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Influence of hexenuronic acids on US bleaching operations

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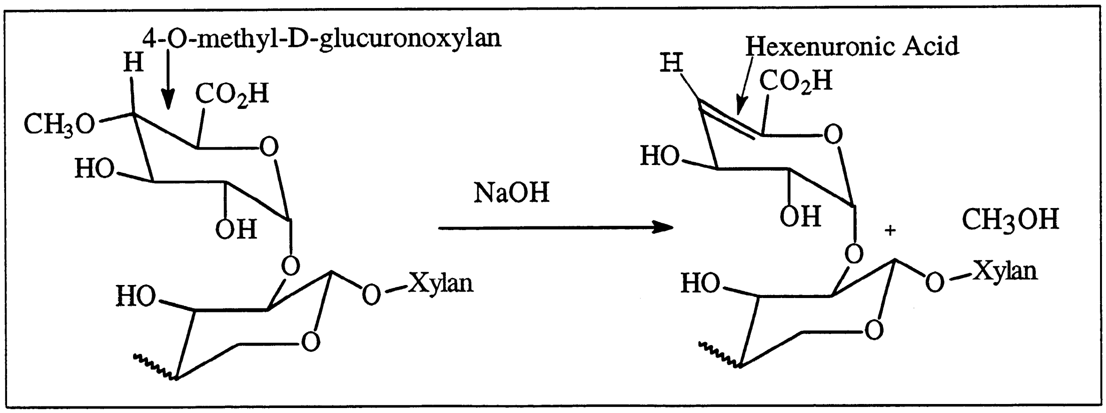
ABSTRACT: Acid hydrolysis of commercial and laboratory HW kraft pulps demonstrated that between 35-55% of the kappa number of these pulps could be attributed to hexenuronic acids. For SW kraft pulps, the contribution of hexenuronic acids to the pulp kappa number was much less. Examination of the xylan and hexenuronic acid content of the kraft pulps indicated that there was a correlation between these two components. Finally, analysis of HW kraft pulps for hexenuronic acid groups indicated that formation of this unsaturated hemicellulose could be controlled by the extent of delignification.

EXECUTIVE STATEMENT: This study examines the role of hexenuronic acids in US HW and SW kraft pulps. The presence of hexenuronic acids was found to be a dominant component of the pulp kappa number for HW kraft pulps, whereas, for SW kraft pulps, it was found to be a minor component. Acid hydrolysis studies suggest that it may be possible to reduce ECF bleaching chemical usage by 35 –50% for HW kraft pulps. The level of hexenuronic acids in a HW kraft pulp can be influenced by the extent of delignification.

