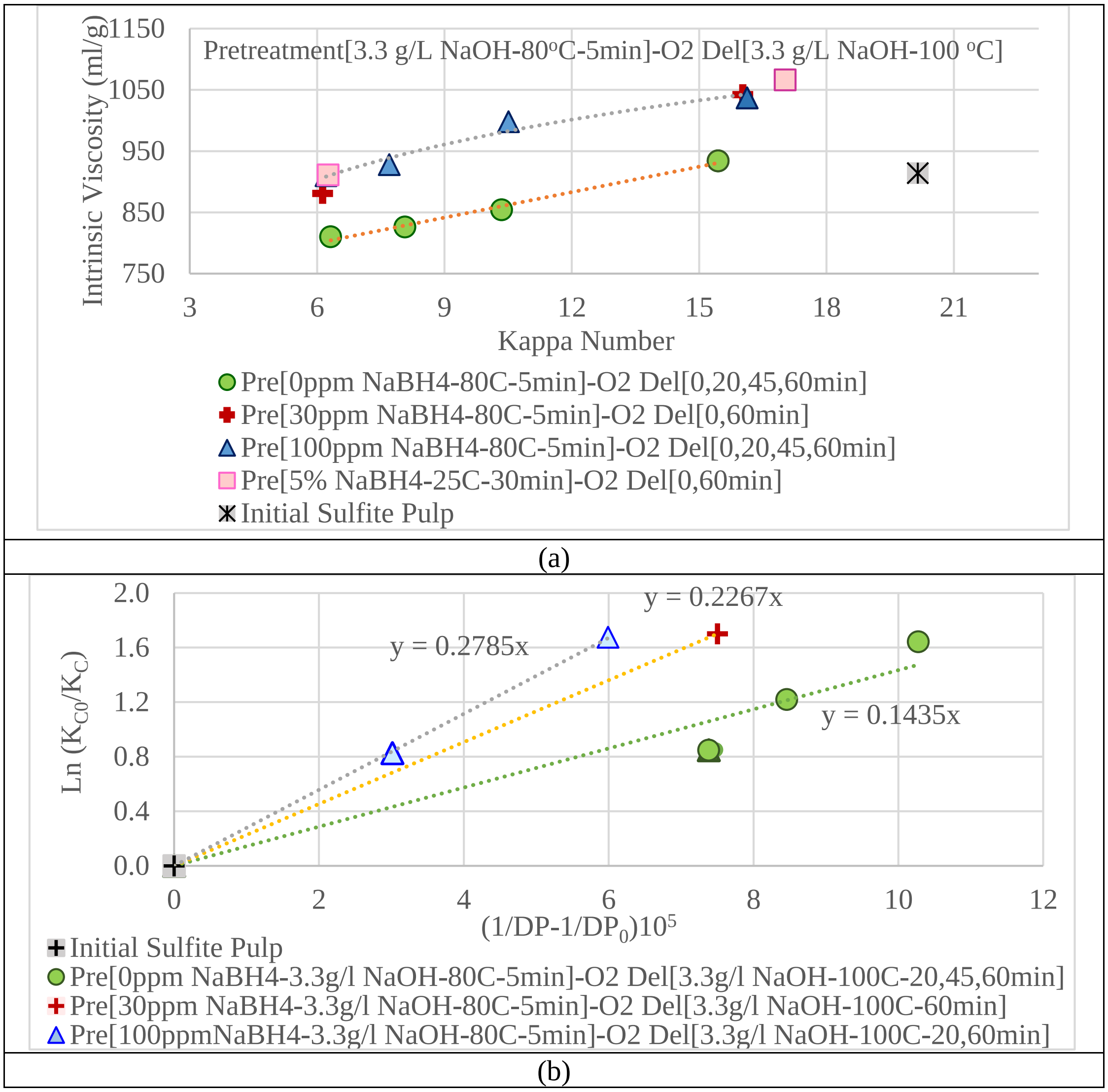


Figure 6.5. Effect of $NaBH_4$ on (a) Viscosity-Kappa Selectivity

(b) $Ln[K_{C0}/K_C]$ versus $(1/DP-1/DP_0)10^5$ Selectivity

In Table 6.4, the influence of $NaBH_4$ on the reduction of carbonyl groups in the sulfite pulp is represented. As can be seen, after 5 min mixing with 0, 30, 100 ppm, and 5% (based on pulp weight) $NaBH_4$ and 3.3 g/L NaOH at 80 ^oC in the absence of oxygen, the carbonyl group content decreases by 9, 25, 31, and 51%. This shows that $NaBH_4$ was able to reduce the carbonyl groups at the pretreatment condition (5 min mixing, 80 ^oC, 3.3 g/L NaOH). After 60 min oxygen delignification, the carbonyl group content was again measured (Table 6.4). It can be seen that the carbonyl groups are (almost) completely removed after 60 minutes. The carbonyl groups remaining after $NaBH_4$ pretreatment are located on hemicellulose and lignin, not on cellulose. Therefore, it suggests that oxygen delignification converts these remaining carbonyl groups to carboxyl groups, and/or they are removed from the pulp by dissolution because these oxidized lignin and hemicellulose fragments are more hydrophilic.

Table 6.4. Effect of Different Concentrations of $NaBH_4$ on Carbonyl Group Content

T (^oC)	$NaBH_4$ (ppm)	Pretreatment Mixing Time (min)	Carbonyl Group Content (mmol/100g o.d. pulp)	O_2-Delignification Time (min)	Carbonyl Group Content (mmol/100g o.d. pulp)
-	-	0	2	0	2
80	0	5	1.82	60	0.167
80	30	5	1.49	60	0
80	100	5	1.37	60	0
25	5% on Pulp weight	30	0.969	60	0

6.3 Kraft Pulp

6.3.1 Effect of Operating Conditions on Selectivity during $NaBH_4$ Pretreatment in CSTR

- **Different Concentrations of $NaBH_4$**

The effect of three different $NaBH_4$ concentrations (0, 30, and 100 ppm) on oxygen delignification/cellulose degradation selectivity was investigated on the conventional kraft pulp (kappa number 24.42, and intrinsic viscosity 996 mL/g). The pretreatment was done in the presence of $NaBH_4$ in 3.3 g/L NaOH solution at 80 °C for 5 minutes mixing, followed by oxygen delignification at 100 °C and 120 psig total pressure with 3.3 g/L NaOH (3.3 g/L NaOH caustic solution saturated with oxygen at 65 psig at room temperature) (see Subchapters 4.4.1 and 4.4.2) for more pretreatment and reaction details respectively). The results in Figure 6.6 show that $NaBH_4$ pretreatment does not significantly improve the viscosity-kappa selectivity compared to no $NaBH_4$ pretreatment. This is understandable since the conventional kraft pulp does not contain carbonyl groups (Table 6.1).

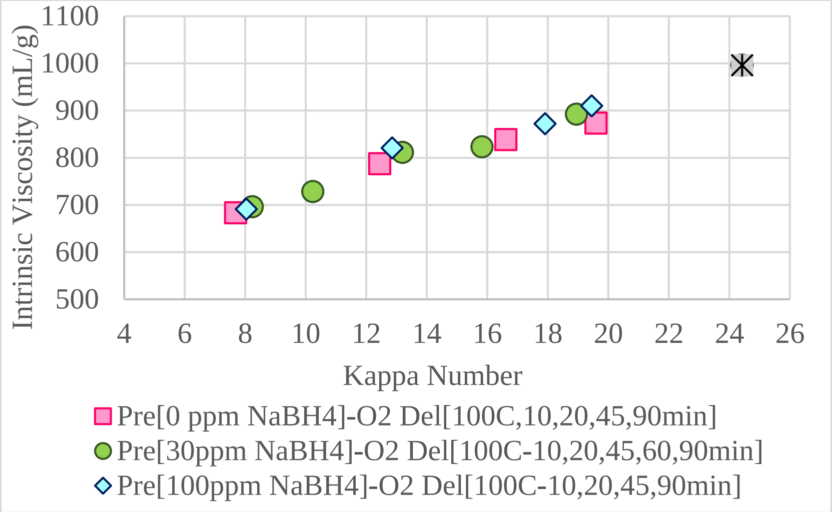


Figure 6.6. Effect of $NaBH_4$ on Selectivity of Kraft Pulp at CSTR Pretreatment[3.3 g/L NaOH-80^{o}C-5min]-O_2 Del[3.3 g/L NaOH-100^{o}C]

In Figure 6.7, the selectivity is investigated by plotting $Ln[K_{c0}/(K_{ct}Y_t)]$ against $1/DP-1/DP_0$ for oxygen delignification of the kraft pulp at 100 °C and 3.3 g/L NaOH for 20, 45, and 90 min after pretreatment with 0 and 100 ppm $NaBH_4$+3.3 g/L NaOH for 5 minutes at 80 °C. K_{c0} and K_{ct} are kappa numbers corrected for HexA (Kappa-HexA/10) at time 0 and t (min) respectively, and Y_t is the oxygen delignification pulp yield at time t. This figure clearly shows that $NaBH_4$ as a reduction agent has no effect on selectivity for conventional kraft pulp.

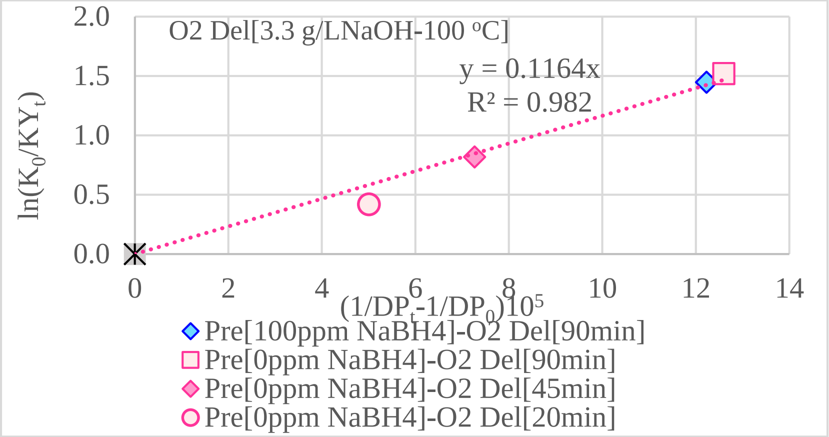


Figure 6.7. Ln[$K_{c0}/(K_{ct}Y_t)$] vs (1/DP-1/DP_0)10^5 of Kraft Pulp at CSTR Pretreatment[3.3g/LNaOH-80°C-5min]-O_2 Del[3.3g/LNaOH-100°C]

- **Effect of Temperature**

In Figure 6.8, the impact of temperature on selectivity in the presence and absence of $NaBH_4$ in the CSTR reactor is investigated. As can be seen by increasing the reaction temperature from 90 to 120 °C, $NaBH_4$ does not affect delignification both at 90 and 120 °C. However, the degree of delignification corrected for HexA increases from 61.9 to 93% by increasing the temperature from 90 to 120°C after 90 min of reaction. This implies that at the higher temperatures (T=120°C), the reactivity of the less reactive lignin moieties (non-phenolic lignin) would increase. Also, as can be seen, the effect of $NaBH_4$ on cellulose degradation is not significant (Figure 6.8) because the cellulose of conventional kraft pulp does not contain carbonyl groups. The data in Figure 6.8 (b) shows that the oxygen delignification selectivity is only slightly higher at 100 °C than at 120 °C. This has also been reported by others (Y. Ji 2007) (Jafari 2015).

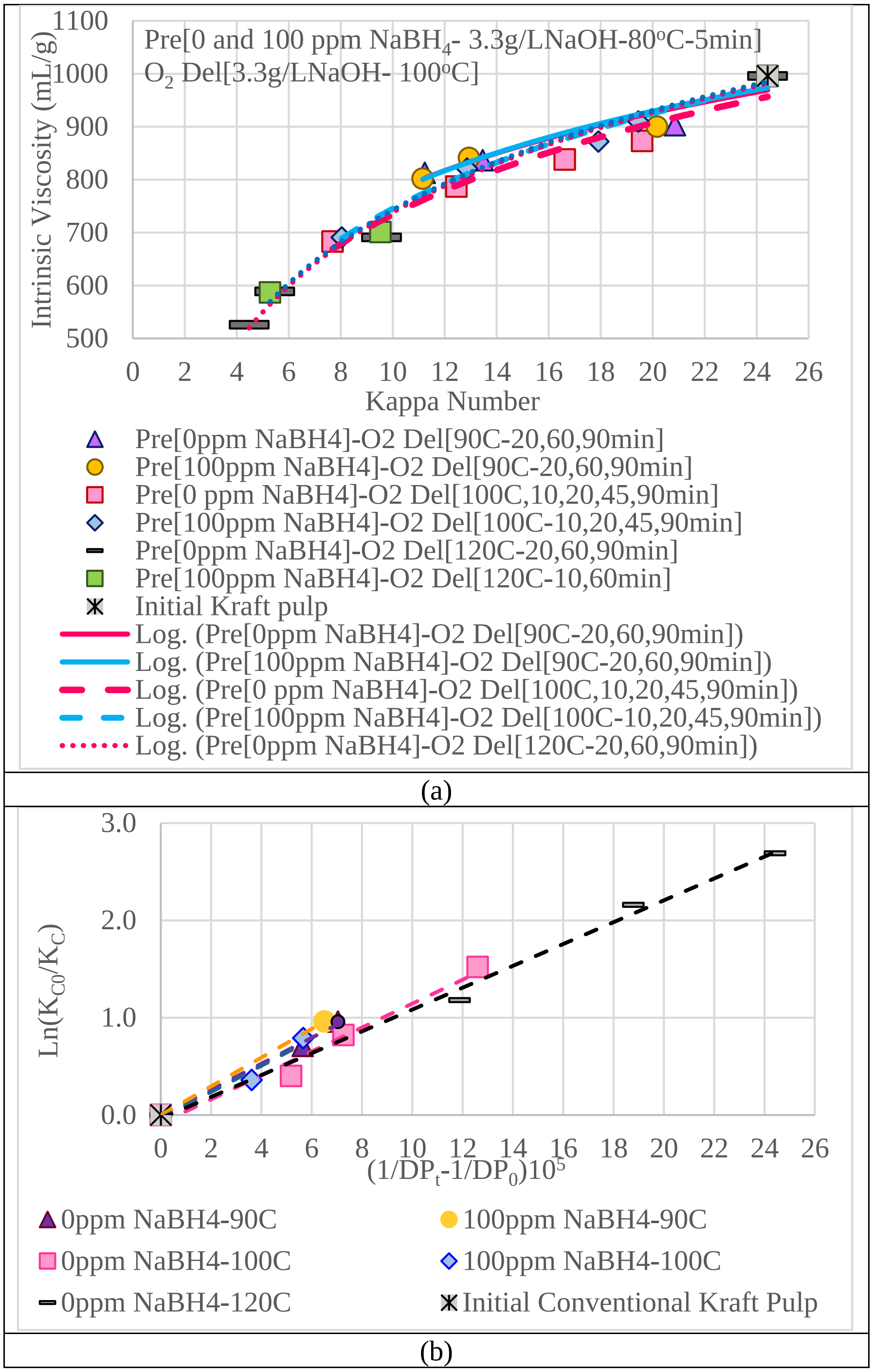
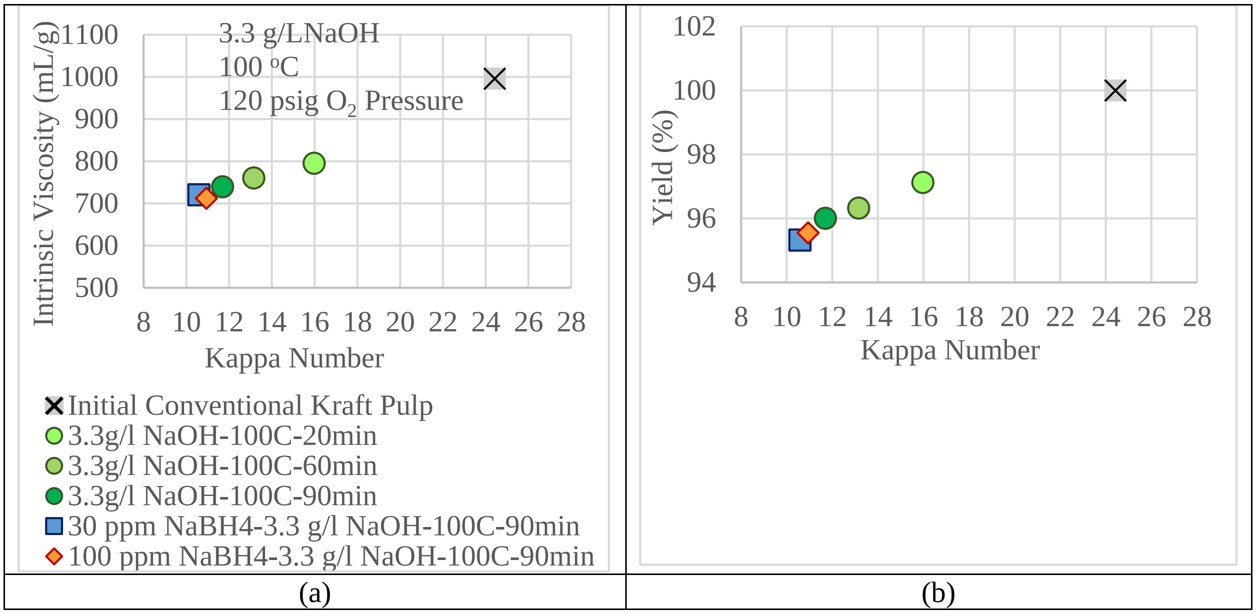


