Influence of Hexenuronic Acids on Kraft Bleaching

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1.0: INTRODUCTION

Over the past ten years there has been a research renaissance in hemicellulose chemistry as it applies to pulping and bleaching operations. Researchers have identified hemicelluloses as an important component influencing pulp yields, strength properties, and pulp bleachability. This report summarizes the research activities undertaken at IPST in the dues funded research consortium (DFRC) project F015 directed at evaluating the role of hemicelluloses in pulp bleachability. Currently, the focus of our studies is directed towards evaluating the impact that hexenuronic acids (HexA) have on chemical pulp production. These unsaturated sugars are formed by base catalyzed elimination of methanol from 4-O-methyl-D-glucurnoxylans during pulping, as shown in Figure 1.1. Clayton,[1] Johansson and Samuelson,[2] and Simkovi et. al[3] established the fundamental chemical pathways involved in alkaline degradation of 4-O-methylglucuronoxylan.

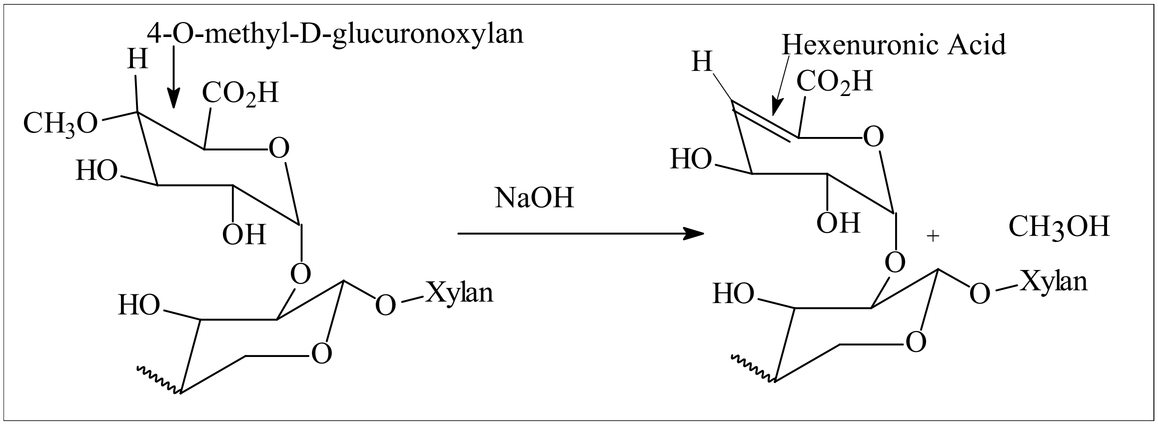


Figure 1.1: Alkali-catalyzed formation of hexenuronic acids.

Following these studies, interest in this field of hemicellulose chemistry wained until Buchert et al.[4] reported that hexenuronic acids present in kraft pulp have a profound effect on pulp bleaching operations. They demonstrated that most of the residual glucuronic acid present in kraft pulps are HexA and not 4-O-methyl-D-gluconoxylan. Furthermore, they established that these unsaturated sugars readily consumed electrophilic reagents such as ozone, peracetic acid, and chlorine dioxide but were relatively inert to alkaline peroxide and oxygen delignification. A careful analysis of the relative rates of acid-catalyzed hydrolysis of hexenuronic acids versus pulp polysaccharides identified hydrolysis conditions under which HexA could be removed from pulp while incurring minimal damage to the pulp fiber. Vuorinen et al. reported[4b] that optimal HexA removal conditions were achieved using a pH 3.0 – 3.5 solution, at 85-115°C for 2 – 4h. Acid catalyzed hydrolysis of HexA was shown to release HexA from the fiber ultimately yielding 2-furoic acid and 5-carboxy-2-furaldehdye as summarized in Figure 1.2.

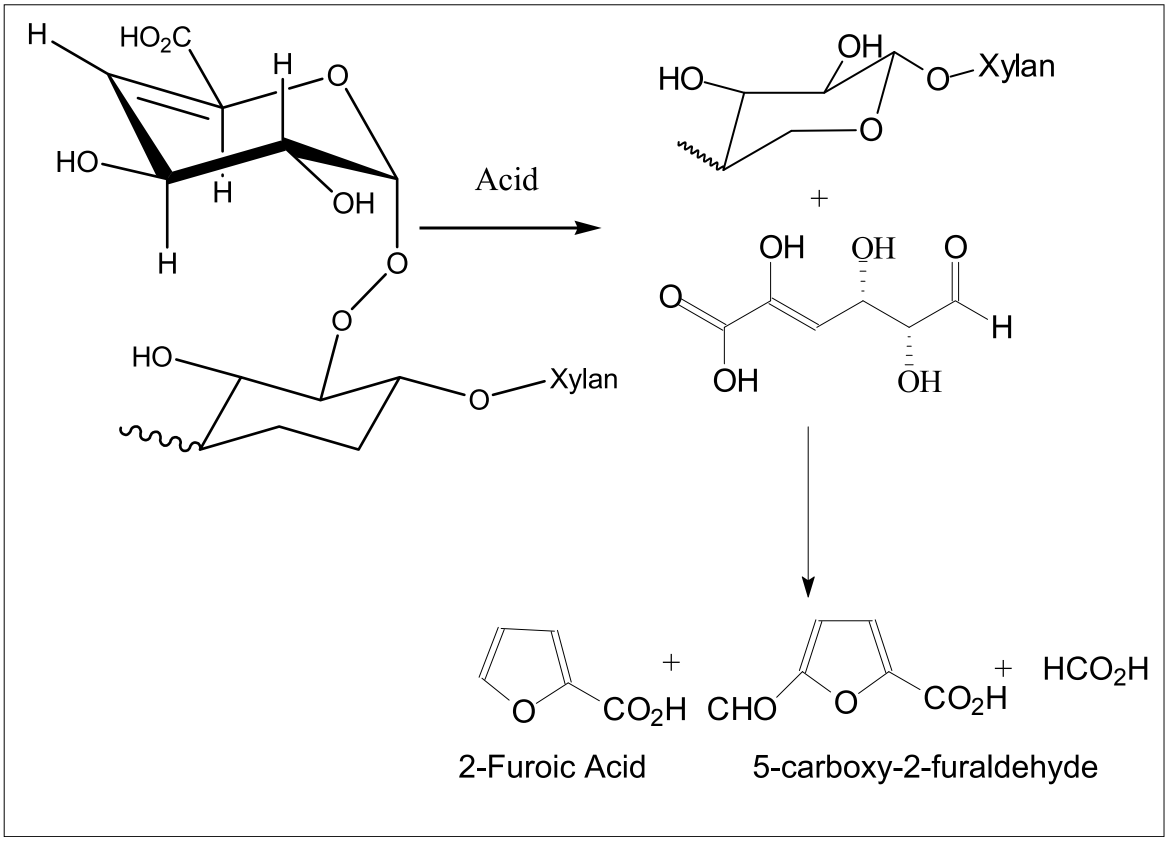


Figure 1.2: Acid catalyzed hydrolysis of HexA.

ECF bleaching studies of birch kraft pulp suggested that an acid hydrolysis stage prior to a D_0-stage could lead to a 50% reduction in bleaching costs. The elimination of HexA in kraft pulps was shown to be also beneficial to TCF pulp bleaching operations and allowed for higher brightness values to be achieved. Accompanying the improved brightness ceilings it was reported that reversion properties for TCF pulps was reduced.

Based on these and other observations, Ragauskas proposed to examine the effects of HexA for US pulp bleaching operations in DFRC project F015. This report summarizes the results of these studies over the past three fiscal years. In general, our studies in this field of research were initially directed toward establishing if HexAs were relevant to US pulp manufacturers. Once we conclusively demonstrated the validity of HexA formation to US manufactures, we focussed our efforts on evaluating their impact on pulp bleachability, methods of HexA generation and removal, and their impact on pulp properties.

RESULTS

2.0 Contribution of hexenuronic acids toward kraft pulp kappa number.

As an initial research goal in this sub-project of F015, PAC recommended that a survey study be performed on a variety of commercial US kraft pulps to determine the relevancy of hexenuronic acids to North American pulp bleaching operations. Analysis of the hexenuronic acid content of kraft pulps was determined by employing an acid hydrolysis procedure. The results of our preliminary HexA studies are summarized in Figure 2.1. Refluxing a commercial HW kraft pulp in a pH 3.5 buffered solution (buffered solution: formic acid: sodium formate) for an extended time period indicated that the acid treatment could reduce the kappa number of the pulp by 50%. The reduction in kappa number was completed within 5 h at 100°C. Based on the studies by Buchert et al. and others one could conclude that approximately 50% of the pulp kappa number could be attributed to HexA.

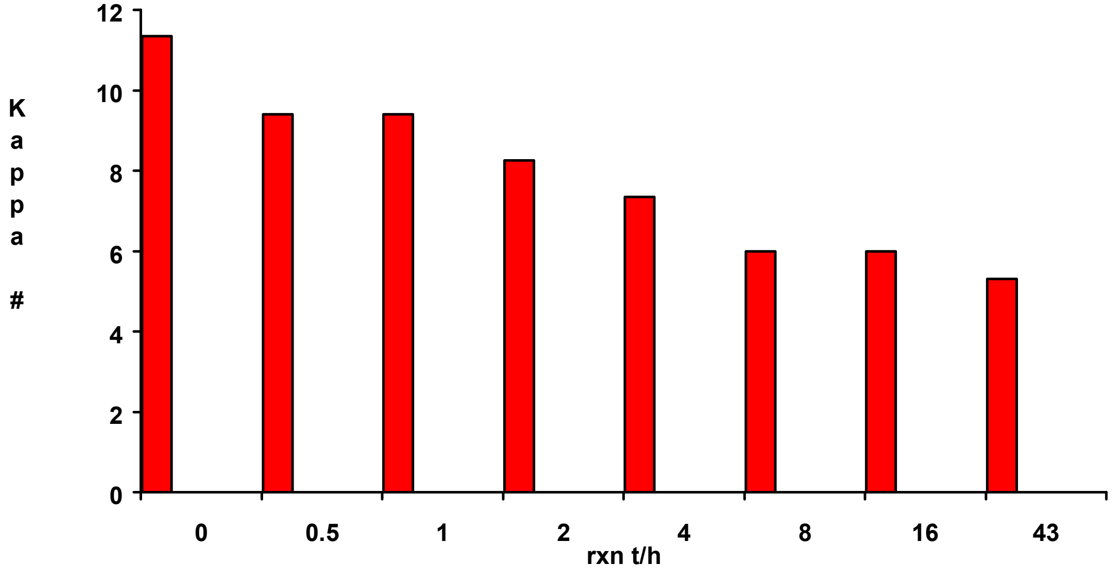


Figure 2.1: Kappa number of a commercial hardwood kraft pulp before and after refluxing in aqueous formic acid-sodium formate solution.

