Selectivity of oxygen delignification for southern softwood kraft pulps with high lignin content

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ABSTRACT: The selectivity of kraft pulping versus the oxygen delignification processes over the range of kappa nos. 25–90 was compared. Kraft pulping was found to be more selective than oxygen delignification for removing lignin from southern softwood kraft pulps. The greater selectivity is thought to be related to hydroxyl radicals that form in the oxygen delignification process that are not present in the kraft process. The hydroxyl radicals attack the carbohydrates and randomly cleave the polymeric chains, causing a significant decrease in the degree of carbohydrate polymerization and thus a loss of viscosity. Kraft pulping generates hydrosulfide ions that are highly selective and attack the lignin. Carbohydrate degradation occurs mainly from peeling reactions, which do not appreciably reduce the degree of polymerization of the cellulose and thus there is less viscosity loss. At low lignin content (i.e., low kappa number), the remaining lignin is likely bound covalently to the carbohydrate portion in both processes. Therefore, removal of the lignin results in significant degradation of the carbohydrates.

Application: Findings from the comparison of the drop in viscosity that occurs during kraft pulping and in oxygen delignification are applicable to fiber lines that contain both processes.

The oxygen delignification process is predominant in modern fiber lines because of its environmental and economic benefits. The process, however has two major disadvantages: poor selectivity and the high capital cost of installing a system. Poor selectivity has limited commercial systems to about 50%–60% lignin removal when measured by kappa number, although new two-stage systems for softwood are pushing this limit higher. The high capital cost is directly associated with the long reaction time and working pressure used in the process.

The kraft pulping process has a significant effect on pulp bleaching and oxygen delignification [1]. Measurement of pulp yield following oxygen delignification for high kappa number pulps has been investigated by Zorn [2] and Bubniak [3]. The amount of lignin remaining in the pulp and its structure will depend on the conditions used in the pulping process. It has been reported that the bleached pulp yield is about 2% higher when the pulping process is terminated at high kappa numbers, than when an oxygen delignification process is applied [2]. Usually, after kraft pulping the target kappa number is about 30 for softwood and 20 for hardwood. Oxygen delignification is employed in place of a conventional D_0 stage to reduce the kappa number 40%–60% prior to bleaching. The extent of delignification depends upon the pulp type, the initial kappa number, and the number of stages employed in the oxygen delignification process. If the target kappa number is raised in the digester in an effort to achieve higher pulp yields, then selectivity becomes an important issue. That is especially true for softwood pulps because intrinsic fiber strength can be reduced significantly due to free radical reactions present during oxygen delignification. Consequently, the study of the selectivity of the oxygen delignification process is an important topic in pulping technology. Pulps with kappa nos. 66 and 90 were investigated due to interest in combined pulping and bleaching and to estimate the selectivity coefficient over a wide range of kappa numbers.

We investigated the selectivity of the oxygen delignification process applied to southern softwood over a wide range of kappa numbers. The study was focused on the selectivity of the oxygen delignification process relative to the continuing pulp delignification using the kraft processes. Four different kraft brown stock pulps were studied over the range of kappa nos. 25–90. The higher kappa number pulps were chosen because of an interest in simultaneous pulping and bleaching. These pulps correspond to lignin contents that varied between 4% and 14% by weight. The effects of initial kappa number, temperature, alkali concentration, oxygen pressure, and reaction time were investigated experimentally. The dependent variables measured were kappa number, intrinsic viscosity, and caustic consumption. The dependent variables were then used to estimate the selectivity coefficients for the process over the kappa nos. 25–90. Pulp yield data following oxygen delignification was outside of the scope the investigation.

PREVIOUS RESEARCH

The mechanism of oxygen bleaching has been studied extensively [4–6] and was summarized by McDonough [7]. Oxygen is an unusual molecule because its normal (lowest energy)

configuration is the triplet state. It contains two electrons that are unpaired, and each of these electrons has an affinity for other electrons of opposite spin. Because oxygen behaves similarly to a free radical, it has a strong tendency to react with organic substances. Free-radical chain reactions begin that liberate hydroperoxy radicals ($HOO^{\cdot}$), hydroxyl free radicals ($OH^{\cdot}$), and superoxide free-radicals ($O_2^{\cdot-}$).

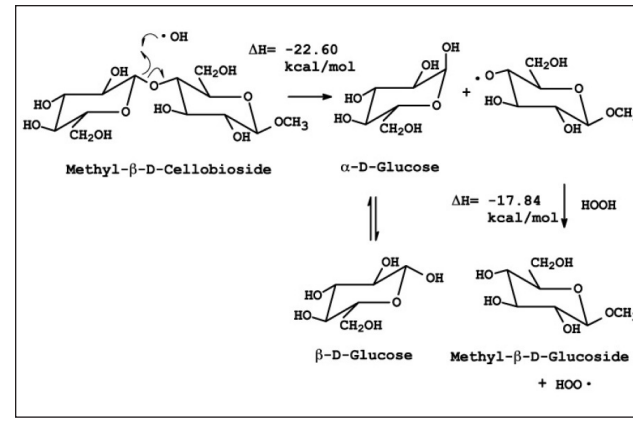
Lignin reactions

Johansson and Ljunggren [8] found that phenolic structures with a conjugated side chain, like stilbene and enol ethers, react very rapidly, whereas diphenylmethane-type condensed structures are particularly resistant to oxygen bleaching. Gellerstedt and Lindfors [9] discussed the structure and reactivity of residual lignin in kraft pulp. Fu and Lucia [10] found that xylan-linked lignin is more resistant to oxidative reactions and tends to remain in the pulp, while galactan-linked lignin tends to dissolve during oxygen delignification. The p-hydroxyphenyl and 5, 5'- biphenolic units in the residual lignin are quite stable and tend to accumulate during oxygen delignification [10, 11]. During oxygen delignification, it was confirmed that the number of phenolic hydroxyl groups and carboxyl groups in the lignin in the pulp decreased and the number of carboxylic acid groups increased. Termination reactions occur that form condensed lignin structures. The degradation products from oxygen delignification are predominately organic acids and carbon dioxide [1].

