Some properties of kraft and kraft–borate pulps of different wood species

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ABSTRACT: Comparative analyses were carried out on the properties of birch, maple, and spruce for conventional kraft pulping and kraft pulping with sodium metaborate added to correspond to 35% autocausticizing. A 1.8% increase was noticed in the screened yield for the kraft–borate pulping of spruce at H-factors higher than 1000. Also, at kappa numbers lower than 50, sodium metaborate increased the total yield in spruce pulping. Sodium borate did not affect the brightness nor the contents of extractives and hexenuronic acid groups (HexA) of the kraft pulps for the species studied. The kappa number corrected for the HexA component, which is a more accurate estimate of the lignin content, showed that kraft delignification was not changed by sodium metaborate at the increasing H-factor. An increase of holocellulose retention was found for the kraft–borate pulps of spruce at the kappa numbers lower than 60, indicating that sodium metaborate has the potential to protect carbohydrates in kraft pulping.

Application: With no detrimental effects observed for maple, spruce, and birch pulps, autocausticizing with sodium metaborate added in the white liquor appears to be an easy way for a causticizing-limited mill to increase its capacity without new equipment.

New insight into autocausticizing reactions has rekindled interest in supplementing or eliminating the calcining and causticizing cycle. An important question regarding the implementation of the borate-based autocausticizing in the kraft process is the effect of sodium metaborate. Sodium metaborate is present in the pulping liquor as the product of the autocausticizing reactions. To understand its effects on kraft pulping, we need to study the properties of kraft pulps produced with white liquor containing sodium metaborate.

Here, we present results obtained in the 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 under the same conditions as used for kraft pulps except that the white liquor contained sodium metaborate at a level that corresponded to 35% autocausticizing.

The screened yields, rejects, and properties of pulps were measured, including kappa number, brightness, and the contents of extractives and hexenuronic acid groups (HexA). In addition, the holocellulose content of spruce wood and pulps was determined and was used to estimate the retention of carbohydrates during pulping.

BACKGROUND

In the 1970s, Janson suggested the application of sodium metaborate ($NaBO_2$) as the most favorable autocausticizing agent [1, 2]. However, the reaction stoichiometry Janson suggested required a relatively large ratio of sodium metaborate to sodium hydroxide (NaOH). Therefore, the proposed process was thought to be economically unattractive. It was also thought that there may be problems in evaporation because of a rise in boiling point and difficulties in black liquor handling because of an increase in black liquor viscosity.

Interest in borate-based autocausticizing was rekindled when Tran *et al.* showed that the autocausticizing reactions are more efficient than Janson had proposed [3]. Tran and coworkers indicated that borate autocausticizing proceeds through the reaction of sodium metaborate and sodium carbonate (Na_2CO_3) in the furnace. This reaction forms trisodium borate (Na_3BO_3) and generates carbon dioxide, as shown in Reaction 1. In the dissolving tank, the trisodium borate undergoes hydrolysis to form sodium hydroxide and regenerate sodium metaborate, as Reaction 2 shows.

$$NaBO_2 + Na_2CO_3 \rightarrow Na_3BO_3 + CO_2 \tag{1}$$

$$Na_3BO_3 + H_2O \rightarrow 2NaOH + NaBO_2 \tag{2}$$

In accordance with 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 autocausticizing is only one-half that indicated by the stoichiometry established earlier [1, 2]. Since less borate is required, the effect of borate on kraft pulping, on the boiling point rise, and on the viscosity of black liquor will be less than observed in earlier work [4–6, 7].

In addition to suggesting the new stoichiometry, Tran and coworkers also proposed that borate autocausticizing offers the possibility of only partially converting the sodium carbonate to sodium hydroxide, with the remaining conversion occurring in the lime cycle. This possibility would give a causticizing-limited mill an easy way to increase its causticizing capacity without installing new equipment. Based on this new understanding, several mill trials with partial autocausticizing 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 autocausticizing levels between 5% and 25%.