Following this initial study, a series of commercial HW kraft pulps were examined for their sensitivity to a hot acid stage. The results of these investigations are summarized in Figures 2.2 – 2.6.

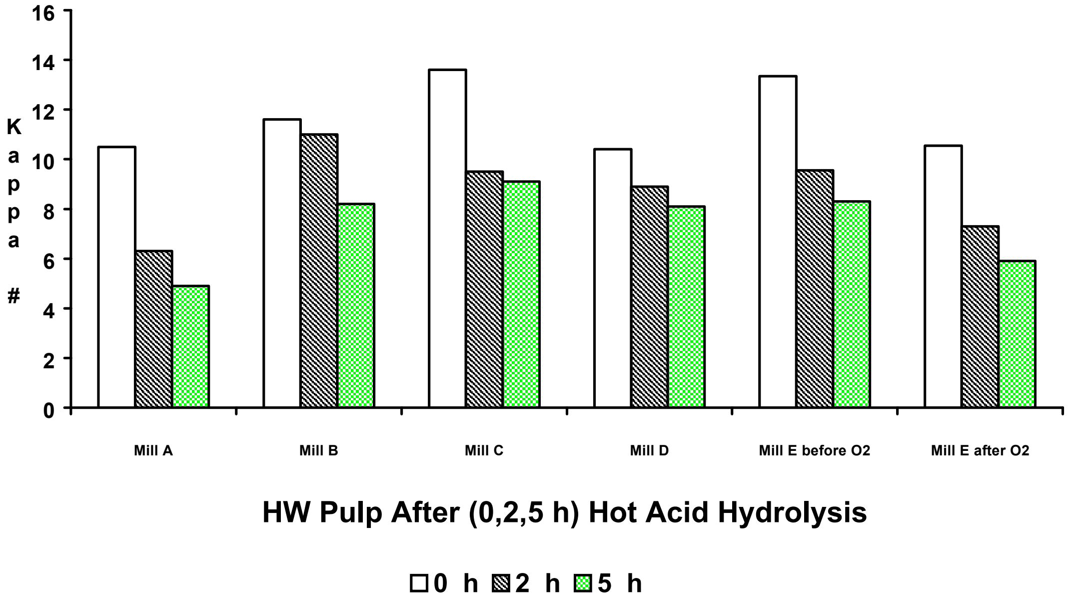


Figure 2.2: Kappa number of commercial HW kraft pulps before and after refluxing in aqueous formic acid-sodium formate solution for 2 and 5 h.

Analysis of the hardwood data suggests that hexenuronic acids contribute approximately 20 to 60% of the total kappa number for the commercial hardwood kraft pulps studied. Interestingly, the ease of acid-catalyzed removal of hexenuronic acids was found to vary substantially for the pulps examined. For most of the hardwood kraft pulps examined, it appeared that the hexenuronic acids are substantially removed after two hours of acidic treatment, whereas pulp from Mill B required five hours. The factors contributing to this phenomenon are currently not understood. Acid hydrolysis of softwood kraft pulps (see Figures 2.3 & 2.4) suggested that the hexenuronic acids contributed approximately 0 to 15% of the total kappa number for these pulps.

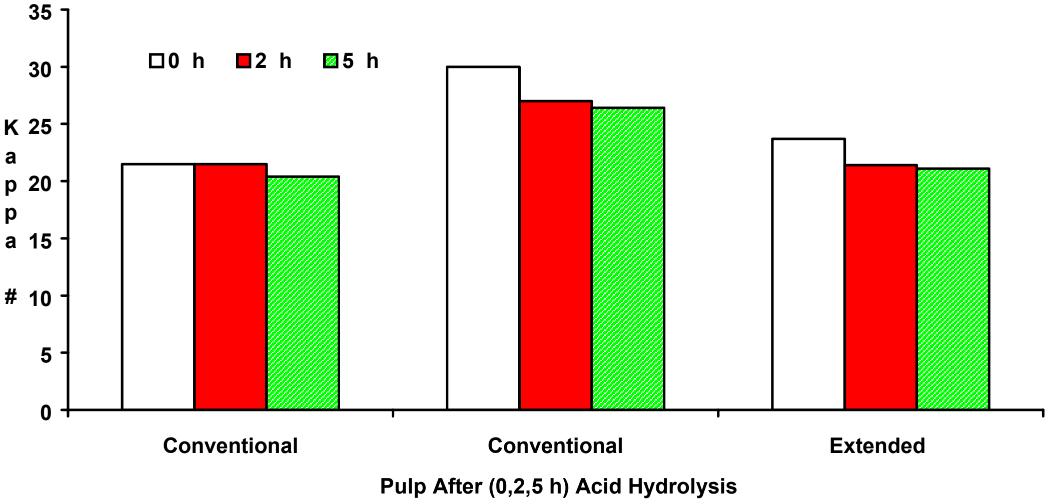


Figure 2.3: Kappa number of commercial softwood kraft pulps before and after refluxing in aqueous formic acid-sodium formate solution for 2 and 5 h.

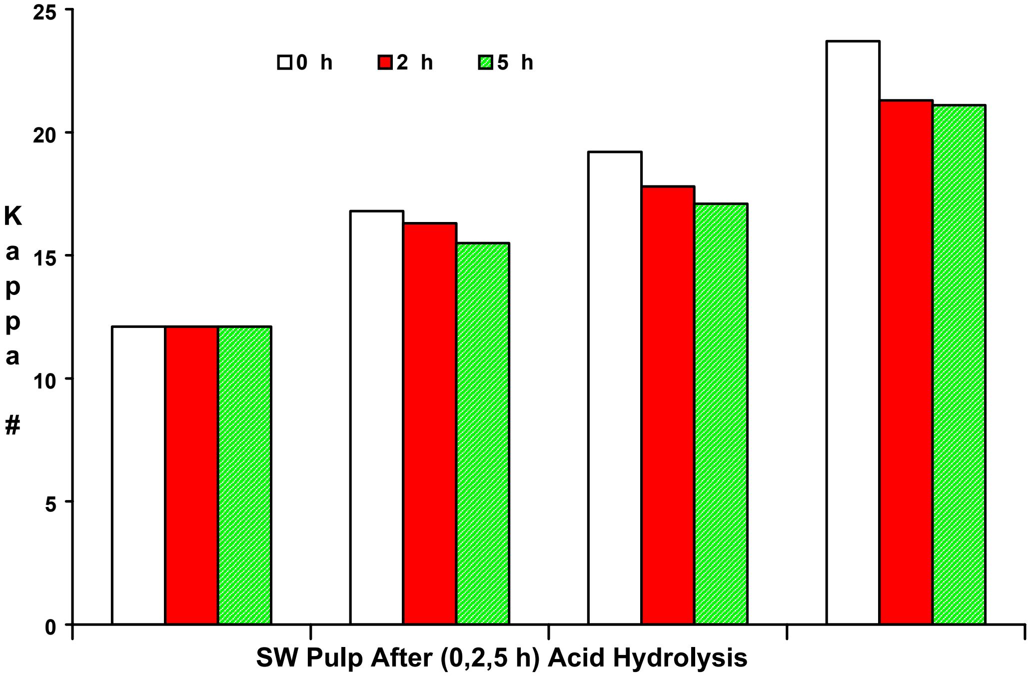


Figure 2.4: Kappa number of laboratory prepared, extended modified softwood kraft pulps before and after refluxing in aqueous formic acid-sodium formate solution for 2 and 5 h.

Along with the kappa number analysis of each starting pulp, the xylan content of each starting pulp was determined. Analysis of the xylan content versus the drop in kappa number after acid hydrolysis suggested a correlation between the xylan content of the starting pulp and the contribution of hexenuronic acids to the kappa number of the pulp (see Fig. 2.5). It appears that as the xylan content of the kraft pulp increases so to does the sensitivity of the kraft pulp increase to kappa reduction by a hot acid stage treatment.

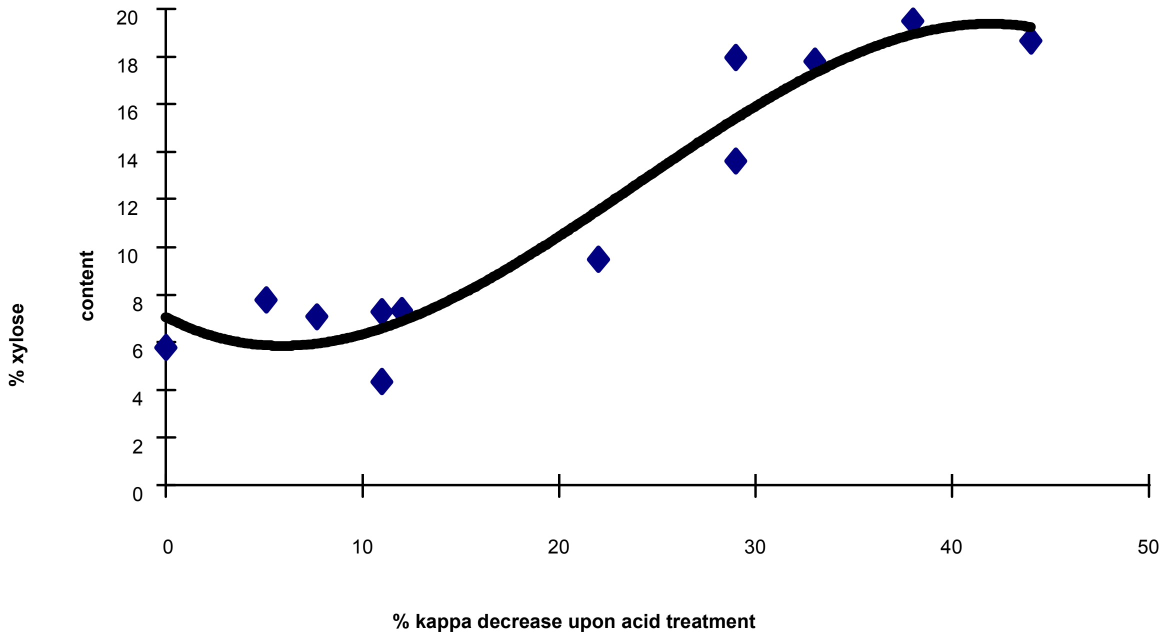


Figure 2.5: Relationship between xylan content of softwood and hardwood kraft pulps and the decrease of kappa number upon acid hydrolysis treatment.

