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EFFECTS OF SODIUM METABORATE ON KRAFT PULPING

by

Biljana M. Bujanovic

A Dissertation
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Doctor of Philosophy
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Biljana M. Bujanovic

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CHAPTER I

SUMMARY

Today, the kraft process is the paper industry's dominant pulping technology. Its main advantages are low demands on wood species and wood quality, and excellent pulp strength properties, while its drawbacks are dark color of pulp and the emission of malodorous compounds into the air and water. The recovery of the pulping chemicals, sodium hydroxide (NaOH) and sodium sulfide (Na_2S) (white liquor) from the spent cooking liquor (black liquor) is an integrated and economically necessary part of kraft technology. While sodium sulfide is regenerated in the recovery boiler/furnace, regeneration of sodium hydroxide occurs in the causticizing vessels by the reaction of sodium carbonate (Na_2CO_3) with calcium hydroxide (Ca(OH)_2 ; slaked lime) – causticizing reaction. The causticizing reaction results in calcium carbonate (CaCO_3) from which calcium hydroxide is regenerated in the lime cycle. The lime cycle starts with a highly endothermic reaction, the incineration of calcium carbonate (calcining reaction), which releases in carbon dioxide (CO_2) and leaves calcium oxide (CaO). Calcium hydroxide is then produced in the slaker by the reaction of calcium oxide and water (slaking) (Fengel, Wegener, 1984, Grace, Malcolm, 1989). Significant energy and capital equipment savings would be possible if calcium hydroxide, as a causticizing agent, could be replaced with some other chemical which does not need a complicated regeneration process. Processes that

form sodium hydroxide or caustic directly, and exclude an independent cycle of the causticizing agent regeneration, are referred to as autocausticizing. Autocausticizing was suggested as a method of the expulsion of carbon dioxide from the smelt in the recovery furnace by the cooking chemicals themselves, without the addition of causticizing compounds that have to be separated later. There are several compounds that may be used as autocausticizing agents and they are, for example, sodium salts of amphoteric oxides as sodium metaborate (NaBO_2), sodium phosphate (NaPO_3), disodium phosphate ($\text{Na}_4\text{P}_2\text{O}_7$), sodium silicate ($\text{Na}_2\text{Si}_2\text{O}_5$), and sodium aluminate (NaAlO_2) (Janson 1977, 1979a).

Janson suggested the application of sodium metaborate as the most favorable autocausticizing agent (Janson 1977, 1978, 1979a). However, the reaction stoichiometry suggested by Janson required a relatively large ratio of sodium metaborate to sodium hydroxide. At that time, the borate-based autocausticizing process was considered unattractive because it was estimated that the large level of required sodium metaborate would double the total inorganic load over the entire recovery system and cause problems in evaporation and liquor handling (Grace, 1981, Janson, Söderhjelm, 1988). However, in 1999, Tran et al. studied the borate-based autocausticizing reactions and concluded that the stoichiometry of these reactions is twice as efficient as suggested earlier. These studies also indicated that the mills with a limited causticizing capacity could use partial autocausticizing as a method of increasing their caustic production without installing new equipment (Tran et al., 1999). Partial autocausticizing refers to a process in which a certain amount of

sodium hydroxide is produced in the borate autocausticizing reactions, while the remaining amount of sodium hydroxide is produced in the causticizer. These findings resulted in a series of successful partial borate autocausticizing trials, which have been conducted in a few mills in North America. The trial in one of these mills is transferring to a commercial application (Kochesfahani, Bair, 2002). Although partial borate autocausticizing is being pursued, little information is available about the effect of borate on kraft pulping, including the quality of pulp and delignification reactions, and on the resulting black liquor properties.

The objectives of this thesis were to determine the effects of sodium metaborate on the delignification of spruce, birch, and maple, and the quality of pulps produced in kraft-borate pulping of these species. In order to accomplish this goal, a detailed characterization of the wood chips and pulps produced in the kraft and kraft-borate pulping experiments, was conducted. White liquor for a major part of the kraft and kraft-borate pulping experiments, was prepared by dissolution of the commercial chemicals in water. White liquor for kraft-borate pulping contained sodium metaborate in the amount corresponding to a desired autocausticizing level. The controlling pulping parameters for the kraft and kraft-borate experiments were the same, i.e. each kraft experiment had its kraft-borate counterpart. A series of the spruce pulping experiments had a goal to evaluate the pulping efficiency of white liquor produced by causticizing in the presence of sodium metaborate. White liquor for these experiments was prepared in the causticizing reaction with and without added sodium metaborate.

Residual lignin (lignin remaining in pulp) was isolated from the spruce kraft and kraft-borate pulps (H-factor 2,000). The structure of the residual lignins was studied to learn more about the effect of sodium metaborate on the kraft delignification chemistry.

The studies included analysis of the black liquor resulting from kraft and kraft-borate (35 % autocauticizing) pulping of birch, maple, and spruce at an H-factor of 1,500. The boiling point rise was measured to evaluate the effect of sodium metaborate on the evaporation phase in the kraft-borate process. The kraft lignins (lignin dissolved in cooking liquor) were isolated from the same black liquors and some of their properties were compared to gain additional information about the structural changes, which take place in the lignin during kraft and kraft-borate pulping. In a separate series of experiments, the black liquor properties, boiling point rise, solubility limit, and viscosity were determined for industrial black liquor with and without sodium metaborate at levels that corresponded to the different autocauticizing levels. The goal of these experiments was to evaluate the effect of sodium metaborate on the black liquor evaporation and handling in kraft-borate process.

Preliminary cooking experiments were performed with spruce at the different autocauticizing levels (from 10 % to 52 % autocauticizing) in order to select an optimal autocauticizing level, which was used further in pulping of spruce, maple, and birch. Based on the results of this study, the 35 % level of autocauticizing was chosen to be studied further. Kraft and kraft-borate pulping experiments were

performed under the same conditions concerning liquor-to-wood ratio, active alkali charge, sulfidity of white liquor, and cooking temperature, at the same and increasing H-factor (Vroom, 1957) (for spruce from 500 to 3,000, for birch and maple from 250 to 1,500). The screened yield, rejects, kappa number, viscosity, brightness, and mechanical properties (after 5,000 rev. PFI milling; CSF, density, tear and tensile strength) of the resulting pulps were determined and compared (TAPPI Test Methods, 1991). Also, chemical composition of pulps was studied. The chemical analyses included determination of the contents of lignin (Klason lignin, acid soluble lignin), extractives, holocellulose, pentosans, hexenuronic acid groups, and phenolic hydroxyl groups (TAPPI Test Methods, 1991, Useful Methods, 1990, Browning, 1967, Bethge, 1964, Chai et al., 2001, de Sousa et al., 2001). The chemical composition of the wood chips used in the pulping experiments was determined and it provided a base for further estimation of the efficiency of the kraft and kraft-borate delignification processes (Fengel, Wegener, 1984, Browning, 1967, Iiyama, Wallis, 1988, Bethge, 1964).

In order to understand better the delignification process performed in the presence of sodium metaborate, residual lignins of spruce kraft and kraft-borate pulps (H factor 2,000) were compared. Residual lignin was isolated by both standard acid hydrolysis (Gellerstedt et al., 1994) and two-step procedure of acid hydrolysis. The isolated lignin samples were characterized by analytical and spectral methods (Dence, 1992, Iiyama, Wallis, 1988, de Sousa et al., 2001, Tamminen, Hortling, 1999, Faix et al., 1992, Wegener, Strobel, 1992). These results enabled a comparison of the kraft

and kraft-borate delignification results and provided an insight into the effect of high temperature on the residual lignin isolation by acid hydrolysis.

Analysis of the black liquors obtained in kraft and kraft-borate pulping of birch, maple, and spruce (H-factor 1,500) included isolation (Lin, 1992) and characterization of the kraft lignin samples (Lin, 1992, Faix, 1991, Faix et al., 1992, de Sousa et al., 2001) and measurements of the boiling point rise (Frederick et al., 1980). Additionally, the effect of sodium metaborate on the properties of black liquor was studied in an independent series of studies conducted using an industrial slash pine black liquor. Sodium metaborate was added to the black liquor at levels equivalent to 30%, 60%, and 120% autocausticizing. The effect of sodium metaborate on the boiling point rise was analyzed at elevated pressures and temperatures, and at atmospheric pressure (Frederick et al., 1980). Also, the effect of sodium metaborate on the solubility limit and viscosity of slash pine black liquor was studied.

This thesis is organized in the six following chapters:

- Chapter I. Summary
- Chapter II. Introduction
- Chapter III. Experimental
- Chapter IV. Effect of sodium metaborate on kraft pulping of spruce, birch, and maple
- Chapter V. Effect of sodium metaborate on the properties of black liquor
- Chapter VI. Conclusions

Autocausticizing process, the objectives of this thesis and the thesis major findings are presented in Chapter I.

The theory of borate-based autocausticizing and new results obtained in this field are discussed in Chapter II. This Chapter also explains the need for studies of both kraft and kraft-borate pulping in the same conditions in order to evaluate the effect of the sodium metaborate on kraft pulping. The material and methods used in the experiments of are presented in Chapter III.

The results of this thesis have been published in peer-reviewed journals and presented at the international conferences as peer-reviewed papers. Chapters IV and V are based on these manuscripts, which represent the chapters' sections. These two chapters also discuss the additional results obtained in the thesis experiments, but not included in the manuscripts.

Chapter IV presents the results obtained in the studies of the effect of sodium metaborate on kraft pulping of spruce, birch, and maple.

Comparative studies of kraft and kraft-borate pulps of birch, maple, and spruce included the chemical characterization of these pulps, analysis of both the kappa number-Klason lignin relationship and the contribution of hexenuronic acid groups to the kappa number, and evaluation of tear and tensile strength. The results of these studies indicated that the basic chemical and mechanical properties of kraft and kraft-borate (at 35 % autocausticizing) pulps of the studied species are the same. However, the screened yield of spruce pulp at the same kappa number was higher in kraft-borate than in kraft pulping. This increase in the screened yield might indicate

the potential of sodium metaborate to protect carbohydrates – hexosans in pulping of spruce. A series of experiments aimed to studying the pulp bleachability showed that the kraft-borate pulps obtained at an increasing level of sodium metaborate in white liquor were delignified with the same efficiency as the kraft pulps. Therefore, it was concluded that partial borate autocauticizing, at the levels ranging from 10 to 52 % is not expected to affect the bleachability of spruce kraft pulps.

In order to learn more about the reactivity of lignin during pulping, residual lignin was isolated from both spruce kraft and kraft-borate (35 % autocauticizing) pulps (H-factor 2,000) by acid hydrolysis (Gellerstedt et al., 1994). Additionally, in order to explore the effect of temperature on lignin isolation, a separate series of experiments under acid hydrolysis was performed in two steps. The first step was acid hydrolysis in an ultrasonic bath at 20 °C, while the second step was standard acid hydrolysis. The yield, the phenolic hydroxyl group content, and the FTIR properties of isolated lignins were compared. The results of this study showed no difference in both the isolation yield and the structure of kraft and kraft-borate residual lignin. Acid hydrolysis conducted at lower temperature resulted in lower yield of lignin transformed in a lesser degree than during acid hydrolysis at reflux temperature.

The main results of the studies are presented in three journal publications and three conference papers/presentations, which provide a base for six sections of Chapter IV. The paper's titles, authors, and publication information are presented in Table I.1. The studies' additional results, not included in the manuscripts, are also a part of Chapter IV.

Table I.1.

Papers Presented in Chapter IV

#	Paper Title, Authors and Publication Information
IV-1	Bujanovic, B., Cameron, J., Yilgor, N.: Comparative Studies of Kraft and Kraft-Borate Pulping of Black Spruce. <i>J. Pulp Paper Sci.</i> , 29 (6): 190-196, (2003).
IV-2	Bujanovic, B., Cameron, J., Yilgor, N.: Some Properties of Kraft and Kraft-Borate Pulps of Different Wood Species. TAPPI Fall Technical Conference, San Diego, CA, Sept. 9-12, 2002, Session 24-3, Oral Presentation, CD of Conference Proceedings; accepted for publication in <i>TAPPI J.</i>
IV-3	Bujanovic, B., Yilgor, N., Cameron, J., Aravamuthan, R.: Chemical Characterization of Birch, Maple, and Spruce Kraft and Kraft-Borate Pulps, submitted for publication in <i>J. Pulp Paper Sci.</i>
IV-4	Bujanovic, B., Cameron, J.H., Subbaiyan, P. R.: Tensile and Tear Strength of Kraft and Kraft-Borate Pulps. TAPPI Fall Technical Conference, Chicago, IL, October 2003, Oral Presentation, CD of the Conference (2003).
IV-5	Genco, J., Cameron, J., Bujanovic, B., Bair, C.: Effect of Borate Autocauticizing on Kraft Pulping. 2001 TAPPI Pulping Conference, Seattle, WA, Nov 4-7, 2001, Poster Presentation (in abstract).
IV-6	Bujanovic, B., Schoffers, E., Cameron, J.: Residual Lignin of Spruce Kraft and Kraft-Borate Pulps. 12 th ISWPC, Madison, Wisconsin, June 8-12 2003, Proceedings, Vol. II: 131-134, (2003).

The results obtained in the studies of the effect of sodium metaborate on the properties of black liquor are presented in Chapter V.

The effect of sodium metaborate on the properties of black liquor was studied in two series of experiments. In the first series, the properties of the black liquors resulting from the kraft and kraft-borate of birch, maple, and spruce were analyzed. These experiments included the boiling point rise (BPR) measurements (Frederick et al., 1980) and structural characterization of kraft lignins (Lin, Dence, 1992). In the second series, the commercial slash pine black liquor boiling point rise, solubility

limit, and viscosity was determined before and after addition of sodium metaborate. Sodium metaborate addition corresponded to the different autocausticizing levels.

The studies of the BPR of black liquors resulting from kraft and kraft-borate (35 % autocausticizing) pulping of birch, maple, and spruce at an H-factor of 1,500 indicated an increase of BPR of kraft-borate black liquor compared to that of corresponding kraft black liquor. This increase was between 2.3 and 2.5 °C, at 70 % solids. The analyses of the kraft lignin samples isolated from the kraft and kraft-borate black liquors of studied species corroborated the analyses of the spruce kraft and kraft-borate residual lignins (Ch. IV). According to these results, sodium metaborate at the 35 % level of autocausticizing did not affect the kraft delignification chemistry.

Commercial slash pine black liquor was used in the second series of experiments studying the black liquor properties. Sodium metaborate was added to the black liquor to simulate 30, 60, and 120 % autocausticizing, and the BPR was measured. The largest effect of borate was observed at an addition level equivalent to 120 % autocausticizing and at over 70 % solids, where borate increased the boiling point rise by about 5 °C. It was confirmed that sodium metaborate is totally soluble in black liquor and increases the solubility of the other black liquor components. Viscosity of black liquor increased in the presence of sodium metaborate. However, only a mild increase of viscosity was observed when the autocausticizing level was increased from 30 % to 120 %.

Results of these studies are presented as a journal publication and the conference papers/presentations. These papers provide a base for four sections of Chapter V. The paper's titles, authors, and publication information are presented in Table I.2.

Table I.2.

Papers Presented in Chapter V

#	Paper Title, Authors and Publication Information
V-1	Bujanovic, B., Cameron, J.H.: Effect of Sodium Metaborate on the Boiling Point Rise of Slash Pine Black Liquor. <i>Ind. Chem. Eng. Res.</i> , 40 (11): 2518-2524 (2001).
V-2	Bujanovic, B., Cameron, J.H., Joyce, M.: Effects of Borate Autocauticizing on the Black Liquor Properties. Int. Chem. Rec. Conf., Whistler, BC, Canada, June 11-14, 2001, Poster Presentations, 93-95 (2001).
V-3	Bujanovic, B., Cameron, J.H., Subbaiyan, P. R.: Some Properties of Black Liquor from Kraft and Kraft-Borate Pulping. TAPPI Fall Technical Conference, Chicago, IL, October 2003, Oral Presentation, CD of the Conference, 2003.
V-4	Bujanovic, B., Cameron, J.H.: Effect of Borate on Boiling Point Rise of Black Liquor. AiChE 2000 Annual Meeting, Los Angeles, CA, Nov 12-17, 2000, Technical Sessions: 318f (in abstract).

While the chapters IV and V discuss the results obtained in the studies of the effect of sodium metaborate on kraft pulping and the properties of pulp, a conclusion based on the discussion and the recommendations for further studies are presented in Chapter VI of this thesis.

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CHAPTER II

INTRODUCTION

There are several advantages of the kraft process, which have led to its dominance in chemical pulping in the last 50 years. These are low demands on wood species and wood quality, excellent pulp strength properties, short cooking times, and well established recovery of the pulping chemicals. The main drawbacks of the kraft process are dark color of the unbleached pulp originating from residual lignin and the sulfur-bearing pollutants, which are emitted into the environment (Fengel, Wegener, 1984, Grace, Malkolm, 1989). The residual lignin structure and alkali-stable bonds between residual lignin and carbohydrates have been studied in order to find the reasons leading to the gradually more difficult delignification (Tamminen, Hortling, 1999). The results of these studies contribute to an improvement of both kraft and bleaching processes. An improvement has already been accomplished regarding the emission of the odorous pollutants, which can be controlled at a low level by proper recovery boiler operation and reduced by catalytic combustion, thermal incineration, adsorption, or wet scrubbing (Smook, 1992).

Two active chemicals perform kraft delignification; sodium hydroxide (NaOH), which is also used in the earlier developed soda process, and sodium sulfide (Na₂S). Sodium sulfide was found to accelerate lignin dissolution and hence, kraft pulp is stronger than soda pulp (kraft means strength or power in German and

Swedish). The regeneration of spent liquor (black liquor) to the cooking chemicals (white liquor) is an integrated and economically necessary part of kraft technology, which generates process energy. The scheme of the kraft recovery process is shown in Fig. II.1.

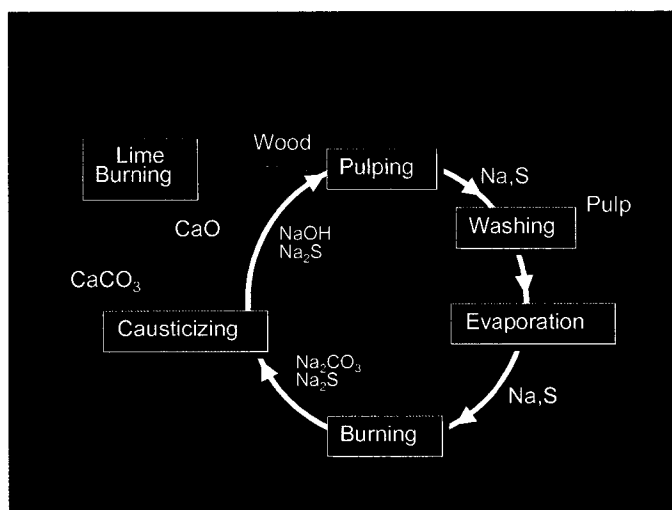
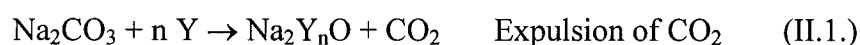


Figure II.1. Conventional Kraft Recovery Process

According to the conventional kraft recovery process, black liquor is concentrated in the multistage vacuum evaporator chain to a solid concentration that supports combustion of the heavy black liquor in the recovery boiler/furnace. In the recovery furnace, the dissolved organic compounds are oxidized to carbon dioxide (CO_2) and water, with heat generation. The inorganic compounds of black liquor together with sodium sulfate (Na_2SO_4), which is added in the recovery furnace, produce an inorganic smelt. After combustion, the inorganic smelt containing mainly sodium carbonate (Na_2CO_3) and sodium sulfide remains at the bottom of the furnace.

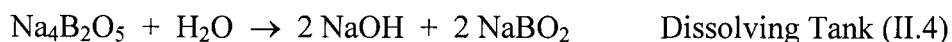
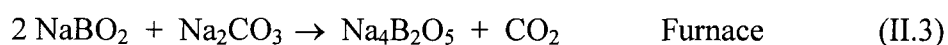
The smelt is dissolved in water to yield green liquor in the dissolving tank. After clarifying by removing of undissolved material (so-called dregs), green liquor is causticized by calcium hydroxide (Ca(OH)_2 , slaked lime). The causticizing reaction results in sodium hydroxide and calcium carbonate (CaCO_3). The calcium carbonate is converted back to calcium hydroxide by incineration in the lime kiln and slaking of the resulting calcium oxide (CaO) with water (Fengel, Wegener, 1984, Grace, Malcolm, 1989). The calcium carbonate incineration is a highly energetically demanding process and significant energy savings could be achieved if alternative, less energy intensive causticizing processes could be developed. The replacement of calcium hydroxide with other chemicals able to accomplish the expulsion of carbon dioxide from sodium carbonate that do not require lime regeneration would lead to the elimination of the slakers, causticizers, and the lime kiln.

Autocausticizing as the formation of a strong alkali from a weaker alkali, which is also the pulping chemical, was suggested as the method of sodium hydroxide regeneration (Janson, 1977, 1978, 1979a,b, 1980). In general term, autocausticizing may be formulated by the equations II.1. and II.2. (Janson, 1979b):



The potential autocausticizing agents are required not only to perform autocausticizing function, but also to be sufficiently alkaline to function as delignification agents. There are several compounds that may fulfill both requirements and hence, be used as the autocausticizing agents. These are for

example, sodium salts of boric, phosphoric, and silicic acids, and aluminium hydroxide. Janson (1977, 1979b) studied different properties of these compounds emphasizing both compatibility with the whole kraft process and efficiency of the corresponding autocausticizing reactions. In the conclusion of these studies, Janson pointed out that “sodium borates seem to be the most promising of the compounds investigated, as regards both pulping and regeneration.” Also, Janson proposed the stoichiometry of two-step borate-based autocausticizing reaction. In accordance with this stoichiometry, sodium carbonate reacts with sodium metaborate (NaBO_2) to generate disodium borate ($\text{Na}_4\text{B}_2\text{O}_5$) in the recovery furnace, reaction II.3. The resulting disodium borate undergoes hydrolysis in the dissolving tank, reaction II.4., when sodium hydroxide is produced and sodium metaborate is regenerated.



Following this stoichiometry, one mole of sodium metaborate is required to generate one mole of sodium hydroxide. Janson (1979a) also suggested that the expulsion of carbon dioxide in the recovery furnace (reaction II.3.) would be severely hindered if the Na/B molar ratio of the reactants is greater than 1.5 and that it would not occur if the ratio is greater than 3. These Na/B ratio requirements implied that only total borate-based autocausticizing leading to the elimination of the lime cycle would be technically feasible. The kraft recovery process with total borate-based autocausticizing is shown in Fig. II.2.

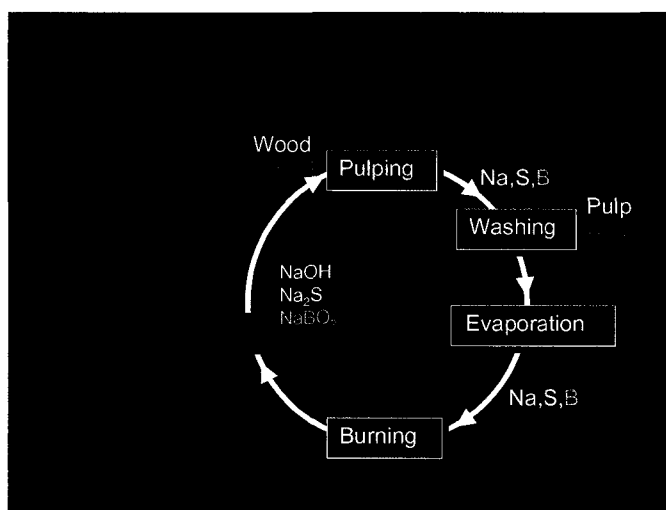
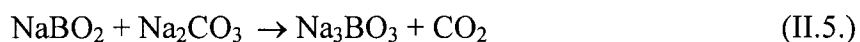


Figure II.2. Kraft Recovery Process with Total Borate-Based Autocauticizing

In the early 1980's, the borate-based autocauticizing mill-scale trials were conducted in Finland. They followed the autocauticizing stoichiometry proposed by Janson. However, at that time, some negative effects of borates on the recovery system were pointed out. For example, the required amount of borates was estimated to double the total inorganic load in the entire recovery system (Grace, 1981). Also, in the studies of the properties of black liquor resulting from the kraft process with borate-based autocauticizing, an increase of the black liquor viscosity was observed (Janson, Söderhjelm, 1988). As solids content and viscosity of black liquor affect the capacity of pumps and heat transfer during evaporation, further efforts on the implementation of borate-based autocauticizing were stopped.

Recently, Tran et al. (1999) found that the amount of sodium metaborate needed to produce the same amount of sodium hydroxide may be less than was previously indicated. Their simultaneous differential and thermogravimetric

(DTA/TGA) studies of the reaction between sodium metaborate and sodium carbonate indicated that decarbonization of sodium carbonate occurred in accordance with reaction II.5., and with trisodium borate (Na_3BO_3) as a reaction product. In water, trisodium borate hydrolyzed to form sodium hydroxide and regenerated sodium metaborate, according to reaction II.6.



These results suggested that the same effect of sodium hydroxide regeneration could be achieved with half of the amount of sodium metaborate indicated by Janson's results. Therefore, the potential effects of borate on the recovery line were expected to be lower than estimated earlier and a new interest for borate-based autocausticizing was launched out.

The work of Tran et al. (1999) also emphasized that partial autocausticizing is feasible and economically attractive. Partial autocausticizing refers to the process in which a certain amount of sodium hydroxide is produced in the borate-based autocausticizing reactions, while the remaining amount of sodium hydroxide is produced in the causticizer. Partial autocausticizing is especially attractive for the mills with a reduced capacity of lime production because it allows higher caustic production without increasing the lime demand. The scheme of recovery process in the kraft mill with partial borate-based autocausticizing is shown in Fig.II.3.

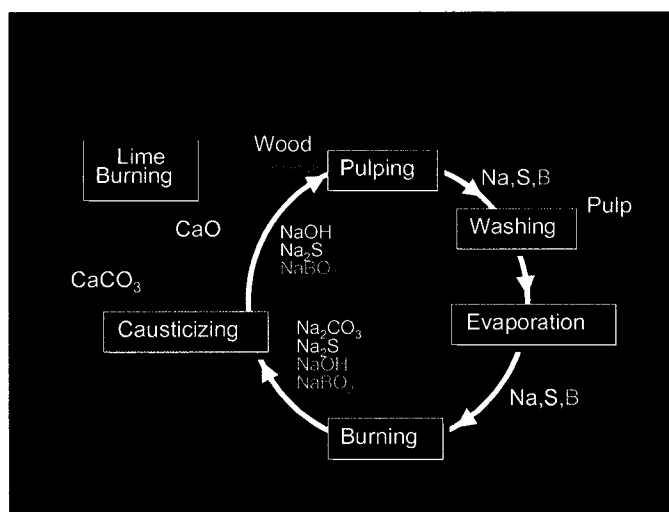
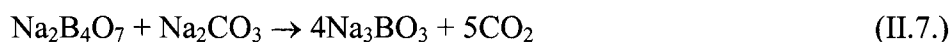


Figure II.3. Kraft Recovery Process with Partial Borate-Based Autocauticizing

As a result of these new findings, a series of partial borate-based autocauticizing trials has been conducted using sodium tetraborate pentahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \times 5\text{H}_2\text{O}$) as an autocauticizing agent (Hunter et al., 2000). Sodium tetraborate was used instead of sodium metaborate because it is capable of performing decarbonization of sodium carbonate in the recovery boiler (reaction II.7.) as sodium metaborate (reaction II.5.), but has the lower Na/B ratio and lower cost (Tran et al., 1999).



Decarbonization of sodium carbonate by sodium tetraborate (reaction II.7.) results in trisodium borate, which hydrolyzes producing sodium metaborate and sodium hydroxide (reaction II.6.). The two-step autocauticizing stoichiometry proposed by the reactions II.5., 6. and II.7., 6. indicates that regardless of the starting material used for borate-based autocauticizing, autocauticizing reactions result in

sodium metaborate. Therefore, the borate-based autocausticizing produces sodium metaborate, which circulates throughout the system and represents an additional chemical during kraft pulping.

One of the first trials was conducted at Georgia-Pacific Corporation, Camas mill, which, at that time, had a production of 1300 tons/day of bleached kraft pulp. The trials lasted for a period of over 16 months and they were conducting at increasing level of autocausticizing from 5 % to 25 %. Sodium tetraborate pentahydrate was introduced into the liquor system in the amount ranged between 0 and 16 tons/day, with average of 1.6 tons/day. This corresponds to 470 lbs of boron. A boron loss during the trial was about 2.5 % (11.75 lbs B/day in average, which corresponds to 0.04 tons $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ /day). More than 80 % of the total boron loss was attributed to the normal washing losses, spills, and leaks, which are typical for a kraft mill. Less than 2 % of the total boron loss was with pulp. It is in accordance with the low level of boron found in the unbleached pulp at 18 % autocausticizing – 35 ppm, which corresponds to 213 ppm of NaBO_2 . The addition of sodium tetraborate pentahydrate was effective in the production of sodium hydroxide and, hence, in the reduction of the amount of lime. Sodium metaborate resulted from the autocausticizing reactions (reaction II.7., 6.) did not affect the quality of pulp regarding viscosity, brightness, and strength (Hunter et. al., 2000).

The trials performed at different levels of borate-based autocausticizing in other mills confirmed that partial autocausticizing reduces the lime consumption without change of the pulp quality. Therefore, a mill, in which 10 % autocausticizing

was trailed for three months, decided to transfer this autocausticizing trail to a commercial application (Kochesfahani, Bair, 2002).

Borate-based autocausticizing has also been included in the current program “The Eco-cyclic Pulp Mill,” which has a goal to propose the alternative ways to improve the efficiency of the kraft process. Developing a complete eco-cyclic system for high quality paper products, Axegård et al. (2002) compared the efficiency of the “Reference Mill” representing the most recent technology in commercial operation in Finland and Sweden, with the efficiency of future “Model Mills.” “Model Mills” included at least one of the sub-processes aimed at improving technology, but not yet commercially implemented. Direct causticizing using borates was proposed as a way to simplify the recovery system with simultaneous reduction of capital investment, net operating costs, emission of “fossil” CO₂, and solid waste. Partial borate causticizing was recommended as the short-term goal (in 1-5 years), while 100 % borate causticizing was recommended as a long-term goal (in ≥ 10 years). The results of “The Eco-cyclic Pulp Mill” program corroborated the results of partial borate autocausticizing trials and indicated a need for further studies in this area.

Implementation of either partial or total borate-based autocausticizing brings a new chemistry into the system. Therefore, its effect on the efficiency of pulping and the operation of recovery line should be evaluated.

In the mill trials conducting partial borate autocausticizing (10 to 25 % autocausticizing level), the operation of recovery line was stable and only minor

adjustments were required. However, further studies and improvements in this area are required (Hunter et al., 2000, Tran et al., 2002, Kochesfahani, Bair, 2002).

The effect of an additional chemical, sodium metaborate in the white liquor on the kraft pulping was studied earlier (Janson, 1980, Prihoda et al., 1996). However, the level of sodium metaborate used in these studies corresponded to the stoichiometry of borate autocausticizing reactions suggesting that one mole of sodium metaborate is needed to regenerate one mole of sodium hydroxide (Janson, 1977, 1979a). The presence of such a high level of sodium metaborate caused a retardation of the kraft pulping of two softwood species (black spruce and pine) (Janson, 1980, Prihoda et al., 1996) and an improvement of the birch kraft pulping (Janson, 1980). These opposite effects of sodium metaborate were discussed either by an increased ionic strength of the pulping liquor (retardation) or by the buffer capacity of borate, which maintains the high alkalinity (improvement).

The opposite effects of sodium metaborate on the pulping of different wood species noticed by Janson (1980) and Prihoda et al. (1996) might also result from the different interactions between sodium metaborate, and the softwood and hardwood wood main chemical constituents. The reactions between sodium metaborate and the main wood constituents, lignin and hemicelluloses were confirmed in previous studies (Lundquist et al., 1995, Vuorinen, Alén, 1999). The formation of a complex between the arylglycerol β -aryl ether structure as a dominant lignin structure and borates was discussed and the different stability of the *erythro* and *threo* form of this complex was proposed (Lundquist et al., 1996). The *erythro* form of arylglycerol β -

aryl ether structure dominates in the hardwood lignins, while almost the same amount of the *erythro* and *threo* form of this structure is present in the softwood lignins (Brunow et al., 1992). Therefore, the different mixtures of *erythro* and *threo* isomers of the arylglycerol β -aryl ether structure found in the hardwood and softwood lignins may lead to differences in the kraft-borate pulping of hardwoods and softwoods (kraft-borate pulping is kraft pulping in the presence of sodium metaborate). Also, borates react with the hydroxyl groups of (galacto)glucomannans (with the vicinal hydroxyl groups of mannose units at C-2 and C-3 positions) and this reaction has been broadly used in the fractionation/purification of hemicelluloses (Vuorinen, Alén, 1999).

In a series of pulping experiments Janson (1978) increased the Na:B ratio from 1.72 to 2.27 (for example, Na:B = 2; mole NaBO_2 per mole NaOH; total solids 105.8 g) and found an increased delignification rate, i.e. delignification increased with the increasing of Na:B ratio in cooking liquor. According to the results of Tran et al. (1999), the Na:B ratio = 3 is required in total borate-based autoausticizing (0.5 mole NaBO_2 per mole NaOH; total solids 72.9g), while this ratio is higher and dependent on the level of autoausticizing in partial autoausticizing. The newly proposed and higher values of the Na:B ratio are expected to have lower effect on delignification than was observed earlier (Janson, 1980, Prihoda et al., 1996). The corresponding decrease of total solids in cooking liquor is expected to lead to a smaller increase in solids content, boiling point rise, and viscosity of black liquor than estimated earlier (Grace, 1981, Janson, Söderhjelm, 1988).

The major objectives of this thesis were to determine the effects of sodium metaborate on the kraft pulping of black spruce (*Picea mariana*), paper birch (*Betula papyrifera*), and sugar maple (*Acer saccharum*). Spruce and birch were selected because previous studies showed the opposite effects of sodium metaborate on the kraft pulping of these two species (Janson, 1980, Prihoda et al., 1996). Maple was selected, as this is one of the most abundant hardwood species in Michigan and frequently used as a pulpwood. Before pulping, the chemical composition of the spruce, maple, and birch woodchips was determined (Dence, 1992, Fengel, Wegener, 1984, Browning, 1967, Iiyama, Wallis, 1988, Bethge, 1964).

In order to evaluate the effects of sodium metaborate on kraft pulping, a comparative analysis of kraft and kraft-borate pulping was performed. Kraft-borate pulping was conducted in the same conditions as kraft pulping, except that white liquor contained sodium metaborate in the amount corresponding to both the desired autocausticizing level and the stoichiometry of the autocausticizing reactions (reactions II.5., 6.). The spruce pulping experiments included pulping at the increasing borate level, corresponding to the increasing partial autocausticizing from 0 to 52 %. In this series of experiments, the controlling pulping parameters, H-factor, sulfidity, active alkali charge, temperature, and wood/liquor ratio were constant. These preliminary experiments studied the effect of the increasing content of sodium metaborate in the white liquor. Then, the kraft-borate pulping experiments using birch, maple, and spruce were performed with the white liquor containing sodium metaborate, in the amount corresponding to 35 % autocausticizing. The 35 %

autocausticizing was chosen since this is a significant autocausticizing level, which is not expected to cause problems in the evaporation and pumping of black liquors (Tran et al., 2002). Pulping was characterized by the yield of pulping, including the screened pulp yield and rejects, and by the kappa number (TAPPI Test Methods, 1991). The chemical and mechanical properties of pulps were determined. The analysis of chemical composition of pulps included determination of the contents of lignin (Klason lignin, acid-soluble lignin), holocellulose, pentosans, extractives, hexenuronic acid groups, and phenolic hydroxyl groups (TAPPI Test Methods, 1991, Useful Methods, 1990, Browning, 1967, Bethge, 1964, Chai et al., 2001, de Sousa et al., 2001). These results and the results obtained in the studies of the chemical composition of birch, maple, and spruce were used to calculate the delignification rate and selectivity of pulping with and without sodium metaborate. Density and tensile and tear strength were measured after the PFI laboratory milling of the kraft and kraft-borate pulps, while “beatability” of the pulps was estimated by the CSF values before and after milling (TAPPI Test Methods, 1991).

Any change in the delignification chemistry caused by the presence of sodium metaborate in the white liquor would affect the structure of both residual (lignin remaining in pulp) and kraft (lignin dissolved in cooking liquor) lignins. Therefore, the residual lignin from the spruce kraft and kraft-borate pulps (H-factor 2,000) was isolated by acid hydrolysis using both the standard procedure (Gellerstedt et al., 1994) and the two-step procedure which efficiency was verified in this thesis. Kraft lignin from the kraft and kraft-borate liquors of birch, maple, and spruce (H-factor 1,500)

was isolated by acidification (Lin, 1992). The obtained kraft and kraft-borate residual and kraft lignin samples were characterized by analytical methods and FTIR spectroscopic analysis and compared (Dence, 1992, Iiyama, Wallis, 1988, de Sousa et al., 2001, Tamminen, Hortling, 1999, Faix, 1991, Faix et al., 1992, Wegener, Strobel, 1992).