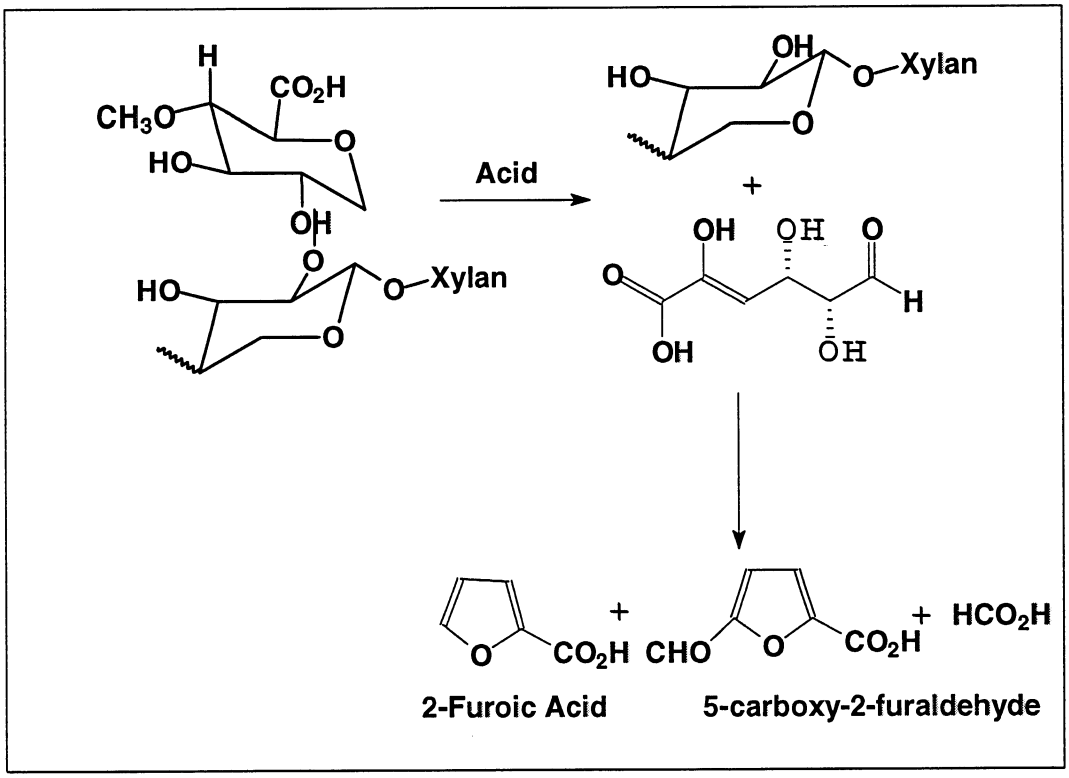
INTRODUCTION: Although fundamental bleaching research has largely focused on lignin chemistry for the past decade, recent studies have begun to readdress this issue and direct more attention toward carbohydrate chemistry. These studies have shown that hemicelluloses influence a variety of important properties throughout pulping, bleaching, and papermaking. The formation of hexenuronic acids during pulping (see Figure. 1) is currently a very active research area that has been shown to have practical mill considerations. Early studies by Clayton examined the behavior of 4-O-methyl-α-D-glucuronoxylans from poplar, white birch, and white elm with alkali at 170°C and found indirect evidence for the formation of hexenuronic acids(*1*).



1. Alkali-catalyzed formation of hexenuronic acids.

Subsequent studies by Johansson and Samuelson (*2*) and Simkovic et al. (*3*) provided additional experimental evidence supporting the formation of hexenuronic acids from 4-O-methyl-α-D-gluconoxylans. Finally, Teleman et al. (*4*) isolated and characterized hexenuronic acids from an enzymatically hydrolyzed, unbleached, kraft pulp.

Studies by Vuorinen et al. (*5*) and Buchert et al. (*6*) further explored the chemistry of hexenuronic acids in kraft pulps. They demonstrated that hexenuronic acids contribute approximately 50% to the kappa number of several northern Scandinavian kraft pulps. Furthermore, these unsaturated sugars were shown to readily consume electrophilic bleaching chemicals such as chlorine dioxide and ozone. A series of well-designed acid hydrolysis studies identified reaction conditions under which hexenuronic acids could be removed from kraft pulps (see Figure 2) without significantly impacting their physical properties.



2. Proposed (5) acid hydrolysis pathway for hexenuronic acid.

Following these reports, several investigators began to explore the impact of hexenuronic acids on pulp bleaching operations. Li and Gellerstedt (*7*) have examined the contribution of hexenuronic acids to a pulp's kappa number. Roberts (*8*) and da Silva Filho et al. (*9*) have reported that the presence of hexenuronic acids is a principal factor controlling the affinity of pulp fibers for nonprocess elements. Senior et al. (*10*) reported that the use of AQ in a kraft cook could influence the amount of hexenuronic acids present in hardwood kraft pulps. Nilvebrant and Reimann (*11*) have shown that hexenuronic acids can contribute to oxalic acid formation from a Z-stage. Lachenal and Chirat (*12*) have demonstrated that the differing rates of reaction for chlorine dioxide with lignin and hexenuronic acid can be employed to improve HW kraft bleaching operations. Despite this significant body of work, few reported studies have examined the presence of hexenuronic acids from commercial North American kraft pulping operations. This paper examines the presence of hexenuronic acids in commercial SW and HW kraft pulps from US operations and evaluates how pulping parameters may influence their formation.

EXPERIMENTAL

Materials

All chemical reagents were commercially purchased and used as received. Commercial hardwood and softwood kraft pulps were acquired from several mills, principally in the US southeast. In addition, a series of softwood and hardwood batch and extended modified kraft cooks were preformed in the laboratory. The laboratory cooks were all preformed from sweetgum or loblolly pine wood sources. All pulps were extensively washed prior to a hot-acid stage.