To understand the effect of borates on kraft pulping, it is necessary to study the properties of pulps and black liquors obtained in kraft pulping with white liquor containing sodium metaborate at the level corresponding to the partial autocausticizing stoichiometry suggested by Tran *et al.* [3]. Therefore, the properties of slash pine black liquor were measured with and without sodium metaborate added at the level corresponding to 30% in another study [9].

SPECIES		K/KB	250	500	750	1000	1500	2000	2500	3000
			H-FACTOR							
Birch	SY**	K	56.2	55.5	53.4*	52.1	51.8	—	—	—
		KB	56.3	55.2	53.6*	52.8	50.3	—	—	—
	R**	K	2.7	1.2	<0.1	<0.1	<0.1	—	—	—
		KB	1.5	1.0	<0.1	<0.1	<0.1	—	—	—
	KN**	K	63.9	36.7	27.8*	21.5	20.7	—	—	—
		KB	61.5	37.7	25.5*	24.0	20.6	—	—	—
Maple	SY**	K	56.3	55.4*	53.5*	52.6	51.7	—	—	—
		KB	58.8	55.1*	55.0*	52.3	51.5	—	—	—
	R**	K	3.3	0.7*	<0.1*	<0.1	<0.1	—	—	—
		KB	0.6	0.1*	0.4*	<0.1	<0.1	—	—	—
	KN**	K	54.3	35.9*	22.8*	18.4	15.2	—	—	—
		KB	55.5	28.8*	28.3*	20.6	16.7	—	—	—
Spruce	SY**	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
	R**	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
	KN**	K	—	125.7	—	76.0*	57.7	48.6*	39.5	39.2
		KB	—	121.5	—	77.9*	59.9	47.5*	42.9	37.0

*the average obtained in two pulping experiments
**Screened Yield (SY); Rejects (R, % OD Wood); Kappa Number (KN).

I. Screened yields and rejects obtained in kraft and kraft–borate pulping of birch, maple and spruce at increasing H-factor.

Although increases were found in both the boiling point rise and the viscosity for black liquor containing sodium metaborate, the increases were relatively small and are not expected to cause problems in the evaporation and pumping of black liquor. An increase in the solubility limit of black liquor, which was also noticed, might decrease the scaling problems in the evaporator.

EXPERIMENTAL

Black spruce (*Picea mariana*), paper birch (*Betula papyrifera*), and sugar maple (*Acer saccharum*) woodchips, supplied by the U.S. Forest Products Laboratory, were used to conduct the kraft (K) and kraft–borate (KB) pulping experiments. Both conventional white liquor and white liquor containing sodium metaborate were prepared in the laboratory. The white liquor parameters were maintained the same for all pulping experiments: 27.2% sulfidity, NaOH 93.4 g/L as Na_2O, and Na_2CO_3 22.45 g/L as Na_2O.

To simulate the white liquor composition corresponding to that at 35% borate autocausticizing, we added sodium metaborate to the white liquor in the amount corresponding to 16.4 g/L as Na_2O. The white liquor parameters were measured with a dual-titrator ion analyzer (U.S. Borax) as a variation of the ABC titration method. The ratio of cooking liquor to wood was 4 L/kg. The active alkali charge was maintained at 16.5% on oven-dry wood. Laboratory pulping was conducted in an M/K digester with 400 g of o.d. wood at the increasing H-factor.

Five H-factors (from 250 to 1500) were used in the pulping of maple and birch, while seven H-factors (from 500 to 3000) were used in the pulping of spruce. The contribution of both the heating and cooling period to H-factor was the same (80). The cooking temperature was 170 °C, and the time at maximum temperature was regulated according to the target H-factor. 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.

We characterized the pulps by determining kappa number (TAPPI T 236 cm-85) and brightness (TAPPI T 217 wd-77). Because both cyclohexane and toluene were recommended to replace benzene in extraction [10], we measured the content of extractives in pulps by successive extractions in ethanol:cyclohexane (1:2) and ethanol for spruce pulps and in ethanol:toluene (1:2) and ethanol for birch and maple pulps. We determined the HexA content by the UV-spectroscopy method recently developed by Chai *et al*. [11]. The holocellulose content of the spruce wood chips and pulps was determined according to the acid-chlorite method [12].

