INCLUSION OF A PRESSURIZED ACIDOLYSIS STAGE IN CHEMICAL PULP BLEACHING

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Hardwood soda-AQ pulps are believed to be rich in benzyl sugar ethers (BSE) that can be partially cleaved by aqueous acidic treatments. The aim of this investigation was to evaluate the effect of acidolysis on final bleached brightness for kraft and soda-AQ (SAQ) hardwood pulps. The increase in final brightness due to acidolysis at 110 °C was twice as high for a eucalyptus SAQ pulp as compared to the kraft pulp. An oxygen delignified maple C-SAQ pulp (carbonate pre-treated SAQ) was acidolyzed at 120 °C and pH 2.6 for 30 min. When 1.60% ClO_2 + 0.25% H_2O_2 on pulp was used in DE_PD final bleaching of the control sample a brightness of 91.5% was achieved. When only 1.00% ClO_2 + 0.25% H_2O_2 on pulp was used for the acidolyzed sample a brightness of 92.0% was attained. Analyses of the maple pulp after the acidolysis showed no major change in lignin content, brightness, or pulp yield. The minor changes suggest that a facile reaction such as benzyl ether cleavage was responsible for the improved bleachability. Preliminary research involving a lignin model compound and commercial birch xylan showed that lignin-carbohydrate condensation products were generated under SAQ cooking conditions. Furthermore, a fraction of these lignin-carbohydrate moieties were subsequently cleaved by acidolysis at pH 2.5 and 105 °C.

Keywords: Alkaline pulping; Hardwood pulps; Lignin-carbohydrate complexes; Acidolysis; Bleachability

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INTRODUCTION

Some of the benefits that could be derived from non-sulfur pulping (and specifically soda-anthraquinone or SAQ pulping) of hardwoods have been described in an earlier publication (Francis et al. 2008). These include 1) precipitation of a significant fraction of the lignin from the pulping effluent or black liquor (BL) without the evolution of hydrogen sulfide, 2) a realistic possibility of implementation of BL gasification followed by Fischer Tropsch synthesis of alkanes due to the low sulfur content of the BL; additional raw biomass could be incorporated into BL gasification, and 3) if a conventional Tomlinson furnace were to be used, energy recovery from the SAQ BL would be significantly higher than for kraft due to the inefficiencies and endothermicity associated with the reduction of Na_2SO_4 to Na_2S.

There are two obstacles associated with the conversion of a hardwood kraft pulp mill to the SAQ process. The first obstacle is that the SAQ process requires 15-30% more NaOH as compared to kraft in the delignification of hardwoods (Francis et al. 2006). This NaOH would be produced by re-causticization of Na_2CO_3 as shown in equations (1) and (2). A retrofit at the mill to increase the re-causticizing rate by 30% would be expensive.

$$Na_2CO_3 + CaO + H_2O \rightarrow 2NaOH + CaCO_3 \quad (1)$$

$$CaCO_3 \rightarrow CaO + CO_2 \quad (2)$$

A promising solution to this problem was recently discovered (Francis and Shin 2007; Bose et al. 2009). Instead of using NaOH at the level of 14% Na_2O on chips for hardwoods, a pretreatment with 4% Na_2O from Na_2CO_3 would be performed, then the remaining Na_2CO_3 (10% Na_2O) would be re-causticized to NaOH. SAQ pulping with a carbonate pretreatment (C-SAQ process) of 4.0% Na_2O followed by 10% Na_2O (from NaOH) in the cooking stage affords a pulp that is vastly superior to SAQ with 14% Na_2O from NaOH. Except for bleachability, the C-SAQ process is also equal or superior to kraft at an equal or lower NaOH application (Francis and Shin 2007). Bose et al. (2009) prepared a kraft pulp from sugar maple (*Acer saccharum*) using 10.5% Na_2O on chips from NaOH plus 4.0% Na_2O from Na_2S and compared it with a C-SAQ pulp using 4.0% Na_2O from Na_2CO_3 followed by 10% Na_2O from NaOH + 0.1% AQ. The C-SAQ pulp had a lower unbleached kappa number, lower rejects and a screened fiber yield that was higher by 1.4% on chips. The total H-factor for the C and SAQ stages was lower than for kraft (Bose et al. 2009). Unfortunately, the brightness of C-SAQ pulp reached only 90.8% ISO in comparison to 92.2% ISO for kraft pulp bleached with equivalent applications of oxygen, chlorine dioxide, and hydrogen peroxide (Bose et al. 2009).

The lower bleached brightness above leads into a discussion of the second and more significant obstacle to converting a hardwood kraft mill to SAQ. The lower brightness of SAQ hardwood pulps is not due to colored complexes between the fibers and AQ or products from its transformation or degradation (Bose et al. 2009). In all probability, the poorer bleachability is due to a higher concentration of condensed lignin structures and/or a higher concentration of lignin-carbohydrate complexes (LCC) in SAQ pulps as compared to kraft pulps from the same chips. A major hindrance in formulating pulping and bleaching strategies to overcome the brightness deficiency of hardwood SAQ pulps is the lack of credible data comparing the concentrations of condensed lignin structures and LCC in the residual lignin (RL) of kraft and SAQ pulps. The residual lignin is that remaining in the pulp fibers, and it can be analyzed in-situ or after its isolation using appropriate techniques. *Only one paper could be found where there was a direct comparison of condensed lignin structures in RL of hardwood kraft and SAQ pulps (Bose et al. 2009).* The effective alkali and H-factor were equivalent for the two processes, and the unbleached kappa numbers were within 3.0 units of each other. *Similarly, only one publication could be found with a direct comparison of LCC in the RL (Choi et al. 2007).* Both publications concluded that the RL in the SAQ pulps contained a higher concentration of condensed lignin structures and LCC, respectively. Both publications were also tentative in their discussion on whether these higher concentrations were due to a lower rate of cleavage of native condensed lignin structure or native LCC (present in the wood chip) when SAQ was used or a higher rate of formation of these structures during SAQ cooking as a result of condensation reactions (Choi et al 2007; Bose et al. 2009).