Carbohydrate degradation reactions

Random chain cleavage and, to a lesser extent, carbohydrate peeling reactions occur during oxygen delignification. These reactions, especially the random chain cleavage, are commonly monitored by measuring the decrease in intrinsic viscosity [η] of the pulp and less commonly by its degree of polymerization (M_n). Random chain cleavage occurs at any glycosidic linkage along the chainlike molecule, while in carbohydrate peeling reactions individual sugar units on the end of the chain are attacked and removed one unit at a time [12]. Although both types of reactions occur during oxygen delignification, random chain cleavage is thought to be the more significant.

Hydroxyl ($OH^{\cdot}$) and superoxide ($O2^{\cdot-}$) free radicals readily occur during oxygen delignification and are thought to randomly attack carbohydrates, ultimately resulting in chain breakage at the point of attack. Guay and coworkers [13] used computational methods to determine that carbohydrate degradation resulting from reaction with the superoxide anion ($O2^{\cdot-}$) is energetically unfavorable but that reaction with the hydroxyl free radical ($OH^{\cdot}$) is thermodynamically possible. Guay and coworkers [14] presented an alternative degradation mechanism predicated on the hydroxyl free radical ($OH^{\cdot}$), as illustrated in **Fig. 1**. A hydroxyl radical substitution reaction at the glycosidic linkage between the two pyranose rings formed methyl β-D-glucoside and D-glucose [13]. The substitution reaction led to chain cleavage and lowering of the molecular weight. A perhydroxyl free radical ($HOO^{\cdot}$) was also formed.



1. Carbohydrate degradation using methyl β-D cellobioside model compound [13].

Primary and secondary peeling reactions, which are responsible for decreasing the yield, are usually of less importance than random chain cleavage in oxygen delignification. Primary peeling occurs at the front unit on the carbohydrate chain and terminates with a stopping reaction. Secondary peeling is initiated on the front sugar unit immediately following random hydrolysis. A new carbonyl unit is created on the front sugar unit of the newly formed chain, which can undergo further peeling until a stopping reaction occurs. Peeling reactions are thought to be minimal in oxygen delignification, compared with that which occurs in the kraft process, because carbonyl groups on the first glucose unit are readily oxidized to carboxylic acid groups that terminate peeling reactions.

Selectivity

Selectivity is defined as the ratio of the oxygen reaction rate with lignin to the reaction rate with the carbohydrate polymers present in the pulp. Selectivity is usually measured as the ratio of the kappa number to the viscosity of the pulp. It is sometimes beneficial to measure the intrinsic viscosity [η] and then convert it to degree of polymerization (DP).

The selectivity coefficient (α) can be readily estimated from the change in lignin content and the initial (DP_0) and final (DP) degrees of polymerization of cellulose at any time (t) during delignification, as in Eq. (1):

$$\alpha = \frac{\Delta K}{1/DP - 1/DP_0} \quad (1)$$

The advantage of the selectivity coefficient (α) is that it can be measured readily as the slope of a plot of ($1/DP-1/DP_0$) versus the change in kappa number (ΔK). Under this definition, perfect selectivity occurs when the selectivity coefficient equals zero (α=0).

Selectivity is affected by the wood species, choice of process conditions, and the presence of contaminants such as

the concentration of transition metals present in the pulp. Most pulps contain appreciable amounts of iron, copper, magnesium, and other metals that catalyze free radicals which lower the molecular weight of carbohydrates. Methods of controlling carbohydrate degradation were studied by Dang [15], who found that improvements in pulp selectivity resulted primarily from a reduction in the transition metals in the pulp. Adding chelating agents [16, 17], washing the brownstock pulp in an acid pretreatment stage, and adding magnesium ion directly to the oxygen stage [16] are all known to improve selectivity.

Lignin removal

The kinetics of oxygen delignification are complex and vary for different wood species and pulping processes [18–24]. Kinetic models are often empirical and incorporate mass transfer effects in the mathematical representation of the data. The most widely used model for lignin removal reactions can be described by a power law equation, as in Eq. (2):

$$-r_a = -\frac{dK}{dt} = k_o \exp(-\frac{E_A}{RT})[OH^-]^m[P_{O_2}]^n K^q \quad (2)$$

where (K) is the kappa number, [OH^-] is the sodium hydroxide concentration and (P_{O2}) represents the oxygen pressure. Also, (T) is the temperature, (EA) is the activation energy, and (R) is the universal gas constant. In some studies, the lignin reaction order is assumed to be 1.0 [18, 23]. Both one- and two-region mathematical models have been proposed.

Carbohydrate degradation

Similar empirical power law models have also been proposed for cellulose degradation in terms of the number average molecular weight (M_n) of cellulose [23], as in Eq. (3):

$$-r_a' = -\frac{dM_n}{dt} = k_0' \exp\left(\frac{E_a}{R\,T}\right)[OH]^{\chi}[P_{O_2}]^{\beta} M_n^{\alpha} \quad (3)$$

The constants in Eqs. (2) and (3) are empirical (m, n, q and α, β, and χ). They are determined by fitting the experimental data to simplified forms of Eqs. (2) and (3). In some studies, the hydroxyl ion concentration was allowed to vary, as is the practice industrially. In other studies, the hydroxyl ion concentration was held constant. Inherent in Eq. (3) is the assumption that the hemicellulose polymers in the pulp do not contribute appreciably to the number average molecular weight (M_n) of the carbohydrates comprising the pulp. Iribarne and Shroeder [23] concluded that polysaccharide cleavage could be modeled using a one-region model having an approximate 0.3-order for both alkali and oxygen. Their results suggested that delignification selectivity can be maximized by low reaction temperatures, a short first stage at high oxygen pressure and high alkali concentration, and a second stage at low pressure and low alkali concentration.

EXPERIMENTAL

The experimental methods were described by Tao [25]. The experimental pulps were prepared from southern yellow pine wood chips that were obtained from a linerboard mill in Louisiana, USA.

