

SOME PROPERTIES OF KRAFT AND KRAFT-BORATE PULPS OF DIFFERENT WOOD SPECIES

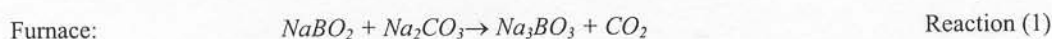
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ABSTRACT

An important question with the implementation of the borate-based autoausticizing in kraft process is the effect of sodium metaborate, which is present in the pulping liquor as the product of the autoausticizing reactions on kraft pulping and properties. This study shows the results obtained for birch, maple and spruce in conventional kraft pulping and in kraft pulping with sodium metaborate added at the level corresponding to 35 % autoausticizing – kraft-borate pulping. An increase in the yield of 1.8 % was noticed in kraft-borate pulping of spruce delignified to the same kappa number, at the H-factors higher than 1,000. Also, sodium metaborate decreased the rejects in kraft-borate pulping of the three studied species. Sodium borate did not affect the brightness and the contents of extractives and hexenuronic acid groups (HexA) of the kraft pulps of studied species. The kappa number corrected for the HexA component, estimating the lignin content in pulps more accurately showed, at the increasing H-factor, that kraft delignification was unchanged in the presence of sodium metaborate. An increase of holocellulose retention was found for the kraft-borate pulps of spruce at the kappa numbers lower than 60, indicating a potential of sodium metaborate to protect carbohydrates in kraft pulping.

INTRODUCTION

Janson [1,2] suggested the application of sodium metaborate (NaBO_2) as the most favorable autoausticizing agent. However, his reaction stoichiometry required a relatively large ratio of sodium metaborate to sodium hydroxide (NaOH). Therefore, the proposed process was thought to be economically unattractive and to have potential problems in evaporation and liquor handling concerning the boiling point rise and increase of black liquor viscosity. An interest in the use of borate-based autoausticizing to supplement or eliminate the calcining/causticizing cycle has been renewed since Tran et al. [3] showed that the autoausticizing reactions are more efficient than were proposed by Janson [1,2]. Tran et al. indicated that borate autoausticizing proceeds through the reaction of sodium metaborate and sodium carbonate (Na_2CO_3) in the furnace. In this reaction trisodium borate (Na_3BO_3) is formed and carbon dioxide (CO_2) is generated, reaction 1. In the dissolving tank, the trisodium borate undergoes hydrolysis to form sodium hydroxide and regenerate sodium metaborate, reaction 2.



In accordance to this stoichiometry, only one mole of sodium metaborate is required for the formation of two moles of sodium hydroxide. Therefore, the amount of sodium metaborate needed for autoausticizing is only one-half that indicated by the earlier established stoichiometry [1,2]. Since less borate is required, the effect of borate on the kraft pulping, and on the boiling point rise and viscosity of black liquor will be lower than observed in the earlier work on the effects of borate on kraft pulping [4-6] and on the viscosity of black liquor [7].

In addition to suggesting the new stoichiometry, Tran et al. [3] also proposed that borate autoausticizing offers the possibility of only partially converting the sodium carbonate to sodium hydroxide with the remaining conversion occurring in lime cycle. This provides an easy method for causticizing limited mills to increase their causticizing capacity without installing new equipment. Based on this new understanding, several mill trials with partial autoausticizing were conducted recently [8]. These trials confirmed the effectiveness of borate in producing caustic and showed no negative effects of borate on pulp quality and mill effluents at autoausticizing levels between 5 and 25 %.

A study of the properties of pulps and black liquors obtained in kraft pulping, with white liquor containing sodium metaborate at the level corresponding to the partial autoausticizing stoichiometry suggested by Tran et al. [3], is necessary to understand the effect of borates on kraft pulping. Therefore, the properties of slash pine black liquor

with and without sodium metaborate added at the level corresponding to 30 % autocausticizing were measured [9]. Although an increase in the boiling point rise and viscosity was found for black liquor containing sodium metaborate, it was relatively small and is not expected to cause problems in the evaporation and pumping of black liquor. An increase of solubility limit of black liquor, which was also noticed, might decrease the scaling problems in the evaporator.