Figure 6.8. Effect of Temperature on Selectivity (a) Viscosity/Kappa Selectivity (b) $Ln(K_{C0}/K_C)/(1/DP_t-1/DP_0)10^5$ Selectivity in the Presence and Absence of $NaBH_4$ Pretreatment[0, 100 ppm $NaBH_4$- 3.3g/LNaOH-80ºC-5min]-O_2 Del[3.3g/LNaOH]

6.3.2 Effect of $NaBH_4$ on Oxygen Delignification Selectivity in Batch Reactor

The impact of 0, 30, and 100 ppm $NaBH_4$ pretreatment on oxygen delignification selectivity and pulp yield in the Batch (Parr) reactor is shown in Figure 6.9 (a and b) respectively. The pretreatment was done with the presence of $NaBH_4$ in 3.3 g/L NaOH solution at 90 °C for 20 min mixing in the absence of oxygen and followed by oxygen delignification at 100 °C and 120 psig O_2 pressure. It can be seen that the selectivity is not affected by the addition of 100 ppm $NaBH_4$ as expected. Based on the absence of carbonyl groups in the kraft pulp matrix (Table 6.1), cellulose cleavage due to alkaline β-elimination will not occur, and treatment with $NaBH_4$ will not improve the pulp viscosity.



(a) (b)

Figure 6.9. Effect of $NaBH_4$ at Different Concentrations (0, 30, and 100 ppm) on (a) Intrinsic Viscosity/Kappa Selectivity (b) Pulp Yield versus Kappa in Batch (Parr) Reactor

The original working hypothesis of the present study was that $NaBH_4$ pretreatment would improve the intrinsic viscosity of conventional kraft pulp sufficiently to overcome the extra degradation of cellulose when oxygen delignification was extended to about 80% kappa reduction.

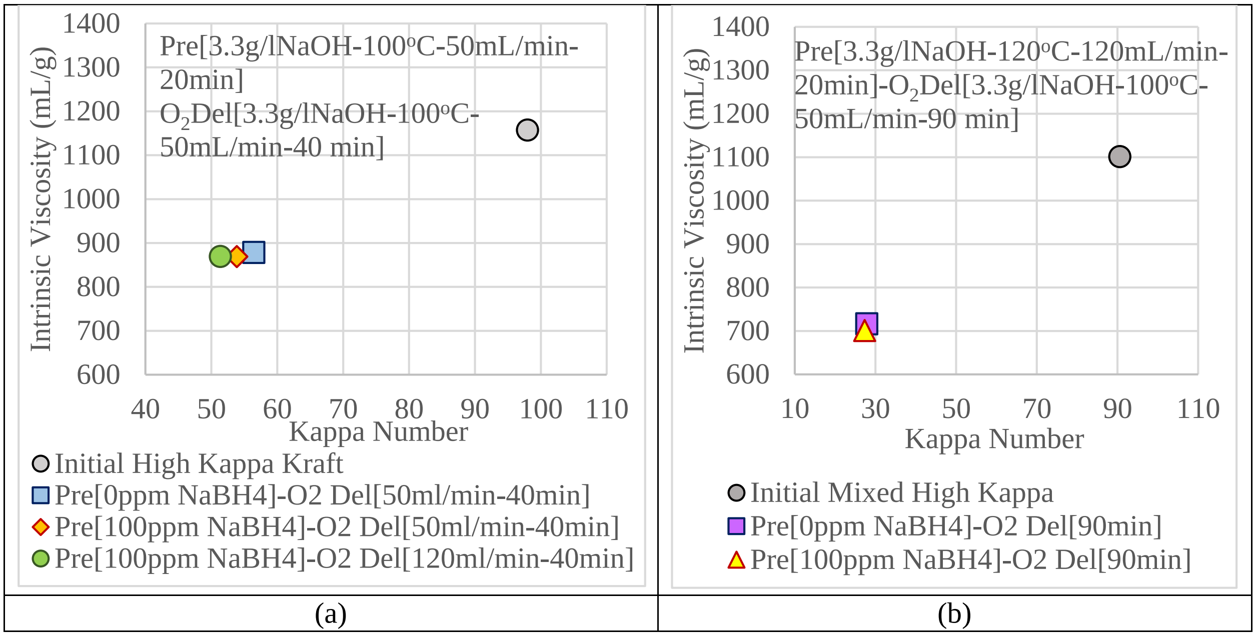
This was based on the significant improvements in intrinsic viscosity obtained by Jafari in 2015 when applying $NaBH_4$ at very small concentrations during oxygen delignification of a high (65) kappa Pine kraft pulp (Jafari 2015). Jafari did not measure the carbonyl group content of the high kappa pulp. However, as shown in Figure 6.8, $NaBH_4$ pretreatment did not result in an improvement of the intrinsic viscosity because the present conventional softwood kraft pulp (kappa 24) did not contain carbonyl groups. Therefore, we decided to test our original working hypothesis on a laboratory-created high kappa Southern Pine kraft pulp (kappa 98) which had a significant amount of carbonyl groups (2.32 mmol/100g o.d. pulp). This will be discussed in the next section.

6.4 High Kappa Kraft Pulp

Since the high kappa kraft contains a high amount of carbonyl groups (Table 6.1) it was expected that $NaBH_4$ pretreatment would protect cellulose from the β-elimination reaction, and thus lead to a significant increase in oxygen delignification selectivity.

However, as shown in Figure 6.10, no improvement in selectivity is obtained with the addition of 100 ppm $NaBH_4$ during pretreatments. In Figure 6.10 (a), the pretreatment was done at 100 ^{o}C at a flow rate of 50 mL/min for 20 min and followed by oxygen delignification at 100 ^{o}C at a flow rate of 50 mL/min for 40. However, no improvement in intrinsic viscosity is observed. In Figure 6.10 (b), the pretreatment was done at a higher temperature (120 ^{o}C) and a high flow rate (120 mL/min), and the oxygen delignification was performed at 100 ^{o}C for a longer reaction time (90min) compared to 40 minutes used for experiments presented in Figure 6.10 (a). The increased flow rate from 50 to 120 mL/min slightly increased delignification which is expected because at a low flow rate the Berty reactor does operate less as a differential reactor. As can be seen, again no improvement in intrinsic viscosity is obtained with or without $NaBH_4$ added during pretreatment. The likely explanation for this behavior is that the carbonyl groups are not located on the cellulose but on hemicellulose and lignin. Potthast and colleagues also believe that in kraft pulp, carbonyl groups are mostly located on hemicellulose rather than cellulose since hemicelluloses act as sacrificial substrates and protect cellulose from being oxidized (Potthast, Rosenau and Kosma 2006).

Alternatively, in this high kappa kraft pulp the presence of a high amount of transition metals (Table 4.3), which may catalyze the formation of radicals, cellulose degradation can be another reason why we did not see any improvement in selectivity by $NaBH_4$ addition.



(a) (b)

Figure 6.10. Effect of $NaBH_4$ on selectivity of the high kappa kraft pulp (CSTR)

(a)Pre[3.3g/lNaOH-100^{o}C-50mL/min-20min]-O_2Del[3.3g/lNaOH-100^{o}C-50mL/min-40 min]

(b)Pre[3.3g/lNaOH-120^{o}C-120mL/min-20min]-O_2Del[3.3g/lNaOH-100^{o}C-50mL/min-90 min]

This raises the question as to why Jafari (2015) obtained an increased selectivity when applying $NaBH_4$ during oxygen delignification to a commercial high (65) kappa Pine kraft pulp, while this was not observed with the present study with a laboratory-created high kappa Southern Pine kraft pulp (kappa 98). Unfortunately, we do not have an answer to this question.

6.5 Effect of Additives and Reaction Conditions on Conventional Kraft Pulp Yield

In Figure 6.11, the carbohydrate degradation is investigated during oxygen delignification. The pulp yield loss (ΔY) is plotted against kappa number reduction (ΔKappa number) at different reaction conditions.

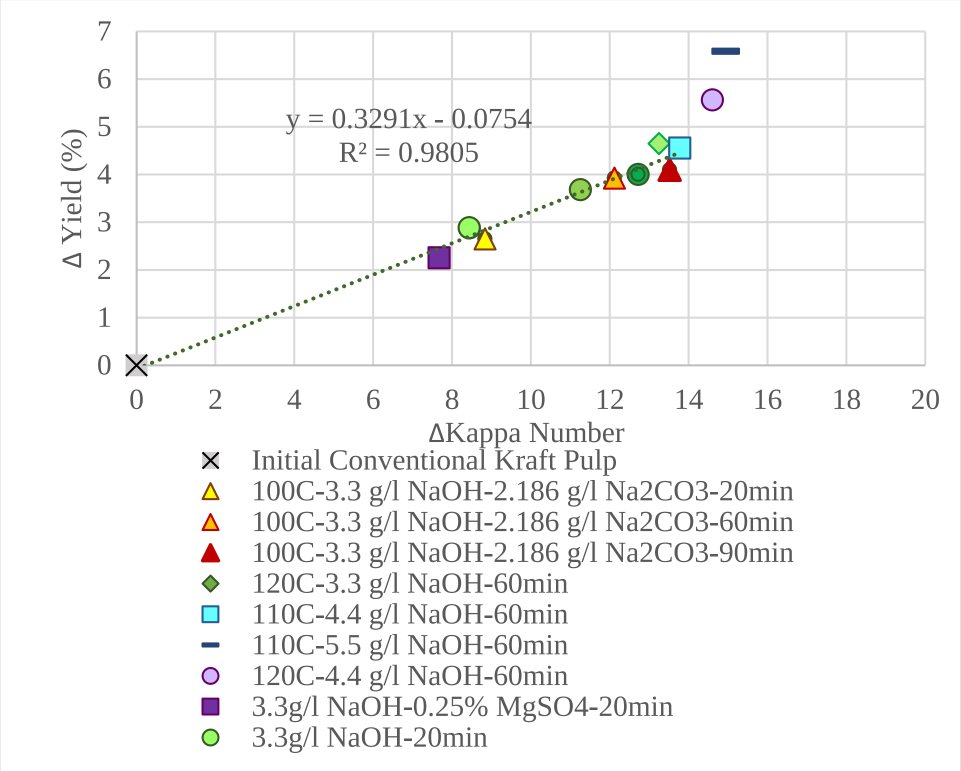


Figure 6.11. ΔYield versus Δkappa Number at

Different Reaction Conditions at Batch Reactor

Figure 6.11 shows a linear increase in pulp yield loss with kappa number reduction for all experimental data except at the highest temperature and alkali concentration (120 ^{o}C- 4.4 g/L NaOH and 110 ^{o}C- 5.5 g/L NaOH) for which pulp yield loss strongly increases with very little corresponding delignification. By ignoring these two extreme reaction conditions (120 ^{o}C, 4.4 g/L NaOH, and 110 ^{o}C, 5.5 g/L NaOH), the pulp yield loss can be described as:

$$\text{Pulp Yield Loss (\%)} = 0.329 \times \Delta\text{Kappa Number} \tag{6.1}$$

where, 0.329 is the slope of $\Delta Y/\Delta \text{Kappa}$ obtained in Figure 6.11.

In order to calculate the amount of carbohydrate remaining in the pulp pad as a function of kappa number reduction (ΔKappa number), the lignin amount in the pulp was measured as Klason lignin and then plotted against the kappa number reduction at different reactions conditions (Figure 6.12).

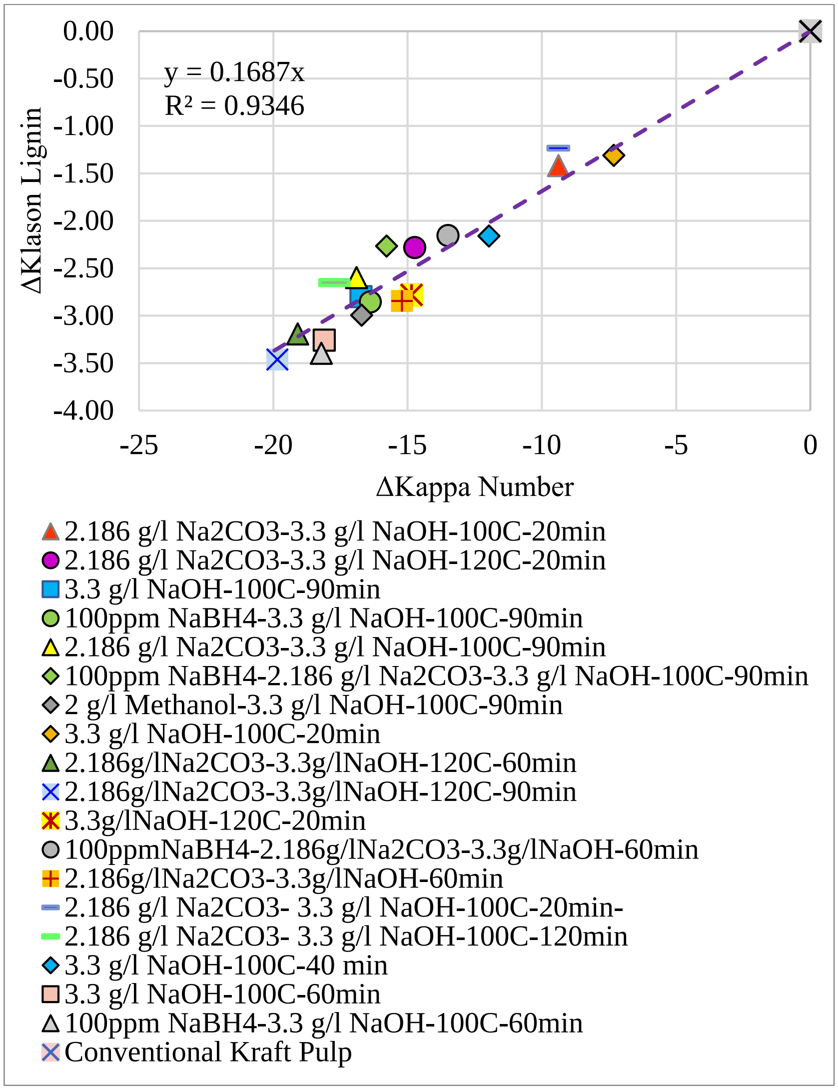


Figure 6.12. ΔKlason Lignin versus Δkappa Number

As can be seen, there is a linear relationship between the ΔKlason lignin and the Δkappa number reduction:

$$\text{Lignin Loss (\%)} = 0.168 \times \Delta\text{Kappa Number} \tag{6.2}$$

Thus, the correlation between ΔKlason lignin and kappa number reduction is 0.168 in softwood kraft pulp. Ji in 2007 took this value to be 0.15 (Y. Ji 2007).

