

EFFECT OF HEMICELLULOSE CONTENT IN KRAFT BROWNSTOCK ON OXYGEN DELIGNIFICATION

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ABSTRACT

Kraft pulping experiments were performed on mixed Northeastern hardwood chips to investigate the effect of hemicellulose content on the response of brownstock pulps to medium consistency oxygen delignification. High levels of anthraquinone were used to produce pulps with high pulp yield which coincided with high hemicellulose content brought about by elevated levels of xylan.

Response variables were found to depend upon hemicellulose content in the brownstock. The kappa number versus time data fit a classical power law model, indicative of lignin fragmentation. There was a systematic increase in the oxygen delignification rate and in the Schoon rate constant as the hemicellulose content decreased in the digester. The pulp selectivity increased with increasing pulp hemicellulose content until a maximum was reached.

Chemical analysis of the pulps indicated that the increase in pulp yield was caused primarily by an increase in the xylan polymer as additional anthraquinone was added in the digester. In the oxygen reactor, the loss in pulp yield resulted from a reduction in the lignin as well as a loss of carbohydrates, primarily from loss of the xylan polymer. The observed results support the hypothesis that oxygen delignification is limited by reduced accessibility due to the presence of increased amounts of xylan.

INTRODUCTION

Oxygen delignification is becoming increasingly important in pulp bleaching technology. Extending oxygen delignification without loss of fiber strength and pulp yield will be an important topic in pulp bleaching research for the near future. A lower kappa number following an oxygen delignification stage results in a lower active chemical charge required to bleach the pulp. This results in savings in chlorine dioxide charge and other chemical requirements to achieve the target brightness. A major unexplored area in oxygen bleaching is the relationship between delignification observed in the oxygen stage and the conditions present in the digester and other unit operations in the fiber line.

Digester operating conditions would be expected to affect the response variables in oxygen delignification and subsequent bleaching stages. Varying the cooking conditions not only affects the final kappa number (lignin content) leaving the digester but also results in different properties for the lignin and hemicellulose at a target kappa number. These differences in chemical structure would be expected to affect oxygen delignification and subsequent bleaching of pulps.

PREVIOUS STUDIES

Backstrom et al. studied the influence of cooking temperature in modified softwood Kraft pulping [1]. Gustavsson et al. present contradictory results in the study of the bleachability of softwood Kraft pulp [2]. They reported that the bleachability was improved by increasing the cooking temperature for low and medium $[\text{OH}^-]$ charges, but found no differences at high $[\text{OH}^-]$ charge.

Chen studied the effect of cooking temperature in conventional birch Kraft pulp on oxygen delignification [3]. He reported that the oxygen delignification efficiency was improved by increasing the cooking temperature from 170 °C to 180 °C. Chen suggested that the different cooking temperatures resulted in a different structure for the residual lignin. The residual lignin in pulp cooked at higher temperature was more easily degraded during oxygen delignification than lignin in pulp cooked at a lower temperature. It has been widely reported that increasing the

effective alkali charge improves the unbleached pulp brightness and the bleachability of the brownstock pulp [2, 4, 5, 6].

Gilbert and Hsieh compared the bleaching response of Kraft pulps and Kraft-AQ pulps prepared from southern pine in ECF bleaching sequences [7]. They reported that the Kraft-AQ pulps exhibited better bleachability, in terms of brightening, chemical requirements, and pulp viscosity, than the Kraft pulps.

Chirat and Lachenal investigated the limits of oxygen delignification using several softwood and hardwood Kraft pulps [8]. In all of the experiments, the delignification essentially stopped after three successive medium consistency oxygen stages which were performed at 100 °C. They found that the limits to oxygen delignification were 75% and 60% for the softwood and hardwood Kraft brownstock pulps, respectively. It was concluded that the residual lignin was most probably attached to carbohydrates by linkages which resist oxygen bleaching.

Tamminen and Hortling compared the effect of the alkaline cooking method--conventional Kraft pulping (CK), polysulfide/anthraquinone (PSAQ) and soda-anthraquinone (SoAQ), on subsequent oxygen delignification [9]. They found that the lignin structures before and after exposure to oxygen could not explain the differences in oxygen delignification. They speculated that the difference in delignification was caused by differences in the hemicellulose to lignin bond structure.

The responses to oxygen delignification by pulps of high hemicellulose content were investigated previously by Zou [10]. This work showed that pulps with high xylan content were more difficult to delignify but had improved selectivity when compared to pulps with low xylan content. The work reported here is an extension of this work.

OBJECTIVE AND SCOPE

Few of the previous studies on oxygen delignification have focused on the effect of carbohydrate content in the brownstock with the same pulping process conditions. Rather, many have focused on optimizing the oxygen delignification process itself.

The objective of the present study was to determine the impact of the hemicellulose content in the brownstock on the performance of an oxygen stage. Northeastern hardwood Kraft pulps were the pulp of interest and were selected because of their difficulty in delignification. The effect of the brownstock composition on oxygen delignification was studied by varying the hemicellulose content of the pulp. Pulps with high hemicellulose content were prepared at the same kappa number by pulping with anthraquinone, which functions as a pulping catalyst. This was achieved by holding the cooking conditions constant while varying the H-factor and the level of anthraquinone.

EXPERIMENTAL

Kraft Pulping

Mixed northeastern hardwood chips were used to prepare Kraft pulps in a two kilogram, electrically heated, batch digester that could be rocked at a frequency between 2 and 6 revolutions per minute through an arc of approximately 135 degrees. The digester was operated at a constant liquor to wood ratio of four to one (4:1). Kraft brownstock pulps were prepared having the same target kappa number (16 to 17) by pulping with 12%EA, 30% sulfidity and different AQ levels. This was accomplished by varying the anthraquinone charge and changing the H-factor by altering the cooking time to meet the kappa number target while keeping the temperature constant (160°C). After cooking, the pulps were well-washed and subjected to oxygen delignification in a medium consistency reactor. Carbohydrate and lignin analyses were performed to determine the component sugars and soluble and insoluble lignin.

Conditions

The pulps were then delignified in a single stage medium consistency oxygen reactor. Details of the experimental conditions and procedures are summarized by Zou [10, 11]. The oxygen delignification experiments were conducted at a temperature of 90 °C using 1.5% caustic based upon pulp, and an oxygen pressure of 0.69 MPa (100

psig). The reaction time was varied from zero (0) to sixty (60) minutes. Magnesium sulfate was used for viscosity protection and was added at 0.1% based upon pulp.

Procedure

In the experiments, the oxygen reactor was preheated to 90 °C. In a separate operation, the magnesium sulfate was added to the pulp initially and mixed in a Hobart mixer. While the pulp was being mixed, caustic was added. Following the mixing operation, the mixture was sealed in a plastic bag and heated to around 90 °C in a microwave oven. The pulp was transferred to the oxygen reactor and the entire mixture brought up to 90 °C. Lastly the oxygen was added to start the reaction. There was approximately a ten (10) minute delay caused by having to heat the entire mixture to 90 °C prior to addition of the oxygen. Thus, there is some extraction of the lignin by the caustic prior to the addition of oxygen. The experimental data were corrected for this extraction step.

Response Variable and Pulp Composition

The response variables were determined using standard methods. The kappa number and intrinsic viscosity were determined by following TAPPI Standards T-236 and ASTM D 1795-62, respectively. The pulp yield was determined gravimetrically. The component carbohydrate content of the pulps as well as the extractives (methylene chloride) and soluble and insoluble lignin were estimated by following the procedures summarized by Genco et al. [12]. Sugar analyses were performed using a Dionex DX 500 ion chromatograph.

