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Soda Pulping of Hardwoods Catalyzed by Anthraquinone and Methyl Substituted Anthraquinones

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Abstract: Black liquor gasification (BLG) as well as the recovery of lignin and other organic compounds from pulping black liquor would be aided if an efficient sulfur-free pulping process could be developed. This has provided new impetus for research on soda pulping with redox catalysts instead of sodium sulfide that is presently used in the kraft process. Soda/anthraquinone (AQ) pulping afforded white birch (*Betula papyrifera*) and sugar maple (*Acer saccharum*) pulps with equal if not superior strength to kraft pulps. However, the delignification rate was significantly lower for soda/AQ pulping. When AQ was replaced by 2-methylantraquinone (2-MAQ) a delignification rate only slightly lower than that of kraft pulping was obtained at the same effective alkali (EA). At a kappa number of ~20, a soda/2-MAQ pulp was produced from sugar maple at a higher yield (1.2% on chips) than for a kraft pulp. 2-MAQ was synthesized, as a powder, at 75% yield using an AlCl_3 -mediated Friedel-Crafts reaction that is one of the methods used for commercial production of AQ.

Keywords: Alkaline pulping, redox catalysts, anthraquinone, 2-methylantraquinone, hardwoods

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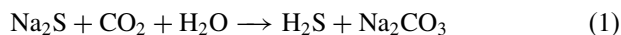
INTRODUCTION

Black liquor gasification (BLG) is a partial combustion process in which the organic compounds in a pulping effluent are converted into fuel gases. It offers the potential for more efficient utilization of the fuel value as compared to concentrating the black liquor (BL) and incinerating it in a conventional recovery furnace.^[1–4] BLG would allow a mill to generate more electricity or use some of the H₂ and CO in the flue gas for chemical synthesis. Another option is to precipitate some of the lignin from the BL before gasification. However, the regeneration of Na₂S from kraft BL would be tedious. Some of the sulfur in the BL would be converted to H₂S in the fuel gases for all BLG processes.^[3] This H₂S has to be selectively removed by adsorption onto a solid sorbent or into a solvent. The H₂S would have to be desorbed from the solid sorbent and the surface re-conditioned for another sulfidation cycle. If the H₂S is absorbed into a solvent then desorption into a non-reactive gas followed by re-absorption into NaOH or Na₂CO₃ would be required.

If an efficient catalyst for soda pulping could be found then the small amount of sulfur entering the system with the wood, chemicals, and fuels could be adsorbed onto a ferric oxide (Fe₂O₃)-containing sorbent to generate FeS. When the sulfidated sorbent was treated with O₂, the products would be Fe₂O₃ and SO₂ gas. The formation of FeS during sulfidation and regeneration of Fe₂O₃ after oxidation (both treatments at 480–580°C) were confirmed for many cycles by X-ray diffraction (XRD) analyses.^[5] Furthermore, no results were reported that indicated that Fe₂O₃ adsorbed CO₂ to form stable products even though the gas mixture that was used contained 5.2% CO₂ and only 1.5% H₂S.^[5] The same basic chemistry appears to occur at higher temperatures as well.^[6] The SO₂ gas could be absorbed into a weak alkaline solution to generate NaHSO₃ that could be reacted with residual oxidants in the bleach plant and discharge as part of the liquid effluent.

The key to this optimistic outcome that would produce saleable products, electricity, chemicals, or sulfur-free lignin, is additional research on non-sulfur pulping. The aim of this research program was to see if soda pulping catalyzed by anthraquinones (AQs) can produce a bleached hardwood pulp equivalent to bleached kraft pulp from the same species. The literature contains credible mechanisms to explain how anthraquinone (AQ) catalyzes lignin depolymerization^[7,8] and retards the rate of alkaline peeling of carbohydrates^[9,10] in a redox cycle involving anthrahydroquinone (AHQ). When AQ is used, it is reported that tear strength^[11,12] and bleached brightness^[11,12] are slightly lower than for a corresponding kraft pulp. Also, the causticizing rate (regeneration of NaOH from Na₂CO₃) would be lower for kraft pulping and conventional recovery. However, the causticizing rate for kraft black liquor increases when BLG is used because more Na₂CO₃ is generated when Na₂S is converted to H₂S

(Equation (1)).



EXPERIMENTAL

Wood Supply

The white birch and sugar maple were grown on properties owned by SUNY College of Environmental Science and Forestry in the Central New York area.