Kraft pulping experiments

Chip samples were screened in a Weyerhaeuser classifier and pulped to develop curves for pulp yield and intrinsic viscosity over the range of kappa nos. 25–105. The pulping experiments were conducted in a rocking digester using the conditions shown in **Table I**. The time at temperature of the wood in the digester was varied to achieve the desired H-factor. The response variables were the kappa number, total yield, intrinsic viscosity, and chemical composition. Pulps above kappa no. 35 were delignified by using a mild treatment of sodium chlorite ($NaClO_2$) before the intrinsic viscosity measurements were made. The pulps with kappa nos. 65.9 and 90.2 were reduced in size using a small laboratory refiner where the particle size was lowered to give CSF freeness values of approximately 700 mL. The refining action did not appreciably affect the oxygen delignification data and confirmed the results published by Agarwal [24].

Item	Value
Wood type	100% southern yellow pine
Liquor ratio (kg liquor/kg wood)	4
Temperature (°C)	157.2
Sulfidity (S)	30
Active alkali (AA, % on wood)	16.60
Effective alkali (EA, % on wood)	14.11
H-factor	Variable

I. Summary of kraft pulping conditions.

Oxygen delignification experiments

The oxygen delignification experiments were performed in a 2-L stainless steel Model No. 4530 Parr batch reactor (Parr Instrument; Moline, IL, USA). It had been determined previously that setting the stirrer speed at 230 rpm was sufficient to minimize mass transfer effects [26]. All of the pulps used in this study were treated with DTPA (diethylenetriaminepentaacetate) at 70°C to remove metal ions before oxygen delignification.

Experimental conditions

The oxygen delignification experiments were conducted using 30 g of pulp calculated on an o.d. basis. Oxygen delignification experiments were performed to investigate the effect of temperature, alkali condition, oxygen pressure, reaction time, and the effect of initial kappa number. Magnesium sulfate ($MgSO_4$) was used to inhibit carbohydrate degradation

reactions at an application rate of 0.3% based on dried pulp in all experiments. The reactor was held at the experimental temperature and pressure for the desired reaction times of 10, 20, 40, and 60 min.

Effect of temperature

The experiments were conducted at temperatures of 100°C, 120°C, and 140°C. The pulp that was used to investigate the effect of temperature had an initial kappa no. of approximately 90.2.

Effect of alkali concentration

The effect of alkali concentration was determined using the high kappa number pulps at alkali application rates of 3% and 6%. The temperatures used in the alkali concentration experiments were 100°C, 120°C, and 140°C.

Effect of pressure on oxygen delignification

Reaction pressures of 45, 75, and 105 psig (3.103, 5.171, and 7.239 bar gage) were used in these experiments for the kappa no. 90 pulp.

Effect of consistency

Oxygen delignification experiments were performed at consistency values of 5% and 10% at temperatures of 140°C and 160°C, respectively. As the temperature was increased, the consistency was decreased to compensate for the reduction in oxygen solubility in the caustic. The caustic application rates were 3% and 9% for each consistency and temperature value at a reaction time of 60 min.

Pulp analysis

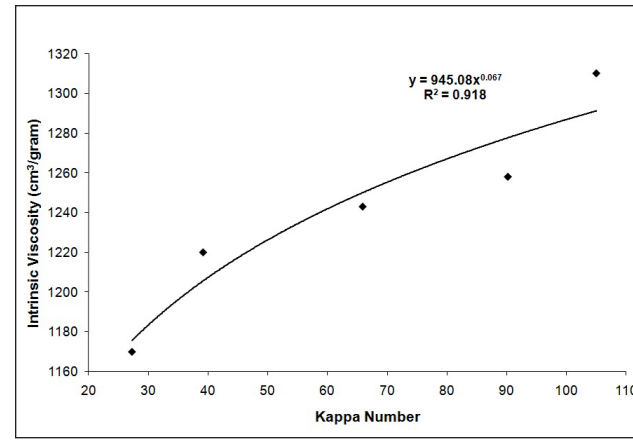
The kappa number and residual alkali were determined by following TAPPI T 236 "Kappa number of pulp" and TAPPI T 625 "Analysis of soda and sulfate black liquor," respectively. The intrinsic viscosity [η] was estimated according to ASTM standard D1795-62 and SCAN-C 15:62. The intrinsic viscosity was converted to DP using the Mark-Houswink-Sakurada relationship, as in Eq. (4):

$$[\eta] = 0.6061 \times DP^{0.90} \quad (4)$$

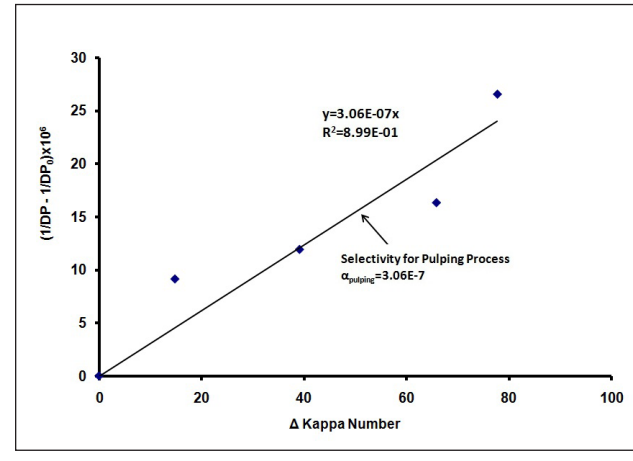
The moles of cellulose in the pulp are related to the number average degree of polymerization (DP_n) by the simple equation (Eq. [5]):

$$m_n = \frac{Grams\ Per\ Metric\ Ton}{Molecular\ Wt\ (Grams/mole)} = \frac{10^6}{162DP_n + 18} \cong \frac{10^6}{162DP_n} = \frac{Gram\ Moles}{Metric\ Ton\ Pulp} \quad (5)$$

In Eq. (5), the factor of 162 is the molecular weight of the anhydro-glucose unit and 18 is the molecular weight of water.



2. Intrinsic viscosity versus kappa number for pulping data [13].



3. Estimation of selectivity during kraft pulping (αpulping).

RESULTS AND DISCUSSION

The experimental results are summarized in **Table II** and the pulping data were determined by Zou [27].