The acid hydrolysis conditions employed in these initial studies were usually detrimental to pulp viscosity as shown in Figures 2.6 and 2.7. These data do not preclude the use of an acid treatment stage to remove hexenuronic acids since further optimization studies could undoubtedly reduce the loss of viscosity while still retaining the reduction in kappa number.

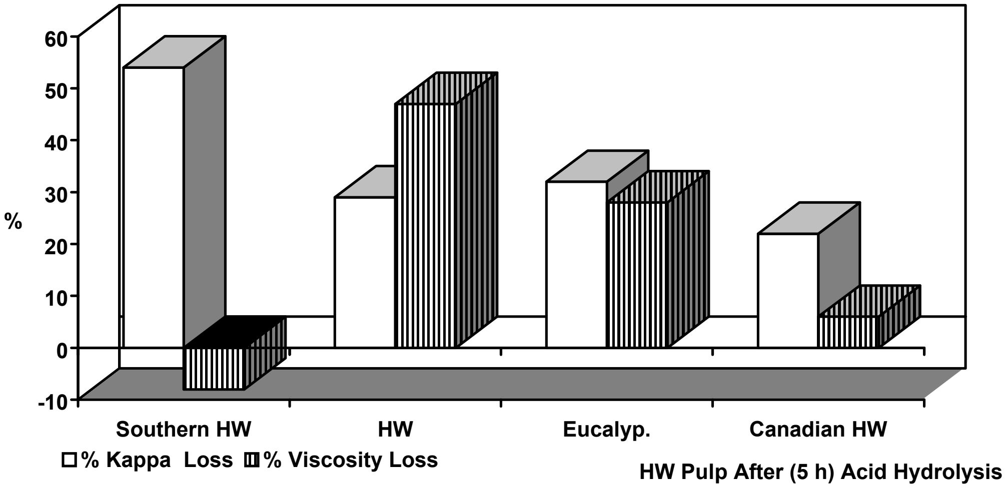


Figure 2.6: Relative changes in viscosity and kappa # of hardwood kraft pulps upon treatment with acid for removal of hexenuronic acid.

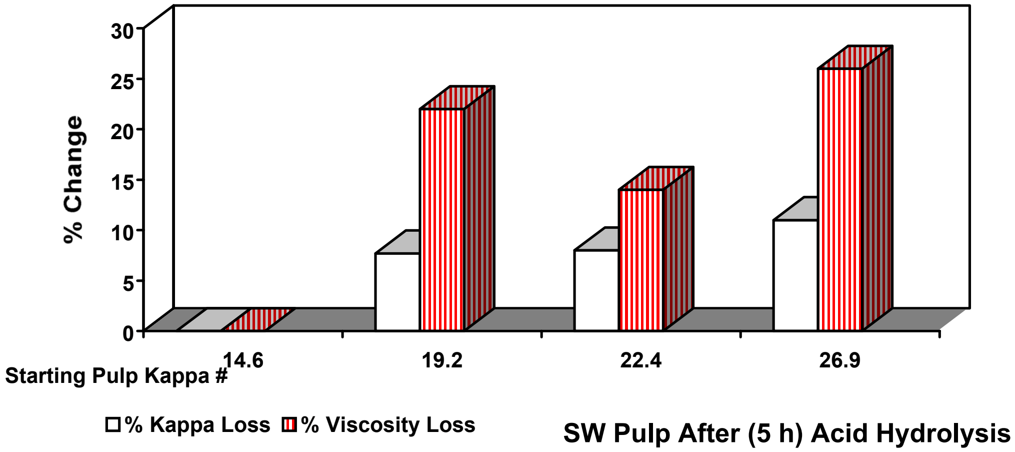


Figure 2.7: Relative changes in viscosity and kappa # of softwood kraft pulps upon treatment with acid for removal of hexenuronic acid.

The results of these analyses demonstrated that hexenuronic acids are a substantial component of the kappa number for North American hardwood kraft pulps and a minor component of softwood kraft pulps. Furthermore, these results suggest that US manufacturers could reduce the kappa number of kraft HW brownstocks using an acid stage and this was anticipated to lead to savings in bleaching costs.

3.0 Influence of HexA on Bleaching Kraft Pulps

The influence that hexenuronic acids have on bleaching was investigated by employing commercial softwood and hardwood kraft pulps with chlorine dioxide and ozone. As summarized in Figure 3.1, acid treatment of an oxygen delignified hardwood kraft pulp reduced the kappa number of the HW pulp by 26%. Subsequent delignification with ZE for the oxygen delignified pulp and OA pulp indicated that the benefits of an A-stage carried through the ZE stages. Indeed, the OAZE pulp was shown to be delignified by an extra 50% over the OZE HW kraft pulp. Performing the same type of experiment for a softwood kraft pulp suggested that acid pretreatment of a kraft pulp could enhance ZE delignification by 50% (see Fig. 3.2).

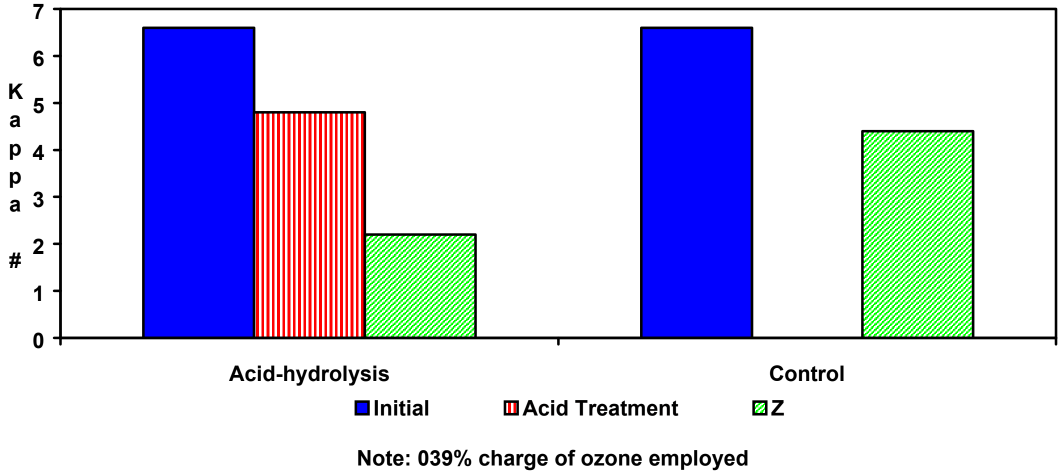


Figure 3.1: ZE bleaching post-O_2 hardwood kraft pulp and hot acid treated (100°C, buffered pH 3.5, 2h) post-O_2 hardwood kraft pulp.

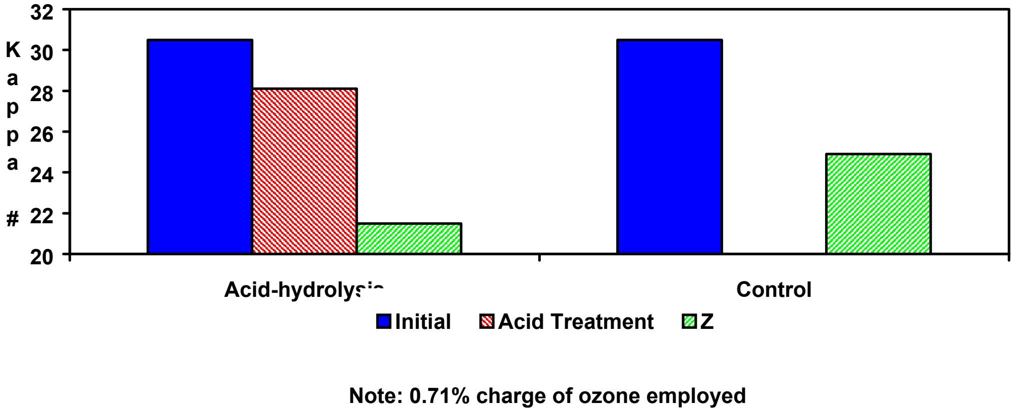
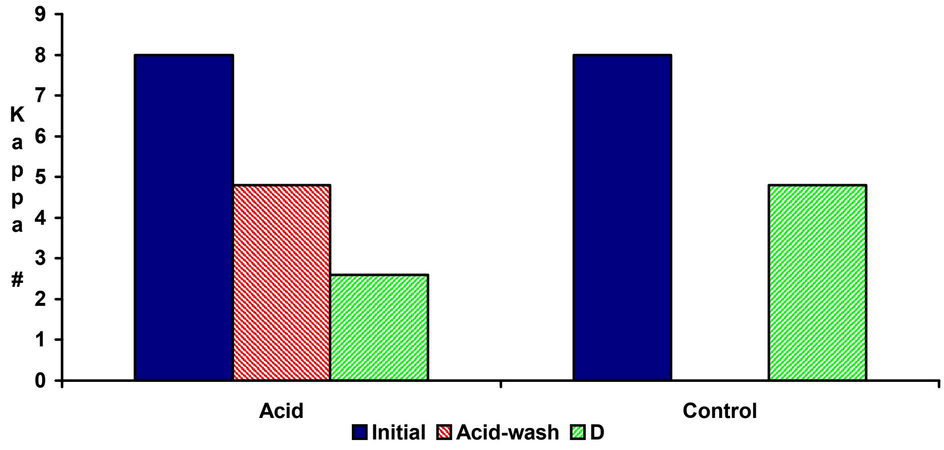


Figure 3.2: ZE bleaching softwood kraft pulp and hot acid treated (100°C, buffered pH 3.5, 2h) softwood kraft pulp.

The benefits noted for acid pretreating a hardwood kraft prior to ozone bleaching were also observed for chlorine dioxide as shown in Figure 3.3. Bleaching a SW kraft pulp with ADE sequence outperformed a DE sequence (Note: employed a 0.61% charge of ClO_2 for both pulps) by 46% with respect to delignification.