As the boiling point rise (BPR) is an important property of black liquor that controls the efficiency of the evaporation phase, the experiments of this thesis included the measurements of BPR. The BPR of the laboratory kraft and kraft-borate (35 % autocausticizing) black liquors of birch, maple, and spruce (H-factor 1,500), and the slash pine commercial black liquor was measured. The BPR of the commercial black liquor was measured before and after addition of different amounts of sodium metaborate that corresponded to the different levels of autocausticizing. Two series of experiments were performed. The first series was conducted at atmospheric pressure, in accordance with the method recommended by Frederick et al. (1980). In the case of the commercial black liquor, these experiments were also designed to examining the effect of sodium metaborate on the solubility limit of black liquor (Zaman et al., 1998). The second series was conducted at elevated pressure and temperature (Peters, 1984). This series of experiments used the commercial slash pine black liquor, with and without sodium metaborate.

In order to estimate the effect of sodium metaborate on viscosity of the black liquor resulting from the kraft process with implemented borate-based

autocausticizing, the viscosity of commercial slash pine black liquor with and without sodium metaborate was analyzed.

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CHAPTER III

EXPERIMENTAL

The U.S. Forest Products Laboratory, Madison, Wisconsin provided the woodchips for the experiments of this thesis. The woodchips were obtained from paper birch (*Betula papyrifera*), sugar maple (*Acer saccharum*), and black spruce (*Picea mariana*) trees grown in northern Minnesota. The chips were stored at 8 °C and used for pulping experiments.

Wood Chemical Composition

Before the pulping experiments, the chemical composition of the woodchips was determined using the classical wet-chemistry methods of wood analysis, combined with UV spectrophotometry. The preparation of wood for chemical analyses included grinding of woodchips (T257 cm-85) and successive extraction of the ground wood (40 mesh) with ethanol/cyclohexane (1:2; 8 h) and ethanol (8 h) (T204 om-88). Cyclohexane was used instead of benzene, as recommended by Fengel and Przyklenk (1983). At the same time, the content of extractives soluble in these solvents was determined. The extractive-free wood was used for the determination of the contents of holocellulose, pentosans, and lignin (Klason, acid-soluble, acetyl-bromide).

The content of holocellulose (wood polysaccharides, cellulose and hemicelluloses) was determined by wood delignification with acidified sodium chlorite – acid-chlorite method (Browning, 1967, Fengel, Wegener, 1984).

The analysis of the pentosan content was performed by the conversion of the pentosans to furfural by hydrobromic acid (3.18 M HBr; Bethge, 1964). The furfural concentration was measured using the UV spectrophotometric method (Browning, 1967). The furfural calibration graph and the absorptivity value at 277.5 nm were obtained using the commercial chemical - 2-furaldehyde, 99 % Aldrich. In the UV-spectrophotometric studies of this thesis, including the furfural measurements, the Lamber-Beer law was used to calculate concentration of the absorbing compound:

$A = abc$ – Lambert-Beer law; a , (molar) absorptivity of the compound at a wavelength of the maximum absorption, $\text{Lg}^{-1}\text{cm}^{-1}$ ($\text{Lmol}^{-1}\text{cm}^{-1}$); $b = 1$ cm, the length of the light path; c , concentration of the compound, gL^{-1} (molL^{-1}). The absorptivity values were either accepted from the literature or calculated using the UV-results and the Minitab statistical program. The calculated furfural absorptivity was

$$a_{\text{furfural}, 277.5} = 6.18 \times 10^{-3} \text{ Lg}^{-1}\text{cm}^{-1}.$$

The lignin content was determined as the acid-insoluble, Klason lignin, according to the Klason method (Dence, 1992). The acid-soluble lignin present in the hydrolysate after the removal of solid Klason lignin was measured by UV-spectrophotometry ($\lambda = 205$ nm, $a = 110 \text{ Lg}^{-1}\text{cm}^{-1}$) (Dence, 1992). Additionally, the lignin content was analyzed by the acetyl bromide method, developed by Iiyama and Wallis (1988). According to this method, wood is treated with acetyl bromide in

acetic acid, in the presence of perchloric acid. The resulting solution absorbs UV light with absorption maximum at 280 nm, which is proportional to the lignin content. The lignin absorptivity value of $20.09 \text{ Lg}^{-1}\text{cm}^{-1}$, which was used in these experiments, was recommended for both softwood and hardwood samples.

Pulping Experiments

The kraft and kraft-kraft borate pulping experiments were performed using the maple, birch, and spruce woodchips after hand-sorting during which bark, knots, fines, and defective and oversized chips were removed. Then, the moisture content of the chips was determined (T 258 om-89). The laboratory pulping was conducted in an M/K digester (Mini-Mill Laboratory Digester, Systems Inc. Danvers, MA) using 500 g OD woodchips, at liquor:wood ratio 4:1 and 16.5 % active alkali charge.

Pulping Temperature and H-factor

The pulping experiments were performed at the maximum (cooking) temperature of 170°C . Time at the maximum temperature was calculated in accordance with the concept of H-factor (Vroom, 1957). During the heating period the vent line valve at the top of the digester was open up to 100°C ; at 100°C the valve was closed and further heating and cooking at the maximum temperature were performed with the valve closed. Upon completion of the pulping, the heaters were turned off, and the cooling period was performed with the vent line valve gradually opened up. It was completely open at 100°C ; then, the pump was stopped and black

liquor was collected under the vent line, by opening the bottom drain valve. The H-factor gained during heating from 100 °C to 170 °C was in average 80 (n=52 - number of cooking experiments, st. dev = 5.95), the same as the H-factor gained during cooling from 170 °C to 100 °C (n=52, st. dev =7.87). The H-factors used in the kraft and kraft-borate pulping of birch, maple, and spruce are shown in Table III.1.

Table III.1.

H-factors Used in the Birch, Maple, and Spruce Kraft and Kraft-Borate Pulping Experiments

Species	H-Factor							
	250	500	750	1000	1500	2000	2500	3000
Birch	X	X	X*	X	X			
Maple	X	X*	X*	X	X			
Spruce		X		X*	X	X*	X	X

*the experiments performed twice under the same conditions

White Liquor Parameters

The kraft and kraft-borate white liquors were prepared for the major part of experiments in the laboratory, by dissolving of the commercial analytical grade chemicals in water. A series of the experiments was performed using the white liquor produced in the laboratory, by causticizing. The causticizing experiments were performed using analytical grade sodium carbonate, sodium borate, sodium sulfide, and industrial burnt lime. Cameron et al. (2002) published earlier the details on the preparation of the white liquor by causticizing.

The white liquor parameters, sulfidity, and sodium hydroxide and sodium carbonate concentration were the same for the kraft and kraft-borate white liquors.

The kraft borate liquors contained sodium metaborate in the amount needed to provide for a desired level of autocausticizing, according to the stoichiometry of borate-based autocausticizing, as explained in Chapter II (equations II.5.,6.). The sodium metaborate source was sodium metaborate dihydrate ($\text{NaBO}_2 \times 2 \text{H}_2\text{O}$) supplied by US Borax Inc. (product name: sodium metaborate 4mol technical (4046), Test sample). The white liquor parameters were determined by using a dual-titrator ion analyzer developed by U.S. Borax Inc. The method used in this analyzer is a variant of the standard ABC titration method and it is performed in two steps (Tran et al., 2002). The first step is the titration of the ammonia solution of white liquor with silver nitrate; this step measures the sulfide concentration (1 ml/200 ml 0.1 M NH_4OH ; 0.1.M AgNO_3)). The second step is the titration of water solution of white liquor with hydrochloric acid; this step measures the concentrations of sodium hydroxide, sodium carbonate, and sodium metaborate (5ml/ 200 ml DI water; 0.1.M HCl). The parameters of the white liquors prepared either by dissolving or by causticizing were approximately the same and they are shown in Table III.2.

The concentration of sodium metaborate in the kraft-borate white liquor depends on the desired level of autocausticizing. A series of the spruce kraft-borate experiments at an H-factor of 2,000 was performed with the white liquors containing increasing concentration of sodium metaborate, which corresponded to the increasing level of autocausticizing from 10 to 52 %. The major part of the birch, maple, and spruce kraft-borate pulping experiments was conducted with the white liquor containing the sodium metaborate at the level corresponding to the 35 %

autocausticizing. The sodium metaborate concentrations used in the kraft-borate pulping experiments and the autocausticizing levels are shown in Table III.3.

Table III.2.

Parameters of the Kraft and Kraft-Borate White Liquors

White liquor prepared by	Sulfidity, % (n; SD)	NaOH, g/L As Na ₂ O (n; SD)	Na ₂ CO ₃ , g/L as Na ₂ O (n; SD)
Dissolving chemicals in water	27.2 (45; 0.314)	93.4 (45; 0.600)	22.46 (45; 0.758)
Causticizing	27.81 (3; 1.04)	92.98 (3; 1.03)	20.29 (3; 1.66)

n– total number of the white liquors prepared; SD – standard deviation

Table III.3.

Concentrations of Sodium Metaborate in the Kraft-Borate White Liquors and the Corresponding Autocausticizing Levels

White liquor prepared by	Autocausticizing Level, %					
	10	20	35	43	45	52
	NaBO ₂ g/L, as Na ₂ O					
Dissolving chemicals in water	4.7	9.4	16.4	20.1		24.3
Causticizing			16.3		21	

Characterization of Kraft and Kraft-Borate Pulps

The pulps were washed with cold water, disintegrated in the laboratory blender, and screened on the vibrating screen (0.016”) using cold water. Using the pulp centrifugal extractor, the pulps were dewatered to approximately 27 % OD fiber. The screened yields and rejects were calculated after weighting and moisture content determination (T 412 om-90). The pulps were stored at 8 °C.

The pulps were characterized using the standard TAPPI methods, listed in Table III.4. These methods included the laboratory refining of pulps and preparation of handsheets for brightness measurements and pulp physical testing.

The data obtained in the birch, maple, and spruce kraft and kraft-borate (35 % autocausticizing) pulping experiments were statistically analyzed to evaluate the effect of sodium metaborate on the pulping yield (screened yield and total yield) and delignification rate (the kappa number dependence on H-factor). The statistical analysis included the test of the equality of coefficients of different regressions (Pindyck, Rubinfeld, 1991).

The chemical composition of the pulps was analyzed and the contents of extractives, holocellulose, pentosans, hexenuronic acid groups, and phenolic hydroxyl groups were determined. The methods of the extractives, holocellulose and pentosan content determination were the same as those used during the determination of wood chemical composition (T 204 om-88, Browning, 1967, Fengel, Wegener, 1984, Bethge, 1964). The hexenuronic acid group (HexA) content in pulps was determined in accordance with the method recently developed by Chai et al. (2001). This method is based on a highly selective hydrolysis of HexA in a solution of mercuric chloride and sodium acetate (22 mmol/L, i.e. 0.6 % HgCl_2 and 0.7 % CH_3COONa) and UV-spectrophotometry of the obtained hydrolysate. The HexA content in pulp is calculated as

$$C_{\text{HexA}} = 0.287V (A_{260} - A_{290})/w \quad (\text{III.1.})$$

where

0.287 $\mu\text{mol/mL}$ - the calibration factor obtained by Chai et al. (2001);

V- volume of the hydrolysis solution, mL;

w – oven-dry weight of pulp, g;

A_{260} , A_{290} - absorption intensities at 260 and 290 nm, respectively;

C_{HexA} – content of hexenuronic acid groups in pulp, $\mu\text{mol/g}$.

Table III.4.

TAPPI Methods Used to Characterize the Kraft and Kraft-Borate Pulps

Method Title	TAPPI Method #
Kappa number of pulp	T 236cm-85
Viscosity of pulp (capillary viscometer method)	T 230 om-89
Acid-insoluble lignin in wood and pulp	T 222 om-88
Acid-soluble lignin in wood and pulp	UM 250
Forming handsheets for reflectance tests of pulp	T 205 om-88
Brightness of pulp, paper and paperboard (directional reflectance at 457 nm)	T 452 om-87
Laboratory beating of pulp (PFI mill method)	T 248 cm-85
Freeness of pulp	T 227 om-85
Physical testing of pulp handsheets	T 220 om-88
Internal tearing resistance of paper (Elmendorf-type method)	T 414 om-88
Tensile breaking properties of paper and paper-board (using constant rate of elongation apparatus)	T 494 om-88

The phenolic hydroxyl group (PhOH) content of pulps was determined using the reagent of Folin and Ciocalteu, heterophosphotungstate-molybdate (Folin & Ciocalteu's reagent, 2.0 N; Sigma). The FC reagent oxidizes the PhOH groups producing the blue chromophore with absorption at 760 nm that is proportional to the total amount of phenolic hydroxyl groups (de Sousa et al., 2001). Vanilin was used for the calibration purposes and calibration was included within each group of samples (vanilin, 4-hydroxy-3-methoxy benzaldehyde, Sigma). The vanilin molar

absorptivity of $13.11 \text{ Lmmol}^{-1}\text{cm}^{-1}$ (st. dev. = 0.393) was obtained in four series of experiments. This value agrees with the vanillin molar absorptivity obtained by Singleton et al. (1999) ($14.9 \text{ Lmmol}^{-1}\text{cm}^{-1}$). Based on the absorption of pulp solution obtained after the treatment with the FC reagent and the calibration diagram, the PhOH group concentration in the pulp solution was calculated. The PhOH group content as mmol per gram lignin was calculated by taking into account the pulp lignin content (total lignin content in pulp = Klason + acid-soluble lignin).

The bleachability of the spruce kraft and kraft-borate pulps was studied in the two-step acid-chlorite delignification. After extraction, the pulps were delignified to either a high or a low bleaching level. For the high level of bleaching (HLB), the pulps were delignified in accordance with the acid-chlorite method of holocellulose isolation (Browning, 1967). This procedure followed the recommended time and temperature (70-80 °C for 5 hours). For the low level of bleaching (LLB), the time and temperature were reduced to one hour, at 65 °C. Brightness (T452 om-87), kappa (T 236 cm-85), and viscosity (T 230 om-89) of both HLB and LLB were measured and compared with the corresponding values obtained for unbleached pulps.

Characterization of Residual Lignin

The spruce kraft and kraft-borate (at 35 % autocausticizing) pulps obtained at an H-factor of 2,000 were used for the residual lignin isolation. These pulps were exhaustively extracted in a multi-step extraction in order to remove the compounds, which might dissolve with lignin during its isolation and disturb its analysis. The

solvents included acetone, dichloromethane, ethanol (8 h each, Soxhlet apparatus), and cold water (48 h). The residual lignin isolation was performed by acid hydrolysis, following the standard method proposed by Gellerstedt et al. (1994). Additionally, a two-step acid hydrolysis procedure aimed toward studying the effect of high temperature on the residual lignin isolation was developed. The first step of this procedure was the same as the original procedure except that hydrolysis was performed in an ultrasonic bath, at 20 °C, without the nitrogen current (treatment of extracted pulp with hydrochloric/dioxane:water (0.1.M HCl in dioxane:water (88:12))). The first fraction of pulp lignin was further isolated in accordance with the steps described in details in the standard procedure (Gellerstedt et al. 1994). The second fraction of residual lignin was isolated from the pulp residue obtained in the first step following the standard procedure (reflux under nitrogen for 2 h in 0.1 M HCl in dioxane/water (82/18)). The lignin isolation yields were measured and compared.

The pulps residues obtained after standard acid hydrolysis, and those obtained after the first and second step of the two-step procedure were analyzed to determine brightness (T 452 om-87), kappa number (T 236 cm-85), and the contents of Klason lignin, acid-soluble lignin (Dence, 1992), and PhOH groups (de Sousa et al., 2001). The residual lignin samples were analyzed to determine the contents of lignin and PhOH groups.

The Klason and acid-soluble lignin content was determined for the residual lignin samples isolated by standard acid hydrolysis (total lignin = Klason lignin + acid-soluble lignin). Afterwards, the same residual lignin samples were used to

determine the absorptivity of residual lignin. These samples (~0.002 g) were dissolved in the acetyl bromide/glacial acetic acid solution (25 % (w/w) AcBr in CH₃COOH; 5 ml) containing perchloric acid (0.2 ml 70 % HClO₄ in 5 ml of solution), in accordance with the acetyl bromide method of the lignin content determination (Iiyama, Wallis, 1988). UV absorbance of the obtained lignin solutions was measured at 280 nm and the absorptivity of residual lignin was calculated. The obtained value of 24.8 Lg⁻¹cm⁻¹ agreed with the pine kraft lignin absorptivity proposed by Marton (1965) (25.0 Lg⁻¹cm⁻¹) and was used during the acetyl bromide determination of the lignin content in the residual lignin samples isolated in the two-step acid hydrolysis.

The content of PhOH groups in the residual lignin samples was analyzed using the reagent of Folin and Ciocalteu (de Sousa et al., 2001). Additionally, in order to compare the different methods of the PhOH group content determination, the content of the PhOH groups (mmol/g lignin) was calculated based on the FTIR spectra of the acetylated samples and equations recommended by Faix et al.(1992) (eq. III.2.) and Wegener and Strobel (1992) (eq. III.3.). These equations use the normalized absorption of the phenolic and aliphatic hydroxyl groups at 1765 cm⁻¹ and 1745 cm⁻¹, respectively.

$$\text{PhOH} = 0.588 [5.66 (A_{1765}/A_{1745}) - 1.37] \quad (\text{III.2.})$$

$$\text{PhOH} = 0.588 [14.75 A_{1765}/(A_{1765}+A_{1745}) - 3.45] \quad (\text{III.3.})$$

Acetylation of the lignin samples was performed with acetic anhydride/pyridine (1:1, v/v), as recommended by Lundquist (1992).

Characterization of Kraft and Kraft-Borate Black Liquors

The black liquor samples analyzed in these experiments were of two origins. The birch, maple, and spruce kraft and kraft-borate (35 % autocausticizing) black liquors were collected during the laboratory pulping experiments pulping at an H-factor of 1,500 – laboratory black liquors. Slash pine kraft black liquor was obtained from International Paper Co. – commercial black liquor. Solids content of the black liquors was measured using the TAPPI standard method (T 650 om-89). The black liquors were stored at 8 °C.

Characterization of Kraft Lignin

Kraft lignin was isolated from the laboratory black liquors. Isolation was performed by acidification of black liquor with 20 % sulfuric acid in the two-step procedure recommended by Lin (1992). Before acidification, the black liquors were concentrated to the solids content of about 40 % by evaporation in a rotary evaporator at 30 °C. After isolation, kraft lignin was extracted in n-pentane (8h, Soxhlet extractor) in order to remove low-molecular weight compounds (Gellerstedt et al., 1994).

Kraft lignin was analyzed by FTIR spectroscopy. The lignin condensation index, CI was calculated according to Faix's equation (1991), which uses the FTIR

absorption maximums (A_{\max}) and minimums (A_{\min}) to evaluate the total number of carbon-carbon bonds between the lignin units (C3-C5, C β -C5, C-C bonds via C2 or C6) (eq. III.4.).

$$CI = \sum A_{\min \text{ between } 1500 \text{ and } 1050 \text{ cm}^{-1}} / \sum A_{\max \text{ between } 1600 \text{ and } 1030 \text{ cm}^{-1}} \quad (\text{III.4.})$$

Kraft lignin was also analyzed for the content of PhOH groups using the FC reagent (de Sousa et al., 2001).

Boiling Point Rise

Boiling point rise (BPR) is the difference between the boiling point of the solution and that of the pure solvent. It is a colligative property, depending upon the solution molality and the solvent properties. The BPR of the black liquor samples was measured in two series of experiments. The first series of experiments was performed at atmospheric pressure, while the second series of experiments was performed at elevated pressures and temperatures. The details explaining both methods and the equipment used in the BPR measurements are presented in the V-1 paper of this thesis (Effect of Sodium Metaborate on the Boiling Point Rise of Slash Pine Black Liquor).

Boiling Point Rise at Atmospheric Pressure

The dependence of the black liquor boiling point rise on the black liquor solids concentration is described by equation III.5., suggested by Frederic et al. (1980).

$$\Delta T_B = K_B S / (1-S) \quad (\text{III.5.})$$

ΔT_B -boiling point rise;

S - solids content of liquor;

K_B – constant, dependent on the composition of the black liquor.

However, it was noticed that eq. III.5. applies only to black liquor below the solubility limit (SL), i.e. the slope of the BPR curve decreases abruptly when the SL is reached. Therefore, Zaman et al. (1998) divided the BPR curves into two parts and suggested two linear equations III.6. and III.7. to describe the first and second part, respectively:

$$\text{BPR} = a S / (1-S) \quad (\text{III.6.})$$

$$\text{BPR} = b' + a' S / (1-S) \quad (\text{III.7.})$$

The parameters a, a', and b' (eq. III.6., 7.) are the pressure dependent constants varying from liquor to liquor because of the differences in the composition of the liquors. The solids content at the breaking point is that of the liquor at saturation, i.e. it is the solubility limit concentration.

The boiling point rise of the laboratory and commercial black liquors was measured by the method described by Frederick et al. (1980). The data obtained during evaporation of the laboratory black liquors were analyzed using the Minitab statistical program.

The test involving the equality of coefficients of different regressions (Pindyck, Rubinfeld, 1991) was used to show whether the BPR of the laboratory kraft and kraft-borate black liquors can be described by the same regression model or two

different regression models must be applied. The increase of the BPR for the birch, maple, and spruce black liquor in the presence of sodium metaborate at the 35 % autocausticizing was estimated.

The BPR of pure commercial liquor and commercial liquor containing different levels of sodium metaborate was measured during the evaporation and dilution cycles. Sodium metaborate was added into the black liquor to correspond 30, 60, or 120 % autocausticizing and the amount was calculated based on the composition of the black liquor solids and the borate-based autocausticizing reactions (Ch. II, reactions 5,6). The calculation is explained in detail in the V-1 paper of this thesis (Effect of Sodium Metaborate on the Boiling Point Rise of Slash Pine Black Liquor). The data obtained in these experiments were processed in accordance with the equations III.6.,7., separately for the evaporation and dilution cycle. The corresponding values of SL were also calculated and compared. In the following experiments, sodium carbonate, sodium sulfate, and calcium carbonate as the inorganic salts known to cause scaling in the kraft evaporators were added to the commercial black liquor. The effect of sodium metaborate on the BPR and SL of the resulting black liquor samples was evaluated.

Boiling Point Rise at Elevated Pressures and Temperatures

The boiling point rise due to material in solution can be also defined as the actual temperature of the mixture minus the temperature of the pure solvent if it exerted the same vapor pressure as the mixture. Dühring's rule, as described by

Peters (1984), is used to show the effect of dissolved materials on the boiling point rise. This rule states that a plot of the temperature solution versus that of the reference solvent, where both the reference solvent and the solution exert the same pressure, results in a straight line. As described by Peters, pure water is often used as the reference solvent.

The pressure-temperature relationship for the commercial black liquor samples was measured using a pressurized reactor. The original black liquor (19.3 % solids content) was concentrated to 40 and 60 %. The vapor pressure was measured as a function of temperature for the three different black liquor samples of increasing solids content (19.3, 40, 60 %) with and without sodium metaborate. The results were processed using the Minitab statistical program and the linear equations were derived.

Viscosity

Viscosity is defined as the ratio of the shear stress to the shear rate for a fluid subjected to a shearing force. For black liquor it varies strongly with the concentration and the temperature. The origin of the black liquor including the wood raw material and degree of delignification can also be of great significance.

In these studies the viscosity of the commercial black liquors samples with and without sodium metaborate was measured. Before the viscosity measurements, the samples were concentrated to 65 % solids content. Three levels of sodium metaborate added to the commercial black liquors corresponded to the

autocausticizing levels of 30, 60 and 120 %. The viscosity measurements were conducted at temperatures between 70 and 75 °C, using couette geometry with a Rheometric Scientific SR-5000 viscometer.

Statistical Analysis of Data

The statistical analysis of the data obtained in these experiments was performed using the Minitab statistical program. The analysis included the test of the equality of coefficients of different regressions (Pindyck, Rubinfeld, 1991). The purpose of the test is to evaluate if two sets of data, in this case the kraft and kraft-borate pulping/black liquor data, can be described by single regression model or two regression models better explain them. The test is based on the null hypothesis, which represents the single equation and the alternative hypothesis, which represents two individual equations. The sum of the error sums of squares of individual equations ($ESS_{UR} = ESS_1 + ESS_2$) is compared with that of the single equation (ESS_R) according to the appropriate F statistic at the 5 % level of significance. The appropriate F statistic is described by equation III.8.,

$$F_{k, N+M-2k} = [(ESS_R - ESS_{UR})/k]/[ESS_{UR}/(N+M-2k)] \quad (III.8.)$$

where

N, M - number of observations in the two sets of data,

k – number of coefficients in the regression model.

If the calculated F statistic is larger than the critical value of the F distribution with k and N+M-2k degrees of freedom, the null hypothesis can be rejected implying that two separate regressions must be estimated (the data cannot be pooled).

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CHAPTER IV

EFFECT OF SODIUM METABORATE ON THE PULP PROPERTIES AND KRAFT PULPING OF BIRCH, MAPLE, AND SPRUCE

Spruce Pulping at Increasing Autocauticizing Level (H-Factor 2,000)

The effect of sodium metaborate on spruce kraft pulping was studied in a series of pulping experiments at a constant H-factor of 2,000 and at increasing levels of sodium metaborate. Kraft-borate (KB) pulping experiments were performed at the corresponding 10, 20, 35, 43, and 52 % level of autocauticizing. These experiments included kraft (K) pulping in the same conditions regarding H-factor, sulfidity, liquor to wood ratio, active alkali charge, and temperature. The white liquor for kraft and kraft-borate pulping was prepared by dissolving of the commercial chemicals in water. The resulting screened yield, total yield, and kappa number are shown at the different autocauticizing levels in Figure IV.1.

The average values of screened and total yields, rejects, kappa number, and brightness obtained in spruce kraft and kraft-borate (10, 20, 35, 43, 52 % autocauticizing) pulping are shown in Table IV.1. Both total and screened yields of kraft-borate pulping are higher than of the corresponding of kraft pulping. This is a potential advantage of implementation of borate-based partial autocauticizing, which was explored further in the experiments at 35 % autocauticizing and at increasing H-factor.

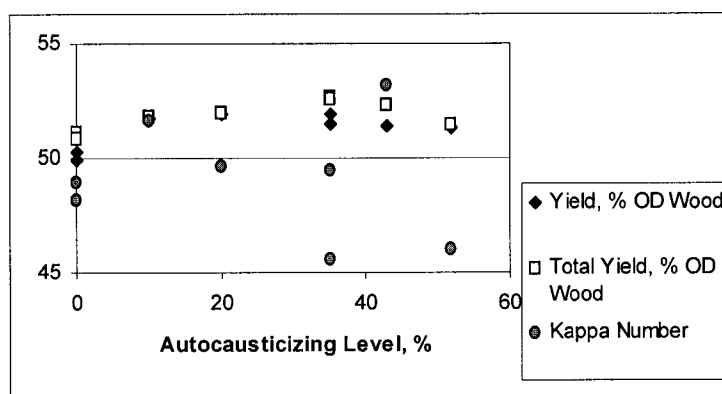


Figure IV.1. Screened Yield, Total Yield, and Kappa Number Obtained in Spruce Kraft and Kraft-Borate Pulping

A slight decrease of rejects was observed in the kraft-borate pulping. However, the corresponding high standard deviation indicated a need for additional studies in this area. The spruce kraft and kraft-borate pulping resulted in pulps of approximately the same kappa number and brightness.

Table IV.1.

Some Properties of Spruce Kraft and Kraft-Borate Pulps
Obtained at 2,000 H-factor

Pulping	Yield (SD)	Rejects (SD)	Total Yield (SD)	Kappa Number (SD)	Brightness (SD)
	% OD Wood				
Kraft ^{a)}	50.1 (0.28)	0.9 (0.14)	51.0 (0.14)	48.6 (0.52)	19.2 (0.14)
Kraft-Borate ^{b)}	51.6 (0.26)	0.53 (0.47)	52.2 (0.47)	49.3 (3.00)	19.5 (0.74)

^{a)} the average obtained for two cooking experiments

^{b)} the average obtained for six cooking experiments; cooking at 35 % autocauticizing was repeated

In order to evaluate the effect of sodium metaborate present during kraft pulping on the next, bleaching phase of pulp production, spruce kraft and kraft-borate

pulps were bleached using the method of acidic chlorite delignification. The pulps were bleached to both low (LLB) and high levels (HLB) of bleaching. Viscosity and kappa number of pulps of LLB and viscosity of pulps of HLB were measured and compared. The results of these experiments are shown in Figure IV.2.

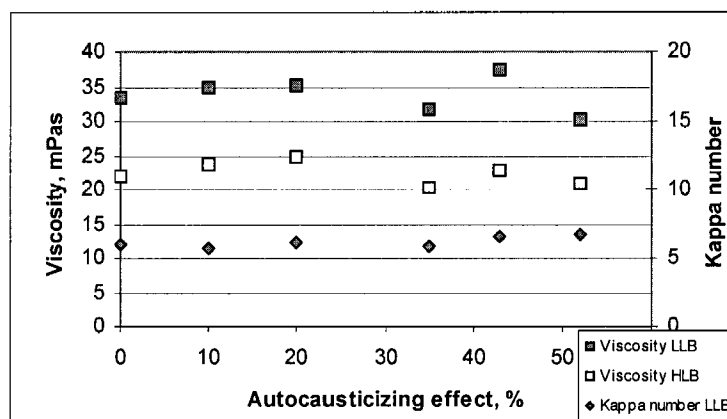


Figure IV.2. Kappa Number and Viscosity of Spruce Bleached (LLB, HLB) and Unbleached Kraft and Kraft-Borate Pulps

Brightness of unbleached pulps and pulps bleached to two bleaching levels was also measured and these results are shown in Figure IV. 3.

During bleaching to a low level of bleaching both kraft and kraft-borate pulps were delignified to the same kappa number (LLB pulps - average kappa number of pulps 6.20; st. dev. 0.39). During bleaching they retained approximately the same viscosity (LLB pulps - average viscosity of 33.9 mPa·s; st. dev. 2.6) (Fig. IV.2.). The brightness gain during this phase of bleaching was approximately the same for kraft and kraft-borate pulps as both unbleached and LLB pulps were characterized by the same brightness (unbleached pulps - Table IV.1., average brightness 19.35 (st. dev. =

0.66); LLB - average brightness 64.45, st. dev. = 2.16) (Fig. IV.3). In the continuation of bleaching to a high level of bleaching, the kraft and kraft-borate pulps were degraded to the same extent as the viscosity of pulps decreased to same value (HLB - average viscosity of 22.4 mPa·s; st. dev. 1.7) (Fig. IV.2.).

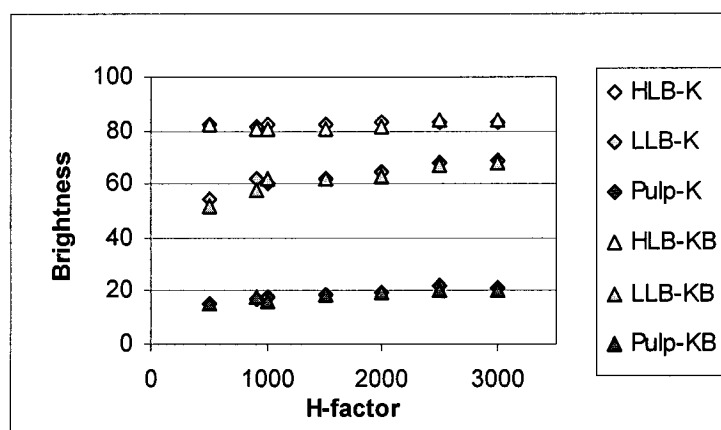


Figure IV.3. Brightness of Bleached (LLB, HLB) and Unbleached Spruce Pulps Obtained at Different Levels of Auto-causticizing

Also, the brightness gain in this phase of bleaching was approximately the same for kraft and kraft borate pulps (HLB – Fig. IV.3., average brightness 82.45, st. dev. 0.72). (Fig. IV.3.). Based on these studies, the implementation of auto-causticizing at the level from 10 to 52 % is not expected to affect the bleachability of spruce kraft pulps.

Birch, Maple, and Spruce Pulping at Increasing H-factor

The kraft and kraft-borate pulping experiments of this series were performed in the same conditions regarding the white liquor parameters, active alkali charge, liquor to wood ratio, temperature, and H-factor. The white liquor used in the kraft-borate pulping experiments contained sodium metaborate in the amount corresponding to 35 % autocausticizing.

Dependence of the screened and total yield on the kappa number obtained in kraft and kraft-borate pulping of birch, maple, and spruce was studied in these experiments. The screened yield/kappa number function is shown in Figure IV-2.2. (p.94), while the total yield/kappa number function is shown in Figure IV.4. As expected, both screened and total yields of hardwood (birch and maple) pulps are higher than the corresponding of spruce pulps at the same kappa number.

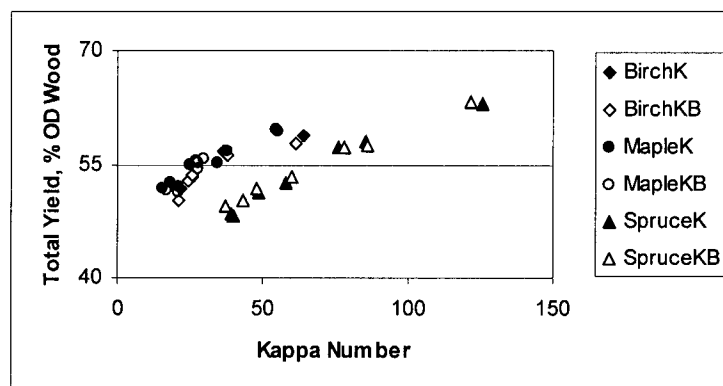


Figure IV.4. Total Yield at Different Kappa Numbers in K and KB (35 % Autocausticizing) Pulping of Birch, Maple, and Spruce

The statistical analysis of pulping results included a test of the equality of coefficients of different regressions (Pindyck, Rubinfeld, 1991). When applied on the pulping yield results, the test confirmed that sodium metaborate increases both screened and total pulp yields in spruce kraft pulping, as the results of spruce pulping at increasing autocauticizing level indicated previously. No effect of sodium metaborate was observed on the screened and total yield in birch and maple pulping experiments. The statistical data for the quadratic regression models describing the dependence of screened/total yield on kappa number are shown in Table IV.2.

Table IV.2.

Statistical Data for the Yield/Kappa Number Regression Models
($Y = a+bK+cK^2$, Y- screened or total yield, %, K- kappa number)

Spec.	K/KB	Screened Yield					Total Yield				
		Regression Model					Regression Model				
		Coefficient			Parameter		Coefficient			Parameter	
		a	b	C	σ	R^2	a	b	C	σ	R^2
Birch	K/KB	42.50	0.545	$-5.21 \cdot 10^{-3}$	0.61	93.0	41.15	0.616	$-5.43 \cdot 10^{-3}$	0.66	95.8
Maple	K/KB	45.95	0.415	$-3.72 \cdot 10^{-3}$	0.88	85.5	45.83	0.402	$-2.80 \cdot 10^{-3}$	0.76	93.1
Spruce	K	38.86	0.253	$-0.55 \cdot 10^{-3}$	0.62	99.0	35.78	0.370	$-1.22 \cdot 10^{-3}$	0.42	99.6
Spruce	KB	42.23	0.207	$-0.35 \cdot 10^{-3}$	0.54	99.1	41.85	0.221	$-0.38 \cdot 10^{-3}$	0.48	99.4

The observed yield increase in kraft-borate pulping of the softwood - spruce, but not of the hardwoods – birch and maple, might be associated with the different chemical properties of the main softwood and hardwood hemicelluloses. While the main softwood hemicelluloses, (galacto)glucomannans form the addition products with the borate ions in the reaction of the vicinal hydroxyl groups of mannose units at C-2 and C-3 positions, the main hardwood hemicelluloses, glucuronoxylans remain stable in the presence of the borate ions (Sjöström, 1981, Vuorinen, Alén, 1999).

Figure IV.5. summarizes the data for the kappa number plotted against the H-factor used in the pulping experiments. It can be noticed that kraft and kraft-borate pulping are characterized by approximately the same decreasing trend of kappa number with increasing of H-factor. As expected, the main difference can be noticed in pulping of the hardwoods – birch and maple, and the softwood – spruce.

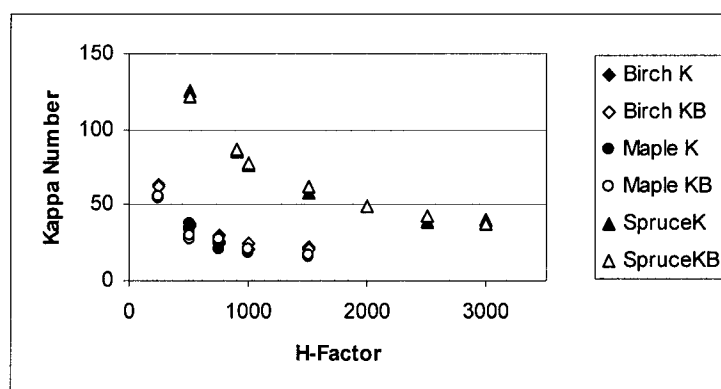


Figure IV.5. Decrease of Kappa Number with the H-factor Increase in Kraft and Kraft-Borate Pulping of Birch, Maple, and Spruce

Test involving the equality of coefficients of different regressions applied on these data showed that the same quadratic regressions can be applied on the kraft and kraft-borate (35 % autocauticizing) pulping data for the three studied species ($K = a + bH + cH^2$, K – kappa number; H- H-factor). Table IV.3. contains the regression models' data, coefficients, and statistical parameters. Therefore, sodium metaborate at the 35 % autocauticizing level should not affect the kappa number decrease during kraft pulping of birch, maple, and spruce.