H-factor (Hour)	Total Yield (%)	Kappa No.	Intrinsic Viscosity (cm³/g)
2518	47.17	25.0	1170
1500	49.15	40.0	1220
885	53.00	65.0	1243
602	56.62	90.2	1258
515	58.13	105	1310

II. Summary of kraft cooking results.

Pulp yield

Pulps with successively lower kappa numbers were obtained with increasing cooking time starting with kappa no. 105 and decreasing to kappa nos. 90.2, 65.9, 39.2, and 27.3. The total pulp yield varied between 58.1% and 47.2% as the kappa no. decreased from 105 to 25. The pulping data were correlated

using a linear regression line which fit the data extremely well (Eq. [6]):

$$Yield(\%) = 0.1403 \times Kappa\ No. + 43.686 \quad (6)$$

The coefficient of determination (R^2) was very close to 1.00. Equation (6) suggests that the pulp yield dropped by about 0.14% for a reduction of each kappa number unit.

Intrinsic viscosity during pulping

Figure 2 illustrates the intrinsic viscosity plotted versus the kappa number for the five pulp samples. The intrinsic viscosity data could be correlated well using a power law regression model where the coefficient of determination (R^2) was 0.92 (Eq. [7]):

$$\left[\eta, cm^3 / gram\right] = 945.08\left[Kappa\ No.\right]^{0.067} \quad (7)$$

Selectivity coefficient

The initial degree of polymerization [DP_0] was estimated from the intrinsic viscosity data taken at kappa no. 105 according to Eq. (4). The data for the change in the degree of polymerization ($1/DP-1/DP_0$) are plotted in **Fig. 3** and illustrate the selectivity coefficient ($\alpha_{pulping}$) for the kraft pulping process. The selectivity coefficient obtained during kraft pulping was estimated to be approximately 0.306 x 10^{-6} and will be compared with similar data obtained by the oxygen delignification process.

Kappa number reduction during oxygen delignification

Effect of initial kappa number

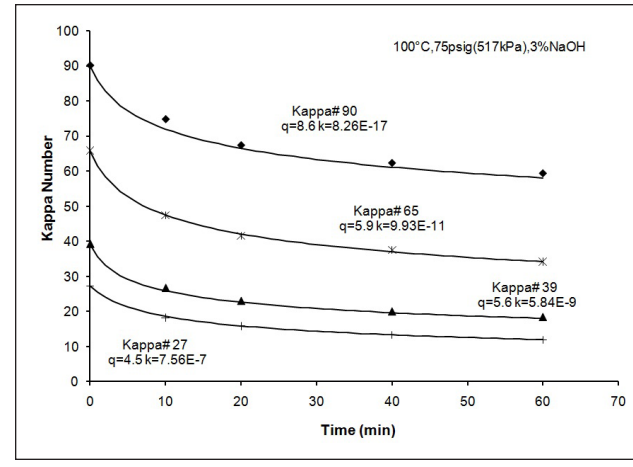
Figure 4 illustrates the effect of the initial kappa number on the reduction in kappa number brought about at a constant set of delignification conditions. Data are shown for the reduction in kappa number versus time for pulps having initial kappa nos. of 90.2, 65.9, 39.2, and 27.3. The conditions used in these experiments were temperature 100 °C, oxygen pressure 75 psig (517 kPa gage), and alkali application rate of 3% NaOH. The continuous lines shown in Fig. 4 represent the analytical expression for the kappa number (K) resulting from a power law model [28] (Eq. [8]):

$$-\frac{dK}{dt} = k_q K^q \quad (8)$$

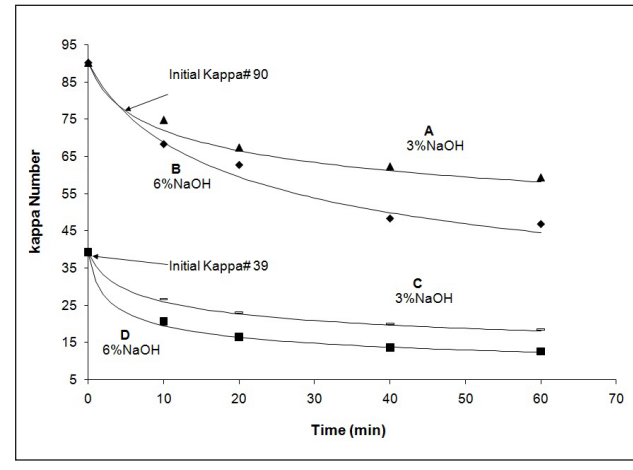
For the experiments conducted in this study, Eq. (8) can be readily integrated by assuming constant hydroxide concentration [24], as in Eq. (9):

$$\left(\frac{1}{K^{q-1}}\right) - \left(\frac{1}{K_0^{q-1}}\right) = k(q-1)t \quad for \quad q \neq 1 \quad (9)$$

In reality, because of the experimental procedure the alkali concentration varied as a function of time. Lignin removal occurred rapidly at the beginning of the experiment but proceeded more slowly with time and reached a floor value. However, the Agarwal model correlated the data well, so including the change in alkali concentration with time only complicated the analysis. The pulps with the higher initial kappa nos. (90.2 and 65.9) had higher rates of delignification at the beginning of the reaction when compared with the pulps with lower initial kappa nos. (39.2 and 27.3).



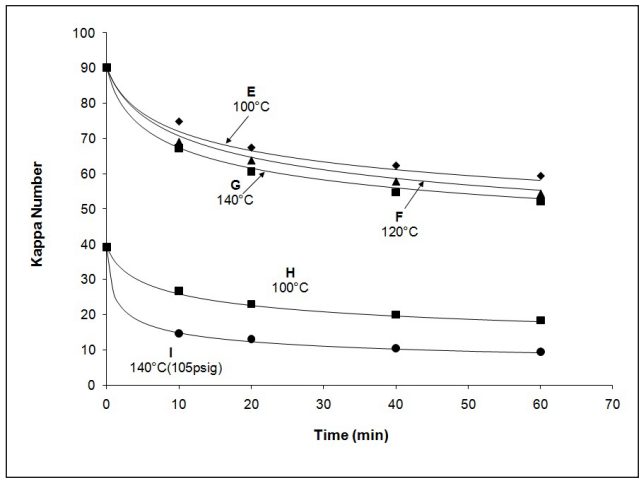
4. Kappa number versus time with different initial kappa numbers.