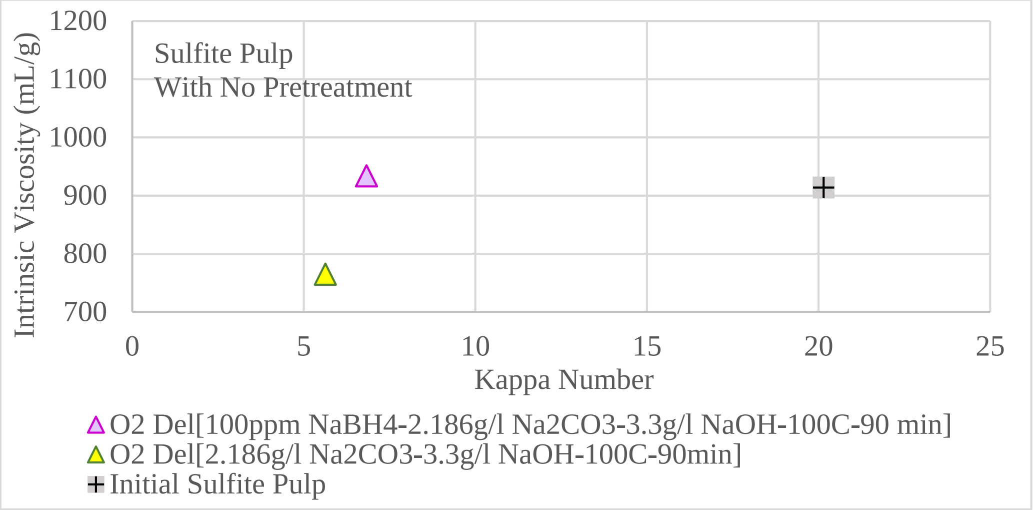
Now, by subtracting the lignin loss equation (6.2) from the pulp yield (6.1), the carbohydrate loss during oxygen delignification can be calculated:

$$\text{Carbohydrate loss (\%)}=0.161\times\Delta\text{Kappa Number} \tag{6.3}$$

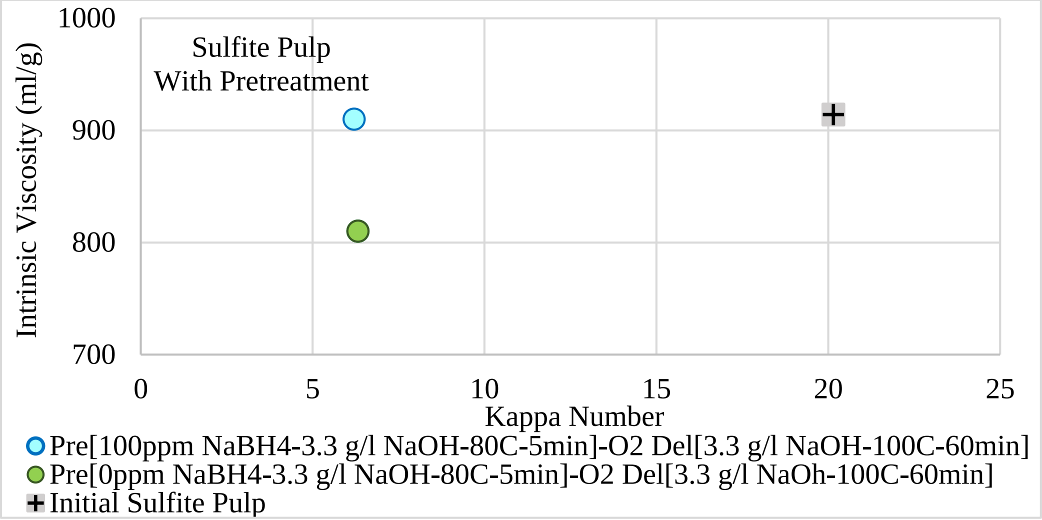
Thus based on Equations (6.2) and (6.3), almost equal weights of carbohydrates as that of lignin are dissolved at mild oxygen delignification conditions over a wide range of kappa removal. This is in agreement with the mechanism that carbohydrates are attacked by unselective oxygen radicals generated by the reaction between phenolic lignins and oxygen under alkali conditions.

6.6 Stability of $NaBH_4$ in an Oxygenated Caustic Solution

During our initial experiments, low concentration $NaBH_4$ (10-100 ppm) caustic solutions were prepared by direct addition to the caustic solution which was then oxygenated overnight and this solution was used to perform oxygen delignification of conventional kraft pulp which was the focus of this thesis. These experiments showed that $NaBH_4$ did not improve the delignification/cellulose degradation selectivity as was found by Jafari (Jafari 2015). This finding was initially blamed on the destruction of $NaBH_4$ by reaction with dissolved oxygen during the overnight oxygenation of the caustic solution. However, later it was found that the lack of selectivity improvement was due to the absence of carbonyl groups on cellulose in kraft pulp, Therefore we tried the original approach with sulfite pulp because this pulp has a carbonyl groups on its cellulose chains. Therefore, $NaBH_4$ was added to a 2.186 g/L Na_2CO_3+3.3 g/L NaOH solution at 100 ppm and subjected to one hour oxygenation at 65 psig at room temperature, followed by 90 minutes oxygen delignification at 100 ^oC. A control (0 ppm $NaBH_4$) was also performed. As can be seen in Figure 6.13 (a), 100 ppm $NaBH_4$ significantly increased the selectivity, thus no reaction between oxygen and $NaBH_4$ takes place duing caustic solution oxygenation. This increase in selectivity can also be seen when 5 minutes $NaBH_4$ pretreatment was performed before 60 minutes oxygen delignification. This confirms that $NaBH_4$ works both with pretreatment and when added to the NaOH (and then oxygenated) solution, thereby proving that $NaBH_4$ does not (or mostly not) react with oxygen in a caustic solution.



(a) No $NaBH_4$ Pretreatment
($NaBH_4$ was Directly Added in Caustic Solution and Then Oxygenated for 1h for O_2 Del)



(b) $NaBH_4$ Pretreatment followed by O_2 Del

Figure 6.13. Effect of $NaBH_4$ in the Oxygenated Caustic Solution on Oxygen Delignification (CSTR-Sulfite Pulp)

The results of the same approach and reaction conditions to conventional kraft pulp (kappa 24), i.e. oxygen delignification in the presence of $NaBH_4$, are seen in Figure 6.14. It shows that with the presence of $NaBH_4$ during oxygen delignification the selectivity is not affected. However, less delignification is obtained. A possible explanation for this effect may be that $NaBH_4$ reduces the reducing ends of hemicellulose in the kraft pulp which causes less delignification since there are lignins attached to the hemicellulose and when hemicellulose detaches from the pulp matrix, these lignins are also removed from the pulp (Y. Ji 2007). Further work must be done to done on this topic.

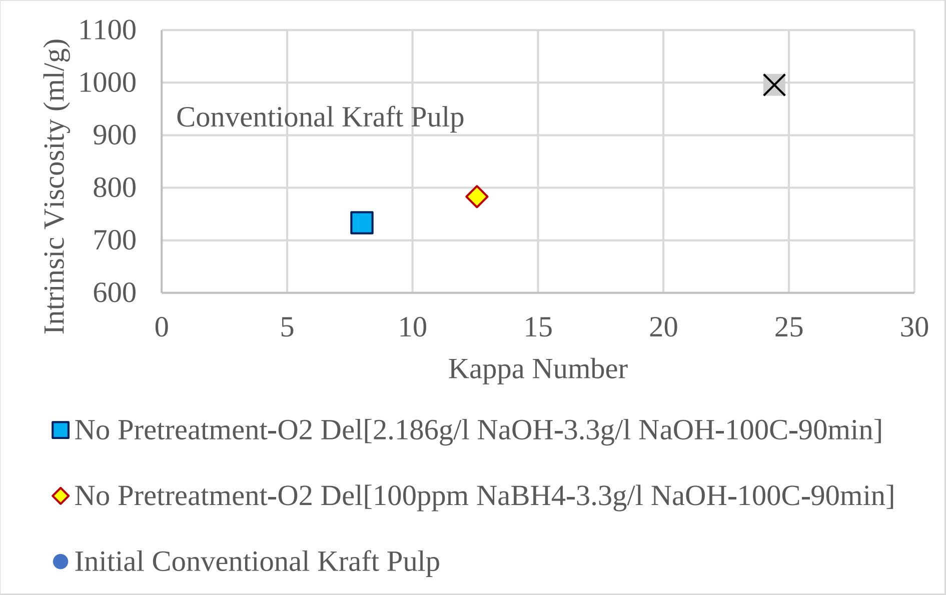


Figure 6.14. Effect of $NaBH_4$ in the Oxygenated Caustic Solution on Oxygen Delignification (No Pretreatment-CSTR-Conventional Kraft Pulp)

6.7 Conclusions

- $NaBH_4$ was able to reduce the carbonyl group content on sulfite pulp by 31% using a 5 minute mixing pretreatment at 80 °C in 3.3 g/L NaOH leading to an improvement in intrinsic viscosity of 100 mL/g and an increase in delignification/cellulose degradation selectivity of a factor 2. A reduction in carbonyl group content during subsequent oxygen delignification was observed as well, but this reduction of carbonyl content is likely caused by oxidation of the carbonyl groups on hemicellulose and lignin to carboxylic groups (Hosoya, et al. 2018)
- For the conventional kraft pulp, the selectivity is not affected by the addition of 100 ppm $NaBH_4$ because of the absence of carbonyl groups on cellulose in the kraft pulp, and no improvement in pulp viscosity and selectivity is seen.
- At mild oxygen delignification conditions over a wide range of kappa removal, almost equal weights of carbohydrates and lignin are dissolved. This is in agreement with the mechanism that carbohydrates and lignin are attacked by unselective oxygen radicals generated by the reaction between phenolic lignins and oxygen at alkaline conditions.
- $NaBH_4$ does not (or mostly not) react with oxygen in an oxygenated caustic solution. Therefore, $NaBH_4$ works both with pretreatment and when added to the NaOH (and then oxygenated) solution Less delignification takes place when $NaBH_4$ is present during oxygen delignification compared to the control without $NaBH_4$ present. This may be because $NaBH_4$ stabilizes the reducing ends of hemicellulose in the kraft pulp which leads to less peeling delignification since there are lignins attached to the hemicellulose and when hemicellulose detaches from the pulp matrix, these lignins are also removed from the pulp (Y. Ji 2007).

CHAPTER 7

IMPROVING SELECTIVITY VIA HYDROXYL RADICAL SCAVENGERS

7.1 Introduction

The cleavage of cellulose chains during oxygen delignification is mostly caused by reactive oxygen species formed when molecular oxygen reacts with phenolic lignin units to form intermediate peroxides. These peroxides then decompose via single electron transfer reactions to hydroxyl and oxyl radicals (A. J. van Heiningen 2019), (Y. V. Ji 2009). These radicals randomly attack the cellulose chains and oxidize them by forming carbonyl groups (T. McDonough 1996).

In this chapter, two pathways of protecting carbohydrates from degradation during oxygen delignification are proposed. One pathway is using additives that scavenge harmful radicals. As mentioned in chapter 3, the produced hydroxyl radicals are very unselective. Hydroxyl radicals can be scavenged via the mechanism of hydrogen atom abstractions and electron abstractions. The other pathway to minimize radical attack is to add chemicals that encapsulate or block the catalytic effect of transition metals on radical generation from peroxides. This will also be studied in this research. However, it would also be very beneficial if by the addition of the additives the degree of delignification could be increased for a standard softwood kraft pulp of 24 kappa numbers up to 80% while maintaining an acceptable cellulose Degree of Polymerization, DP, as calculated from the measured pulp intrinsic viscosity and also be environmentally and economically friendly.

Based on information gathered , we chose sodium carbonate, methanol, and glycerol as the radical scavengers (Stenman, et al. 2003) (Hu, et al. 2015), and magnesium sulfate as the transition metal encapsulator during oxygen delignification for the conventional kraft pulp in a through-flow reactor set-up (Berty reactor) and Batch (Parr Reactor).

7.2 Sodium Carbonate

It has been reported that carbonate ions react with hydroxyl radicals to form the more selective carbonate ion radicals (Equation (7.1).

$$CO_3^{-2} + HO^{\cdot} \rightarrow CO_3^{\cdot -} + OH^{-} \qquad (7.1)$$

It should be mentioned that the reaction rate constant of the carbonate anion radical ($CO_3^{2-\cdot}$) with carbohydrates and lignin model compounds are 10^5-10^6 and 10^8-10^9 ($M^{-1}s^{-1}$) respectively (at a pH of around 12), and the reaction rate constants of hydroxyl radical with both carbohydrates and lignin model compounds are 10^9-10^{10} ($M^{-1}s^{-1}$) (at a pH of around 12) (Carlsson, et al. 2003). Therefore, it was tested whether the addition of 2.186 g/LNa_2CO_3 (equivalent to 1.65 g/L NaOH relative to a 3.3 g/LNaOH solution) would improve the pulp intrinsic viscosity.

7.2.1 Oxygen Delignification with Sodium Carbonate in CSTR

In Figure 7.1, it is shown that the selectivity is increasing by the addition of 2.186 g/L Na_2CO_3 into the 1.65 and 3.3 g/L NaOH solution at 100 °C.

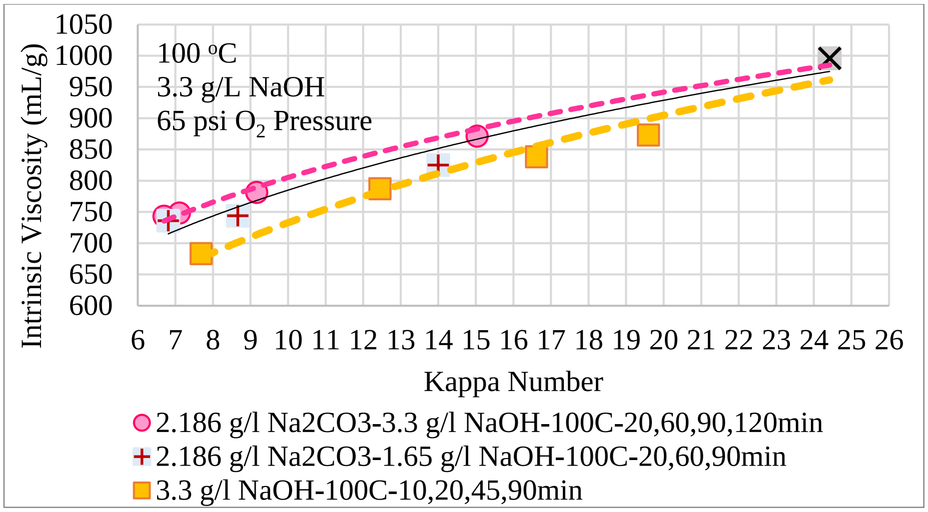


Figure 7.1. Intrinsic Viscosity/Kappa Selectivity at 100 °C-CSTR

When the data is plotted in terms of Equation (4.4) ($S_{\mathrm{KC}} = \frac{\ln\frac{L_0}{L_t \mathrm{Y}}}{\frac{1}{\mathrm{DP}_t}-\frac{1}{\mathrm{DP}_0}} = \frac{\ln\frac{(\mathrm{K}_0-\frac{\mathrm{HexA}}{10})\times 1.5}{(K_t-\mathrm{HexA}/10)\times 1.5\times \mathrm{Y}}}{\frac{1}{\mathrm{DP}_t}-\frac{1}{\mathrm{DP}_0}}$) in Figure 7.2, it can clearly be seen that the slope, S_{KC}, at 100 °C is about 43% higher with Na_2CO_3 addition.