RESULTS

Kraft Pulping

The experiments are summarized in Table 1. It is well known that cooking with AQ leads to pulps with higher hemicellulose content and thus higher pulp yield. In this set of experiments, four levels of anthraquinone (0, 0.1%, 1%, and 4%) were added to the digester during the Kraft pulping process. In each case a target kappa number of 16 to 17 was achieved. Commercially, AQ levels added to the digester are typically between 0.05 to 0.1% for economic reasons.

Table 1.
Summary of Kraft-AQ pulping results

| ID | AQ (%) | Time at temp. min | H-factor | Screened Yield (%) | Reject (%) | Total Yield (%) | Kappa No. | Intrinsic Viscosity (ml/g) | Brightness (% ISO) |
|---------|--------|-------------------|----------|--------------------|------------|-----------------|-----------|----------------------------|--------------------|
| Control | | 464 | 3065 | 49.94 | 0.151 | 50.10 | 16.3 | 1244 | 27.10 |
| AQ 0.1% | 0.1 | 246 | 1694 | 52.22 | 0.285 | 52.50 | 17.5 | 1239 | 29.52 |
| AQ 1.0% | 1.0 | 185 | 1271 | 54.11 | 0.200 | 54.31 | 17.2 | 1157 | 26.31 |
| AQ 4.0% | 4.0 | 171 | 1247 | 56.06 | 0.250 | 56.31 | 17.6 | 1130 | 27.13 |

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

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

Pulp Viscosity. Increasing the AQ charge increased the brownstock pulp yield; it also decreased the pulp viscosity (Table 1). Although pulping with AQ in the digester reduced the cooking time to achieve a target kappa number, no improvement could be measured for the brightness of the brownstock pulp.

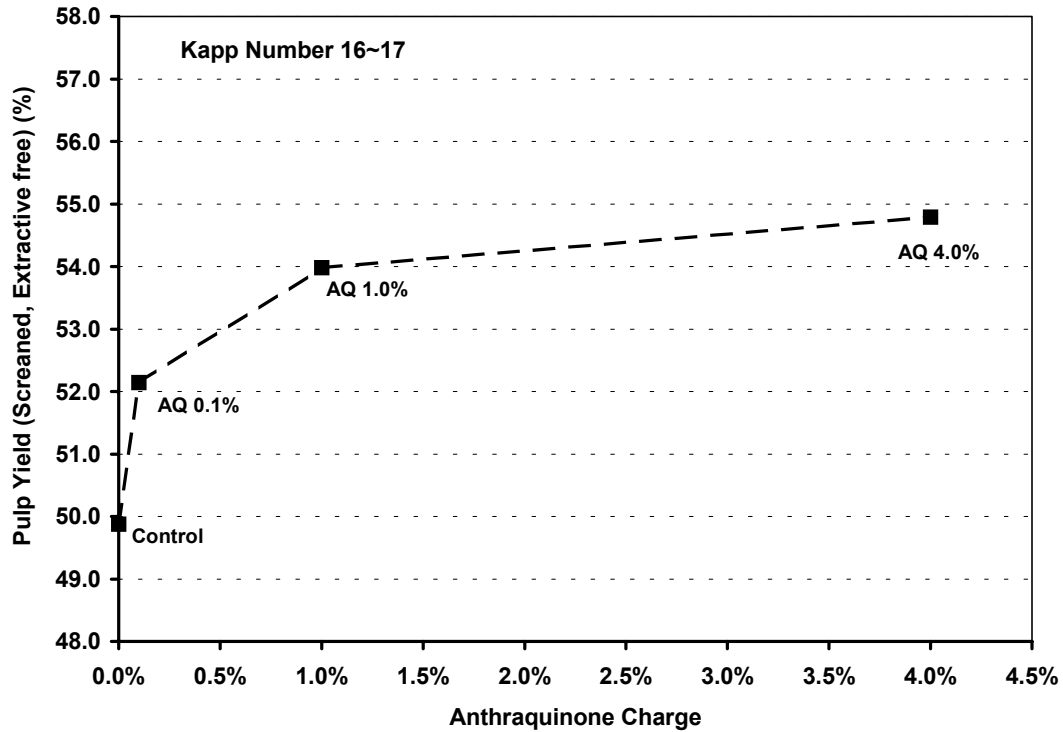


Figure 1. Pulp yield versus AQ charge in the digester.

Pulp Composition. The data for the carbohydrate composition for the brownstock pulps produced using AQ in the digester are summarized in Table 2.

Table 2.
Summary of brownstock pulp composition analysis

| Sample ID | Ash (%) | Extractives (%) | Total Lignin (%) | Uronic Anhydride (%) | Arabinan (%) | Galatan (%) | Glucan (%) | Xylan (%) | Mannan (%) | Cellulose (%) | Hemicellulose (%) |
|-----------|---------|-----------------|------------------|----------------------|--------------|-------------|------------|-----------|------------|---------------|-------------------|
| Control | 0.12 | 0.12 | 2.31 | 0.24 | 0.10 | 0.23 | 74.98 | 21.56 | 0.56 | 74.65 | 23.04 |
| AQ0.1% | 0.17 | 0.14 | 2.33 | 0.24 | 0.46 | 0.47 | 73.36 | 22.37 | 0.76 | 72.91 | 24.75 |
| AQ1.0% | 0.16 | 0.23 | 2.24 | 0.18 | 0.13 | 0.31 | 72.25 | 23.64 | 1.23 | 71.53 | 26.24 |
| AQ4.0% | 0.18 | * | 2.32 | 0.17 | 0.22 | 0.27 | 71.70 | 24.09 | 1.23 | 70.97 | 26.71 |

(*) Data not available

The chemical analysis showed that these four (4) pulps had the same lignin contents, which was about 2.3%. On an absolute basis (x_i^P) (pulp), the hemicellulose contents of the four (4) pulps were found to increase while the cellulose content was found to decrease. By contrast the retention of both the hemicellulose and cellulose polymers was found to increase when cooking with anthraquinone. This can be seen if the carbohydrate contents of the pulps are expressed on the basis of wood going to the digester (x_i^W).

$$x_i^W = \frac{y_{Pulp} * x_i^P}{100} \quad (1)$$

where y_{Pulp} is the pulp yield following Kraft pulping and x_i^P is the weight fraction of the carbohydrates in the pulp on an absolute basis. These data are shown in Figures 2 and 3. The data of Figure 2 clearly show that both the cellulose and hemicellulose polymers are retained as the AQ to the digester is increases. Although both the cellulose and hemicellulose contents of the pulp increase, the greater yield gain originated from the retention of the hemicellulose (xylan) polymers. This increase in the hemicellulose contents results because the AQ reduces aldehyde end groups on the carbohydrates and increases the rate of delignification. Also, the hemicellulose polymers are more accessible to the alkali in the pulping liquor and more prone to undergo peeling reactions compared to cellulose because of their amorphous structure.

Dependence of Pulp Yield on Hemicellulose Content. For the brownstock pulps produced using AQ, there was an excellent linear relationship between pulp yield and the hemicellulose content in the pulp (Figure 4). For pulps produced at the same kappa number, invariably, pulps with higher yield contained greater amounts of the hemicellulose polymers and less cellulose. Approximately 70% of the increase in pulp yield can be attributed to the increase in the hemicellulose polymers and only 30% resulted from improved cellulose retention. Xylan is a dominant component in the hemicellulose polymers comprising northeastern hardwoods. Invariable, the retention of xylan increased with increasing pulp yield (Figure 5).