Laboratory Kraft Cooks

Conventional HW kraft cooking trials were performed at a 4:1 liquor/wood ratio using 30% white liquor sulfidity (active alkali basis). Sweetgum chips and cooking liquor were heated to 165°C for 90 minutes and kept at that temperature until the desired H-factor was reached.

RDH kraft cooking trials were performed using a fully automated control system employing white liquor with 30% sulfidity (active alkali basis) and a cooking temperature of 165°C. White liquor addition was split into warm and hot black liquor pretreatments. The wood chips were pretreated with warm and hot black liquors before cooking with white liquor. At the end of the cook, hot cooking liquor inside the digester was displaced back to the hot and the warm black liquor accumulators using washer filtrate from a brownstock washing system. Table 1 summarizes some of the important HW kraft cooking parameters and pulp properties.

A series of extended modified continuous laboratory cooks were performed using loblolly pine wood chips. The cooking conditions used for these pulps has been previously described by Froass et al. (13)

Acid Hydrolysis

The content of hexenuronic acids in kraft pulps was measured indirectly by refluxing the pulps in a formic acid/sodium formate buffer solution (pH: 3.0) for 2 and 5 hours. The acid treated pulps were all analyzed for kappa number. Selected pulps were analyzed for viscosity values after a 5 houracid hydrolysis stage. Typically, viscosity values decreased by 10 – 35% for the HW kraft samples studied and 20 – 25% for the SW kraft pulp samples.

Selected acid hydrolysis effluents were analyzed by UV/Vis for the presence of 2-furoic acid (5). In addition, selected kraft pulps were analyzed for their xylan content following standard literature methods (14).

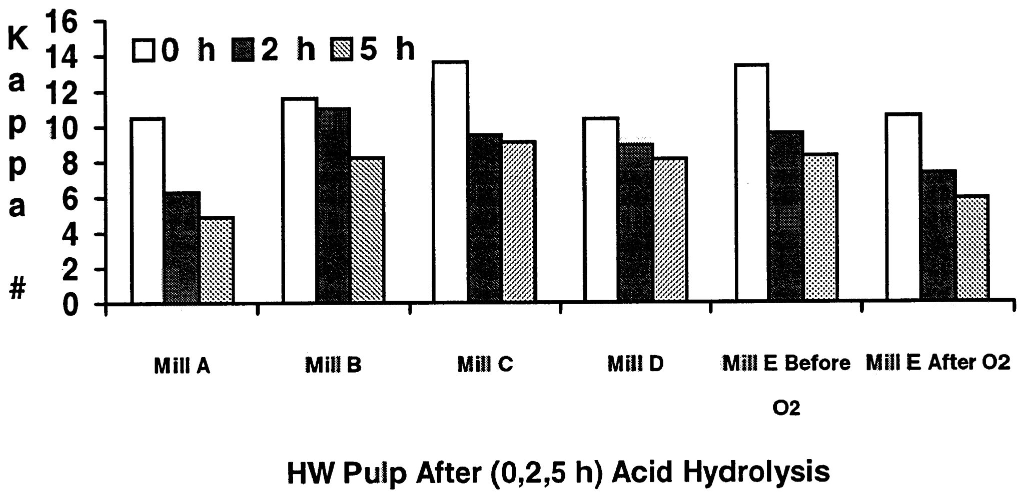
Table 1. HW kraft pulping conditions and pulp properties.

Cook Type	%EA charged on wood as Na_2O	H-factor	Kappa Number	Total Yield (%)	Brightness (ISO)
Conventional Kraft	15.7	1,800	11.4	48.8	33.1
	14.9	1,400	11.8	49.5	34.9
	13.6	1,100	14.4	50.3	32.4
	12.8	800	15.2	51.0	32.8
RDH Kraft	NA	1,000	7.8	46.5	38.8
	14.5	500	12.3	48.9	37.3
	13.9	300	13.4	50.0	37.3
	13.8	400	13.8	NA	36.8
	NA	250	16.6	50.7	34.3
	11.2	200	22.9	52.0	32.3