In Figure 7.1, it is also shown that the kappa number at 100 °C for 90 minutes of oxygen delignification in the presence of 2.186 g/L Na_2CO_3 is about 7.1, which is equivalent to a HexA-corrected delignification of about 81%. This shows that we could extend the oxygen removable delignification up to 80% of conventional Southern Pine kraft pulp (about 24.4 kappa number) while maintaining acceptable intrinsic viscosity (>700 mL/g).

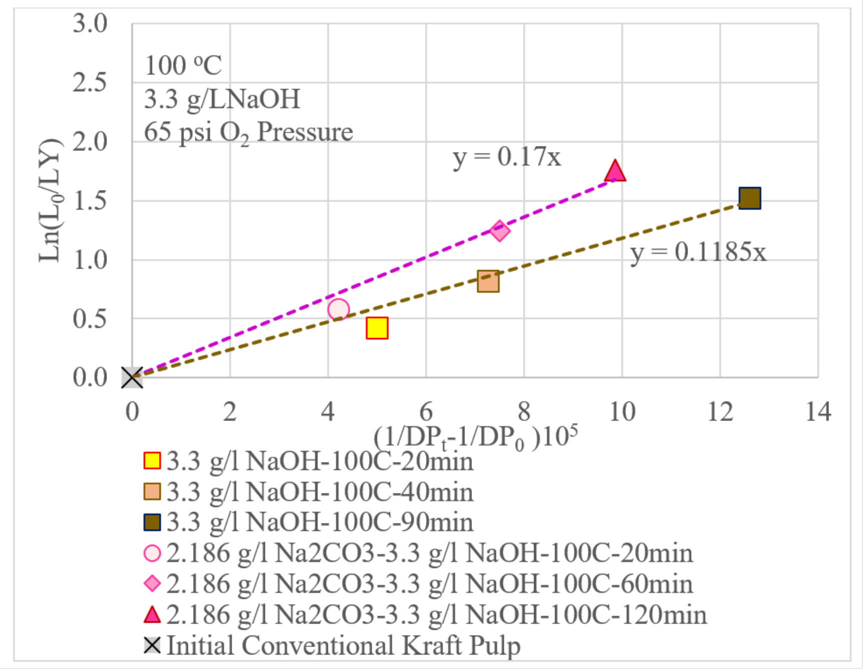


Figure 7.2. Ln[L_0/LY]/(1/DP_t-1/DP_0)10^5 Selectivity at 100 °C

The increase in selectivity by Na_2CO_3 addition suggests that at this range of alkalinity (12.55<pH<12.9), the positive radical scavenging effect of carbonate ions dominates the negative effect of increased pH on the selectivity (Norgren and Lindstrom 2000) at these operating conditions. As shown in Figure 3.1, the pKa of the equilibrium between hydroxyl and oxyl radicals is 11.9. It is known that oxyl radicals are even more unselective than hydroxyl radicals, and thus when the pH increases from slightly below to higher than pH 12, oxygen radicals will become more unselective. However, by adding 2.186 g/L Na_2CO_3 into a 1.65 or 3.3 g/L NaOH solution with the pH value of 12.55 and 12.9 respectively, the hydroxyl radicals may be scavenged by carbonate ions and then replaced by the selective radical ($CO_3^{2-\cdot}$), (Equation (*7.1*). Therefore, less hydroxyl radicals may be present in the system to cause cellulose degradation or even be converted into the more unselective radical (oxyl radical) at higher pH. This may be the explanation as to why at higher pH by increasing the NaOH concentration from 1.65 to 3.3 g/L in the presence of 2.186 g/L Na_2CO_3 (equivalent to 1.65 g/L NaOH) does not affect the reduction of kappa number and intrinsic viscosity (Figure 7.1). By adding 2.186 g/L of Na_2CO_3 into the 1.65 and/or 3.3 g/L NaOH, the pH of the solutions barely increases (the former and latter solutions have pH values of 12.5 and 12.8 respectively).

In Figure 7.3, it is shown that oxygen delignification at 120 ^{o}C decreases the kappa number down to 4.5 after 90 minutes for both 0 and 2.186 g/L Na_2CO_3+3.3 g/L NaOH caustic solutions, but at 40 mL/g higher intrinsic viscosity for the experiment with Na_2CO_3 addition.

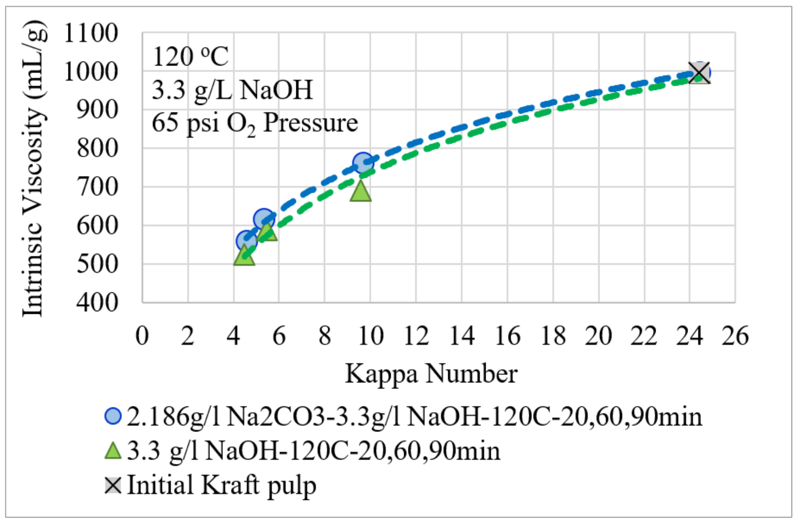


Figure 7.3 Intrinsic Viscosity/Kappa Selectivity at 120 °C

After correction for the non-reactive HexA content of 3 kappa units, this level of delignification to 4.5 - 3.0 = 1.5 kappa unit is equivalent to almost 93% HexA-corrected delignification. In comparison the kappa number at 100 °C for both systems after 90 minutes is about 7, which is equivalent to a HexA-corrected delignification of about 81%, showing that the delignification is greatly increased by increasing temperature. However, the intrinsic viscosity is also significantly reduced after 90 minutes at 120 °C.

The selectivity improvement by the addition of Na_2CO_3 at 120 °C is also shown in the selectivity plot in Figure 7.4.

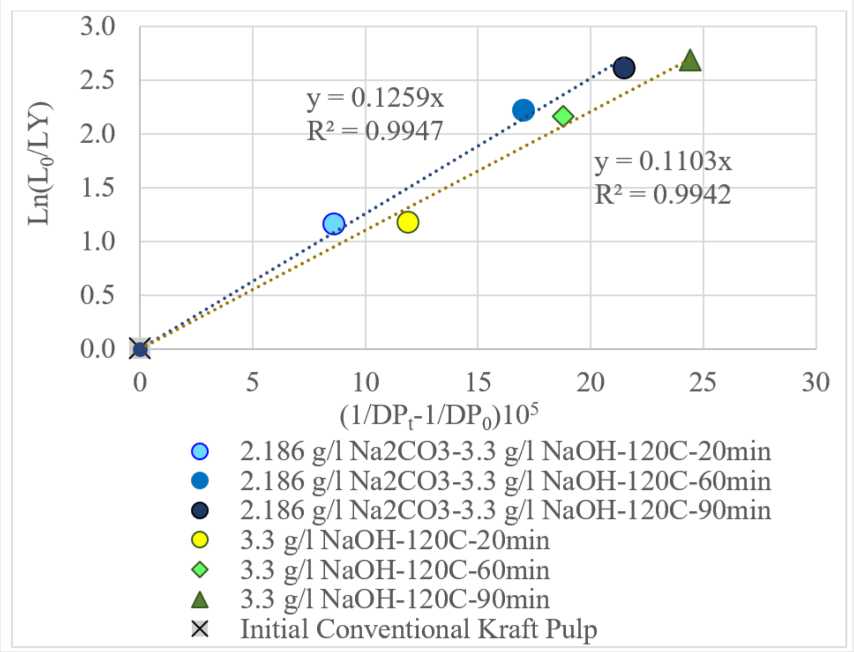


Figure 7.4 Ln[L_0/LY]/(1/DP_t-1/DP_0)10^5 Selectivity at 120 °C

This Figure shows that the addition of Na_2CO_3 leads to a selectivity (slope) improvement from 0.110 to 0.126 or a selectivity improvement of 15%. This improvement is smaller than the 43% improvement in selectivity seen in Figure 7.2, where the selectivity slope increased from 0.119 at 100 °C with only NaOH to 0.17 with 2.186 g/LNa_2CO_3 added to 3.3 g/L NaOH. The selectivity of the 4 cases is compared in Figure 7.5. This implies that by increasing the reaction temperature the lignin reactivity is significantly improved, but unfortunately, the improvement in the selectivity by the addition of 2.186 g/L Na_2CO_3 diminishes at the higher temperature.

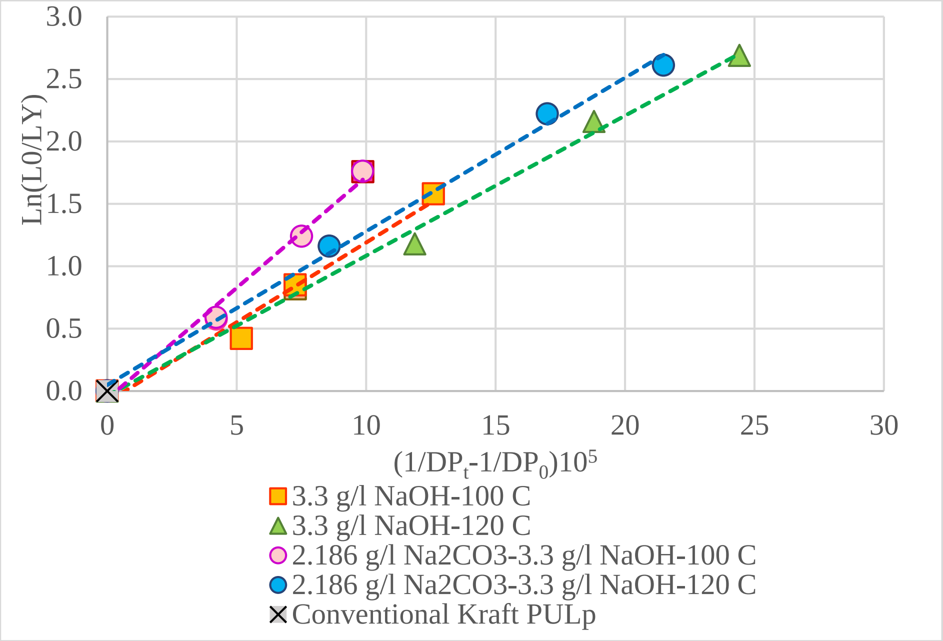


Figure 7.5 $\mathrm{Ln}[L_0/LY]/(1/DP_t-1/DP_0)10^5$ Selectivity at 120 °C

This suggests that the capture efficiency of the hydroxyl/oxyl radicals by carbonate diminishes at a higher temperature.

As can be seen in Figure 7.6, by increasing the amount of Na_2CO_3 from 2.184 to 4.372 g/L (equivalent to 1.65 and 3.3 g/L NaOH respectively) at 100 °C the selectivity does not increase further relative to the control of 3.3 g/L NaOH without any Na_2CO_3 addition.

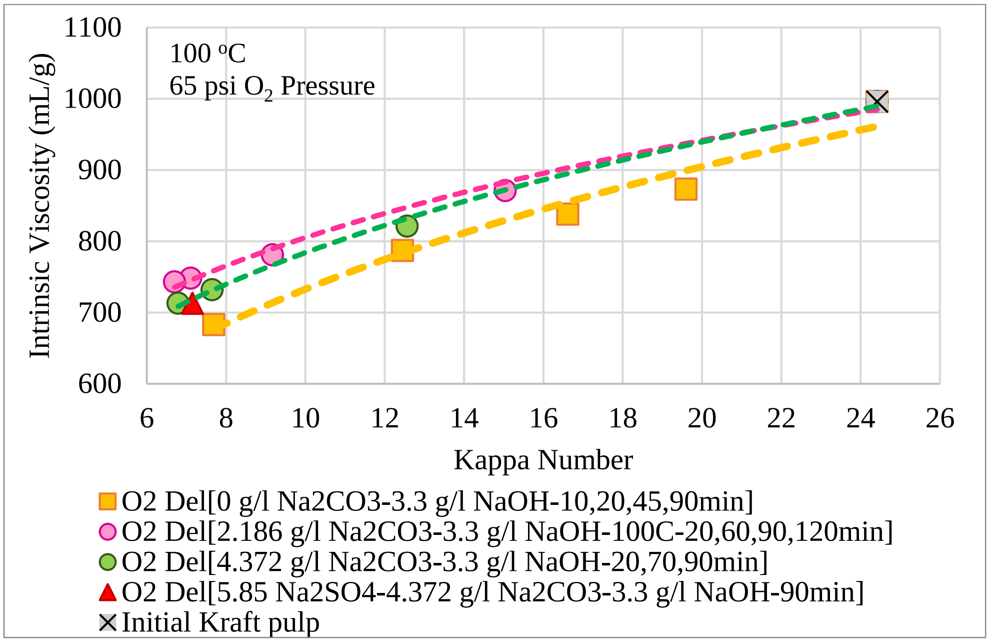


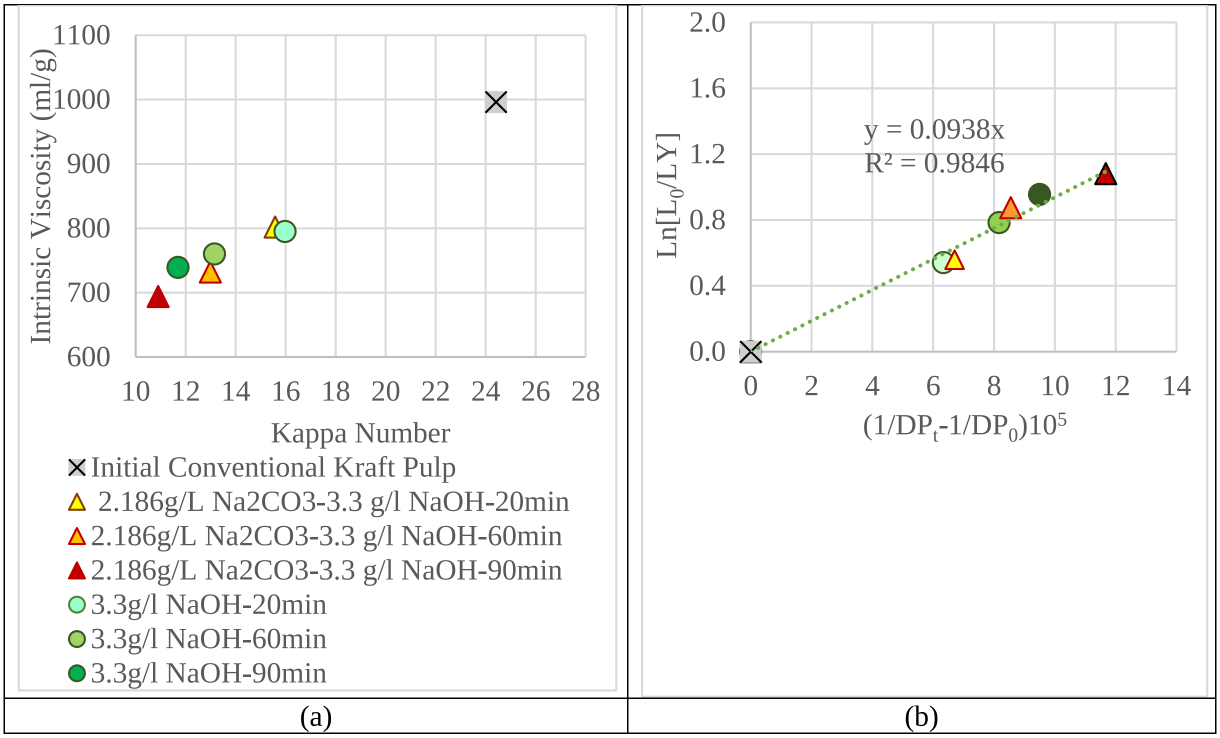
Figure 7.6. Effect of Different Concentrations of Na_2CO_3 and NaOH on Selectivity of Kraft pulp During Oxygen Delignification at 100 °C

It shows that the addition of 2.186 g/L Na_2CO_3 (50% as NaOH based on mol) is optimal for scavenging hydroxyl radical, and increasing the Na_2CO_3 concentration higher than 2.186 g/L would not cause any more improvement on selectivity. Thus it appears there is an optimum Na_2CO_3/NaOH molar ratio of about 0.5 to obtain the highest selectivity improvement by Na_2CO_3 addition.