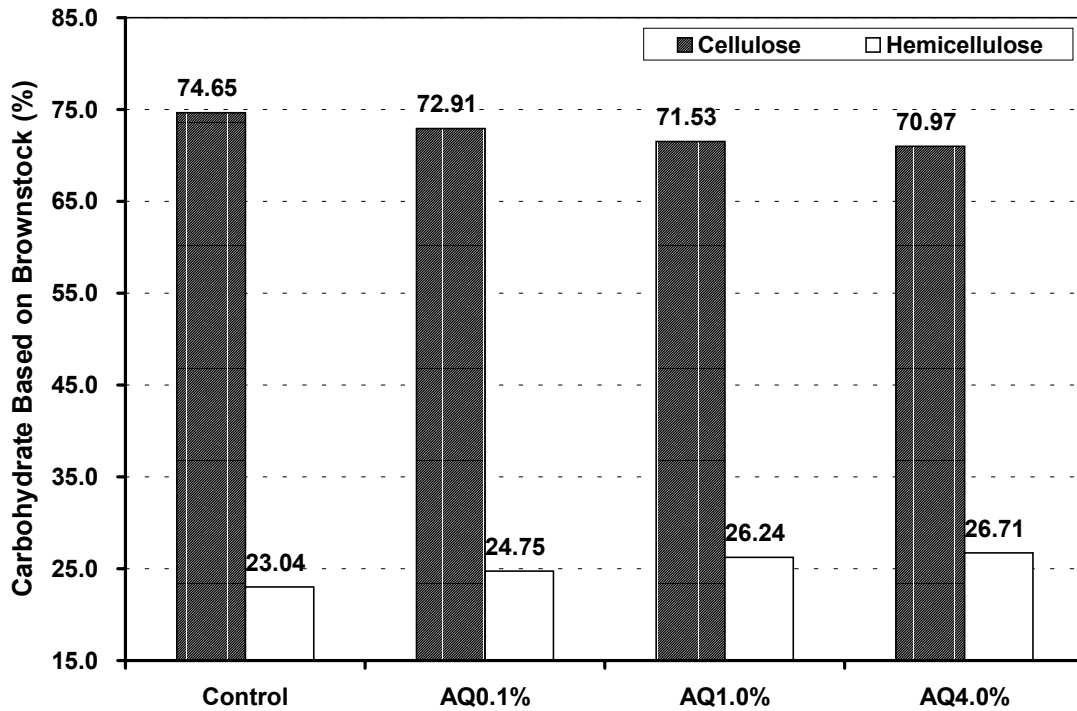


Figure 2. Carbohydrate content based upon brownstock (absolute basis).

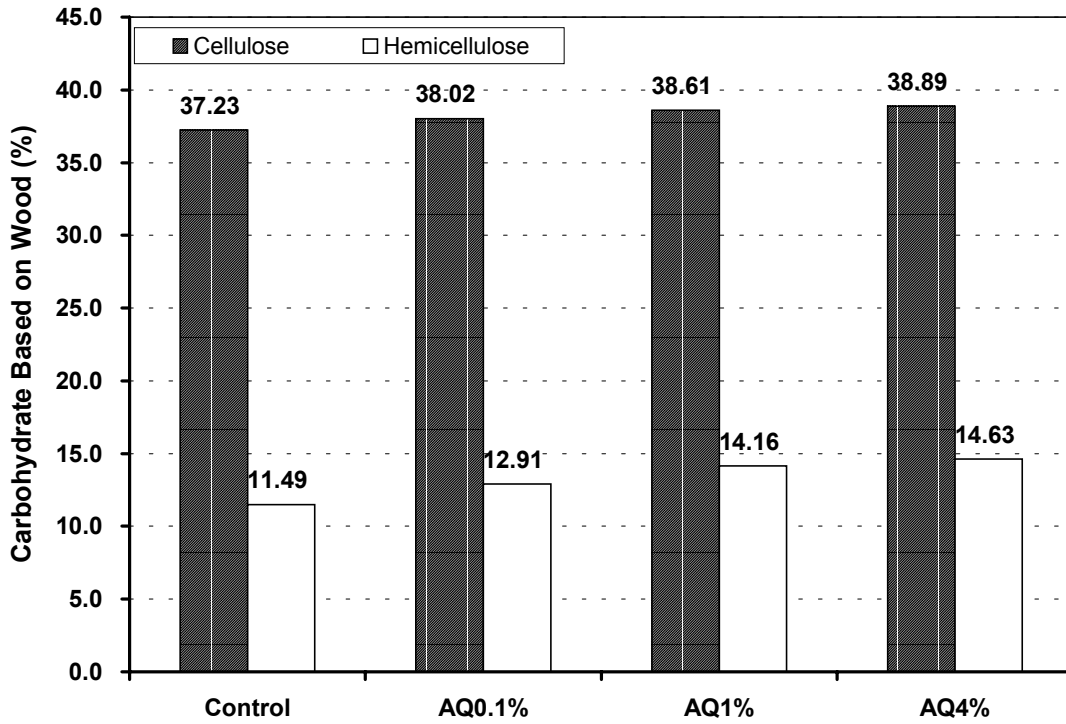


Figure 3. Carbohydrate content based upon wood versus AQ charge in the digester.

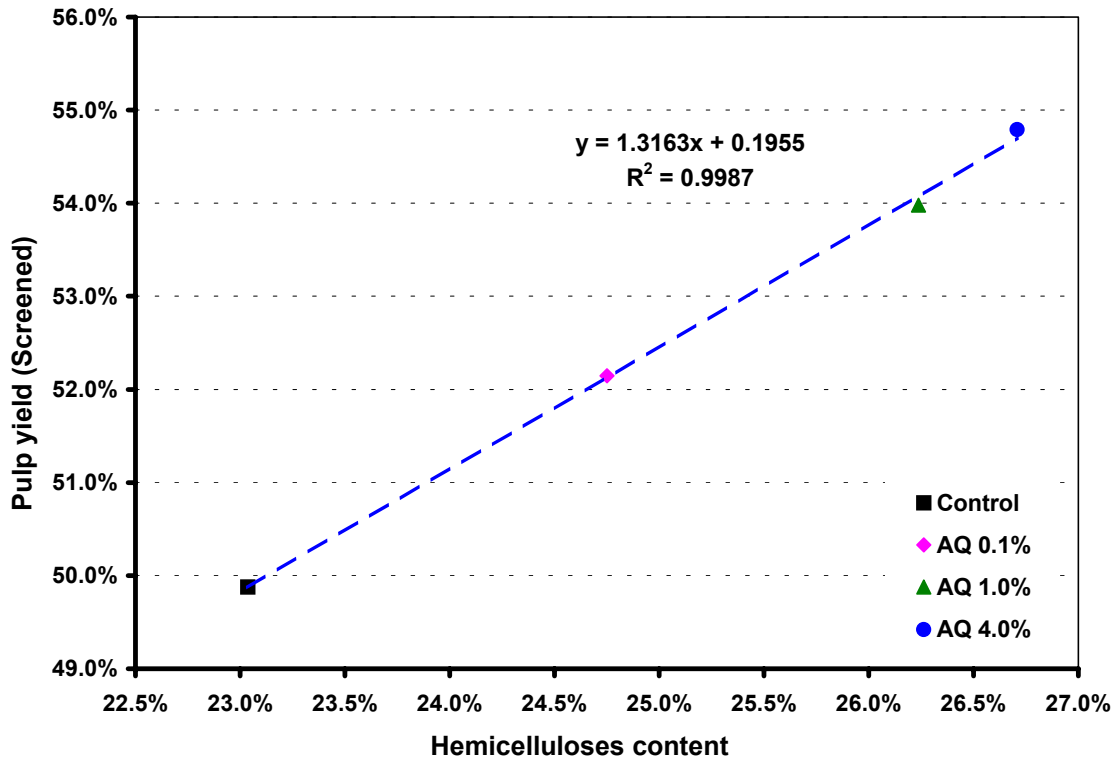


Figure 4. Kraft Screened yield versus hemicellulose content in the brownstock pulps produced using AQ (absolute basis).