Table IV.3.

Statistical Data for the Kappa Number/H-Factor Regression Models
 $(K = a+bH+cH^2, H- H\text{-factor}, K- \text{kappa number})$

Species	Pulping	Regression Model				
		Coefficients			Parameters	
		A	b	c	σ	R^2
Birch	K/KB	86.5	-0.116	$4.8 \cdot 10^{-5}$	3.01	96.7
Maple	K/KB	72.5	-0.092	$3.7 \cdot 10^{-5}$	4.00	91.5
Spruce	K/KB	161	-0.097	$1.9 \cdot 10^{-5}$	5.14	97.4

Viscosity of pulps was measured for the unbleached birch and maple pulps and the results are plotted versus kappa number in Figure IV.6. The data comparing kraft and kraft-borate pulping indicate that sodium metaborate did not affect viscosity of the pulps at the kappa numbers ranged between 15 and 40.

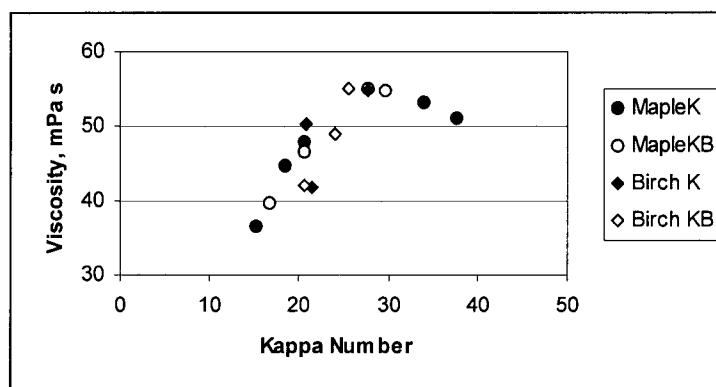


Figure IV.6. Viscosity of the Unbleached Kraft and Kraft-Borate Birch and Maple Pulps vs. Kappa Number

The spruce pulps produced at the H-factors between 500 and 2,000 were bleached to a low level of bleaching (LLB). Then, viscosity and kappa number of the bleached pulps were measured. The results presented in Figure IV.7. show that

during bleaching kraft and kraft-borate pulps were delignified approximately to the same kappa number, retaining approximately the same viscosity. Based on these results, sodium metaborate present in white liquor at the level corresponding to 35 % autocausticizing produces no effect on the spruce pulp viscosity, in kraft pulping at the H-factors from 500 to 2,000. However, pulp viscosity slightly increased with kraft-borate pulping at the H-factors 2,500 and 3,000 and this higher viscosity was preserved through bleaching (Figure IV-1.7.).

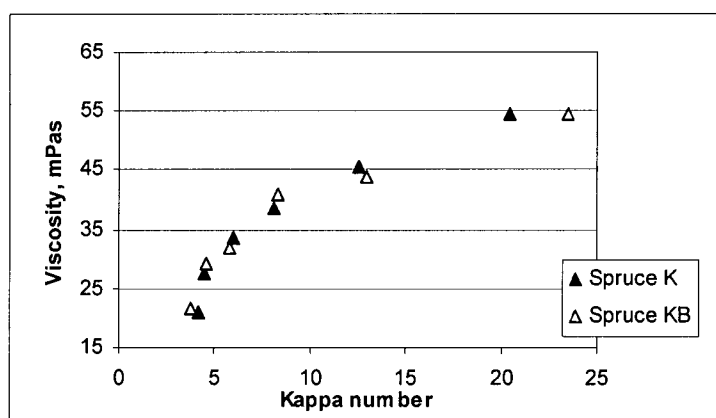


Figure IV.7. Viscosity of Spruce Kraft and Kraft-Borate Pulps Bleached to a Low Level of Bleaching (LLB)

These results indicate that sodium metaborate at the level corresponding to 35 % autocausticizing has a potential to improve spruce pulp viscosity, which should be explored in the next studies.

Spruce Pulping with White Liquor Prepared by Causticizing

Spruce kraft and kraft-borate pulping experiments with white liquor prepared by causticizing were performed at the H-factors of 1,500 and 2,500. White liquor for the kraft-borate pulping experiments was produced in the same conditions as white liquor for kraft pulping except that causticizing was performed in the presence of sodium metaborate at the level corresponding to 35 % autocausticizing (Cameron et al., 2002). The screened pulping yields and kappa numbers were measured and compared. The results were compared with those obtained in pulping at the same conditions including H-factor, temperature, liquor to wood ratio, white liquor sulfidity, and active alkali charge, but with the laboratory prepared kraft and kraft-borate white liquors (from the commercial chemicals by dissolving in water). The screened yields obtained in kraft and kraft-borate pulping with causticized (Kcaust, KBcaust) and laboratory (K, KB) white liquors are shown in Figure IV.8.

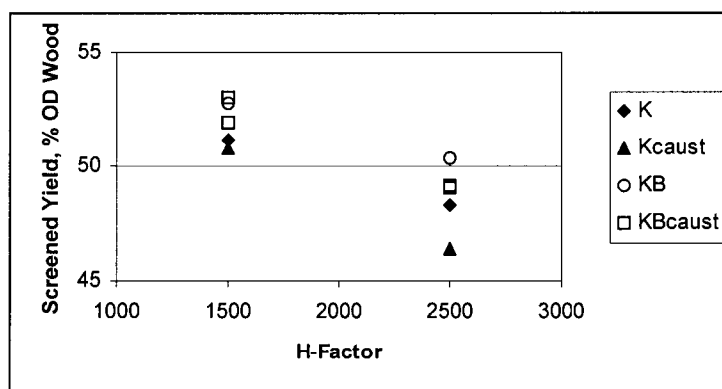


Figure IV.8. Screened Yield of Spruce Pulps Obtained in K and KB Pulping with Causticized and Laboratory White Liquor

Pulping with the kraft-borate causticized white liquor resulted in higher screened yield than pulping with the kraft causticized white liquor. The difference between the screened yields obtained in pulping with causticized white liquors increased with increasing of H-factor, with kraft-borate yields being higher (H1500, Y, % OD wood: Kcaust = 50.8, KBcaust = 52.4; H2000 Y, % OD wood: Kcaust = 46.4, KBcaust = 49.1). It was in accordance with the results obtained in the kraft and kraft-borate pulping with the laboratory prepared white liquor (H1,500, Y, % OD wood: K = 51.1, KB = 52.8; H2,500 Y, % OD wood: K = 48.3, KB = 50.3). The pulp screened yields were plotted against kappa number in Figure IV.9.

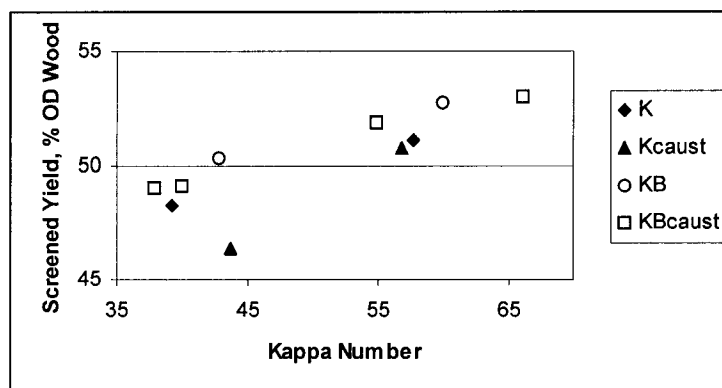


Figure IV.9. Screened Yield vs. Kappa Number of Spruce Pulps Obtained in K and KB Pulping with Causticized and Laboratory White Liquor

Kappa number of pulps obtained in kraft and kraft-borate pulping with causticized white liquor was very similar (H1500, Kappa number: Kcaust = 56.8, KBcaust = 60.6; H2500 Kappa number: Kcaust = 43.7, KBcaust = 39.0). This indicates that kraft-borate pulping with causticized white liquor results in higher

screened yield, at the same kappa number. These results corroborated the previously observed increase of screened pulp yield in kraft-borate pulping with the laboratory white liquor (Paper IV-1. Comparative Studies of Kraft and Kraft-Borate Pulping of Black Spruce, Bujanovic et al., 2003a). Also, they were in accordance with the results obtained in pulping conducted on western hemlock with white liquor prepared in mill trials using the autocausticizing process (Genco et al., 2002). Therefore, an increase of screened yield of spruce pulp obtained in kraft process with partial borate autocausticizing can be expected.

IV-1. Comparative Studies of Kraft and Kraft-Borate Pulping of Black Spruce

Abstract

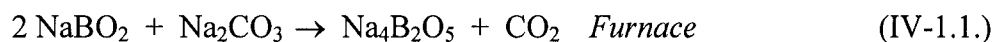
Borate autocausticizing can either replace - total autocausticizing - or supplement the kraft lime cycle - partial autocausticizing. Partial autocausticizing has recently been commercialized in one kraft mill and is undergoing trials in several additional mills. Although it is known that borate reacts with lignin, little information is available on the effect of borates on kraft pulp yield or fibre properties. The objectives of this study were to determine the effect of sodium metaborate, which is the borate product from autocausticizing, on kraft pulping and on the properties of black spruce pulps. The major findings of this study suggest that borate increases yield, can decrease rejects, improves the selectivity of lignin removal, does not affect the delignification rate and can increase pulp viscosity at the same kappa number.

Introduction

Autocausticizing processes are non-conventional causticizing processes based on the use of amphoteric salts to release carbon dioxide (CO_2) from sodium carbonate (Na_2CO_3) in the kraft furnace and generate sodium hydroxide (NaOH) in the green-liquor dissolving tank. The most promising of the autocausticizing processes is borate-based autocausticizing (Janson, 1977, 1978, 1979a,b), which can supply either part or all of the sodium hydroxide requirements in the kraft pulping process. When autocausticizing supplies the entire hydroxide requirement, the calcining/causticizing

process is eliminated, and when autocausticizing supplies part of the hydroxide, the material and energy requirements of calcining and causticizing are reduced.

Janson (Janson 1977, 1978, 1979a,b, 1980) was the first to recognize that borate can directly form caustic and produce a high enough pH for use in the kraft process. Janson proposed that borate autocausticizing involves two steps; first, sodium carbonate (Na_2CO_3) reacts with sodium metaborate (NaBO_2) in the molten smelt to generate disodium borate ($\text{Na}_4\text{B}_2\text{O}_5$), reaction (IV-1.1.), and second, in the dissolving tank, the disodium borate is hydrolyzed to form sodium hydroxide and regenerate sodium metaborate, reaction (IV-1.2.).



With this stoichiometry, one mole of sodium metaborate is required to generate one mole of sodium hydroxide. Janson (1979a) also suggested that reaction (IV-1.1.) would be severely hindered if the Na/B molar ratio of the reactants is greater than 1.5 and that it would not even occur if it is greater than 3. Sodium to boron ratios less than 3 require extremely high borate loadings and eliminate the possibility of partial autocausticizing.

Further studies on pulping with the caustic generated through borate autocausticizing include the continuing work of Janson and work at Paprican (Janson 1980, Prihoda et al., 1996, Koran et al., 1996). Both of these groups studied the effects of sodium metaborate on kraft pulping and pulp properties at the low Na/B ratios described above. The high level of borate used in these experiments retarded

the delignification of pine and black spruce. When describing the effect of borate on the kraft pulping of pine, Janson (1980) stated, "The replacement of sodium hydroxide by disodium borate retards the cooks a little", and the Paprican authors stated in their conclusions regarding the effect of borate on the kraft pulping of black spruce that, "The retardation of kraft pulping caused by borates could easily be compensated by a 4 °C increase in cooking temperature" (Koran et al., 1996). Although Janson (1978) found that borate slightly retarded pulping, he recognized that the retardation effect would be less at higher Na/B ratios. In the work described in this paper, the Na/B ratios are higher by factors of 2 to 10 than those used in the earlier studies.

In his review of alternative sulfate recovery methods, Grace (1981) estimates that borate autocausticizing as proposed by Janson would double the inorganic deadload of the black liquor. The resulting liquor would also have a high viscosity and low heating value. Therefore, borate autocausticizing was believed to be difficult to implement and this technology was not pursued for some time.

Recently, Tran, et al. (1999) published experimental results that show the actual autocausticizing reactions are considerably more efficient than were proposed by Janson. Their findings showed that borate autocausticizing proceeds through the reaction of sodium metaborate and sodium carbonate in the furnace to form trisodium borate (Na_3BO_3), and generate carbon dioxide, reaction (IV-1.3.). On dissolving, the trisodium borate reacts with water to form sodium hydroxide and generate the metaborate, reaction (IV-1.4.).



Compared to the earlier stoichiometry, reactions (IV-1.3.) and (IV-1.4.) require half the borate for the same amount of hydroxide formation.

In addition to suggesting the new stoichiometry, Tran et al. (1999) also proposed that borate autocausticizing offers the possibility of only partially converting the sodium carbonate into sodium hydroxide, with the remaining conversion occurring in the 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 autocausticizing were recently conducted and confirmed the new stoichiometry (Hunter et al., 2001).

The lower level of borate required with this new stoichiometry results in a corresponding decrease of total solids in cooking liquor, leading to a smaller increase in solids content in the black liquor and, therefore, a smaller increase in the boiling point rise and viscosity of the resulting black liquor. Indeed, in the mill trials no change in boiling point rise was apparent at 6 % and 18 % autocausticizing nor was an increase in viscosity noticed (Hunter et al., 2001).

Since less borate is used, it would be expected that the borate would have less effect on delignification than was observed by Janson (1980) and later by the Paprican group (Prihoda et al., 1996, Koran et al., 1996) in the kraft-borate pulping of pine and black spruce.

The main objective of this study was to determine the effect of sodium metaborate on kraft delignification with sodium metaborate present in the white liquor in the amount corresponding to that generated by partial autoausticizing in accordance with the stoichiometry described by reactions (IV-1.3.) and (IV-1.4.). The main questions were; what are the effects of borate on pulping rate, yield and pulp properties?

To answer these questions, two series of pulping experiments were performed. In the first series of experiments, the effects of increasing borate levels were determined at a constant H-factor of 2,000 and in the second series, the effects of a constant borate level were determined at different H-factors. The yield, holocellulose and lignin content, viscosity and brightness of the resulting pulps were measured for pulping with and without borate.

Experimental

The pulping experiments were conducted using black spruce (*Picea mariana*) woodchips from northern Minnesota supplied by The U.S. Forest Products Laboratory, Madison, Wisconsin. The chips had moisture content of 32.47 % (wet basis) (TAPPI, T 258 om-89). They were stored at 8 °C. Conventional white liquor (kraft) and white liquor containing sodium metaborate (kraft-borate) were prepared in the laboratory. The white liquor parameters were determined by using a dual-titrator

ion analyzer, which is a variant of the standard ABC titration method¹, developed by U.S. Borax Inc (Tran et al., 2002). The experimental conditions for the pulping experiments are described in Table IV-1.1. To simulate the white liquor composition with borate autocauticizing pulping, metaborate ($\text{NaBO}_2 - 2\text{xH}_2\text{O}$) – the product of the autocauticizing reactions- was added to the white liquor. As is shown in Table IV-1.1., the amount of sodium metaborate added to the white liquor was adjusted to correspond to different autocauticizing levels, according to the borate autocauticizing reactions (equations IV-1.3., 4.). Laboratory pulping was performed in an M/K digester. The pulps were washed with cold water, disintegrated and screened. The screened yield and rejects were calculated after weighing and moisture content determination (T 208 om-89).

Before determination of the holocellulose and lignin levels, the pulps were extracted in a two-step procedure (T 204 om-88) first with ethanol:cyclohexane (1:2, EC), as cyclohexane was recommended to replace benzene for extraction purposes, and then with ethanol (E). The Klason (T 222 om-88) and acid-soluble lignin content (TAPPI Useful Method, UM 250) were then determined. The contents of extractives (in EC, E), Klason lignin, acid- soluble lignin, acetyl bromide lignin, holocellulose, and the acetyl bromide lignin level remaining in the holocellulose were also determined for the black spruce wood chips (T 258 om-89, T 204 om-88, Fengel, Przyklenk, 1983, T 222 om-88, UM 250, Browning, 1967, Iiyama, Wallis, 1988).

¹ The dual-titrator equipment was purchased from the Brinkmann Corporation; The program and equations used in the titrator were developed by U.S. Borax (U.S. Borax Inc., 26877 Tourney Road, Valencia, CA

Table IV-1.1.

Pulping Conditions

White Liquor: Sulphidity 27.2 %, NaOH 93.4 g/L as Na₂O, Na₂CO₃ 22.45 g/L as Na₂O;
 Liquor/Wood ratio: 4:1 (g/g); Active Alkali Charge: 16.5 % OD Wood

Series-Exp No	NaBO ₂ g/L as Na ₂ O	Na/B molar ratio*	Autocausticizing Level, %**	H-factor
I-1 (II-9)	-	-	0	2,000
I-2	4.7	21.10	10	2,000
I-3	9.4	10.38	20	2,000
I-4 (II-10)	16.4	6.69	35	2,000
I-5	20.1	5.65	43	2,000
I-6	24.3	4.80	52	2,000
II-1	-	-	0	500
II-2	16.4	6.69	35	500
II-3	-	-	0	900
II-4	16.4	6.69	35	900
II-5	-	-	0	1,000 (repeated)
II-6	16.4	6.69	35	1,000 (repeated)
II-7	-	-	0	1,500
II-8	16.4	6.69	35	1,500
II-9 (I-1)	-	-	0	2,000
II-10 (I-4)	16.4	6.69	35	2,000
II-11	-	-	0	2,500
II-12	16.4	6.69	35	2,500
II-13	-	-	0	3,000
II-14	16.4	6.69	35	3,000

*Na in NaOH and NaBO₂; **Degree of autocauticizing that corresponds to NaBO₂ addition based on autocauticizing reactions 3 and 4

After extraction, the pulps were further delignified to either a high or low bleaching level. This was done to determine the ease of bleaching of the kraft-borate pulps compared to the kraft pulps. For the high level of bleaching (HLB), the pulps were delignified in accordance with the acid-chlorite method of holocellulose isolation (Browning, 1967). This procedure followed the recommended time and temperature (70-80°C for 5 hours). For the low level of bleaching (LLB), the time and temperature were reduced to one hour at 65°C. The delignification agents in

bleaching according to the acid-chlorite method are chlorine dioxide, the main degradation product of sodium chlorite in acid solution, and chlorine and chlorate ions, as its by-products (Browning, 1967).

The bleached and unbleached pulps were analyzed for kappa number (T 236 cm-85), viscosity (T 230 om-89), and brightness (T 217 wd-77).

As mentioned in the introduction, the effect of the sodium metaborate on kraft pulping was followed in two series of pulping experiments. In the first series, the H-factor of 2,000 was constant and the pulping liquors contained increasing amounts of sodium metaborate, which corresponded to increasing autocausticizing levels from 0 to 52 %. In the second series of experiments, the level of sodium metaborate was held constant and the H-factor was increased from 500 to 3,000.

Results and Discussion

The chemical composition of the black spruce (*Picea mariana*) used in these pulping experiments is shown in Table IV-1.2. The level of extractives soluble in ethanol:cyclohexane (1:2) followed by ethanol, and the levels of Klason, acid-soluble and acetyl bromide lignin were obtained. Holocellulose was isolated from the extractive-free wood by the acid-chlorite method (84.9 % OD Wood, SD 0.38 (SD = Standard Deviation) (Browning, 1967). Residual lignin in the holocellulose was determined (11.10 % based on OD wood, SD 0.15) by the acetyl bromide method (Iiyama, Wallis, 1988) and the holocellulose level (total polysaccharides = cellulose + hemicelluloses) was corrected for this residual lignin. The levels of lignin and

holocellulose in the black spruce were used as a base for further calculations of residual lignin and retained holocellulose in the pulps.

Table IV-1.2.

Chemical Composition of Black Spruce (Percent OD Wood)

COMPONENT	%	% Total (SD)
Extractives in Ethanol:Cyclohexane (1:2)	1.27	
Extractives in Ethanol	0.09	
Extractives		1.36 (0.054)
Holocellulose		73.80 (0.530)
Klason Lignin	27.41	
Acid-Soluble Lignin	0.29	
Lignin		27.70 (0.226)
Acetyl Bromide Lignin	27.05	

Pulping Experiments at 2,000 H-Factor at Increasing Autocauticizing Level

Table IV-1.3. shows the pulp properties obtained in the first series of experiments at a constant H-factor (2,000) and with increasing levels of sodium metaborate, representing increasing autocauticizing. At all sodium metaborate levels, the screened pulp yields obtained with kraft-borate pulping were higher than that obtained with kraft pulping and were not dependant on the level of borate. After the initial increase in yield at a borate level corresponding to 10 % autocauticizing, the yield remained constant despite increasing borate levels. The average yield of screened pulp for kraft-borate pulping was 51.6 % (SD 0.19) compared to 50.1 % (SD 0.28) for kraft pulping.

In addition to increasing yield, these results suggest that sodium metaborate can decrease the rejects level in kraft pulping of black spruce (Table IV-1.3.). To confirm this observation, one of the objectives of the next series of experiments was the comparison of rejects in kraft and kraft-borate pulping at different H-factors.

Table IV-1.3.

Properties of Kraft and Kraft-Borate Pulps (2,000 H-Factor)

PULP PROPERTY	AUTOCAUSTICIZING LEVEL, %					
	0 ^b	10	20	35 ^b	43	52
	Kraft	Kraft-Borate				
Screened Yield, % OD Wood	50.1	51.7	51.9	51.7	51.4	51.3
Rejects, % OD Wood	1.0	0.1	0.1	1.0	0.9	0.2
Kappa Number	48.56	51.63	49.67	47.51	53.17	46.03
Brightness	19.2	20.2	19.4	19.9	19.1	18.3
Extractives ^a , % OD Pulp	0.72	0.49	0.48	0.72	0.47	0.41
Holocellulose ^c , % OD Pulp	90.10	91.02	91.2	90.18	90.11	90.24
Klason lignin, % OD Pulp	6.87	7.15	7.43	6.99	7.75	6.85
Acid-Soluble Lignin % OD Pulp	0.43	0.40	0.38	0.42	0.36	0.37
Total Lignin, % OD Pulp	7.30	7.55	7.81	7.41	8.11	7.22

^aTotal Extractives – Extractives soluble in ethanol:cyclohexane (1:2) and in ethanol

^bThe values are the average of two experiments (at 0 % of I-1 and II-9 and at 35 % of I-4 and II-10; repeatability lower than 2 %)

^cNot corrected for the residual lignin content as the corresponding kappa numbers were lower than 2 (Table IV.1.4.)

The results of this series of experiments suggest that the addition of sodium metaborate to the white liquor does not affect the kappa number since kraft pulps were characterized by almost the same kappa number (48.56; SD 0.52) as kraft-borate pulps (49.25; SD 2.90). The higher standard deviation of the kappa number for the kraft-borate pulps was further explored in the next series of kraft and kraft-borate (35 % autocausticizing) pulping experiments, as described later in this paper.

While in kraft-borate pulping the kappa number remained approximately the same as in kraft pulping, the addition of sodium metaborate to the white liquor increased the retention of carbohydrates, i.e. decreased the loss of carbohydrates, as shown in Figure IV-1.1. In this figure, the removal of carbohydrates (as holocellulose) is plotted versus autocausticizing level.

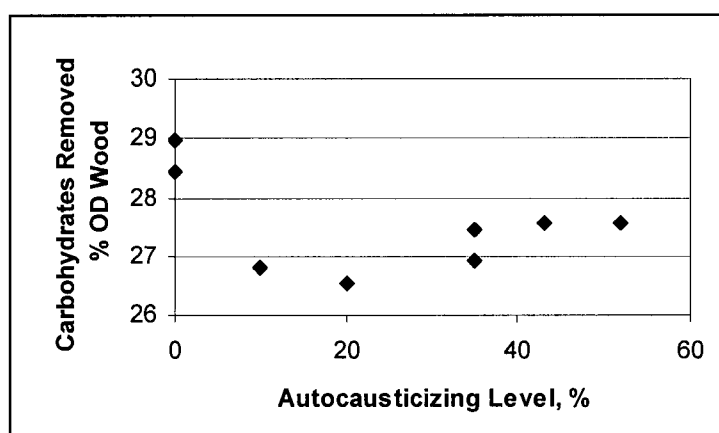


Figure IV-1.1. Removal of Carbohydrates with Kraft and Kraft-Borate Pulping vs. Autocausticizing Level (%)

The average removal of carbohydrates was 28.71 % OD Wood (SD 0.360) in kraft pulping (0 % autocausticizing) decreasing to 27.14 % OD Wood (SD 0.440) in kraft-borate pulping (10 % to 52 % autocausticizing). This higher retention of carbohydrates is one of the reasons for the increase of screened yield with kraft-borate pulping. Another reason may be the reduction in rejects with borates.

The brightness, kappa number and viscosity were determined for kraft and kraft-borate pulps after low and high levels of bleaching, as described in the Experimental Section. These results are shown in Table IV-1.4.

Table IV-1.4.

Some Properties of Kraft and Kraft-Borate Pulps (2,000 H-Factor)
after Bleaching (LLB, HLB)

Autocausticizing level %	Brightness		Kappa		Viscosity mPa·s	
	LLB	HLB	LLB	HLB	LLB	HLB
0	64.3	83.5	5.98	<2	33.38	21.94
10	68.4	83.0	5.78	<2	34.89	23.66
20	65.2	82.6	6.18	<2	35.20	24.72
35	62.6	81.6	5.80	<2	31.81	20.36
43	62.8	81.7	6.51	<2	37.53	22.73
52	63.4	82.3	6.75	<2	30.29	20.86

After bleaching, the viscosities of the kraft and kraft-borate pulps were approximately the same. The average viscosities for the kraft and kraft-borate pulps were, at LLB, 33.38 mPa·s (SD 0.47) and 33.94 mPa·s (SD 2.88) and at HLB 21.94 mPa·s (SD 0.29) and 22.47 mPa·s (SD 1.84), respectively. These results indicate that the polysaccharides of both kraft and kraft-borate pulps degrade to the same extent during acid-chlorite delignification.

Bleached kraft and kraft-borate pulps had the same kappa number and brightness, Table IV-1.4. This is shown both for the low level of bleaching, where the kappa numbers were approximately 6, and for the high level of bleaching, where the kappa numbers were less than 2. These findings show that kraft and kraft-borate pulps have the same bleachability.

Among the major findings of this first series of experiments is that kraft-borate pulping increases screened yield, results in better protection of holocellulose, and tends to reduce rejects. The objectives of the next series of experiments were to determine the effect of H-factor on kraft-borate pulping and to further explore the findings of the first series of experiments.

Pulping Experiments at Increasing H-Factor in Kraft and Kraft-Borate (35 % Autocauticizing) Conditions

In this series of experiments, the effect of H-factor on kraft-borate pulp at a constant metaborate addition level (35 % of autocauticizing) was compared to the effect of H-factor on kraft pulp. The 35 % level was chosen since this is a significant autocauticizing level, and represents the highest partial autocauticizing studied in the on-going mill trials. At 35 % autocauticizing, the increases in black liquor viscosity and boiling point rise are not expected to cause the problems in the evaporation and pumping of black liquors (Bujanovic, Cameron, 2001, Bujanovic et al., 2001). The properties of kraft and kraft-borate pulps obtained at increasing H-factor from 500 to 3,000 in this series of experiments are presented in Table IV-1.5.

The increase of screened pulp yield and decrease of rejects in kraft-borate pulping found in the first series of experiments were confirmed in this second series of experiments. As shown in Table IV-1.5. and Figure IV-1.2., the addition of borate increases the screen pulp yield at the same kappa number.

Table IV-1.5.

Some Properties of Kraft and Kraft-Borate (35 % Autocausticizing) Pulps
Obtained at Increasing H-Factor (500-3,000)

PULP PROPERTY	PULP	H-FACTOR						
		500	900	1,000 ^b	1,500	2,000 ^b	2,500	3,000
Screened Yield % OD Wood	Kraft	62.1	56.1	55.8	51.1	50.1	48.3	47.7
	Kraft-Borate	62.2	57.1	56.9	52.8	51.7	50.3	49.4
Reject % OD Wood	Kraft	1.0	2.0	1.5	1.7	1.20	0.2	0.5
	Kraft-Borate	1.0	0.5	0.5	0.7	0.15	0.1	0.1
Kappa Number	Kraft	125.69	85.49	75.96	57.69	48.56	39.24	39.47
	Kraft-Borate	121.59	86.28	77.89	59.92	47.51	42.85	37.02
Brightness	Kraft	14.9	16.9	17.4	18.8	19.2	22.2	21.5
	Kraft-Borate	15.5	17.7	16.5	18.4	19.9	20.3	20.3
Extractives ^a % OD Pulp	Kraft	0.5	0.41	0.65	0.57	0.72	0.59	0.59
	Kraft-Borate	0.5	0.46	0.65	0.49	0.72	0.58	0.49
Holocellulose ^c % OD Pulp	Kraft	78.65	85.49	86.22	88.74	90.10	92.51	93.2
	Kraft-Borate	78.42	84.03	84.59	88.21	90.18	92.53	92.2
Klason lignin % OD Pulp	Kraft	18.65	12.55	11.85	8.84	6.87	5.17	5.46
	Kraft-Borate	18.23	11.90	11.66	9.54	6.99	5.71	5.06
Acid-Soluble Lignin % OD Pulp	Kraft	0.42	0.34	0.47	0.47	0.43	0.39	0.42
	Kraft-Borate	0.42	0.36	0.47	0.41	0.42	0.39	0.44
Total Lignin % OD Pulp	Kraft	19.07	12.89	12.32	9.31	7.30	5.56	5.88
	Kraft-Borate	18.65	12.26	12.13	9.95	7.41	6.10	5.50

^aTotal Extractives - Extractives soluble in ethanol:cyclohexane (1:2) and in ethanol

^bThe values are the average of two experiments (at 1,000 and 2,000 H-factor; repeatability lower than 2 %)

^cNot corrected for the residual lignin content as the corresponding kappa numbers were lower than 2

In the statistical analysis of the results obtained in kraft and kraft-borate pulping, a test involving the equality of coefficients of different regressions was used (Pindyck, Rubinfeld, 1991). In this test the null hypothesis in which the regression models for two sets of data are identical – single equation - is considered against the alternative hypothesis in which the regression models are different – individual

equations. Then, the sum of the error sums of squares of individual equations is compared with that of the single equation according to the appropriate F statistic. Based on the screened yield - kappa number data and this test, the null hypothesis was rejected. This indicates that two different models apply for kraft and kraft-borate pulping, at the 5 percent level of significance (equations IV-1.5.,6.).

Kraft:

$$\text{Screened Yield, \%} = 41.8 + 0.166 \text{ Kappa, } \sigma = 0.746, R^2 = 98.3 \% \quad (\text{IV-1.5.})$$

Kraft-Borate:

$$\text{Screened Yield, \%} = 43.9 + 0.153 \text{ Kappa, } \sigma = 0.594, R^2 = 98.6 \% \quad (\text{IV-1.6.})$$

Equations IV-1.5. and IV-1.6. show that the screened yield is higher in kraft-borate than in kraft pulping at the same kappa number. Also, the difference between the yields increases with decreasing kappa number and increasing H-factor, with kraft-borate yields being higher. In pulping at H-factors higher than 1,000, the kraft-borate yields were on average 1.8 % (SD 0.18) higher than kraft yields. A decrease of rejects in pulping in kraft-borate conditions, which was indicated based on the first series of experiments, was also obtained in the second series of experiments. However, the standard deviation of the difference in the rejects between kraft and corresponding kraft-borate pulping experiments is rather high (the reject levels were about 0.6 % lower for kraft-borate than for kraft pulping with SD 0.4) (Table IV-1.5.).

Table IV-1.5. illustrates the effect of H-factor on the composition of the resulting pulps. The extractive content in kraft and kraft-borate pulps was almost the same at the same H-factor, varied between 0.4 and 0.7 % OD pulp and did not depend

on the H-factor. As expected, the Klason lignin content in the pulps gradually decreased with H- factor. At the same time, the acid-soluble lignin content varied between 0.34 % and 0.47 % OD pulp and was always higher than that of the wood before delignification (Table IV-1.2.). This increase in acid-soluble lignin is primarily because of the decrease in the molecular weight of the lignin during pulping (Tamminen, Hortling, 1999). As shown in Figure IV-1.3., the delignification rates, expressed as the residual lignin in pulp in percentages of original wood lignin versus H-factor, were almost the same for kraft and kraft-borate pulping.

Figure IV-1.3. shows that the addition of borate at a 35% autocausticizing level does not retard pulping. This is in contrast to the results of Janson and the Paprican authors (Janon, 1980, Prihoda et al., 1996, Koran et al., 1996) where borate slightly decreased delignification; however, these previous experiments were conducted at higher borate addition levels so comparison is difficult. Nevertheless, these results confirmed Janson's expectations that lower borate levels would have less effect on lignin retardation.

The conversion factors between kappa number and Klason lignin were almost the same for kraft and kraft-borate pulps. This indicates the same content of structures are undergoing oxidation with potassium permanganate during the kappa number determination, which are mainly lignin and hexenuronic acid groups, but also other types of oxidizable structures like aliphatic double bonds, aldehyde groups, and α -keto-carboxylic groups (Li, Gellerstedt, 1998). This factor was 0.148 for kraft

pulps ($R^2 = 99.83 \%$, $\sigma = 0.471$) and 0.149 for kraft-borate pulps ($R^2 = 99.84 \%$, $\sigma = 0.461$).

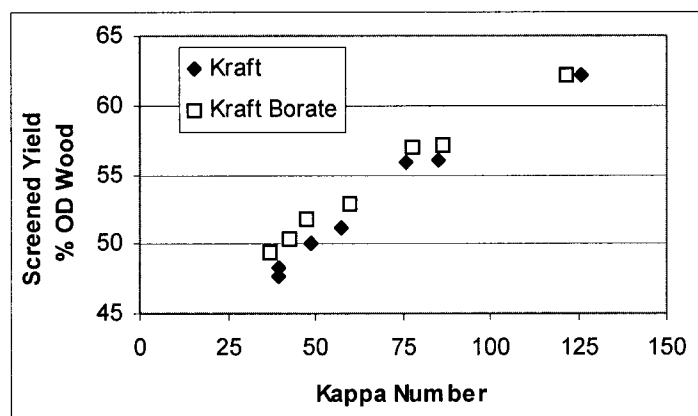


Figure IV-1.2. Yield of Screened Kraft and Kraft-Borate (35 % Autocauticizing) Pulps vs. Kappa Number

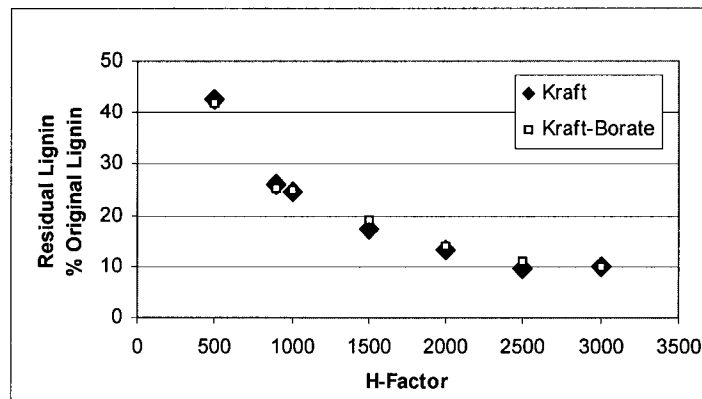


Figure IV-1.3. Lignin Removal in Kraft and Kraft-Borate (35 % Autocauticizing) Pulping

Figure IV-1.4. illustrates the effect of H-factor on kappa number for both unbleached and partially bleached kraft and kraft-borate pulps. The test of the

equality of coefficients of different regressions (Pindyck, Rubinfeld, 1991) was used again here to analyze the kappa number-H-factor data for kraft and kraft- borate pulps before and after low level of bleaching. It was shown that according to the F statistics the same linear regression model can be used for pulps obtained in kraft and kraft- borate pulping, at the 5 percent level of significance (equation IV-1.7.).

$$\text{Kappa}_{K,KB \text{ Pulp}} = 161 - 9.65 \times 10^{-2} \times H + 1.9 \times 10^{-5} \times H^2, R^2 = 97.4 \%, \sigma = 5.136 \quad (\text{IV-1.7.})$$

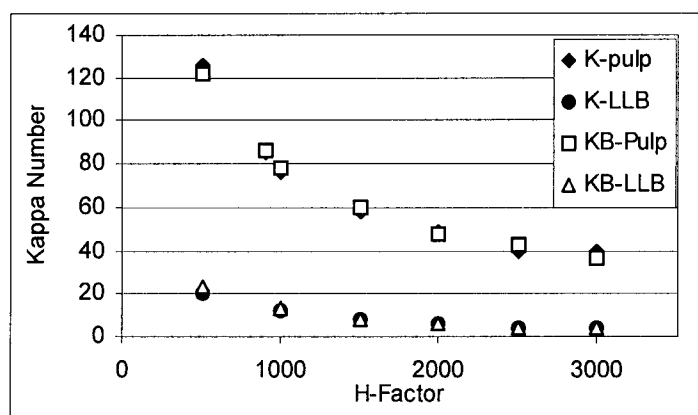


Figure IV-1.4. Kappa Number of Kraft and Kraft-Borate (35 % Autocauticizing) Pulps Before and After Bleaching (LLB) versus H-Factor

It was also found that one regression model can be used for kraft and kraft- borate pulps after low level of bleaching (LLB), also at the 5 percent level of significance (equation IV-1.8.).

$$\text{Kappa}_{K,KB \text{ LLB}} = 30.5 - 2.07 \times 10^{-2} \times H + 4.0 \times 10^{-6} \times H^2, R^2 = 97.6 \%, \sigma = 1.116 \quad (\text{IV-1.8.})$$

Equations (IV-1.7.) and (IV-1.8.) combined with the data shown in Figure IV-1.3., suggest that the addition of sodium metaborate does not affect the delignification

rate or the bleachability of the pulps. Therefore, the structure of the kraft and kraft-borate residual lignin would be expected to be similar (Tamminen, Hortling, 1999). Also, there is no evidence that kraft-borate pulps contain a lignin-borate complex, which might be formed in kraft-borate pulping as the formation of this complex was reported earlier in the studies of the β -O-4 lignin structure (Lundquist et al., 1996).