If the SAQ process is to replace kraft for hardwoods, it is imperative that more data be collected to support or refute the limited data already reported, showing whether a higher concentration of condensed lignin structure and/or LCC is the likely reason for the poorer bleachability of SAQ pulps. The objective of this research was to use an indirect approach, cleavage of benzyl-sugar ethers by aqueous acidolysis, to investigate whether SAQ hardwood pulps have higher BSE concentrations that corresponding kraft pulps.

EXPERIMENTAL PROCEDURES

Pulping and Bleaching

Eucalyptus pulp research at Andritz Laboratory, Glens Falls, New York

Chips from an unknown eucalyptus species were obtained from a South American mill. They were screened then delignified by the kraft and SAQ processes using the Lo-solids technique, as described by Gomide et al. (2007). The liquor to wood ratio (L:W) was 3.5 : 1 for both kraft and SAQ.

The total effective alkali (EA) applied for kraft was 13.2% Na_2O with a liquor sulfidity of 35.9%. A 15 min impregnation was conducted at 110°C, and the upper section and lower section cooking temperature was 153°C for durations corresponding to total H-Factor of 610. Three kraft pulps were prepared with respective total yield of 54.0%, 54.0%, and 54.7%. The amount of rejects after screening were 0.06%, 0.11%, and 0.13% (based on initial chip mass), and the kappa numbers of the screened pulps were 15.7, 15.6, and 15.6, respectively. The mixture of the three pulps had a kappa number of 15.7, 80.7 cP viscosity, and 40.5% ISO brightness. These values were changed to 9.7, 52.5 cP, and 61.3% ISO, respectively, after oxygen delignification (75 min at 100 °C, 10% consistency, 1.2% NaOH, and 0.25% $MgSO_4 \cdot 7H_2O$ on pulp, 0.57 MPa of O_2). The total EA applied for SAQ was also 13.2% Na_2O (from NaOH only), a 30 min impregnation was conducted at 130 °C, and the upper section and lower section cooking temperature was 157 °C for durations corresponding to a total H-Factor of 880. The AQ (0.1% on chips) was added to the impregnation stage. Four SAQ pulps were prepared with respective total yield of 54.1%, 53.4%, 53.9%, and 53.8%. The amounts of rejects after screening were 0.06%, 0.04%, 0.08, and 0.08% (based on initial chip mass), and kappa numbers of the screened pulps were 16.1, 16.1, 16.3, and 16.4, respectively. The SAQ pulp mixture had a kappa number of 16.2, 42.1 cP viscosity, and 39.4% ISO brightness. These values were changed to 9.9, 31.5 cP, and 57.7% ISO, respectively, after oxygen delignification (same as above but with 1.4% NaOH on pulp).

The kraft and SAQ Eucalyptus pulps were bleached using the A/D_0EopD_1 sequence.

A/D_0 Stage: The oxygen delignified pulps were treated with a dilute H_2SO_4 solution (pH~3.0) at 95 °C or 110 °C at 10% consistency in a Quantum reactor for retention times varying from 30 to 240 min. Chlorine dioxide along with chilled water were then injected to give a temperature of 85 °C, and the pulp was allowed to be oxidized by ClO_2 for 15 min at that temperature.

Eop Stage: This was performed in the Quantum reactor at 85 °C with 1.0% NaOH, 0.5% H_2O_2, and 0.2% $MgSO_4 \cdot 7H_2O$ on pulp. The stage was performed at 10% consistency with 0.43 MPa of O_2 for 60 min.

D_1 Stage: These treatments were performed in plastic bags in a water bath at 70°C and 10% consistency for 120 min. ClO_2 applications of 0.3%, 0.5%, and 0.7% on pulp were used along with small NaOH or H_2SO_4 applications to achieve an end pH of ca. 4.0. The chemicals were mixed into the fibers at room temperature, heated to approximately 70°C in a microwave oven, then placed in the water bath. Only a minor fraction of the Eop bleached pulp was used for the D_1 stage, and the treatment was repeated if effluent end pH was outside of the range of 3.6 to 4.5.

Sugar maple pulp research at SUNY – ESF, Syracuse, New York

C-SAQ pulps were prepared by pre-treating chips at 4:1 L:W ratio with 4.0% Na_2O (from Na_2CO_3) for 30 min to 150 °C and 30 min at that temperature. The C-stage (carbonate) liquor was then drained off and water, NaOH, AQ, and Na_2SO_3 (O_2 scavenger) were added to restore a 4:1 L:W ratio based on initial chip mass. The NaOH dose was 11.0% Na_2O on initial chip mass, and it was added along with 0.1% AQ and 0.25% Na_2SO_3. The temperature was increased to 165 °C in ca. 40 min and kept at that temperature for 90 min (H-Factor of 961). Four cooks were performed, and the variations in kappa number and pulp yield were minimal. The pulp used for bleaching was a mixture of the four pulps with kappa number 19.9, screened yield of 55.0%, and 39.7% Elrepho brightness. The bleaching and acidolysis stages were:

O stage: Conducted in a Quantum Mark IV reactor at 12% consistency, 0.72 MPa of O_2, 2.0% NaOH, and 0.5% $MgSO_4 \cdot 7H_2O$ on pulp at 90 °C for 60 min.