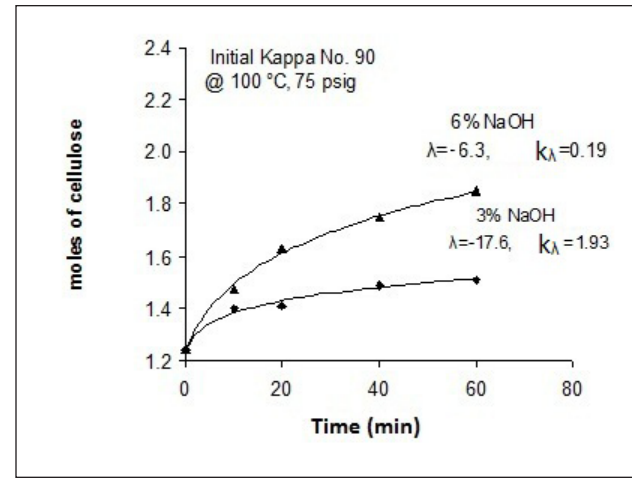
5. Kappa number versus time at different alkali concentrations for initial kappa no. 90 pulp and kappa no. 39 pulp at 100°C and 75 psig (517 kPa).

Effect of alkali concentration

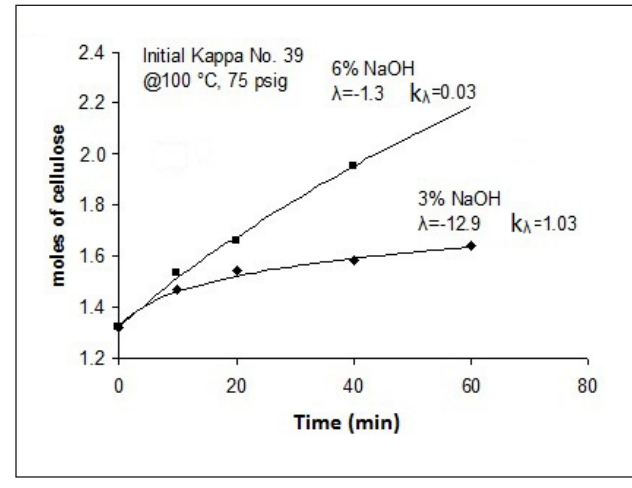
Figure 5 illustrates the effect of alkali level on the delignification of the southern softwood pulps. (The figures show data for the pulps having initial kappa nos. of 90.2 and 39.2 but are typical of the data taken for all the samples.) The caustic application rate used in these experiments was 3% and 6% based the mass of o.d. pulp. The figures illustrate the reduction in kappa number with time when the temperature and oxygen pressure were held constant and the initial alkali was varied. In both instances, the greater reduction in kappa number was observed at 6% caustic application. In the experi-



6. Kappa number versus time at different temperature for pulps with initial kappa nos. 90 and 39 at 3% NaOH and 75 psig (517 kPa gage).



7. Effect of alkali application rate on cellulose cleavage during oxygen delignification with initial kappa no. 90.



8. Effect of alkali application rate on cellulose cleavage during oxygen delignification with initial kappa no. 39.

ments conducted at 100 °C, shown in **Fig. 6**, the addition of 6% caustic resulted in a reduction in the kappa no. from 90 to 35 for the initial kappa no. 90 pulp (B) and from 39 to 15 for the initial kappa no. 39 pulp (D). By contrast, the addition of 3% NaOH showed only a reduction in kappa no. from 90 to 60 for kappa no. 90 pulp (A) and from 39 to 23 for kappa no. 39 pulp (C). The same phenomena were observed in the experiments conducted at 120 °C (not shown). The rate of delignification (dK/dt) was greater over a longer time for the higher caustic application rates. At time (t) equal to zero, however, the initial delignification rates were very similar.

Effect of temperature on the kappa number reduction

Figure 6 illustrates the effect of temperature on the kappa number drop, while the pressure and alkali application level were held constant. The caustic application level used in these experiments was 3% based upon the mass of o.d. pulp, and the pressure was kept constant. Figure 5 shows the results at 100°C, 120°C, and 140°C for the kappa no. 90 pulp and results at 100°C and 140°C for the kappa no. 39 pulp. The greatest reduction in kappa number was obtained at the highest temperature, 140 °C. The kappa no. dropped from 90 to 52 (G). In the experiments conducted at 100°C and 120°C, the reduction in kappa no. was only from 90 to 65 and 57, respectively, for the initial kappa no. 90 pulp (E and F). Similar results were obtained in the experiments conducted with initial kappa no. 39 pulp (H and I).

Cellulose degradation during oxygen delignification

The cleavage of polysaccharide chains was monitored by using the increase in the number-average moles of cellulose per metric ton of pulp (m_n) as a parameter. Iribarne and Schroeder [23] described the kinetics for the apparent polysaccharide cleavage using a power law mathematical model (Eq. [10]) similar to Eq. (3).

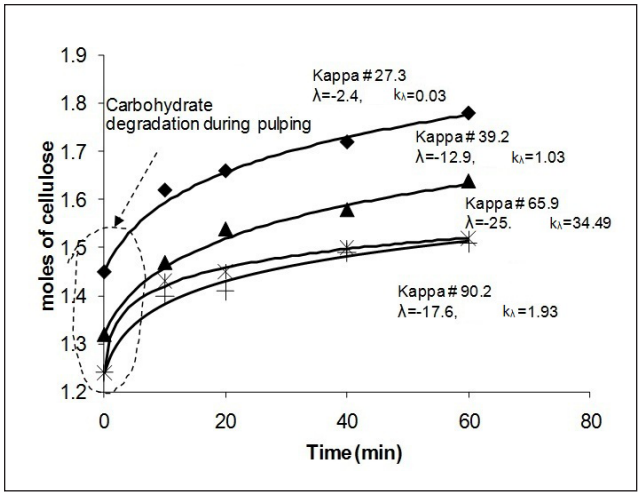
$$\frac{dm_n}{dt} = k_\lambda m_n^{\lambda} \tag{10}$$