This paper presents the results obtained in comparative analysis of the properties of kraft (K) and kraft-borate (KB) pulps of birch, maple and spruce obtained at the same gradually increasing H-factors. Kraft-borate pulps were obtained in the same conditions as kraft pulps except that the white liquor contained sodium metaborate at the level corresponding to 35 % autocausticizing - kraft-borate white liquor. The screened yields, rejects and properties of pulps including kappa number, brightness, and contents of extractives and hexenuronic acid groups (HexA) were measured. Also, the holocellulose content of spruce wood and pulps was determined and used to estimate the retention of carbohydrates during pulping.

EXPERIMENTAL

Black spruce (*Picea mariana*), paper birch (*Betula papyrifera*) and sugar maple (*Acer saccharum*) woodchips, supplied by The U.S. Forest Product Laboratory, Madison, Wisconsin, were used to conduct the kraft (K) and kraft-borate (KB) pulping experiments. Both conventional white liquor (kraft) and white liquor containing sodium metaborate (kraft-borate) were prepared in the laboratory. The white liquor parameters were maintained the same for all pulping experiments: sulfidity 27.2%; NaOH 93.4g/L as Na₂O; Na₂CO₃ 22.45g/L as Na₂O. To simulate the white liquor composition corresponding to that at 35% borate autocausticizing, sodium metaborate, which is the product of the autocausticizing reactions, was added to the white liquor in the amount corresponding to 16.4g/L as Na₂O. The white liquor parameters were measured using a duo-titrator ion analyzer developed by U.S. Borax Inc. (variant of the TAPPI Standard ABC titration method). The ratio of cooking liquor to wood was 4L/kg. The active alkali charge was maintained at 16.5% on oven-dry wood. Laboratory pulping was conducted in M/K digester using 400g oven-dry wood at the increasing H-factor. Five H-factors (250, 500, 750, 1,000 and 1,500) were used in pulping of maple and birch, while seven H-factors between (500, 900, 1000, 1500, 2,000, 2,500 and 3,000) were used in pulping of spruce. The pulps were washed with cold water, disintegrated in the laboratory blender and then screened on the vibrating screen. The screened yields and rejects were determined.

The pulps were characterized by determination of kappa number (TAPPI T 236 cm-85) and brightness (TAPPI T217 wd-77). The content of extractives in pulps was measured by the successive extraction either in ethanol:cyclohexane (1:2) and ethanol (spruce pulps) or in ethanol:toluene (1:2) and ethanol (birch and maple pulps), as both cyclohexane and toluene were recommended to replace benzene in extraction [10]. Hexenuronic acid groups (HexA) content in pulps was determined by the method recently developed by Chai et al. [11]. This method is based on a highly selective hydrolysis of HexA in a mercuric chloride - sodium acetate solution and UV-spectrophotometry of the obtained hydrolysate: $C_{\text{HexA}} = 0.287V (A_{260} - A_{290})/w$; V-the volume of the hydrolysis solution, mL; w - the oven-dry weight of pulp, g; A_{260} , A_{290} - the absorption intensities at 260 and 290 nm, respectively; C_{HexA} - the content of hexenuronic acid groups in pulp, $\mu\text{mol/g}$. The holocellulose content of the spruce woodchips and pulps was determined in accordance to the acid-chlorite method [12].

RESULTS AND DISCUSSION

Yield, Reject and Kappa Number

The yields and rejects obtained in kraft and kraft-borate pulping of birch, maple and spruce at different H-factors are shown in Table I.

Table I Yields and Rejects Obtained in Kraft and Kraft-Borate Pulping of Birch, Maple and Spruce at Increasing H-Factor