Chemicals

Anthraquinone (AQ) and 2-methylantraquinone (2-MAQ) were purchased from the Aldrich Chemical Company. The purity of the AQ was 97% whereas the 2-MAQ consisted of 95% 2-MAQ and ~3.5% 1-MAQ. This MAQ mixture is defined as MAQ-Ald. to differentiate it from a mixture that was synthesized using the method of Danielsen,^[13] with some modifications. The reaction scheme is shown in Figure 1. Phthalic anhydride (1.50 g), toluene (7.5 mL), and aluminum chloride (3.0 g) in a 100 mL Erlenmeyer flask were carefully heated to 65°C with a heating mantle, until evolution of HCl gas practically ceased. After being cooled to room temperature, the products were mixed with 10 g of crushed ice and 1 mL of conc. HCl. The products were extracted with diethyl ether (2 × 20 mL) and the organic layer was collected, dried over sodium sulfate, and concentrated to ~5 mL. Petroleum ether (2 mL, b.p. 60–80°C) was then added and the products were allowed to precipitate.

The precipitate was dried and weighed. A small fraction was purified with silica gel column chromatography (hexane-acetone mixture) and the product was identified as 2-(4-methylbenzoyl)-benzoic acid (MBBA), the intermediate in Figure 1. Another fraction of the crude product was silylated and analyzed by gas chromatography (GC) using a DB-17 capillary column. The response

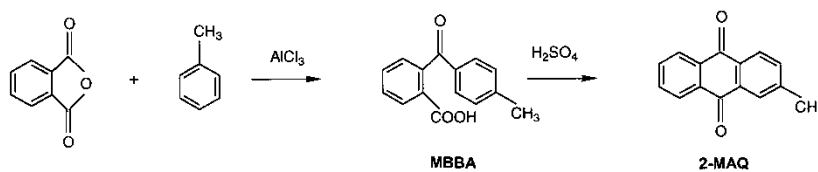


Figure 1. Synthesis of 2-methylantraquinone by the AlCl₃-mediated Friedel-Crafts reaction.

factor of the purified MBBA was determined relative to diphenyl ether. The yield of MBBA in the crude product was 92% based on the limiting reactant, phthalic anhydride.

The purified MBBA had a melting point of 138–139°C and the MS and ¹H-NMR data are: MS (m/z): 240 (M⁺, 15), 181 (10), 149 (20), 119 (100), 91 (35), 65 (25). ¹H-NMR (CDCl₃): 2.3973 (s, -CH₃), 7.2065 (d, arom), 7.2605 (CDCl₃), 7.3501 (d, arom), 7.5983 (m, arom), 8.0677 (d, arom), 8.2750 (broad, -COOH).

The ring closure or cyclization step (Figure 1) was performed with conc. H₂SO₄ (20 mL) at 100°C for 60 min. After cooling, the reaction products were poured onto crushed ice and stirred. The precipitate was filtered, washed with water, and dried. The crude product was characterized by thin layer chromatography (TLC) using silica gel plates and toluene-ethyl formate-formic acid (5:4:1). Only two spots were observed and they corresponded to 2-MAQ and MBBA. Cold water (~20°C) was used to make a slurry of the crude product that was then filtered. This washing procedure was repeated three times. The filter cake was then washed with hot water in a Buchner funnel. The final product had a purity of ~95% and the yield of 2-MAQ was 75% based on phthalic anhydride. The melting point of the product was 169–172°C and its ¹H-NMR data were as follows: ¹H-NMR (CDCl₃): 2.5253 (s, -CH₃), 7.5253 (CDCl₃), 7.5806 (d, arom), 7.7848 (m, arom), 8.0836 (s, arom.), 8.1883 (d, arom), 8.2805 (m, arom).

A comparison of the purchased and synthesized 2-MAQ MS spectra is presented in the Results and Discussion section.

Standard Pulping Conditions

A liquor-to-wood ratio of 5:1 was used and 90 min to maximum temperature. Sodium sulfite (0.5% on chips) was added as an oxygen scavenger to all soda cooks that were catalyzed by an anthraquinone.

Bleaching

D₀ Stage: In plastic bottles at 3.0–3.5% consistency, 70°C, 2 h with initial pH ~3.5 (before the addition of ClO₂) and end pH ~2.3. A kappa factor of 0.20 (% equiv. Cl₂/kappa number) was used on all occasions.

Ep Stage: In plastic bags at 12% consistency, 80°C, 2 h with 2.0% NaOH, 0.25% H₂O₂, and 0.1% MgSO₄ · 7H₂O on pulp. The end pH was always in the range of 11.2–11.6.