The effect of ionic strength on selectivity was also studied to investigate whether the increased sodium ion concentration has any effect on the selectivity when 4.372 g/L Na_2CO_3 was added to the 3.3 g/L NaOH solution during oxygen delignification. Brannvall and Lindstrom in 2007 stated that a high ionic strength can slow delignification and lead to lower strength pulp during kraft cooking (Brännvall and Lindström 2007). Therefore, 5.85 g/L Na_2SO_4 (100% as NaOH) was added to the 4.372 g/L Na_2CO_3-3.3 g/L NaOH solution to increase the concentration of sodium in the solution. As can be seen in Figure 7.6, the addition of sodium sulfate did not significantly change the degree of delignification or cellulose degradation. Thus the ionic strength has no influence on the selectivity and delignification rate during oxygen delignification.

7.2.2 Oxygen Delignification with Sodium Carbonate in the Batch Reactor

Because oxygen delignification selectivity could be improved in the Berty reactor by the addition of Na_2CO_3, this effect was also studied in the Parr batch reactor. The effect of sodium carbonate on oxygen delignification and selectivity in the Batch reactor is shown in Figure 7.7 (a and b).



(a) (b)

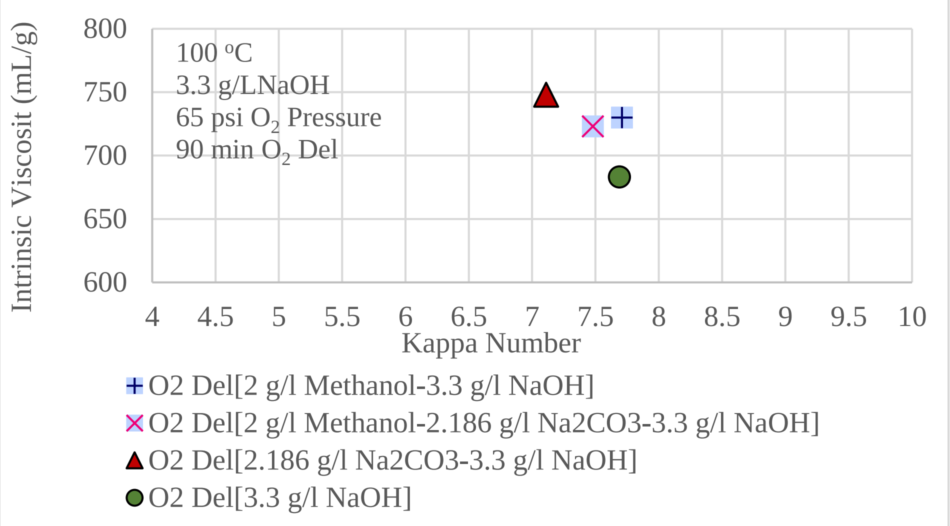
Figure 7.7. Effect of Na_2CO_3 on Selectivity at 100 ^{o}C

(a) Intrinsic Viscosity/Kappa Selectivity (b) $Ln[L_0/LY]/(1/DP_t-1/DP_0)10^5$ Selectivity

In Figure 7.7 (a), it can be seen that the data plots related to 20 and 60 min with and without 2.186 g/L Na_2CO_3 are almost on top of each other, and 2.186 g/L Na_2CO_3 increases delignification by one more kappa unit when the oxygen delignification is extended from 60 to 90 minutes. However by adding 2.186 g/L Na_2CO_3 no impact can be seen on selectivity (Figure 7.7. b). This is surprising and differs with the CSTR results. The key difference between the two reactor systems is that in the batch reactor the alkalinity decreases rapidly over time, while it remains constant in the CSTR. Thus most of the time the batch reactor operates at a high Na_2CO_3/NaOH molar ratio which as was shown earlier was not as efficient in scavenging hydroxyl radicals. However, Na_2CO_3 can increase delignification because it acts as a buffer (CO_3^{-2}/HCO_3^-) and does not let the pH inside the batch reactor drop by generating more NaOH ($Na_2CO_3 + 2H_2O \rightarrow 2NaOH + H_2O + CO_2$) during the oxygen delignification. As mentioned before, in the batch reactor the pH drops very fast because of the consumption of NaOH by organic acids formed during oxygen delignification. In Figure 7.11 (will be presented later) it can also be seen when the oxygen delignification is extended from 60 to 90 minutes, almost all of the effective alkali as NaOH is consumed since the pH of the oxygen delignification liquor is lower than 11.3 which is the limit for the existence of effective alkali as NaOH (SCAN-N 33:94). Thus it can be emplies that after 60 min oxygen delignification when almost all amount of NaOH is consumed, the addition of 2.186 g/L Na_2CO_3, the pH of the pulp suspension would not drop below 10, and lignin (with the pK_α of about 10.5) can still be dissociated and then be attacked by dissolved oxygen which causes more delignification.

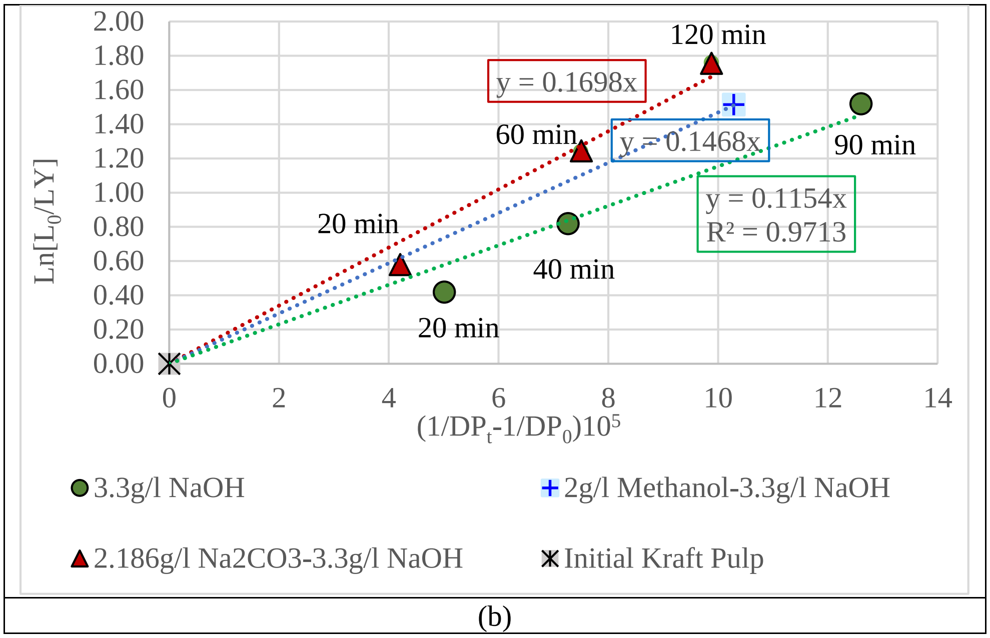
7.3 Effect of Methanol on Selectivity in the CSTR Reactor

Figure 7.8 (a) shows the impact of methanol addition on selectivity during oxygen delignification. By adding 2 g/L methanol into the caustic control (3.3 g/L NaOH), the intrinsic viscosity increases by nearly 50 mL/g, while the kappa number stayed the same as the control after 90 minutes at 100 ^{o}C. To evaluate whether there would be a synergy in the selectivity improvement by adding both methanol and Na_2CO_3, a mixture of 2 g/L CH_3OH and 2.186 g/L Na_2CO_3 in 3.3 g/L NaOH was also investigated. It can be seen that after 90 minutes of oxygen delignification this caustic mixture produced essentially the same selectivity and delignification as the 2 g/L methanol in 3.3 g/LNaOH, while the 2.186 g/L Na_2CO_3 in 3.3 g/L NaOH experiment achieved an increase in the intrinsic viscosity of about 70 mL/g and the kappa number decreased 0.6 units relative to the caustic control (3.3 g/L NaOH). Thus unfortunately there is no synergy between methanol and Na_2CO_3 as an additive with radical scavenging properties.



(a)

Figure 7.8 Continued.



(b)

Figure 7.8. Effect of Methanol on Selectivity in Comparison with Other Additives

(a) Intrinsic Viscosity/Kappa Selectivity (b) $Ln[L_0/LY]/(1/DP_t-1/DP_0)10^5$ Selectivity

7.4 Magnesium Sulfate Addition in the Batch Reactor

In Figure 7.9, the effect of magnesium sulfate on selectivity is investigated in the Batch reactor. As previously mentioned, $MgSO_4$ can protect cellulose chains by encapsulating the transition metals which accelerate the generation of radicals through the Fenton reaction. Therefore, 0.25 and 1% $MgSO_4$ (based on pulp weight) were used as an additive. As can be seen in Figure 7.9, addition of $MgSO_4$ has no effect on the selectivity.

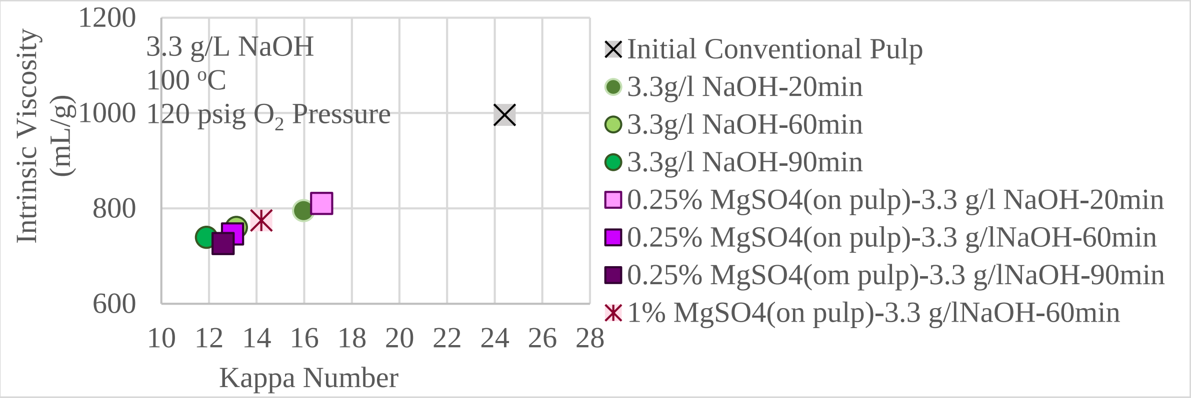


Figure 7.9. Impact of $MgSO_4$ on Viscosity/Kappa Selectivity

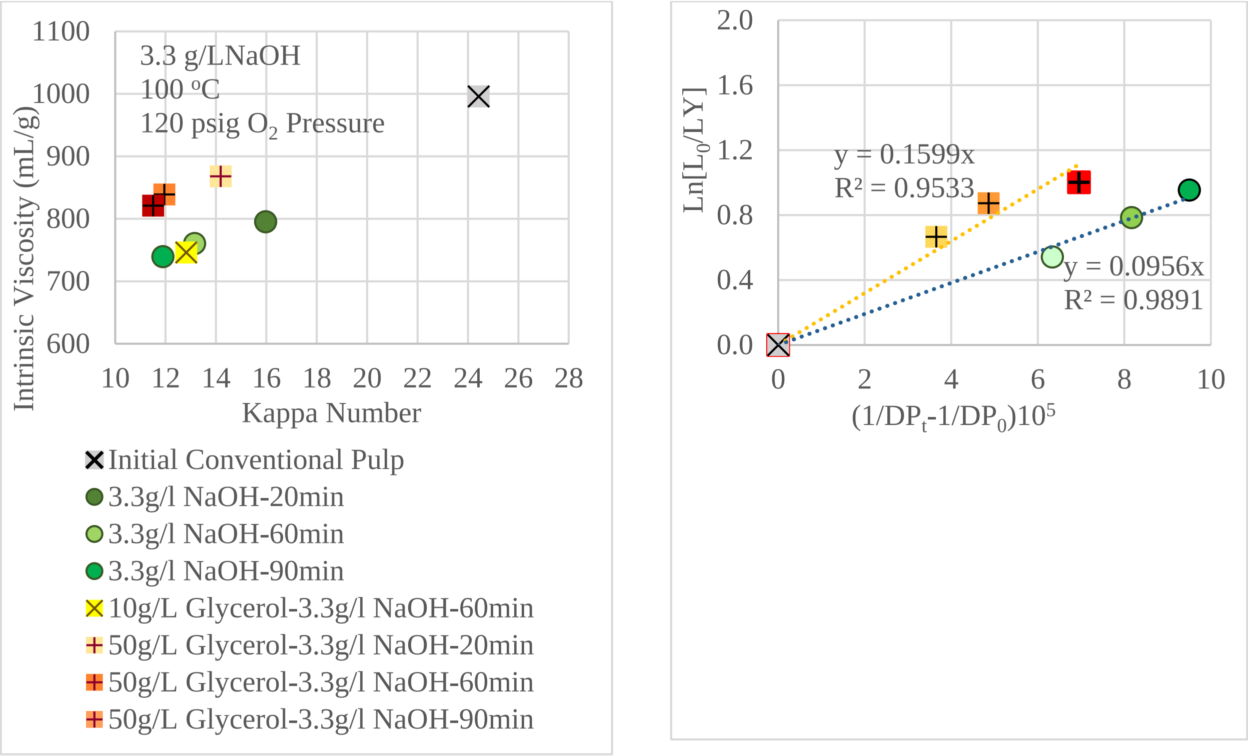
Since no improvement was obtained by the addition of 0.25 or 1% $MgSO_4$ (based on pulp weight), the transition metal contents of the pulp were also measured before and after each oxygen delignification reaction in the presence and absence of $MgSO_4$ (Table 7.1). As shown below, magnesium sulfate addition reduced the Fe^{+2} and Mn^{+2} content in the pulp after 60 min oxygen delignification, but the levels of Fe^{+2} and Mn^{+2} are still high. Huang and his colleagues in 2021 found that even 20 ppm metal (Mn^{2+}, Fe^{2+}, Cu^{2+}) can be enough for accelerating the generation of radicals. They also believe that $MgSO_4$ is more effective when there is a low level of Fe^{2+}, Cu^{2+}, and Mn^{2+} (Huang, H, et al. 2021). Thus, 0.25 and 1% $MgSO_4$ might not be sufficient for encapsulating and trapping the transition metals for our pulp with a high level of transition metals. Another possible explanation might be that the stainless steel Parr reactor might introduce these transition metals in the pulp by the intensive contact between the pulp and the reactor wall due to the pulp mixing by the rotating motion of the reactor.