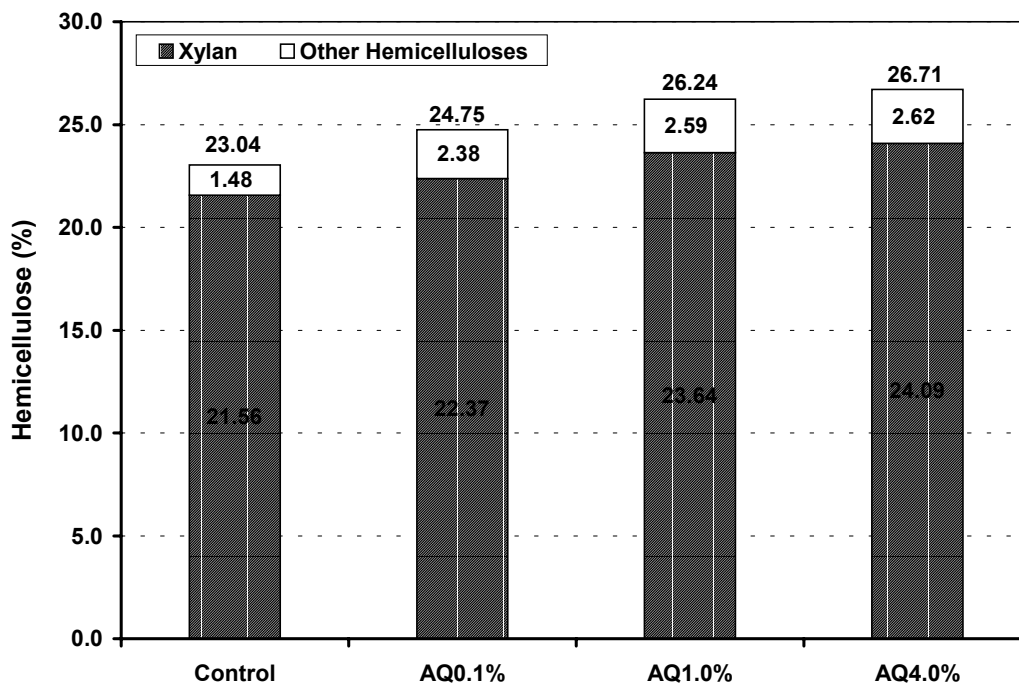


Figure 5. Xylan and other hemicellulose contents in brownstock pulps produced using AQ.

Results of Oxygen Delignification

Kinetics. Schoon's model [13], developed for depolymerization reactions that occur by a infinite number of parallel first order reactions, was used to analyze the data for the oxygen delignification kinetics (Table 3). Treatment of kinetic data for oxygen delignification has been described previously by Agarwal and co-workers [14]. The objective of the current work was to develop data for the kinetic rate constant (k') and order of the reaction (q) and permits a direct comparison of the kinetics for the delignification reaction at variable hemicellulose content in the brownstock. The kappa number data are shown graphically in Figure 6. The initial kappa number has been shifted slightly or modified so that all of experiments start at an initial kappa number value of 15.5. The data have also been corrected for extraction of lignin that occurred during the heat up period, approximately 10 minutes, in which no oxygen was entered into the reactor.

$$\frac{K^{(1-q)} - K_0^{1-q}}{q-1} = k' \cdot t \quad (2)$$

Table 3.
Oxygen delignification rate constant (k') and order of the reaction ($q=7.7$).

| ID | R ² | k' |
|---------|----------------|-----------|
| Control | 0.9990 | 4.246E-10 |
| AQ0.1% | 0.9878 | 2.639E-10 |
| AQ1.0% | 0.9956 | 2.602E-10 |
| AQ4.0% | 0.9977 | 1.702E-10 |

The experimental data fit Schoon's model very well as seen by the high values for the coefficient of regression (R^2). The reaction rate order for oxygen delignification "q" is 7.7 when the kappa number data are corrected for the reduction that takes place during the caustic extraction in the preheating stage. The value for the reaction order (q) of 7.7 coincided with the results reported by Agarwal for mixed southern hardwoods having a kappa number of 13.

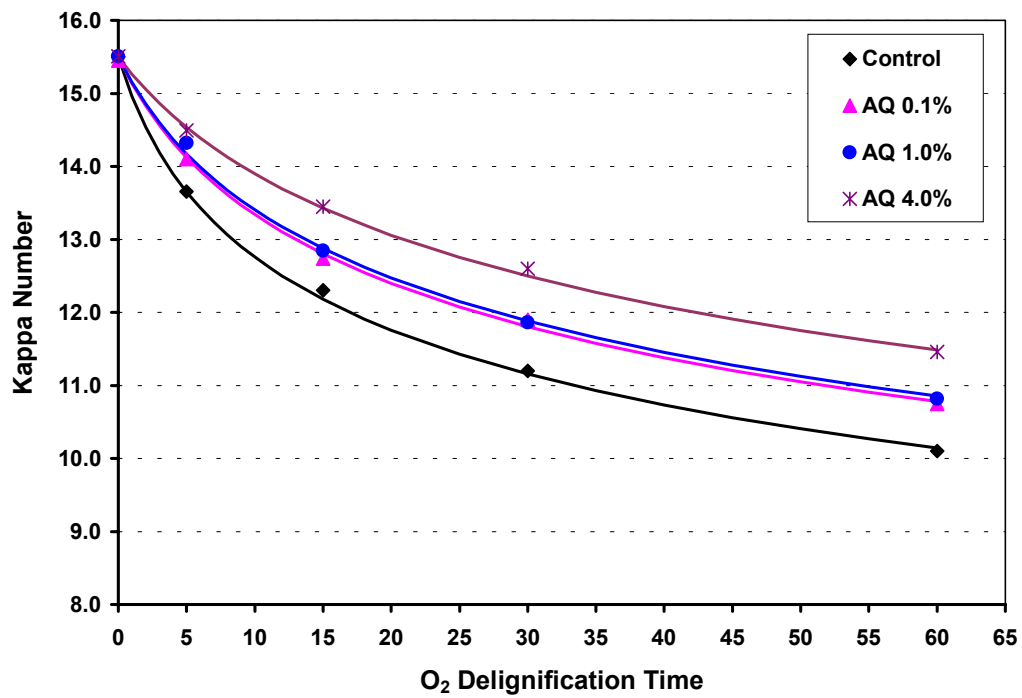


Figure 6. Effect of hemicellulose content on oxygen delignification.