Species	Yields and Rejects	K/KB	H-Factor							
			250	500	750	1,000	1,500	2,000	2,500	3,000
Birch	Yield	K	56.2	55.5	53.4*	52.1	51.8	-	-	-
		KB	56.3	55.2	53.6*	52.8	50.3	-	-	-
	Reject	K	2.7	1.2	<0.1*	<0.1	<0.1	-	-	-
		KB	1.5	1.0	<0.1*	<0.1	<0.1	-	-	-
Maple	Yield	K	56.3	55.4*	53.5*	52.6	51.7	-	-	-
		KB	58.8	55.1*	55.0*	52.3	51.5	-	-	-
	Reject	K	3.3	0.7*	<0.1*	<0.1	<0.1	-	-	-
		KB	0.6	0.1*	0.4*	<0.1	<0.1	-	-	-
Spruce	Yield	K	-	62.1	-	55.8*	51.1	50.1*	48.3	47.7
		KB	-	62.2	-	56.9*	52.8	51.7*	50.3	49.4
	Reject	K	-	1.0	-	1.5*	1.7	1.2*	0.2	0.5
		KB	-	1.0	-	0.5*	0.7	0.2*	0.1	0.1

*the average obtained in two pulping experiments

The yields of kraft and kraft-borate pulps of birch and maple obtained at the same H-factors were approximately the same, while the yields of spruce pulps were higher in kraft-borate than in kraft pulping, especially at the H-factors higher than 1,000. The rejects in kraft-borate pulping of birch and maple were lower than corresponding in kraft pulping at the H-factors lower than 750, while the rejects in kraft-borate pulping of spruce were lower at all studied H-factors (500-3,000). Based on these results, a potential of sodium metaborate to decrease the rejects in pulping of maple, birch and spruce and to increase the yields in pulping of spruce is indicated. To estimate the residual lignin in the obtained pulps, the kappa numbers of the pulps were determined and the diagrams of yield vs. kappa number were made and are shown here in Fig. 1.

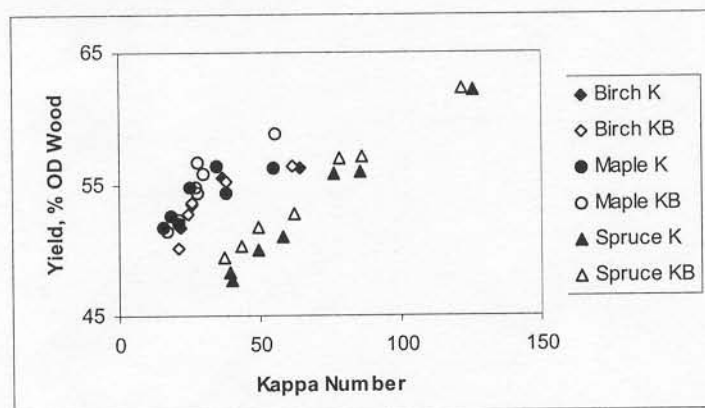


Fig. 1. Yield vs. Kappa Number for Kraft and Kraft-Borate Pulps of Birch, Maple and Spruce

It is well known that the yields of birch and maple kraft pulp are higher than that of spruce kraft pulp at the same kappa number [13]. This result was found for both kraft and kraft-borate pulping, as shown in Fig. 1. Also, the yields of birch and maple pulps characterized by the same kappa numbers were not affected by sodium metaborate, while sodium metaborate increased the yield of spruce kraft pulps delignified at the same kappa number. This

increase is especially evident at the H-factors higher than 1,000, where the yields of kraft-borate pulps were higher in average for 1.8 % (st. dev. 0.18) than those of kraft pulps (Table I, Fig. 1).

Brightness and Extractives

The brightness of kraft and kraft-borate pulps of studied wood species at the same kappa number was decreasing in accordance to the series: maple > birch > spruce, as it is shown in Fig. 2. No effect of sodium metaborate on the pulp brightness, i.e. formation of chromophoric structures during pulping course, was noticed as the kraft and kraft-borate pulps of the same species at the same kappa number were characterized by approximately the same brightness.