Note: 0.61% charge of ClO_2 employed

Figure 3.3: Chlorine dioxide bleaching hardwood kraft pulp and hot acid treated (100°C, buffered pH 3.5, 2h).

In summary, the bleaching results from Figures 3.1 – 3.3 confirm the hypothesis that hexenuronic acids play an important role in consuming electrophilic bleaching agents such as ozone and chlorine dioxide. Removal and/or modification of hexenuronic acids prior to bleaching could result in substantial savings in bleaching chemical costs.

4.0 Effects of HexA removal on Full Sequence ECF Bleaching.

The limited bleaching studies presented in section 3 suggested a direct benefit for removing hexenuronic acids from kraft pulps prior to the first stage of TCF or ECF delignification. To determine if the hot-acid stage bleaching benefits were transferable to subsequent bleaching operations, a pre and post-O_2 kraft pulp were subjected to a hot acid stage and then bleached to full brightness. The pre-O_2 HW kraft pulp was bleached with a DEDED sequence and the post-O_2 was bleached with a DED sequence. Experimental conditions and chemical charges employed are summarized in Table 4.1.

Table 4.1 Bleaching conditions employed to bleach pre- and post-O_2 delignified HW kraft pulps.

DEDED and ADEDED
Brownstock kappa #: 11.4
Brownstock kappa # after acid hydrolysis[1]: 5.6
A-stage: formic acid/sodium formate pH:3, 3 h.
D_0: 0.20 k.f. 3.5% csc, 45 min., 50^{o}C
D_1 Charge: 0.6%; Consistency:10%; 3 h; 75^{o}C
D_2 Charge: 0.1, 0.2, 0.4, 0.6%; Consistency:10%; 3 h; 75^{o}C
DED and ADED
Brownstock kappa #: 8.5
Brownstock kappa # after acid hydrolysis[1]: 2.8
A-stage: formic acid/sodium formate pH:3, 3 h.
D_0: 0.20 k.f. 3.5% csc, 45 min., 50^{o}C
D_1 Charge: 0.1, 0.2, 0.4, 0.6%; Consistency:10%; 3 h; 75^{o}C

[1] acid stage was preformed at 100^{o}C, 2-h pH 3 (buffered).

The changes in TAPPI brightness values and pulp viscosity values were followed throughout the bleaching sequences and these data are summarized in Figures 4.1, 4.2, and Table 4.2

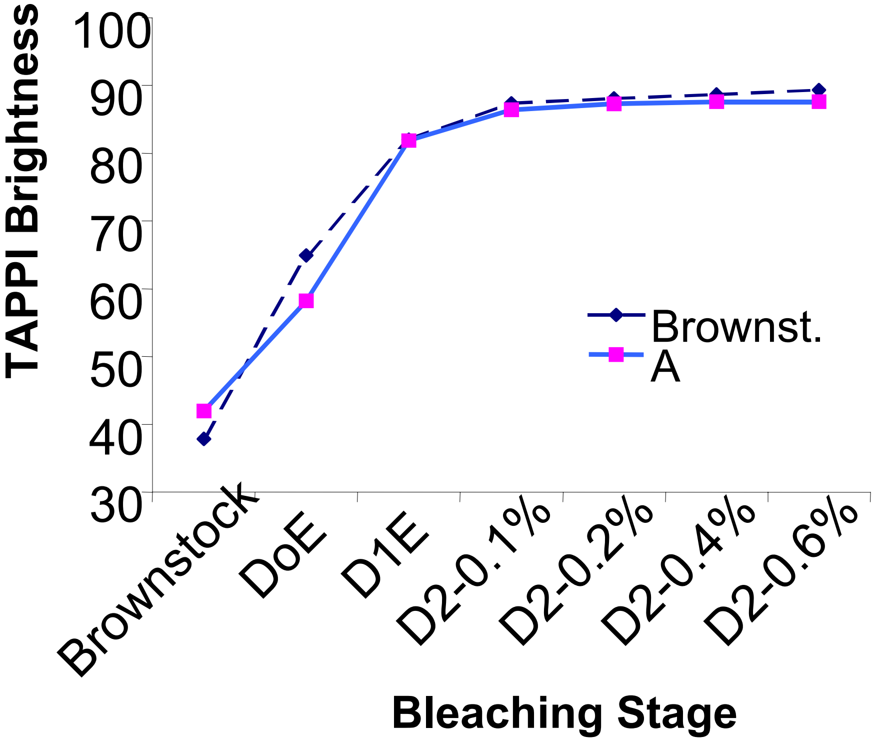


Figure 4.1: Changes in TAPPI brightness for HW kraft pulp bleached DEDED and ADEDED.

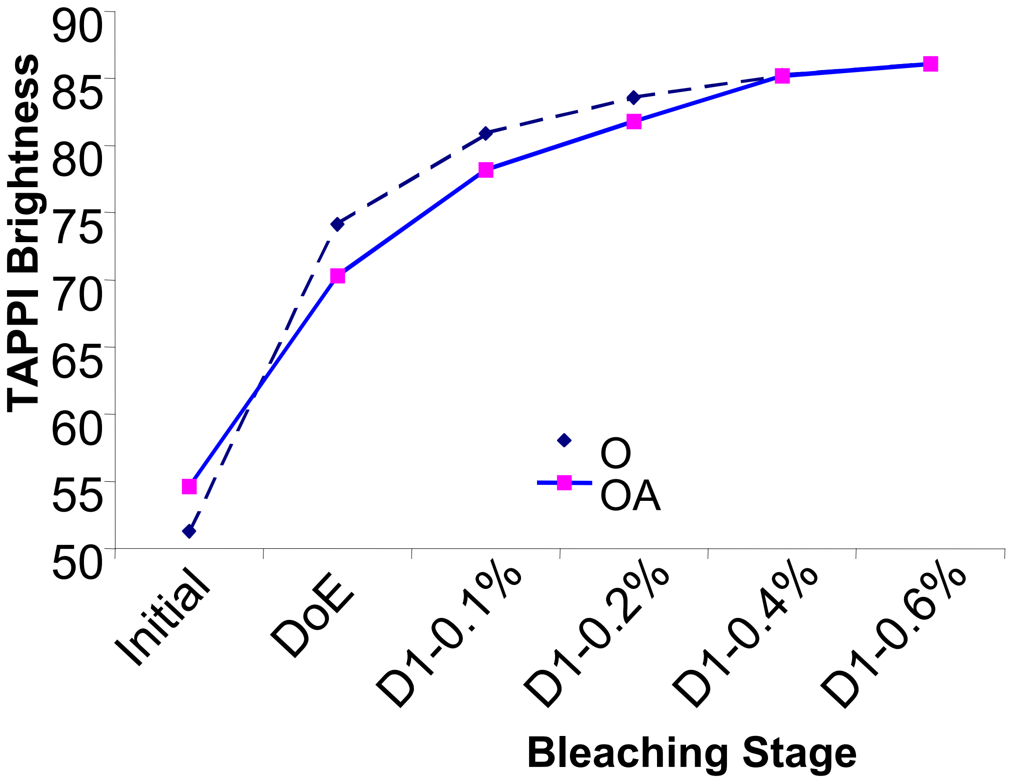


Figure 4.2: Changes in TAPPI brightness for oxygen delignified HW kraft pulp bleached DED and ADED.

Table 4.2: Changes in viscosity for HW kraft pulps bleached DEDED, ADEDED, ODED, and AODED.

Pulp	Viscosity/cP
Brownstock	24.0
Brownstock(A)	18.7
DEDED	
D2: 0.1% charge	23.1
D2: 0.2%	21.6
D2: 0.4%	21.8
D2: 0.6%	19.7
ADEDED	
D2: 0.1%	19.3
D2: 0.2%	19.0
D2: 0.4%	18.9
D2: 0.6%	17.3
O	21.8
OA	19.9
ODED	
D1: 0.1%	21.4
D1: 0.2%	20.4
D1: 0.4%	20.4
D1: 0.6%	19.7
OADED	
D1: 0.1%	16.1
D1: 0.2%	16.2
D1: 0.4%	15.8
D1: 0.6%	15.2

The results of the ECF bleaching studies indicate that the acid hydrolyzed kraft pulps yield final brightness properties comparable to the unhydrolyzed kraft pulps. Of greater significance is the approximately 50% savings in chemical bleaching agent for the A-stage treated pulps.

As has been previously observed, there is a slight decrease in viscosity after the hot acid treatment of kraft pulps and this was observed again for the pre and post-O2 delignified kraft pulps, as summarized in Table 4.2. The differences in viscosity values do narrow as the pulps are bleached to full brightness but nonetheless, the fully bleached A-treated pulps exhibit slightly reduced viscosity values.

5.0 Influence of Pulping Technologies on Hexenuronic Acids in Kraft Pulps.

The formation of HexAs have been shown to occur during pulping by hydroxide catalyzed elimination of methanol from 4-O-methyl-D-glucurnoxylans. (see Figure 1.1) Given the mechanism of formation, it was anticipated that kraft-pulping technology could influence the amount of HexAs formed during pulping. Our initial investigations in this field were targeted toward examining the influence of AQ and polysulfide (PS) on formation of HexAs during pulping. The interest in AQ was based on the well-appreciated yield benefits that occur when AQ is used during pulping. These yield benefits have been shown to be due to an increased retention of hemicelluloses in the pulp. PS kraft pulps were of interest since recent publications by Berthold, Lindgren, and Lindström[6] have suggested that PS can act as a reducing agent for unsaturated side-chains present in lignin (see Fig. 5.1) and by extrapolation we had envisaged a comparable reduction process that could potentially occur with the double bond in HexAs.

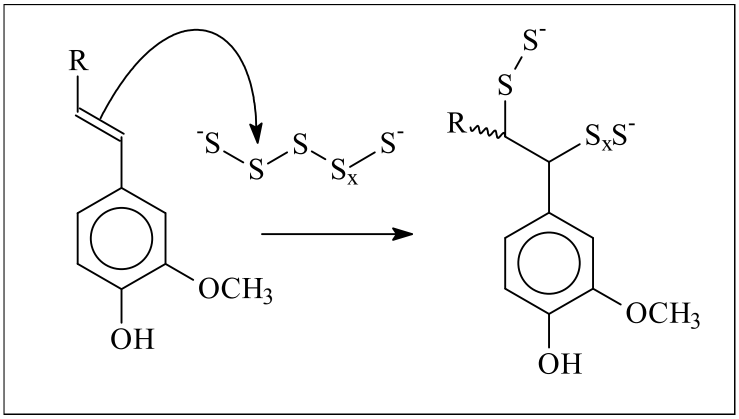


Figure 5.1: Proposed reductive chemistry of polysulfide with lignin.