Pulp Acidolysis (A stage): The oxygen delignified pulp (kappa number 10.3) was pre-heated to 100 ^oC in a Quantum Mark IV reactor (10% consistency). Sulfuric acid was then added to give solution phase concentrations of 0.012M (pH 2.6) or 0.015 (pH 2.2). The slurry was then heated to 120 ^oC (20 min) and held at that temperature for 30 min. The pulp was then removed and washed in a Buchner funnel. The entire sample was then soaked for ca. 20 h in a dilute slurry (ca. 2% consistency) consisting of pulp, $NaHCO_3$, and water (pH 7.0 to 7.5). A small stainless steel autoclave was used to determine yield loss during acidolysis. Twenty grams of pulp were placed in the autoclave at 10% consistency and 0.015M H_2SO_4. The autoclave was sealed at room temperature and placed in a 120 °C oil bath for 50 min. Based on accurate vapor pressure measurements for deionized water in the autoclave the internal temperature profile was estimated to be 12 min to 118 °C and 38 min at that temperature. The fibers were recovered, washed, and soaked in dilute $NaHCO_3$.

D_0 Stage: This was done in plastic bags at 10% consistency, 70 °C, 2h with initial pH approximately 4.0 (before the addition of $C1O_2$) and end pH 2.5 to 3.0. The ClO_2 and dilute H_2SO_4 were mixed into the fibers at room temperature, heated to approximately 70 °C in a 1.1 kW microwave oven, and then placed in a water bath.

Mixing at room temperature followed by microwave heating was used for all of the following stages.

E_P Stage: In plastic bags at 12% consistency, 80 °C, 2h with 2.0% NaOH, 0.25% H_2O_2, and 0.1% $MgSO_4•7H_2O$ on pulp. The end pH was always greater than 11.2.

D_1 Stage: In plastic bags at 10% consistency, 70 °C, 3h, and 0.5% $C1O_2$ on pulp. Sodium hydroxide (0.05%-0.15% on pulp) was used to ensure an end pH in the range of 3.8 to 4.5. One-half of the pulp was bleached in this stage, and the treatment was repeated with the other half if effluent end pH was outside of the range mentioned above.

E_2 Stage: In plastic bags at 12% consistency, 80 °C, 2h with 0.5% NaOH on pulp. The end pH was 11.1 for the one sample that was treated.

D_2 Stage: In a plastic bag at 10% consistency, 70 °C, 3h, and 0.3% $C1O_2$ on pulp. The end pH was 4.5 for the one sample that was treated.

Q-stage: In plastic bag at 10% consistency, 80 °C, 60 min. and with 0.2% Na_5DTPA and 2.5% SO_2 on pulp (from $NaHSO_3$). The end pH was 5.4 for the one sample treated.

P-Stage: In a plastic bag at 12% consistency, 80 °C, 2h and with 0.1% $MgSO_4•7H_2O$, 0.25% H_2O_2, and 1.0% NaOH on pulp. The end pH was 10.9 for the one sample treated.

LMC – xylan reactions

Apocynol (AP in Fig. 2) was added to 60 mL of 0.4 M NaOH solution in 100 mL stainless steel autoclaves either by itself or in combination with 0.3 g of the commercial birch xylan (Sigma-Aldrich). The AP dose was always 0.5 g, and it was added along with a small dose of Na_2S (0.1 g/l) to scavenge oxygen. Each autoclave was sealed and placed in a 165 °C oil bath for 60 min. The time to maximum temperature of ca. 163 °C was ca. 14 min (based on vapor pressure measurements). After the reaction, the autoclave was cooled by flowing cold water. Aliquots of the reaction mixture (10 ml each) were acidified to pH 2.5 ± 0.1 using 4 N H_2SO_4. Some of the pH 2.5 samples were extracted to recover un-reacted AP that was quantified by gas chromatographic (GC) analysis. Extraction was performed using dichloromethane (DCM) followed by ethyl acetate (EA). Other pH 2.5 samples were placed in a 105 °C oven in thick-walled glass vials for 1.0 h to observe the change in AP concentration due to the mild acidolysis. These solutions were also extracted and analyzed by GC. The organic extract (DCM + EA) was concentrated to ca. 1.0 ml *in vacuo* and analyzed without derivatization of functional groups.

Gas Chromatography and Other Analyses

A HP 5890A gas chromatograph equipped with a flame ionization detector (FID) and an EC-1 (dimethylpolysiloxane) capillary column (30m x 0.25mm; film thickness 0.25 µm); nitrogen as carrier gas (1 mL/min); split ratio 1:32; injector temperature of 250 ºC and detector temperature of 270 ºC were used. The following temperature profile was used: initial temperature 120 ºC, holding time at initial temperature 5 min, a ramp from 120 ºC to 270 ºC at 5 ºC/min, and a hold at maximum temperature for 5 minutes. Hexenuronic content (HexA) was determined by a UV spectroscopic method (Vuorinen et al. 1999). The chemical composition of the birch xylan was determined by two-stage

H_2SO_4 hydrolysis followed by sugar analyses by ^{1}H NMR (Bose et al. 2009). The first stage was conducted in 72% H_2SO_4 for 2 h at 25 ºC, while the second stage was performed in 40% H_2SO_4 for 1 h at 80 ºC. The transition metal contents of a pulp sample was determined by its conversion to an ash at 575 ºC followed by nitric acid dissolution and ICP-AES analysis.