The brightness of the kraft and kraft-borate pulps, before and after bleaching, is illustrated in Figure IV-1.5. Here, both pulps have the same brightness; supporting the conclusion that borate does not affect bleachability.

Figure IV-1.6. shows the selectivity of lignin removal in kraft and kraft-borate pulping. The selectivity was calculated based on the chemical composition of black spruce, the yield, and the chemical composition of kraft and kraft-borate pulps. The higher selectivity of kraft-borate pulping is evident, especially in the later phases of delignification. For example, at 25 % lignin removal, 29.7 % of the carbohydrates are removed with kraft pulping, but only 28.3 % with kraft-borate (all expressed as % of original wood).

The apparent higher selectivity of kraft-borate pulping supports the conclusion that there is better carbohydrate retention with kraft-borate pulping, which is shown in Figure IV-1.1. The lower removal of carbohydrates in kraft-borate pulping agrees with the work of Partlow (1967) who reported that borate protects α -cellulose during cold caustic refining of sulfite cellulose.

The higher selectivity of kraft-borate pulping occurs at H-factors higher than 1,500. Therefore, the viscosities of kraft and kraft-borate pulps at H-factors 2,500 and 3,000, before and after bleaching were measured and are shown in Figure IV-1.7.

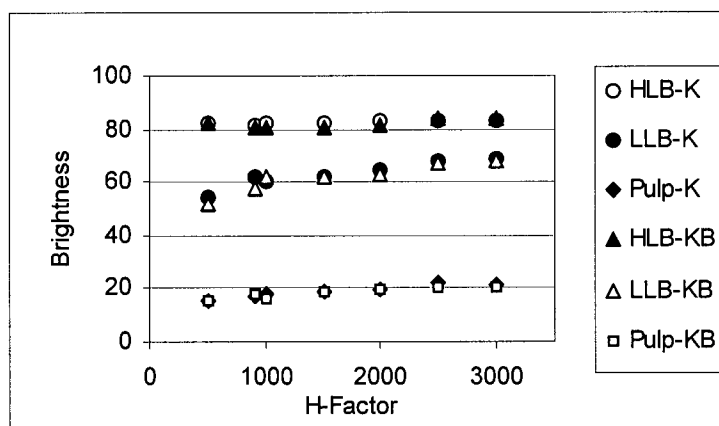


Figure IV-1.5. Brightness of Kraft and Kraft-Borate (35 % Autocauticizing) Pulps Before and After Bleaching (LLB, HLB) versus H-factor

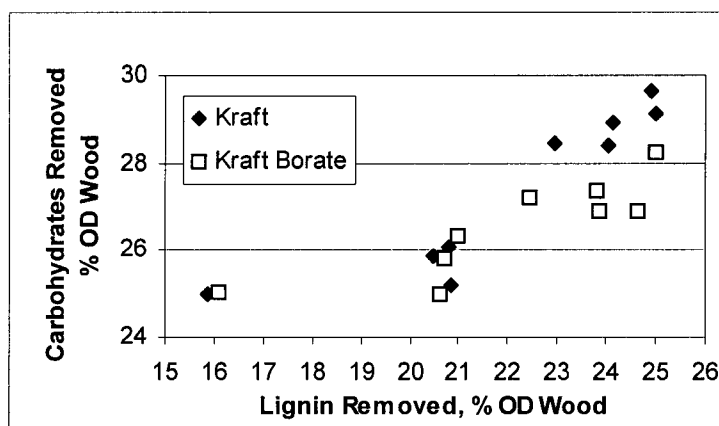


Figure IV-1.6. Selectivity of Lignin Removal in Kraft and Kraft-Borate (35 % Autocauticizing) Pulping

Pulp viscosity increased with kraft-borate pulping. The increase in viscosity relative to kraft pulp was 5.2 % at 2,500 H-factor and 6.8 % at 3,000 H-factor. In most cases this increase of viscosity was preserved through bleaching. Based on these results, the higher selectivity of pulping with borate may be due to borate protecting the holocellulose.

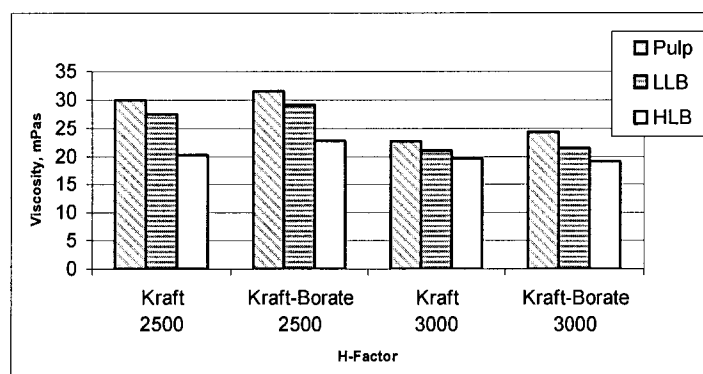


Figure IV-1.7. Viscosity of Kraft and Kraft-Borate (35 % Autocauticizing) Pulps at 2,500 and 3,000 H-Factor Before and After Bleaching (LLB, HLB)

Conclusions

This paper describes the effect of the addition of borate on kraft pulping of black spruce. The conclusions of this work are summarized below.

Higher screened pulp yield: The screened pulp yield increased with kraft-borate pulping compared to kraft pulping; this increase was about 1.8% in kraft-borate pulping at the 35 % autocauticizing level at H-factors higher than 1,000.

Potential of sodium metaborate to lower rejects: Although the SD (0.4) was somewhat high, the reject levels decreased and were about 0.6% lower for kraft-borate pulping at 35 % autocauticizing level than for kraft pulping.

Same Delignification Rate: The addition of borate at a 35% autocauticizing level did not retard kraft pulping.

Higher Selectivity of Lignin Removal: At the same level of lignin removal, kraft-borate pulps retained more holocellulose. This higher selectivity is believed to be due to borate protecting the holocellulose during pulping, which was found in pulping at H-factor 2,500 and 3,000.

The addition of sodium metaborate to kraft pulping increased screened yield and indicated a decrease in rejects. These important additional advantages of borate autocauticizing should be further explored in mill trials and included in economic analyses for this technology.

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IV-2. Some Properties of Kraft and Kraft-Borate Pulps of Different Wood Species

Abstract

An important question regarding the implementation of the borate-based autocausticizing in the kraft process is the effect of sodium metaborate, which is present in the pulping liquor as the product of the autocausticizing reactions on kraft pulping and the properties of pulp. 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 % autocausticizing – kraft-borate pulping. An increase in the screened 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, at kappa number lower than 50, sodium metaborate increased the total yield in spruce pulping. 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, “HexA-free” kappa number, which provides a more accurate estimation of the lignin content in pulp 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 (1977, 1979a) suggested the application of sodium metaborate ($NaBO_2$) as the most favorable autocausticizing agent. However, the reaction stoichiometry suggested at that time 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 autocausticizing to supplement or eliminate the calcining/causticizing cycle has been renewed since Tran et al. (1999) showed that the autocausticizing reactions are more efficient than were proposed by Janson. Tran et al. indicated that borate autocausticizing 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. In the dissolving tank, the trisodium borate undergoes hydrolysis to form sodium hydroxide and regenerate sodium metaborate.

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 autocausticizing is only one-half that indicated by the earlier established stoichiometry (Janson, 1977, 1979a). 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 (Janson, 1980, Prihoda et al., 1996, Koran et al., 1996) and on the viscosity of black liquor (Janson, Söderhjelm, 1988).

In addition to suggesting the new stoichiometry, Tran et al. (1999) also proposed that borate autocausticizing 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 autocausticizing were conducted recently (Hunter et al., 2000). 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 %.

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 autocausticizing stoichiometry suggested by Tran et al. (1999), 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 (Bujanovic et al., 2001). 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 Na_2O ; Na_2CO_3 22.45g/L as Na_2O . To simulate the white liquor composition corresponding to that at 35% borate autocausticizing, sodium metaborate was added to the white liquor in the amount corresponding to 16.4g/L as Na_2O . The white liquor parameters were measured using a dual-titrator ion analyzer developed by U.S. Borax Inc. (variant of the 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 an M/K digester using 400g oven-dry wood at the increasing H-factor. Five H-factors (from 250 to 1,500) were used in pulping of maple and birch, while seven H-factors (from 500 to 3,000) were used in 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, while the time at the maximum temperature was regulated according to the desirable 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.

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 (Fengel, Wegener, 1984). Hexenuronic acid group (HexA) content in pulps was determined by the method recently developed by Chai et al. (2001a). The holocellulose content of the spruce woodchips and pulps was determined in accordance to the acid-chlorite method (Browning, 1967).

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 IV-2.1.

Table IV-2.1.

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

Species	Yield ^{a)} / Rejects ^{b)} / Kappa Number	K/KB	H-Factor							
			250	500	750	1,000	1,500	2,000	2,500	3,000
Birch	Y	K	56.2	55.5	53.4 ^{c)}	52.1	51.8	-	-	-
		KB	56.3	55.2	53.6 ^{c)}	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 ^{c)}	21.5	20.7	-	-	-
		KB	61.5	37.7	25.5 ^{c)}	24.0	20.6	-	-	-
Maple	Y	K	56.3	55.4 ^{c)}	53.5 ^{c)}	52.6	51.7	-	-	-
		KB	58.8	55.1 ^{c)}	55.0 ^{c)}	52.3	51.5	-	-	-
	R	K	3.3	0.7 ^{c)}	<0.1 ^{c)}	<0.1	<0.1	-	-	-
		KB	0.6	0.1 ^{c)}	0.4 ^{c)}	<0.1	<0.1	-	-	-
	KN	K	54.3	35.9 ^{c)}	22.8 ^{c)}	18.4	15.2	-	-	-
		KB	55.5	28.8 ^{c)}	28.3 ^{c)}	20.6	16.7	-	-	-
Spruce	Y	K	-	62.1	-	55.8 ^{c)}	51.1	50.1 ^{c)}	48.3	47.7
		KB	-	62.2	-	56.9 ^{c)}	52.8	51.7 ^{c)}	50.3	49.4
	R	K	-	1.0	-	1.5 ^{c)}	1.7	1.2 ^{c)}	0.2	0.5
		KB	-	1.0	-	0.5 ^{c)}	0.7	0.2 ^{c)}	0.1	0.1
	KN	K	-	125.7	-	76.0 ^{c)}	57.7	48.6 ^{c)}	39.5	39.2
		KB	-	121.5	-	77.9 ^{c)}	59.9	47.5 ^{c)}	42.9	37.0

^{a)}screened yield, % OD wood; ^{b)} rejects, % OD wood; ^{c)}the average obtained in two pulping experiments

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 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). However, at H-factor $>2,000$ the difference in the rejects between kraft and kraft-borate pulping was lower than on the lower H-factors. Based on these results, a potential of sodium metaborate 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 screened yield vs. kappa number were made as shown in Fig. IV-2.1.

It is well known that the screened yields of birch and maple kraft pulp are higher than that of spruce kraft pulp at the same kappa number (Sjöström, 1981). This result was found for both kraft and kraft-borate pulping, as shown in Fig. IV-2.1. Also, the screened 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 kappa number < 60 (H-factor $> 1,000$), where the screened yields of kraft-borate pulps were, on average, 1.8 % (st. dev. 0.18) higher than those of kraft pulps (Table IV-2.1., Fig. IV-2.1).

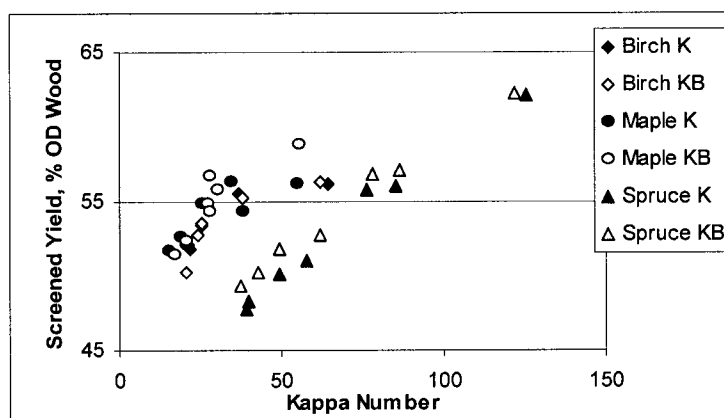


Figure IV-2.1. Screened Yield vs. Kappa Number for Birch, Maple, and Spruce Kraft and Kraft-Borate Pulps

Brightness and Extractives

The brightness of kraft and kraft-borate pulps at the same kappa number was decreasing in accordance to the series: maple > birch > spruce (Fig. IV-2.2.).

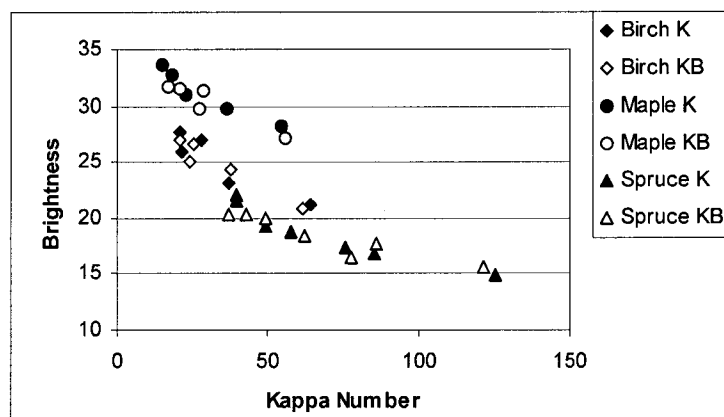


Figure IV-2.2. Brightness vs. Kappa Number for Birch, Maple, and Spruce Kraft and Kraft-Borate Pulps

No effect of sodium metaborate on the pulp brightness, i.e. formation of chromophoric structures during pulping, 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.

Even that the lignin chromophoric structures affect pulp brightness the most, other chromophoric structures, including those in the organic low-molecular weight compounds soluble in organic solvents i.e. extractives, also cause a decrease of pulp brightness (Dence, Reeve, 1996). Several of the extractives in unbleached pulps, which contain one or more double bonds, are extremely reactive towards bleaching agents and increase their consumption in the bleaching phase (Dence, Reeve, 1996). 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. IV-2.3.

The extractives content in birch pulps was 1 to 2 %, while in maple and spruce pulps it was about 0.6 %. No effect of sodium metaborate on the extractives content of pulps was noticed. 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 brightness improvement. For example, maple kraft pulp (H-factor 1,000, kappa number 18.5) originally had 32.7 brightness and after extraction 34.9 (6.9 % increase), while for birch kraft-borate pulp (H-factor 1,000, kappa number 24) the corresponding values were 25.1 and 27.2 (8.1 % increase).

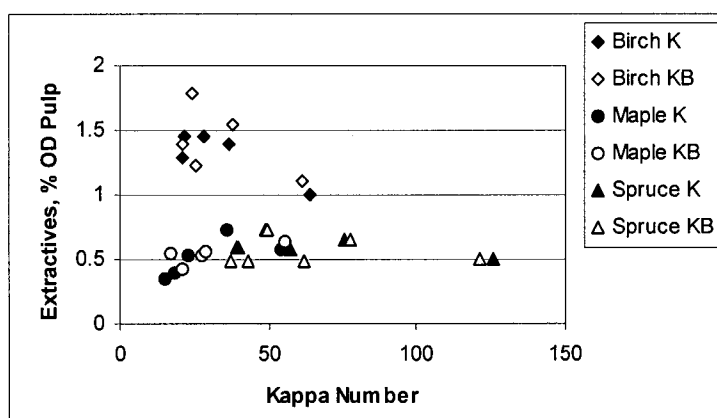


Figure IV-2.3. Extractives vs. Kappa Number for Birch, Maple, and Spruce Kraft and Kraft-Borate Pulp

Also, kappa number of pulps decreased after the pulp extraction. Kappa number reduction of 4.2 % and 4.1 % was obtained for K and KB birch pulps obtained at H-factor 1,500, respectively (K 21.52; KB 21.40; after extraction K 20.67; KB 20.56).

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. 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 (Chai et al., 2001a, Jiang et al., 2000, Li, Gellerstedt, 1997). In this study, the HexA content was determined by UV-spectroscopic method developed by Chai et al. (2001a). 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 (Chai et al., 2001a,b) and with the xylans/4-O-methyl-D-glucuronic acid groups content in studied species (Sjöström, 1981). Also it was found that approximately the same HexA content characterized the kraft and corresponding kraft-borate pulps, produced at the same H-factor. The HexA content of studied pulps is shown in Figure IV-2.4.

In addition to lignin and HexA, the kappa number is affected by other types of oxidizable structures including extractives (Li, Gellerstedt, 1998). However, an error in estimation of the residual lignin in pulp based on the kappa number can be significantly decreased by correction of kappa number for its HexA component. As it was found that 10 μmol of hexenuronic acid correspond to 0.85 kappa units (Li, Gellerstedt, 1997), the hexenuronic acid component of kappa numbers was calculated, and subtracted from the corresponding kappa number.

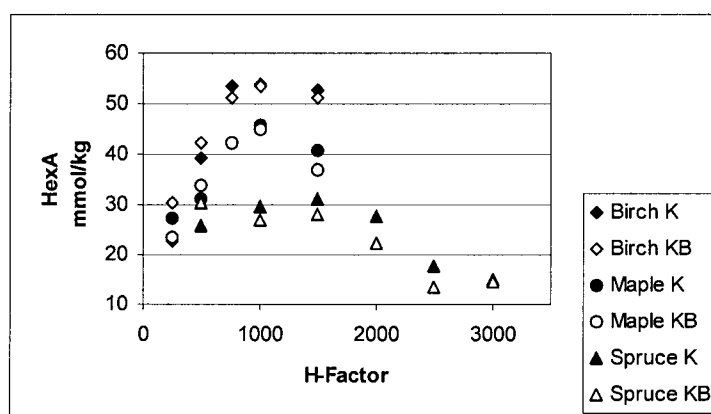


Figure IV-2.4. Hexeneuronic Acid (HexA) Content in K and KB Pulps of Birch, Maple, and Spruce Obtained at Increasing H-Factor

The kappa numbers corrected for the HexA component ("HexA-free" Kappa Number) were plotted against the corresponding H-factor as it is shown in Fig. IV-2.5. and Fig. IV-2.6. for birch and maple, respectively, and in Fig. IV-2.7. for spruce.

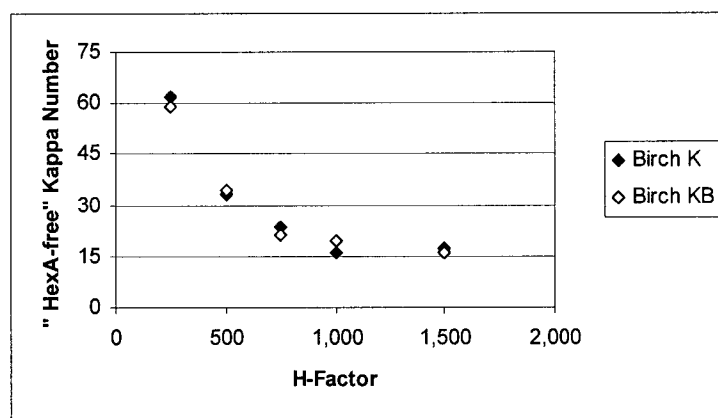


Figure IV-2. 5. Kappa Number Corrected for the HexA Component vs. H-Factor in Kraft and Kraft-Borate Pulping of Birch

(Kappa,K = $88.7 - 0.129 H + 5.5 \times 10^{-5} H^2$, $R^2 = 97.9 \%$; $\sigma = 3.84$; SE Coef: Const 7.01; H 0.018; $H^2 1.02 \times 10^{-5}$; Kappa, KB = $82.6 - 0.115 H + 4.7 \times 10^{-5} H^2$, $R^2 = 97.1 \%$; $\sigma = 4.23$; SE Coef: Const 7.71; H 0.020; $H^2 1.12 \times 10^{-5}$)

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

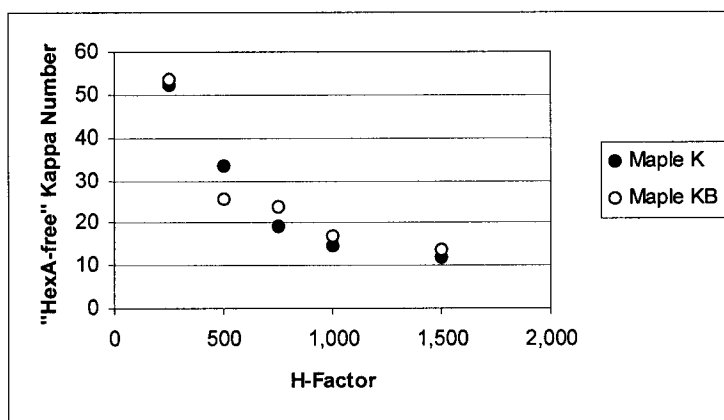


Figure IV-2.6. Kappa Number Corrected for the HexA Component vs. H-Factor in Kraft and Kraft-Borate Pulping of Maple

(Kappa,K = $74.5 - 0.102 H + 4.0 \times 10^{-5} H^2$, $R^2 = 99.5 \%$; $\sigma = 1.70$; SE Coef: Const 3.10; H 0.008; $H^2 4.48 \times 10^{-6}$; Kappa,KB = $71.6 - 0.096 H + 3.9 \times 10^{-5} H^2$, $R^2 = 92.0 \%$; $\sigma = 6.31$; SE Coef: Const 11.52; H 0.030; $H^2 1.67 \times 10^{-5}$)

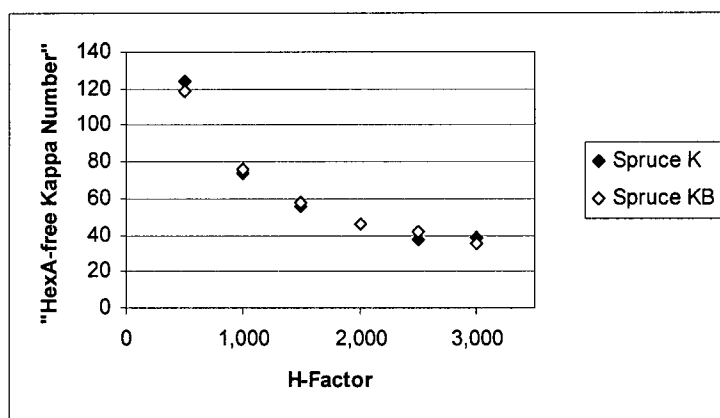


Figure IV-2.7. Kappa Number Corrected for the HexA Component vs. H-Factor in Kraft and Kraft-Borate Pulping of Spruce

(Kappa,K = $165 - 0.104 H + 2.1 \times 10^{-5} H^2$, $R^2 = 97.3 \%$; $\sigma = 6.94$; SE Coef: Const 12.41; H 0.016; $H^2 4.54 \times 10^{-6}$; Kappa, KB = $156 - 0.0913 H + 1.7 \times 10^{-5} H^2$, $R^2 = 97.9 \%$; $\sigma = 5.86$; SE Coef: Const 10.48; H 0.014; $H^2 3.84 \times 10^{-6}$)

Retention of Carbohydrates in Kraft Pulping of Spruce

An increase in the yield of spruce kraft pulps was found in the presence of sodium metaborate in pulping to the approximately same kappa number (Table IV-2.1, Fig. IV-2.1.). 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. IV-2.8. These data represent the retention of holocellulose versus kappa number.

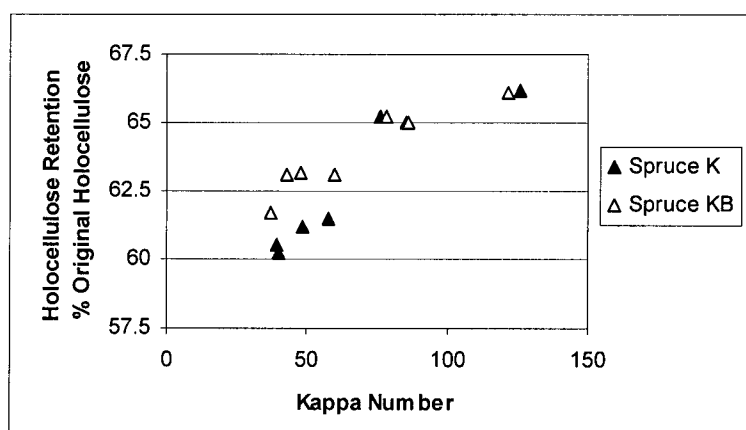


Figure IV-2.8. Retention of Holocellulose in Kraft and Kraft-Borate Pulps of Spruce vs. Kappa Number

As shown in Fig. IV-2.8., 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 % autocausticizing – 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 (“HexA-free” Kappa Number) 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.

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IV-3. Chemical Characterization of Birch, Maple, and Spruce Kraft and Kraft-Borate Pulps

Abstract

In order to evaluate the quality of pulping in the presence of sodium metaborate corresponding to 35 % borate-autocausticizing, the chemical constituents of birch, maple, and spruce kraft and kraft-borate pulps produced in the same conditions were analyzed. The chemical analyses of pulps included determination of kappa number, and the contents of Klason lignin, hexenuronic acid groups (HexA), phenolic hydroxyl groups (PhOH), holocellulose, and pentosans. Conversion factors between Klason lignin and kappa number/“HexA-free” kappa number were calculated. The same conversion factors between Klason lignin and “HexA-free” kappa number found for maple and spruce pulps indicate that these pulps contain equal levels of oxidizable structures originating dominantly from lignin. The higher level of oxidizable structures estimated for birch pulps may be attributed to the high content of extractives. The level of oxidizable structures was the same in kraft and corresponding kraft-borate pulps. Sodium metaborate did not influence dissolution of pentosans, however, an observed stabilization of hexosans might be the reason for an increased screened yield found in spruce kraft-borate pulping. The equal PhOH content of the residual lignin of kraft and corresponding kraft-borate pulps, in combination with the same rate of lignin removal, is a good indicator that the delignification path is similar for both kraft and kraft-borate (at 35 % autocausticizing) pulping of the studied species.

Introduction

Borate autocausticizing as an alternative technology aimed toward improving the energy efficiency of kraft process was suggested in the 1970's (Janson, 1977). This technology is based on the removal of carbon dioxide (CO_2) from sodium carbonate (Na_2CO_3) by the action of sodium metaborate (NaBO_2) in the recovery boiler and the production of sodium hydroxide (NaOH) in the dissolving tank. According to this reaction path, sodium hydroxide is a component of green liquor and, hence, the implementation of borate autocausticizing would eliminate the need for the causticizing plant. The stoichiometry of the borate autocausticizing reactions suggested by Janson in the 1970's indicated that one mole of sodium metaborate is required to produce one mole of sodium hydroxide (Janson, 1977). This is a relatively large amount of sodium metaborate, which might lead to an unacceptably high inorganic load over the entire recovery system (Grace, 1981). This concern resulted in a low interest in the implementation of borate autocausticizing until the end of the 1990's. However, in 1999, Tran et al. (1999) studied the borate-based autocausticizing reactions and observed that the stoichiometry of these reactions is twice as efficient as suggested earlier. These studies also indicated that the causticizer limited mills can use a partial autocausticizing (part of the required sodium hydroxide is produced in the borate autocausticizing reactions, while another part is produced in the causticizer) as a method of increasing their causticizing capacity without installing new equipment (Tran et al., 1999). These findings

resulted in a series of successful partial borate autocausticizing trials in a few mills in North America. The trial in one of these mills has led to a commercial application (Kochesfahani, Bair, 2002). Additional confirmation of these results can be seen by the fact that Swedish researchers recommend the partial borate causticizing technology as a short-term goal (1-5 years) and 100 % borate direct causticizing as a long-term goal (≥ 10 years) in the development of "The Eco-cyclic Pulp Mill." They also propose that borate causticizing decreases both the emission of "fossil" CO₂ and production of solid waste, and increases the level of sold power in the kraft mill (Axegård et al., 2002).

In order to implement borate autocausticizing technology in the kraft mills, the studies of the effect of sodium metaborate on the overall recovery operation, the pulping process, and the properties of pulp should be performed. In the mill trials so far, the operation of the recovery line in partial borate autocausticizing (10 to 25 % autocausticizing effect) was stable and only minor adjustments were required. However, further studies and improvements in this area are necessary (Kochesfahani, Bair, 2002, Tran et al., 2002). Laboratory experiments were conducted to obtain a better understanding of the optimal conditions in which borate autocausticizing reactions take place (Tran et al., 2002, Yusuf, Cameron, 2001). Additionally, the laboratory experiments showed no negative effect of sodium metaborate on the causticizing reaction (in the partial borate autocausticizing technology a portion of sodium hydroxide is produced in causticizing) (Cameron et al., 2002). The pulping process and the properties of pulp were studied in kraft-borate pulping earlier, but the

level of sodium metaborate in these studies corresponded to the stoichiometry of borate autocausticizing reactions suggesting that one mole of sodium metaborate is needed to regenerate one mole of sodium hydroxide (Janson, 1977). The presence of such a high level of sodium metaborate caused opposite effects on the kraft pulping of black spruce and birch; while the black spruce kraft pulping was retarded (Janson, 1980, Prihoda et al., 1996), an enhancement of birch kraft pulping was noticed (Janson, 1980).

In more recent pulping experiments, the level of sodium metaborate in the white liquor was adjusted to correspond to more efficient stoichiometry of borate autocausticizing reactions proposed by Tran et al. (1999). The kraft and kraft-borate pulping of softwoods were conducted using either the mill liquors - conventional and autocausticized (10 % autocausticizing level) - when western hemlock was pulped (Genco et al., 2002) or the liquors prepared from commercial chemicals - kraft and kraft-borate (35 % autocausticizing level) - when spruce was pulped (Bujanovic et al., 2003a). Both series of pulping experiments in the presence of sodium metaborate, i.e. kraft pulping with mill autocausticized white liquor and kraft-borate pulping, resulted in an increase of screened pulp yield at the same kappa number. No similar effect of sodium metaborate was noticed in kraft-borate (35 % autocausticizing level) pulping of hardwoods (birch and maple) (Bujanovic et al., 2003b). No difference in the delignification (kappa number vs. H-factor) was noticed in the previous comparative studies of kraft and kraft-borate pulping (35 % autocausticizing level) of spruce, birch, and maple (Bujanovic et al., 2003a, b). However, the results obtained in the

pulping of western hemlock with mill conventional and autocauticized (10 % autocauticizing level) liquors, showed that an 8 % increase in the H-factor is needed in the pulping with the autocauticized white liquor to achieve a kappa number of 30 (Genco et al., 2002). These different results obtained in pulping of different wood species at the different levels of autocauticizing might indicate that different levels of sodium metaborate in the pulping liquor vary in the effect on delignification rate and this effect may be wood species dependent. The pulping studies of western hemlock and spruce in the presence of sodium metaborate corresponding to 10 % and 35 % autocauticizing respectively, showed a potential of sodium metaborate to protect cellulose in kraft pulping (Genco et al., 2002, Bujanovic et al., 2003b).

The current studies represent the continuation of the previous studies of the kraft and kraft-borate (35 % autocauticizing) pulps of spruce, birch, and maple conducted in order to learn more about the effect of sodium metaborate on the kraft pulping.

Kappa Number – Lignin Content – Hexenuronic Acid Groups - Extractives

The lignin content in wood is determined by the Klason method, which is based on the complete acid-catalyzed hydrolysis of polysaccharides while most of the lignin remains as an insoluble residue. It is required that this method be followed by the UV-spectral determination (absorption at 205 nm) of the acid-soluble lignin (T 222 om-88, UM 250). The lignin content in kraft pulp is determined most often by the kappa method, which is based on the principle that lignin consumes permanganate

at a much higher rate than the carbohydrate component of the pulp. For a long time, consumption of permanganate was attributed exclusively to the lignin oxidation. Klason lignin in kraft pulp is calculated from kappa number using an empirically determined conversion factor ($\% \text{ Klason lignin} = \text{kappa number} \times 0.15$) (T 236 cm-85, Dence, 1992). However, Li and Gellerstedt detected that, during kappa number determination, permanganate is consumed not only by lignin, but also by every other oxidizable pulp structure, most notably by hexenuronic acid groups (HexA) (Li, Gellerstedt, 1997, 1998). The HexA groups are formed in xylans from their 4-O-methyl-D-glucuronic acid groups (GlcpA) by elimination of CH_3O at C_4 followed by hydrogen elimination at C_5 (Sjöström, 1981). Li and Gellerstedt demonstrated that 10 μmol of hexenuronic acid correspond to 0.84 - 0.86 kappa units (Li, Gellerstedt, 1997). According to this finding, there is a need for both estimation of the contribution of the HexA groups to the kappa number and correction of the conversion factor between kappa number and Klason lignin. In addition to lignin and the HexA groups, permanganate is consumed by other oxidizable structures such as a free aldehyde group, a double bond, an α,β -unsaturated carbonyl group, and an α -keto-carboxylic acid group (Li, Gellerstedt, 1998). Therefore, it can be expected that different aromatic and aliphatic structures found in pulp extractives increase the measured kappa number. Gellerstedt et al. (1994) found that kappa numbers were reduced after extraction of the unbleached laboratory and industrial pulps (extraction in acetone and dichloromethane). Kappa number decreased from 16.1 to 15.7 for birch laboratory pulp and from 18.2 to 16.8 for birch industrial pulp. In this study,

the kappa number was corrected for the HexA component and conversion factors relating kappa number with Klason lignin were calculated for kraft and kraft-borate pulps of birch, maple, and spruce. As it was shown that acid-soluble lignin originates predominantly from carbohydrates, it was not considered in these studies (Li, Gellerstedt, 1998).

Hemicelluloses - Hexenuronic Acid Groups

Although kraft pulping results in the loss of a large part of the original wood hemicelluloses (40-60 %), hemicelluloses are important constituents of pulp. They improve pulp beatability and, hence, positively affect the inter-fiber bonds (d. A. Clark, 1985). For softwood kraft pulps, the remaining hemicelluloses are glucomannans and arabinoglucuronoxylans (pine kraft pulp: 8.5 % glucomannans, 10.6 % xylans), while hardwood kraft pulps are rich in glucuronoxylans (birch kraft pulp: 30.2 % xylans, 1.9 % glucomannans). The high difference in the content of xylans in softwood and hardwood kraft pulps is explained by the higher xylans content of hardwoods and the higher resistance of xylans compared to glucomannans in alkaline pulping conditions (Sjöström, 1981). Due to the higher content of xylans, the content of HexA groups in the hardwood pulps is higher than in the softwood pulps despite the higher ratio of 4-O-methylglucuronic acid/xylose (GlcA/Xylp) in softwoods (this ratio is 1:5 for softwoods and 1:10 for hardwoods, (Sjöström, 1981)). The relationship between the content of pentosans, the content of HexA groups, and kappa number was analyzed here in order to determine the effect of sodium

metaborate on the retention of pentosans and the HexA groups/Xylp ratio during kraft pulping of the studied species, birch, maple, and spruce. Also, based on the results of the holocellulose and pentosans determination the retention of hexosans was estimated. Based on the retention of pentosans and hexosans in kraft and kraft-borate pulping, the probable reasons of the screened yield increase in kraft-borate pulping of spruce were proposed.

Phenolic Hydroxyl Group Content

Lignin reactivity is largely determined by its phenolic hydroxyl group (PhOH) content as lignin phenolic phenylpropane units are preferably attacked in most chemical reactions. During kraft pulping, cleavage of the α - and β -aryl ether bonds results in the formation of new phenolic hydroxyl groups. Hence, the lignin reactivity and solubility in the cooking liquor are enhanced. Also, the PhOH groups play a prominent role in the pulp bleaching processes; the bleaching agents reacting through a peroxide type reaction (oxygen, peroxide) primarily attack phenolic lignin units; chlorine dioxide and ozone react with both phenolic and non-phenolic lignin units. But, in the case of chlorine dioxide, reaction with non-phenolic units occurs at a much slower rate (Dence, 1996). Therefore, the content of PhOH groups in pulps is a good indicator of the pulp bleachability. In this study, it was used to further evaluate the effect of sodium metaborate on the kraft pulping of birch, maple, and spruce.

Experimental

These experiments were a continuation of the kraft and kraft-borate pulping experiments conducted at Western Michigan University as an integral part of the broader studies on the borate-based autoausticizing.