To examine the effects of AQ on the formation of HexAs in kraft pulps, we prepared a series of HW kraft pulps with and without AQ and examined their response to a hot acid stage. Table 5.1 summarizes some of the important physical properties of the pulps. Each pulp in Table 5.1 was treated at low consistency with a pH 3.5 formic acid-sodium formate buffer at 110°C for 1h. The acid hydrolyzed pulps were analyzed for kappa number and the effluents characterized by UV/Vis for the presence of 2-furoic acid (see Figure 1.2). The results of this analysis are summarized in Table 5.2 and Figures 5.1 – 5.3.

Table 5.1: Hardwood kraft pulps employed for hexenuronic acid studies.

Pulp	**Kappa #**	**% AQ**	**%EA**
Industrial pre-O2	15.7	--	--
Industrial post-O2	10.6	--	--
Lab* kraft	47.0	--	13
lab-AQ kraft	43.2	0.050	13
lab-AQ kraft	38.4	0.100	13
lab-AQ kraft	36.0	0.025	14
lab-AQ kraft	33.5	0.075	14
Lab kraft	32.1	0	15
lab-AQ kraft	27.3	0.050	15
Lab kraft	24.3	0	17
lab-AQ kraft	24.3	0.025	16
lab-AQ kraft	22.4	0.050	17
lab-AQ kraft	20.2	0.100	17

*denotes a pulp prepared in a laboratory.

Analysis of the results noted for the low kappa pulps (see Table 5.2) and for the high kappa pulps (see Figure 5.1 – 5.3) clearly indicates a difference in the contribution of hexenuronic acids to the pulp kappa number. Presumably, the different cooking conditions employed to acquire these pulps influence the content of hexenuronic acids. The results of the acid hydrolysis experiments with the high kappa HW kraft pulps (see Figures 5.1 – 5.3) suggest that the generation of hexenuronic acids in a pulp is not simply a linear relationship with extent of delignification. Furthermore, this data suggests that a substantial increase in hexenuronic acids may be occurring as the kappa number of the hardwood pulps is reduced below a value of twenty. It is also interesting to note that the AQ pulps appear to have a higher level of hexenuronic acids.

Table 5.2: Changes in kappa number and concentration of 2-furoic acid in the effluents of industrial hardwood kraft pulps treated with pressurized acid: pH 3.5, 110^{o}C, 1 h.

Starting Pulp	Kappa # of pulp before & after acid treatment	Concentration of 2-furoic (mmol/kg pulp)
Commercial pre-O_2	15.7 - 7.9	7.30
Commercial post-O_2	10.6 - 4.2	5.11

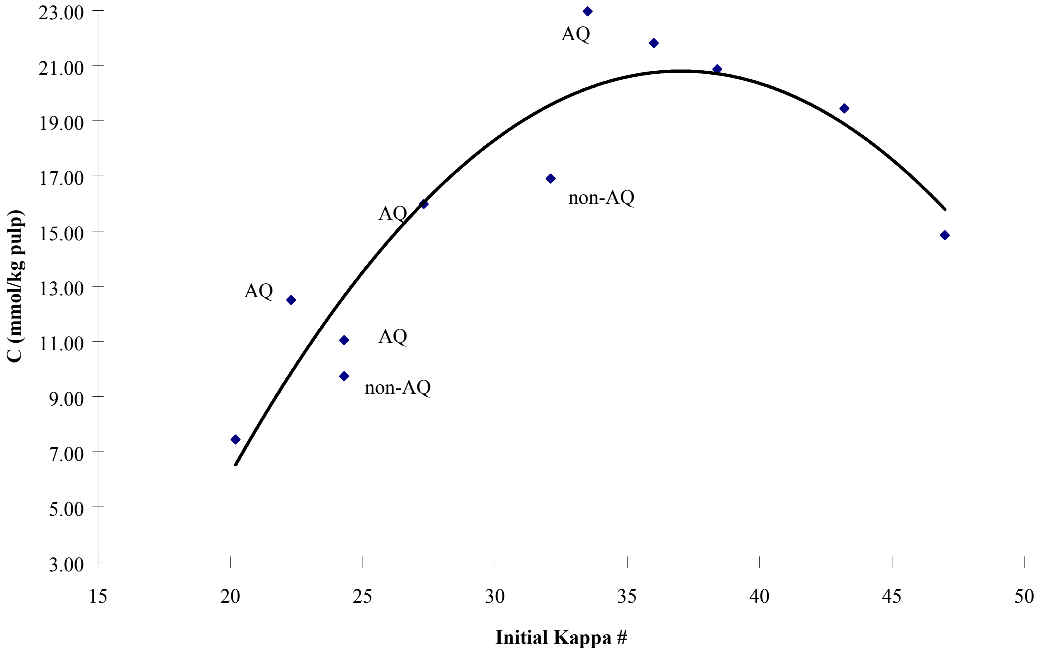


Figure 5.1: Concentration of 2-furoic acid in effluents from treating lab (see Table 1) HW kraft pulps with pressurized formic acid: pH 3.5,110°C, 1 h.

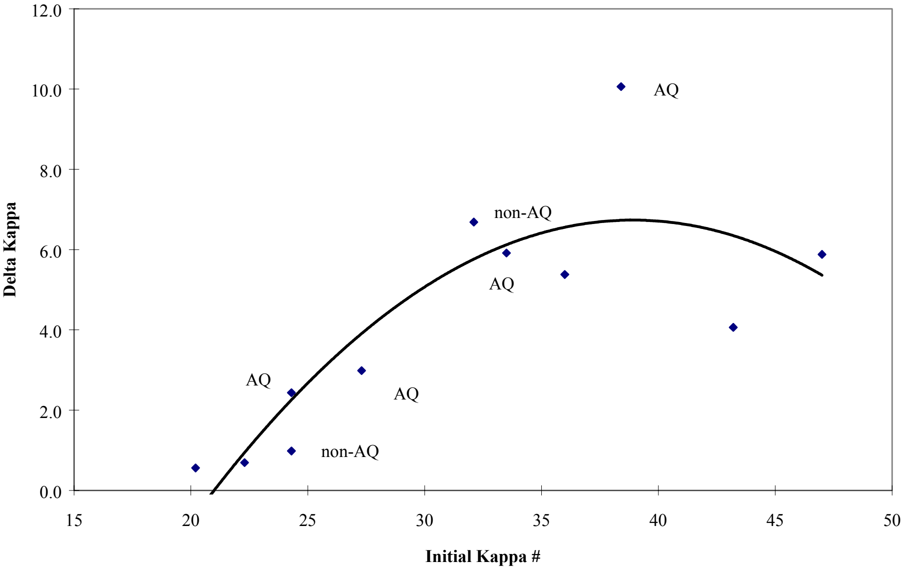


Figure 5.2: Change in kappa number for hardwood lab pulps (see Table 5.1) treated under pressurized acidic conditions: pH 3.5,110°C, 1 h.

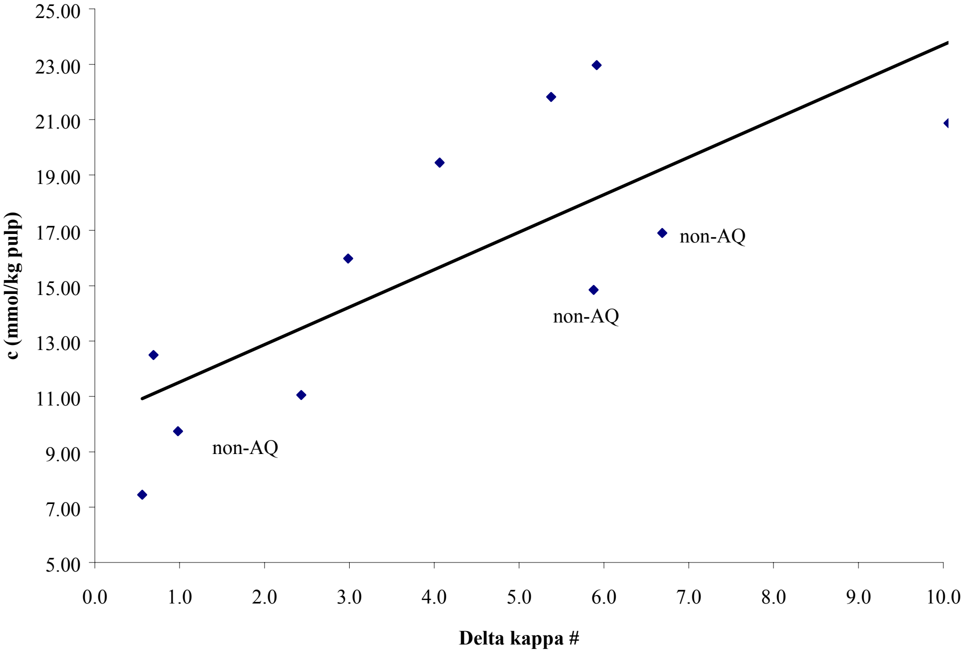


Figure 5.3: Correlation between generation of 2-furoic acid and change in kappa number upon treatment of high-kappa hardwood pulps under pressurized acidic conditions: pH 3.5,110°C, 1 h.

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To further investigate the effects of AQ on hexenuronic acid formation during kraft pulping, a series of conventional and AQ hardwood kraft pulps were acquired and treated with a hot acid stage. The kappa number of the pulps was determined before treatment and after 2 and 5 h of refluxing in a pH 3 buffered solution. The results of these investigations are summarized in Figures 5.4 and 5.5. An examination of these data suggests that at any given kappa number, the pulp prepared with AQ responded more favorably to a hot acid treatment (i.e., the AQ pulps has a greater drop in kappa number upon treatment with acid). These results suggest that a conventional pulp has more lignin and less HexA than an AQ kraft pulp at the same kappa number.