D₁ Stage: In plastic bags at 10% consistency, 70°C, 3 h, 0.8% ClO₂ and 0.2–0.3% NaOH on pulp. The end pH was always in the range of 3.5–4.1.

Analyses

TAPPI Standard Methods were used for kappa number, viscosity, and strength properties whereas brightness was determined on an Elrepho brightness meter in the range of 90% brightness. A Kajaani FS 100 analyzer was used to determine weight (mass)-weighted average fiber length, i.e. $L_w = (\sum n_i L_i^3) / (\sum n_i L_i^2)$, where $i = 1, 2, 3, \dots, n$ = fiber count, L = contour length.

RESULTS AND DISCUSSION

Preliminary Research with White Birch

The first issue investigated was tear strength for soda/AQ pulps. White birch was chosen because of its unusually long fibers. This species should give an advantage to the soda/AQ process if it uses a higher effective alkali (EA) than would be used for kraft pulping. The intrinsic fiber strength may be lower for the soda/AQ pulp but if the average fiber length is equal to that of a kraft pulp and is in the range of 1.5 mm you may achieve equivalent strength. One would expect that as fiber length increases the contribution to pulp strength caused by fiber-fiber bonding and entanglement increases in significance compared to intrinsic fiber strength.

A kraft pulp was produced using 18% active alkali ($\text{NaOH} + \text{Na}_2\text{S}$, Na_2O basis) and 25% sulfidity whereas a soda/AQ pulp was produced using 18.6% active alkali (AA) and 0.1% AQ. Two h at 165°C was used for both processes (see Experimental for other standard pulping conditions). The effective alkali (EA) ($\text{NaOH} + \frac{1}{2}\text{Na}_2\text{S}$, Na_2O basis) was 15.8% on chips for kraft pulping and 18.6% for soda/AQ pulping. Pulps with nearly equivalent kappa numbers (~ 20), screened yields ($\sim 51.5\%$ on chips), and average fiber length (~ 1.4 mm) were obtained. The tensile-tear plots for the two pulps are shown in Figure 2. It can be seen that they are nearly identical. The strength of the soda/AQ pulp would be expected to increase if the alkalinity of the pulping liquor were to be lowered. Random chain cleavage of cellulose is known to decrease with decreasing alkalinity.^[14]

Kraft, Soda/AQ, and Soda/MAQ Pulps from Sugar Maple

Sugar maple was chosen for a more detailed comparison of the pulping processes because of its abundance in the northeastern and north-central regions of the United States and because it produces a relatively strong kraft pulp^[15,16] despite having an average fiber length of only ~ 0.7 mm.^[16,17]

Some properties of a kraft pulp and three soda/AQ pulps are presented in Table 1. Lower EA was used compared to pulping of birch. The time at maximum temperature was 2 h for all of these cooks. Despite a higher EA

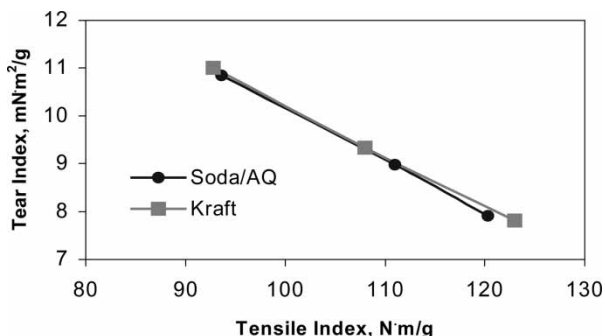


Figure 2. Tensile-tear plots for unbleached kraft and soda/AQ pulps from white birch.

application, soda/AQ pulping (0.1% AQ) at 165°C afforded less delignification than kraft pulping at the same temperature. However, when the maximum temperature was increased to 170°C a soda/AQ pulp that was equivalent to the kraft pulp in terms of kappa number, yield, and tear strength was obtained. When the EA for soda/AQ was decreased from 15.5% to 14.0% and the AQ dose was increased to 0.15% a 5-point decrease in kappa number was obtained

Soda/MAQ Pulping

Based on the results in Table 1, soda/AQ can not achieve the low kappa number of kraft pulping at equivalent temperature, time, and EA application. 2-methylantraquinone (2-MAQ) is reported to be a more effective catalyst than AQ.^[18,19] Furthermore, it appears possible that a plant producing AQ could be used to produce 2-MAQ at approximately the same cost (to be discussed later). Not only is 2-MAQ reported to give a lower kappa number than AQ it is also reported to give a higher pulp yield. When the two

Table 1. Kraft and soda/AQ pulping of sugar maple

Chemical application	Temp., °C	Effective alkali (%)	Kappa number ^b	Yield, ^c %
16% AA and 30% sulfidity ^a (kraft)	165	13.6	20.7	53.5
20% NaOH, 0.1% AQ	165	15.5	28.0	54.2
20% NaOH, 0.1% AQ	170	15.5	20.3	53.3
18% NaOH, 0.15% AQ	170	14.0	15.4	52.1

^aAA = Active alkali as % Na₂O on chips.