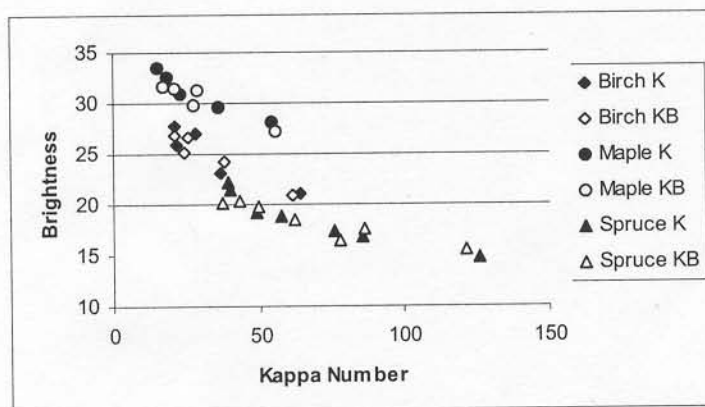


Fig. 2. Brightness vs. Kappa Number for Kraft and Kraft-Borate Pulps of Birch, Maple and Spruce

Even that the lignin chromophoric structures remained in pulp affect pulp brightness the most, other chromophoric structures, including those in the organic low-molecular weight compounds soluble in organic solvents i.e. extractives, cause a decrease of pulp brightness [14]. Therefore, the content of extractives in studied pulps was determined by successive extraction in organic solvents as described in the experimental section. The obtained results are shown in Fig. 3.

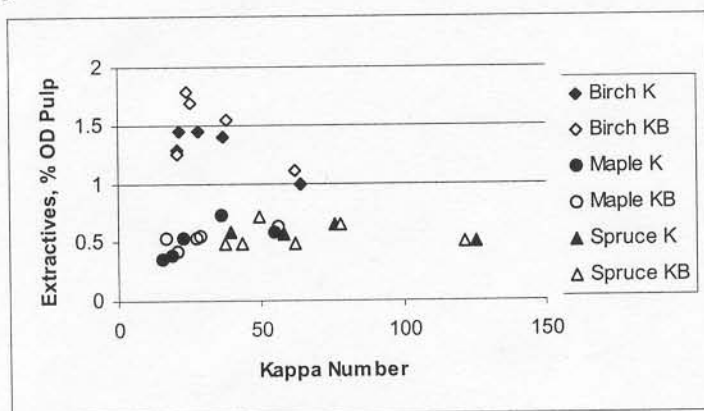


Fig. 3. Extractives vs. Kappa Number for Kraft and Kraft-Borate Pulps of Birch, Maple and Spruce

The content of extractives in birch pulps was 1 to 2 %, while in maple and spruce pulps it was about 0.5 %. No effect of sodium metaborate on the extractives content of pulps was noticed. Removal of the extractives increased the brightness of the both kraft and kraft-borate pulps. For example, maple kraft pulp (H-factor 1,000, kappa number 18.5) originally had brightness 32.66 and after extraction 34.9 (6.9 % increase). Also, birch kraft-borate pulp (H-factor 1,000, kappa number 24) originally had brightness 25.12 and after extraction 27.15 (8.1 % increase). These results show the negative effect of extractives on the pulp brightness, especially in the case of birch pulps.

Hexenuronic Acid Groups (HexA) and Correction of Kappa Number

Hexenuronic acid groups are formed in xylans by methanol elimination from 4-O-methyl-D-glucuronic acid groups [11, 15]. They protect xylan chains in kraft pulping, contribute significantly to the measured value of the kappa number by potassium permanganate consumption, and interfere with the bleaching processes based on chlorine dioxide and ozone [15, 16]. In this study, the HexA content was determined by UV-spectroscopic method developed by Chai et al. [11]. As expected, the HexA content decreased in pulps of studied species in accordance to the series: birch > maple > spruce, which agrees with the results of previous studies on HexA content in pulp [11, 15-17] and with the xylans/4-O-methyl-D-glucuronic acid groups content in studied species [13]. Essentially, the same HexA content characterized the kraft and corresponding kraft-borate pulps.

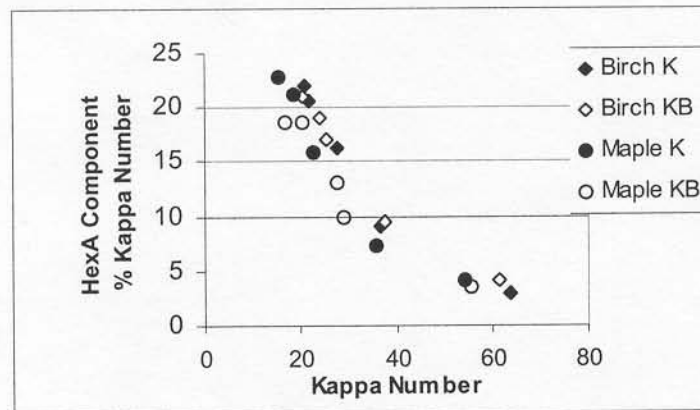


Fig. 4. Hexenuronic Acid Groups Component of Kappa Number vs. Kappa number for Kraft and Kraft-Borate Pulps of Birch and Maple

