Mechanistic Differences Between Kraft and Soda/AQ Pulping. Part 1: Results from Wood Chips and Pulps

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Mechanistic Differences Between Kraft and Soda/AQ Pulping. Part 1: Results from Wood Chips and Pulps

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Abstract: Soda pulping catalyzed by anthraquinone (AQ) or 2-methylanthraquinone (MAQ) can produce hardwood chemical pulps similar to kraft pulps in all respect but for bleachability. Results accumulated in our laboratory suggest that the residual lignin in pulps from anthraquinone catalyzed processes is less reactive toward bleaching chemicals than that in kraft pulps. Analyses of pulps by periodate and permanganate oxidations suggest that the residual lignin from the non-sulfur processes contained more condensed structures than kraft residual lignin. The low reactivity of these structures is believed to be responsible for the lower brightness of bleached soda-AQ (SAQ) pulps. Pulping and bleaching trials with hardwood chips demonstrated that shortening of the cooking time and/or increasing the alkalinity is one strategy for improving bleachability of SAQ pulps. When sugar maple *(Acer saccharum)* chips were SAQ cooked for 1.0 and 2.0 h at 165°C, the higher kappa number pulp produced after 1.0 h of cooking bleached to a significantly higher brightness with a small increase in the chlorine dioxide application.

Keywords: Alkaline pulping, anthraquinones, lignin condensation, periodate oxidation, permanganate oxidation

INTRODUCTION

Kraft pulping is the dominant process for the delignification of wood chips into pulp fibers in North America. The key to the kraft process is the Tomlinson or kraft recovery furnace that is quite efficient at recovering the pulping chemicals, NaOH and Na_2S. However, energy efficiency is becoming more important each

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passing year and there is a sense of inevitability that gasification of the pulping effluent or black liquor (BL) will replace the Tomlinson furnace for chemical and energy recovery. The current estimates are that an optimized Tomlinson furnace would produce excess energy in the amount of approximately 900 kWh or 3.2 GJ per ton of pulp produced (approximately 2 dry tons of wood/ton of pulp) whereas a gasifier or steam reformer would net around 2,200 kWh or 7.9 GJ per ton of pulp produced.[1,2] However, the regeneration of Na_2S from kraft BL would be tedious for all gasification processes. Some of the sulfur in the BL will be converted to H_2S in the fuel gases (Eq. [1]). This H_2S has to be selectively removed by adsorption onto a solid sorbent or absorption into a solvent. The H_2S would have to be desorbed from the solid sorbent and the surface reconditioned for another sulfidation cycle. If the H_2S is absorbed into a solvent then desorption into a non-reactive gas followed by re-absorption into NaOH or Na_2CO_3 would be required.

$$Na_2S + CO_2 + H_2O \rightarrow H_2S + Na_2CO_3 \tag{1}$$
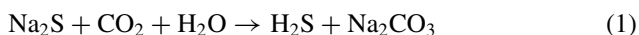
The technical feasibility of black liquor gasification (BLG) would improve significantly if a non-sulfur pulping process were to replace kraft.[3,4] Therefore, research is being performed to improve the efficacy of soda-AQ (SAQ) pulping to a point where it becomes equal or superior to kraft. The probability of success is higher for hardwoods as compared to softwoods. Consequently, most of the effort is focused on deciduous wood at the present time.

The major disadvantages of SAQ pulping as compared to the kraft pulping are (1) a pulp that is more difficult to bleach and (2) a higher NaOH requirement that calls for increased re-causticizing (Na_2CO_3 to NaOH). When an active alkali (AA = NaOH + Na_2S on a Na_2O basis) of 16.0% Na_2O on chips and 30% sulfidity (Na_2O from Na_2S/AA) is used for kraft pulping, 11.2% of the AA would come from NaOH and 4.8% from Na_2S. In the kraft pulping process, the recovery of almost all the sulfur is as Na_2S, and re-causticizing would then be required to convert Na_2CO_3 into NaOH, so that 11.2% Na_2O on chips is achieved. In SAQ pulping of hardwoods, approximately the same amount of effective alkali (EA = NaOH + $\frac{1}{2}$ Na_2S on a Na_2O basis) is required as in kraft pulping.[3] In the earlier case, the EA for the kraft pulping would be 13.6% Na_2O on chips, and a similar amount of alkali would be required for the SAQ pulping but from NaOH alone. The NaOH requirement for SAQ pulping can be decreased to a level equal to or lower than for kraft pulping if a carbonate (SAQ green liquor) pretreatment is used.[5] The poorer bleachability of SAQ pulps is the objective of this communication, and several analytical techniques will be used to show that a higher ratio of condensed structures (C-C bond formations among aromatic rings and side chains) in the lignin from SAQ pulping as compared to kraft pulping is most likely responsible.