RESULTS AND DISCUSSION

Screened yield, rejects, and kappa number

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

The screened yields of kraft and kraft–borate pulps of birch and maple obtained at the same H-factors were approximately the same, while the screened yields of spruce pulps were higher in kraft–borate pulping than in kraft pulping, especially at the H-factors higher than 1000. The rejects in kraft–borate pulping of birch and maple were lower than in kraft pulping at the H-factors lower than 750. For spruce, the rejects in kraft–borate pulping were lower at all studied H-factors (500–3000). However, at H-factor greater than 2000, the difference in the rejects between kraft and kraft–borate pulping was lower than at the lower H-factors. As these results indicate, sodium metaborate has the potential to increase the yields in the pulping of spruce.

To estimate the residual lignin in the pulps obtained, we determined the kappa numbers of the pulps and made diagrams of screened yield vs. kappa number, as shown in **Fig. 1**. The screened 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 the figure shows. Also, the screened yields of birch and maple pulps were not affected by sodium metaborate, while sodium metaborate increased the yield of spruce kraft pulps. This increase is especially evident at kappa numbers greater than 60 (H-factor > 1000), where the screened yields of kraft–borate pulps were, on average, 1.8% higher than those of kraft pulps (Table I, Fig. 1).

Brightness and extractives

The brightness of kraft and kraft–borate pulps decreased from maple to birch to spruce, as shown in Fig. 1. We noticed no effect of sodium metaborate on the pulp brightness (*i.e.*, the formation of chromophoric structures), because the kraft and kraft–borate pulps of the same species had approximately the same brightness at the same kappa number.

Even though the lignin chromophoric structures that remain in pulp affect pulp brightness the most, other chromophoric structures cause a decrease in pulp brightness as well [14]. Some of these structures are extractives, which are low-molecular-weight organic compounds soluble in organic solvents.

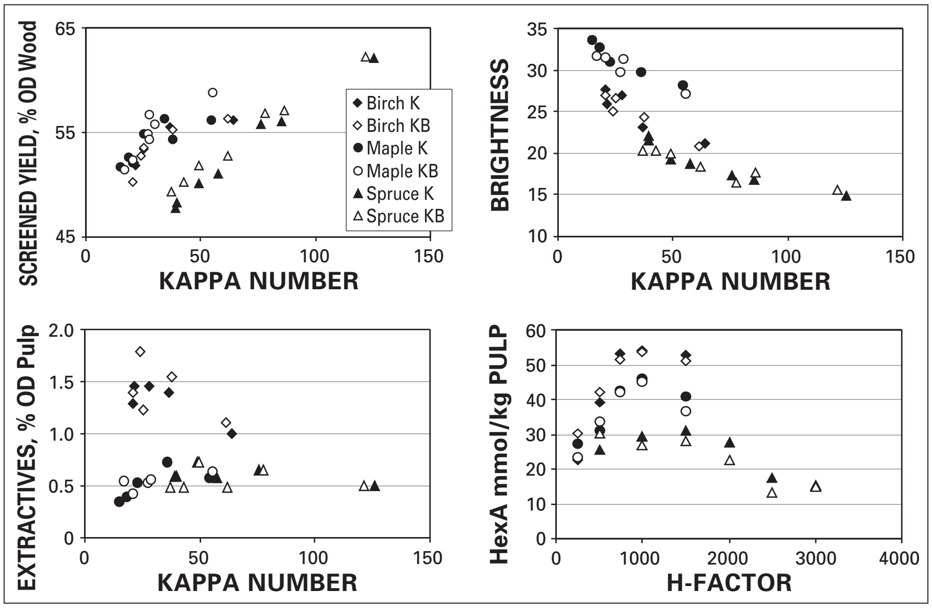
Of the extractives in unbleached pulps, several contain one or more double bonds. They are extremely reactive towards bleaching agents, and can increase their consumption in the bleaching phase [14]. Therefore, we determined the content of extractives in the pulps studied by successive extraction in organic solvents, as already described. The results are shown in Fig. 1.