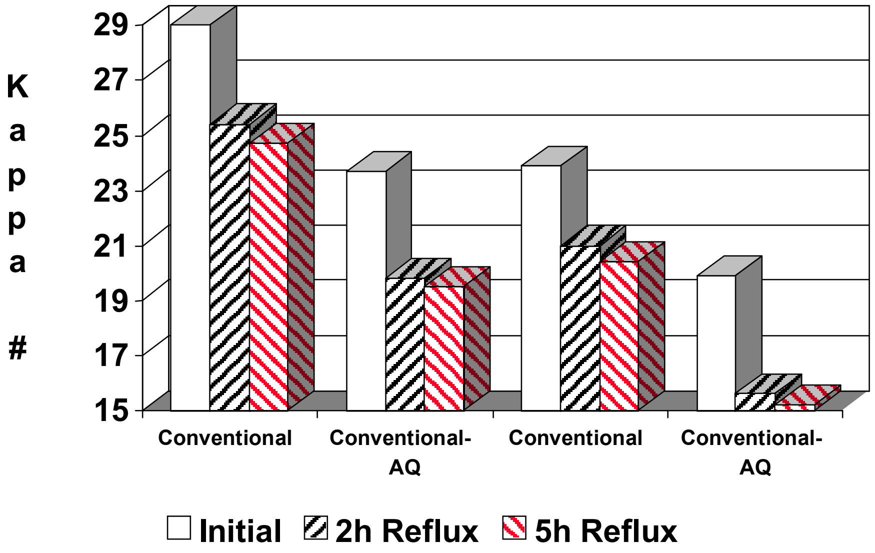


Figure 5.4. Changes in kappa number for conventional, and AQ HW kraft pulps treated to a 2 and 5 hr hot acid stage buffered at pH 3.

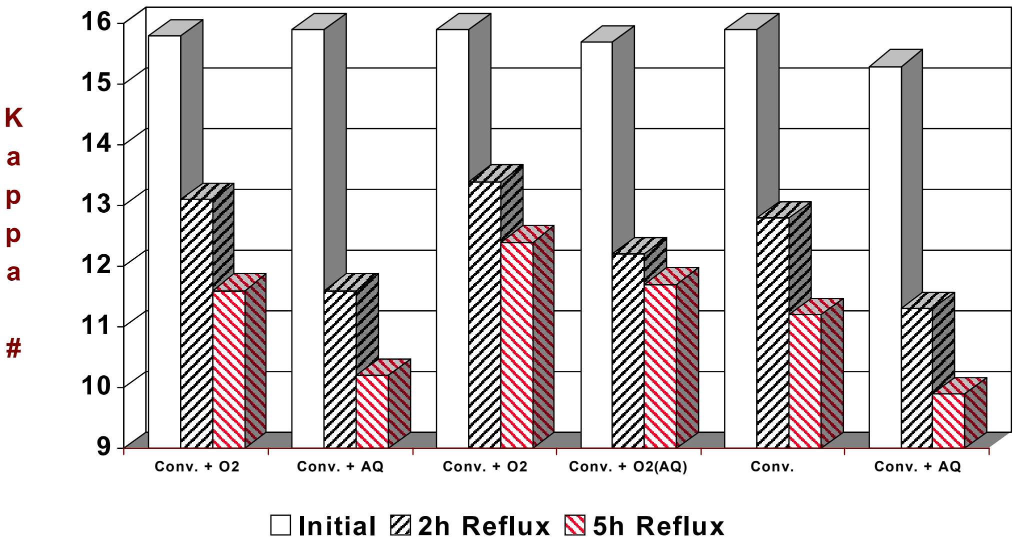


Figure 5.5. Changes in kappa number for conventional, AQ, conventional-O_2 delignified HW kraft pulps treated with a 2 and 5 h hot acid stage buffered at pH 3.

To explore the role of polysulfide/AQ in hexenuronic acid formation during kraft pulping, a series of conventional and polysulfide/AQ hardwood kraft pulps was acquired, hot acid treated, and analyzed for kappa number. Tables 5.3 and 5.4 highlight the results of these studies.

Table 5.3. Physical properties of conventional and polysulfide/AQ hardwood kraft lab prepared pulps.

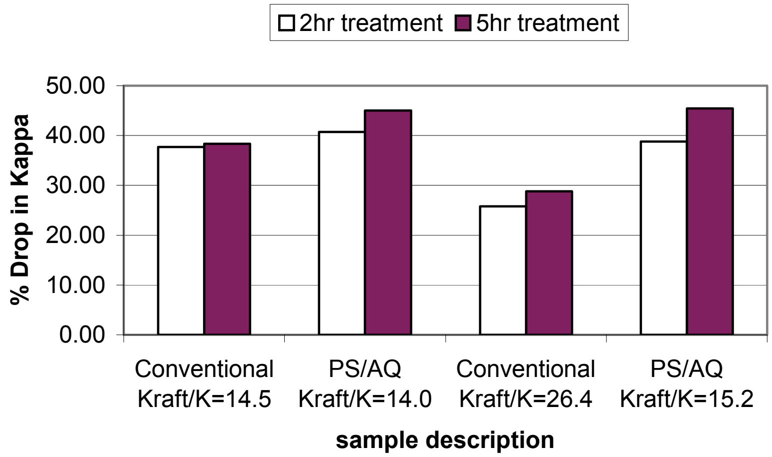
Pulp	**Kappa number**	**Carbohydrate Composition**			
		Glucan	**Xylan**	**Arabinan**	**Mannan**
Conventional Kraft	14.6	67.5	18.2	0.45	1.42
Conventional Kraft	26.4	63.4	18.2	0.09	1.28
Polysulfide/AQ	14.0	67.1	19.2	0.45	1.03
Polysulfide/AQ	15.2	63.1	18.0	0.00	1.39

Table 5.4. Changes in kappa number and viscosity for conventional and polysulfide/AQ hardwood kraft pulps after 2 and 5 hr of hot acid treatment.

Pulp	**Initial Kappa number**	**Initial Viscosity/cP**	**Kappa number after 2 h hot acid-stage**	**Kappa number after 5 h hot acid-stage**	**Viscosity/cP after 5 h hot acid-stage**
Conventional Kraft	14.6	36.5	9.1	9.0	37.0
PS/AQ –low polysulfide	14.0	29.9	8.3	7.7	27.0
Conventional Kraft	26.4	51.1	19.6	18.8	37.1
PS/AQ –high polysulfide	15.2	33.6	9.3	8.3	26.7

The data in Table 5.4 suggests that the polysulfide/AQ pulps have a slight enrichment in hexenuronic acids that could be attributed to the AQ. Figure 5.6 summarizes the % changes in kappa number after a 2 and 5 hr hot acid stage. These results suggest that the polysulfide does not decrease the amounts of HexA present in a pulp.

Figure 5.6. Relative decreases in kappa number for conventional and PS/AQ hardwood kraft pulps (see Table 5.4) treated to a hot acid stage.



This conclusion is also supported by the UV-analysis of the effluents of the hot acid stage. Figure 5.7 summarizes our UV/Vis-studies of the hot acid stage effluents for the conventional and PS/AQ kraft pulps described in Table 5.4.

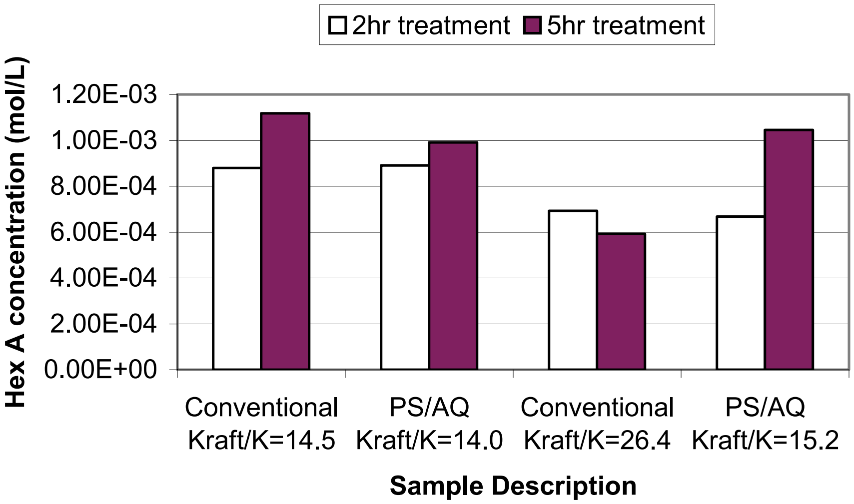


Figure 5.7. Amounts of HexA released during hot acid treatment of conventional and PS/AQ hardwood kraft pulps (see Table 5.4).

6.0 Pulp NPEs and Interaction with Hot Acid Stage.

The treatment of a kraft pulp with a hot acid stage will not only hydrolyze HexA groups but also function as a very effective acid-catalyzed metal purge. It is now well established that an acidic stage can remove metals from a kraft pulp and based on first principels, a hot acid stage should strip the pulp of nonprocess elements (NPE). To explore this phenomenon, a series of laboratory HW kraft pulps were analyzed for NPE content before and after a hot acid stage. The results of this investigation are presented in Table 6.1.

Table 6.1. Changes in kappa number and NPE profile for a series of hardwood kraft pulps refluxed in pH 3 buffer for 5 hr.