MATERIALS AND METHODS

Wood Supply

Two batches of sugar maple (*Acer saccharum*) logs (SM 1 and SM 2) were harvested from different regions of Central New York. Paper birch (*Betula papyrifera*) and cottonwood (*Populus deltoides*) were also harvested in Central New York while loblolly pine (*Pinus taeda*) logs were donated by a pulp mill in the southern United States.

Pulping

A liquor-to-wood ratio of 5:1 and a ramp time of 90 min (to maximum temperature) were used for SM 1. Kraft pulping of SM 1 was conducted for 2 h at 165°C with an active alkali of 16.0% Na_2O on chips (OD basis in all cases) and 25% sulfidity. SAQ pulping of SM 1 was for 2 h at 170°C with 14% Na_2O (18% NaOH) and 0.15% AQ on chips. SMAQ pulping of SM 1 was for 2 h at 165°C with 14% Na_2O and 0.12% or 0.25% MAQ on chips. A 1:1:1 chip mixture of SM 1, birch and cottonwood (MBC) was also used to produce kraft, SAQ and SMAQ pulps. A cooking time of 2 h at 165°C and a 4:1 liquor to wood ratio were used. Kraft pulping was with 16% AA and 25% sulfidity; SAQ was with 14% AA and 0.15% AQ while SMAQ used 14% AA and 0.12% MAQ.

Ninety minutes to 165°C and a 4:1 liquor to wood ratio was used for kraft and SAQ pulping of SM 2. The carbonate pretreatment was performed with 4.0% Na_2O (from Na_2CO_3) on chips at a 4:1 L to W ratio. The treatment was for 30 min at 150°C with a 30 min ramp time. After the C stage (carbonate pretreatment) the free effluent was drained off and 10% Na_2O and 0.1% AQ (both based on initial chip mass) along with fresh water were added and the temperature ramped back up to 165°C in ∼ 40 min. Loblolly pine kraft pulp was prepared using a 4:1 liquor to wood ratio, 18% active alkali on chips and 25% sulfidity. The time to reach the maximum temperature of 175°C was 90 min and the duration at 175°C was 100 min. SMAQ pulping was performed with 16.3% Na_2O (21% NaOH), 0.14% MAQ and a 4:1 liquor to wood ratio. The temperature profile was similar to kraft but with 120 minutes at 175°C instead of 100 minutes.

Pulp Bleaching

O-Stage (SM 1): Conducted in a Quantum Mark IV reactor at 12% consistency, 0.72 MPa of O_2, 2.0% NaOH, and 0.5% MgSO4*7H2O on pulp at 90°C for 1 h.

O-Stage (SM 2): Conducted in a Quantum Mark IV reactor at 12% consistency, 0.72 MPa of O_2, 1.0% NaOH, 1.0% Na_2CO_3 and 0.5% MgSO4*7H2O on

pulp at 90°C for 30 min. The O_2 pressure was released, an additional 1.0% NaOH added and the system re-pressurized to 0.72 MPa. Delignification was allowed to continue for 30 min more at 90°C.

O-Stage (Loblolly pine): Same as for SM1 but with 3.0% NaOH on pulp.

D_0-Stage: In plastic bottles at 3.0–3.5% consistency, 70°C, 2 h with initial pH approximately 4.0 (before the addition of ClO_2) and end pH 2.6–3.0. A ClO_2 application (wt% on pulp) of $0.076 \times$ incoming kappa number (kappa factor of 0.20) was used on all occasions.

E_P-Stage: In plastic bags at 12% consistency, 80°C, 2 h with 2.0% NaOH, 0.25% H_2O_2, and 0.1% $MgSO_4.7H_2O$ on pulp. The chemicals were mixed into the fibers at room temperature, heated to approximately 80°C in a 1.1 kW microwave oven and then placed in a water bath. The end pH was always greater than 11.2.