Black spruce (*Picea mariana*), paper birch (*Betula papyrifera*), and sugar maple (*Acer saccharum*) chips were supplied by The U.S. Forest Products Laboratory, Madison, Wisconsin. Chemical composition of wood chips was analyzed according to the standard methods for determination of the contents of extractives (two-step extraction in toluene:ethanol (2/1) and ethanol) (T 204 om-88, Fengel, Przyklenk, 1983), holocellulose (Browning, 1967), acetyl bromide lignin in holocellulose (Dence, 1992, Iiyama, Wallis, 1988), pentosans (Bethge, 1964), and Klason and acid-soluble lignin content (T 222 om-88, UM 250, Dence, 1992). The details about the pulping procedure and conditions were published earlier (Bujanovic et al., 2003a,b). Kraft and kraft-borate pulping were performed under the same conditions except that white liquor used in the kraft-borate pulping contained sodium metaborate ($\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$) in the amount corresponding to 35 % autoausticizing. The kappa number (T 236 cm-85), and the Klason lignin content (T 222 om-88) in kraft and kraft-borate pulps were analyzed using the TAPPI Methods. The pulps were also analyzed for the content of extractives (T 204 om-88, Fengel, Przyklenk, 1983), holocellulose (Browning, 1967), pentosans (Bethge, 1964), hexenuronic acid groups, and phenolic hydroxyl groups. The content of hexenuronic acid groups (HexA) in pulps was determined by the method recently developed by Chai et al.

(2001). The results of HexA group determination were published earlier together with the contents of extractives (Bujanovic et al., 2003b). The phenolic hydroxyl group (PhOH) content in pulps was determined using the method originally recommended for determination of the concentration of PhOH in proteins, wines, and fruit juices, and recently applied on lignins and lignin-containing materials by de Sousa et al. (2001). This method uses the reagent of Folin and Ciocalteu (FC; supplied by Sigma-Aldrich), which is a heterophosphotungstate-molybdate. The FC reagent reacts selectively with PhOH giving a blue color with absorption proportional to the total amount of PhOH at 760 nm. Vanillin (Sigma-Aldrich) was used for calibration purposes. The PhOH content results were calculated using the Klason lignin content in the pulps.

Results and Discussion

Wood Chemical Composition

In order to evaluate kraft and kraft-borate pulping of birch, maple, and spruce, the global chemical composition of these species was studied, i.e. the contents of extractives, lignin, holocellulose and pentosans were determined. The holocellulose (polysaccharides; cellulose+xylans+(galacto)glucomannans) content was obtained after correction for the content of residual lignin determined by the acetyl bromide method (Iiyama, Wallis, 1988). The residual lignin contents were in agreement with the literature data; lower for the hardwood holocelluloses (maple: 7.18 %, birch: 6.68 % based on OD wood) than for the spruce holocellulose (11.10 % based on OD

wood) (Fengel, Wegener, 1984). Table IV-3.1. presents the chemical composition data obtained for birch, maple, and spruce in this study. It also includes the results obtained in the earlier studies (Sjöström, 1981, Fengel, Wegener, 1984, Rowell, 1984). As expected, the content of pentosans increased according to the series: spruce < maple < birch, while the content of lignin decreased in the same order. The higher acid-soluble lignin content found for birch and maple is in accordance with less condensed/more soluble GS-lignin (guaiacyl-syringyl) of hardwoods (Fengel, Wegener, 1984).

Table IV-3.1.

Chemical Composition of Birch, Maple, and Spruce

SPECIES [Ref]	COMPONENT, % OD Wood							
	Extractives			Holocel.	Pents.	Lignin		
	TE	E	Total			Klason	Acid-sol.	Total
Birch	3.51	0.18	3.69	76.3	25.4	17.8	3.08	20.9
1)			3	78	23	18		
2)			2.6	73.9	29.7			21.4
Maple	1.60	0.54	2.14	73.9	18.80	21.30	2.83	24.1
3)					15.6	22.7		
1)			3		17	22		
2)			2.5	71.5				25.2
Spruce	1.20	0.08	1.28	73.8	8.07	27.4	0.29	27.7
3)			2.6	71.7	7.6	27.3		
1)			2		12	27		

1) Rowell 1984; 2) Sjöström 1981; 3) Fengel, Wegener, 1984

Kappa number – Lignin Content – Hexenuronic Acid Groups – Extractives

As shown in Figure IV-3.1. (a-Birch; b-Maple; c-Spruce), straight-line relationships were obtained for Klason lignin content vs. kappa number for each of the studied kraft and kraft-borate pulps. The slopes of these lines are the conversion

factors between kappa number and Klason lignin content (C). They were calculated for the kraft and kraft-borate pulps as shown in Table IV-3.2. This table also shows the statistical data – coefficient of determination (R^2), standard error of regression (σ), and standard error of coefficient, i.e. standard error of calculated conversion factor (SE). Also, the tests involving the equality of coefficients of different regression were included in the statistical analysis of the data to test whether the assumption of the different regression model, i.e. different conversion factors for kraft and kraft-borate pulping, is correct (Pindyck, Rubinfeld, 1991).

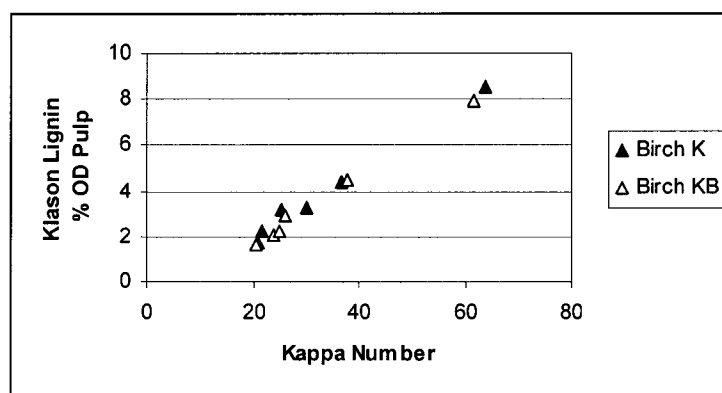


Figure IV-3.1.a. Klason Lignin vs. Kappa Number for Birch Kraft and Kraft-Borate Pulps

The C's (conversion factor to determine Klason lignin from kappa number) for birch, maple, and spruce pulps were different indicating the different level of oxidizable structures contributing to the measured kappa number. However, the test of the equality of coefficients of different regressions showed that the identical regression models are viable for kraft and corresponding kraft-borate pulps, i.e. the

equal C's can be applied for kraft (K) and corresponding kraft-borate (KB) pulps (Table II, MapleK/KB, Birch K/KB, Spruce K/KB).

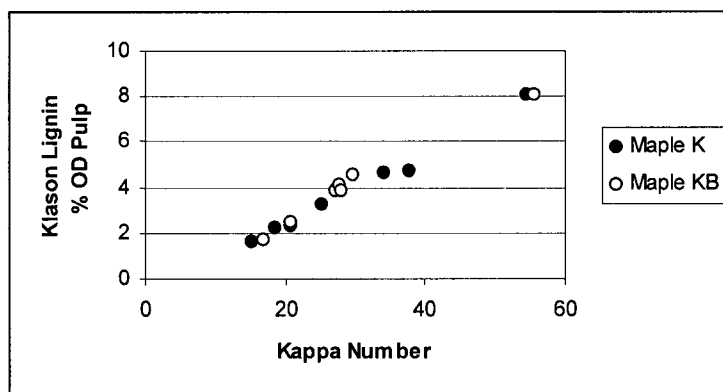


Figure IV-3.1.b. Klason Lignin vs. Kappa Number for Maple Kraft and Kraft-Borate Pulps

These data indicate that sodium metaborate did not affect the level of total permanganate oxidizable structures formed in pulping of birch, maple, and spruce (lignin, HexA groups, aliphatic double bonds, aldehyde groups, α -keto-carboxylic acid groups (Li, Gellerstedt, 1997, 1998)).

The C for spruce pulps (Spruce K/KB, $C=0.149$) was almost equal to the conversion factor recommended in the literature - 0.15 (T 236 cm-85, Dence, 1992). It might indicate that the conversion factor recommended in the literature is more applicable for softwood than for hardwood pulps. The C's calculated for birch and maple pulps (Birch K/KB, $C=0.120$; Maple K/KB, $C=0.140$) were expected to be lower than that calculated spruce pulps as the higher content of HexA groups was found in maple and birch pulps than in spruce pulps. The observed lower C's found

for birch compared to maple pulps can be explained by the higher contents of both HexA groups and extractives, i.e. higher content of oxidizable structures other than lignin, in birch than in maple pulps (Table IV-3.2.).

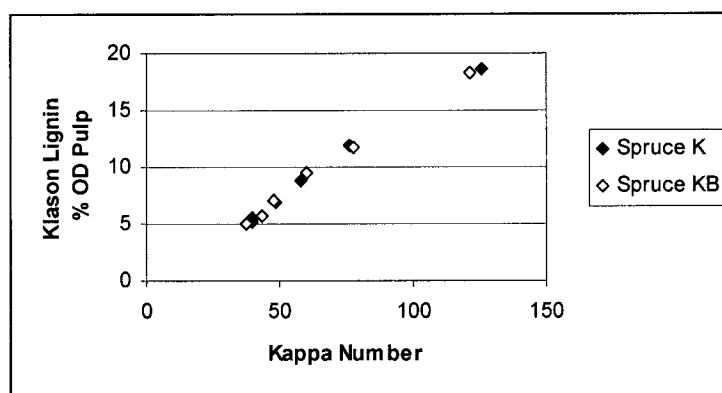


Figure IV-3.1.c. Klason Lignin vs. Kappa Number for Spruce Kraft and Kraft-Borate Pulps

The contribution of HexA groups to the measured kappa number for the studied pulps was calculated using the molar equivalent of 8.5 (Dence, 1992). The plots of the HexA component of kappa number at different kappa numbers for birch and maple kraft and kraft-borate pulps are shown in Figure IV-3.2., and for spruce kraft and kraft-borate pulps in Figure IV-3.3.

In accordance with the higher contents of HexA groups found in birch and maple pulps, the HexA contribution to the measured kappa number is higher for these pulps than for spruce pulps. For maple kraft pulp, the highest contribution of HexA to the kappa number was found at kappa number 15.2 when 3.48 kappa units or 22.9 % of the measured kappa number originated from HexA. The highest contribution of

HexA to the kappa number for spruce pulps was much lower and was found for spruce kraft pulp at kappa number 48.6 where 2.4 kappa units or only 4.9 % of measured kappa number resulted from HexA groups.

Table IV-3.2.

Conversion Factors (Kappa Number/"HexA – free" Kappa Number to Klason Lignin Content) and Average Contents of Extractives and HexA groups in Pulps

PULP	C ¹ (R ² , %)	σ (SE)	C-HA ² (R ² , %)	σ (SE)	Extractives Average Content % OD Pulp (St.dev)	HexA Average Content μmol/g pulp (St.dev)
BirchK	0.123 (98.77)	0.5441 (0.0061)	0.135 (99.69)	0.2723 (0.0034)	1.32 (0.17)	44.3 (13.6)
BirchKB	0.116 (97.79)	0.6756 (0.0078)	0.129 (99.05)	0.4422 (0.0056)	1.43 (0.28)	45.7 (9.6)
BirchK/KB	0.120 (98.24)	0.5980 (0.0048)	0.132 (99.34)	0.3673 (0.0033)	1.38 (0.23)	45.0 (11.1)
MapleK	0.136 (99.14)	0.4355 (0.0051)	0.149 (99.72)	0.2499 (0.0032)	0.56 (0.15)	37.5 (7.9)
MapleKB	0.143 (99.46)	0.3582 (0.0043)	0.157 (99.60)	0.3073 (0.0040)	0.58 (0.10)	36.2 (8.4)
MapleK/KB	0.140 (99.24)	0.4006 (0.0034)	0.153 (99.59)	0.2945 (0.0027)	0.57 (0.12)	36.9 (7.7)
SpruceK	0.148 (99.83)	0.4709 (0.0027)	0.153 (99.83)	0.4817 (0.0028)	0.58 (0.1)	24.5 (6.6)
SpruceKB	0.149 (99.84)	0.4605 (0.0027)	0.153 (99.82)	0.4848 (0.0029)	0.56 (0.1)	22.7 (7.2)
SpruceK/KB	0.149 (99.83)	0.4448 (0.0018)	0.153 (99.83)	0.4613 (0.0019)	0.57 (0.10)	23.6 (6.7)

¹C = Conversion factor; Klason lignin = C x Kappa number

²C-HA = Conversion factor; Klason lignin = C-HA x "HexA – free" Kappa number

"HexA-free" Kappa number = Kappa number – 8.5 x HexA (mol/g)

No effect of sodium metaborate was observed on the content of HexA groups in the pulps (Bujanovic et al., 2003b) and hence, on the contribution of HexA to the measured kappa number (Figures IV-3.2., 3). The kappa number units originated from HexA were subtracted from the corresponding kappa numbers and the kappa numbers corrected for the contribution of HexA ("HexA-free" Kappa Number) were

obtained. Figure IV-3.4. shows the plot of Klason lignin vs. “HexA-free” kappa number for kraft and kraft-borate pulps, while Table IV-3.2. contains the calculated conversion factors – C-HA ($\text{Klason Lignin} = \text{C-HA} \times \text{“HexA-free” Kappa Number}$).

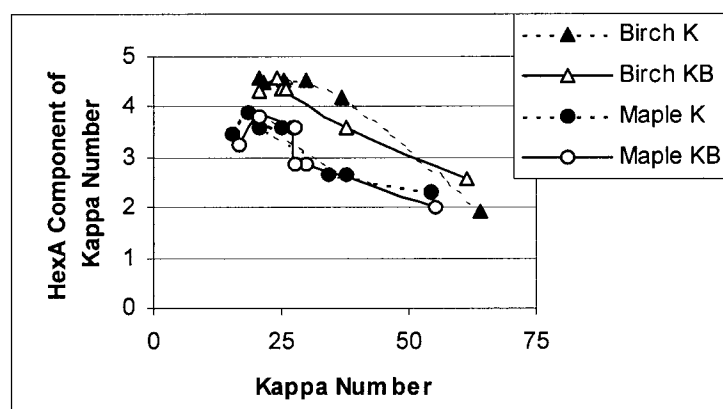


Figure IV-3.2. HexA Groups Contribution to Kappa Number at Different Kappa Numbers for Birch and Maple Kraft and Kraft-Borate Pulps

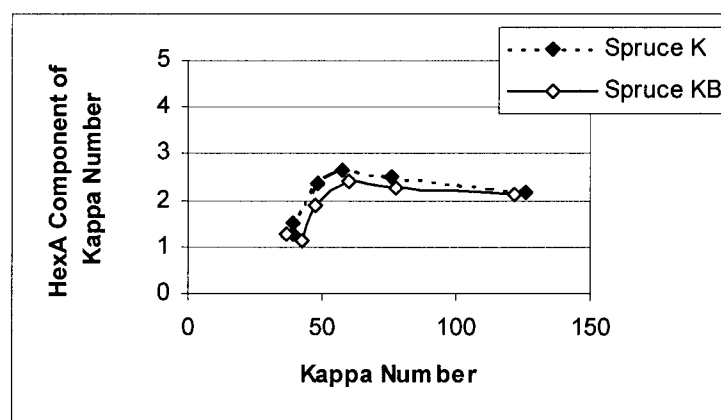


Figure IV-3.3. HexA Groups Contribution to Kappa Number at Different Kappa Numbers for Spruce Kraft and Kraft-Borate Pulps

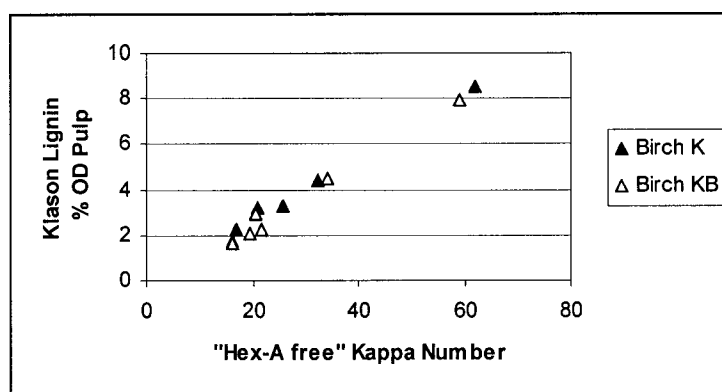


Figure IV-3.4a. Klason Lignin vs. "HexA-free" Kappa Number for Birch Kraft and Kraft-Borate Pulps

The increasing order of conversion factors calculated for kappa number/Klason lignin $C - HA_{BirchK / KB} < C - HA_{MapleK / KB} < C - HA_{SpruceK / KB}$ was changed to $C - HA_{BirchK / KB} < C - HA_{MapleK / KB} = C - HA_{SpruceK / KB}$ for conversion factors calculated for "HexA-free" kappa number/Klason lignin. According to this result, "HexA-free" kappa number of birch pulps includes the contribution of oxidizable structures other than lignin in higher degree than in the case of spruce and maple pulps (birch pulps consume permanganate at higher rate than maple and spruce pulps).

Some of these structures belong to the birch pulp extractives (higher content of extractives found in birch than in maple and spruce pulps, Table IV-3.2.). The test of the equality of coefficients of different regressions showed that the identical C-HA could be estimated for kraft and corresponding kraft-borate pulps (Birch K/KB C-HA= 0.132; Maple K/KB C-HA = 0.153; Spruce K/KB C-HA = 0.153). The same

C-HA's together with the same C's which characterize kraft and kraft-borate pulps shows that sodium metaborate has no effect on the formation of the oxidizable structures in kraft-borate pulping of birch, maple, and spruce, at 35 % autocausticizing level. This is an important conclusion regarding the consumption of bleaching agents in bleaching phase.

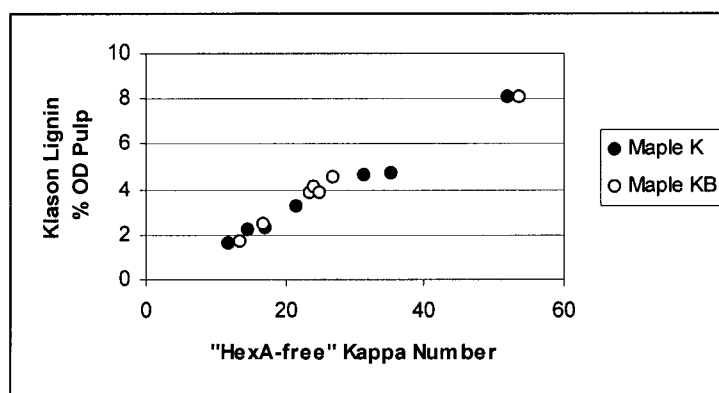


Figure IV-3.4b. Klason Lignin vs. "HexA-free" Kappa Number for Maple Kraft and Kraft-Borate Pulps

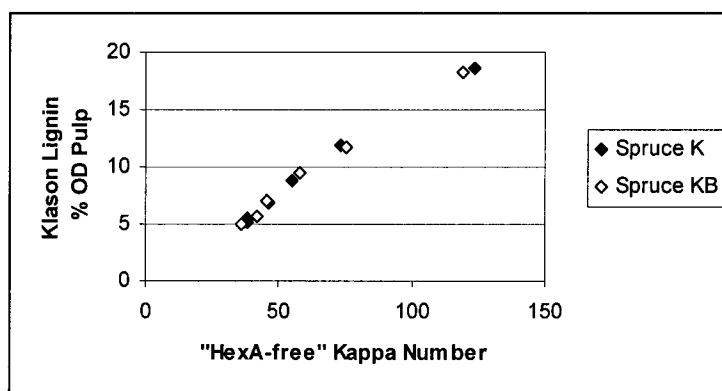


Figure IV-3.4c. Klason Lignin vs. "HexA-free" Kappa Number for Spruce Kraft and Kraft-Borate Pulps

Pentosans - Hexenuronic Acid Groups

The pentosans content as a function of kappa number for birch, maple, and spruce kraft and kraft-borate pulps is shown in Figure IV-3.5. The same increasing order of the pentosans content found for wood species, spruce < maple < birch, was found for both kraft and kraft-borate pulps.

The pentosans retention in percent of the wood pentosans was calculated during kraft and kraft-borate pulping as shown in Figure V-3.6. (the screened pulp yield data have been reported earlier (Bujanovic et al., 2003a,b)). It was found that the retention of birch and maple pentosans is higher than the retention of spruce pentosans. The retention of spruce pentosans decreased continually, i.e. the spruce pentosans continually dissolved during pulping from kappa number 120 to kappa number 40. At kappa number 40, the retention of spruce pentosans was approximately 44 % of original pentosans, while the retention of birch and maple pentosans was approximately 54 % of original pentosans. No effect of sodium metaborate was observed on the pentosans retention in pulping of these three species.

The pentosans retention is examined further in an analysis of the content of HexA groups in pentosans. The pentosans retained in pulps can be considered as xylans, since arabinose, which is a building unit of softwoods arabinoglucuronoxylans, is easily eliminated during the course of the alkaline degradation of polysaccharides (Sjöström, 1981). Therefore, the molar ratio of HexA/Xylp (hexenuronic acid groups/xylose) during pulping can be calculated.

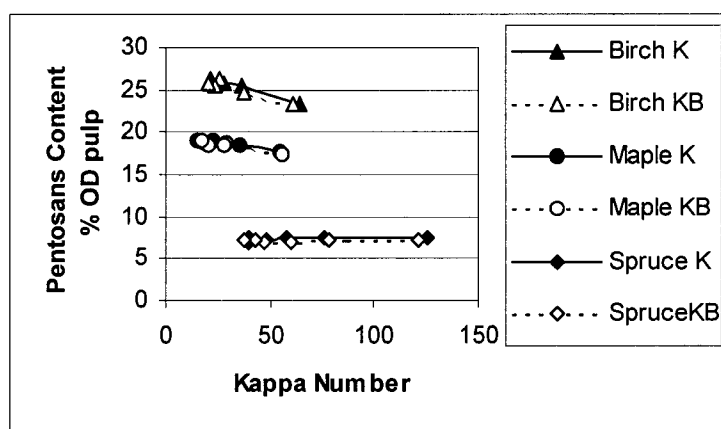


Figure IV-3.5. Pentosans Content in Birch, Maple, and Spruce Kraft and Kraft-Borate Pulps vs. Kappa Number

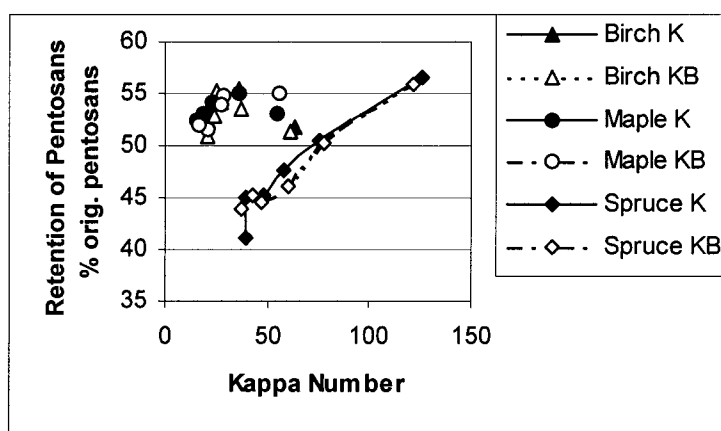


Figure IV-3.6. Retention of Pentosans in Birch, Maple, and Spruce Kraft and Kraft-Borate Pulps at Different Kappa Numbers

The HexA/Xylp ratio of hardwood pulps slightly increased in pulping from kappa number ~60 to kappa number ~30 as shown in Figure IV-3.7.

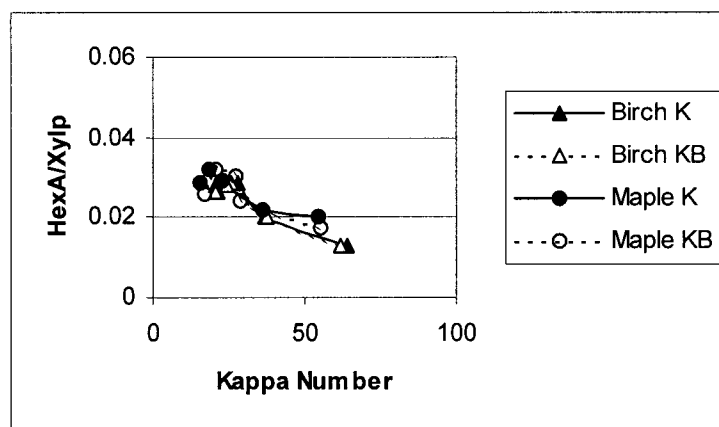


Figure IV-3.7. Content of HexA Groups in Pentosans (Xylans) of Birch and Maple Kraft and Kraft-Borate Pulps at Different Kappa Numbers

The corresponding number of xylose units per one HexA group decreased from ~55 to ~35. At the same time, the retention of pentosans was stable and approximately 54 % of original pentosans. The observed increase of HexA content in birch and maple pulp pentosans resulted from a relatively high effective alkali concentration (EA) in this pulping phase as Chai et al. found that HexA formation from GlcpA strongly depends on the EA (Chai et al., 2001).

This increase of HexA content in pentosans had a beneficial effect on the retention of pentosans as Jiang et al. (2000) reported the stabilizing role of HexA groups in preventing the peeling reactions of xylans (pentosans) during kraft pulping. In further pulping, in conditions of reduced effective alkali concentration (EA), a slight decrease of the HexA content in pentosans and, hence, the pentosans dissolution was observed (Fig's IV-3.6.,7). The results obtained here for birch and maple pulping are in agreement with both earlier reported effects - positive effect of

HexA groups on the xylans retention and strong effect of EA concentration on the HexA groups formation/dissolution (Chai et al., 2001, Jiang et al., 2000).

The spruce pulp pentosans were characterized by slight increase of the content of HexA in pulps of decreasing kappa number from ~120 to ~60 as shown in Figure IV-3.8. (corresponding H-factors increased from 500 to 1500). During this pulping period, the number of xylose units per one HexA group decreased from ~23 to ~18, while the spruce xylans degraded almost linearly (Fig. IV-3.6.). This indicates that the dissolved xylans were of lower HexA content or new HexA groups were formed. The former would be in support of the HexA stabilizing role in preventing xylans dissolution in kraft pulping (Jiang et al., 2000).

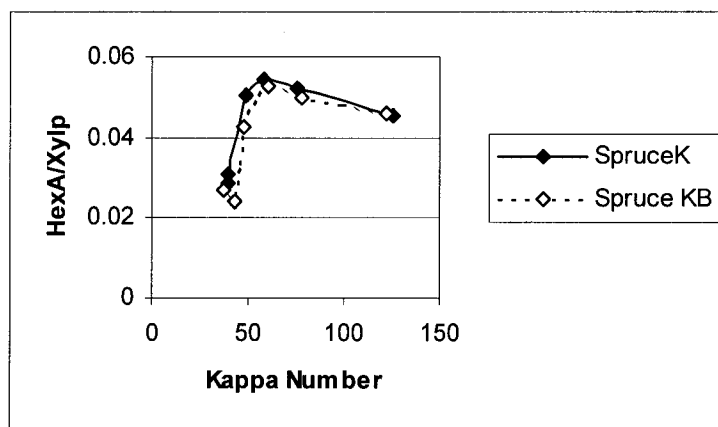


Figure IV-3.8. Content of HexA Groups in Pentosans (Xylans) of Spruce Kraft and Kraft-Borate Pulps at Different Kappa Numbers

In further pulping at H-factor higher than 1500, the HexA groups were dissolved more readily than the xylans (Fig. IV-3.6.), since the HexA content in

xylans was decreasing in the corresponding pulps (kappa number lower than 50). This may indicate that the reduced EA concentration in this late pulping phase led to an acceleration of HexA dissolution (Chai et al., 2001).

Hexosans (Cellulose+Glucomannans) Retention

It was shown that, at the same kappa number, the screened yield of spruce kraft-borate pulps is higher than the screened yield of spruce kraft pulps (Bujanovic et al., 2003a), while the screened yields of birch and maple kraft pulps were approximately equal to the screened yield of birch and maple kraft-borate pulps, respectively (Bujanovic et al., 2003b). The holocellulose (cellulose+xylans+glucomannans) contents of the pulps were determined according to the acid-chlorite method (Browning, 1967). Based on the screened yields, the holocellulose and the pentosans contents determined for wood and corresponding pulps, the retention of hexosans, which include cellulose and glucomannans (% original hexosans) was calculated in pulps of different kappa number. The results are shown for birch and maple in Figure IV-3.9. and for spruce in Figure IV-3.10.

Retention of hexosans decreased in the series maple > birch > spruce. No effect of sodium metaborate on the retention of hexosans is observed in pulping of hardwoods – birch and maple (Fig. IV-3.9.). However, kraft-borate pulping of spruce resulted in higher retention of hexosans than in kraft pulping at kappa numbers lower than ~60 as shown in Figure IV-3.10. Consequently, higher screened yield of spruce kraft-borate pulps might be a result of higher retention of hexosans. The potential

role of sodium metaborate in protection of hexosans during kraft pulping is in agreement with a recently observed potential of sodium metaborate to protect cellulose in kraft pulping (Genco et al., 2002, Bujanovic et al., 2003a).

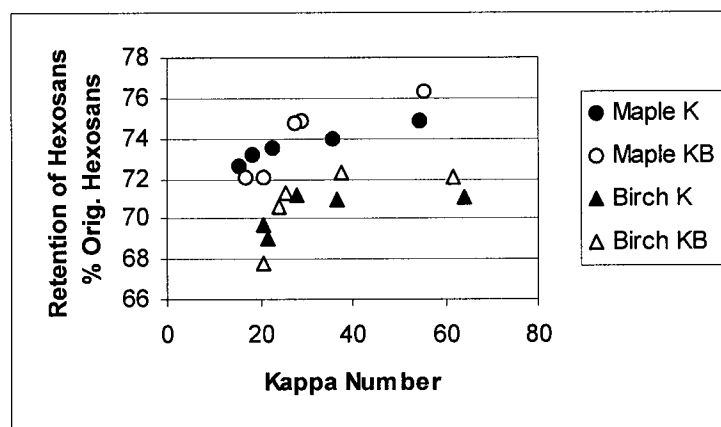


Figure IV-3.9. Retention of Hexosans in Birch and Maple Kraft and Kraft-Borate Pulping

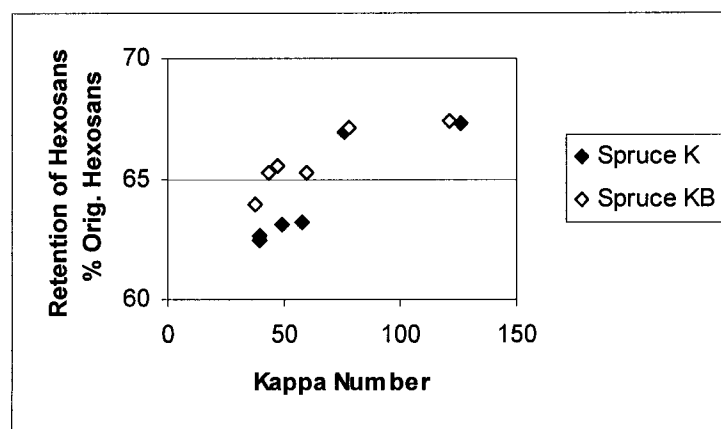


Figure IV-3.10. Retention of Hexosans in Spruce Kraft and Kraft-Borate Pulping

Phenolic Hydroxyl Group Content

The original PhOH content in the lignin of hardwood species is lower than that in the lignin of softwood species. The proportion of phenolic units in percent of the phenylpropane (C9) units is 13 % in softwoods and is in 7-11 % range in hardwoods (for example, approximately 70 mmol PhOH/100 g lignin - Norway spruce; 50 mmol PhOH/100 g lignin – aspen) (Chen et al., 19997, Lai, 1992).

The main reaction leading to the lignin fragmentation in kraft pulping is cleavage of aryl ether bonds in phenolic and nonphenolic β -aryl ether structures. The result of this type of reaction is an increase of the PhOH content in lignin. As softwood lignins contain less β -aryl ether structures than hardwood lignins (spruce (*Picea abies*) – 48 %, birch (*Betula verrucosa*) – 60 % bonds in lignin are arylglycerol- β -aryl ether structures (Sjöström, 1981) kraft pulping results in higher content of PhOH groups in hardwood than in softwood lignins.

The content of phenolic hydroxyl groups in the pulps was determined using the Folin and Ciocalteu method, which was suggested recently as a simple and rapid method of providing reliable results (de Sousa, 2001). The PhOH content was plotted against kappa number as shown in Figure IV-3.11. for birch and maple pulping and as shown in Figure IV-3.12. for spruce pulping. As expected, the PhOH content in pulp residual lignin increased in the following order spruce < birch ~ maple.

No effect of sodium metaborate was observed on the level of PhOH groups in the residual lignin. The kraft and kraft-borate pulps of studied species contained lignin of the same PhOH content during pulping.

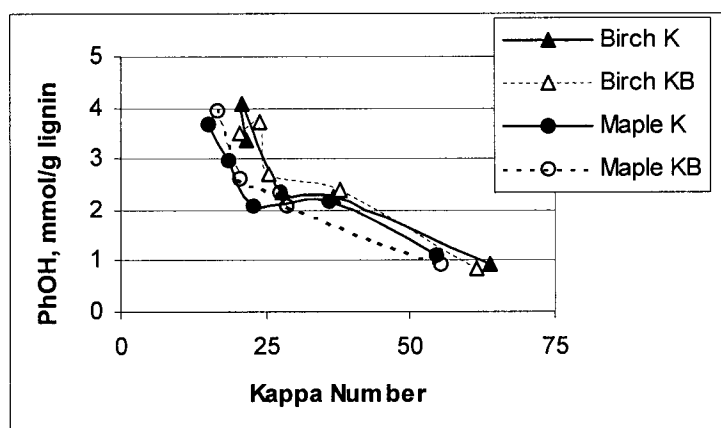


Figure IV-3.11. Content of PhOH Groups in Lignin of Birch and Maple Kraft and Kraft-Borate Pulps vs. Kappa Number

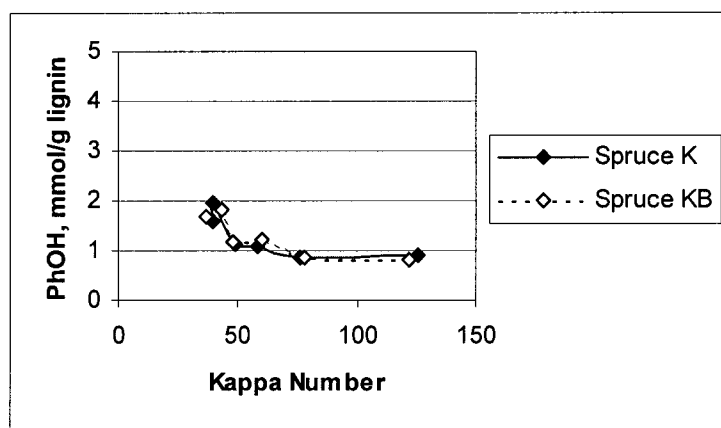


Figure IV-3.12. Content of PhOH Groups in Lignin of Spruce Kraft and Kraft-Borate Pulps vs. Kappa Number

As the phenolic hydroxyl groups represent the most reactive sites in pulping and bleaching reactions, these results indicate that kraft-borate pulping at 35 % borate-based autocausticizing results in lignin of basically the same reactivity as kraft pulping. The results obtained in this study are in accordance with the results obtained earlier in the studies of residual lignin isolated by acid-hydrolysis from spruce kraft and kraft-borate (35 % autocausticizing) pulps as both pulps resulted in lignin of the same yield and composition (Bujanovic et al., 2003c). The similar/same bleachability of spruce kraft and kraft-borate pulps might be expected as pulping at the same H-factor resulted in pulps of approximately the same kappa numbers, contents of extractives, HexA, PhOH, and residual lignin of similar structure.

Conclusions

Previous studies showed that the delignification path of birch, maple, and spruce in kraft and kraft-borate (sodium metaborate present in white liquor in the amount corresponding to 35 % autocausticizing) pulping was essentially the same. In a continuation of these studies, sodium metaborate was not observed to affect the chemical properties of birch, maple, and spruce pulps. Chemical composition of pulp, including the content of pentosans, HexA, the ratio of HexA/Xylp, and the content of PhOH groups for birch, spruce, and maple was not changed in kraft-borate pulping. While the pentosans retention remained the same in kraft and kraft-borate pulping of the studied species, kraft-borate pulping of spruce led to a stabilization of hexosans – cellulose and glucomannans. This result should be explored further, as it

would be a beneficial side effect of the implementation of borate-based partial autocausticizing in the kraft pulping of spruce. Conversion factors between kappa number/"free HexA" kappa number and Klason lignin for kraft and corresponding kraft-borate pulps of birch, maple, and spruce were the same. Therefore, sodium metaborate did not affect the level of oxidizable structures in kraft and kraft-borate pulps. Based on these results and the chemical structure of spruce pulp residual lignin, which was studied recently, similar bleachability of spruce kraft and kraft-borate pulps is expected.

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IV-4. Tensile and Tear Strength of Kraft and Kraft-Borate Pulps

Abstract

In order to study the effect of sodium metaborate as an autocauticizing agent on the kraft process and the properties of pulp, the kraft and kraft-borate pulps of birch, maple, and spruce were produced and analyzed in our previous experiments. The results of these experiments showed that sodium metaborate, present in the white liquor in the amount corresponding to the 35 % autocauticizing level, does not affect the pulping process and the chemical properties of pulp. In a continuation of this study, the physical properties of the kraft and kraft-borate pulps were analyzed. The pulps were refined (PFI mill, 5,000 rpm). The CSF of the pulps was measured before and after refining. Test handsheets for determining the physical properties of pulp were formed from the refined pulps. It was found that the mechanical properties, density, tensile, and tear strength of kraft and kraft-borate pulps of birch, maple, and spruce refined in a PFI mill at 5,000 rpm were the same.