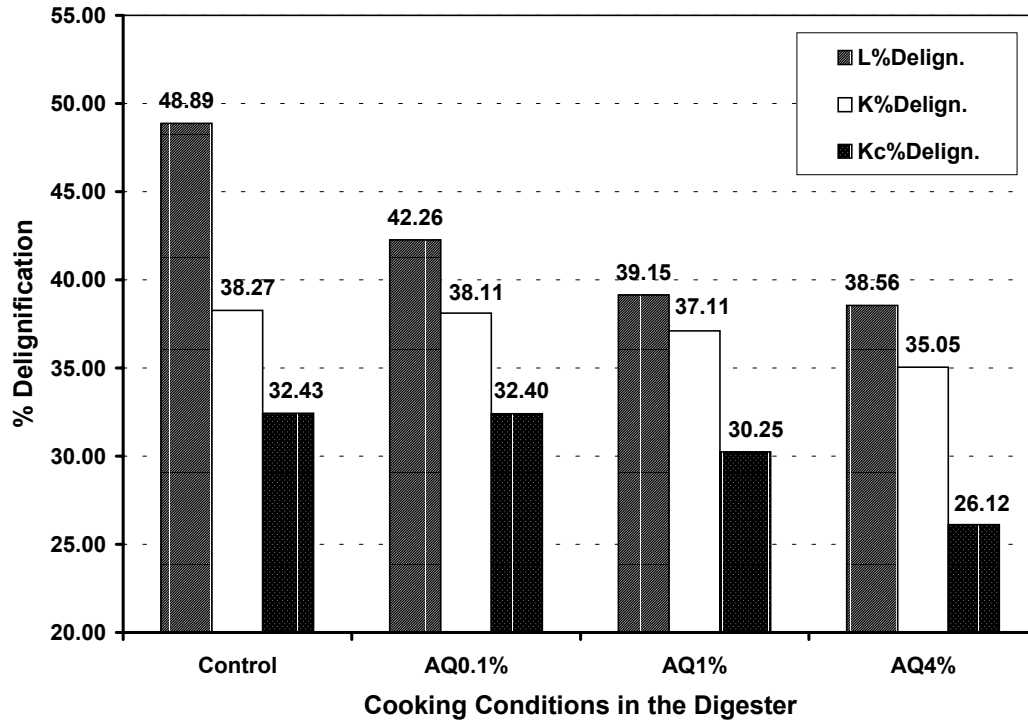


Figure 7. Delignification rate versus cooking conditions in the digester.

Hence, the “q” value in the oxygen delignification for northern mixed hardwood appears to be close to 7.7. The oxygen delignification rate decreased significantly with an increase in the hemicellulose content in the brownstock. These results are similar to our earlier work reported by Zou in which it was concluded that hardwood pulps with high hemicellulose content in the brownstock hinder oxygen delignification and result in lower efficiency [10].

Data for the percent delignification are shown in Figure 7. Three different methods were used to measure the degree of delignification. These were the change in kappa number (K), the change in total lignin content (L) and the change in corrected kappa number (K_C) after correcting for the lignin extraction during the heat-up period in the oxygen reactor. No matter what basis is chosen, it can be seen that the oxygen delignification reaction was decreased with an increase in the hemicellulose content of the brownstock. The brownstock pulp cooked with 4% AQ additive had the highest hemicellulose content (highest pulp yield); it also presented the lowest extent of delignification. Contrarily, pulp cooked with no AQ additive (control) presented the highest oxygen delignification efficiency. Pulp prepared using the soda process (data not shown) had very low hemicellulose content compared to the pulps presented here and had much higher levels of delignification.

Selectivity

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

$$MW_{Ave} = x_1 * MW_{Cellulose} + (1-x_1)*MW_{Hemicelluloses} \quad (3)$$

The DP of the cellulose is considerably greater than that of the hemicellulose polymers. During pulping and bleaching processes, the DP of the hemicellulose polymers does not change appreciably because the DP is inherently low [15]. By contrast, the DP of the cellulose changes appreciably primarily because of cellulose degradation by random hydrolysis. Consequently, if cellulose degradation occurs at a faster rate than the increase in the cellulose content, the DP of the pulp and hence, the viscosity of the pulp, will decrease. This situation occurs in most pulping and bleaching processes -- pulp viscosity generally decreases with an increase in cellulose content.

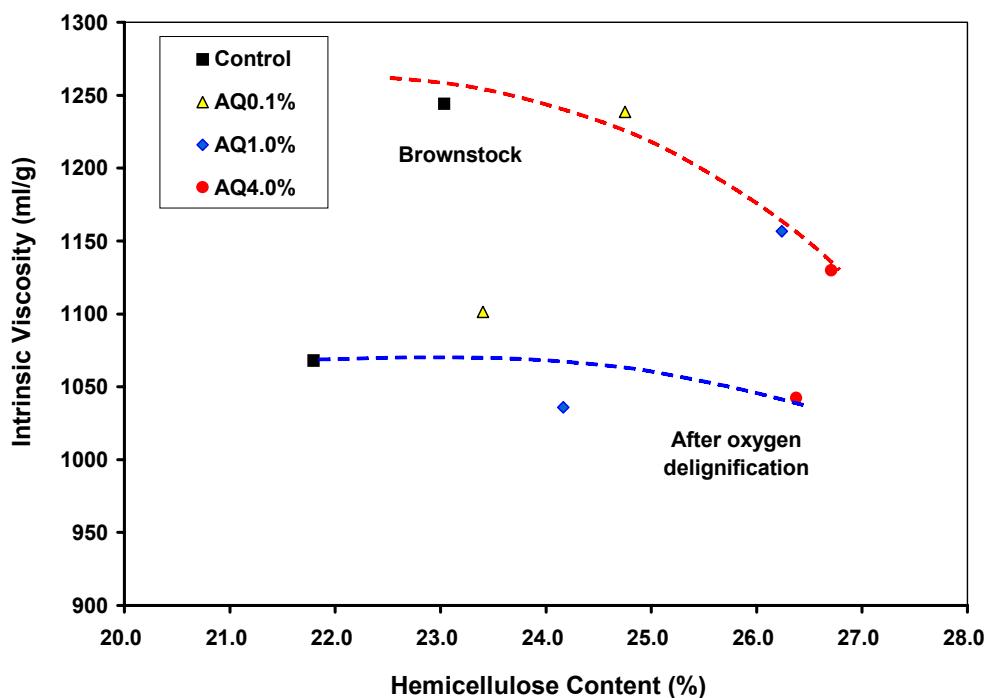


Figure 8. Intrinsic viscosity versus pulp hemicellulose content for brownstock pulp and following oxygen delignification at 60 minutes.

If the pulp was cooked under the best possible conditions, that is, under low EA and low cooking temperature, the cellulose would not be significantly degraded; and since the pulp had a high content of low molecular weight hemicelluloses, the pulp would exhibit lower viscosity because of the increase in the hemicellulose content. This is shown in Figure 8 (brownstock). The pulp with the highest viscosity was the control that was cooked without AQ. Under these conditions the cellulose would not be degraded significantly and the DP of the cellulose would be high. As the cooking time was decreased with addition of AQ at constant EA (12%) while cooking under conditions similar to the control, pulps with progressively greater hemicellulose content (greater pulp yield) would be produced without degrading the cellulose. This would give rise to pulps with progressively lower viscosity at constant kappa number. Cooking with 4% AQ that is cooking with the shortest time resulted in the highest hemicellulose content and the lowest viscosity at constant kappa number (Figure 8).