D_1-Stage: In plastic bags at 10% consistency, 70°C, 3 h, and 0.5% ClO_2 on pulp. Sodium hydroxide (0.1–0.2% on pulp) was used to ensure an end pH in the range of 3.8–4.5. The chemicals were mixed into the fibers at room temperature, heated to approximately 70°C in a 1.1 kW microwave oven then placed in a water bath. 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 earlier.

P-Stage: In plastic bags at 12% consistency, 80°C, 2 h and with 0.1% $MgSO_4.7H_2O$, 0.5% H_2O_2, and 1.5% NaOH.on pulp. The chemicals were mixed into the fibers at room temperature, heated to approximately 80°C in a 1.1 kW microwave oven and then placed in a water bath.

Chemical Analyses

Phenolic hydroxyl groups (PhOH) were determined by periodate oxidation[6,7] while hexeneuronic acids were determined by the method of Chai et al.[8] The permanganate oxidation method is described elsewhere[9,10] and was used to analyze lignin and pulp samples as well as an α-5 and a β-5 dimer. The α-5 dimer was provided by CanSyn Chemical Corp., Toronto, Canada while the β-5 dimer was prepared as previously reported.[10] The two chemical structures will be shown in the Results and Discussion.

RESULTS AND DISCUSSION

Inclusion of Oxygen Delignification in the Bleaching Sequence

Kraft, SAQ, and SMAQ pulps from sugar maple were bleached by the $D_0E_PD_1$ sequence in an earlier investigation.[3] Enough of the kraft and SAQ pulps remained for oxygen delignification trials. However, the SMAQ pulp was

Table 1. Bleaching results for kraft, SAQ, and SMAQ from sugar maple (SM 1)

	Kappa number		Brightness			
	Unbl.	O_2	Unbl.	O_2	Final	k (m^2/kg)[1]
Kraft (53.0%)[2]	18.5	9.9	38.6	56.2	91.6 (91.3)[3]	0.181
SAQ (52.1%)	15.4	9.0	40.5	54.1	90.5 (91.1)	0.235
SMAQ[4] (54.9%)	18.9	10.9	38.9	49.7	89.5 (90.4)	0.290
SMAQ[5] (54.5%)	18.0	10.7	39.5	51.1	89.9	0.267

[1]Light absorption coeff.; average light scattering coeff. of 47.1 m^2/kg.
[2]Screened Yield; rejects were <0.4% on chips for all pulps.
[3]Brightness after $D_0E_PD_1$ bleaching in parentheses; Data from Ref. [3].
[4]SMAQ cooking with 0.12% MAQ on chips.
[5]SMAQ cooking with 0.25% MAQ on chips.

depleted. A new SMAQ pulp was produced using 0.12% MAQ on chips and using the same sugar maple (SM 1) from the earlier investigation. Previously, a SMAQ with kappa number 20.4 and screened yield of 54.7% was obtained.[3] The corresponding values in the present case were kappa number 18.9 and screened yield of 54.9%. The kraft, SAQ and SMAQ pulps were bleached by the $OD_0E_PD_1$ sequence and the results are presented in Table 1.

The brightness gap between kraft and SAQ pulps increased from 0.2 point for $D_0E_PD_1$ bleaching to 1.1 points for the $OD_0E_PD_1$ sequence (Table 1). Similarly, the difference between kraft and SMAQ increased from 0.9 point to 2.1 points (Table 1). When the $D_0E_PD_1$ sequence was used, $\sim$ 2.2% ClO_2 on pulp was applied[3] while only $\sim$ 1.3% was used in $OD_0E_PD_1$. As compared to kraft pulp, it appears that there are more chemical moieties in the SAQ and SMAQ pulps that are less reactive to O_2. The $OD_0E_PD_1$ sequence afforded a higher brightness than $D_0E_PD_1$ for the kraft pulp but lower brightness for the SAQ and SMAQ pulps. Condensed lignin structures may be the unreactive moieties. These structures are known to be more difficult to oxidize and solubilize during O_2 bleaching.[11,12] A condensed C_9 unit is defined as one containing a C-C bond at any ring position except for C-1 (sidechain) or connected to another C_9 unit by a diaryl ether linkage.[9,10]

Before an intensive investigation was initiated on the quantification of condensed structures it was necessary to rule out an obvious possibility of the formation of colored complexes between the anthraquinones (or chemicals formed from them) and fiber components. SMAQ pulping was repeated but with an increase in the MAQ dose from 0.12% to 0.25% on chips. The higher MAQ application lowered the unbleached kappa number by 0.9 units and did not have a statistically significant effect on pulp yield (Table 1). It would be expected that more of the yellow MAQ or products from it would end up on the pulp when 0.25% was used. However, this pulp had a slightly higher bleach

brightness than the one produced when 0.12% was used (Table 1). It does not appear that bound MAQ or products from it are responsible for the lower bleached brightness of SMAQ pulps.