Table 7.1. Effect of $MgSO_4$ on Reducing Transition Metals

Samples	Metal Content (mg /kg o.d. Pulp)						
	Ca	Cr	Cu	Fe	Mg	Mn	Ni
Initial Kraft Pulp	2360	UN	59.5	39.5	392	52	UN
3.3 g/LNaOH-100C-60min	1476	< 2.0	< 2.0	5128	496	71.1	< 2.0
1% $MgSO_4$-3.3 g/LNaOH-60 min	1910	< 2.0	37.3	3606	1697	36.8	< 2.0
0.25% $MgSO_4$-3.3 g/LNaOH-60 min	1913	< 2.0	27.0	2532	758	5.29	< 2.0

7.5 Effect of Glycerol on Selectivity at Batch Reactor

In Figure 7.10, the impact of glycerol addition on selectivity is investigated. As can be seen, the addition of 50 g/Lglycerol increased the selectivity ($S_{\mathrm{KC}} = \frac{\ln\frac{L_0}{L_t\mathrm{Y}}}{\frac{1}{\mathrm{DP}_t}-\frac{1}{\mathrm{DP}_0}}$) by 43% (Figure 7.10. b) which can be considered a significant improvement. Surprisingly, 10 g/L glycerol was ineffective in increasing the selectivity (Figure 7.10 a). The main mechanism of the positive effect of glycerol on selectivity is scavenging unselective radicals (Rosenblum and El-Sabban 1982).



(a) (b)

Figure 7.10. Effect of Glycerol on Selectivity at 100 ºC

(a) Intrinsic Viscosity/Kappa Selectivity

(b) $\mathrm{Ln}[L_0/LY]/(1/DP_t-1/DP_0)10^5$ Selectivity

It can be mentioned that the 50 g/L glycerol increases the selectivity because glycerol could reduce the carbonyl groups formed by the unselective radicals attack. This can be obtained from

Figure 7.14 (This figure will be presented later) that by addition of 50 g/L glycerol the carbonyl group decrease from 0.14 to 0.05 mmol/100g pulp o.d which is significant. In Figure 7.10, it is shown that there is minimal further delignification (and cellulose degradation) when the oxygen delignification is extended from 60 to 90 minutes. It was suspected that this was due to the consumption of almost all NaOH at 60 minutes. This was confirmed by the pH of the oxygen delignification liquor which was 11.15. This pH value is lower than 11.3 which is the limit for the existence of effective alkali as NaOH (SCAN-N 33:94). Therefore, phenolic delignification stops and thus also the associated hydroxyl radical generation and cellulose degradation.

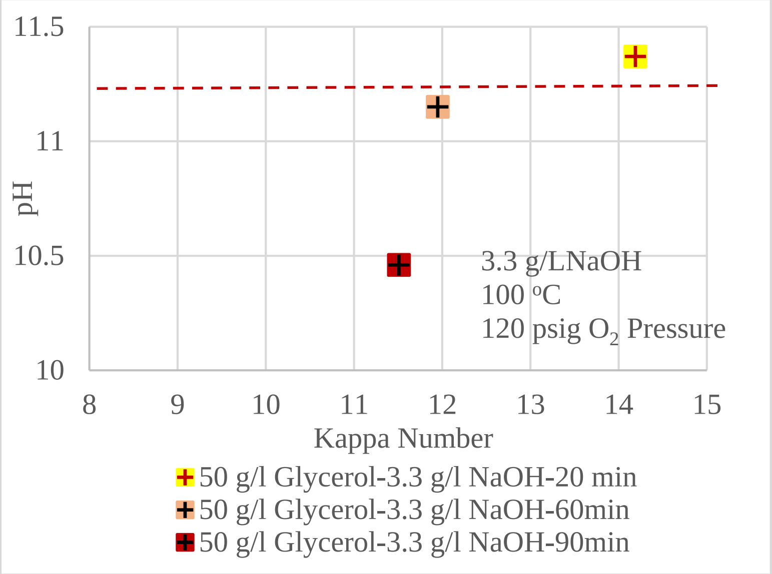


Figure 7.11. pH versus Kappa Number (T=100 °C)

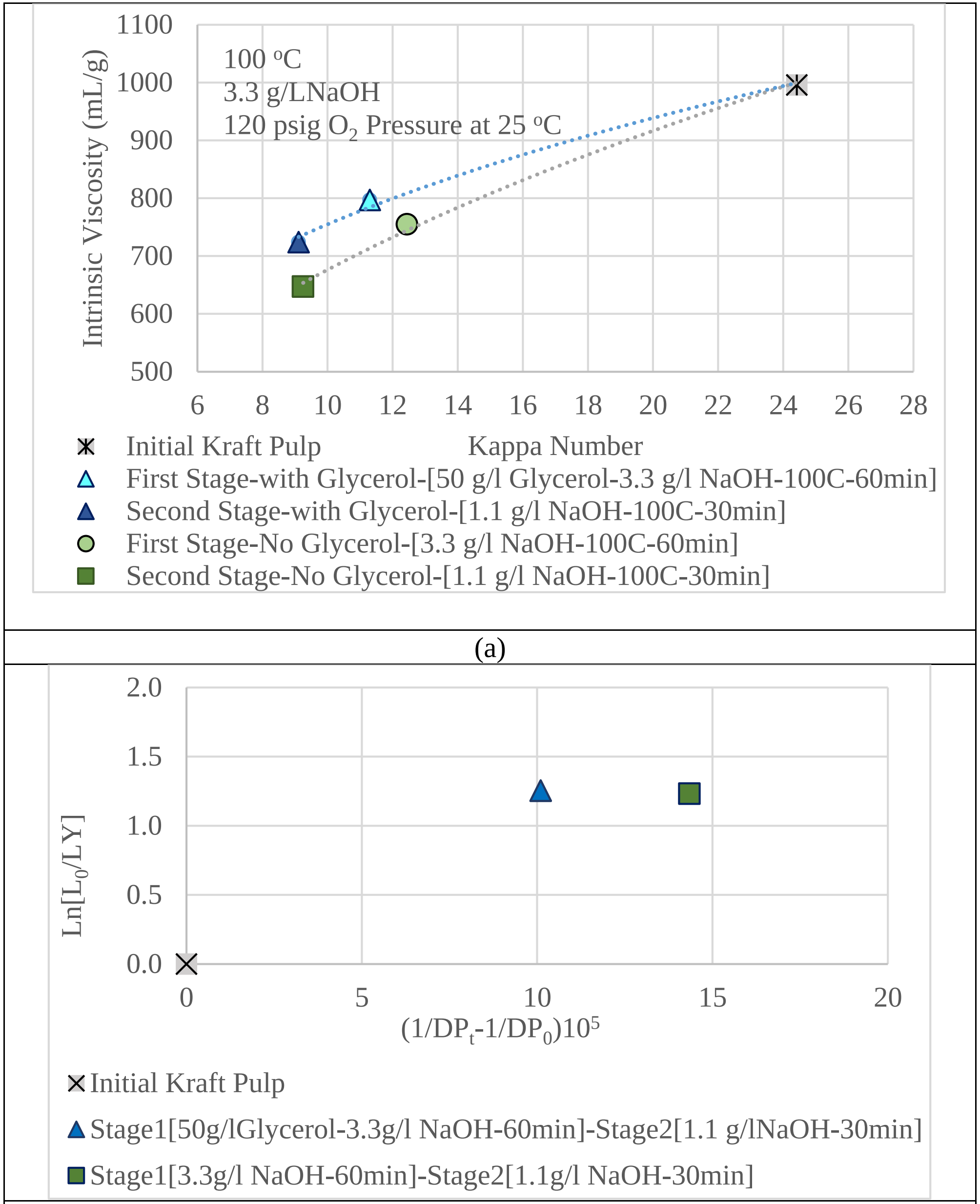
7.6 Oxygen Delignification using Multiple Batch Stages

As previously shown (Figure 7.11), by extending the reaction time by more than 60 min, delignification does not proceed much further because of the lack of effective alkali. On the other hand, increasing the initial alkalinity is not very effective because a high alkali concentration leads to more cellulose degradation (Y. Ji 2007). Based on the results obtained in the CSTR, a constant alkali concentration of 3.3 g/L at 100 °C leads to delignification at longer times with still reasonable selectivity. Thus in this section, the oxygen delignification process in the Parr reactor will be split into two or three stages with the addition of fresh alkali at each stage at different charges to see whether the delignification can be extended at improved selectivity. To improve the intrinsic viscosity, based on the previous results shown in Figure 7.10, 50 g/L glycerol is chosen as the additive to be added just in the first stage.

7.6.1 Two-Stage Oxygen Delignification in Batch Reactor

In this section, the effect of glycerol on selectivity in two-stage batch oxygen delignification is investigated and then compared with a single-stage process at the same reaction time and temperature. In the first stage of oxygen delignification, 3.3 g/L NaOH solution was used in the presence and absence of 50 g/Lglycerol at 100 °C for 60 minutes. In the second stage, 1.1 g/L NaOH was added into the black liquor to increase the level of the residual affective alkali in the pulp suspension. Thus, instead of 90 min single-stage reaction, two-stage oxygen delignification in 60 and 30 min reactions with the addition of extra NaOH between the stages was considered to increase the level of the effective alkali. This was done since after 60 min oxygen delignification (at 100 °C with 3.3 g/LNaOH), the amount of residual effective alkali becomes zero (Figure 7.11).

As shown in Figure 7.12 (a), by splitting the 90 min oxygen delignification into 60 and 30 min with the addition of an extra 1.1 g/L NaOH in the second stage, the kappa number and intrinsic viscosity at the end of the second stage decrease to 9.1 and 9.3 kappa units and 724 and 647 mL/g in the presence and absence of 50 g/Lglycerol respectively. This shows that by adding 50 g/L glycerol just in the first stage of oxygen delignification, we can still have an acceptable intrinsic viscosity ([µ]>700 mg/L) at the end of the second stage. Figure 7.12 (b) also shows that by the addition of 50 g/L glycerol, the selectivity ($\mathrm{S_{KC}} = \frac{\ln\frac{L_0}{L_t \mathrm{Y}}}{\frac{1}{\mathrm{DP}_t} - \frac{1}{\mathrm{DP}_0}}$) is still higher than the alkali control.



(a)

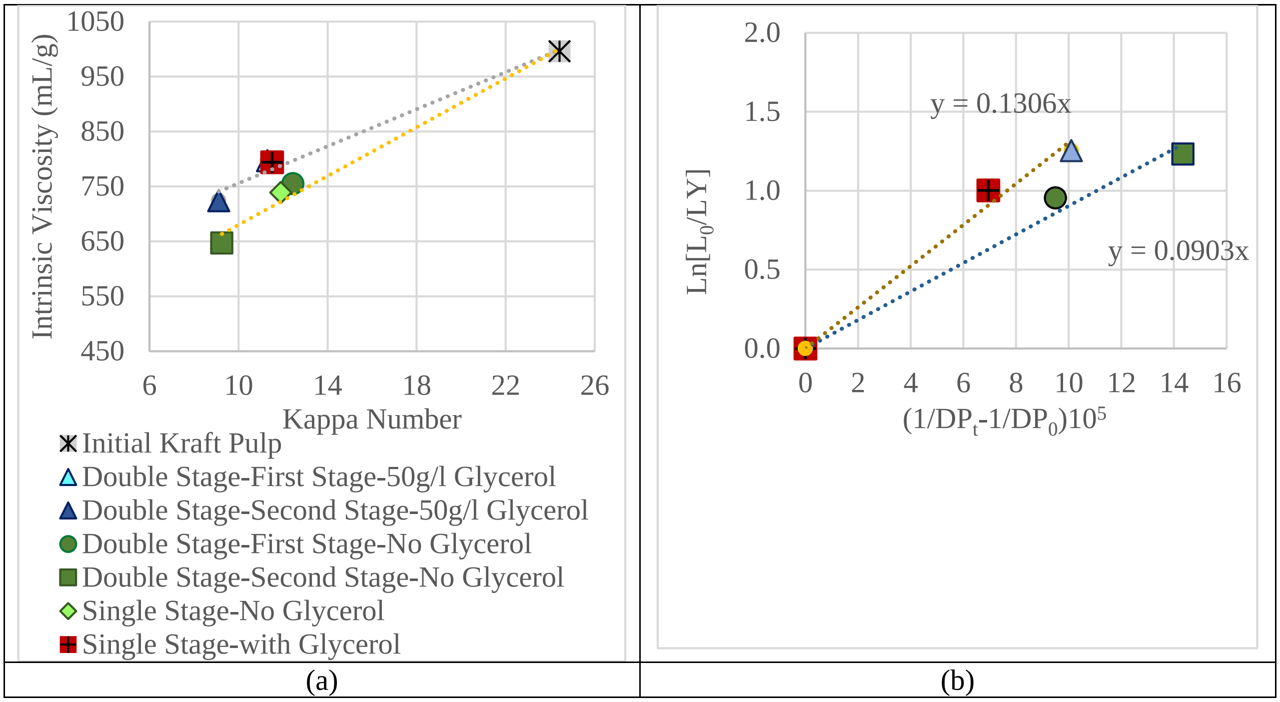
(b)

Figure 7.12. Oxygen Delignification in Two Stages

(a) Intrinsic Viscosity/Kappa Selectivity

(b) $Ln[L_0/LY]/(1/DP_t-1/DP_0)10^5$ Selectivity

In Figure 7.13, the double-stage oxygen delignification is compared with the single-stage. It is clearly shown that by using two stages instead of one stage of oxygen delignification at the same reaction time and temperature but with the extra addition of NaOH (1.1 g/L) in the second stage, delignification continues down to kappa numbers of 9.11 and 9.25 for 0 and 50 g/Lglycerol respectively (Figure 7.13. a). However, the selectivity ($S_{KC} = \frac{\ln\frac{L_0}{L_t Y}}{\frac{1}{DP_t}-\frac{1}{DP_0}}$) in the double and single stage are the same (Figure 7.13. b).



(a) (b)

Figure 7.13. Oxygen Delignification in One and Two Stages

Stage 1[0,50g/lGlycerol-3.3g/LNaOH-100°C-60min], Stage 2[1.1g/LNaOH-100°C-30min]

(a) Intrinsic Viscosity/Kappa Selectivity

(b) $Ln[L_0/LY]/(1/DP_t-1/DP_0)10^5$ Selectivity

At the end of 90 min oxygen delignification with and without 50 g/Lglycerol in the double-stage, the carbonyl group of the pulp samples was determined. As shown in Figure 7.14, by the addition of 50 g/Lglycerol the carbonyl group content decreases from 0.14 to 0.05 mmol/100 g pulp o.d. This implies that glycerol effectively reduces the carbonyl groups formed during oxygen delignification in the Batch reactor.

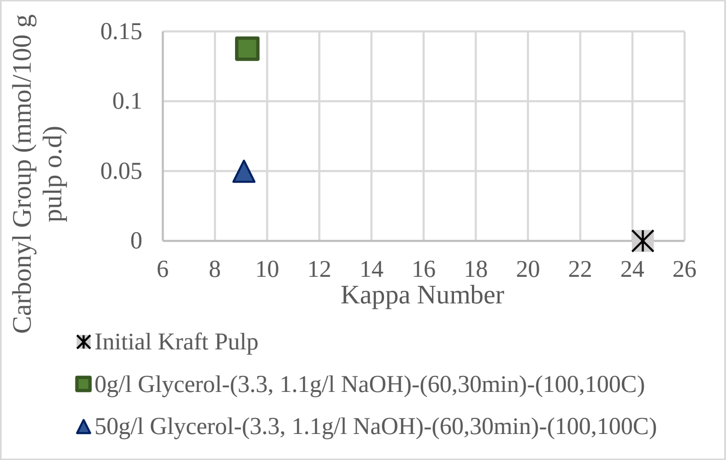


Figure 7.14. Effect of 50 g/LGlycerol on Reducing Carbonyl Groups

7.6.2 Effect of Temperature on Selectivity in Two-Stage Batch Oxygen Delignification

The effect of temperature on two-stage oxygen delignification in the presence of glycerol was investigated as an approach of extending delignification while minimizing cellulose degradation.