The model described by Bubniak, which is shown in equation (4), was used to correlate the intrinsic viscosity data in terms of the selectivity parameter (α) [16]. In equation (4), K_0 and DP_0 are the properties after the ten minutes extraction without oxygen present (see Experimental).

$$\left(\frac{1}{DP}\right) - \left(\frac{1}{DP_0}\right) = -\alpha \cdot (K - K_0) \quad (4)$$

The selectivity parameter (α) is defined by equation (5) in terms $\Delta(1/DP)$ and ΔK which are the change in degree of polymerization and change in kappa number respectively.

$$\alpha = -\frac{\Delta\left(\frac{1}{DP}\right)}{\Delta K} = \frac{\left(\frac{1}{DP_t} - \frac{1}{DP_0}\right)}{(K_0 - K)} \quad (5)$$

By this definition, the higher the value of the selectivity factor (α) the poorer will be the pulp selectivity.

The effect of the hemicellulose content on the selectivity of oxygen delignification is summarized in Figures 9 and 10. Table 4 shows the selectivity parameter (α) for these pulps. The data for the selectivity parameters shown in Table 4 are plotted versus the hemicellulose content in Figures 10. Generally, during oxygen delignification, the pulp selectivity will improve with an increase in the hemicellulose content in brownstock pulp. Rather than increasing continuously, a shallow minimum occurred in selectivity versus hemicellulose contents curves (Figure 10). This minimum occurred at a total hemicellulose content of approximately 25.6%.

Table 4.
Summary of selectivity data in terms of coefficient (α)

| ID | Additives % | Hemicellulose content (%) | α |
|---------|-------------|---------------------------|----------|
| Control | | 23.04 | 7.258E-6 |
| AQ 0.1% | 0.1% AQ | 24.75 | 5.631E-6 |
| AQ 1.0% | 1.0% AQ | 26.24 | 5.421E-6 |
| AQ 4.0% | 4.0% AQ | 26.71 | 5.592E-6 |

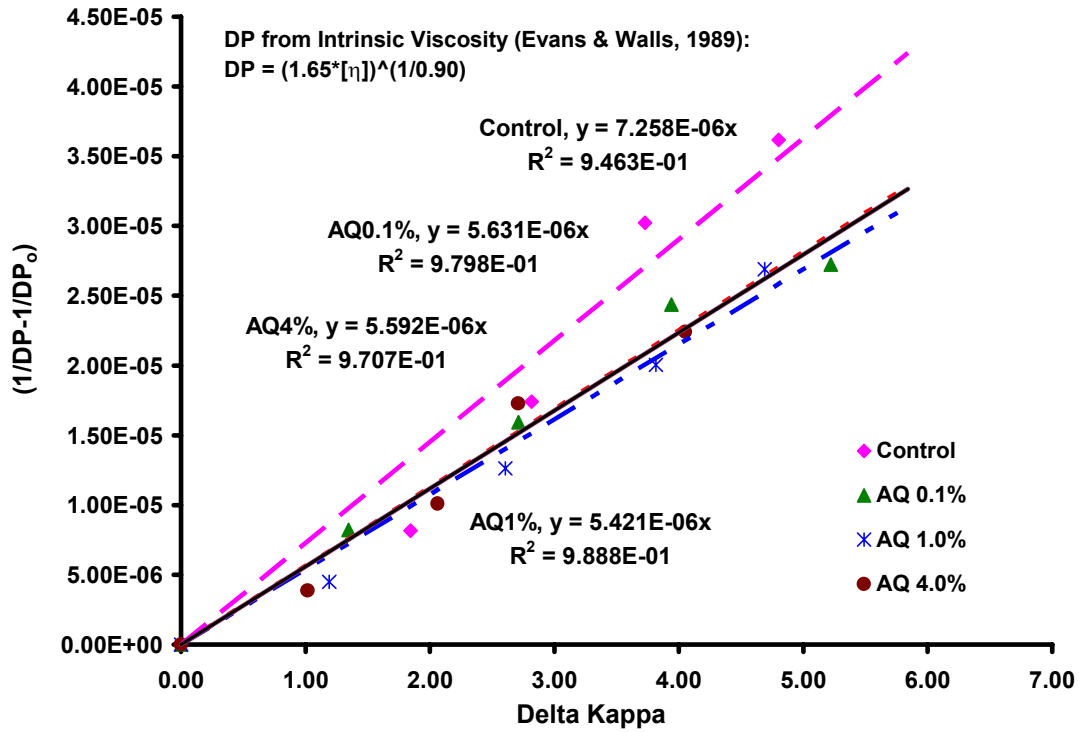


Figure 9. Effect of hemicellulose content on oxygen delignification selectivity.

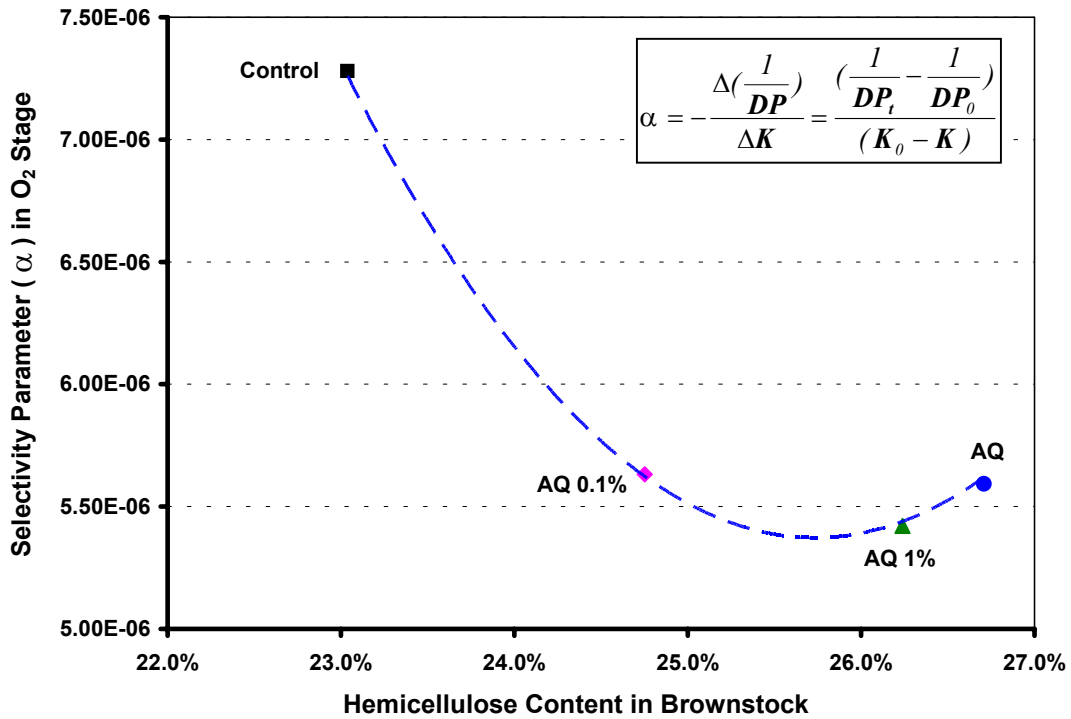


Figure 10. Effect of hemicellulose content on oxygen delignification selectivity.

Pulp Yield Following Oxygen Delignification.

The data for the pulp yield loss are presented versus the change in kappa number in Figure 11. The pulp yield loss data at the 4% AQ addition rate are suspect because the pulp may contain residual AQ. The pulp with highest absolute yield loss and the greatest slope was the pulp produced using 4% AQ during cooking. This pulp also had the highest yield following cooking. As a general rule, pulps with high yield in the digester resulting from the use of AQ exhibited high yield loss in the oxygen reactor. This was thought to result from dissolution of carbohydrates in the caustic because of the high xylan content.