Analyses by Periodate Oxidation

When the 18.5 kappa number kraft and the 18.9 kappa number SMAQ pulps (Table 1) were delignified with oxygen the kappa number decrease was 46% for the kraft pulp (18.5 to 9.9) but only 42% for the SMAQ pulp (18.9 to 10.9). The pulps contained nearly identical concentrations of hexeneuronic acids (HexA) groups both before and after O_2 delignification ($\sim$ 55 mmoles/kg before and $\sim$ 45 mmoles/kg after). The PhOH contents of the unbleached and O_2-delignified pulps were determined by periodate oxidation. The unbleached SMAQ pulp contained 32 PhOH/100 C_9 units while the O_2-treated pulp contained 21 PhOH/100 C_9 units. The corresponding values for the kraft pulp were 28 PhOH/100 C_9 units and 15 PhOH/100 C_9 units. The lignin in the SMAQ pulp contained more PhOH than that in the kraft pulp but they were less reactive during O_2-treatment. Pulps from loblolly pine were then analyzed (kappa numbers of 25.4 and 11.9 for unbleached and O_2-delignified kraft pulps and corresponding values of 27.1 and 12.8 for the SMAQ pulps). The phenolic contents were 37 and 19 PhOH/100C_9 units for unbleached and O_2-delignified SMAQ pulps and 29 and 16 PhOH/100C_9 units for the corresponding kraft pulps. Both the O_2-delignified SMAQ pulps from hardwoods and softwoods failed to achieved kappa number as low as kraft but contained a higher PhOH content at the end of the stage. The end pH ($\sim$ 12.0) and O_2 pressure after the 60 min O stages were still very high and did not limit additional delignification. When 30 min O stages were performed on these pulps the decrease in kappa number was at least 75% of that obtained for the 60 min treatment. The reaction conditions selected for these pulps were to insurance extensive oxidation of all reactive structures and the asymptotic limits in kappa number described by McDonough[13] were achieved.

Condensed PhOH are known to be much less reactive toward O_2 than uncondensed PhOH.[11,12] From the results above, it appears as if dissolved lignin units with PhOH were condensing on to the residual lignin to a greater extent during SMAQ pulping thus increasing the PhOH content of the SMAQ residual lignin. One of the principal alkaline condensation reactions is shown in Figure 1.[14]

Analyses by Permanganate Oxidation

Kraft, SMAQ, and SAQ formulations were used to extract >90% of the lignin from the maple/birch/cottonwood (1:1:1) chip mixture (MBC). The lignin in
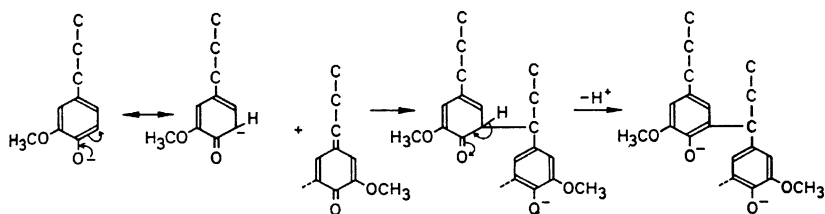
Figure 1. Lignin condensation reaction leading to a α-5 structure (Ref. [14]).

the wood meals as well as lignin in black liquors and lignin remaining in the pulps (residual lignin) were analyzed by permanganate oxidation. The reaction scheme for permanganate oxidation is shown in Figure 2 and the products from hardwood lignin are shown in Figure 3. This method was chosen because it always affords credible results for biphenyls (VIII in Figure 3) and other C-5 condensed structures (III) when samples are effectively pre-methylated with dimethyl sulfate.[10] A CuO pretreatment can be used to increase the PhOH content of the sample prior to methylation and $KMnO_4$ oxidation resulting in higher yields of I–VIII. Previous data in the literature[9] as well as our data indicate that mono-methylated biphenyl structures are oxidized to III in high yields. This is particularly true for CuO hydrolyzed samples. For these samples one mole of III can be subtracted and one mole of VIII (two monomers) added if such a correction normalizes the yield of VIII. However, such a correction should be made only if it has a minor effect on the data, that is, an increase in the yield of VIII corresponding to <15% of that obtained. The yields of VIII for pulp samples were normalized in the present study and this was based on the fact that the yields of VI + VII (diaryls) were almost equal for kraft, SMAQ, and SAQ pulps.