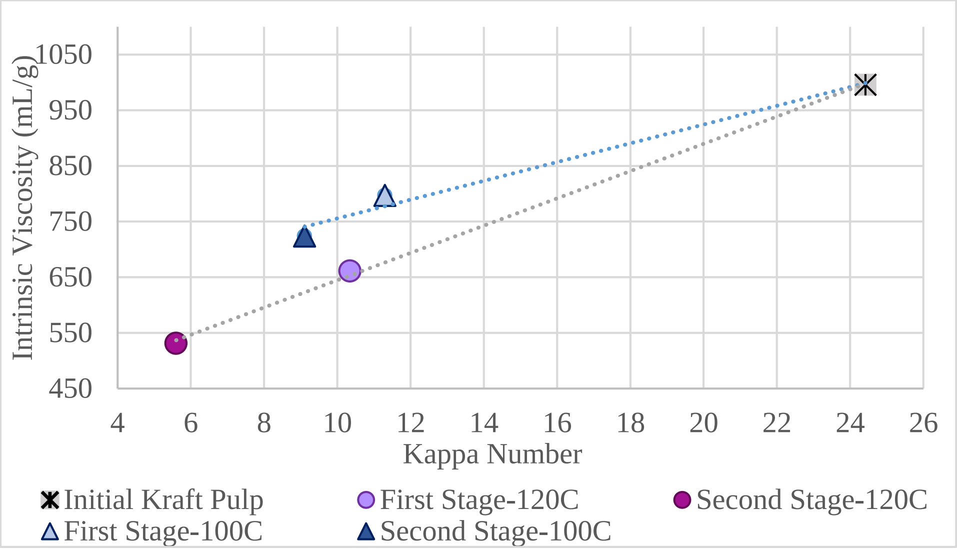


Figure 7.15. Effect of Temperature on Viscosity/Kappa Selectivity

First Stage O_2 Del [50g/LGlycerol-3.3 g/LNaOH-60min-100 or120 ^{o}C]-

Second Stage O_2 Del [1.1g/LNaOH-30min-100 or120 ^{o}C]

As shown in Figure 7.15, by increasing the reaction temperature from 100 to 120 ^{o}C in both stages, the kappa number decreases down to 5.6 kappa or 2.6 kappa units when corrected for

HexA content. This means 87% delignification (corrected for HexA) with an intrinsic viscosity of almost 550 mL/g.

7.6.3 Three-Stage Batch Oxygen Delignification

The 90 min oxygen delignification was split into three stages at 25, 30, and 35 min with the addition of NaOH in each stage to extend the delignification while minimizing cellulose degradation by keeping the NaOH concentration low. The three-stage of oxygen delignification was done at two different conditions. In one set of experiments, a constant concentration of NaOH (3.3 g/l) was added in each stage (9.9 g/LNaOH in total). The temperature was 100 ^{o}C for all three stages. In the other set of experiments, a different concentration of NaOH (3.3, 2.2, 1.1 g/l) was added in each stage (6.6 g/LNaOH in total). The purpose of decreasing the total amount of NaOH and adding it from high to low concentrations was to reduce the total charge of NaOH but keeping the NaOH concentration at a reasonable level until the end the process. The temperature for the first and second stages was set at 100 ^{o}C, and for the third stage, the temperature was increased to 120 ^{o}C to increase the reactivity of the residual lignin. As can be seen in Figure 7.16 (a), the experiment with different NaOH concentrations (3.3, 2.2, 1.1 g/l) has an 8% higher intrinsic viscosity (520 vs 480 mL/g) and a 17% lower kappa number (6 vs 7.25). In Figure 7.16 (b), it is shown that the experiment with the constant amount of NaOH (3.3 g/l) in three stages still contains effective alkali after the end of the third stage since the pH of the black liquor is above 11.3, while NaOH in the other experiment with different NaOH concentrations (3.3, 2.2, 1.1 g/L) is all consumed as the pH of the black liquor after the third stage is less than 11.3. Thus having three-stage with 3.3, 2.2, 1.1 g/LNaOH at 100, 100, 120 ^{o}C respectively is beneficial in terms of delignification and viscosity/kappa selectivity compared to charging the same NaOH concentration (3.3 g/L) in three stages at a total charge of 9.9 g/LNaOH at the constant temperature (100 ^{o}C) for all operating stages.

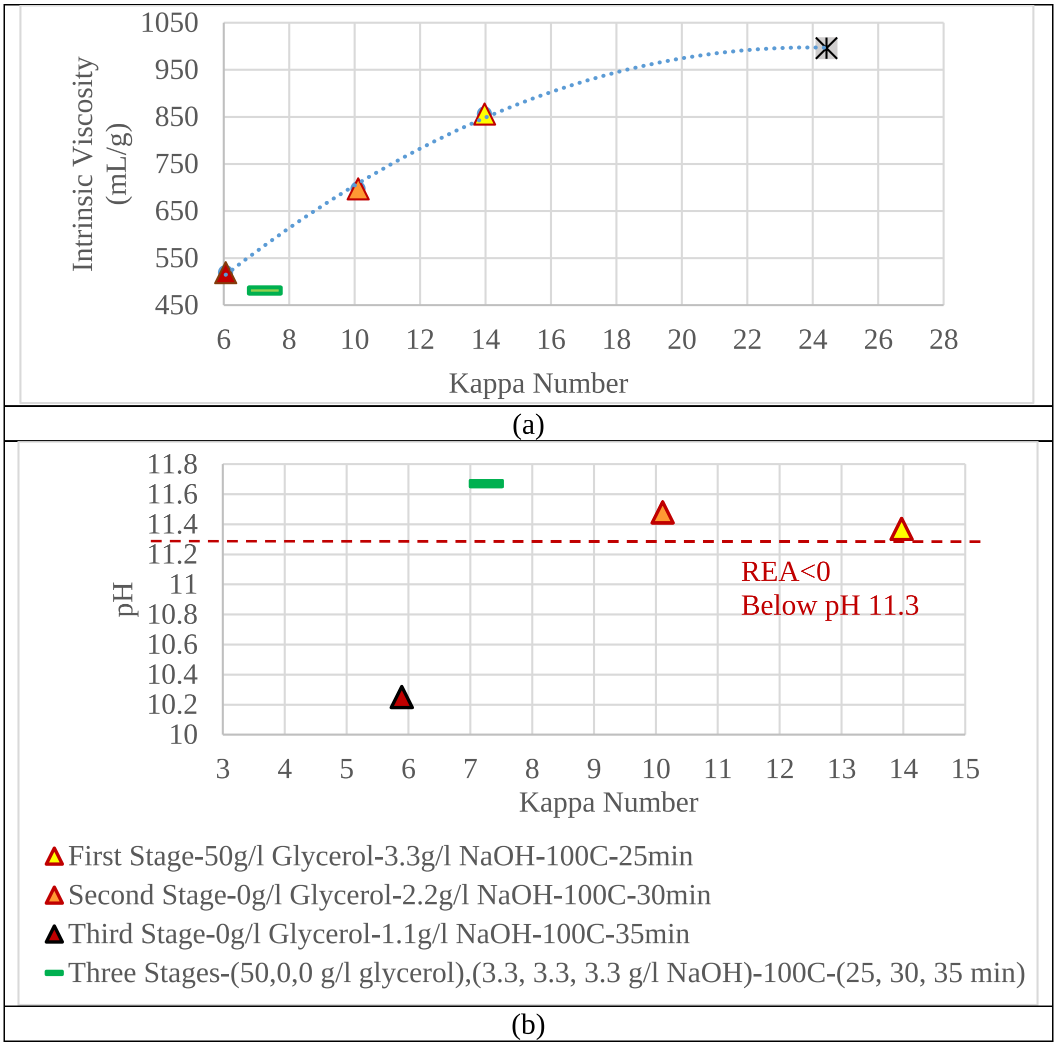


Figure 7.16. Oxygen Delignification in Three Stages in the Presence of 50g/LGlycerol at Different NaOH Concentrations and Temperatures

(a) Intrinsic Viscosity versus Kappa Number

(b) pH versus Kappa Number Measured at the End of Each Stage Oxygen Delignification

7.6.4 Comparing the Single, Double, and Triple-Stage Batch Oxygen Delignification

In Figure 7.17, the single, double, and triple stage oxygen delignification experiments are compared. It can be seen that in the two-stage oxygen delignification the final kappa number decreases by 2 more units (kappa 9) compared to the single-stage oxygen delignification (kappa 11). By increasing the temperature in the two-stage oxygen delignification from 100 to 120 °C, the intrinsic viscosity drops to 530 mL/g, and the kappa number decreases to 5.6 or 2.6 when corrected for HexA which means 87% total delignification based on the HexA-free kappa number (3) of the original pulp. On the other hand, by splitting 90 min oxygen delignification into three stages (3.3, 2.2, 1.1 g/L NaOH, 100, 100, 120 °C), the same final results were obtained at the end of 90 min reaction when compared to the double-stage (3.3, 1.1 g/L NaOH) oxygen delignification at 120 °C.

As can be seen below, the three-stage oxygen delignification is also used with the same amount of NaOH (3.3 g/L) and temperature (100 °C) in each stage with the presence of 50 g/Lglycerol (3.3, 3.3, 3.3 g/LNaOH-100, 100, 100 °C, 25, 30, 35 min), but less delignification and lower intrinsic viscosity take place in comparison with the three-stage reaction at a higher temperature but a lower amount of alkalinity in total (3.3, 2.2, 1.1 g/LNaOH-100, 100, 120 °C- 25, 30, 35 min). This shows that the lower addition of the alkali and increasing the temperature up to 120 °C at the third stage when a higher fraction of unreactive lignin is left in the pulp could have a better impact on removing lignin while keeping intrinsic viscosity from decreasing.

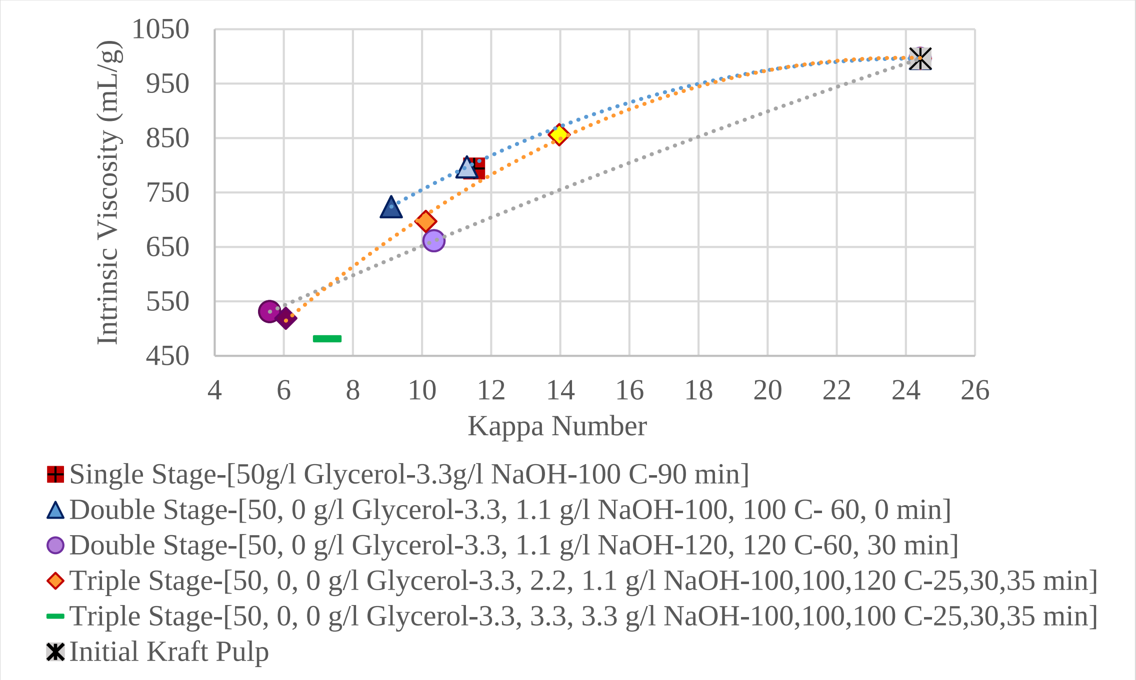


Figure 7.17. Overview of Single, Double, and Triple-Stage Oxygen Delignification

7.7 Difference Between CSTR and Batch Reactor

In order to compare the delignification/cellulose degradation selectivity in the Parr and Berty reactors, Ln[(Kappa$_0$-HexA/10)/(Kappa$_t$-HexA/10)yield] is plotted against 1/DP-1/DP$_0$ for 20, 45, and 90 minutes of oxygen delignification in the CSTR and for 90 minutes in the batch reactor. The initial concentration and temperature were 3.3 g/L and 100 °C for both without and with the addition of 2.186 g/L Na_2CO_3 (Figure 7.18). In this figure, the same selectivity is obtained in the CSTR and batch reactor, but more delignification is achieved in the CSTR because the NaOH concentration is maintained at the initial value throughout the process, while the caustic concentration decreases over time in the batch reactor. It is known that the selectivity improves at lower alkalinity. However, in the batch reactor, the dissolved lignin concentration increases with time, and further reactions with oxygen will create more radical species which may degrade cellulose (Jafari thesis). Therefore these opposing effects on selectivity in the batch reactor may cancel out each other. Still, the finding of the same selectivity in the present batch and CSTR reactor experiments is different from Ji et al. (Ji, Wheeler and van Heiningen 2007) who found that the selectivity in the CSTR decreases at a high degree of delignification obtained at very long delignification times (up to 180 minutes). Their explanation for the decreasing selectivity is an additional contribution to cellulose degradation by alkaline hydrolysis, which is small compared to attack by radicals generated by oxygen delignification, but which cumulatively becomes important at long oxygen delignification times because the alkalinity remains high in the CSTR. However, it is known that alkaline hydrolysis of cellulose only becomes important above 130 °C while the experiments performed by Ji et al were done at 90 °C and our present experiments at 100 °C (Y. Ji 2007). Therefore we do not have an explanation for the difference between the results of Ji et al. and our present findings (Y. Ji 2007).

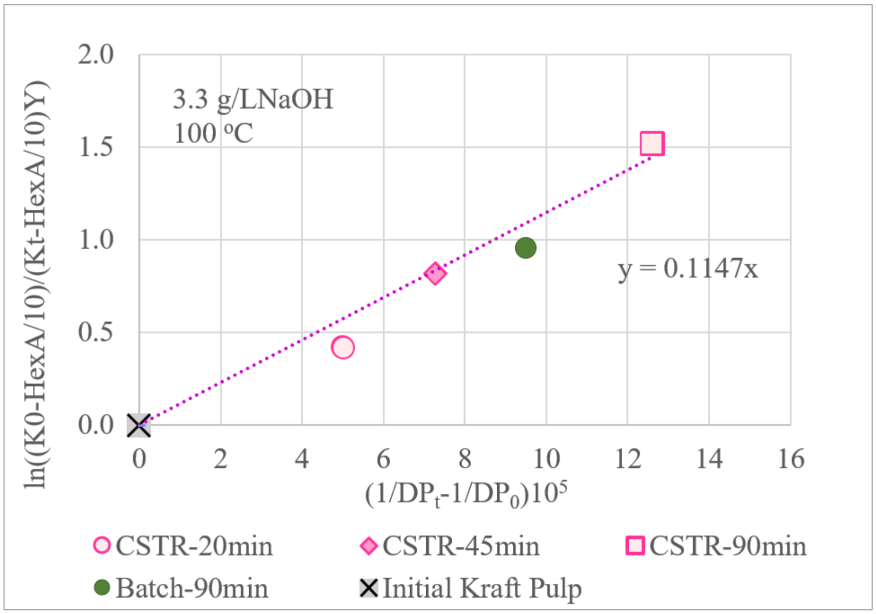


Figure 7.18. $Ln[L_0/LY]/(1/DP_t-1/DP_0)10^5$ Selectivity

for CSTR and Batch Reactor at Different Reaction conditions

7.8 Conclusions

- By the addition of 2.186 g/L Na_2CO_3 (equivalent to 1.65 g/L NaOH) into the 1.65 and 3.3 g/L NaOH (overnight oxygenated at 65 psi O_2 pressure at room temperature) at 100 °C, sodium carbonate increased the selectivity, $S_{KC} = \frac{\ln\frac{L_0}{L_t Y}}{\frac{1}{DP_t} - \frac{1}{DP_0}}$, by about 43% in comparison to the caustic control (3.3 g/L NaOH) in the CSTR. This improvement can be explained by Na_2CO_3 scavenging of hydroxyl radicals formed by phenolic delignification.
- Also, the kappa number at 100 ^{o}C for 90 minutes of oxygen delignification in the presence of 2.186 g/L Na_2CO_3 brings the kappa number down to about 7.1 kappa units, which is equivalent to a HexA-corrected degree of delignification of about 81%. The intrinsic viscosity is also maintained at an acceptable value (748 mL/g). This shows that we could extend the oxygen delignification up to 80% of conventional Southern Pine kraft pulp (about 24.4 kappa number) while maintaining an acceptable intrinsic viscosity (>700 mL/g).
- In the presence of 2.186 g/L Na_2CO_3 (equivalent to 1.65 g/L NaOH), no effect of the kappa reduction was seen when the ph of the caustic solution increases by adding more NaOH (from 1.65 to 3.3 g/L). The explanation may be that the concentration of 2.186 g/L Na_2CO_3 is sufficiently high to scavenge the hydroxyl radicals generated by phenolic oxidation at 1.65 g/L NaOH. At the higher 3.3 g/L NaOH concentration more of the hydroxyl radicals are converted to more selective radicals ($CO_3^{2-\cdot}$). However at the higher pH more unselective oxyl radicals are present which may compensate the higher efficiency of hydroxyl radical conversion into carbonate radicals.