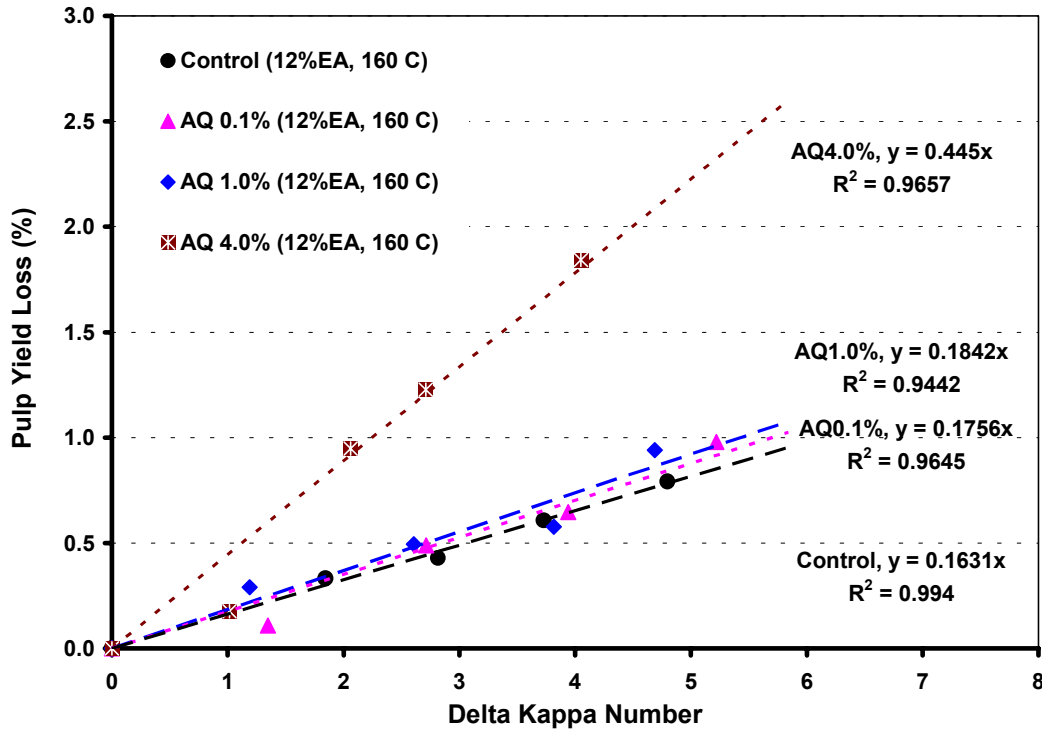


Figure 11. Pulp yield loss versus delta kappa number for pulps produced with AQ.

Carbohydrate Degradation.

Simoes and Castro method of analysis was used to estimate the rate of carbohydrate scissions during oxygen delignification (equation 6) [17].

$$\Psi = \left(\frac{1}{DP} - \frac{1}{DP_0} \right) \cdot \frac{6.023 \times 10^{23}}{162} \times \frac{1}{\text{reaction time}} \quad (6)$$

Pulps with high hemicellulose content in brownstock that would be expected to affect the carbohydrate scission rate. The effect of the hemicellulose content on carbohydrate degradation is shown in Figure 12. All of the curves show a decrease in scission rate with time in the oxygen reactor. Also, the higher the hemicellulose content in the pulp, the lower was the carbohydrate scission rate in the oxygen delignification. The brownstock pulp that was produced using 4% AQ had the highest hemicellulose content and also the lowest cellulose degradation rate. The pulp with the highest carbohydrate degradation rate was the control pulp. This pulp also had the lowest hemicellulose content. These results suggest that the hemicellulose polymers present in the pulp are protecting the cellulose from degradation by hydroxyl free radicals (OH•) present during oxygen delignification as suggested by Guay [18]. The hemicellulose polymers, which have a low molecular weight, compete with the cellulose for hydroxyl free radicals and thus avoid undue loss of molecular weight of the cellulose.

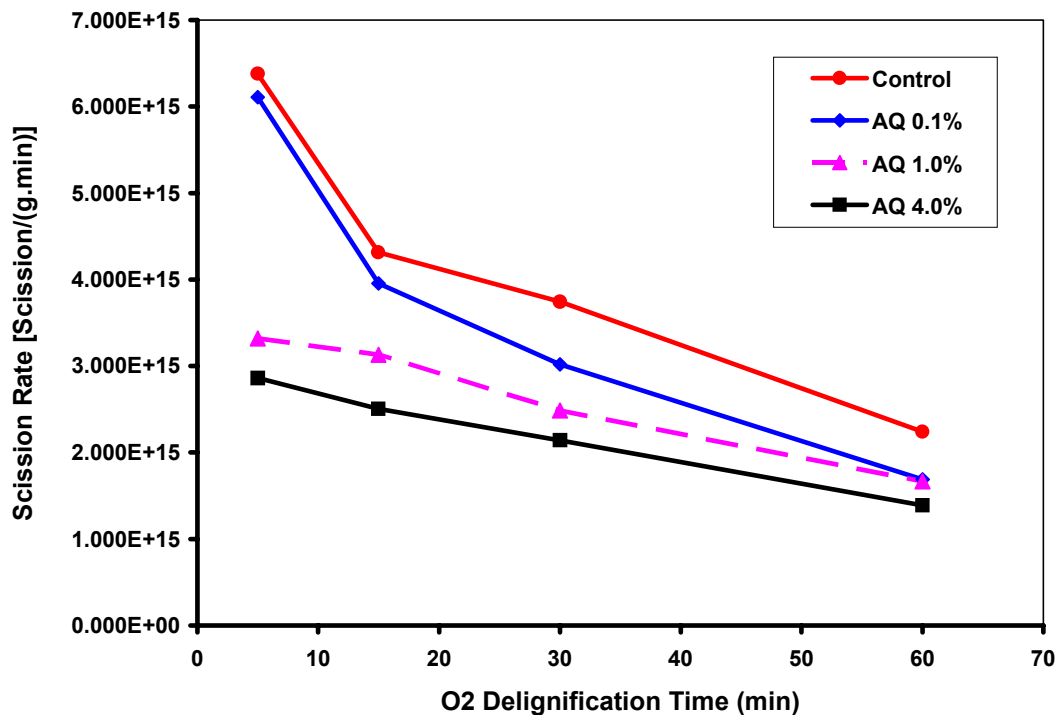


Figure 12. Effect of hemicellulose content on carbohydrate scission rate in the oxygen delignification stage.

Glucan Content after Oxygen Delignification.

The data for the glucan contents of the pulp before and after oxygen delignification are shown in Figure 13. These data are based upon the brownstock using an equation similar to equation (1). When based upon the brownstock, there was almost no loss in the glucan content following oxygen delignification for these high hemicellulose content pulps. When the data were plotted in terms of the weight fraction of xylan in the pulp (data not shown), invariably a higher glucan content was observed after oxygen delignification when compared to the brownstock. This occurred because the lignin and hemicellulose polymers are being preferentially removed with little loss of cellulose.

Xylan Contents after Oxygen Delignification.

The xylan content before and after oxygen delignification is shown in Figure 14. Here again the data are based on brownstock using an equation similar to equation (1). In all cases there was a removal of the xylan polymer from the pulp during oxygen delignification. On an absolute basis, the xylan weight fraction in all of the pulps decreased with exposure to oxygen (data not shown) when compared to the brownstock. From these data it can be seen that the primary loss in yield of the carbohydrates results from the loss of the xylan polymer.