Equation (10) can be integrated between the initial number of moles of cellulose present at time equal to zero (m_0), and any value for the moles of cellulose (m_n) present at time (t), provided the reaction coefficient (k_λ) and reaction order (λ) are approximately constant, as in Eq. (11):

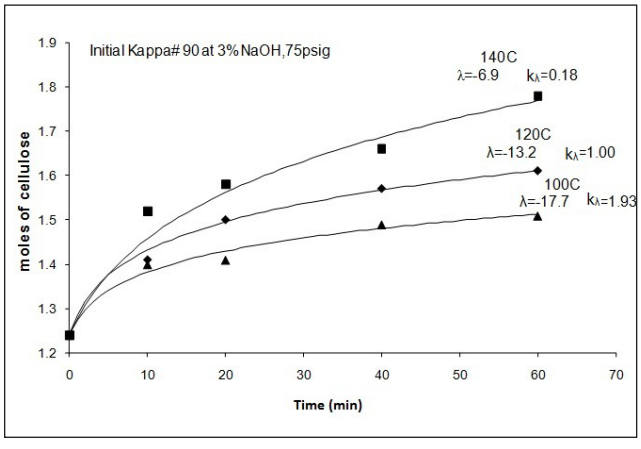
$$\left(\frac{1}{m_n^{\lambda-1}}\right) - \left(\frac{1}{m_{n0}^{\lambda-1}}\right) = k_\lambda (1-\lambda) t \quad for \quad \lambda \neq 1 \tag{11}$$

Effect of caustic application level on cellulose degradation

The data for the kappa no. 90 and 39 pulps are shown in **Figs. 7** and **8**. The solid lines in both figures represent a power law model line with reaction order (λ) and the rate constant (k_m), while the points in the figure are the exper-



9. Effect of initial kappa number on cellulose degradation during oxygen delignification at 100°C, 75 psig (517 kPa gage), and 3% NaOH.

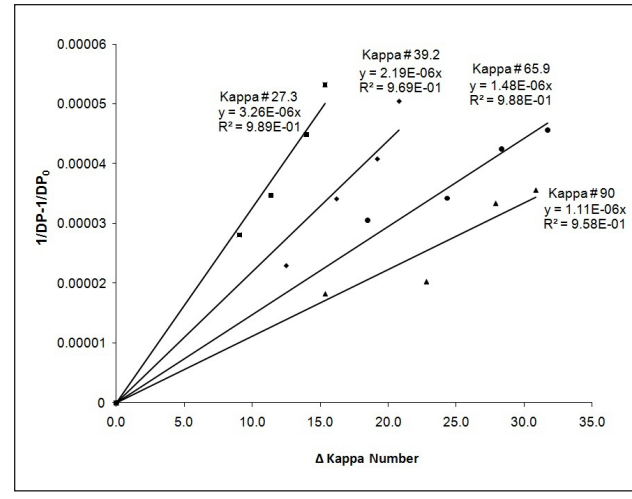


10. Effect of temperature on the moles of cellulose formed during oxygen delignification for kappa no. 90 pulp.

imental data. The experimental conditions were 100°C and 75 psig (517 kPa gage), while the alkali application level was a parameter at 3% and 6% NaOH. Figs. 7 and 8 show that that moles of cellulose in the pulp increased with increasing reaction time and the caustic addition rate was a major variable affecting the cellulose degradation rate.

Effect of initial kappa number

Figure 9 illustrates the effect of the initial kappa number on the cellulose degradation rate for the conditions of temperature 100°C, pressure 75 psig (517 kPa gage), and 3% alkali application rate. The initial kappa number also had a large effect on moles of cellulose, as Fig. 9 shows. The reduction in molecular weight of cellulose was less at the higher kappa number values. The change in the moles of cellulose at the zero (0) time in Fig. 9 presents the degradation of cellulose taking place in the digester during pulping.



11. Effect of initial kappa number on selectivity at 100 °C, 3% NaOH, and 75 psig (517 kPa gage).

Effect of temperature

Figure 10 presents the results at 100°C, 120°C, and 140°C for the kappa no. 90 pulp, while the oxygen pressure and alkali application level were kept constant. Raising the temperature greatly increased the level of cellulose degradation. High temperature and alkali concentration accelerated the degradation of cellulose.

Selectivity coefficient

The selectivity coefficient (α) is related to the ratio of the rate constants for carbohydrate degradation (k_λ) to that for lignin removal (k_q) as explained in Appendix A (Eq. [12]):

$$\frac{k_\lambda}{k_q} = \frac{\alpha \times 10^6}{162} \qquad (12)$$

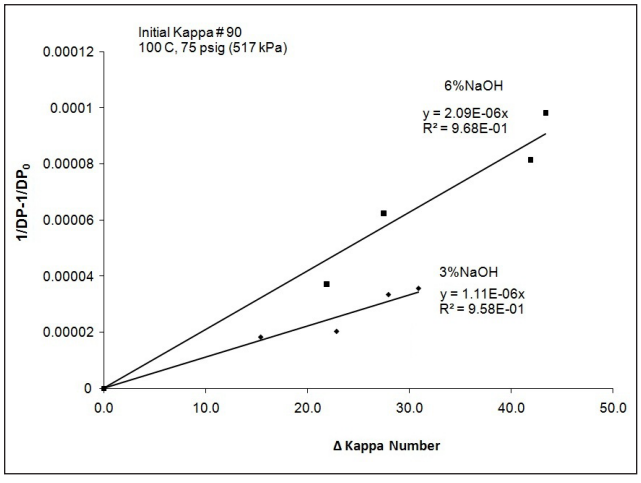
Effect of initial kappa number

Figure 11 shows the effect of the initial kappa number on the selectivity. The oxygen delignification experiments were conducted at 100°C, 75 psig (517 kPa), and an alkali application level of 3%. Figure 11 illustrates that there was higher selectivity for the higher initial kappa number pulps; that is, the slopes were lower for the pulps with higher kappa numbers and thus the ratio of the reaction rate coefficient (k_λ/k_q) is lower. For example, at an initial kappa no. of 27.3, the selectivity coefficient (α) was estimated to be 3.26×10^{-6} while at kappa no. 90.2 the selectivity coefficient was 1.14×10^{-6}. The conclusion drawn from these data is that initial kappa number has a significant effect on pulp selectivity. The data shown in Fig. 11 suggest that, as the lignin content increases, the free radicals that cause oxygen delignification have a higher probability of reacting with lignin as opposed to the cellulose in the pulp. However, even at a high kappa number, since the pulp is predominately carbohydrates (**Table III**), carbohydrate degradation is appreciable.