- The optimum Na_2CO_3/NaOH molar ratio to obtain the highest selectivity improvement by Na_2CO_3 addition is about 0.5 because of doubling the Na_2CO_3 concentration to 4.372 g/l at 3.3 g/L NaOH did not increase selectivity.
- Contrary to the CSTR results, Na_2CO_3 addition did not increase the selectivity in the Batch (Parr) reactor. The key difference between the two reactor systems is that in the Batch reactor the alkalinity decreases rapidly over time, while it remains constant in the CSTR. However, Na_2CO_3 can increase the degree of oxygen delignification because it acts as a buffer (CO_3^{-2}/HCO_3^-) and does prevents the pH inside the Batch reactor drop below 10 by supplying more NaOH ($Na_2CO_3 + 2H_2O \rightarrow 2NaOH + H_2O + CO_2$). Therefore by adding Na_2CO_3, phenolic lignin (with a pK_α of about 10.5) can still be dissociated and then be attacked by dissolved oxygen.
- With the presence of 2 g/L methanol into the caustic control (3.3 g/L NaOH), the intrinsic viscosity increases by nearly 50 mL/g, while the kappa number remains the same as that of the control after 90 minutes of oxygen delignification at 100 ^{o}C.
- No improvement was obtained by the addition of 0.25 or 1% $MgSO_4$ (based on pulp weight). Magnesium sulfate addition reduced the Fe^{+2} and Mn^{+2} content in the pulp after 60 min oxygen delignification, but the levels of Fe^{+2} and Mn^{+2} are still relatively high because the metal concentrations in the fresh kraft pulp are high. Thus, 0.25 or 1% $MgSO_4$ might not be sufficient for encapsulating and trapping the transition metals for our pulp with a high level of transition metals.
- The impact of glycerol on selectivity is investigated in the Batch (Parr) reactor. The addition of 50 g/L glycerol increased the selectivity ($S_{\mathrm{KC}} = \frac{\ln\frac{L_0}{L_t \mathrm{Y}}}{\frac{1}{\mathrm{DP}_t} - \frac{1}{\mathrm{DP}_0}}$) by 43% which can be considered

a significant improvement. The intrinsic viscosity and kappa number after 90 minutes of oxygen delignification are 730 ml/g and 7.7 kappa unit (or HexA free kappa of 4.7) which is equivalent to a HexA-corrected delignification of about 78%. Surprisingly, 10 g/L glycerol was ineffective in increasing selectivity. A possible explanation for why 50 g/L glycerol increases the selectivity might be that at this high glycerol concentration less carbonyl groups remain formed by the unselective radical attack. By adding 50 g/L glycerol into 3.3 g/L NaOH caustic solution, the carbonyl group decreases from 0.14 to 0.05 mmol/100g pulp o.d which is significant.

- For oxygen delignification at 100 °C with the oxygenated 3.3 g/L NaOH caustic solution, the same selectivity ($Ln[L_0/LY]/(1/DP_t-1/DP_0)10^5$) was obtained in the CSTR as in the batch reactor. However, more delignification was achieved in the CSTR because the NaOH concentration is maintained at the initial value throughout the process, while the caustic concentration decreases over time in the batch reactor.

Future Work

To better understand the oxygen delignification mechanism of softwood kraft pulp and increase the degree of delignification while maintaining an acceptable cellulose Degree of Polymerization, DP, we suggest future work in the following areas of research:

- Study the composition of the unreactive lignin and investigate ways of removing this lignin.
- Obtain a better understanding of the mechanism and kinetics of the relevant reactions during kraft pulp oxygen delignification in the presence of sodium carbonate and sodium hydroxide at different pHs.

- Study the effect of crude sodium-based industrial glycerol generated as a waste stream in the biodiesel industry on the selectivity and lignin removal during oxygen delignification of kraft pulp.

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APPENDIX A

Kinetics Calculation

A.1. Calculations of Reaction Order in Lignin, q

The reaction order in lignin, q, is calculated from the general power-law kinetic model.

$$r_{(t)} = -\frac{dL_C}{dt} = k_\alpha[O_2]^m[OH]^n(L_c - L_\infty)^q \qquad \text{(Equation A.1)}$$

At constant oxygen and alkali concentrations, Equation A.1 can be written:

$$L_{Ck} = k_\alpha[O_2]^m[OH]^n(L_C - L_\infty)^q \qquad \text{(Equation A.2)}$$

$$r_{(t)} = -\frac{d(L_C - L_\infty)}{dt} = k_\alpha(L_C - L_\infty)^q \qquad \text{(Equation A.3)}$$

$$-d(L_C - L_\infty) = k_\alpha(L_C - L_\infty)^q dt \qquad \text{(Equation A.4)}$$

$$\int_{K_{C0}}^{K_{Ct}} \frac{-d(L_C - L_\infty)}{(L_C - L_\infty)^q} = \int_0^t k_\alpha dt \qquad \text{(Equation A.5)}$$

$$(L_C - L_\infty) = [(L_{C0} - L_\infty)^{1-q} - k_\alpha(1-q)t]^{\frac{1}{1-q}} \qquad q \neq 1 \qquad \text{(Equation A.6)}$$

$$Ln\frac{L_{C0} - L_\infty}{L_C - L_\infty} = k_\alpha t \qquad q = 1 \qquad \text{(Equation A.7)}$$

$$y = \frac{(L_{C0} - L_\infty)^{1-q} \quad - (L_C - L_\infty)^{1-q}}{(q-1)} = k_\alpha \mathrm{t} \qquad \text{(Equation A.8)}$$

where, r is the reaction rate (mg/min)

L_C is the residual lignin corrected for HexA (mg/g pulp)

m is the reaction order (unitless)

n is the reaction order (unitless)

q is the reaction order (unitless)

t is time (min)

[OH] is the caustic concentration (mol/l)

$[O_2]$ is the oxygen concentration (mol/l)

k_α is the reaction rate constant

In this way, the reaction order q is obtained by a trial and error method. Therefore different q were predicted and used in Equation A.8, then the kappa number versus time data were plotted and the correlation coefficient (R^2) was found for each chosen q. The highest R^2 (the closest to one) would give the right values of q.

A.2. Estimation of Rate Order q in CSTR

As can be seen in Table A.1, the q values are chosen from 0.001 to 10, and the $y=\frac{(L_{C0}-L_\infty)^{1-q} \;\; -(L_C-L_\infty)^{1-q}}{(q-1)}$ values are calculated from Equation A.8 for residual lignins (corrected for unreactive lignin) at different reaction times. The correlation coefficient (R^2) for alkali delignification is obtained for each q value and presented in Table A.1.

Table A.1.

$y=\frac{(L_{C0}-L_\infty)^{1-q} \;\; -(L_C-L_\infty)^{1-q}}{(q-1)}$						R^2
t = time $L_{C,t}-L_\infty$	0 min $L_{C,0}-L_\infty$	10 min $L_{C,10}-L_\infty$	20 min $L_{C,20}-L_\infty$	45 min $L_{C,45}-L_\infty$	90 min $L_{C,90}-L_\infty$	
q	y_0	y_1	y_2	y_3	y_4	
0.001	-3.6979	3.509	8.2951	14.205	21.467	0.8897
0.01	-3.5907	3.4119	8.074	13.849	20.993	0.891
0.1	-2.6758	2.5767	6.1631	10.747	16.815	0.908
0.5	-0.7242	0.74	1.8584	3.5037	6.4774	0.9685
0.99	-0.1461	0.1606	0.4292	0.9	2.1766	0.999
1.05	-0.1201	0.1332	0.3588	0.7628	1.9163	0.999
1.5	-0.0276	0.0328	0.0937	0.2223	0.7697	0.9815
2	-0.0054	0.0069	0.0212	0.0573	0.3039	0.947
3	-0.0002	0.0003	0.0011	0.004	0.0586	0.8717
4	-8E-06	1E-05	6E-05	0.0003	0.0136	0.8418
6	-1E-08	3E-08	2E-07	2E-06	0.001	0.829
8	-2E-11	5E-11	5E-10	1E-08	8E-05	0.8279
10	-3E-14	1E-13	1E-12	1E-10	8E-06	0.8278

As can be seen in Figure A.1, the best value for q for alkali delignification in the CSTR should be one (R^2=0.999).

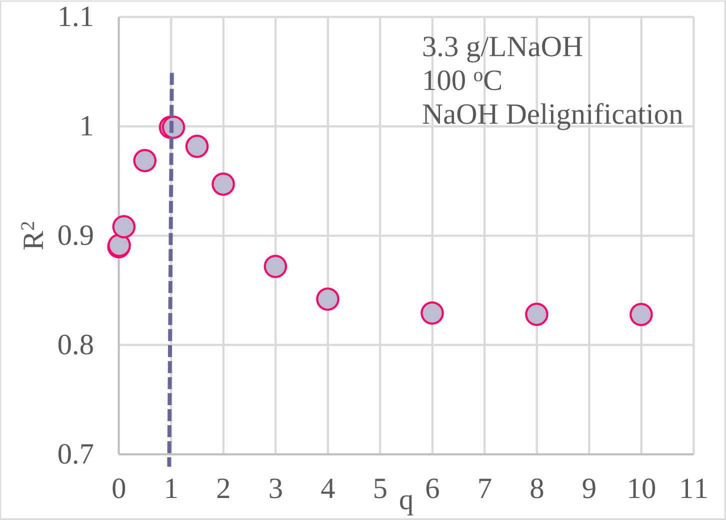

Figure A.1

A.3. **Reaction Rate Constant k_α**

As shown in Equation A.7, the reaction rate constant is the slope of $Ln\frac{L_{C0}-L_\infty}{L_C-L_\infty}$ versus time when the reaction order q is equal to 1.

$$Ln\frac{L_{C0}-L_\infty}{L_C-L_\infty}=k_\alpha t \qquad q=1 \qquad \text{(Equation A.7)}$$

In Figure A.2, $Ln\frac{L_{C0}-L_\infty}{L_C-L_\infty}$ is plotted against time for the CSTR data. The value of the reaction rate constant is 0.0254 which is obtained from the slope represented in Figure A.2.

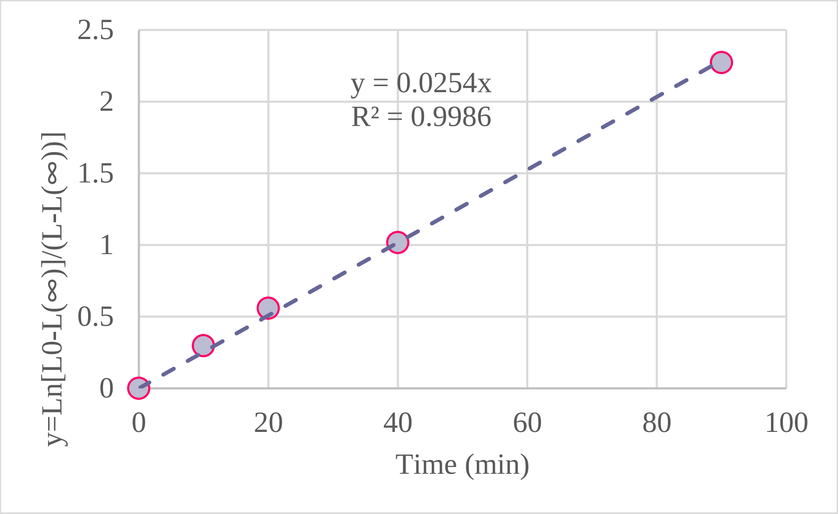

Figure A.3. y=$\frac{(L_{C0}-L_{\infty})^{1-q}\ \ -(L_{C}-L_{\infty})^{1-q}}{(q-1)}$ versus time

A.4. Model Verification

In order to investigate the validation of the model for an alkali delignification, the predicted residual lignin is plotted against the measured residual lignin (corrected for unreactive lignin) for the CSTR data. As shown in Figure A.5, there is a linear relationship between the predicted kappa number and the measured kappa number with the slope of 1.02 (R^2=0.997). This implies the predicted kappa number is very close to the measured kappa data in the CSTR.

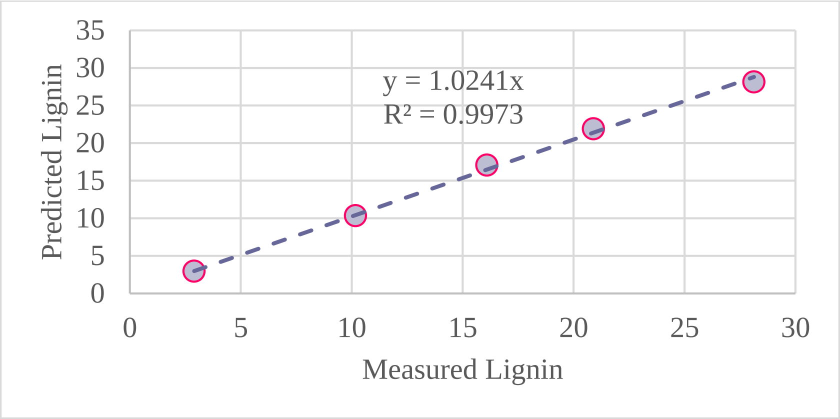

Figure. A.5

BIOGRAPHY OF THE AUTHOR

Azadeh Pahlevanzadeh was born in Leeds, U.K (1987) and grow up in Iran in an educated family with strong social values of hard work. She attended Sharif University of Technology which is one of the best universities in Iran in 2006 with a Bachelor's degree in Chemical Engineering. In the fifth semester of her education, she got an opportunity to go to South Africa with her family because of her father's sabbatical at Kwazulu Natal University so she got permission for one semester. During this time she participated at Durban University of Technology as an auditor student in a unit operation course. Her hard work in studying her courses and other contents out of the textbooks during her B.Sc. gained her an overall GPA of 15.59 out of 20. Her two last GPA also were 16.6 and 17.6 since all of the courses she took were proficiency and labs which were her favorites so her GPA became very good. In 2013, She attended University of Tehran with a Master's degree in Energy and Environmental Engineering. Her overall GPA was 19.09 out of 20 and she was the top student among students in her field. Her project was on extracting lipid from microalgae for producing biodiesel. She was really interested in this field since chemical engineering and bioscience are combined with each other to produce a biofuel that is friendly with the environment. Azadeh is a candidate for the Doctor of Philosophy degree in Chemical Engineering from the University of Maine in May 2022.