Introduction

There is considerable interest in the use of borate to autocauticize sodium carbonate, that is, produce sodium hydroxide without the use of the causticizing-calcining cycle. Autocauticizing offers several advantages in terms of required capital investment and energy efficiency because its full implementation would eliminate the lime kiln, slaker, and causticizing vessels. Also, the causticizing limited

mills can use a partial borate autocausticizing as a method of increasing the mill causticizing capacity without installing new equipment (Tran et al., 1999, Kochesfahani, Bair, 2002). Swedish researchers recommend the partial borate causticizing technology as a short-term goal (1-5 years) and 100 % borate direct causticizing as a long-term goal (≥ 10 years) in the development of “The Eco-cyclic Pulp Mill.” They also propose that borate causticizing decreases both the emission of “fossil” carbon dioxide and production of solid waste and increases the level of sold power in kraft mill (Axegård, 2002).

In the kraft technology with partial borate autocausticizing, borates circulate within the cycle autocausticizing the liquor. In several mill trials it was found that when the liquor is loaded with borate, only make-up borate is required to keep the autocausticizing level at the target (at 20 % autocausticizing level make-up borate was 3.44 % of the total required amount of sodium metaborate) (Kochesfahani, Bair, 2002). Therefore, in the kraft technology with borate autocausticizing, pulping process is performed in the presence of sodium metaborate. The effect of sodium metaborate on the delignification and the properties of pulp should be explored. In the recent studies, the kraft and kraft-borate pulping of softwoods were carried out using either the mill conventional and autocausticized (10 % autocausticizing level) liquors when western hemlock was pulped (Genco et al., 2002) or the kraft and kraft-borate (35 % autocausticizing level) liquors prepared from commercial chemicals when spruce was pulped (Bujanovic et al., 2003a). Both series of pulping experiments in the presence of sodium metaborate, i.e. kraft pulping with mill

autocausticized white liquor and kraft-borate pulping, resulted in an increase of screened pulp yield at the same kappa number. No similar effect of sodium metaborate was noticed in kraft-borate (35 % autocausticizing level) pulping of hardwoods, birch and maple (Bujanovic et al., 2003b). No difference in the delignification was noticed in the previous comparative studies of kraft and kraft-borate pulping of spruce, birch, and maple (Bujanovic et al., 2003a, b). However, the results obtained in the pulping of western hemlock with mill conventional and autocausticized liquors showed that an 8 % increase in the H-factor is needed in pulping with the autocausticized white liquor to achieve a kappa number of 30 (Genco et al., 2002). These different results obtained in pulping of different wood species at the different levels of autocausticizing suggest that different levels of sodium metaborate in the pulping liquor vary in the effect on delignification rate and this effect may also be wood species dependent. The pulping studies of western hemlock and spruce in the presence of sodium metaborate corresponding to 10 % and 35 % autocausticizing respectively, showed a potential of sodium metaborate to protect cellulose during kraft pulping (Bujanovic et al., 2003a, b).

Experimental

These experiments were a continuation of the kraft and kraft-borate pulping experiments conducted at Western Michigan University as an integral part of the broader studies on the borate-based autocausticizing.

Black spruce (*Picea mariana*), paper birch (*Betula papyrifera*), and sugar maple (*Acer saccharum*) chips were supplied by The U.S. Forest Products Laboratory, Madison, Wisconsin. The details about the pulping procedure and conditions were published earlier (Bujanovic et al., 2003a, b). Kraft and kraft-borate pulping were performed under exactly the same conditions except that white liquor used in the kraft-borate pulping contained sodium metaborate ($\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$) in the amount corresponding to 35 % autocauticizing. The kappa number of kraft and kraft-borate pulps was analyzed using the TAPPI Method (T 236 cm-85). The pulps used in these experiments along with the H-factors at which they were produced and the resulting kappa numbers are shown in Table IV-4.1.

Table IV-4.1.

Kraft and Kraft-Borate Pulps Used in the Experiments

Species	H-Factor	Kappa Number	
		Kraft - K	Kraft-Borate – KB
Birch	500	36.7	37.7
	1000	20.7	24.0
	1500	21.5	20.6
Maple	500	35.9	28.8
	1000	18.4	20.6
	1500	15.2	16.7
Spruce	1000	76.0	77.9
	1500	57.7	59.9
	2000	48.6	47.5

Freeness of pulps was measured following the TAPPI freeness method (T 227 om-85) before and after refining of pulps in a PFI (T 248 cm-85: Laboratory beating of pulp (PFI mill method)). After refining, the laboratory handsheets were made (T 205 om-88: Forming handsheets for physical tests of pulp). The density, tensile and

tear strenght were determined in accordance with the TAPPI Methods (T220 om-88: Physical testing of pulp handsheets; T414 om-88: Internal tearing resistance of paper (Elmendorf-type method); T 494 om-88: Tensile breaking properties of paper and paperboard (Using constant rate of elongation apparatus)).

Results and Discussion

The previous studies showed that delignification of birch, maple, and spruce is not affected by sodium metaborate, which is present in the white liquor in the amount corresponding to 35 % autocausticizing level. The statistical analysis showed that the same kappa number/H-factor regression models can be applied for the kraft and corresponding kraft-borate pulping (Bujanovic et al., 2003b). Therefore, at the 35 % borate autocausticizing level, retardation of delignification is not expected in pulping of birch, maple, and spruce. Chemical analysis showed that basically there is no difference in chemical composition between the kraft and corresponding kraft-borate pulps of these species (Bujanovic et al., 2003a, b, d). Some mechanical properties of these pulps were analyzed in the current studies.

The CSF of the studied kraft and kraft-borate pulps (Table IV-4.1.) before and after refining in a PFI mill at 5,000 rpm are shown in Table IV-4.2.

The CSF of studied pulps was in the expected range for unrefined kraft pulps in the order: spruce > birch > maple. This corresponds to the decreasing order of lignin content in pulps (Table IV-4.1.). The “beatability” of pulps at 5,000 rpm in a

Table IV-4.2.

CSF of Raw Pulps and After PFI Mill Refining at 5,000 rpm.

PULP	H-FACTOR							
	500		1000		1500		2000	
	CSF		CSF		CSF		CSF	
	Raw	Refined	Raw	Refined	Raw	Refined	Raw	Refined
BirchK	700	150	695	190	705	160		
BirchKB	710	185	705	140	695	170		
MapleK	585	330	525	275	525	255		
MapleKB	550	330	550	325	525	235		
SpruceK			725	675	720	510	705	500
SpruceKB			725	635	705	525	705	485

PFI mill decreased in the following order: birch > maple > spruce, based on the CSF's before and after refining. "Beatability", as an important pulp characteristic, is mostly controlled by the thinness of the fiber walls and the content of lignin and hemicelluloses. Higher "beatability", i.e. easier refining of hardwood pulps, which are enriched with hemicelluloses, was confirmed in this study (d'A. Clark, 1985, Peel, 1999). The CSF's of raw and refined pulps were approximately the same for kraft and corresponding kraft-borate pulps and no effect of borate was noticed on the pulp refining.

Density of the laboratory handsheets made from refined pulps was determined. The density of pulps increased with the decreasing kappa number. It was found that the kraft and kraft-borate pulps at the same kappa number have approximately the same density as shown for birch, maple, and spruce in the Figures IV-4.1., 2., and 3., respectively. Statistical analysis of the data indicates that density of pulps at the same kappa number decreases in the following order: spruce>birch>maple.

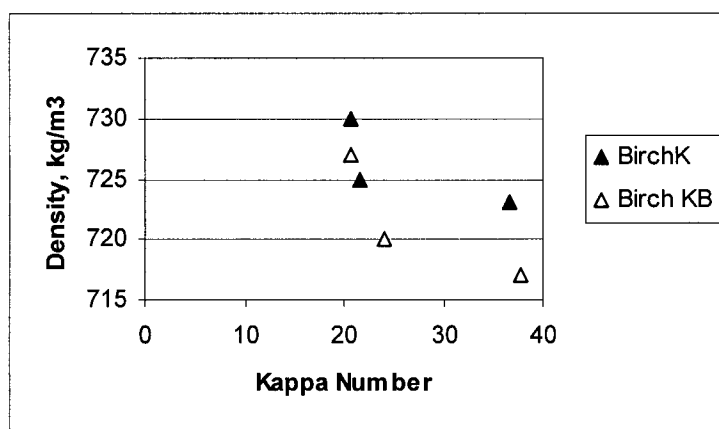


Figure IV-4.1. Kappa Number Dependence of Density of Sheets Made from Birch Kraft and Kraft-Borate Pulps

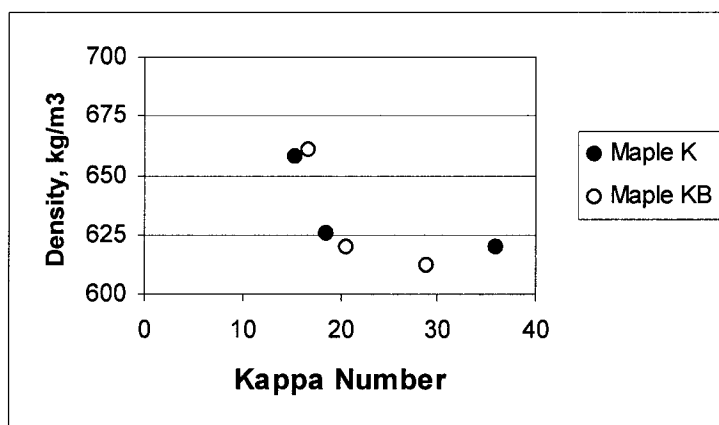


Figure IV-4.2. Kappa Number Dependence of Density of Sheets Made from Maple Kraft and Kraft-Borate Pulps

Tensile index was measured, and the values obtained for the kraft and kraft-borate pulps were compared at the same density as shown in Figures IV-4.4., 5., and 6. for birch, maple, and spruce, respectively.

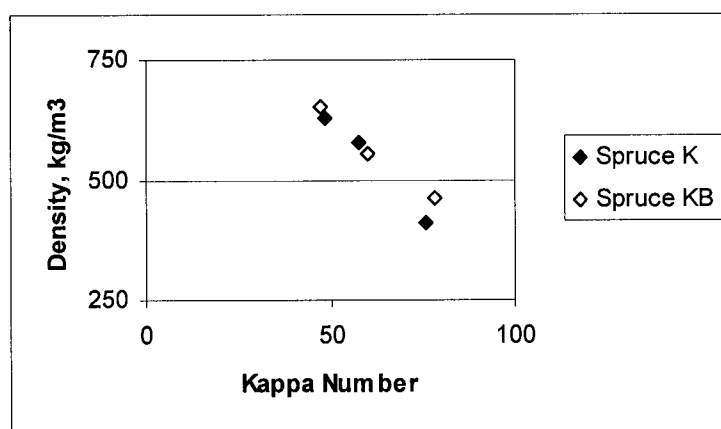


Figure IV-4.3. Kappa Number Dependence of Density of Sheets Made from Spruce Kraft and Kraft-Borate pulps

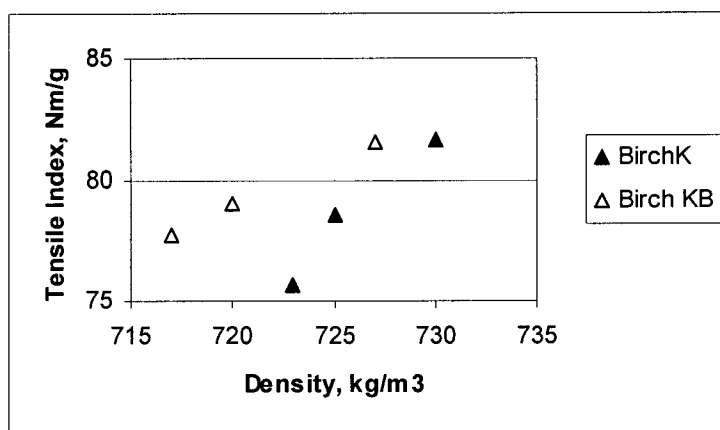


Figure IV-4.4. Tensile Index vs. Density of Sheets Made from Birch Kraft and Kraft-Borate Pulps

While the results obtained for spruce pulps indicate that kraft and kraft-borate pulps have the same tensile index at the same density, the results obtained for birch and maple pulps indicate a slightly higher tensile index of kraft-borate pulps at the

same density. This potential positive effect of sodium metaborate on the tensile strength of birch and maple pulps should be further explored in upcoming studies.

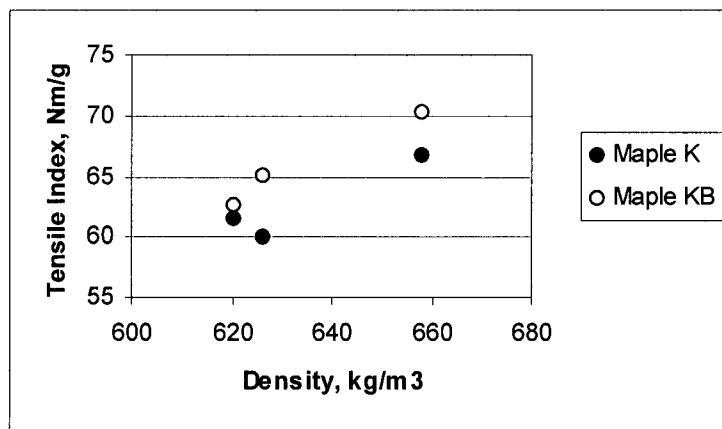


Figure IV-4.5. Tensile Index vs. Density of Sheets Made from Maple Kraft and Kraft-Borate Pulps

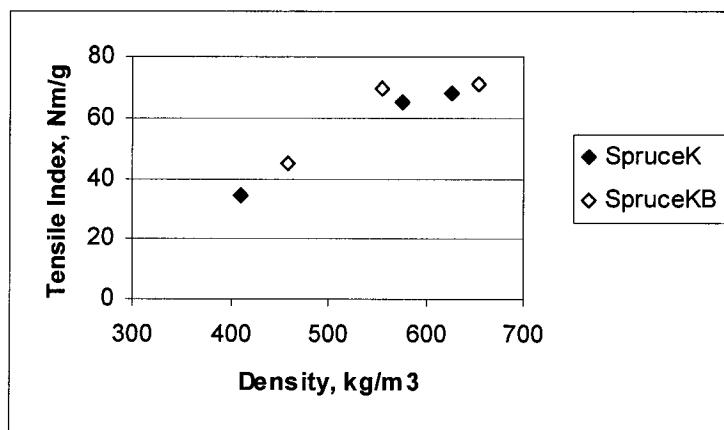


Figure IV-4.6. Tensile Index vs. Density of Sheets Made from Spruce Kraft and Kraft-Borate Pulps

The effect of sodium metaborate on the mechanical properties of pulp was studied further by determination of tear index of kraft and kraft borate pulps. Then, the previously found tensile indices were plotted against tear indices. The plots for birch, maple and spruce pulps are shown in Figures IV-4.7., 8., and 9., respectively.

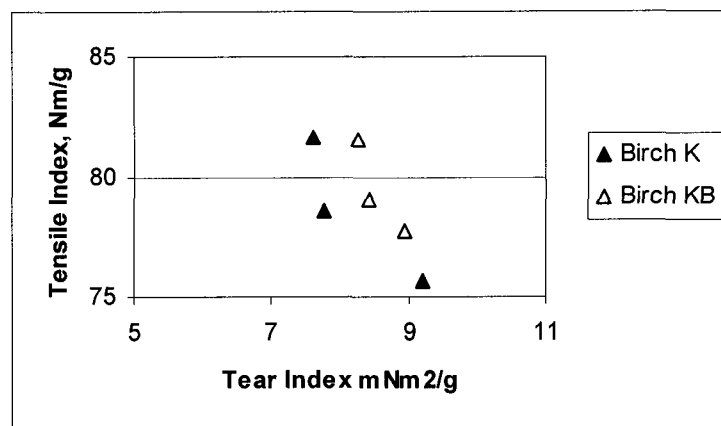


Figure IV-4.7. Tensile Index vs. Tear Index for Birch Kraft and Kraft-Borate Pulps

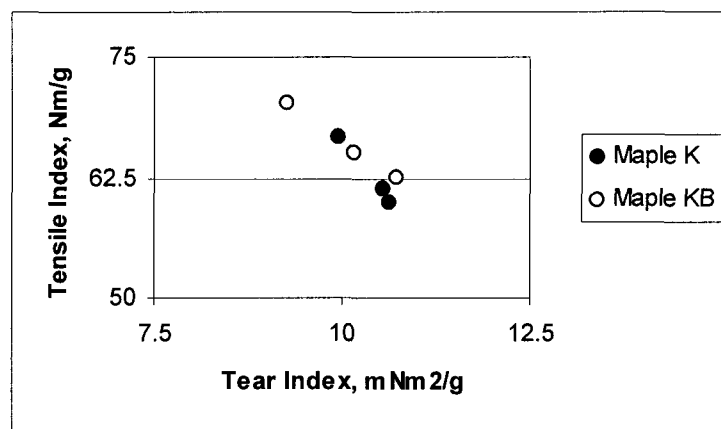


Figure IV-4.8. Tensile Index vs. Tear Index for Maple Kraft and Kraft-Borate Pulps

As expected, the tear resistance decrease is followed by the tensile strength increase (fiber shortening and stronger fiber bonding at lower kappa number, i.e. at higher H-factors) which is the same for kraft and kraft-borate pulps. This indicates that sodium metaborate does not affect the basic mechanical properties of birch, maple, and spruce pulps.

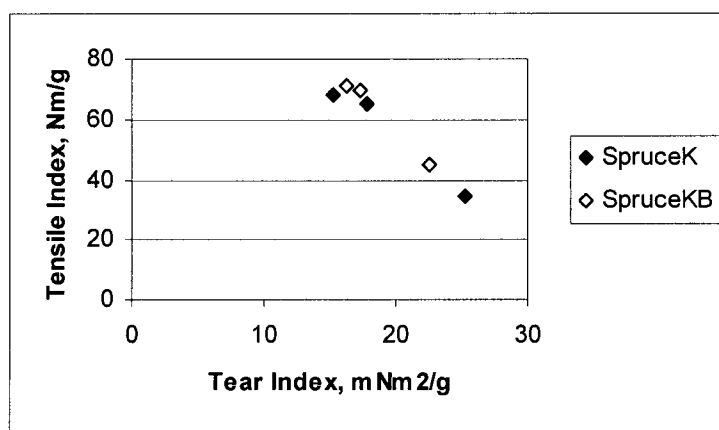


Figure IV-4.9. Tensile Index vs. Tear Index for Spruce Kraft and Kraft-Borate Pulps

Conclusion

Sodium metaborate, which is used in kraft technology as a partial autoausticizing agent, was studied to determine its effect on the mechanical properties of pulp at 35 % level of autoausticizing. These studies indicated that the mechanical properties, density, tensile, and tear strength of kraft and kraft-borate pulps of birch, maple, and spruce refined in a PFI mill at 5,000 rpm. are the same.

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IV-5. Effect of Borate Autocausticizing on Kraft Pulping

Abstract

Partial autocausticizing using boron has become a viable option for removing recausticizing bottlenecks in the chemical recovery cycle of kraft pulp mills. Several full-scale trials in North America have shown the technology to work efficiently in the recovery process.

Previously, it has been thought that the inorganic borate in the recovery liquor was an inactive chemical in the digester. Recent work at the University of Maine (J. Genco) and work currently underway at Western Michigan University (J. Cameron/B. Bujanovic) indicate that the borate liquor makes a positive contribution in the digestion process.

The poster session presents initial findings on kraft pulping using borate containing white liquor produced: 1) in an autocausticizing mill trial, 2) synthetically in a laboratory. Data will be presented illustrating the effect of borate on screened pulp yield and the rate of digestion of wood chips. The data reflects the yield behavior at various degrees of autocaustizing following the H-factor curve. The results show an increase in screened yield as well as a drop in rejects. Recent mills trials have shown that borate accelerates pulping and allows the liquor to wood ration to be reduced in the digester.

IV-6. Residual Lignin of Spruce Kraft and Kraft-Borate Pulps

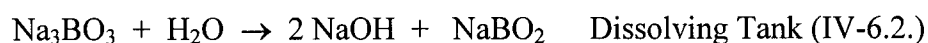
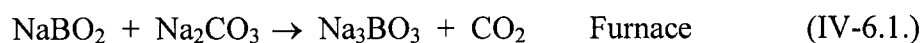
Abstract

Aimed at comparing the delignification results in kraft and kraft-borate (kraft pulping in the presence of sodium metaborate corresponding to 35 % autocauticizing) pulping, residual lignin from the spruce kraft and kraft-borate pulps was isolated by acid hydrolysis. Being performed at the boiling point, the standard method of acid hydrolysis could lead to undesirable lignin transformations. Therefore, in this study, acid hydrolysis was conducted in two steps - on the extracted pulps at 20 °C in an ultrasonic bath, and on the pulp residues at the boiling point under nitrogen. For comparative purposes, lignin was isolated by standard acid hydrolysis.

The results of this study showed no differences in the structure of lignin isolated from kraft and kraft-borate pulp. The yield of lignin isolated by acid hydrolysis at 20 °C was about three times lower than the yield of lignin isolated at higher temperatures. The results of lignin content determination and FTIR data indicated a high purity of the isolated residual lignin samples regardless of the conditions applied during acid hydrolysis. Based on the PhOH content, the residual lignins isolated at 20 °C were less altered than those isolated under boiling point conditions. However, additional information about the lignin structure is needed to elucidate more thoroughly the effect of temperature on the lignin isolation by acid hydrolysis.

Introduction

In kraft pulping, borate-based partial autocausticizing has been proposed as a technology that can reduce the lime consumption and hence the energy requirements (Tran et al., 1999). This occurs through sodium hydroxide formation in reactions performed in the furnace (reaction IV-6.1.) and the dissolving tank (reaction IV-6.2.).



According to these reactions, sodium metaborate (NaBO_2) is an additional chemical present in kraft pulping and its effect on the delignification process and the quality of pulp should be explored. Our previous studies of kraft and kraft-borate pulping of black spruce showed that NaBO_2 added in the amount corresponding to 35 % autocausticizing did not affect the delignification rate and increased the screened pulp yield at the same kappa number (Bujanovic et al., 2003a). The results of acidic chlorite delignification conducted in these studies in two steps (low and high level of bleaching), indicated the same bleachability of the kraft and kraft-borate pulps. As the pulp bleachability is mainly dependent on the lignin structure, in a continuation of the studies of the effect of NaBO_2 on kraft pulping of spruce, residual lignin of the kraft and kraft-borate pulps was isolated and analyzed.

Enzymatic (EH) and acid-catalyzed (AH) hydrolysis have been suggested for the isolation of the residual lignin from kraft pulp (Hortling et al., 1990, Gellerstedt et al., 1994). However, neither of them produces a high yield of unchanged lignin in the

form suitable for lignin analysis. EH occurs in high yield (> 80 %) of unchanged lignin, but it is a multiple-step and time-consuming procedure, and impurities of carbohydrate and protein origin make this lignin unsuitable for analysis. AH results in lignin devoid of contaminants, but its yield is significantly lower than that obtained by EH (~40%). Because AH is performed for two hours at boiling point of 0.1 M HCl in dioxane:water (82:18), transformation of lignin occurs. These conditions promote cleavage of both benzyl ethers and β -aryl ethers with benzyl alcoholic groups resulting in an increase of the content of phenolic hydroxyl groups (PhOH) in lignin (Tamminen, Hortling, 1999, Jääskäläinen et al., 2001). Also, lignin condensation is a possible side reaction during AH, as the studies of the lignin model compounds under weakly acidic conditions at high temperature and the spruce wood lignin under the treatment in dioxane-water-HCl have indicated (Lundquist, 2001, Solar, Kačik, 1995).

In these studies, lignin was isolated from spruce kraft and kraft-borate pulps following the method of acid hydrolysis. Additionally, in order to explore the effect of temperature on lignin isolation, a separate series of experiments under acid hydrolysis was performed in two steps. The first step was acid hydrolysis in an ultrasonic bath at 20 °C, while the second step was standard acid hydrolysis. The yields, the PhOH contents, and the FTIR properties of isolated lignins were compared.

Material and Methods

Wood

The pulping experiments were conducted using the black spruce chips (*Picea mariana*) from northern Minnesota supplied by The U.S. Forest Products Laboratory, Madison, Wisconsin.

Pulping

Kraft pulp (K) was produced in an M/K digester; pulping conditions: sulfidity 27.2%, AA 16.5 %, liquor-to-wood ratio = 4:1; cooking temperature 170 °C; H-factor 2,000. Spruce kraft-borate pulp (KB) was produced in the same conditions as spruce kraft pulp (K) except that the white liquor contained $\text{NaBO}_2 \cdot 2\text{xH}_2\text{O}$ in the amount corresponding to 35 % autocausticizing (Bujanovic et al., 2003a).

Extraction

In order to remove all of the compounds that might dissolve with lignin during its isolation and disturb its analysis, the pulps were successively extracted in acetone, dichloromethane, ethanol (8 h each, Soxhlet apparatus), and water (cold water, 48 h).

Residual Lignin Isolation

Residual lignin was isolated from the pulps by acid hydrolysis that was applied in two different ways. The scheme of lignin isolation is shown in Table IV-6.1. Lignin was isolated by acid hydrolysis following the method described earlier (acid hydrolysis, standard, AH) (Gellerstedt et al., 1994). Also, lignin was isolated by a two-step acid hydrolysis procedure. In the first step, acid hydrolysis was performed at 20 °C in the ultrasonic bath (AH1) and then the first fraction of pulp lignin was isolated following the same procedure as outlined in the standard acid hydrolysis (Gellerstedt et al., 1994). Standard acid hydrolysis was performed on pulp residue obtained in the first step of acid hydrolysis (AH2) and the second fraction of lignin was isolated.

Pulp Characterization

Kappa number, Klason and acid-soluble lignin, and brightness were measured on both the extracted pulps and the pulp residues after acid hydrolysis, according to the standard TAPPI methods. The phenolic hydroxyl group content (PhOH) was measured on both the extracted pulps and the pulp residues using the method of Folin and Ciocalteu (FC method). This method is based on a color reaction of the PhOH groups with a hetero-phosphotungstate-molybdate. Absorbance of the obtained solution at 760 nm is proportional to the concentration of PhOH (de Sousa et al., 2001). In these studies, vanillin was used for calibration purposes.

Table IV-6.1.

Scheme of Residual Lignin Isolation

Spruce Kraft Pulp K Extracted	Acid Hydrolysis Standard (AH)	Lignin KAH		
		Pulp Residue KAH _{res}		
	Acid Hydrolysis Ultrasonic Bath 20 ⁰ C (AH1)	Lignin KAH1		
		Pulp Residue KAH1 _{res}	Acid hydrolysis Standard (AH2)	Lignin KAH2
				Pulp Residue KAH2 _{res}
Spruce Kraft- Borate Pulp KB Extracted	Acid Hydrolysis Standard (AH)	Lignin KBAH		
		Pulp Residue KBAH _{res}		
	Acid Hydrolysis Ultrasonic Bath 20 ⁰ C (AH1)	Lignin KBAH1		
		Pulp Residue KBAH1 _{res}	Acid hydrolysis Standard (AH2)	Lignin KBAH2
				Pulp Residue KBAH2 _{res}

Residual Lignin Characterization

The Klason and acid-soluble lignin content were determined in the residual lignin samples isolated by standard acid hydrolysis (KAH, KBAH) (Dence, 1992). The acetyl bromide lignin was determined in the remaining isolated lignin samples (KAH1, KBAH1, KAH2, KBAH2) (Iiyama, Wallis, 1988). The PhOH content in lignin samples was determined using the FC method (de Sousa et al., 2001). Also, the PhOH content in lignin samples was calculated based on FTIR spectral data of the acetylated lignin samples using the equations suggested earlier. Two different equations based on the normalized absorption of the phenolic and aliphatic hydroxyl groups at 1765 and 1745 cm⁻¹, respectively, were used (Faix, et al., 1992, Wegener,

Strobel, 1992). Additionally, the FTIR spectra for raw lignin samples were compared.

Results and Discussion

Some Properties of Spruce Kraft and Kraft-Borate Pulps

Spruce kraft and kraft-borate (35 % autocauticizing) pulps produced at the same H-factor (2,000) were characterized by approximately the same kappa number and brightness as shown in Table IV-6.2. An exhaustive extraction of pulps in organic solvents and water affected both the kappa number and brightness. A decrease of kappa number and an increase of brightness after pulp extraction show that the pulp extractives carry oxidizable and chromophoric structures and, hence, might affect the bleaching process. Based on the results obtained in this study, an effect of the extractives is expected to be the same in the bleaching of both the kraft and the kraft-borate pulps (Table IV-6.2).

The Klason and acid-soluble lignin contents and the PhOH content were determined on the extractive-free pulps. The content of PhOH groups (mmol/g lignin) was calculated based on the total lignin content (Klason + acid-soluble lignin). The PhOH contents found for the kraft and kraft-borate pulps were almost the same (Table IV-6.2.). This is a very important observation regarding the effect of NaBO_2 on kraft pulping because the lignin reactivity highly depends on the PhOH content. The PhOH contents determined for the kraft and kraft-borate pulps in this study were

very similar to those found for unbleached pulp from conventional kraft cooking of pine using the same FC method (de Sousa et al., 2001).

Table IV-6.2.

Some Properties of Spruce Kraft and
Kraft-Borate Pulps (H 2,000)

Pulp Property	Spruce Pulp	
	K	KB
Brightness BE (AE)	19.0 (19.7)	18.9 (19.6)
Kappa number BE (AE)	43.1 (40.8)	42.9 (40.7)
Klason lignin, %	6.47	6.39
Acid-soluble lignin, %	0.43	0.42
Total lignin, %	6.90	6.81
PhOH, mmol/g lignin	1.20	1.28
Extractives in:		
Acetone, %	0.25	0.30
Dichloromethane, %	0.07	0.07
Ethanol, %	0.18	0.16
Cold water, %	3.38	3.25
Total extractives, %	3.88	3.78

BE-Before Extraction; AE – After Extraction

Acid hydrolysis of spruce kraft and kraft-borate pulps: The yields of residual lignin isolated from the kraft and kraft-borate pulps using the standard method of acid hydrolysis (AH) and the two-step acid hydrolysis (AH1, AH2) are illustrated in Figure IV-6.1. The yields are based on the total lignin content of pulps (Klason + acid-soluble lignin).

The yields of residual lignin isolated from the kraft and kraft-borate pulps in the standard method of acid hydrolysis and in the two-step method of acid hydrolysis were almost the same ($KAH \cong KBAH$; $KAH1 \cong KBAH1$; $KAH2 \cong KBAH2$). Based on

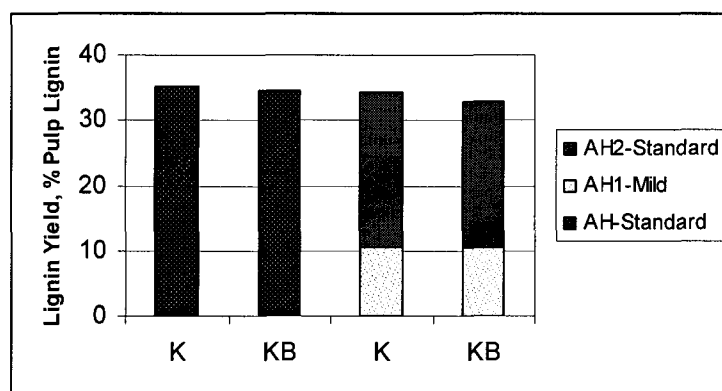


Figure IV-6.1. Yields of Residual Lignin Isolation from Spruce Kraft and Kraft-Borate Pulps by Standard Acid Hydrolysis (AH) and Two-Step Acid Hydrolysis (AH1, AH2)

the same amounts of released lignins, the kraft and kraft-borate pulps are likely to have the same residual lignin structure and the same type/frequency of lignin-carbohydrate bonds. The yield of residual lignin isolated in the first step of the two-step acid hydrolysis (AH1) was approximately three times lower than that of residual lignin isolated during standard acid hydrolysis (AH). This result was expected as “the release of lignin from kraft pulps requires higher temperatures during acid hydrolysis (Gellerstedt et al., 1994).” However, the total lignin yield obtained in the two-step acid hydrolysis was slightly lower than that obtained in the standard acid hydrolysis (Fig. IV-6.1.). The properties of the pulp residues after the standard and two-step acid hydrolysis are shown in Table IV-6.3.

In accordance with the obtained lignin yields, the total lignin content, i.e. the kappa number of the pulp residues after acid hydrolysis, was following the next order:

$KAH_{res} \cong KBAH_{res} < KAH2_{res} \cong KBAH2_{res} < KAH1_{res} \cong KBAH1_{res}$. However, the

KAH_{2res} and KBAH_{2res} had the highest brightness, which indicates that a removal of the chromophoric lignin structures occurred more readily in the two-step procedure than during standard acid hydrolysis. The PhOH content of the pulps remained almost unchanged during both the standard and the two-step acid hydrolysis.

Table IV-6.3.

Some Properties of Spruce Pulp Residues after Acid Hydrolysis

Pulp Residue	B*	Kappa	PhOH**	Lignin %		
				K	AS	Total
KAH _{res}	25.3	24.78	1.10	3.93	0.35	4.28
KBAH _{res}	25.5	24.17	1.35	3.82	0.32	4.14
KAH1 _{res}	20.8	36.41	1.25	5.32	0.40	5.72
KBAH1 _{res}	21.1	37.12	1.15	5.40	0.40	5.80
KAH2 _{res}	28.2	26.80	1.36	4.04	0.36	4.40
KBAH2 _{res}	28.4	26.71	1.39	3.95	0.35	4.30

*B – Brightness; **PhOH, mmol/g lignin

Residual Lignin Properties

The lignin content in all of the residual lignin samples isolated in this study was higher than 97.5 % (Table IV-6.4.).

The lignin content of the KAH and KBAH samples was determined by the Klason/acid-soluble method. Afterward they were dissolved in the AcBr/CH₃COOH solution and the 280 nm absorbance of the obtained solutions was measured (AcBr method (Iiyama, Wallis, 1988)). Based on these results, the Beer-Lambert relationship, and the Klason+acid-soluble lignin content in the KAH and KBAH samples, the residual lignin absorptivity was calculated. The value of 24.8 lg⁻¹cm⁻¹, which was found for both the KAH and KBAH lignin samples, agrees with the pine

kraft lignin absorptivity of $25.0 \text{ lg}^{-1}\text{cm}^{-1}$ proposed earlier by Marton (1965). Using this value of lignin absorptivity, the lignin content in the KAH1, KBAH1, KAH2, and KBAH2 lignin samples was determined by the AcBr method (Iiyama, Wallis, 1988).

Table IV-6.4.

Properties of Residual Lignin Samples

Lignin Sample	Lignin Content %		PhOH mmol/g lignin		
	Total	AcBr	FC	FTIR	
				1*	2**
KAH	97.8		2.63	2.20	2.36
KBAH	97.5		2.49	2.26	2.45
KAH1		98.6	2.23	2.02	2.12
KBAH1		98.0	2.17	1.94	2.00
KAH2		97.4	2.27	2.07	2.18
KBAH2		97.6	2.39	2.22	2.34

* FTIR – 1: $\text{PhOH, mmol/g lignin} = 0.588 [5.66 (A_{1765}/A_{1745}) - 1.37]$ (Faix et al., 1992)

**FTIR – 2 $\text{PhOH, mmol/g lignin} = 0.588 [14.75 A_{1765}/(A_{1765}+A_{1745}) - 3.45]$ (Wegener, Strobel, 1992)

The results of the determination of the PhOH content in the residual lignin samples by the FC method and the FTIR method based on two equations (FTIR-1 (Faix et al., 1992); FTIR-2 (Wegener, Strobel, 1992)) are shown in Table IV-6.4. The PhOH content data obtained by these methods were somewhat different and were decreasing in the next order: $\text{FC} > \text{FTIR} - 2 > \text{FTIR} - 1$. Regardless of the applied method, all of the residual lignin samples were characterized by the higher PhOH content than the corresponding pulps from which they have been isolated (Tables IV-6.2., 3). The PhOH content of residual lignin isolated from the kraft and kraft-borate pulps was basically the same indicating a similar reactivity of the residual lignin of

kraft and kraft-borate pulp. An increase of the PhOH content in lignin during acid hydrolysis results from the cleavage of acid-labile aryl ether units in lignin (benzyl ethers and β -aryl ethers with benzyl alcoholic group (Tamminen, Hortling, 1999, Jääskeläinen et al., 2001)). However, acid hydrolysis performed at 20 °C in the ultrasonic bath (AH1) decreased this effect as the PhOH content of KAH1 and KBAH1 was lower than KAH and KBAH, respectively, and somewhat lower than KAH2 and KBAH2, respectively.

The residual lignins isolated here resulted in a similar FTIR spectrum in the region 2000– 800 cm^{-1} . FTIR data clearly indicated the lignin dominance in all of the residual lignins. FTIR spectra of KAH1 and KBAH1 are shown in Figure IV-6.2.