RESULTS AND DISCUSSION

Acidolysis of Eucalyptus Pulps in an A/D_0 Stage

Isolated residual lignin (IRL) was produced from kraft and SAQ hardwood pulps by Choi et al. (2007) using an enzymatic hydrolysis procedure. The pulps were made from beech (*Fagus sylvatica*) chips, and the IRLs contained approximately 7% to 10% sugars by weight (Choi et al. 2007). Those authors used 2,3-dicholoro-5,6-dicyanobenzoquinone (DDQ) oxidation to cleave benzyl ether linkages between lignin and carbohydrates with the generation of new hydroxyl groups in the sugar moieties. It was determined that 1 to 3% of the C_9 units in the kraft IRL were connected to sugar moieties by benzyl ether bonds, while the value was 7 to 8% for the SAQ IRL (Choi et al. 2007). Two possibilities were presented to explain the difference. The first was that the lignin-carbohydrate complexes (LCC) in the starting wood (native LCC) were cleaved to a lesser degree during SAQ due to the absence of the strong sulfide nucleophiles. The other explanation was that some of BSE were generated during cooking (Choi et al. 2007). When the total xylose units cleaved from the $C\alpha$ positions of lignin were calculated as a percentage of total liberated sugars, the value for kraft IRL was 50% higher than for the native LCC, while the value for the SAQ IRL was >100% higher (Choi et al. 2007). The xylose fraction of the total sugar would be insignificant for the kraft IRL due to its low concentration of benzyl-sugar ethers. However, for SAQ pulping there are two possibilities to explain xylose enrichment in the IRL. Either benzyl-xylan ethers in the native LCC are more resistant to cleavage than benzyl ethers with other sugar moieties and as such they accumulate in the residual lignin, or benzyl-xylan ethers are generated via OH groups in xylose units reacting with $C\alpha$ positions of C_9 units in the lignin.

Irrespective of the explanation behind the high number of BSE in the SAQ pulp, if these ethers are partially cleaved by mild acidolysis (100 °C to 120 °C, pH 2 to 3) as reported in the literature (Jonaik et al. 1987; Taneda et al. 1987; Lawoko et al. 2006), then such treatments should cleave some of the LCC in pulps and make the lignin more accessible to chemical reactions during bleaching. This should improve bleachability, and particularly so for hardwood SAQ pulps. The bleaching sequence normally used to whiten hardwood chemical pulps is $OD_0E_{OP}D_1$ or $D_0E_{OP}D_1E_2D_2$ (where O is a pressurized alkaline O_2 stage; D_0 is chlorine dioxide delignification with an end pH of 2-3; E_{OP} is alkaline extraction with sodium hydroxide plus O_2 and H_2O_2 for incremental delignification and brightening; E_2 is extraction with NaOH only; and D_1 and D_2 are chlorine dioxide brightening stages with an end pH of 3.7 to 5.5). Data on LCC recovered from kraft pulp (Lawoko et al. 2004) and effluent (Laine and Tamminen 2002) after O_2 delignification would suggest that only minimal cleavage of the strong lignin-carbohydrate linkages should be expected in O, Eop, and Ep (NaOH + H_2O_2) bleaching stages.

This research was initiated in the Andritz laboratory with the assumption that BSE would not be significantly cleaved in a D_0, A/D_0 or D_{HT} stage, where typically the maximum temperature is 95 °C (Colodette et al. 2008; Barros et al. 2008). The acronym D_0 stands for a conventional ClO_2 delignification stage performed at 50 °C to 70 °C; the A/D_0 stage starts with acidolysis at ca. 95 °C and pH ca. 3.0 then chilled ClO_2 plus chilled water are added to lower the D_0 temperature to <90°C; in the D_{HT} treatment ClO_2 is applied to the pulp at ca. 95 °C (Colodette et al. 2008; Barros et al. 2008). In a conventional D_0 stage a fraction of the oxidizing equivalents is consumed by hexenuronic acid (HexA) (Vuorinen et al. 1999; Ragnar and Lindstrom 2004; Ventorim et al. 2008). However, in an A/D_0 stage the pre-acidolysis converts most of the hydrolyzed HexA to 2-furoic acid and formic acid, which are believed to be quite un-reactive toward the oxidants (ClO_2, HOCl, Cl_2) in a D_0 stage (Teleman et al. 1996; Vuorinen et al. 1999). The experimental design was to perform the A/$D_0E_{OP}D_1$ sequence on O_2 delignified pulp and use A-pretreatment temperatures of 95 °C and 110 °C. The working assumption was that almost all of the HexA and only a small fraction of the BSE would be cleaved at 95 °C while almost all of the HexA and a significant fraction of the BSE would be cleaved at 110 °C.

It should be noted, however, that there is controversy surrounding the savings in bleaching chemicals that is associated with an A-pretreatment at <100 °C. Some results suggest that only 6 to 14% in total oxidizing equivalents is saved (Ragnar and Lindstrom 2004; Colodette et al. 2008; Barros et al. 2008) while others indicate a saving in the range of 30% (Vourinen et al. 1996, 1997, 1999, 2004). Results will be presented later where AD_0 was compared to D_0 for the maple C-SAQ pulp. In that AD_0 treatment the pulp was washed after the A-pretreatment, which was performed at 120 °C.

Both the oxygen-delignified kraft and SAQ pulps from eucalyptus were bleached by the A/D_0EopD_1 sequence. The HexA content of the oxygen delignified pulps were 54.6 meq/kg for kraft and 51.4 meq/kg for SAQ. The pre-hydrolysis section of the A/D_0 stage was performed at 95 °C for 60, 120, and 240 min and also at 110 °C for 30 min. The initial and end pH were always in the range of 2.8 to 3.0. The results for the kraft pulp are summarized in Table 1, while those for the SAQ pulps are in Table 2.