The α-5 and β-5 dimers in Figure 4 were also investigated. The mass spectrum for α-5 compound was identical to that reported by Pavlickova et al.[15] who assigned a fragment for all the major m/z values. The mass spectrum for the β-5 compound was previously reported.[10] When the two dimers were oxidized by $KMnO_4$ the yield of III was 47% and 48%, respectively. The $KMnO_4$ bond cleavages to generate III from α-5 and β-5 structures are shown in Figure 5. Permanganate oxidation appears to be applicable for a wide range of C-5 condensed lignin structures.

Analysis of the MBC woodmeal gave 6.9 moles of III and 4.4 moles of VIII (monomeric basis) per 100 C_9 units of lignin. β-5 structures in the native
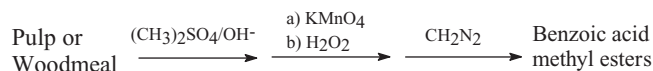

Figure 2. Reaction scheme for lignin analysis by permanganate oxidation.
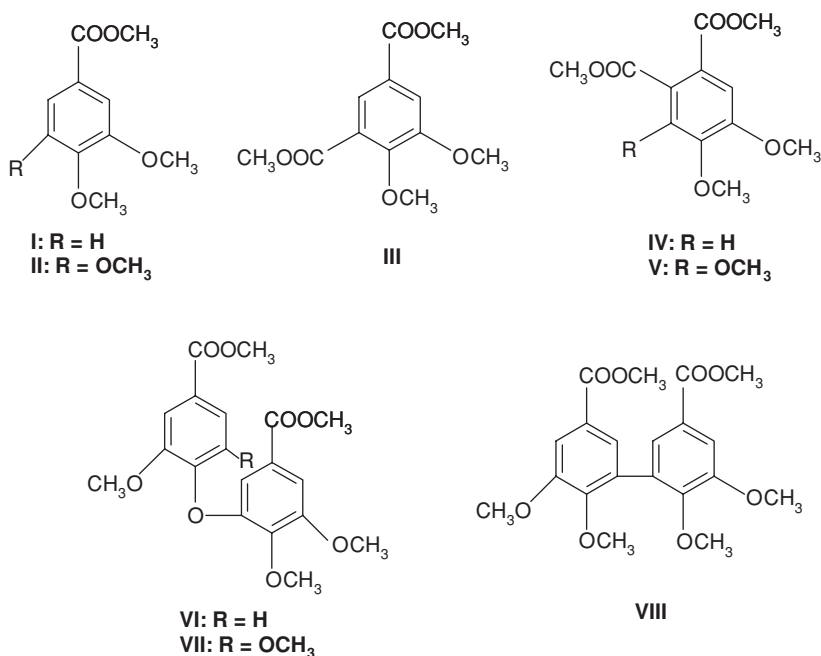
Figure 3. Products from permanganate oxidation of hardwood lignin.

lignin would be primarily responsible for the yield of III. The dissolved lignin from the kraft and SAQ cooks were then analyzed and a higher yield of III was observed for the SAQ process (Table 2). This may be indicating the formation of α-5 structures via C-5 condensation at a higher rate among dissolved degraded lignin fragments during SAQ pulping as compared to kraft pulping. There was a decrease in VIII for the dissolved lignin as compared to the native lignin.

Figure 4. α-5 and β-5 compounds that were methylated and oxidized to III by $KMnO_4$.

Figure 5. C-5 condensed dimers and KMnO$_4$ bond cleavages to give III.