As it was found that 10 μmol of hexenuronic acid correspond to 0.85 kappa units [16], the hexenuronic acid component of kappa numbers was calculated, expressed in % of kappa number, and plotted against kappa number. These plots are shown in Fig. 4 for kraft and kraft-borate pulps of birch and maple and in Fig. 5 for kraft and kraft-borate pulps of spruce.

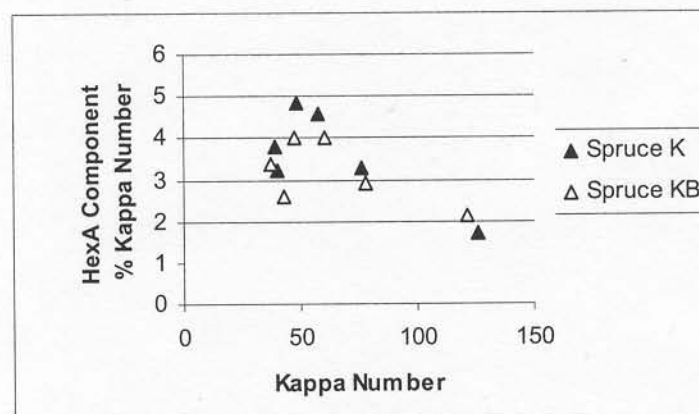


Fig. 5. Hexenuronic Acid Groups Component of Kappa Number vs. Kappa number for Kraft and Kraft-Borate Pulps of Spruce

The HexA component of kappa number of birch and maple pulps was increasing with the decreasing kappa number and was about 20 % at kappa numbers between 15 and 20. The highest HexA contribution of 22.9 % to the kappa number was found for maple kraft pulp at kappa number 15.2. The HexA component of kappa number of spruce pulps was much lower. This was 2 % of kappa number at kappa numbers higher than 100 and 3 to 5 % at kappa numbers lower than 80. At the same kappa number, the HexA component of kappa number for kraft and kraft-borate pulps was approximately equal.

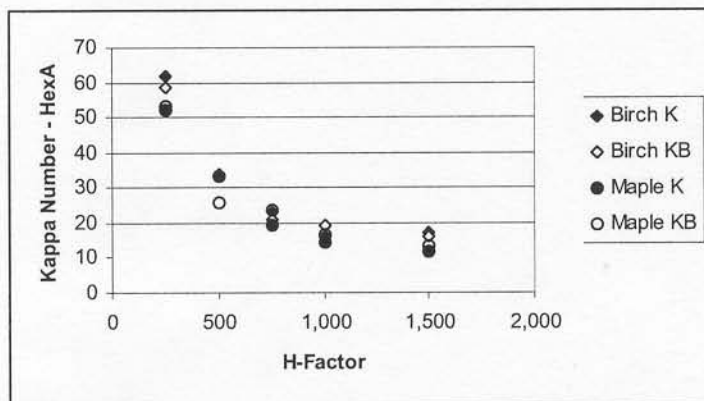


Fig. 6. Kappa Number Corrected for the HexA Component vs. H-Factor in Kraft and Kraft-Borate Pulping of Birch and Maple

Although it is known that besides lignin and HexA, the kappa number is affected by other types of oxidizable structures [18], the main error in estimation of the residual lignin in pulp based on the kappa number was avoided by correction of kappa number for HexA. The kappa numbers corrected for the HexA component (Kappa Number – HexA) were plotted against the corresponding H-factor as it is shown in Fig. 6 for maple and birch and in Fig. 7 for spruce. The data illustrated in these Figures indicate that kraft delignification of birch, maple, and spruce is essentially unchanged in the presence of sodium metaborate at the level corresponding to 35 % autocausticizing.