Pressure Condition	Selectivity Coefficient ($\alpha \times 10^{-6}$)	Coefficient of Determination (R^2)
45 psig (3.013 bar gage)	1.26	0.95
75 psig (5.171 bar gage)	1.37	0.96
105 psig (7.239 bar gage)	1.39	0.99

[a] Temperature equal to 120°C and caustic application rate equal to 3% NaOH.

III. Selectivity coefficient (α) showing the effect of pressure [a].



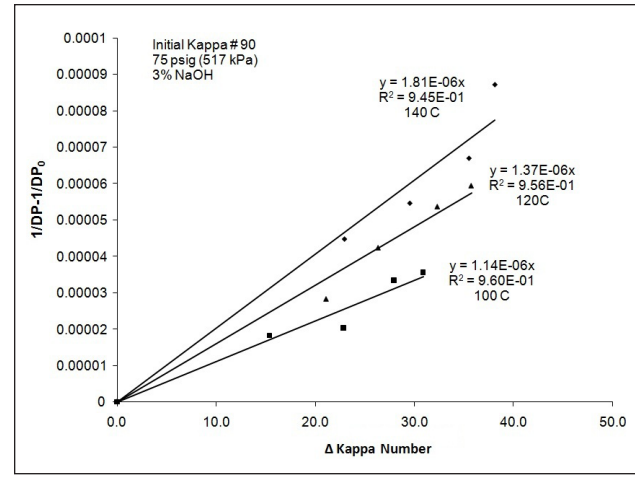
12. Effect of alkali concentration on selectivity at 100°C and 75 psig (517 kPa gage) for kappa no. 90 pulp.

Effect of alkali concentration

Figure 12 shows the effect of alkali application level on the selectivity for the oxygen delignification experiments that were performed at 100°C and 75 psig (517 kPa gage) for the kappa no. 90 brownstock pulp. Similar data were obtained for the kappa no. 39 pulp. It is apparent that a lower level of carbohydrate degradation occurred in the experiments with the lower caustic application rate; that is, the selectivity coefficient was lower in the low alkali application rate experiments. The difference between the two slopes is approximately 0.8×10^{-6} selectivity units for the initial kappa no. 90 pulp and 0.9×10^{-6} selectivity units for the initial kappa no. 39.2 (data not shown).

Effect of temperature and oxygen pressure

The effect of temperature on selectivity is illustrated in **Fig. 13** for a caustic application rate of 3% for the kappa no. 90 pulp. In these experiments, the temperature was varied from 100°C to 140°C. The selectivity coefficients in Fig. 13 for the experiments conducted at 100°C and 120°C are quite similar: about 1.14×10^{-6} at 100°C and 1.37×10^{-6} at 120°C for the initial kappa no. 90. The experiments conducted at 140°C by



13. Effect of temperature on selectivity for kappa no. 90 pulp at 75 psig (7.171 bar gage) and 3% NaOH.

contrast had a higher selectivity coefficient (about 1.81×10^{-6}). Changing the caustic application rate gives rise to different selectivity values.

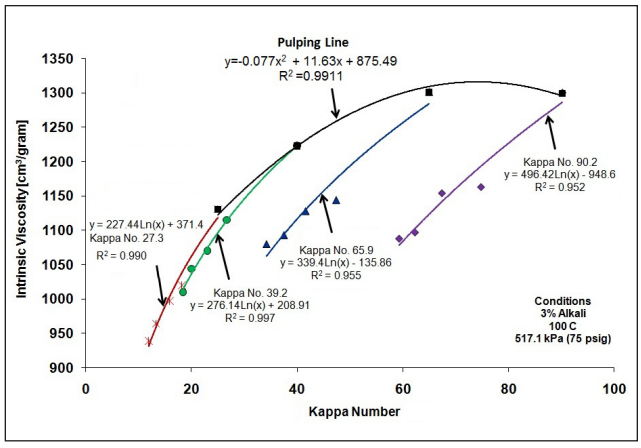
Experiments were performed at pressures of 45 psig (3.013 bar), 75 psig (5.171 bar), and 105 psig (7.239 bar) while the temperature and alkali application rate were kept constant at 120°C and 3% NaOH, respectively. These data show that the three selectivity lines had almost the same slope (Table III). Thus, we concluded that varying the pressure did not have a major effect on carbohydrate degradation.

Comparison of kraft pulping and oxygen delignification

The data in **Table IV** and **Fig. 14** illustrate the difference in selectivity between delignification resulting from kraft pulping and from oxygen delignification. In Fig. 14, the intrinsic viscosity [η] obtained for the pulping line is compared to the intrinsic viscosity data obtained for the four pulps delignified using the oxygen delignification process; that is, the pulps with initial kappa nos. of 90.2, 65, 40, and 25. The oxygen delignification experiments were conducted using constant conditions of 100 °C, 3% alkali application level and 75 psig (5.171 bar gage). The data for the selectivity coefficient (α) in Table IV result from that shown in Figs. 3 and 11.

Removal of lignin by kraft pulping is clearly much more selective, especially for high lignin pulps, than by the oxygen delignification process. This difference in selectivity can be explained by the chemistry occurring in the two systems. During oxygen delignification, hydroxyl radicals are generated. The hydroxyl radicals attack the anomeric position in the carbohydrate chains, cleaving the polymeric chains anywhere along the chain as shown in Fig. 1 [13, 29]. This cleavage can cause a significant decrease in the degree of polymerization of the carbohydrates and thus, a substantial loss of viscosity [14].

In kraft pulping, however, hydroxyl radicals are not produced. The hydrosulfide ions that are responsible for lignin degradation are highly selective toward attack on the lignin



14. Intrinsic viscosity [η] versus kappa number for pulps used in this study (oxygen delignification at 100°C, 75 psig [7.171 bar gage], 3% NaOH).