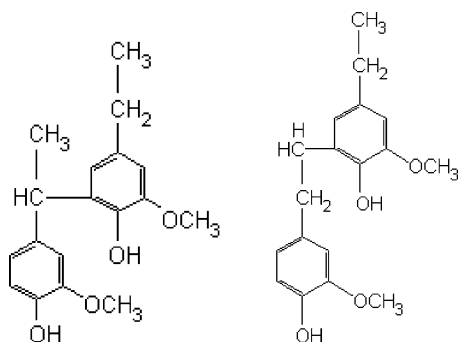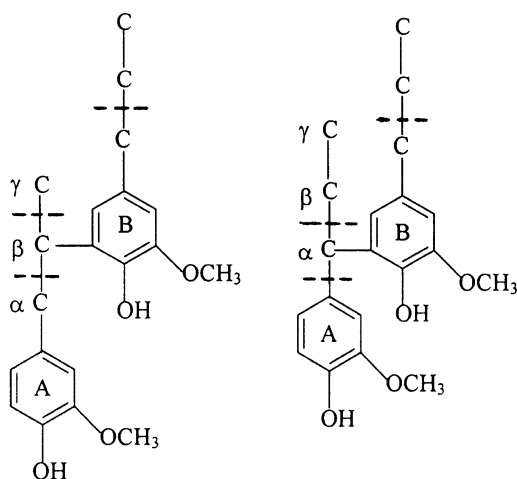Biphenyl and β-5 structures are known to solubilize at a lower rate during kraft pulping.[16] Similar to biphenyl structures, a decrease in the concentration of β-5 structures in the dissolved lignin would also have been expected. However, there was an increase in III as compared to the native lignin and this is likely due to formation of α-5 structures in the dissolved phase for both the kraft and SAQ pulping processes. All of the pulps were then given a CuO pretreatment and analyzed by KMnO$_4$ oxidation. The SAQ and SMAQ pulps afforded ~3 more moles of III per 100 moles of C$_9$ units as compared to the kraft pulp when the yield of VIII was normalized (Table 2). The expected accumulation of biphenyls and β-5 structures in the residual lignin was observed. It is our belief that the residual lignin from the kraft pulp contain only a few C$_9$ units

Table 2. Yield of III and VIII from native, dissolved, and residual hardwood lignins

Sample	III	VIII
Woodmeal	6.9	4.4[1]
Dissolved kraft	8.0	3.8
Dissolved SAQ	10.6	3.1
Residual kraft	13.6	14.6
Residual SAQ	17.0	14.5
Residual SMAQ	16.8	14.5

[1]Monomers/100 C$_9$ units.

from condensation reactions and a majority of the 13.6 moles of III/100 moles of C_9 units (Table 2) are from the accumulation of native β-5 structures.

It would be expected that higher concentrations of condensed structures in SAQ and SMAQ pulps (Table 2) would make them more difficult to bleach because these structures are less reactive to bleaching chemicals (previously discussed).

Cooking Optimization to Retard the rate of Lignin Condensation

When sugar maple is SAQ delignified with 14% or 15% Na_2O on chips, the NaOH concentration typically decrease from an initial value of $\sim$ 1.0 M to $\sim$ 0.5 M after the 90 min ramp time to 165°C and to $\sim$ 0.2 M after 2 h at that temperature. It is our suspicion that reactions like those in Figure 1 do not occur at a high rate early in the cook when the lignin polymers would contain more RO^- groups due to the higher alkalinity and repel each other. Instead they occur in the residual phase of cooking where the alkalinity is lower and dissociation of alcoholic OH groups would be minimal.

A group of kraft and SAQ pulps were prepared from sugar maple chips with varying alkalinity and cooking time for the SAQ samples. A ramp time of 90 min was used for all the cooks except for the CSAQ (carbonate pretreated SAQ) where it took only $\sim$ 40 min to increase the temperature of the warm carbonate pretreated chips ($\sim$ 80°C) up to 165°C. It was expected that bleachability would be improved if the cooking time were to be shortened or if the pulping alkalinity were to be increased.

The pulping results are summarized in Table 3 while the bleaching results are in Table 4. It can be seen in Table 4 that SAQ pulps with shorter cooking

Table 3. Effect of cooking variable on kappa number and yield for kraft and SAQ pulps from sugar maple (SM 2)

Process	Time at 165°C	NaOH applied[1]	Residual alkali[1]	Kappa number	Screened yield
Kraft	120	10.5[2]	2.1	21.3	53.1 (0.4)[3]
SAQ	120	14.0	2.4	20.6	52.7 (0.4)
SAQ	90	15.0	2.8	22.0	53.4 (0.5)
CSAQ[4]	75	10.0	2.3	20.2	54.5 (0.3)
SAQ	60	14.0	—	31.9	56.9 (1.0)[5]

[1] As% Na_2O on chips in the pulping stage.
[2] Plus 4.0% Na_2O from Na_2S.
[3] Rejects;% on chips.
[4] Carbonate pretreatment followed by SAQ pulping.
[5] Pulp was refined in order to decrease reject content.