The HexA contents of the kraft pulp was decreased from 54.6 meq/kg to 24.2, 12.9, and 4.8 meq/kg, respectively, for A-pretreatments of 60 min, 120 min, and 240 min at 95 °C. As the HexA content entering the D_0-stage decreased, more of the oxidizing equivalents that were applied ended up being consumed by lignin, and pulp brightness after the D_0-stage increased from 79.9% for 60 min of acidolysis to 83.2% for 240 min. It is well established that every meq/kg of HexA hydrolyzed and washed out of chemical pulps decreases kappa number by 0.085 units (Li and Gellerstedt 1997; Chai et al. 2001). If it is assumed that HexA hydrolyzed in the A-pretreatment eventually does not consume much ClO_2, then 60 min of hydrolysis at 95 °C in this case would have lowered the kappa number of the pulp entering D_0 by ca. 2.6 units ((54.6-24.2)x0.085), while the 240 min treatment would have lowered it by ca. 4.2 units ((54.6-4.8)x0.085). Therefore, 0.66% ClO_2 was consumed by the two pulps entering D_0 with respective kappa numbers of ca. 7.1 (9.7 minus 2.6) and ca. 5.5 (9.7 minus 4.2). However, the corresponding final brightness values increased from 91.8% to only 92.2% for a 0.5% ClO_2 application in the D_1-stage (Table 1). *For the same overall chemical consumption in bleaching, using the A-pretreatment at 95°C to lower the HexA content from 24.2 meq/kg to 4.8 meq/kg resulted in a brightness increase of only 0.4 point.* It should be noted, however, that pulp brightness increases very slowly with incremental bleaching in the region of the "brightness ceiling" for the particular sample being used. It is unclear from the present results if an A-pretreatment at 95 °C would significantly decrease the amount of oxidizing equivalents required to attain 91.0% ISO brightness.

When an acidolysis temperature of 110 °C was used for 30 min, equal or less HexA were hydrolyzed from the pulp as compared to the 240 min treatment at 95 °C. However, higher brightness values were obtained after both the D_0 and D_1-stages (Table 1). *There is clearly an acidolysis effect not related to HexA that was observed at 110 °C and to the best of the authors' knowledge there is no prior report describing this effect.*

Table 1. A/$D_0E_{OP}D_1$ Bleaching Results for Oxygen Delignified Eucalyptus Kraft Pulp (Kappa number = 9.7)

A/D_0 Stage				
A-Temperature, °C	95	95	95	110
A-Time, min	60	120	240	30
HexA, meq/kg^a	24.2	12.9	4.8	6.4
D_0 end pH	2.6	2.5	2.6	2.7
$C1O_2$ consumed, %^{b}	0.66	0.66	0.66	0.66
Brightness, % ISO	79.9	80.4	83.2	84.1
E_{OP} Stage				
Kappa Number	1.5	0.9	0.6	0.6
Viscosity, cP	33.2	32.8	29.3	24.3
Brightness, % ISO	88.2	88.0	88.9	89.9
D_1 Stage				
Brightness, 0.3%^{c}	91.5	91.7	92.0	92.3
Brightness, 0.5%	91.8	92.0	92.2	92.5
Brightness, 0.7%	92.0	92.1	92.4	92.5

[a] HexA content entering D_0 (54.6 meq/kg entering A stage)
[b] % on pulp
[c] 0.3% ClO_2 on pulp

When the SAQ pulp was investigated, the trend of higher brightness values with increased A-pretreatment retention at 95 °C was repeated. The 110 °C treatment also resulted in a pulp with an equal or higher HexA content entering the D_0 stage but higher brightness values after D_0 and D_1-stages as compared to the 240 min treatment at 95 °C. When A-stage treatments at 95 °C for 60 min and 110 °C for 30 min are compared for the kraft pulp, the later treatment caused a brightness increase varying from 0.5 to 0.8 points for the three ClO_2 applications in D_1 stages (Table 1 and Fig. 1). However, when a similar comparison is made for the SAQ pulp, the brightness increase varied from 1.3 to 1.6 points (Table 2 and Fig. 1). The more significant increase in bleached brightness for the SAQ pulp as a result of acidolysis would appear to be consistent with the data of Choi et al. (2007). If the SAQ pulp contains 3 to 4 times as much LCC as the kraft pulp and these LCC are partially cleaved by acidolysis, then one would expect a more significant amelioration of bleaching problems when acidolysis was performed on the SAQ pulp.

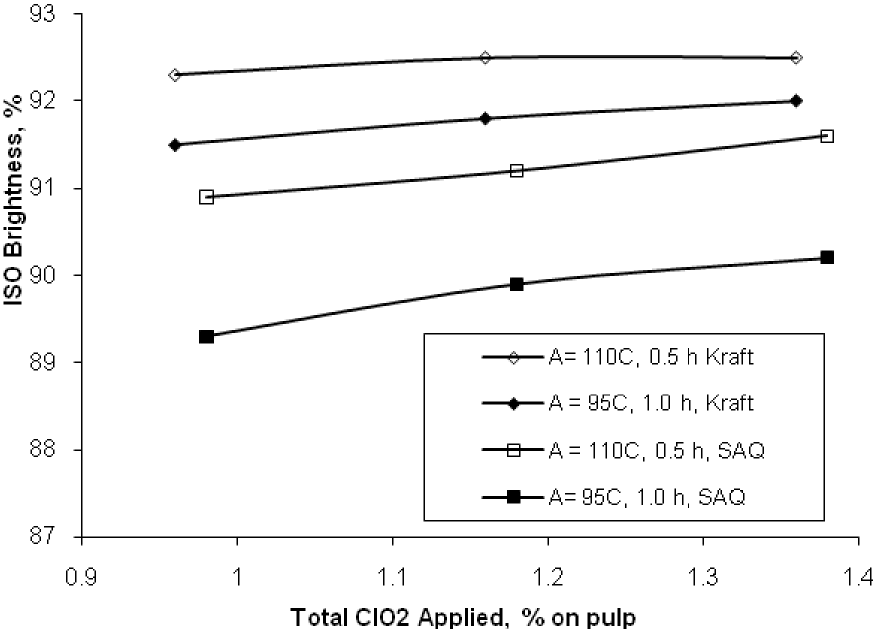

Figure 1. Effect of acidolysis at 110 °C on the final brightness of kraft and SAQ pulps after $OD_0E_{OP}D_1$ bleaching. Acidolysis was performed after the O stage.