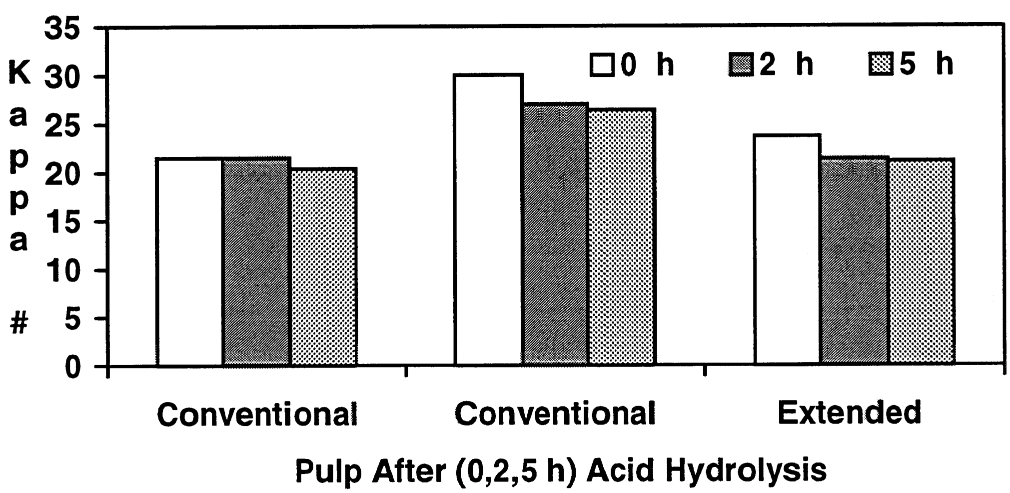
RESULTS AND DISCUSSION

Although the presence of hexenuronic acids has been well documented for Northern European kraft fiber pulps, the presence of these unsaturated sugars in North American fiber sources has not been as extensively studied. To examine this issue, we acquired pulp samples from several mills in the US. Each pulp sample was exhaustively washed and analyzed for kappa number and viscosity. The pulps were then refluxed at 3% consistency in a pH 3 buffered solution for 2 and 5 hours. Under these conditions, hexenuronic acids are released from the hemicellulose chains and are converted to 2-carboxy-2-furaldehdye and 2-furoic acid. As shown in Figure 3, all the commercial hardwood kraft pulps exhibited a significant reduction in kappa number after acid hydrolysis ranging in value from 22% to 53%. Interestingly, the ease of acid-catalyzed removal of hexenuronic acids from kraft pulp was found to vary substantially for some pulps. For most of the hardwood kraft pulps examined, a two hour acidic treatment significantly reduced the kappa number of the pulp. For the pulp from Mill B, a five-hour acid stage was required to maximize the drop in kappa number. The factors contributing to this diversity in response to a hot acid-stage remains yet to be determined.

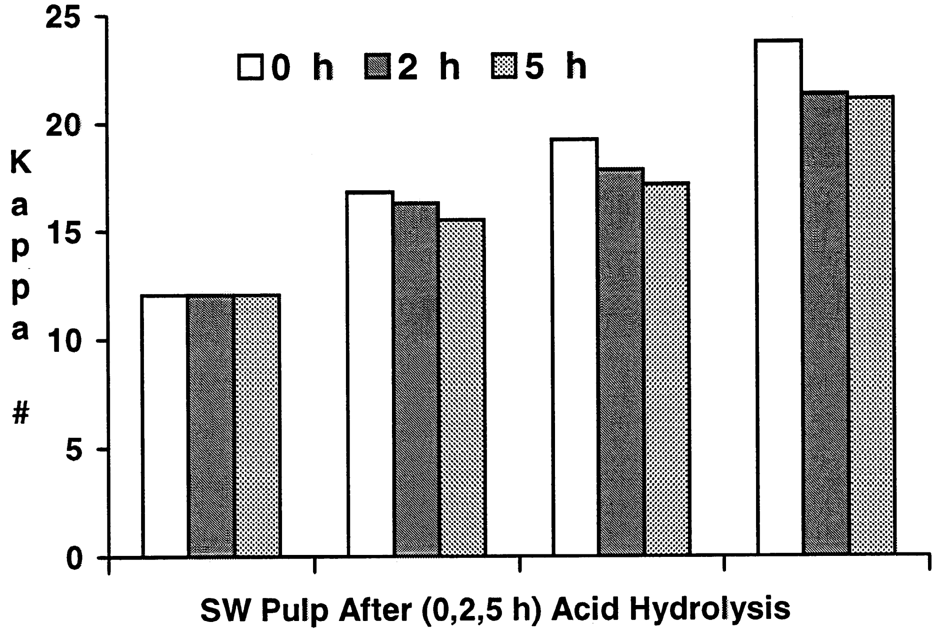
Acid hydrolysis of commercial softwood kraft pulps was not as effective at reducing the kappa number of the pulps as shown in Figure 4. Repeating the acid stage with a series of laboratory-prepared loblolly pine, continuous extended modified kraft pulps yielded comparable results as summarized in Figure 5. The results from acid hydrolysis of SW mill and lab kraft cooks suggest that only a small proportion of the pulp kappa number can be attributed to acid-sensitive hexenuronic acid groups. These results suggest that the minor presence of hexenuronic acids is further reduced as delignification of SW kraft pulps is extended from kappa number 30 to a kappa number of 20.