The extractives content in birch pulps was 1–2%, while in maple and spruce pulps it was about 0.6%. We noticed no effect of sodium metaborate on the extractives content of pulps. However, the extractives negatively affect the brightness and kappa number of both kraft and kraft–borate pulps. Because they contain chromophoric groups, extractives decrease the pulp brightness, and their removal leads to an improvement in brightness. For example, maple kraft pulp (H-factor 1000, kappa no. 18.5) originally had a brightness of 32.66, but after extraction it had a brightness of 34.9 (an increase of 6.9%). On the other hand, the corresponding values for the birch kraft–borate pulp (H-factor 1000, kappa no. 24) were 25.12 and 27.15 (an 8.1% increase).

Furthermore, after extractives were removed, the kappa numbers of pulps decreased. Kappa number reductions of 4.14% for birch kraft and 4.06% for kraft–borate pulp were obtained at an H-factor of 1500 (K = 21.52 and KB = 21.40 before extraction and K = 20.67 and KB = 20.56 after extraction).

HexA and kappa number correction

Hexenuronic acid groups are formed in xylans by methanol elimination from 4-O-methyl-D-glucuronic acid groups [11, 15]. HexA groups protect xylan chains in kraft pulping, contribute to the measured value of the kappa number by consuming potassium permanganate, and interfere with chlorine dioxide and ozone bleaching [15, 16]. As mentioned, we determined the HexA content by a UV-spectroscopic method, and the HexA content decreased from birch to maple to spruce. This order of decrease is in agreement with the results of previous studies on HexA content in pulp [11, 15–17] and is consistent with the content of xylans and 4-O-methyl-D-glucuronic acid groups in the species studied [13]. We also found that approximately the same HexA content characterized the kraft and kraft–borate pulps produced at the same H-factor. The HexA content of the pulps studied is shown in Fig. 1.



1. Screened yield, brightness, and extractives vs. kappa no. for kraft and kraft–borate pulps of birch, maple, and spruce. HexA content in kraft and kraft–borate pulps of birch, maple and spruce obtained at increasing H-factor.

In addition to lignin and HexA, the kappa number is affected by other types of oxidizable structures [18] including extractives, as shown in this study. However, an error in estimating the residual lignin in pulp based on the kappa number can be decreased by correcting the kappa number for its HexA component. Because 10 μmol of hexenuronic acid correspond to 0.85 kappa units [16], we calculated the hexenuronic acid component of kappa numbers and subtracted these contributions from the kappa numbers. We plotted these corrected kappa numbers against the corresponding H-factors. **Figure 2** shows the graphs for birch, maple, and spruce.

The data illustrated in these figures indicate that the kraft delignification of birch, maple, and spruce is essentially unchanged in the presence of sodium metaborate at the level corresponding to 35% autocausticizing.