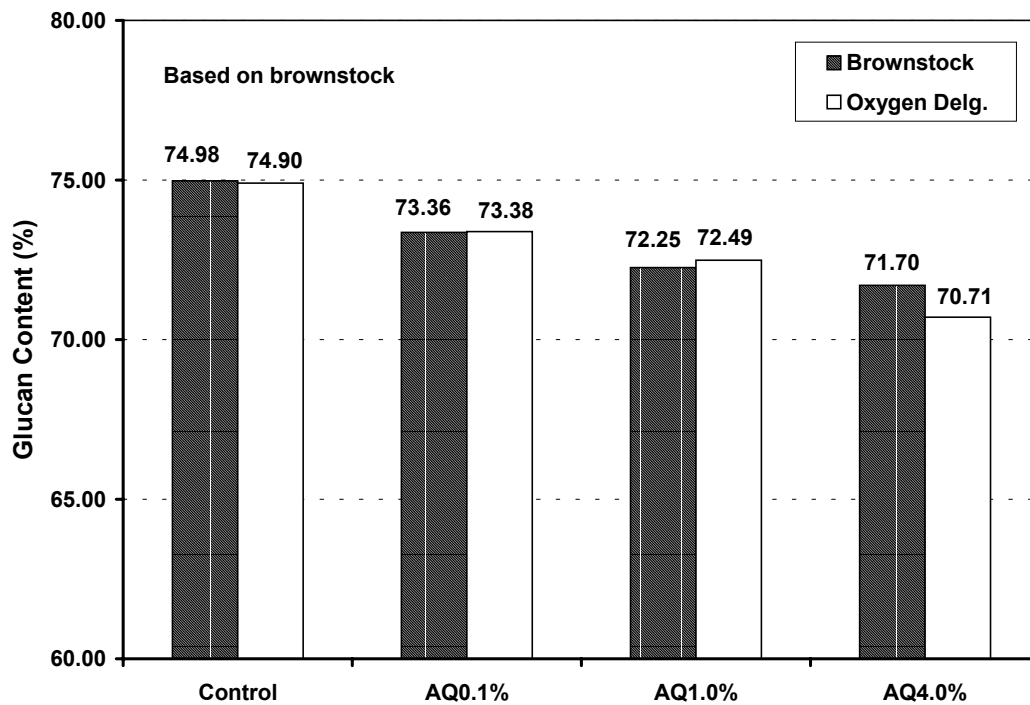


Figure 13. Glucan content in pulp before and after oxygen delignification (based on brownstock).

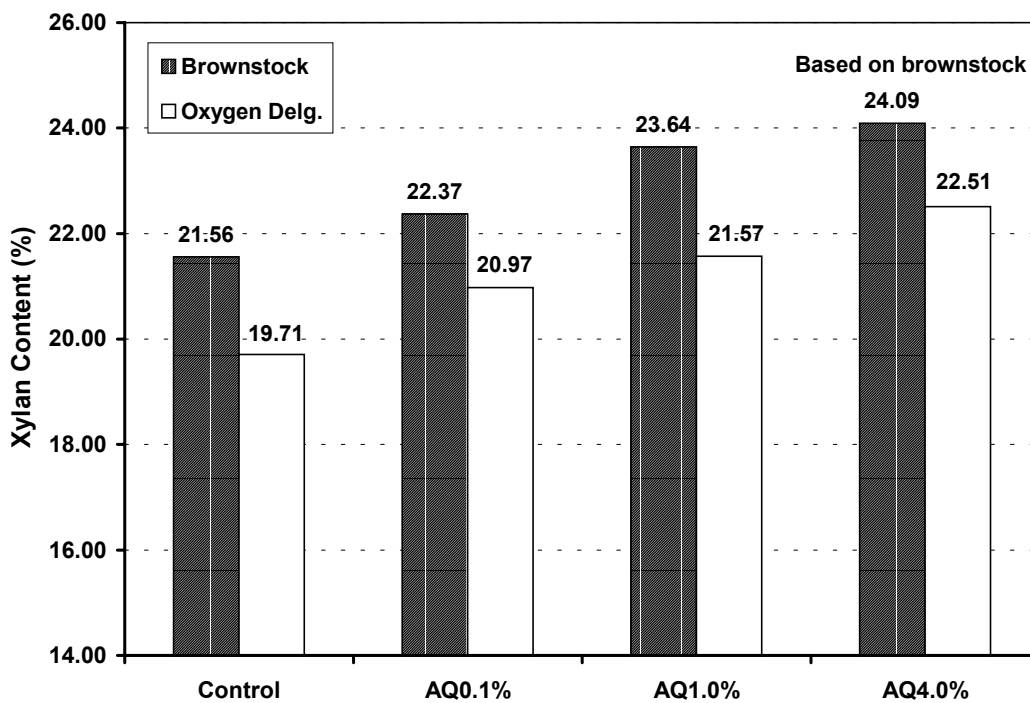


Figure 14. Change in the xylan content of the pulps before and after oxygen delignification (based on brownstock).

DISCUSSION

Similarly to the observations reported here on the effect of the hemicellulose content on oxygen delignification, Buchert observed that pulps with high xylan content inhibit delignification [19]. The exact mechanism for the observed results in both Buchert's work and in the present study is unknown, but several mechanisms suggest themselves.

First, the hemicellulose polymers function as an encrustation substance and surround elementary crystallites of cellulose (Fengel and Wegener [20]). The hemicelluloses are also known to be bound to the lignin and are amorphous. Consequently, chemical reagents are physically present in higher concentrations in the amorphous regions as compared to the cellulose crystallites due to transport limitations. The hydroxyl free radicals ($\text{OH}\bullet$) are formed in situ from decomposition of hydrogen peroxide and as products of reaction of oxygen anion with lignin. Organic radicals are also expected to be formed. Thus physically, the hemicellulose polymers would act to protect the cellulose from radical attack (Violette and van Heiningen) [21]. Since the molecular weight of the hemicellulose polymers is low, perhaps DP 100 to 200 or lower compared to 1000 to 2000 for cellulose in unbleached pulp, the overall viscosity will not be greatly lowered. There will of course be some decrease in yield.

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

Other possibilities for explaining the experimental results have been suggested by Argyropoulos and also Tamminen and Hortling [22, 9]. Argyropoulos suggests that delignification in an oxygen stage is hindered by refractory lignin moieties formed in the pulping process. The work by Tamminen and Hortling suggest that it is the lignin-to-carbohydrate linkages that inhibit delignification, that is -- the superoxide free radicals present under the conditions of oxygen delignification do not react with the lignin to carbohydrate linkages. Obviously, considerable fundamental study is required to elucidate the exact mechanism.

CONCLUSIONS

Adding anthraquinone to the digester increased the pulp yield and shortened the cooking time (lower H-factor). Very high pulp yields were obtained by using high levels of AQ.

Cooking mixed northeastern hardwood chips with AQ to the same brownstock kappa number greatly affected the rate of oxygen delignification for well-washed pulps when the change in kappa number was used as the indicator of delignification. The power law model, suggested by Schoon for hindered chemical reactions, can adequately describe the kinetic rate data for oxygen delignification. The observations made in this and other studies suggest that the high reaction order can be explained by assuming that delignification proceeds through a great number of parallel, first-order reactions taking place simultaneous with the different lignin moieties reacting at different rates as suggested by Schoon [13].

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

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