^bTwo h at maximum temperature.

^cScreened yield; rejects were <0.4% (chip basis) for all pulps in this study.

additives (0.1% on chips) were used to catalyze soda pulping of loblolly pine (*Pinus taeda*), AQ afforded a kappa number of 34.2 at a yield of 44.8% whereas the 2-MAQ afforded a kappa number of 33.4 at 46.4% yield.^[19] The results for the 2-MAQ were quite impressive for loblolly pine, a softwood that responds poorly to alkaline pulping.

A preliminary comparison was made between kraft, soda/AQ, and soda/2-MAQ pulping of sugar maple. All pulps were produced in duplicate because yield data were now more important. If more pulp is obtained for soda/2-MAQ compared to kraft pulping then the sale of the incremental pulp could be used to offset the cost of the 2-MAQ. For all pulps produced in duplicate the most significant difference in kappa number was about one unit and 0.3% (chip basis) in screened and total yield.

The results in Table 2 show that 0.075% 2-MAQ was indeed superior to 0.1% AQ and that soda/2-MAQ gave a higher yield than kraft pulping, albeit at a slightly higher kappa number. The differences in yield and kappa number for the kraft pulps in Tables 1 and 2 are most likely due to the use of different M&K digesters and not to the minor changes in the composition of the cooking liquor. All of the pulps in Table 2 were produced in the same reaction vessel (digester). The ultimate outcome that is being sought is a non-sulfur pulp with the same kappa number as the kraft pulp when the same EA, reaction time, and temperature are used. A cooking time of 2.5 h was used for the soda/AQ and soda/2-MAQ pulps above whereas 2 h was used for the kraft pulp (Table 2). When the 2-MAQ dose was increased to 0.116% a pulp with kappa number 20.4 was obtained at 54.7% yield (Table 2). This yield is 1.7% (chip basis) higher than for the kraft pulp in Table 2, 1.2% higher than the kraft pulp in Table 1, and 0.9% on chips higher than for the soda/AQ pulp in Table 2.

Synthesis of 2-MAQ

The synthesis described in the Experimental section could actually be performed in commercial facilities that are already in existence. The AlCl_3 -

Table 2. Kraft, soda/AQ and soda/2-MAQ pulping of sugar maple at 165°C

Chemical applications	Time at 165°C, h	EA	Kappa number	Yield, %
16% A.A. and 25% sulfidity (kraft)	2.0	14.0	18.5	53.0
18% NaOH, 0.1% AQ	2.5	14.0	23.3	53.8
18% NaOH, 0.075% 2-MAQ ^a	2.5	14.0	20.0	54.2
18% NaOH, 0.116% 2-MAQ	2.0	14.0	20.4	54.7

^aMAQ-Ald. (Experimental) was used; 0.003% 1-MAQ on chips was contained in the 2-MAQ.

mediated Friedel-Crafts reaction in Figure 1 is one of the commercial methods for the synthesis of AQ. Replacing benzene (AQ) with toluene (2-MAQ) may be the only change required. Furthermore, toluene is generally less expensive than benzene on a mass basis. The Chemical Marketing Reporter listed \$0.40/kg for benzene and \$0.36/kg for toluene in January 2003.^[20] More recently (March 2005) the reported prices were \$1.13/kg and \$0.70/kg, respectively.^[21]

It was necessary to conduct the synthesis to get some idea about the yields of 1- and 2-MAQ that were possible. Somewhat surprisingly not much information on these yields could be found in the published literature. Although 2-MAQ is superior to AQ as a catalyst, results in the literature suggest that 1-MAQ is an inferior catalyst.^[18]

No evidence was found indicating that the formation of 1-MAQ was significant. Also, we project a final yield of 2-MAQ even higher than 75% in a commercial plant where recycle would be possible. Only 2-MAQ and the MBBA intermediate in Figure 1 were detected in the crude final product by TLC. Although not quantified, there was a loss of mass when the crude product was washed with water and this would be consistent with the loss of MBBA that contains a carboxylic group. If the wash effluent were to be vacuum dried and the MBBA recycled then yield loss in the cyclization step may be minimal and the 2-MAQ yield may approach 92%, that is, the yield of MBBA from phthalic anhydride and toluene.