3. Kappa number of commercial HW kraft pulps before and after refluxing in pH 3 aqueous buffer solution for 2 and 5 h.



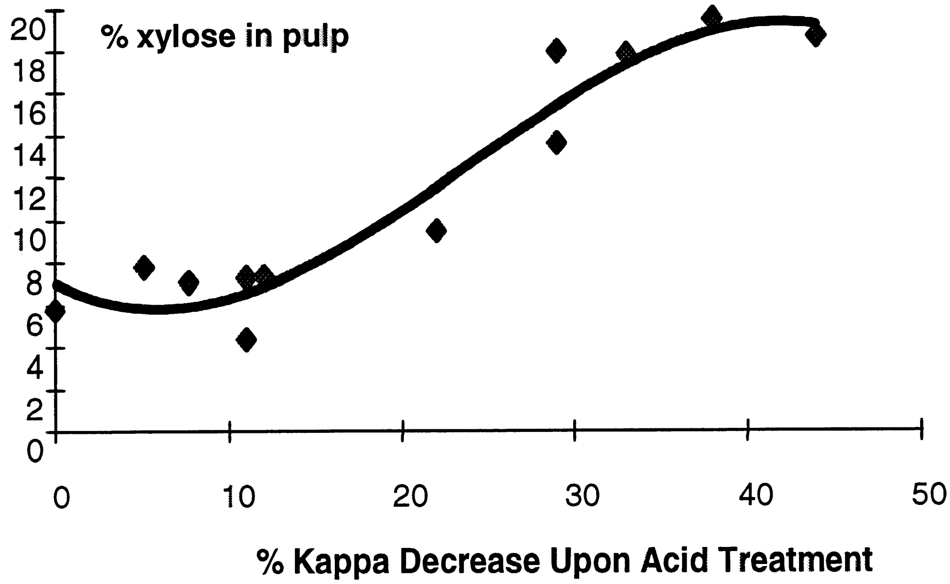
4. Kappa number of commercial softwood kraft pulps before and after refluxing in an pH 3 aqueous buffer solution for 2 and 5 h



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

The acid hydrolysis stage not only lowers the kappa of the kraft pulps but also reduces the pulp viscosity values. The HW kraft pulps typically incurred viscosity losses of 10 to 35% after refluxing in the hot acid stage for 5 h. For the SW kraft pulps, the acid hydrolysis resulted in 20 – 25% decreases in viscosity values. The acid hydrolysis conditions we employed were directed at maximizing the removal of acid-sensitive functional groups from the pulps. Based on literature considerations, the observed losses in viscosity could be minimized with additional optimization studies (15).