Condition	Selectivity Coefficient (α x 10⁶)
Kraft process	0.31
Oxygen delignification process	
Kappa no. 90.2 pulp	1.14
Kappa no. 65.9 pulp	1.48
Kappa no. 39.2 pulp	2.19
Kappa no. 27.3 pulp	3.26

IV. Summary of data for selectivity coefficient.

while carbohydrate degradation occurs only from peeling reactions. The endwise peeling process does not reduce the degree of polymerization as significantly as that which occurs by random cleavage and the viscosity loss is less. For both kraft pulping and oxygen delignification, at low lignin content (i.e., low kappa number), the remaining lignin is likely bound covalently to the carbohydrate portion, so removal of the lignin results in significant degradation of the carbohydrates. This is observed as poor selectivity in both kraft pulping and oxygen delignification.

CONCLUSIONS

The kraft pulping process is more selective than the oxygen delignification process for removing lignin from the higher kappa number pulps (kappa no. 90 and 65). The lower selectivity of the oxygen delignification process was thought to result from the presence of hydroxyl free radicals present in the oxygen delignification process that are not present in the kraft pulping process.

The alkali application rate was found to have a large effect on the rate of oxygen delignification. At a fixed temperature, the greatest reduction in kappa number was obtained by a high rate of application of alkali. This was true for both the high- and low-kappa number pulps. However, the alkali charge was found to have a high negative effect on pulp selectivity. Consequently, a balance must be achieved between lignin removal and pulp selectivity when selecting the alkali application rate.

In addition to the caustic application level, temperature was found to have a great effect on the oxygen delignification process. Raising the temperature increased the oxygen delignification rate for pulps with both high and low initial kappa numbers, provided there was sufficient oxygen dissolved in the pulping liquor. For example, raising the delignification temperature to 140°C required that the consistency be lowered from 10% to 5%. At high consistency and high temperature, for example 10% at 140 °C, insufficient oxygen was present and the pulps blackened and burned. Thus, we concluded that sufficient oxygen must be present in the liquid phase to permit the reactions to proceed. Raising the temperature during the oxygen delignification process reduced the selectivity but to a much lesser extent than raising the caustic concentration. A disadvantage of operating at elevated temperature in the oxygen delignification process is the consumption of additional steam, which increases the operating costs.

The initial kappa number was found to have a great effect on the delignification rate and the selectivity. The higher initial kappa number pulps exhibited higher delignification rates in the initial period and higher selectivity compared with the lower kappa number pulps. Thus, we concluded that removing lignin is easier in high kappa number pulps and there is less viscosity lost.

Over the range of oxygen pressure of 45 psig (3.103 bar) to 75 psig (5.171 bar), the oxygen pressure had a relatively small effect on the reduction in kappa number, intrinsic viscosity drop, and selectivity compared with the caustic application rate and the temperature. The reduction in kappa number appeared to be enhanced at high pressures, for example 105 psig (7.239 bar). The capital cost for the oxygen delignification process increased as the pressure increased, however. **TJ**

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APPENDIX A. SELECTIVITY COEFFICIENT (α)

The selectivity coefficient (α) is estimated from the slope of a plot of $[1/DP_n - 1/DP_0]$ versus the change in kappa number (ΔK). The slope of the graph $(1/DP_n - 1/DP_0)$ versus ΔK is proportional to the chain scissions per monomer unit of cellulose given in Eq. (4) as described by Evans and Wallis [29].The inherent assumption in this definition of the selectivity coefficient (α) is that the reaction order for both kappa number and the moles of cellulose are both zero order. Equation (1) in the main text can be obtained by assuming a power law to describe the change in number of moles of cellulose and the decrease in the lignin content. By taking the ratio of the rate

equations for the kappa number and the moles of cellulose given in Eqs. (2) and (3), we obtain Eq. (A1):

$$\frac{dm_n / dt}{dK / dt} = \frac{k_\lambda m_n^{\ \lambda}}{-k_q K^q} \quad \text{(A1)}$$

The dependence of temperature, pressure, and caustic concentration has been incorporated into the coefficients (kλ and kq). If the rate orders (λ and q) are both taken to be zero, Eq. (A1) can be integrated between the initial value (m0 and K0) at time zero to any value (m and K) at time (t) (Eq. [A2]):

$$m_n - m_0 = -\frac{k_\lambda}{k_q}(K - K_0) \quad \text{(A2)}$$

The moles of cellulose (m) can be converted to the degree of polymerization by using the definition for the moles of cellulose given by Eq. 4 (Eq. [A3]):

$$\left[\frac{1}{DP} - \frac{1}{DP_0}\right] = \left[\frac{k_\lambda}{k_q}\frac{162}{10^6}\right](K_0 - K) \quad \text{(A3)}$$

The selectivity coefficient (α) is given by the ratio of the rate constants (kλ and kq) and is given by the expression Eq. (A4):

$$\alpha = \frac{k_\lambda}{k_q}\frac{162}{10^6} \quad \text{(A4)}$$

Clearly, the assumption that the rate order (q) for kappa number reduction is zero is incorrect. However Eq. (1) is useful in comparing the selectivity of delignification processes.

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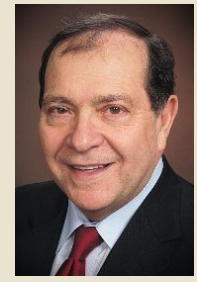
ABOUT THE AUTHORS

This work was done as part of the University of Maine's research effort to understand oxygen delignification. It complements research performed by Adriaan van Heiningen and others on the selectivity of oxygen delignification.

The most difficult aspect of this work was trying to perform oxygen delignification on samples at very high kappa numbers (kappa nos. 65 and 90). We had to partially refine or fiberize the samples to assist in oxygen penetration into the pulp. The most interesting aspect of the research was the conclusion that oxygen delignification is less selective than conventional kraft pulping. We had always assumed that the opposite was true.

Mills can benefit from knowing that kraft pulping is more selective than oxygen delignification. Future work will include an examination of the selectivity of oxygen delignification of southern hardwoods, which are extremely difficult to delignify using oxygen delignification.


Tao


Genco


Cole


Fort

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