No pulping research was performed with the synthesized 2-MAQ. However, its mass spectrum is compared to that of the purchased MAQ in Figure 3. They are almost identical.

Bleachability and Strength of Sugar Maple Pulps

The kraft pulps in Tables 1 and 2, the two soda/AQ pulps cooked at 170°C (Table 1), and the 20.4 kappa number soda/2-MAQ pulp (Table 2) were bleached by a DoEpD₁ sequence. This was to see if the soda/AQ and 2-MAQ pulps were more difficult to bleach and also to see if yield loss during bleaching was more significant for the soda/2-MAQ pulp that had the highest unbleached pulp yield. The results are presented in Table 3. It appears that the soda/AQ and 2-MAQ pulps give slightly lower brightness but there was no significant difference in yield loss during bleaching.

The 18.5 kappa number kraft pulp, the 20.3 kappa number soda/AQ pulp, and the 20.4 kappa number soda/2-MAQ pulp from Table 3 were analyzed for strength properties. The results in Figure 4 suggest that the soda/AQ and 2-MAQ pulps are slightly stronger than the kraft pulp. The average fiber length for the kraft pulp was 0.69 mm, which is typical for sugar maple.^[16,17] Also, the maximum tear of 9.0 mN·m²/g for the kraft pulp is almost identical to two other reported values.^[15,16]

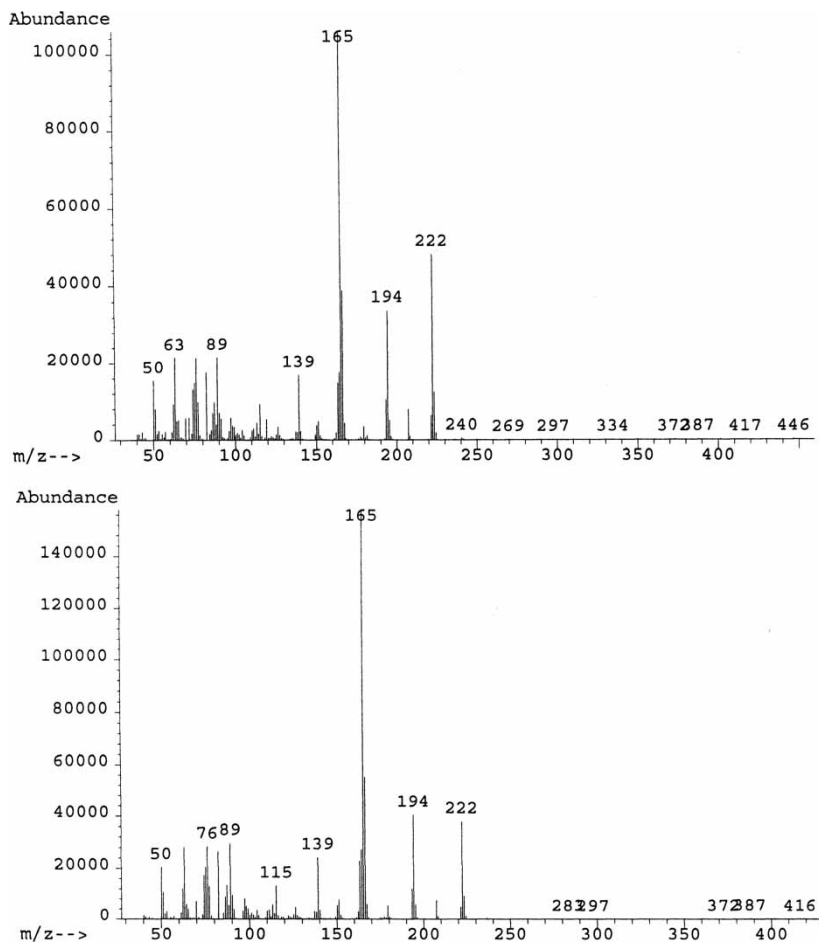


Figure 3. Solid-probe mass spectra of synthesized (top) and purchased (bottom) 2-methylantraquinone.