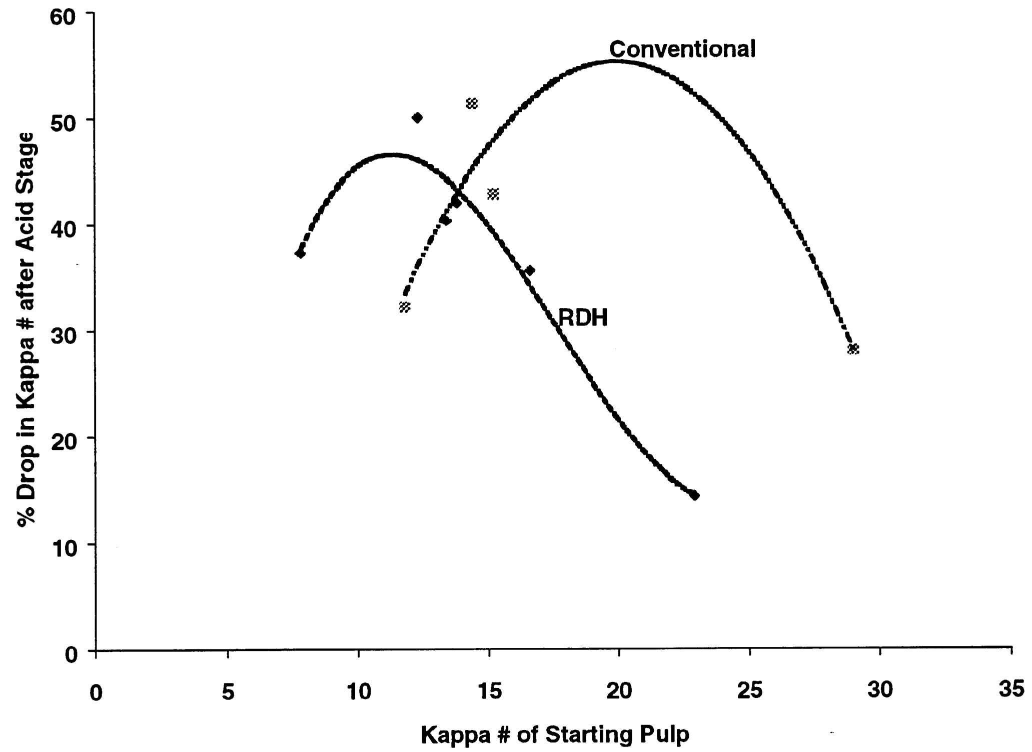
Along with the kappa number analysis of each kraft pulp, the xylan content of each starting pulp was determined. Figure 6 presents the results of relating the xylan content of the kraft brownstocks to the drop in kappa number after a 5-hour acid hydrolysis treatment. These results suggest that there is a correlation between the xylan content of the starting pulp and the contribution of hexenuronic acids to the kappa number of the pulp. This result is consistent with the proposed mechanism of hexenuronic acid formation and its contribution to pulp kappa number.



6. Relationship between xylan content of softwood and hardwood kraft pulps and the decrease of kappa number upon 5-houracid hydrolysis stage.

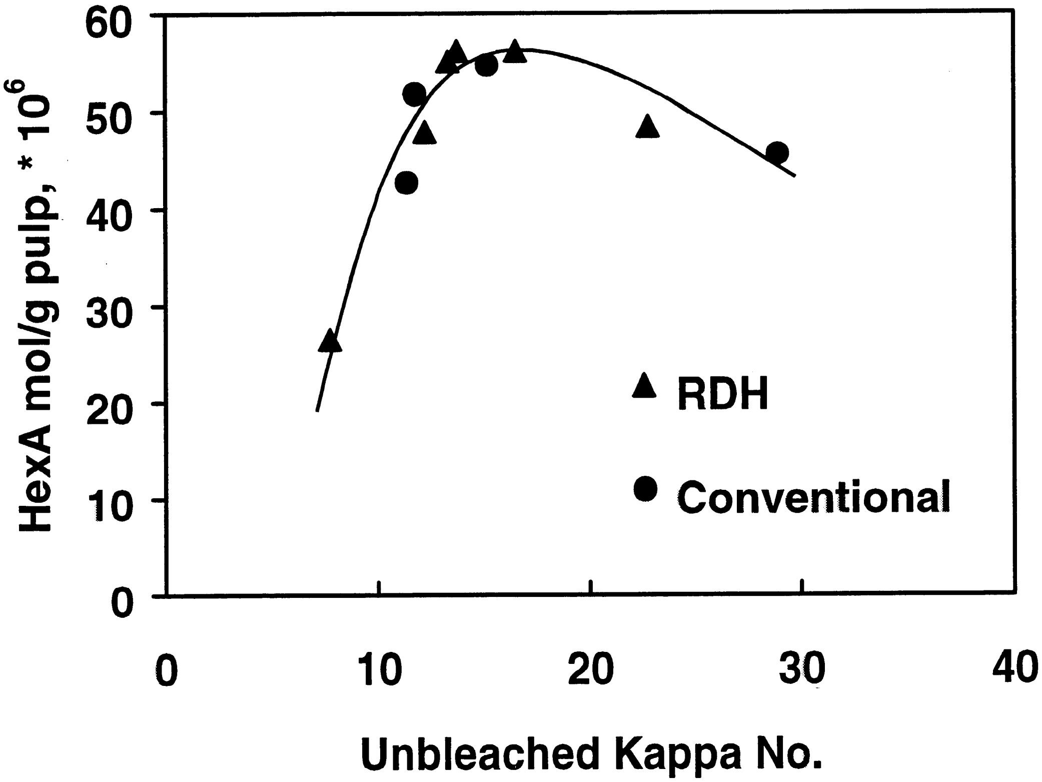
To examine how kraft-cooking technologies can influence the formation of hexenuronic acids for hardwood kraft pulps, we preformed a series of conventional and extended modified batch cooks. These cooks were all accomplished from a common sweetgum wood source to minimize experimental variability due to the fiber source. Table 1 summarizes some of the important cooking and pulp parameters for these hardwood kraft pulps.