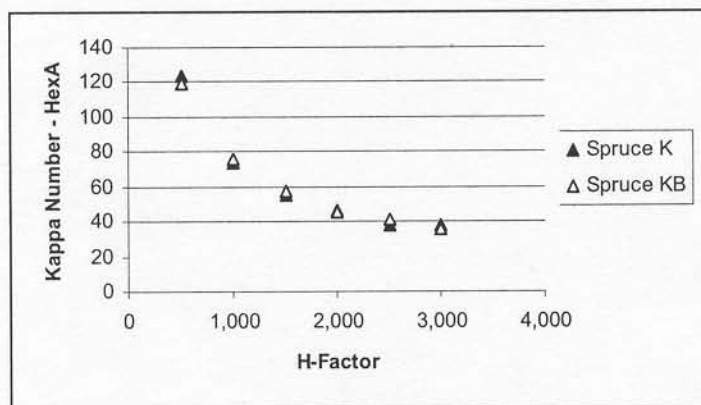


Fig. 7. Kappa Number Corrected for the HexA Component vs. H-Factor in Kraft and Kraft-Borate Pulping of Spruce

Retention of Carbohydrates in Kraft Pulping of Spruce

An increase of the yield of spruce kraft pulps was found in the presence of sodium metaborate in pulping to the approximately same kappa number (Table I, Fig. 1). This effect of sodium metaborate on kraft pulping of spruce was further studied by determination of the holocellulose content in the spruce kraft and kraft-borate pulps, as well as in the spruce woodchips. The results, obtained based on the holocellulose contents and corresponding screened pulp yields, are shown in Fig. 10. These data represent the retention of holocellulose versus kappa number.

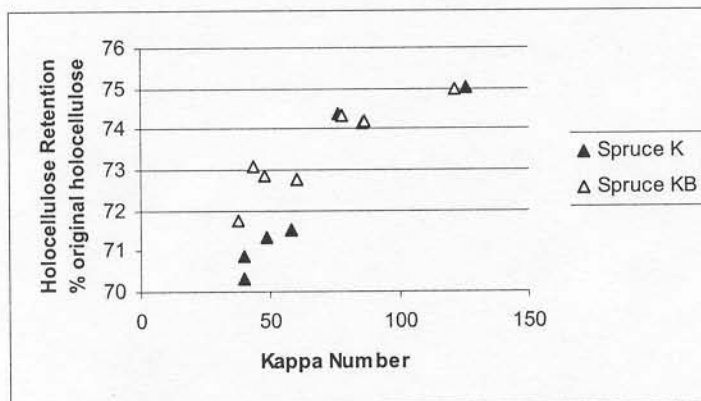


Fig. 10. Retention of Holocellulose in Kraft and Kraft-Borate Pulps of Spruce vs. Kappa Number

As it is shown in Fig. 10, the retention of holocellulose increased in kraft-borate pulping at kappa numbers lower than 60, indicating a potential of sodium metaborate to protect carbohydrates in kraft pulping.

CONCLUSIONS

This study shows the results obtained for birch, maple and spruce in conventional kraft pulping and in kraft pulping with sodium metaborate added at the level corresponding to 35 % autoausticizing – kraft-borate pulping. A potential of sodium metaborate to increase the yield of spruce kraft pulp delignified to the same kappa number, at H-factors higher than 1,000, in average for 1.8 %, was found. Also, the rejects were reduced in kraft-borate pulping of maple and birch at H-factors lower than 750 and in kraft-borate pulping of spruce at H-factors 500 to 3,000. No effect of sodium borate on the kraft delignification of studied species or on the properties of kraft pulps of birch and maple was observed. Sodium borate did not affect the brightness and the contents of extractives and hexenuronic acid groups (HexA) of the kraft pulps of studied species. The kappa number corrected for the HexA component estimating the lignin content in pulps more accurately showed, at the increasing H-factor, that kraft delignification was unchanged in the presence of sodium metaborate. An increase of holocellulose retention was found for the kraft-borate pulps of spruce at kappa numbers lower than 60, indicating a potential of sodium metaborate to protect carbohydrates in kraft pulping.

ACKNOWLEDGEMENTS

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