Table 4. Bleachability of kraft and SAQ pulps in Table 3

Process	Kappa number		Brightness,%ISO	
	Unbleach.	After O_2	After D_1	After P
Kraft	21.3	8.4	92.2	93.3
SAQ	20.6	10.7	89.3 (89.8)[1]	92.1 (92.5)[1]
SAQ	22.0	9.7	90.6	92.6
CSAQ	20.2	9.8	90.8	92.4
SAQ	31.9	16.3	92.6[1]	93.5[1]

[1]0.8% ClO_2 on pulp in D_1 stage (instead of 0.5%).

times and/or a higher alkalinity bleached to a higher brightness. The results in Table 4 are also important because of what they imply about the significance of native LCC on bleachability. One would expect that the SAQ cook with 14% Na_2O that was terminated after 60 min would contain more native LCC than the cook that was terminated after 120 min. However, the 60 min pulp bleached to a significantly higher brightness than the 120 min pulp (Table 4). It would appear that in straight alkaline pulping the concentration of the residual native LCC in the pulp does not significantly influence bleachability. It should be noted that it is possible that condensation between carbohydrate-rich material and secondary quinone methides during alkaline pulping could produce another class of LCC and this issue will be discussed in Part 2 of this series (this issue).

Furthermore, it also appears as if there is a distinction between alkaline-labile and acid-labile LCC. There is ample evidence that a mild hot water pre-extraction of chips (end pH 3.5–4.0) that would be expected to hydrolyze some LCC[17] does accelerate kraft and to a greater extent SAQ pulping.[4,18] Hot water pretreatments can decrease the ramp time of batch SAQ cooking (to 165°C) by ∼ 50 min and the time at 165°C by an additional 30–60 min.[4,18] Based on the results in Table 4, this shortening of the cooking time would be expected to improve bleachability of SAQ pulps and this is indeed observed.[4,18] Improved bleachability is observed for both kraft and SAQ pulps when mild hot water pre-extraction (acidolysis) precedes alkaline cooking and the improvement is more significant for the SAQ process. It appears that cleavage of acid-labile LCC is a significant contributor to the increase in alkaline pulping rate and bleachability. Generation of reducing end groups during acidolysis appears to enhance the rate of AQ reduction to AHQ[19] early in the subsequent SAQ stage and this is believed to be responsible for the more significant effect of hot water pre-extraction on the SAQ process. AHQ (anthrahydroquinone) is the active nucleophile in SAQ pulping.[20,21]

CONCLUSIONS

Kraft pulping was compared to SAQ and SMAQ pulping of sugar maple and a maple/birch/cottonwood chip mixture. SAQ was slightly inferior while SMAQ was equal to kraft for the production of unbleached pulps. A SMAQ pulp with equivalent kappa number and strength[3] as a kraft pulp could be produced at a higher fiber yield. However, it appears that SAQ and SMAQ pulps are more difficult to bleach than kraft pulps and results from lignin analyses (phenolic groups by periodate oxidation and condensed structures by permanganate oxidation) suggest that condensation reactions occur at a higher rate during SAQ and SMAQ pulping. Most condensed lignin structures are less reactive to conventional bleaching chemicals as compared to uncondensed structures. Pulping and bleaching trials demonstrated that shortening of the cooking time and/or increasing alkalinity is one strategy for improving the bleachability of hardwood SAQ pulps. It is inferred that the rate of lignin condensation is higher later in the cook when the alkalinity is lower.