Retention of carbohydrates in kraft pulping of spruce

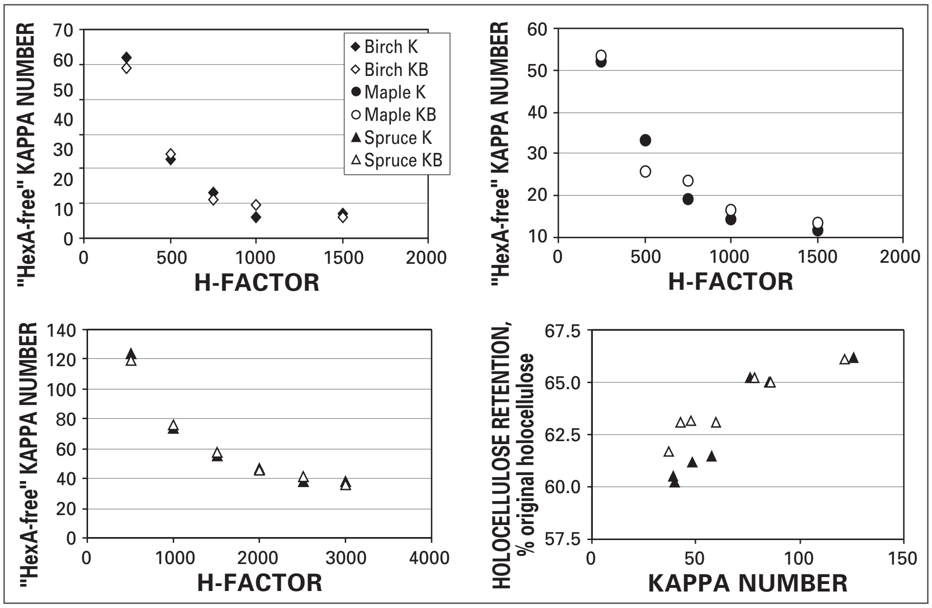
The yield of spruce kraft pulps was found to increase in the presence of sodium metaborate (Table I, Fig. 1). We studied this effect further by determining the holocellulose content in the spruce kraft and kraft–borate pulps, as well as in the spruce wood chips. The results, based on the holocellulose contents and corresponding screened pulp yields, are shown in Fig. 2. These data represent the retention of holocellulose vs. kappa number.

As Fig. 2 shows, the retention of holocellulose increased in kraft–borate pulping at kappa numbers lower than 60. This outcome indicates that sodium metaborate has the potential to protect carbohydrates in kraft pulping.

CONCLUSIONS

Birch, maple, and spruce were processed by conventional kraft pulping and by kraft pulping with sodium metaborate added at a level corresponding to 35% autocausticizing. Sodium metaborate was found to have the potential to increase by an average of 1.8% the yield of spruce kraft pulp at H-factors higher than 1000. 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 of 500 to 3000.

We did not observe that sodium borate has an effect on the kraft delignification of studied species or on the properties of kraft pulps of birch and maple. Sodium borate did not affect the brightness nor the contents of extractives and hexenuronic acid groups of the kraft pulps studied. The kappa numbers corrected for the HexA component showed that kraft delignification was unchanged in the presence of sodium metaborate, at increasing H-factor. An increase of holocellulose retention was found for the kraft–borate pulps of spruce at kappa numbers lower than 60, indicating that sodium metaborate has the potential to protect carbohydrates in kraft pulping. **TJ**



2. Kappa number corrected for the HexA component vs. H-factor in kraft and kraft–borate pulping of birch, maple, and spruce. Retention of holocellulose in kraft and kraft-borate pulps of spruce vs. kappa number.

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INSIGHTS FROM THE AUTHORS

We chose this topic to gain understanding of the effect of sodium metaborate on pulping and the pulp properties. This understanding will aid the implementation of borate-based autocausticizing as an efficient way of saving energy and capital investment in the kraft process. These pulping experiments were conducted with less than one-half the level of sodium metaborate used in previous studies, corresponding to the newly defined stoichiometry of borate-based autocausticizing.

To compare delignification in kraft and kraft-borate pulping, we needed to eliminate the error in estimation of the residual lignin content in pulp based on kappa number due to hexenuronic acid. This proved to be the most difficult aspect of our studies.

The most interesting results of these studies indicate that the screened yield of spruce pulp produced in the kraft-borate pulping at 35 % autocausticizing is higher than that produced under the same conditions in the kraft pulping. Borate-based autocausticizing not only saves energy and capital equipment, but in the case of spruce pulping, it should increase pulp production with no additional capital or energy investment.

An increase of screened yield was observed for kraft-borate pulping of spruce, but not for birch and maple; this should be further explored by the variation of both the amount of sodium metaborate in the white liquor and the pulping conditions.

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