Pulp	Kappa #	Na	Ca	Ba	K	Mg	Mn	Fe
Birch								
Initial	28.1	1175	1795	7.46	57.5	279	6.9	49.6
5h	24.3	71.1	527	3.06	<6.02	69.5	2.0	48.4
Birch								
Initial	16.2	1735	1100	5.11	24.0	103.0	4.8	12.7
5h	10.0	83.1	224	1.18	6.79	19.1	0.95	9.4
Birch								
Initial	14.7	56.7	2435	11.3	20.4	212.0	5.61	23.0
5h	9.6	25.8	280	4.31	14.1	19.6	0.62	11.6
Birch								
Initial	13.9	49.8	1919	4.72	10.2	185.0	3.62	34.2
5h	9.1	15.5	266	1.51	<7.6	21.6	0.48	12.2
Maple								
Initial	23.8	1465	1345	8.01	25.8	173	25.5	226
5h	15.0	52	380	3.44	<9.3	33.8	7.5	218
Maple								
Initial	20.5	1360	920	9.15	22.1	150	31.4	248
5h	13.9	33.8	374	2.53	<10	38.2	7.8	232
Maple								
Initial	19.9	1320	721	7.0	15.0	127	32.1	12.5
5h	15.1	37.6	185	2.2	<5.9	21.3	4.6	8.9
Maple								
Initial	19.8	1480	1325	13.2	29.3	195	41.0	6.9
5h	14.7	73.1	310	4.47	7.34	34.3	7.13	7.7
Maple								
Initial	18.7	1475	1285	9.14	61.2	205	34.9	44.5
5h	13.0	104	308	3.55	<9.8	40.5	8.5	52.0
Maple								
Initial	17.1	1260	1190	8.14	43.6	201	33.3	177
5h	11.6	50.4	200	2.42	9.2	27.7	6.1	78.7
Maple								
Initial	16.2	68.7	1875	8.72	20.1	203	15.3	25.3
5h	8.5	23.4	337	3.92	20.2	22	1.4	11.6
Maple								
Initial	14.5	347	1945	8.64	19.7	245	25.1	12.1
5h	9.5	29.3	176	2.54	<6.8	26.6	2.3	6.9
Maple								
Initial	14.1	775	775	12.2	26.1	128	24.3	12.7
5h	8.5	42.1	110	3.46	8.2	16.4	2.9	7.5

continued

Pulp	Kappa #	Na	Ca	Ba	K	Mg	Mn	Fe
Maple								
Initial	13.5	503	1360	8.33	37.5	246	25.7	16.6
5h	7.6	26.8	205	1.63	<7.9	24.1	2.07	16.0
Maple								
Initial	12.1	1760	1013	13.7	23.1	171	36.8	16.8
5h	7.5	53.6	147	6.24	<7.8	21	4.5	13.1
Maple								
Initial	12.0	43.2	1725	6.81	11.6	195	1.83	55.0
5h	8.3	10.8	203	1.94	5.14	15	18.3	26.5
Maple								
Initial	11.7	67.8	1780	8.54	19.2	200	9.68	10.5
5h	7.0	16.9	250	5.17	11	17.8	0.91	5.6

This data clearly demonstrates that a typical A-stage usually removes greater than 70% of the magnesium, sodium, manganesium, calcium and barium from a pulp fiber. In addition, approximately 50% of the iron in a pulp fiber will be removed during an A-stage.

The retention of NPEs in a fiber occurs primarily due to functional groups in the pulp that can chelate NPEs. Many functional groups in pulp can chelate NPEs including guaiacyl and syringyl phenolics, catechols, condensed phenolics, and carboxylic acid groups from lignin and polysaccharides. The removal of HexAs from a pulp fiber should not only lead to the removal of NPEs from a fiber but also reduce the metal binding capacity of kraft pulp fibers. To examine this issue, we treated a HW kraft pulp to a Q-stage and an A-stage (A: buffered pH 3 solution, 100°C for 0.5, 1.0 and 2.0 h). All pulps (i.e., brownstock, Q-stage and A-stage pulps) were then immersed in a 1.0 N NaCl solution overnight. The resulting pulps were washed with deionized water and analyzed for metals analysis. The results of this analysis are summarized in Table 6.2 and this data clearly demonstrates that the A-stage treated pulps have a significantly reduced affinity for sodium.

Table 6.2: Sodium binding capacity for HW kraft pulp brownstock, Q-stage and A-stage treated pulp immersed in 1.0 NaCl for 16 h.

Pulp[1]	Na Binding(mg/kg od pulp)				
	Brownstock	Q-stage[2]	0.5h	1.0 h	2.0 h A-stage[3]
Pre-O_2	2500	2434	1080	970	800

[1] HW kraft pulp starting kappa #:15.8; [2] chelated with EDTA, pH 5 for 2 h; [3] refluxed in a pH 3 buffer solution for 0.5, 1.0 and 2 h, kappa # of the pulp after 0.5 h refluxing was 12.5, after 1 h of refluxing it was 12.0 and after 2 h of refluxing it was 10.5.

These results are best attributed to a loss of HexA in the pulp fiber and therefore the pulp has a reduced affinity of sodium. These results suggest that not only does a hot acid stage remove metals, but it also eliminates the binding sites in the pulp.

7.0: Effect of Alternative Acid Treatment on HexA Removal.

The role of the conjugate base on the overall acid hydrolysis procedure was examined by performing the hot acid treatment of a hardwood kraft pulp using formic acid, nitric acid, phosphoric acid, and p-toluenesulfonic acid. For each acid stage, a 3% consistency hardwood kraft pulp was pH adjusted to 3.0 and heated to either 80°, 90°, or 95°C for periods of 1, 2, and 5 h. In addition, a 3% csc HW kraft pulp was acidified to pH 2.2 using a D_0 effluent. This latter pulp suspension was reacted for 5 h at temperatures of 80°, 90°, or 95°C. In each case, the acid treated pulps were then washed with water and analyzed for kappa and viscosity. The results of these studies are summarized in Table 7.1.

Table 7.1: Results of treating a commercial HW kraft pulp with an acidic aqueous solution.

Acid Treatment (initial pH) – Bleaching Temperature(C)	Initial Kappa #:13.5 Initial Viscosity:28.7 cP Pulp Properties After Acid Treatment 1 h		2 h		5 h	
	Kappa	Visc.	Kappa	Visc.	Kappa	Visc.
Formic Acid/Sodium Formate (3) 80°	12.8	21.1	10.8	21.9	10.9	22.5
90°	11.2	22.2	10.4	22.2	9.8	22.6
95°	11.1	24.4	10.0	26.0	8.2	22.5
Nitric Acid (3) 80°	12.0	29.3	11.5	29.2	10.5	21.4
90°	10.9	28.7	10.2	22.5	7.9	22.5
95°	10.5	22.8	9.4	23.1	7.7	22.6
Phosphoric Acid (3) 80°	12.6	22.1	12.5	23.5	10.6	23.1
90°	11.8	24.2	11.1	24.8	9.1	21.9
95°	11.2	24.9	10.3	26.2	9.0	20.0
p-toluenesulfonic acid (3) 80°	12.5	27.0	11.6	20.7	10.3	23.2
90°	12.0	24.9	10.4	26.7	8.9	24.5
95°	10.6	22.5	9.6	22.8	8.4	20.6
Do (2) 80°	-	-	-	-	10.9	22.5
90°	-	-	-	-	9.5	21.0
95°	-	-	-	-	9.3	19.8

The results of this investigation demonstrated that the removal of hexenuronic acids from a HW kraft was virtually independent of the acid source. The three key parameters controlling the efficiency of hexenuronic acid removal are the pH of the solution, reaction time and reaction temperature. Based on these results, it is obvious that the use of D_0 effluents to remove hexenuronic acids is a viable, low-cost approach to controlling HexAs in hardwood kraft pulps.

8.0: Effects of HexA Removal on Pulp Yield.

The effect of the hot acid treatment on pulp yields remains an issue of extreme concern. Early research activities in this project had noted that experimental yields for treating HW kraft pulps with formic acid/sodium formate buffer (pH 3) at 100°C were usually in the range 98 – 98.6% (i.e., Gravimetric yields (:% mass pulp recovered/mass of starting pulp)). We have continued to determine pulp yields for acid hydrolyzed HW kraft pulps employing either dilute sulfuric acid or D_0 effluents. The results of these studies are summarized in Table 8.1.

Table 8.1. Yield and changes in physical properties of HW kraft pulps treated with a hot acid stage.

Pulp	Kappa #	Viscosity/cP	Yield (% mass recovered)
1. Brownstock -initial	11.4	24.9	
A[1]	5.6	22.8	98.2 (performed on 30 gr. Scale)
A[1]	6.2	--	97.8 (performed on 100gr scale)
2. O – initial	8.5	21.8	
OA[1]	2.8	19.9	98.1 (performed on 30 gr. Scale)
OA[1]	3.7	--	98.1 (performed on 100gr scale)
3. HW Brown. – initial	14.1	29.6	
A[1]	12.7	--	98.4 (performed on 100gr scale)
A[2]	10.2	--	98.0 (performed on 100gr scale)

[1] Pulp slurry was adjusted to pH 3 with 4N H_2SO_4, 2% csc and refluxed for 3 h. [2] Pulp was refluxed in D_0 effluent pH 2.8, 3% csc for 3 h.

Interestingly, the use of either sulfuric acid, formic acid/sodium formate, or D_0 effluent provided comparable yields to the hot acid treatments of HW kraft pulps.

9.0 Evaluate the Effect of Consistency on HexA Removal for a HW kraft pulp.

The effects of consistency on the acid catalyzed removal of HexAs was studied with three commercial HW kraft pulps. In each case, the pulps were exhaustively washed, diluted with water, and adjusted to pH 3 with 4 N H_2SO_4. The three pulps were acid hydrolyzed at 2 and 10% consistency. The acid treated pulps were analyzed for kappa number, Klason lignin, and viscosity. In addition, selected acid hydrolysis effluents were characterized for color and COD. The results of these investigations are summarized in Table 9.1

Table 9.1: Physical properties of HW kraft pulps and effluents treated with an aqueous pH 3 (dilute H_2SO_4) solution at 2 and 10% consistency at 100°C.

Pulp	Kappa #	Viscosity/cP	Klason Lignin	Color[1]	COD[2]
Pulp 1 Brownstock	14.1	29.6	2.10	-	-
H^+ 1 h medium csc	11.5	27.9	1.76	-	620
H^+ 2 h medium csc	10.5	26.8	1.75	-	950
H^+ 5 h medium csc	8.1	26.1	1.47	-	1200
H^+ 5 h low csc	9.1	29.4	1.28	170	270
Pulp 2 Brownstock	11.6	24.9	1.63	-	-
H^+ 1 h medium csc	8.0	22.5	0.76	-	1000
H^+ 2 h medium csc	6.7	--	--	-	1300
H^+ 5 h medium csc	5.5	19.3	1.18		1600
H^+ 5 h low csc	5.2	19.2	0.98	120	430
Pulp 3 Brownstock	14.2	36.6	1.63	-	-
H^+ 1 h medium csc	10.5	35.6	1.62	-	1200
H^+ 2 h medium csc	9.8	33.7	1.41	-	1400
H^+ 5 h medium csc	8.0	32.9	1.42	-	1500
H^+ 5 h low csc	7.5	32.5	1.21	220	380

[1] mg/l; [2] PCU.