Economic Ramifications

If the black liquors were to be gasified, the causticizing rate would be approximately equal for kraft and soda/MAQ. When an AA of 16.0% Na_2O and 30% sulfidity is used for kraft pulping, 11.2% of the AA would come from NaOH and 4.8% from Na_2S . In conventional recovery where all the sulfur is recovered as Na_2S , causticizing would be required to convert Na_2CO_3 to NaOH so that 11.2% Na_2O on chips is achieved. However, if BLG is used and 50% of the Na_2S is converted to H_2S in accordance with Equation (1), the causticizing rate would increase to

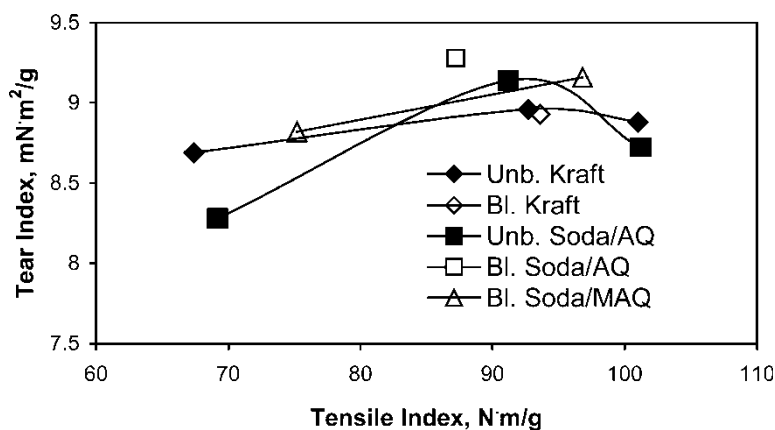
Table 3. Brightness and fiber yield of sugar maple pulps after DoEpD₁ bleaching

Pulping process	Unbleached. kappa number	Bleached brightness ^a (%)	Fiber yield, % ^b
Kraft	20.7	91.0	96.0
Kraft	18.5	91.3	96.3
Soda/AQ	20.3	89.4	96.1
Soda/AQ	15.4	91.1	96.3
Soda/2-MAQ	20.4	90.4	96.2

^a% Elrepho.^bBased on unbleached pulp ($\pm 0.3\%$).

13.6% Na₂O on chips. This is a value similar to the 14.0% used for soda/2-MAQ pulping (Tables 2 and 3).

The situation simplifies to a kraft pulp with kappa number 20.7 at 53.5% yield (Table 2) and a sulfur-free, soda/2-MAQ pulp at 20.4 kappa number and 54.7% yield (Table 3) when the reaction time, temperature, and causticizing rate are approximately equal. It would require 1947 metric tons of chips to produce 1000 metric tons of bleached kraft pulp (53.5% yield after pulping and 96.0% yield after bleaching). That same amount of chips would produce 1024 metric tons of bleached soda/2-MAQ pulp. The extra 24 tons of pulp could be sold for ~\$12,000. At 1.2 kg of 2-MAQ/ton of chips (0.12%), the 2-MAQ requirement for 1947 metric tons would be 2336 kg. Currently, the cost of AQ in the United States is in the range of \$3.50 to \$4.00/kg.^[22] Even if the 2-MAQ costs \$4.50/kg the total catalyst cost

**Figure 4.** Tensile-tear plots for kraft, soda/AQ, and soda/MAQ pulps from sugar maple.

would be ~\$10,500. The difference between incremental pulp sales and MAQ cost would be ~\$1500 that could be used for additional bleaching chemicals for 1065 metric tons of unbleached soda/2-MAQ pulp. An extra expenditure of ~\$1.50/ton in bleaching cost may be able to eliminate the apparent brightness gap between kraft and soda/2-MAQ pulp. The economic benefit to the mill would be the potentially higher value associated with the sulfur-free BL or precipitated lignin.

SUMMARY

Gasification offers the potential for more efficient utilization of the fuel value of the dissolved organics in black liquors compared to the use of a conventional recovery furnace. Soda pulping catalyzed by AQs avoids sodium sulfide that is used in kraft pulping. This is favorable for both gasification and the recovery of lignin and other organic compounds from the black liquor. These organics may be a future source of bio-based products. Also, CO and H₂ from gasification can be used to generate a wide range of chemicals.^[23]

Kraft pulping was compared to soda/AQ and soda/2-MAQ pulping of sugar maple. Soda/AQ was slightly inferior whereas soda/MAQ was equal to kraft for the production of unbleached pulps. Bleaching trials aimed at eliminating the ~1.0 point brightness gap between the soda pulps catalyzed by AQs and the kraft pulp are now in progress.

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