Additional information about the lignin structure is needed to recognize the differences between lignins obtained under different acid hydrolysis procedures (AH, AH1, AH2) using different pulps (K, KB).

Conclusion

Residual lignins from the spruce kraft and kraft-borate pulp were compared in these studies. Lignin was isolated from pulps by acid hydrolysis. Acid hydrolysis was performed in the 0.1 M HCl in dioxane: water (82/18) at boiling point temperature under nitrogen (AH) and at 20 °C in an ultrasonic bath (AH1). These two different ways of acid hydrolysis were applied in order to study the effect of higher temperature on the lignin isolation. The results of lignin content determination and FTIR data indicated a high purity of the isolated residual lignin samples

regardless of the conditions applied during acid hydrolysis. The results of this study showed no differences in the structure of lignin isolated from kraft and kraft-borate pulp. The yield of lignin isolated at 20 °C (KAH1, KBAH1) was about three times lower than the yield of lignin isolated at the boiling point (KAH, KBAH). Based on the PhOH content, the KAH1 and KBAH1 lignins were less altered than the KAH and KBAH lignins. However, additional information about the lignin structure is needed to corroborate the effect of temperature on lignin isolation under acid hydrolysis.

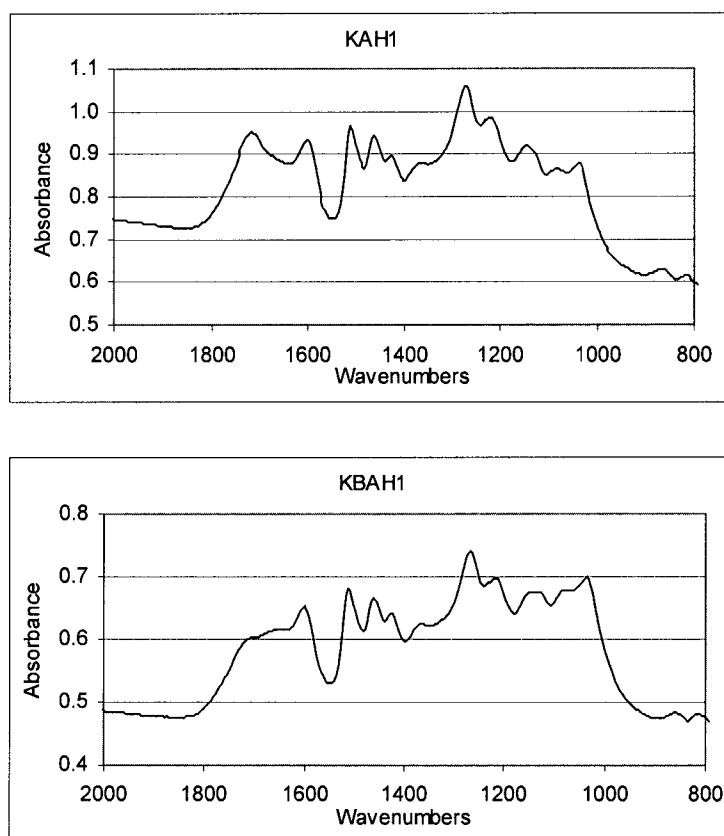


Figure IV-6.2. FTIR Spectra of KAH1 and KBAH1

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CHAPTER V

EFFECT OF SODIUM METABORATE ON THE PROPERTIES OF BLACK LIQUOR

V-1. Effect of Sodium Metaborate on the Boiling Point Rise of Slash Pine Black Liquor

Abstract

Borate can be used as either a total or partial autocausticizing agent for conversion of Na_2CO_3 to NaOH . For every mole of Na_2CO_3 converted, a mole of NaBO_2 is generated and remains in the black liquor. The objective of this study is to determine the effect of this additional NaBO_2 on the boiling point rise (BPR) of the resulting black liquor. Commercial black liquor was obtained, and borate was added at levels equivalent to 30, 60, and 120 % autocausticizing. With borate present, the BPR observed during evaporation was greater than that observed during dilution. This phenomenon was not seen for black liquor without borate nor for black liquor with only Na_2CO_3 added. It is proposed that this difference is due to the formation of a complex between kraft lignin and borate. Borate was also found to be totally soluble in black liquor and to increase the solubility of the other components. The addition of borate had little effect on the BPR of the black liquor. The largest effect of borate was observed at an addition level equivalent to 120 % autocausticizing and at over 70% solids, where borate increased the BPR by about 5 K.

Introduction

The kraft pulping process is by far the dominant pulping process, accounting for over 95 % of all chemical pulps produced in the United States. One of the main reasons for the dominance of the kraft pulping process is its efficient chemical recovery process. In the chemical recovery process, the inorganic pulping chemicals sodium sulfide (Na_2S) and sodium hydroxide (NaOH) are regenerated and the waste organic materials are burnt to supply the energy necessary for the operation of the pulp mill. Sodium sulfide and sodium carbonate (Na_2CO_3) are formed during the burning of black liquor and are dissolved in water to form green liquor. This green liquor containing sodium carbonate is converted to the pulping liquor containing sodium hydroxide through a calcium carbonate (CaCO_3) based calcining-causticizing cycle.

Before the waste liquor from the pulping process (black liquor) is burned, it is necessary to concentrate it from weak black liquor, which is about 20 % solids, to a firing concentration of 65 % or greater. This concentration is accomplished using cascade evaporators, where 1 lb. of steam typically evaporates 5 lb. of water. As noted by Grace (1989), "Even though energy efficient systems are used, liquor concentration consumes up to 25 % of the total energy needed for a bleached grade kraft pulp mill."

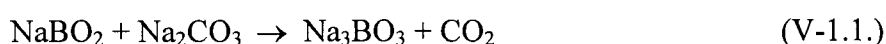
One limitation to the liquor evaporator efficiency is the boiling point rise (BPR) of the black liquor. The BPR of a solution is the difference between the

boiling point of the solution and the boiling point of the solvent at a given pressure. As BPR of the solution increases, the temperature difference between the condensing steam on the outside of the evaporator tubes and the temperature of the boiling liquor inside the tubes decreases. This reduces the driving force for evaporation and results in less evaporation per unit surface area.

There is a considerable interest in the use of borate to autocausticize sodium carbonate, that is, produce sodium hydroxide without the use of the calcium-based calcining-causticizing cycle. Autocausticizing offers several advantages in terms of required capital investment and energy efficiency. For example, if the calcining-causticizing cycle was replaced by autocausticizing, this would eliminate the lime kiln, slaker and causticizing vessels required by the current kraft process or if the calcining-causticizing process was production limiting, the mill capacity could be increased using autocausticizing. To implement this technology, it is necessary to understand the effect of the borate on the overall kraft pulping process including its effect on the properties of the resulting black liquor.

The use of sodium borate to causticize smelt directly in kraft recovery boilers was first suggested by Janson (1980) and more recently by Tran et al. (1999). Janson proposed that borate conversion of sodium carbonate to sodium hydroxide is only feasible at sodium-to-borate ratios of less than 2 and that 2 mol of sodium metaborate (NaBO_2) is needed to decarbonate 1 mol of Na_2CO_3 . Because of the amount of borate required based on the proposed borate/sodium ratio, this process was thought to be technically difficult and uneconomical. However, later work by Tran et al.

(1999) showed that the borate-based autocausticizing reactions are more effective than had been proposed by Janson (1980). According to these authors, the overall autocausticizing reactions can be summarized by the reaction of sodium carbonate with sodium metaborate in the molten smelt to form trisodium borate (Na_3BO_3), reaction (V-1.1.), and the subsequent reaction of trisodium borate in the green liquor dissolving tank to form sodium hydroxide, reaction (V-1.2.).



Among the concerns with the use of borate are changes in the resulting black liquor characteristics, especially its BPR. The experiments conducted in this study are designed to determine the effect of the sodium metaborate addition on the vapor pressure and BPR of commercial black liquor. On the basis of the results of the BPR measurements, the solubility limit (SL) of the black liquor, the point where the partially soluble salts precipitate, was also determined. Two types of experiments were performed using slash pine black liquor. In the first type of experiments, the effect of borate on the vapor pressure of the black liquor was determined by heating the black liquor in a pressurized reactor and measuring the temperature and pressure. In the second type of experiments, the atmospheric boiling point of the black liquor containing different levels of borate was determined during evaporation and dilution cycles. For reference purposes, the effect of sodium carbonate (Na_2CO_3) on the BPR of the black liquor was also determined. Sodium carbonate was chosen for comparison because it is an important inorganic component of black liquor. It is one

of the first to precipitate during evaporation as a constituent of the double salt $2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$ and is a constituent of sodium sulfate-carbonate scales formed in black liquor evaporators (Grace, 1989).

Boiling Point Rise at Elevated Pressures and Temperatures

A solution boils when its vapor pressure equals the pressure of the surroundings. Thus, a solution of a nonvolatile material in water must be heated above the boiling point of pure water before boiling can occur. The BPR due to material in the solution can be defined as the actual boiling temperature of the mixture minus the temperature of the pure solvent where it exerts the same vapor pressure as the mixture. Dühring's rule, as described by Peters (1984), has been used to show the effect of dissolved materials on the BPR. This rule states that a plot of the temperature of the solution versus that of the reference solvent, where both the reference solvent and the solution exert the same pressure, results in a straight line. A major advantage of Dühring's rule is that only two experimental values of the vapor pressure and temperature for a solution of fixed concentration are needed to determine the Dühring's line for a given mixture. This rule is important in obtaining the BPR data and the development of empirical BPR models. As described by Peters, pure water is often used as the reference solvent. Although several authors have reported the BPR data for black liquor, none have applied Dühring's rule to their data. In this study, Dühring's lines are plotted for different concentrations of the slash pine

black liquor with different levels of sodium metaborate added, as explained in the Experimental section.

Boiling Point Rise at Atmospheric Pressure

The BPR is a colligative property, depending upon the solution molality and the properties of the solvent. For the black liquor, the BPR, as suggested by Frederick et al. (1980), can be expressed according to the equation (V-1.3.),

$$\text{BPR} = K_B S / (1-S) \quad (\text{V-1.3.})$$

where:

S = solids content of liquor (weight fraction solids),

K_B = constant which depends on the composition of the black liquor.

Frederick et al. (1980) noticed that this equation only applied to black liquor below the solubility limit (SL). When the SL is reached, the slope of the BPR curves decreases abruptly. Zaman et al. (1998) considered this fact and divided the BPR curve into two parts described by linear equations. In the first part of this curve,

$$\text{BPR} = a S / (1-S) \quad (\text{V-1.4.})$$

while in the second part of this curve

$$\text{BPR} = b' + a' S / (1-S) \quad (\text{V-1.5.})$$

where a, a', and b' are constants that are pressure-dependent and vary from liquor to liquor because of the differences in the composition of the liquors. The intersection of these two equations defines the SL for the corresponding black liquor.

The BPR was measured for slash pine black liquor with different levels of sodium metaborate added. These measurements were performed using the technique originally described by Frederick et al. (1980) and called the boiling temperature measurements by Adams and Frederick (1988). The results obtained by this procedure were analyzed in accordance with the Frederick et al. (1980) and Zaman et al. (1998) equations shown above.

Experimental Section

Black Liquor Characteristics and Metaborate Addition

The black liquor used in this study was kraft slash pine liquor obtained from International Paper Co. It was collected after pulp washing and before evaporation at 19.3 % solids. The black liquor was stored at 281 K until used in the study.

To determine the amount of sodium metaborate that would be present in the black liquor after autocausticizing, the level of sodium carbonate present in the green liquor (the liquor before the causticizing cycle) must be determined. The amount of sodium carbonate initially present in the green liquor was determined using an elementary balance on the sodium and potassium content of the slash pine black liquor. The amount of metaborate needed for a given conversion was determined based on the chemical composition of the commercial black liquor, shown in Table V-1.1. and the stoichiometry shown in equations V-1.1., 2. It was assumed that all sodium and potassium, not present as sulfides, sulfates, or chlorides, were present as carbonates (K_2CO_3 , Na_2CO_3). Because the level of potassium is low compared to the

level of sodium, it was also assumed that all carbonate is sodium carbonate. On the basis of this balance, 0.25 mol (26.5 g) of sodium carbonate was present in the green liquor for every 100 g of the black liquor solids in the resulting black liquor.

Table V-1.1.

Inorganic Content of Black Liquor as Received at 19.3 % Solids
on the Basis of 100 g of Black Liquor Solids

Species	Analysis and basis Wt %	as a sodium compound wt %	as a sodium compound mol
Na_2S	5.81 as Na_2O	7.3 as Na_2S	0.0937
Na_2SO_4	4.1 as Na_2O	9.39 as Na_2SO_4	0.0662
Na_2CO_3	5.18 as CO_3	9.15 as Na_2CO_3	0.0863
NaOH	1.72 as Na_2O	2.22 as NaOH	0.0555
NaCl	0.45 as Cl	0.741 as NaCl	0.0127
Na	1.8 as Na		0.782 as Na
K	1.7 as K		0.0435 as K

On the basis of the above calculations, sodium metaborate (NaBO_2) was added at 5, 10, and 20 % of the original black liquor solids or 5, 10, and 20 g/100 g solids. This corresponds to conversions of about 30, 60, and 120 % of the original carbonate to hydroxide through autocausticizing with borate. The borate was added as sodium metaborate tetrahydrate ($\text{NaBO}_2 \times 4\text{H}_2\text{O}$), and the water of hydration was accounted for as part of the total water in the liquor.

Experimental Techniques

Boiling Point Rise at Elevated Pressures and Temperatures. The pressure-temperature relationship for slash pine black liquor with addition of sodium metaborate was measured using a pressurized reactor. In these experiments, the

original black liquor with 19.3 % solid concentration was concentrated to 40 and 60 % in a separate vessel and transferred to the pressurized reactor. The vapor pressure was then measured as a function of temperature for the three different black liquor samples (19.3, 40.0, and 60.0 % initial solids) with and without the addition of sodium metaborate. The black liquors samples used in these experiments are shown in Table V-1.2.

Table V-1.2.

Black Liquor Samples Used in the Study^a

No	BL	BL solids before addition of borate g/100 g	NaBO ₂ ·4H ₂ O (Na ₂ CO ₃) added g/100 g BL	NaBO ₂ (Na ₂ CO ₃) added g/100 g BL solids	% AC	BL solids after borate (carbonate) addition g/100 g
1	BL20	19.3	0	0	0	19.3
2	BL20+MB5	19.3	2.02	5	30	19.9
3	BL20+MB10	19.3	4.04	10	60	20.4
4	BL20+MB20	19.3	8.10	20	120	21.4
5	BL40	40	0	0	0	40
6	BL40+MB5	40	4.19	5	30	40.0
7	BL40+MB10	40	8.38	10	60	40.6
8	BL40+MB20	40	16.76	20	120	41.1
9	BL60	60	0	0	0	60
10	BL60+MB5	60	6.28	5	30	59.3
11	BL60+MB10	60	12.56	10	60	58.6
12	BL60+MB20	60	25.12	20	120	57.5
13	BL20+C20	19.3		(20)		(22.3)

^a BL-slash pine black liquor; MB – sodium metaborate; C – sodium carbonate

An important aspect of this work is the accuracy of the temperature measurements. The temperatures were measured using a type E thermocouple with a ± 0.1 K resolution. An analysis of the error associated with the data acquisition system used in this study is contained in the Spring 1998 issue of *PC Measurement News* (1998). The sources of error in the thermocouple measurements are the

thermocouple, cold junction compensation, and noise. With relative temperature measurements, such as those used in this study and the E-type thermocouple, these data acquisition systems have a maximum error of ± 0.3 K.

In addition to the temperature sensor, the pressurized reactor (Autoclave Engineers, Inc. Erie, PA; 5400psi at 650 F) contained two pressure-sensors (a bourdon gauge and a force transducer). The two pressure sensors provided a method of verifying the pressure. During heating of the pressure vessel to 373 K, the reactor was vented to remove all air; after the air was removed, the reactor vent was closed and the temperature-pressure data obtained. To ensure that all air was removed from the vessel before the measurements were made, similar experiments were conducted using distilled water. At pressures from 100 to 400 kPa, the corresponding temperatures agreed with the literature data to within ± 0.2 K. Figure V-1.1. shows the pressured reactor used for these experiments.

Boiling Point Rise at Atmospheric Pressure. To determine the effect of sodium metaborate on the BPR of black liquor at atmospheric pressure, different levels of sodium metaborate were added to the black liquor before evaporation. For comparative purposes, the effect of sodium carbonate at a level equal to the highest level of sodium borate added was also determined. These samples are shown in Table V-1.2.

The BPR for these samples was determined by the method described by Frederick et al. (1980). The apparatus for the boiling point rise measurements is

shown in Figure V-1.2. The corresponding boiling point of water was also measured several times during the course of this work.

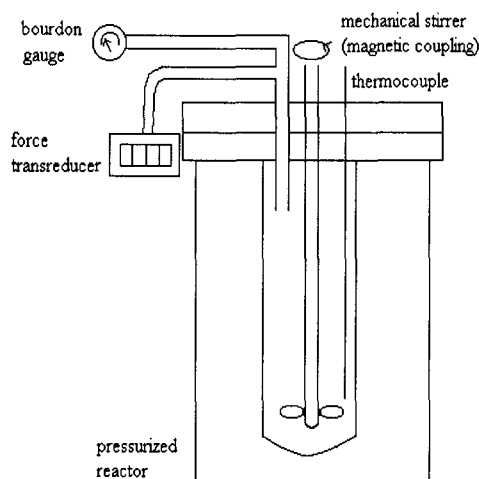


Figure V-1.1. Apparatus for Vapor-Pressure Measurements

This technique is a multi-stage procedure that includes the following:

1. Measurement of the boiling point during reflux of the black liquor at the starting concentration. The reported boiling point was an average value recorded in a 5 min period when the temperature changed within ± 0.05 K.
2. Distillation to the next target solid concentration and collection of the condensate.
3. Measurement of the boiling point during reflux of the black liquor at the desired solids.

This procedure was repeated to 75 % solids. This series of experiments is called evaporation. In the reverse procedure, “dilution”, the collected condensate was returned to the liquor in increments and the boiling point was measured during reflux

of the black liquor. The solids level after each addition increment was calculated based on the amount of condensate added.

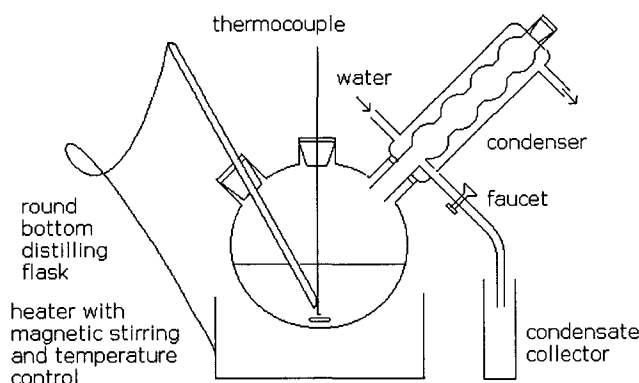


Figure V-1.2. Apparatus for Measurements of the BPR at Atmospheric Pressure

The obtained data were analyzed in accordance with the models developed by Frederick et al. (1980) and Zaman et al. (1998) equations (eqs. V-1.4., 5.). The results obtained in the evaporation and dilution series are treated separately, and two curves are obtained for each sample. The SLs during the evaporation and dilution series were also calculated.

Results

Boiling Point Rise at Elevated Pressures and Temperatures

Figure V-1.3. shows Dühring's lines for the slash pine black liquor at different solids levels. Here, the BPR is about 10 K at 60% solids.

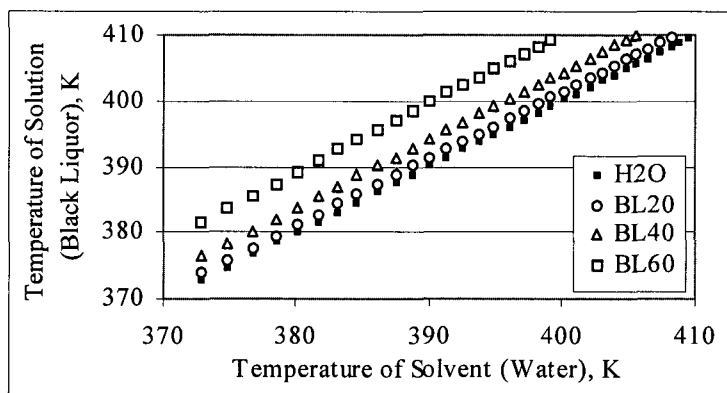


Figure V-1.3. Dühring's Lines for the Slash Pine Black Liquor at Different Solids Levels

Figure V-1.4. shows the effect of the sodium metaborate addition on the BPR of 60 % solids slash pine black liquor. The addition of sodium metaborate to the black liquor did not significantly affect the corresponding Dühring's lines.

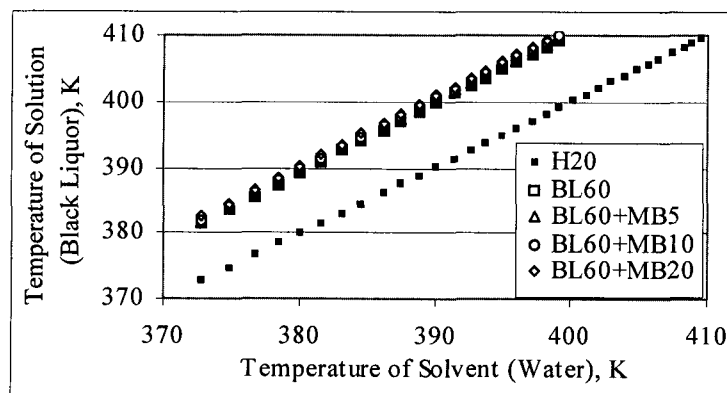


Figure V-1.4. Dühring's Lines for the 60 % Slash Pine Black Liquor with Different NaBO₂ Levels

BPR at Atmospheric Pressure

To confirm the accuracy of the experimental techniques employed in this study and to determine if the commercial black liquor is comparable to softwood black liquors used in other studies, the BPR data obtained in this study were compared with earlier published data. Figure V-1.5. compares the BPR measured in this study with those measured in studies using either boiling temperature measurements (Zaman et al., 1998) or oil dispersion co-distillation techniques (Clay, Karnofski, 1981, Clay, Grace, 1984).

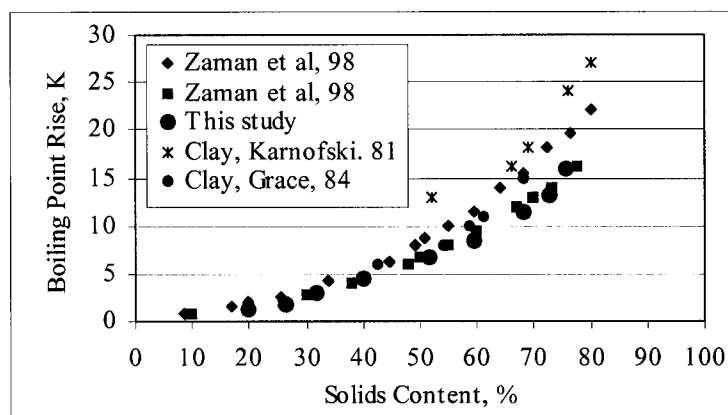


Figure V-1.5. Black Liquor BPR – Comparative Results

The BPR results shown in Figure V-1.5., are within the same range as those obtained in the referenced studies that used various experimental techniques. The BPR was measured up to 75 % solids. Although there is a concern that mass-transfer effects become significant after 60% solids with this technique (Adams, Frederick, 1988), no discontinuity was observed in the data and no major differences were

observed at the higher concentrations compared to the results reported by other authors.

Figure V-1.6. shows the BPR results obtained during evaporation and dilution of the slash pine black liquor without any salts added. As shown in this figure, the BPR during evaporation is the same as that obtained during dilution.

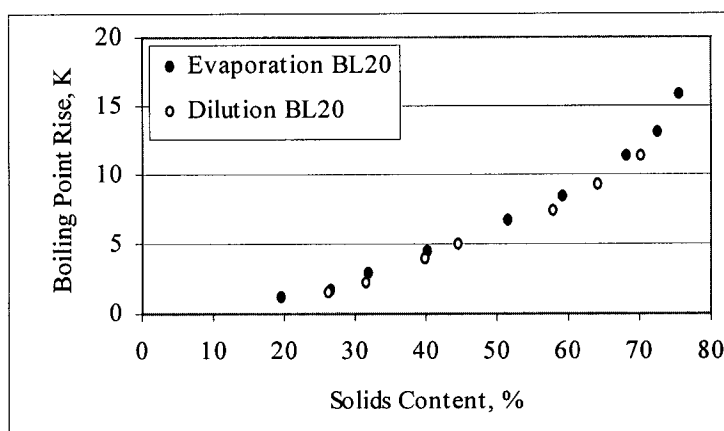


Figure V-1.6. BPR of the Slash Pine Black Liquor

Figure V-1.7. shows the BPR during evaporation for the original black liquor (BL20) and during evaporation and dilution for this black liquor with 20% sodium metaborate added (BL20+MB20).

As will be discussed later, it is also apparent that a hysteresis occurs in the BPR data for the black liquor with sodium metaborate. Once sodium metaborate is added, the BPR during dilution is considerably lower than that observed during the evaporation.

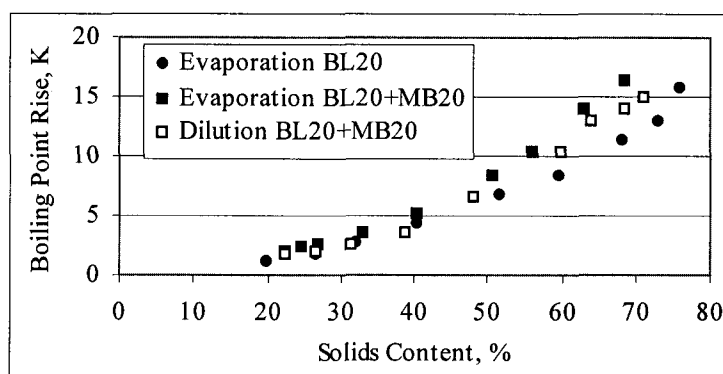


Figure V-1.7. BPR of the Slash Pine Black Liquor with 20 % NaBO_2

Because sodium carbonate is present in commercial black liquor as a result of incomplete causticizing and is important in evaporator scaling, it was used for comparative purposes in this study. As opposed to sodium metaborate, which is totally soluble in black liquor, sodium carbonate is only slightly soluble. Therefore, the addition of sodium carbonate should not affect the BPR of black liquor above its SL. Once the SL is reached, the BPR does not increase as rapidly with increasing solids. This effect is shown in Figures V-1.8. and 9.

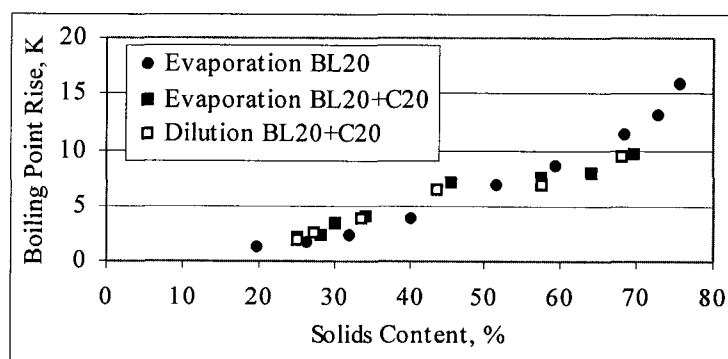


Figure V-1.8. BPR of the Slash Pine Black Liquor with 20 % Na_2CO_3

Comparing Figure V-1.7. to Figure V-1.8. shows that, as opposed to sodium carbonate, sodium metaborate does not precipitate during black liquor evaporation. In addition, no hysteresis was observed in the BPR data for black liquor with the addition of sodium carbonate.

Figure V-1.9. shows an increase in the BPR with increasing solids for the slash pine black liquor with the different levels of sodium metaborate added and for only sodium carbonate added. The data were analyzed using the linear models (Frederick et al., 1980, Zaman et al., 1998) described in eqs V-1.4., 5. The solids are total solids, which include the black liquor and sodium metaborate/carbonate solids, minus the water of hydration present in sodium metaborate tetrahydrate. The water of hydration is added to the total water in the system.

In Figure V-1.10., the BPR is plotted versus the dissolved solids/water ratio, using the linear models (Frederick et al., 1980, Zaman et al., 1998), for the slash pine black liquor without sodium metaborate during evaporation and dilution.

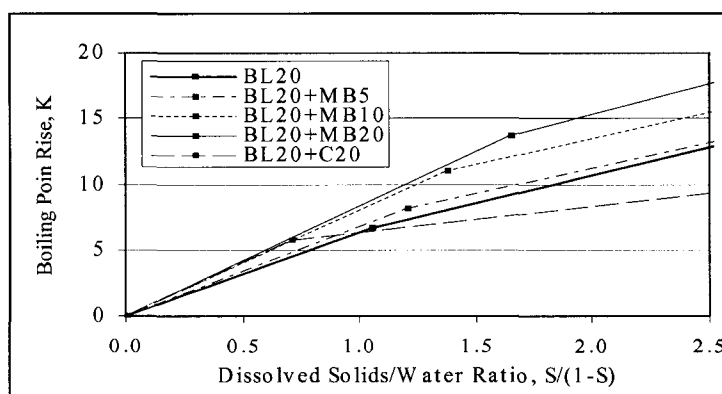


Figure V-1.9. BPR During Evaporation of the Slash Pine Black Liquor with/Without $\text{NaBO}_2/\text{Na}_2\text{CO}_3$

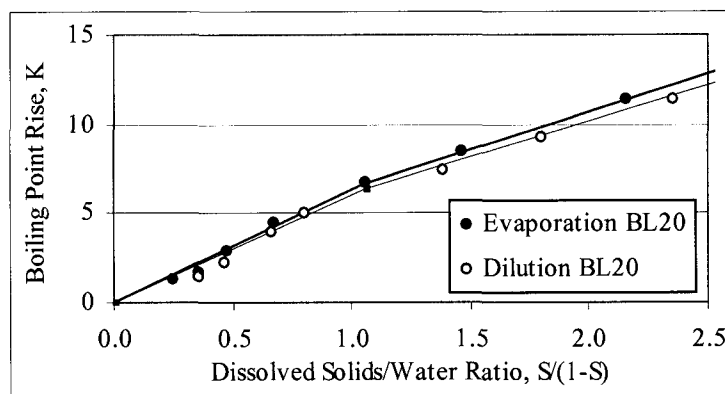


Figure V-1.10. BPR for the Slash Pine Black Liquor During Evaporation and Dilution

In Figure V-1.11., the BPR of the slash pine black liquor with 20 % sodium metaborate added, using the linear models (Frederick et al., 1980, Zaman et al., 1998) is plotted versus the dissolved solids/water ratio during evaporation and dilution. Again, the BPR during dilution is considerably lower than that obtained during evaporation. This result was observed for all the borate-treated black liquors, but not for the untreated or sodium carbonate-treated black liquors.

Effect of Inorganic Portion of Black Liquor on Boiling Point Rise

As will be discussed later, the hysteresis in the BPR of black liquor with sodium metaborate is believed to be due to a known reaction between lignin and borate (Lundquist et al., 1996). However, another possibility is that this hysteresis is due to a reaction between borate and the inorganic portion of the black liquor. To test this possibility, metaborate was added to a formulated inorganic portion of the black liquor. The evaporation and dilution BPR curves for this formulated solution of

sodium hydroxide, sodium carbonate, sodium sulfate, and sodium metaborate are shown in Figure V-1.12.

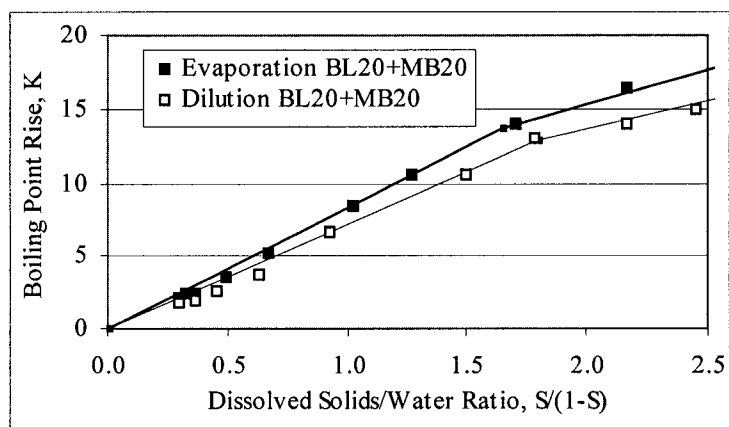


Figure V-1.11. BPR for the Slash Pine Black Liquor with 20 % NaBO_2 During Evaporation and Dilution

As shown in Figure V-1.12., the inorganic portion of the black liquor with the addition of NaBO_2 does not have the hysteresis associated with the addition of NaBO_2 to the black liquor.

Linear Equations Model

From the data obtained during evaporation and dilution of the different black liquors, parameters of equations V-1.4. and 5. that describe the BPR were determined. These parameters and the SLs are shown in Tables V-1.3. and 4 for evaporation and dilution, respectively.

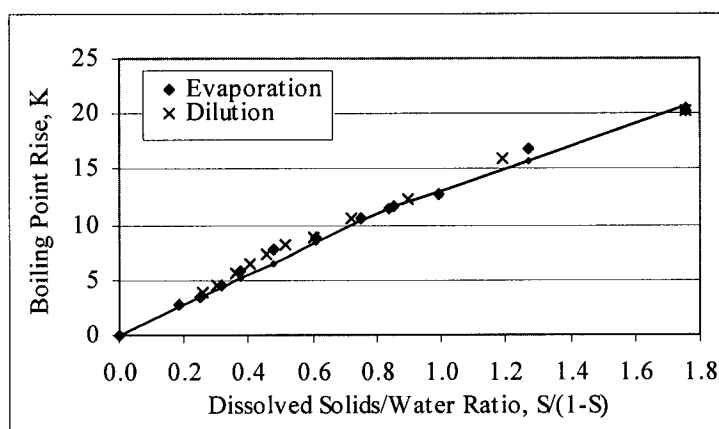


Figure V-1.12. BPR of a $\text{NaOH} + \text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{NaBO}_2$ Water Solution During Evaporation and Dilution

Table V-1.3.

Parameters of Linear Equations of BPR vs. the Dissolved Solids Water Ratio for Evaporation^a

SAMPLE	PARAMETER							
	a	r^2	a'	b'	R^2	SL		
						S/(1-S)	S, %	SBL, %
BL	6.30	0.98	4.27	2.13	0.99	1.05	51.20	51.20
BL+MB5	6.79	0.99	3.88	3.50	0.87	1.20	54.60	52.00
BL+MB10	7.99	0.99	3.97	5.50	0.98	1.37	57.77	52.52
BL+MB20	8.33	0.99	4.65	6.03	0.98	1.64	62.10	51.75
BL+C20	8.08	0.96	1.99	4.30	0.94	0.71	41.39	34.39

S, % – total solids in black liquor (solids originating from black liquor plus added salt)

SBL, % – black liquor originating solids in black liquor

r^2 – statistical indication of the ability of straight line to fit data

The solids level that corresponds to the calculated SL can be expressed either as the total solids in the black liquors after addition of the inorganic salt or as the solids originally present in the black liquor. It was found that the total solids concentration (including the added sodium metaborate) at SL increases with increasing sodium metaborate, while the solids concentration due to the black liquor

(without including sodium metaborate) remains almost the same. This occurs because sodium metaborate is totally soluble in the black liquor. For sodium carbonate addition, both the total solids concentration and the solids concentration originating from the black liquor significantly decrease at the SL compared to the black liquor without sodium carbonate added. This occurs not only because sodium carbonate is partially soluble in the black liquor, but also because it reduces the solubility of the other black liquor components. This behavior is shown in Table V-1.3. and 4.

Table V-1.4.

Parameters of Linear Equations of BPR vs. the Dissolved Solids
Water Ratio for Dilution^a

SAMPLE	PARAMETER							
	a	r ²	a'	b'	R ²	SL		
						S/(1-S)	S, %	SBL, %
BL	5.94	0.94	4.06	2.00	0.99	1.06	51.55	51.55
BL+MB5	6.42	0.99	3.74	3.30	0.98	1.23	55.18	52.55
BL+MB10	7.25	0.98	3.76	5.00	0.98	1.43	58.89	53.54
BL+MB20	7.18	0.98	3.78	6.09	0.86	1.79	64.17	53.48
BL+C20	7.93	0.95	2.00	4.20	0.95	0.71	41.46	34.55

S, % – total solids in black liquor (solids originating from black liquor plus added salt)

SBL, % – black liquor originating solids in black liquor

r² – statistical indication of the ability of straight line to fit data

Discussion

Effect of Metaborate on the BPR

As shown by the Dühring Plot in Figure V-1.4., where the effect of sodium metaborate tetrahydrate on the BPR was measured, the BPR increased by only 2 K

with the addition of 20 g of sodium metaborate tetrahydrate/100 g of black liquor solids to a 60 % solids in liquor. However, it should be noted that sodium metaborate tetrahydrate is about 50 % water and its addition does not greatly affect the percent solids (Table V-1.2.). If we consider Figure V-1.7., the addition of 20 g of sodium metaborate/100 g of black liquor solids (MB20) to a 60 % solids in liquor increases the solids concentration to a 64.2 % solids. When the BPR of a 60 % nonborated liquor is compared to that of a 64.2 % borated liquor, it can be seen that the BPR increases by about 5 K. With a MB20 addition, the expected autocausticizing is about 120 %. Because this is a higher addition level than what would be used even at full autocausticizing, the expected increase in the BPR for commercial autocausticizing would be expected to be less than 5 K at 64 % solids.