Table 2. A/D_0E_{OP} D_1 Bleaching Results for Oxygen Delignified SAQ Pulp (Kappa number = 9.9)

A/D_0 Stage				
A-Temperature, °C	95	95	95	110
A-Time, min	60	120	240	30
HexA, meq/kg[a]	22.3	12.7	5.1	8.3
D_0 end pH	2.8	2.9	2.6	2.6
ClO_2 consumed, %[b]	0.68	0.68	0.68	0.68
Brightness, % ISO	76.0	77.2	79.0	79.7
E_{OP} Stage				
Kappa Number	1.6	1.1	1.0	0.9
Viscosity, cP	22.0	20.6	19.3	18.0
Brightness, % ISO	84.3	85.2	85.8	86.4
D_1 Stage				
Brightness, 0.3%[c]	89.3	89.9	90.0	90.9
Brightness, 0.5%	89.9	90.1	90.6	91.2
Brightness, 0.7%	90.2	90.4	90.7	91.6

[a] HexA content entering D_0 (51.4 meq/kg entering A stage)
[b] % on pulp
[c] 0.3% ClO_2 on pulp

Acidolysis of Sugar Maple SAQ Pulp Ahead of Final Bleaching

This research was performed in order to obtain some idea whether an even more significant effect would be seen if the A-pretreatment were to be performed at 120 °C and slightly lower pH. Also, it would provide an opportunity to compare AD_0 to D_0 and not A/D_0 at 95 °C versus A/D_0 at 110 °C. On this occasion hydrolyzed HexA and its degradation products were washed out of the pulp after the A-pretreatment. The acidolyzed pulps were analyzed for kappa number, HexA content, viscosity, brightness, and yield loss in order to gain some insight as to how significantly they had been modified. The results are summarized in Table 3. Interestingly, there appeared to be no major changes in the pulp properties other than for viscosity, which is used as an indirect measure of the degree of depolymerization (DP) of the carbohydrate fraction. It appeared as if carbohydrate depolymerization was significant and that was expected considering the low pH and high temperature of the acidolysis treatments. However, viscosity values >12.0 cP (Table 3) still correlated to an average DP greater than 1,000 (Negri et al. 1998), and such values are high enough that cellulose solubilization should be minimal. The decreases in kappa number appear to correlate as expected with HexA hydrolysis. The decrease in HexA concentration (34.4 – 2.3 = 32.1 meq/kg) should cause a 2.7 unit decrease in kappa number (32.1 x 0.085). The decreases observed were 4.2 units and 3.9 units for A1 and A2, respectively. The additional 1.2-1.5 units decrease in kappa number is probably due to the removal of acid soluble lignin. There were only minor decreases in pulp brightness after the A-pretreatment (Table 3). Pulp yield was measured on three separate occasions, and values of 99.0%, 98.6%, and 99.2% were obtained (average = 98.9%). The small yield loss would suggest that other than cleavage of glycosidic linkages, there was not a major modification of the carbohydrate fraction. Of the 1.1% yield loss, HexA hydrolysis would account for about 0.5%, with other reactions responsible for the remaining 0.6% on pulp. The molecular weight of HexA in anhydro form is 159 and ca. 0.032 gmole/kg of pulp (32.1 meq/kg) was removed. This corresponds to 5.09 g/kg pulp or 0.5 wt%. In their entirety these data point to a very facile reaction/modification as being responsible for any improvements to be seen in pulp bleaching. Two likely possibilities are: 1) transition metals removal that would improve the Ep stage (Manning et al. 2006; Francis et al. 2008) and 2) benzyl ether cleavage (Jonaik et al. 1987; Taneda et al. 1987; Lawoko et al. 2006) that would have liberated the lignin.

Table 3. Effect of 120 °C Acidolysis on Properties for an O_2-Delignified C-SAQ Pulp

	Untreated	A1	A2
H_2SO_4 conc., M	-	0.012 (pH 2.6)	0.015 (pH 2.2)
Kappa Number	10.3	6.1	6.4
Viscosity, cP	21.4	12.6	12.9
HexA Content, meq/kg	34.4	2.3	3.1
Brightness, % Elrepho	53.7	52.9	53.5
Pulp Yield, %	-	-	98.9

The O_2-delignified pulp along with the acidolyzed samples were first bleached by D_0EpD_1 using varying doses of ClO_2 in D_0. The results for the control pulp are presented in Table 4, while those for the acidolyzed sample are shown in Table 5. When 1.28% total ClO_2 + 0.25% H_2O_2 was applied to both the control and acidolyzed pulps the bleached brightness was 90.1% and 93.0%, respectively. An increase of 2.9 points beyond the 90% level is quite significant. The total ClO_2 was increased from 1.28% to 1.60% for the control pulp, while that for the acidolyzed sample was decreased from 1.28% to 1.00%. Despite a much lower ClO_2 application (0.6% on pulp), the acidolyzed sample afforded a bleached brightness that was higher than for the control, 92.0% vs. 91.5%.