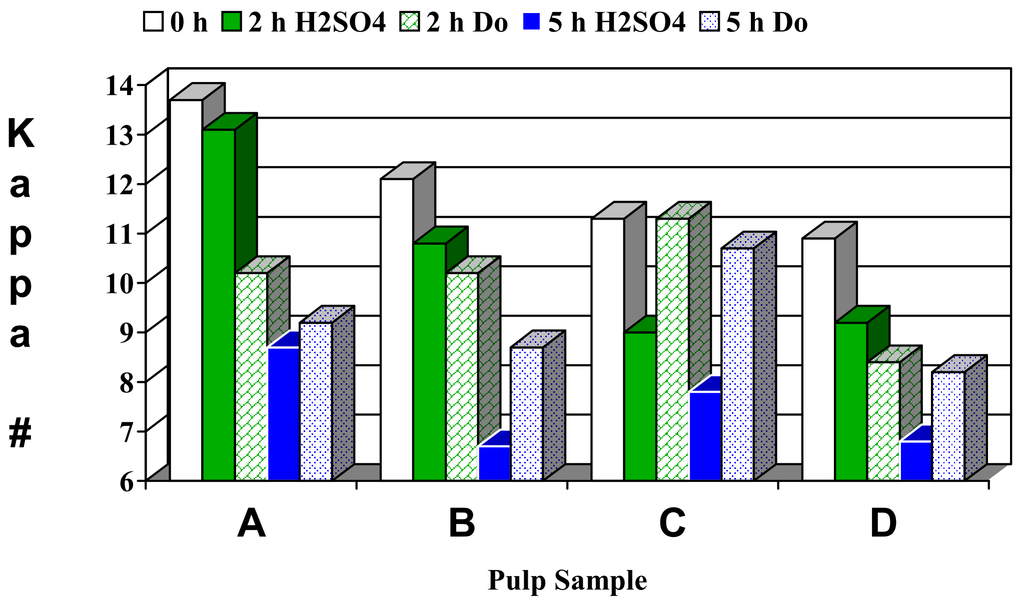
Several important conclusions can be drawn from the data presented in Table 9.1. The most significant conclusion is that for extended hot acid treatments (i.e. 5 h), the removal of HexA can be accomplished equally effective with low and medium consistency pulp slurries. It is also important to note that the hot acid treatment resulted in reducing the amount of Klason lignin in the pulps and the reduction was proportional to the reaction time. Clearly, this effect can not be attributed to the removal of HexA and this latter result suggests that a portion of the observed kappa reduction during a hot acid treatment is due to lignin removal in addition to the removal of HexAs.

The relative effectiveness of using D_0 effluents as an acid source for a hot acid treatment of hardwood kraft pulps was further examined employing a series of commercial HW kraft pulp and D_0 samples. Commercial pulps and D_0 mill effluents were provided to the PI from interested PAC members and, in each case, these pulps were exhaustively washed until the effluents were pH neutral and colorless. Table 9.2 provides a brief description of the pulps and effluents provided to the PI.

Table 9.2: Description of commercial HW kraft pulps and bleach effluents employed for HexA studies.

Mill	Pulp Sample: kappa number	First Stage Bleach Effluent
A	Brownstock: 13.7	C/D pH: 2.5
B	Brownstock: 12.1	D_0 pH: 3.4
C	Pre O_2: 11.3	pH: 2.8
D	Brownstock: 10.9	D_0 pH: 2.3
E	Brownstock: 9.8	D_0 pH: 2.3
F	Post O_2: 8.9	D_0 pH: 2.6
G	Post O_2: 7.8	Acid pressate pH: 2.6
H	Post D_0	Hydrolyzed with pH 3 - H_2SO_4 solution

The washed pulps were then treated with mill bleach effluents at 10% consistency for 2 and 5 hours at 99°C. As a control, all pulp samples were also treated with a dilute sulfuric acid solution (pH: 2.8) at 10% consistency for 2 and 5 hours at 99°C. The resulting pulps were analyzed for changes in kappa number, TAPPI brightness, and viscosity; these results are summarized in Figures 9.1 and 9.2 and Table 9.3.



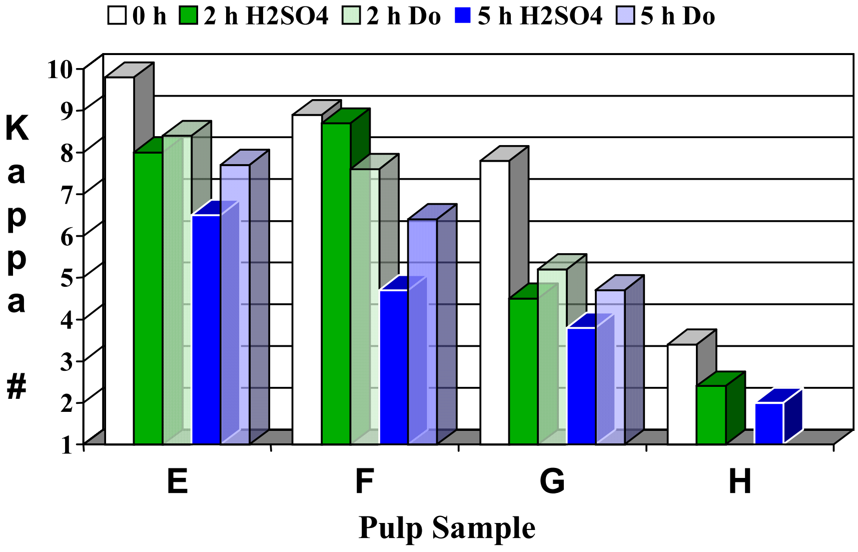


Figure 9.1. Changes in kappa of HW kraft pulps heated to 99°C in dilute sulfuric acid (pH 2.8) and D_0 effluents for 2 and 5 h.

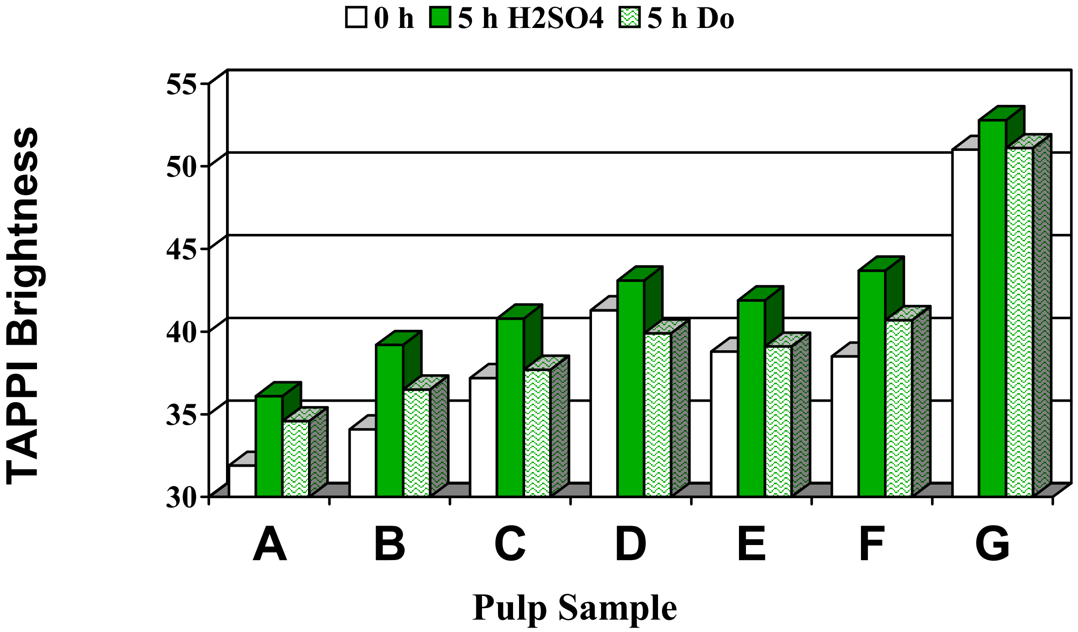


Figure 9.2. Changes in TAPPI brightness of HW kraft pulps heated to 99°C in dilute sulfuric acid (pH 2.8) and D_0 effluents for 2 and 5 h.

Table 9.3: Changes in pulp viscosity when HW kraft pulps were heat-treated (99°C) with dilute sulfuric acid (pH: 2.8) and D_0 effluents for 2 and 5 h.

Pulp Sample	**Pulp Viscosity Values/cP**				
	Initial	**2 h H_2SO_4**	**2h D_0**	**5 h H_2SO_4**	**5 h D_0**
A	31.2	29.7	26.5	25.6	24.5
B	36.9	30.0	31.5	16.0	28.5
C	29.1	28.3	31.1	26.4	29.8
D	35.9	28.3	21.1	--	14.2
E	24.3	19.8	19.4	13.4	16.7
F	16.2	16.9	16.6	9.2	15.8
G	24.5	14.6	22.0	12.0	18.7
H	32.0	15.8	--	--	--

The results of the kappa number analysis indicate that all pulps undergo a reduction in kappa number when heated in either dilute sulfuric acid or first stage bleach effluent. In most cases, the use of a hot sulfuric acid treatment maximized the decrease in kappa number although the difference with the D_0 hydrolyzed pulps was frequently less than 1.5 kappa number units. The sulfuric acid treatments, therefore, provide a measure of the maximum kappa number reduction for these hardwood pulps whereas the D_0 effluent treatments represent a more practical mill technology approach.

(Note: The use of 5 hours of hot sulfuric acid treatment is undoubtedly excessive and caused significant degradation of pulp viscosities, see Table 9.3. This reaction time was selected as a means for rapidly determining the HexA content of the mill pulps studied.)

Interestingly, almost all pulps exhibited a slight increase in brightness when treated with dilute acid at 99°C for 5 hours (see Fig. 1.6). This latter result suggests that the removal of HexA with a hot acid treatment will not detrimentally impact the optical properties of the pulp.

10 HexA Summary

The studies undertaken in DFRC project F0-15 have clearly demonstrated that, for U.S. HW kraft pulping and bleaching operations, HexAs assume an important role. These modified carbohydrates influence bleaching chemical consumption and NPE retention by pulp fibers. Their removal can be accomplished using any acid source including D_0 effluent. Pulping studies have shown that the amounts of HexA in a HW pulp can be influenced by the presence of AQ. Preliminary studies also suggest that pulping can influence the level of HexA in a pulp, but additional studies need to be undertaken to fully define this effect.

Note: The information and conclusions are advisory and the reader must decide for themselves the best approach to solving any problems they may have and how, or whether, this reported information should be considered in its approach. The author does not recommend particular products, procedures, materials, or service. These that are included only in the interest of completeness within a laboratory context and budgetary constraint. Actual products, procedures, materials, and services used may differ and are peculiar to the operations of each company. In no event shall the author have any obligation or liability for damages including, but not limited to, consequential damages arising out of or in connection with any use of or inability to use the reported information.

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