The conventional and RDH HW kraft pulps were refluxed in a pH 3 buffered solution for 5 hours, and the kappa number of the pulps was analyzed before and after the hot acid stage. The results of the kappa number analysis are summarized in Figure 7. This data suggests that differences in batch cooking do not significantly alter the formation of hexenuronic acids in kraft pulps, although there does appear to be a small reduction in the formation of hexenuronic acid groups for the RDH pulps. Of greater significance is the observed increase in kappa number that can be attributed to hexenuronic acid groups as the final pulp kappa number is reduced. The acid hydrolysis data presented in Figure 7 suggests that the HW kraft pulps with a kappa number of approximately 14 have the largest amount of hexenuronic acids contributing to the observed kappa number. As the delignification is extended, the pulps respond less favorably to an acid hydrolysis stage. This is presumably due to a loss of acid-sensitive hexenuronic acid groups to the kraft cooking conditions.



7. Change in kappa number for HW kraft pulps upon acid hydrolysis (5 hourat 100°C, 3%csc, and buffer pH 3 solution) versus starting kappa number of conventional and RDH kraft pulps.

Along with the kappa number analysis of the acid hydrolyzed pulps, the hydrolysis effluents were analyzed by UV/Vis for the presence of 2-furoic acid. As summarized in Figure 2, 2-furoic acid can be used to measure the amounts of hexenuronic acids released from the pulp during a hot acid stage. The results of this analysis are summarized in Figure 8, and this data agrees with the drop in kappa number observed for the acid hydrolyzed pulps. It furthermore supports the hypothesis that for the sweetgum pulps studied, the content of hexenuronic acid groups in pulp increases as delignification is extended from kappa number 30 to approximately 14. Further depletion of hexenuronic acids was observed as delignification was extended. Further fundamental studies will be needed to conclusively establish the pulping chemistry mechanisms contributing to this effect.



8. Hexenuronic acid content of unbleached RDH and conventional kraft pulps from sweetgum as determined by measuring the concentration of 2-furoic acid in the effluents from acid hydrolysis stages of the HW kraft pulps.

CONCLUSIONS

The response of commercial HW kraft pulps to a hot acid stage suggests that hexenuronic acids are important components to the kappa number and significantly influence pulp bleachability. Commercial acid hydrolysis stages could undoubtedly reduce the kappa number of HW kraft pulps prior to ECF bleaching operations. In all likelihood, the observed changes in hexenuronic acids concentration in HW kraft pulps as delignification is extended is due to a series of competitive chemical reactions between cooking chemicals, lignin, and carbohydrates. The details of these reactions are yet to be determined. As these issues are resolved, pulp manufacturers will be able to further control the quality and bleachability of their hardwood furnish. Certainly, future studies into pulp bleachability of North American hardwood kraft pulps must take into account hexenuronic acids and not focus solely on lignin.

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