Table 4. Bleaching Profile of O_2-Delignified C-SAQ pulp with ClO_2 and H_2O_2

	C-SAQ O_2	**C-SAQ O_2**	**C-SAQ O_2**	**C-SAQ O_2**
D_0 Stage				
Entering kappa no.	10.3	10.3	10.3	10.3
ClO_2, % on pulp	0.78	1.10	0.78	0.78
End pH	2.8	2.6	2.6	2.6
Ep Stage				
Kappa number	3.0	2.1	3.0	3.0
Brightness, % Elrepho	83.1	85.9	83.1	83.1
D_1 Stage				
Brightness, % Elrepho	90.1	91.5	90.1	90.1
QP Stages				
Brightness, % Elrepho			91.2	
E_2D_2 Stages				
Brightness, % Elrepho				91.9
Final Fiber Yield. % [a]	52.7	52.7		
Total ClO_2, % on pulp	1.28	1.60	1.28	1.58
Total H_2O_2, % on pulp	0.25	0.25	0.50	0.25

[a] Based on starting chips

The first of the additional experiments investigated the possible role of transition metals removal by acidolysis. Even when the ClO_2 dose in D_0 was increased from 0.78% to 1.10% on the control pulp, the kappa number after Ep decreased from 3.0 to only 2.1 (Table 4), while the value for the acidolyzed pulps was ca. 1.5 for D_0 applications of 0.5% and 0.78% ClO_2 (Table 5). It is possible that the A-pretreatment effectively demineralized the pulp and the subsequent Ep stage was more effective due to less decomposition of H_2O_2 (Manning et al. 2006; Francis et al. 2008).

The control pulp with brightness of 90.1% (kappa factor 0.20) was found to contain only 3.9 ppm Mn, 2.1 ppm Fe and <1.0 ppm Cu. When this pulp was given a chelation treatment and bleached with 0.25% H_2O_2 (QP), its brightness only increased from 90.1% to 91.2%. It appears unlikely that a more efficient utilization of the 0.25% H_2O_2 on pulp that was applied in Ep was the cause of the significant brightness gain observed for the acidolyzed pulps. Also, when the control pulp with 90.1% brightness was bleached with an additional 0.3% ClO_2 in E_2D_2 stages final brightness increased only to 91.9%.

Table 5. Bleaching Profile of Acidolyzed O_2-Delignified C-SAQ Pulp with ClO_2 and H_2O_2

	C-SAQ O_2A1	C-SAQ O_2A1	C-SAQ O_2A2	C-SAQ O_2A2
D_0 Stage				
Entering kappa no.	6.1	6.1	6.4	6.4
ClO_2, % on pulp	0.78	0.5	0.78	0.5
End pH	2.6	2.7	2.6	2.7
Ep Stage				
Kappa number	~1.5	~1.5	~1.5	~1.5
Brightness, % Elrepho	86.1	85.1	86.5	84.9
D_1 Stage				
Brightness, % Elrepho	92.9	92.0	93.1	92.0
Final Fiber Yield. % [a]			52.6	
Total ClO_2, % on pulp	1.28	1.00	1.28	1.00
Total H_2O_2, % on pulp	0.25	0.25	0.25	0.25

[a] Based on starting chips

It appears that SAQ and C-SAQ pulps contain low concentrations of colored moieties after OD_0EopD_1 or OD_0EpD_1 bleaching and that these structures are difficult to degrade using conventional bleaching chemicals. Based on literature data and the results obtained in this investigation it appears likely that these structures are LCC and specifically benzyl-sugar ethers that would be partially cleaved by acidolysis at $pH \leq 3.0$ and temperature >95 °C.

Alkaline LMC-Xylan Reaction and Subsequent Hydrolysis of LCC

The aim of this research was to collect preliminary/rudimentary data regarding the possibility of LCC formation under alkaline cooking conditions and to see if the generated LCC would be susceptible to partial hydrolysis at pH 2.5 and 105 °C. The reaction in Fig. 2 is one that is reported to occur under neutral conditions (Tanaka et al. 1979; Leary et al. 1983), hot alkaline conditions (Ohara et al. 1980; Glasser 1981), and in the presence of a strong nucleophile such as HSO_3^- (Ohara et al. 1980; Glasser 1981). The reaction is written specifically for alkaline situations where the quinone methide (QM) is derived from the phenolate anion. It should be noted that several other mechanisms have been postulated for LCC formation under alkaline cooking conditions (Gierer and Wannstrom 1984; Fullerton and Wilkins 1985; Gierer and Wannstrom 1986; Iverson and Wannstrom 1986; Karlsson and Westmerk 1996; Tenkanen et al. 1999), and the aim of this preliminary investigation was not to procure data in support of any specific mechanism. The objective was simply to see if apocynol (AP), which rearranges to a quinone methide (QM), condenses with xylan. The mechanism in Fig. 2 was highlighted because it is well established that 4 to 5 times as much coniferyl alcohol (CA) is generated from lignin depolymerization during SAQ as compared to kraft pulping (Mortimer 1982; Kondo and Sarkanen 1984; Alen and Vikkula 1989). Phenolic structures like CA with an α-β double bond in their sidechain can rearrange to QMs (Gierer and Lindeberg 1978; Mortimer 1982). Therefore, if a reaction such as that in Fig. 2 were to occur, then one would expect a higher rate of LCC formation in SAQ as compared to kraft pulping.