The above results show that the SL of the borate containing liquors is higher during dilution than during evaporation. It was also observed that the BPR of the slash pine black liquor with sodium metaborate added is lower during dilution than during evaporation. This suggests that a complex is formed between sodium metaborate and black liquor (mixture of inorganic salts, degradation compounds of carbohydrates and lignin, and kraft lignin). Such a lignin-borate complex is suggested by the work of Gierer and Norén (1962) and Lundquist et al. (1996), who found that borate forms a complex with lignin and also with the lignin transformation products formed during kraft process. In accordance with the results of these authors, lignin alkali transformation products characterized by 1,2-diol and 1,3-diol including β -O-4 structure react with borate forming five-member and six-member rings,

respectively. The arylglycerol- β -aryl ether structure represents the dominant lignin bond in wood and is the most reactive structure in kraft pulping (Argyropoulos, Menachem, 1997). However, the β -O-4 structure is still present in lignin dissolved during kraft pulping (Froass et al., 1998). Because the 1,2- and 1,3-diol and β -O-4 structures present in the black liquor are known to complex with borate, it is suggested that this is the borate-lignin complex that is responsible for the reduced BPR.

Future work will include confirmation of the formation of the borate lignin using borate-based pulping experiments and determination of the effect of this complex on the rheology properties including viscosity of the resulting black liquor. On the basis of the results presented in this study, it is expected that borate will complex with the lignin in the black liquor and reduce the resulting BPR.

Conclusions

1. It is shown that Dühring's rule can be applied to black liquor.
2. The BPR of the black liquor used in this study and the experimental techniques employed compare favorably with those of other studies using softwood black liquors and different experimental techniques.
3. The addition of sodium metaborate to 60 % solids liquor at a 120 % autocaustizing level increases the solids concentration to 64 % and increases the boiling point by about 5 K. At less than 120 % autocausticizing, the boiling point would be lower.

4. The addition of sodium metaborate to slash pine black liquor results in a hysteresis of the BPR data obtained during the evaporation and dilution of the black liquor. It is proposed that this difference is due to the formation of a complex between kraft lignin and borate.

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V-2. Effects of Borate Autocausticizing on the Black Liquor Properties

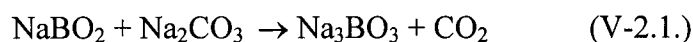
Abstract

This paper presents a study of the effects of sodium metaborate addition on the black liquor properties. The results show that borate increases the boiling point rise, solubility limit, and viscosity of the slash pine black liquor. However, because of a proposed complex between borate and lignin and possible increase causticizing efficiency, the increase of the boiling point rise is expected to be less than that found in these experiments. The greatest increase of viscosity was observed at 30 % autocausticizing effect. Only a mild increase of viscosity was observed at higher borate levels. Based on the results of the measurements of boiling point rise and viscosity, the formation of the borate-black liquor complex is proposed.

Introduction

The application of sodium metaborate (NaBO_2) as an autocausticizing agent was suggested by Janson (1980). However, the reaction stoichiometry suggested by Janson required a relatively large ratio of NaBO_2 to Na_2CO_3 . Because of the large level of sodium metaborate required, the proposed process was thought to be economically unattractive and to have potential problems in evaporation and liquor handling because of the increased boiling point rise and black liquor viscosity. Recently, Tran and coworkers (1999) reexamined the borate autocausticizing reactions and found that the reactions were twice as effective as proposed by Janson.

The use of simultaneous differential and thermogravimetric (DTA/TGA) studies of the reaction between NaBO_2 and Na_2CO_3 indicated that the decarbonization of Na_2CO_3 occurred in accordance with Reaction V-2.1., with trisodium borate (Na_3BO_3) as the reaction product. In water, Na_3BO_3 hydrolyzes to form NaOH and regenerates NaBO_2 , according to Reaction V-2.2.



In addition, Tran and coworkers (1999) proposed that partial autocausticizing is possible with borates. These findings renewed the interest in borate based autocausticizing. The boiling point rise (BPR) and corresponding solubility limit (SL) of the commercial slash pine black liquor with sodium metaborate, at addition level corresponding to 60 % causticizing, are determined in this study.

Sodium carbonate (Na_2CO_3) and sodium sulfate (Na_2SO_4) are the components of a double salt called burkeite known to precipitate the first during the black liquor evaporation (Adams, Frederick, 1988). Calcium carbonate (CaCO_3) can cause scaling especially in kraft pulping of wood with significant amount of bark and in kraft pulping of hardwoods (Frederick, Grace, 1979). These three inorganic compounds were added to the slash pine black liquor. The effect of sodium metaborate on the boiling point rise and solubility limit of the resulting black liquor samples was evaluated. The viscosity of the slash pine black liquor with sodium metaborate added at levels corresponding to 0, 30, 60, and 120 % autocausticizing was measured at a total solids level of 65 %.

Methods and Materials

The slash pine black liquor used in this study was obtained by International Paper Company, Pine Bluff Mill. It was collected with 19.3 % solids (BL20) before evaporation of the black liquor. Upon arrival, the black liquor was stored at 4°C.

The amount of sodium metaborate required for the partial autocausticizing is based on the chemical composition of the commercial black liquor and the equations describing autocausticizing (Equations V-2.1.,2.). It was assumed that all sodium and potassium, which are not present as sulfides, sulfates, or chlorides, are originally present carbonates (K_2CO_3 , Na_2CO_3). Since it was found that the amount of potassium was less than 10 % of that of sodium, the combined potassium and sodium salts are referred to as sodium salts. Sodium metaborate was added at a level corresponding to 10 % of the original black liquor solids or 10 g /100 g solids (MB10). This corresponds to an autocausticizing conversion of about 60%. Sodium borate tetrahydrate ($NaBO_2 \times 4H_2O$) was added to the black liquor based on the desired level of sodium metaborate.

In addition to sodium metaborate, calcium carbonate, sodium carbonate, and sodium sulfate ($CaCO_3$ - CC, Na_2CO_3 - C, Na_2SO_4 - S), inorganic compounds known to cause scaling problems in the kraft evaporators, were added to evaluate the effect of their interaction with sodium metaborate on scaling. The amount of these salts added to the black liquor is expressed as a percentage of the solids content originally present in the black liquor (for example, C20 represents the amount of sodium carbonate corresponding to 20 % black liquor solids).

In these experiments, the boiling point rise was determined by the method developed by Frederick and co-workers (1980) using the technique of evaporation and dilution. Evaporation is a multiple procedure representing the successive evaporation and the measurement of the boiling point of black liquor at increasing concentrations. Dilution is the opposite procedure and was used to evaluate the possible hysteresis effect. The data obtained in these experiments were analyzed in accordance with the equations developed by Frederick et al. and Zaman et al. (1980, 1998). In accordance with their findings, the boiling point rise depends on the liquor to solid ratio following two linear curves in which intersection the solubility limit is defined. The solids in the diagrams shown in this paper are total solids, including black liquor solids and added salt(s), minus water of hydration present in sodium borate tetrahydrate. The water of hydration is added to the total water in the system.

The viscosity measurements were performed using couette geometry with a Rheometric Scientific SR-5000 instrument. The viscosity of slash pine black liquor samples with sodium metaborate added at levels 0.0 %, 5 % (MB5), 10 % (MB10), and 20 % (MB20) of total black liquor solids was measured. The black liquor used for the viscosity study was concentrated to 65 % after the sodium metaborate addition.

Results

Boiling Point Rise and Solubility

Figure V-2.1. shows the effect of the solids mass fraction, $S/(1-S)$, on the black liquor's boiling point rise, at 0 % and 10 % (60 % autocauticizing) sodium metaborate addition. The black liquor had an initial solids content of 20 % and the boiling point rise was measured during evaporation and dilution. The hysteresis (between evaporation and dilution) is very evident for the samples containing borate, but was not seen with samples not containing borate.

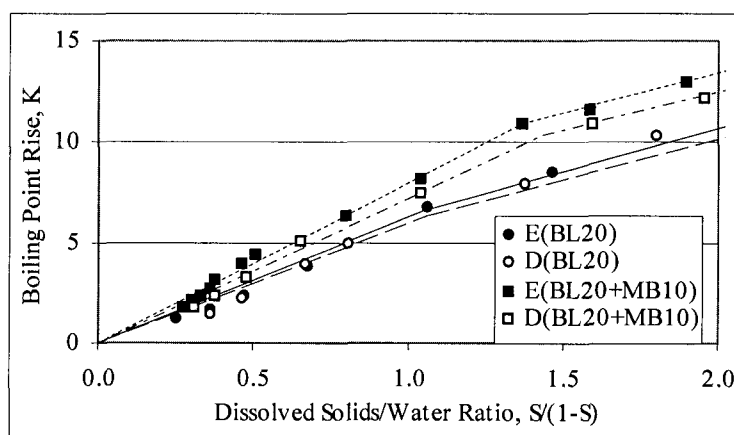


Figure V-2.1. BPR of Slash Pine Black Liquor (BL20) with/Without the 10 % NaBO_2 (MB10); Evaporation, Dilution

The addition of the sodium metaborate at a level corresponding to 10 % of the black liquor total solids increased the boiling point rise by about 2 °C at a solids/water ratio of 2.0. In addition to the increase in the boiling point rise, the solubility limit of the resulting black liquor increased from 51.2 % for BL20 to 57.8 % for

BL+MB10. This solubility limit increase is an advantage in the use of sodium metaborate as an autocausticizing agent concerning the scaling of evaporators. The hysteresis noticed in Figure V-2.1. suggests that sodium metaborate reacts with a component of the black liquor. The reactive species could be kraft lignin and other degradation products of lignin. The reaction between sodium metaborate and 1,2- and 1,3-diol structures, including β -O-4 lignin structure was confirmed earlier by two groups of researchers (Gierer, Norén, 1962, Lundquist et al., 1996).

Because of their partial solubility in the black liquor, the addition of sodium carbonate (C) and sodium sulfate (S) reduced both the boiling point rise and solubility limit of the resulting black liquor. The addition of either sodium carbonate or a mixture of sodium carbonate and sodium sulfate had the same effect on both the boiling point rise and solubility level of the black liquor. This indicates that the solubility limit of these salts is the same. No hysteresis was observed for the evaporation and dilution series of experiments with the addition of sodium carbonate/sodium sulfate. The addition of 10 % sodium metaborate (MB10) to the black liquor containing 20 % of sodium carbonate (C20) and 10 % of sodium sulfate (S10) slightly increased both the boiling point rise and the solubility limit. The boiling point rise obtained at the different dissolved solids/water ratios in this series of experiments is shown in Figure V-2.2. (BL+C20+S10; BL+C20+S10+MB10).

The solubility limit for BL+C20+S10 was 44.5 % with the BPR of 5.5 °C, while SL for BL+C20+S10+MB10 was 46 % with BPR of 6.7 °C.

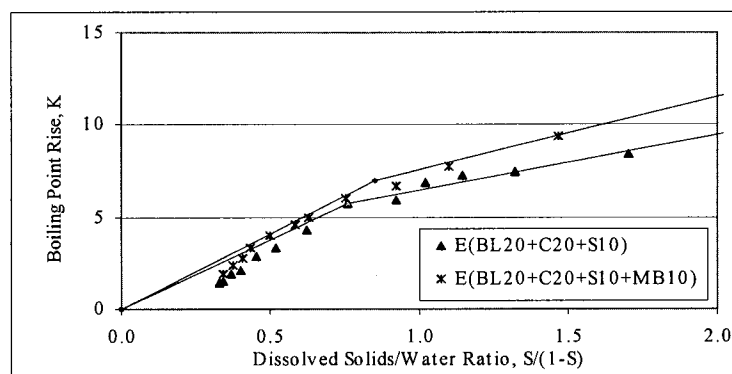


Figure V-2.2. BPR of Slash Pine Black Liquor (BL20) with 20 % Na_2CO_3 (C20), 10 % Na_2SO_4 (S10) with/without 10 % NaBO_2 (MB10); Evaporation

The addition of calcium carbonate (CC), which is completely insoluble in the black liquor, did not change the solubility limit but decreased the boiling point rise. The decrease of the boiling point rise is a consequence of calcium carbonate not being soluble in black liquor. No hysteresis was observed in these experiments. The addition of 10 % sodium metaborate (MB10) to the black liquor containing 20 % calcium carbonate (CC20) significantly increased the solubility limit to a total solids level of 58 %. This is a higher solubility limit than that of the initial black liquor, which is 51.2 %. These results are shown in Figure V-2.3. (BL20+CC20; BL20+CC20+MB10).

Viscosity

At temperatures between 70 and 75 °C, it was found that the slash pine black liquor with sodium metaborate has Newtonian viscosity behavior, in the range of shear rate 10^1 to $3 \times 10^2 \text{ s}^{-1}$. The slash pine black liquor of 65 % solids has a viscosity

of 3 P at 74 °C, which agrees with data published by Adams and Frederick (1988). The addition of sodium metaborate slightly increased the viscosity. However, the viscosity increase was highest at an addition level of 5 % of sodium metaborate. Further addition of sodium metaborate did not significantly increase the viscosity at 70 °C, as shown in Figure V-2.4.

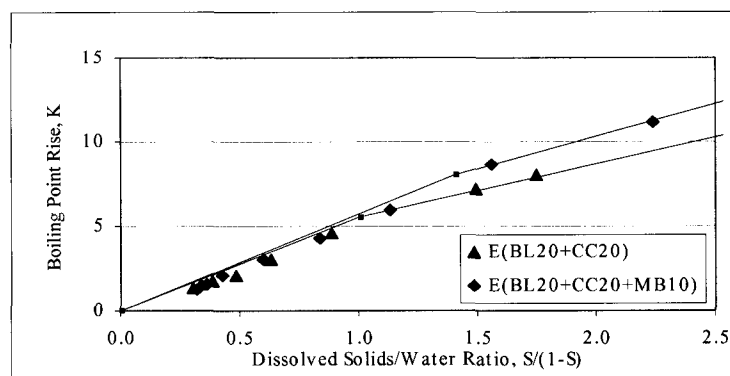


Figure V-2.3. BPR of Slash Pine Black Liquor (BL20) with 20 % CaCO_3 (CC20) with/Without 10 % NaBO_2 (MB10); Evaporation

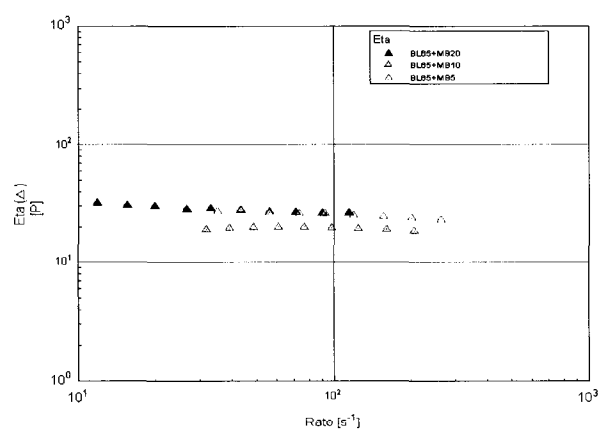


Figure V-2.4. Effect of Shear Rate on Viscosity of Slash Pine Black Liquor with/Without 5, 10, and 20 % NaBO_2 at 65 % Total Solids, 70 °C

Janson and Söderhjelm (1988) also found an increase of the viscosity of borate-based black liquor from pinewood compared to non-borate pinewood black liquor.

Conclusions

The data obtained in this study show that borate slightly increases both the boiling point rise and solubility limit of the slash pine black liquor. The addition of borate also results in a hysteresis between evaporation and dilution. This hysteresis suggests that borate forms a complex with kraft black liquor. The addition of sodium metaborate increased the solubility limit of the black liquor. This was evident for the initial black liquor and for the liquor with the three different inorganic compounds. This increase in solubility limit should be an advantage concerning the scaling problems in kraft evaporators. After the beginning increase of the black liquor viscosity, further addition of sodium metaborate at the levels higher than 5 % had only slight effect on the black liquor viscosity.

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V-3. Some Properties of Black Liquor from Kraft and Kraft-Borate Pulping

Abstract

Implementation of the partial borate autocausticizing requires the study of the operation of both pulping and recovery lines in the kraft process. The recovery line, especially its first evaporation phase, is governed by the black liquor properties, such as the boiling point rise (BPR). The BPR measurements should be included in the analyses of the black liquor resulting from the kraft process with the partial borate autocausticizing since an additional chemical, sodium metaborate, is present in this process. Also, there is a concern that sodium metaborate might affect the pulping chemistry. Studies of lignin dissolved in the black liquor (kraft lignin) during kraft and kraft-borate pulping can provide insights into this question. In this paper, the boiling point rise of black liquor resulted from kraft and kraft-borate (35 % autocausticizing level) pulping of spruce, birch, and maple was studied. Corresponding kraft lignins were isolated and compared regarding the phenolic hydroxyl group content and the characteristics of FTIR spectra. The effect of sodium metaborate at the level of 35 % autocausticizing on the boiling point rise of black liquor and the kraft lignin properties are discussed.

Introduction

There is considerable interest in the use of sodium metaborate ($NaBO_2$) in the kraft technology because it is an autocausticizing agent that can reduce or eliminate

the calcium-based causticizing cycle (Tran et al., 1999). Based on the energy efficiency of the process, its capital requirements, and the system's effect on the emission of fossil fuel derived carbon dioxide, both partial and 100 % borate causticizing technologies are recommended in the development of "The Eco-cyclic Pulp Mill," as short-term and long-term goal, respectively (Axegård et al., 2002). Borate autocausticizing proceeds through the reaction of sodium metaborate and sodium carbonate (Na_2CO_3) taking place in the furnace and resulting in trisodium borate (Na_3BO_3) and carbon dioxide (CO_2). In the dissolving tank, the trisodium borate undergoes hydrolysis to form sodium hydroxide ($NaOH$) and regenerate sodium metaborate (Tran et al., 1999). Therefore, borate circulates within the kraft cycle, performing an autocausticizing function and representing an additional chemical in the pulping process. Trials on borate-based partial autocausticizing have recently been conducted at several kraft pulp mills (Tran et al., 2002, Koshesfahani, Bair, 2002). The results of mill trials showed that the addition of borate in the liquor cycle provides an effective way of producing caustic directly. However, to fully implement this technology, it is necessary to understand the effect of borate on the efficiency of both pulping and recovery processes. The comparative studies of the kraft lignin and the boiling point rise (BPR) of black liquor resulting from kraft and kraft-borate pulping contributed to resolving the dilemma regarding the pulping efficiency and black liquor evaporation in partial borate-based autocausticizing technology.

Kraft Lignin

In order to better understand the structural changes taking place in lignin during kraft pulping and the importance of these changes for delignification, kraft lignin should be isolated and analyzed. Kraft lignin is usually isolated by acidification of concentrated black liquor with a mineral acid (Lin, 1992). Kraft lignin analyses include FTIR spectral analysis (Faix, 1992), determination of the phenolic hydroxyl groups (PhOH) (de Sousa et al., 2001), and calculation of index of condensation (CI) (Faix, 1991).

Boiling Point Rise (BPR)

Before burning the waste liquor from the pulping process (black liquor), it is necessary to concentrate it from weak black liquor, which is about 20 % solids, to a firing concentration of 65 % or greater. One limitation to the liquor evaporator efficiency is the boiling point rise of the black liquor. The boiling point rise of a solution is the difference between the boiling point of the solution and the boiling point of the solvent at a given pressure. As the boiling point rise of the solution increases, the temperature difference between the condensing steam on the outside of the evaporator tubes and the temperature of the boiling liquor inside the tubes decreases. This reduces the driving force for evaporation and results in less evaporation per unit surface area. The BPR of black liquor can be measured by the method recommended by Frederick et al. (1980).

This study describes some properties of kraft lignin and the BPR of the black liquors resulting from kraft and kraft-borate (at 35 % autocausticizing level) pulping of birch, maple, and spruce.

Experimental

Black spruce (*Picea mariana*), paper birch (*Betula papyrifera*) and sugar maple (*Acer saccharum*) woodchips, supplied by The U.S. Forest Products 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 %; $NaOH$ 93.4 g/L as Na_2O ; Na_2CO_3 22.45 g/L as Na_2O . To simulate the white liquor composition corresponding to that at 35 % borate autocausticizing, sodium metaborate was added to the white liquor in the amount corresponding to 16.4 g/L as Na_2O . 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 using 400 g oven-dry wood at 1,500 H-factor. The contribution of both the heating and cooling period to H-factor was the same (80); the cooking temperature was 170 °C.

The black liquor samples were collected after pulping and before washing of pulps. Solids content of black liquors was determined following the TAPPI standard method (T 650 om-690). The parameters of both white and black liquors were

measured using a dual-titrator ion analyzer developed by U.S. Borax Inc. (variant of the ABC titration method).

Kraft Lignin Isolation and Analysis

Isolation of kraft lignin from the studied black liquors (K, KB) was performed by two-step acidification of black liquor by 20 % sulfuric acid (Lin, 1992). After isolation, kraft lignin was extracted in n-pentane (Soxhlet extractor, 8 h) in order to remove low-molecular weight compounds. The phenolic hydroxyl group content (PhOH) was measured in the kraft lignins of K and KB black liquors using the method of Folin and Ciocalteu (FC method). This method is based on a color reaction of the PhOH groups with a hetero-phosphotungstate-molybdate. Absorbance of the obtained solution at 760 nm is proportional to the concentration of PhOH (de Sousa et al., 2001). In these studies, vanillin was used for the calibration purposes. FTIR spectra of kraft lignins were recorded and compared, and the lignin condensation indices were calculated: $CI = \sum A_{\text{min between 1500 and 1050 cm}^{-1}} / \sum A_{\text{max between 1600 and 1030 cm}^{-1}}$ (Faix, 1991).

Boiling Point Rise Measurements

The BPR of the studied black liquors (K, KB) was determined by the method recommended by Frederick et al (1980). The apparatus used in this study was described in detail earlier (Bujanovic, Cameron, 2001). Using this method/apparatus the boiling point of water was measured several times in order to confirm the

accuracy of the obtained results. The results were analyzed using the Minitab statistical program. The regression models estimating the black liquor boiling point rise at different solids concentration were obtained.

Results and Discussion

Some parameters of the black liquors resulted from kraft and kraft-borate pulping of birch, maple, and spruce as the pH, content of solids, and concentration of sodium metaborate are shown in Table V-3.1.

Table V-3.1.

Some Parameters of Kraft and Kraft-Borate Black Liquors of
Birch, Maple and Spruce

Species	K/KB	Black Liquor Parameter		
		pH	NaBO ₂ as Na ₂ O g/L	Solids Content %
Birch	K	11.74	-	16.75
	KB	11.78	11.05	17.64
Maple	K	11.93	-	17.65
	KB	11.83	11.23	18.32
Spruce	K	12.32	-	16.83
	KB	12.33	10.71	17.22

The pH's of black liquors obtained in the kraft and kraft-borate pulping of birch, maple, and spruce were the same indicating that sodium metaborate does not affect the level of residual alkali in the cooking liquor. Therefore, regarding the residual alkali concentration, kraft-borate pulping should not reduce the delignification rate. The sodium metaborate concentration in the kraft-borate white liquor was corresponding to 35 % autocauticizing, i.e. 16.4 g/L as Na₂O. According

to the results obtained in the dual-titration, the concentration of sodium metaborate in the KB black liquors decreased on average for 33 % (Table V-3.1). This result is not expected since the makeup amount of sodium metaborate was only 3.57 % of its required amount as estimated for the mill trials at 20 % autocauticizing (Koshesfahani, Bair, 2002). The noticed decrease of sodium metaborate concentration in the KB black liquors might be attributed to the loss of sodium metaborate with pulp, which can be recovered after washing pulp – the weak liquor. Also, sodium metaborate may react with the black liquor components and hence, become untitratable during the dual-titration (Lundquist et al., 1996, Sjöström, 1981). The solids content in the KB black liquors was higher than in the corresponding K black liquors on average for 3.8 %.

Kraft Lignin

The differences observed between FTIR spectra of softwood and hardwood lignins are still visible in comparisons of FTIR spectra of studied K and KB lignins of maple, birch, and spruce. No differences between the basic FTIR spectral characteristics (major absorption bands and the relations between the intensities at these bands) of K and corresponding KB lignins were observed. The lignin condensation indices (CI) were calculated and they are presented in Table V-3.2. The CI's of spruce kraft lignins were higher than that found for spruce MWL (milled wood lignins) ($CI_{MWLSpruce} = 0.42$) and the CI's of birch and maple kraft lignins were higher than those found for MWL of hardwoods ($CI_{MWLASpen} = 0.38$; $CI_{MWLBeech} =$

0.37) (Faix, 1991). It indicates that the pulping reactions resulted in the lignin, which is dissolved in the cooking liquor with more condensed structure than the native lignin. This study showed that the spruce K and KB lignins were characterized by higher CI than the maple and birch K and KB lignins. No differences were noticed between CI of K and KB lignins of the same species.

Table V-3.2.

Some Properties of Lignins Isolated from
Kraft and Kraft-Borate Black Liquors

Species	K/KB	Lignin Property	
		PhOH (mmol/ g lignin)	CI
Birch	K	4.20	0.45
	KB	4.56	0.46
Maple	K	4.50	0.47
	KB	4.45	0.45
Spruce	K	3.75	0.63
	KB	3.62	0.65

The phenolic hydroxyl groups (PhOH) increase hydrophilic nature of lignin and, hence, positively affect the lignin solubility in the cooking liquor. The contents of PhOH groups of K and KB lignins studied in these experiments were approximately the same (Table V-3.2.). The content of PhOH groups found for spruce K and KB kraft lignins was in accordance with the contents of PhOH determined in pine kraft lignins using aminolysis by Robert et al. (1984).

The equal levels of the calculated CI's and measured contents of PhOH groups of K and KB kraft lignins indicate similar delignification path and lignin solubility in kraft and kraft-borate pulping of birch, maple, and spruce. A similar

conclusion regarding the lignin reactivity in kraft and kraft-borate pulping was drawn recently in the study of residual lignin isolated from spruce kraft and kraft-borate (35 % autocauticizing) pulps (Bujanovic et al., 2003).

Boiling Point Rise

Figures V-3.1.-3. show the boiling point rise obtained during evaporation of the K and KB black liquors of beach, maple, and spruce. The initial contents of solids of the black liquors are shown in Table V-3.1., while the final contents of solids were between 68 and 72 %.

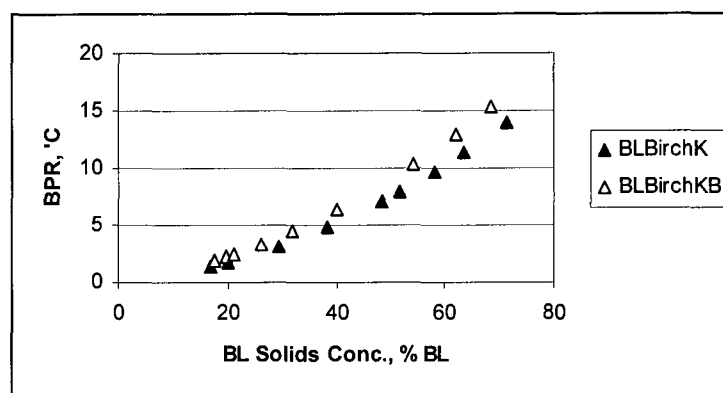


Figure V-3.1. BPR of Birch K and KB Black Liquors

Regression lines were developed for kraft and kraft-borate black liquors – $BPR = aS^2 + bS$, S (kg solids/kg black liquor). The coefficients of these equations, including the statistical parameters - coefficient of determination (R^2) and standard error of regression (σ), are shown in Table V-3.3. The tests involving the equality of

coefficients of different regressions were included in the statistical analysis of the BPR/S data. This test showed that the assumption of the different regression models for kraft and kraft-borate black liquors is correct (Pindyck, Rubinfeld, 1991).

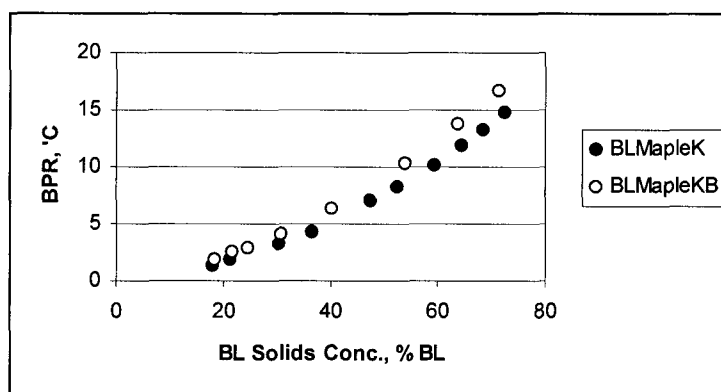


Figure V-3.2. BPR of Maple K and KB Black Liquors

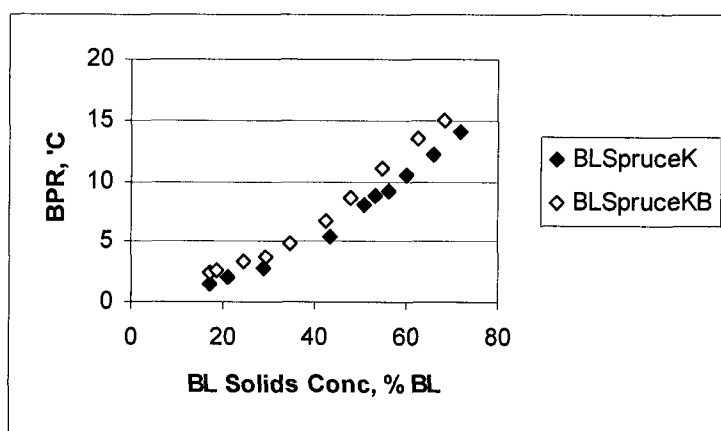


Figure V-3.3. BPR of Spruce K and KB Black Liquors

According to the data in Table V-3.3., the BPR's of kraft-borate black liquor of birch, maple, and spruce are higher than those of corresponding kraft black liquors for 2.3-2.5 °C at 70 % solids content of black liquor.

Table V-3.3.

BPR of Kraft and Kraft-Borate Black Liquors: Statistical Data of Regression Models

$$\text{BPR} = aS^2 + bS, S, \text{ kg solids/kg black liquor}$$

Species	K/KB	Regression Model			
		Coefficients		Parameters	
		a	b	R ²	σ
Birch	K	21.6	4.10	99.7	0.4559
	KB	23.2	6.47	99.8	0.3726
Maple	K	23.1	3.73	99.6	0.5865
	KB	23.9	6.51	99.9	0.2774
Spruce	K	20.7	4.80	99.9	0.2417
	KB	21.7	7.57	99.8	0.4061

Conclusion

Properties of black liquors obtained in kraft and kraft-borate (at 35 % autocauticizing level) pulping of birch, maple, and spruce were compared. Kraft lignins isolated from these black liquors were analyzed. The content of phenolic hydroxyl groups, which positively affect the lignin solubility in the cooking liquor, was not influenced by sodium metaborate. Based on the FTIR data, lignins from kraft and corresponding kraft-borate black liquors were characterized by the same condensation level indicating that kraft-borate pulping is basically characterized by the same reaction path as kraft pulping. As expected, kraft-borate black liquors were

characterized by the higher boiling point rise than corresponding kraft black liquors.

At 70 % solids, the increase of BPR was 2.3-2.5 °C.

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V-4. Effect of Borate on Boiling Point Rise of Black Liquor

Abstract

There is considerable interest in the use of borate-based autocausticizing to supplement or eliminate the calcining/causticizing cycle. On-going mill trials have produced promising results and indicate that this may be economical feasible alternative to the conventional procedure of green liquor causticizing with calcium hydroxide. A common situation is where 5-25 % additional calcining/causticizing capacity is required. This requirement can be met by the addition of sodium borate to the liquor cycle.

An important question with the addition of borate to the liquor cycle is its effect on the resulting black liquor properties. In order to provide an insight into this question, the boiling point rise (BPR) and solubility limit (SL) of the commercial slash pine black liquor were studied. The experiments were performed at different levels of sodium metaborate and inorganic salts known to cause scaling in kraft liquor evaporators – sodium carbonate, sodium sulfate, and calcium carbonate.

An increase of both the BPR and SL of slash pine black liquor containing sodium metaborate was found in this study. The black liquor containing sodium metaborate showed the different BPR results in evaporation and dilution cycle – hysteresis. The hysteresis can indicate formation of lignin-borate complex, which affects the BPR to be lower than expected for a salt completely soluble in black liquor

such sodium metaborate. The SL increase can have a favorable effect on the reduction of the evaporators scaling.

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CHAPTER VI

CONCLUSIONS

Effect of Sodium Metaborate on the Pulp Properties and Kraft Pulping of Birch, Maple, and Spruce

This study presents the results obtained for birch, maple, and spruce in kraft pulping and in kraft pulping with sodium metaborate, kraft-borate pulping. The level of sodium metaborate added in white liquor for kraft-borate pulping was calculated based on a desired level of partial autocausticizing and the autocausticizing stoichiometry proposing that one mol of sodium metaborate is required to generate one mol of sodium hydroxide. Major part of kraft-borate experiments was conducted with white liquor containing sodium metaborate at the level corresponding to 35 % autocausticizing. For spruce, the studies also included the evaluation of the effect of an increasing level of sodium metaborate on pulping at a constant H-factor.

Spruce kraft-borate pulping results in a higher screened yield than kraft pulping, under the same conditions. This result was obtained for spruce in both series of experiments: at a constant H-factor (2,000) with an increasing level of sodium metaborate corresponding to 10 to 52 % autocausticizing, and at an increasing H-factor (500 to 3,000) with the same level of sodium metaborate (35 % autocausticizing). In kraft-borate pulping, at H-factors higher than 1,000, the screened yield increase was ~1.8 %.

It was proposed that sodium metaborate has a potential to protect hexosans in pulping. Since hexosans are more abundant in spruce, an increase of the screened yield in pulping of spruce is more noticeable than in pulping of birch and maple.

Although the SD (0.4) was high, the reject levels decreased and were ~0.6 % lower for spruce kraft-borate (35 % autocauticizing) than for spruce kraft pulping in these experiments. Therefore, spruce pulping in kraft process with implemented partial borate autocauticizing might result in a lower level of rejects than spruce pulping in conventional kraft process.

The comparisons of kraft and kraft-borate pulping of the studied species indicated that delignification is not affected by sodium metaborate. It was also shown that the conversion factors between “HexA-free” kappa number and the Klason lignin content are approximately the same for the kraft and kraft-borate pulps of the same species. Therefore, residual lignin in kraft and kraft-borate pulps is characterized by the same level of oxidizable structures contributing to the measured “HexA-free” kappa number. The same brightness and the same contents of extractives, HexA, and PhOH groups were measured for the kraft and kraft-borate pulps. Based on these results, similar bleachability of kraft and kraft-borate pulps is expected. This conclusion is in agreement with the same bleachability obtained during acidic chlorite delignification of spruce kraft and kraft-borate pulps, and the same residual lignin structure found in spruce kraft and kraft-borate pulps.

The physical properties of pulps were studied. These studies showed no difference in density, and tensile and tear strength of kraft and corresponding kraft-

borate pulps. Also, “beatability,” measured as a decrease of CSF after refining, was the same for both types of studied pulps. Therefore, implementation of the partial autocausticizing, at 35 % level, should not affect the pulp strength.

Effect of Sodium Metaborate on the Properties of Black Liquor

In the studies of the black liquor properties, the boiling point rise was measured for the laboratory prepared kraft and kraft-borate black liquors, and for the commercial black liquor, at different levels of added sodium metaborate. It was shown that in the presence of sodium metaborate, the boiling point rise increases. The highest increase of 5 °C was observed for the commercial slash pine black liquor, at the sodium metaborate level corresponding to 120 % autocausticizing. The BPR's of kraft-borate liquors of birch, maple, and spruce were higher for 2.3 - 2.5 °C than those of corresponding kraft liquors, at 70 % solids.

The hysteresis observed in evaporation and dilution phase of the slash pine black liquor containing sodium metaborate was proposed to be an effect of the formation of a complex between kraft lignin and borate. Similar hysteresis was noticed neither in the studies of the slash pine black liquor nor in the studies of the slash pine black liquor containing sodium carbonate.

An increase of the solubility limit of the slash pine black liquor (initial and in the presence of three different inorganic salts) was observed in the presence of sodium metaborate. This increase in solubility might cause the evaporator scaling problems to be reduced in kraft process with partial borate-based autocausticizing.

The studies of the BPR at elevated pressures and temperatures showed that Dühring's rule applies to black liquor (a plot of the temperature of the solution versus that of the reference solvent, where both the reference solvent and the solution exert the same pressure, results in a straight line). Also, Dühring's lines for the slash pine black liquor and for the slash pine black liquor after addition of sodium metaborate (30, 60 % autocausticizing) are overlapping.

Kraft lignin was isolated from the birch, maple, and spruce kraft and kraft-borate black liquors. The results of kraft lignin characterization based on the content of phenolic hydroxyl groups and the level of condensation indicated that sodium metaborate does not affect a solubility of kraft lignin in black liquor. It is in accordance with the result obtained in the studies of the kraft and kraft-borate pulps that delignification path is not affected by the presence of sodium metaborate (corresponding to 35 % autocausticizing) in kraft pulping.

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