REFERENCES

1. Larson, E.D.; Raymond, D.L. Commercializing black liquor and biomass gasifier/ gas turbine technology. Tappi J. **1997**, *80*(12), 50–57.
2. Mansour, M.N.; Chandran, R.R.; Rockvam, L. The Evolution of and Advances in Steam Reforming of Black Liquor. Proceeding of 2002 Tappi Pulping Conf. (San Diego, CA), TAPPI PRESS, Atlanta, 2002.
3. Francis, R.C.; Shin, S.-J.; Omori, S.; Amidon, T.E.; Blain, T.J. Soda pulping of hardwoods catalyzed by AQ and methyl substituted AQs. J. Wood Chem. Technol. **2006**, *26*, 141–152.
4. Francis, R.C.; Bolton, T. S.; Abdoulmoumine, N.; Lavrykova, N.; Bose, S.K. Positive and negative aspects of soda/anthraquinone pulping of hardwoods. Biores. Technol. **2008**, *99*, 8453–8457.
5. Francis, R.C.; Shin, N.-H. Methods for carbonate pretreatment and pulping of cellulosic material. US Patent Appl. 2007/0284068 (12/13/2007) or PCT Appl. WO 2007/137127 (11/29/2007).
6. Lai, Y.-Z.; Guo, X.-P.; Situ, W. Estimation of phenolic hydroxyl groups in wood by a periodate oxidation method. J. Wood Chem. Technol. **1990**, *10*, 365–377.
7. Francis, R.C.; Lai, Y.-Z.; Dence, C.W.; Alexander, T.C. Estimation of Phenolic Hydroxyl groups in wood pulps. Tappi J. **1991**, *74*(9), 219–224.
8. Chai, X.-S.; Zhu, J.Y.; Li, J. A simple and rapid method to determine Hexeneuronic Acid groups in chemical pulps. L. Pulp Pap. Sci. **2001**, *27*, 165–168.
9. Gellerstedt, G. Chemical degradation methods: Permanganate oxidation. In *Methods in Lignin Chemistry*; Lin, S.Y. and Dence, C.W., Eds.; Springer-Verlag, Berlin, 1992; 322–333.
10. Bose, S.K.; Wilson, K.L.; Francis, R.C.; Aoyama, M. Lignin analysis by permanganate oxidation. I. Native spruce lignin. Holzforschung **1998**, *52*, 297–303.

11. Gellerstedt, G.; Gustafsson, K.; Lindfors, E.L. Structural changes in lignin during oxygen bleaching. Nordic Pulp Pap. Res. J. **1986**, *1*(3), 14–17.

12. Akim, L.; Colodette, J.; Argyropoulos, D.S. Factors limiting oxygen delignification of kraft pulp. Can. J. Chem. **2001**, *79*, 201–210.

13. McDonough, T.J. Oxygen delignification. In *Pulp Bleaching—Principles and Practice*, Dence, C.W., Reeve, D.W. (Eds.); TAPPI PRESS, Atlanta, 1996; 213–239.

14. Gierer, J. Chemical aspects of kraft pulping. Wood Sci. Technol. **1980**, *14*, 241–266.

15. Pavlickova, L.; Koutek, B.; Ubik, K.; Soucek, M. Oligomeric products from basic hydrolysis of 4-hydroxybenzyl phenyl sulfones. Collection Czechoslov. Chem. Commun. **1976**, *41*, 299–310 (in English).

16. Gellerstedt, G.; Lindfors, E.L. Structural changes in lignin during kraft pulping. Holzforschung **1984**, *38*, 151–158.

17. Lawako, M.; Henriksson, G.; Gellerstedt, G. Characterization of lignin-carbohydrate complexes from spruce sulfite pulp. Holzforschung. **2006**, *60*, 162–165.

18. Amidon, T.E.; Francis, R.C.; Scott, G.M.; Bartholomew, J. et al. New product and processes from an integrated forest refinery. PCT Appl. WO 2006/121634 (11/16/2006). USPTO Appl. 20070079944 at http://www.uspto.gov/patft/index.html

19. Bolton, T.S.; Francis, R.C.; Amidon, T.E. Chemical and physical changes due to acidolysis of chips ahead of alkaline pulping. Proceed. 14th Int. Symp. of Wood, Pulp, Fiber Chem., Durban, South Africa, June 25–28, 2007.

20. Landucci, L.L. Quinones in alkaline pulping: Characterization of an AHQ-quinone methide intermediate. Tappi J. **1980**, *63*(7), 95–99.

21. Dimmel, D.R. Electron transfer reactions in pulping systems. Part 1. Theory and applicability to anthraquinone pulping. J. Wood Chem. Technol. **1985**, *5*, 1–14.