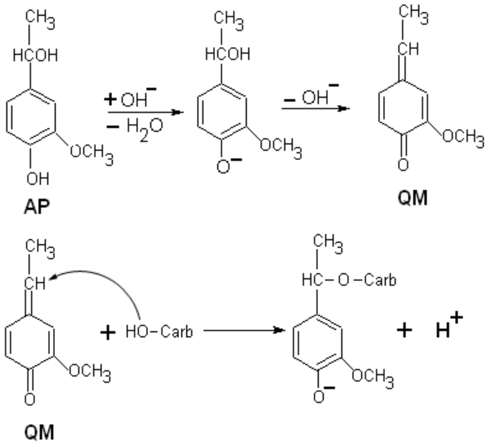

Figure 2. A possible reaction scheme for LCC formation from AP and birch xylan

The chemical composition of the birch xylan is shown in Table 6. The summative analysis was 94.4% using a method with a modified H_2SO_4 hydrolysis protocol followed by NMR analysis of the sugar monomers (Experimental). Compared to the conventional protocol in TAPPI Method T 249 cm-85 (TAPPI 1985), a longer reaction time was used in the first stage of hydrolysis and a higher H_2SO_4 concentration was used in the second stage (Bose et al. 2009). No glucose, mannose, or galactose was detected for this sample, and these sugar monomers would likely have been degraded if they were originally present in the xylan powder as low molecular weight oligomers (Bose et al. 2009; Alves et al. 2010). A recent analysis of xylan extracted from birch wood contained 66.9% xylan plus glucose, mannose, and galactose, totaling 6.9% (Westbye et al. 2008). The xylan content for the birch xylan in the present case was 69.6% (Table 6). The only assumption that was made was that the xylan contained 15.0 wt% of uronic acids. This value is typical of the xylan in birch wood (Kaar and Brink 1991) and consistent with measured values of 11.3% to 15.4% for four different fractions of the birch xylan in the other study (Westbye et al. 2008).

Table 6. Chemical Composition of Birch Xylan

	Birch Xylan
Xylan[a, b]	69.6
Acetyl group	3.1
Uronic acids[c]	15.0
Arabinan	2.6
Glucan	-
Galactan	-
Mannan	-
Rhamnan	2.3
Lignin	1.8
Total	94.4

[a] wt% of starting birch xylan
[b] All carbohydrate derived material expressed as anhydro sugars or anhydrides
[c] Estimated based on literature data for birch (Kaar and Brink 1991)

AP (0.5 g) was self-condensed in 0.4 M NaOH and two 10 mL aliquots of the product mixture were analyzed for residual (un-reacted) AP. After acidification to pH 2.5 ± 0.1, the product mixture was extracted by DCM followed by EA. Duplicate analyses gave values of 13.8% and 13.9% of un-reacted AP (Table 7). Two 10 mL aliquots of the alkaline reaction products were also adjusted to pH 2.5 ± 0.1 and acidolyzed at 105 °C. After the acidolysis, the yield of residual AP was 9.1% and 9.6% of the initial amount (entering alkaline condensation). A second alkaline self-condensation of AP was performed, and on this occasion the residual AP after alkaline treatment was 15.5%, and that value decreased to 7.7% after acidolysis (Table 7). The likely cause of AP disappearance during acidolysis is acid-catalyzed condensation of the AP to the C-6 position of other aromatic rings, which occurs at a higher rate in water alone as compared to water/solvent mixtures (Bose et al. 1999). Two 8 mL aliquots of the acidified reaction products were then supplemented with 2 mL of n-propanol before being acidolyzed. The duplicate values for residual AP after acidolysis were 8.8% and 9.5%, up from 7.7% recovery in the purely aqueous solution.

Table 7. Acidolysis of Oligomeric and Polymeric Reaction Products from Alkaline Treatment of AP and AP/birch Xylan

Alkaline Treatment	Acidolysis Solvent	AP Residual after Alkaline, %[a]	AP Residual after Acidolysis, %[a]
AP[b]	H_2O	13.8, 13.9[c]	9.1, 9.6[d]
AP[b]	H_2O	15.5	7.7
AP[b]	n-Propanol/H_2O[e]	15.5	8.8,9.5[d]
AP + Xylan[f]	H_2O	4.6	6.1

[a] % of initial AP entering alkaline treatment
[b] 0.5g AP (Experimental)
[c] Duplicate analyses of same alkaline product mixture
[d] Acidolysis performed in duplicates
[e] See text for explanation
[f] 0.5g AP + 0.3g birch xylan

When 0.3 g of the birch xylan was added to alkaline AP condensation, the yield of un-reacted AP decreased from values of 13.9% and 15.5% to only 4.6%. It appears that moieties in the xylan or moieties generated from it under alkaline conditions were condensing with AP. Interestingly, when an aliquot of the alkaline reaction products was acidolyzed, the yield of AP increased from 4.6% to 6.1% (Table 7). This serves as evidence of LCC being hydrolyzed, because acidolysis of the AP self-condensation products did not liberate but consumed AP.

We recommend further research on the quantification of BSE in pulps. If their hydrolysis was really the cause of the dramatic improvement in bleachability observed in the present study then research should be extended to investigate the possible use of isolated etherase enzymes (Kim and Engesser 2004; Jaeger et al. 2005) to cleave BSE in SAQ hardwood pulps. The enzyme treatment would be carried out at <100 °C, and no pressurized tower would be needed. The capital cost of enzyme treatment would in all likelihood be much less than for an A-pretreatment at >100 °C.

CONCLUSIONS

It was observed that mild acidolysis dramatically improved the bleached brightness of hardwood SAQ pulps. The empirical findings suggest that BSE cleavage is a likely mechanism to explain the acidolysis effect. Preliminary/rudimentary results were obtained showing bond formation between a phenolic compound and birch xylan under alkaline conditions. Subsequently, some of the bonds generated in alkali were partially hydrolyzed at pH 2.5 and 105 °C.

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