

## GENERAL RESEARCH

# Effect of Sodium Metaborate on the Boiling Point Rise of Slash Pine Black Liquor

Biljana Bujanovic and John H. Cameron\*

College of Engineering, Western Michigan University, Kalamazoo, Michigan 49008

Borate can be used as either a total or partial autocausticizing agent for conversion of  $\text{Na}_2\text{CO}_3$  to  $\text{NaOH}$ . For every mole of  $\text{Na}_2\text{CO}_3$  converted, a mole of  $\text{NaBO}_2$  is generated and remains in the black liquor. The objective of this study is to determine the effect of this additional  $\text{NaBO}_2$  on the boiling point rise 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 boiling point rise observed during evaporation was greater than that observed during dilution. This phenomenon was not seen for black liquor without borate added nor for black liquor with only  $\text{Na}_2\text{CO}_3$  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 boiling point rise 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 boiling point rise by about 5 K.

### Introduction

The kraft pulping process is by far the dominant pulping process, accounting for over 95% of all chemical pulp 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 ( $\text{Na}_2\text{S}$ ) and sodium hydroxide ( $\text{NaOH}$ ), 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 ( $\text{Na}_2\text{CO}_3$ ) 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 ( $\text{CaCO}_3$ ) 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,<sup>1</sup> “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

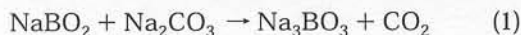
given pressure. As the BPR of the solution increases, the temperature difference between the condensing steam on the outside of the evaporator tubes and the temperature of the boiling liquor inside the tubes decreases. This reduces the driving force for evaporation and results in less evaporation per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

There is 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<sup>2</sup> and more recently by Tran et al.<sup>3</sup> 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 ( $\text{NaBO}_2$ ) is needed to decarbonate 1 mol of  $\text{Na}_2\text{CO}_3$ . 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.<sup>3</sup> showed that the borate-based autocausticizing reactions are more effective than had been proposed by Janson.<sup>2</sup> According to these authors, the overall autocausticizing reactions can be sum-

\* To whom correspondence should be addressed. E-mail: Cameron@wmich.edu. Fax: 616-387-2768.

marized by the reaction of sodium carbonate with sodium metaborate in the molten smelt to form trisodium borate ( $\text{Na}_3\text{BO}_3$ ), reaction (1), and the subsequent reaction of trisodium borate in the green liquor dissolving tank to form sodium hydroxide, reaction (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 experiment, 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 experiment, 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 ( $\text{Na}_2\text{CO}_3$ ) on the BPR of the black liquor was also determined. Sodium carbonate was chosen for comparison purposes 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.<sup>1</sup>

#### BPR 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,<sup>4</sup> 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 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.

**BPR 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.,<sup>5</sup> can be expressed according to eq 3, where  $S$  = solids content

**Table 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
$\text{Na}_2\text{S}$	5.81 as $\text{Na}_2\text{O}$	7.3 as $\text{Na}_2\text{S}$	0.0937
$\text{Na}_2\text{SO}_4$	4.1 as $\text{Na}_2\text{O}$	9.39 as $\text{Na}_2\text{SO}_4$	0.0662
$\text{Na}_2\text{CO}_3$	5.18 as $\text{CO}_3$	9.15 as $\text{Na}_2\text{CO}_3$	0.0863
$\text{NaOH}$	1.72 as $\text{Na}_2\text{O}$	2.22 as $\text{NaOH}$	0.0555
$\text{NaCl}$	0.45 as $\text{Cl}$	0.741 as $\text{NaCl}$	0.0127
$\text{Na}$	18 as $\text{Na}$		0.782 as $\text{Na}$
$\text{K}$	1.7 as $\text{K}$		0.0435 as $\text{K}$

of liquor (weight fraction of solids) and  $K_B$  = constant, which depends on the composition of the black liquor.

$$\text{BPR} = K_B S / (1 - S) \quad (3)$$

Frederick et al.<sup>5</sup> noticed that this equation only applied to black liquor below its SL. When the SL is reached, the slope of the BPR curves decreases abruptly. Zaman et al.<sup>6</sup> considered this fact and divided the BPR curve into two parts with each described by a linear equation. In the first part of this curve

$$\text{BPR} = aS / (1 - S) \quad (4)$$

while in the second part of this curve

$$\text{BPR} = b' + a'S / (1 - S) \quad (5)$$

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.<sup>5</sup> and called the boiling temperature measurements by Adams and Frederick.<sup>7</sup> The results obtained by this procedure were analyzed in accordance to the Frederick et al.<sup>5</sup> and Zaman et al.<sup>6</sup> 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. Upon arrival, 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 autocauticizing, 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 contents 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 1 and the stoichiometry shown in eqs 1 and 2. It was assumed that all sodium and potassium, not present as sulfides, sulfates, or chlorides, were present as carbonates ( $\text{K}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3$ ). 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

Table 2. Black Liquor Samples Used in This Study<sup>a</sup>

no.	black liquor	black liquor solids before addition of borate, g/100 g	NaBO <sub>2</sub> ·4H <sub>2</sub> O (Na <sub>2</sub> CO <sub>3</sub> ) added, g/100 g of BL	NaBO <sub>2</sub> (Na <sub>2</sub> CO <sub>3</sub> ) added, g/100 g of BL solids	% autocausticizing	black liquor solids after addition of borate (carbonate), 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
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)

<sup>a</sup> BL = slash pine black liquor; MB = sodium metaborate; C = sodium carbonate.

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.

On the basis of the above calculations, sodium metaborate (NaBO<sub>2</sub>) was added at 5, 10, and 20% of the original black liquor solids or 5, 10, and 20 g/100 g of 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 (NaBO<sub>2</sub>·4H<sub>2</sub>O), and the water of hydration was accounted for as part of the total water in the liquor.

## Experimental Techniques

### BPR at Elevated Pressures and Temperatures.

The pressure-temperature relationship for slash pine black liquor with the addition of sodium metaborate was measured using a pressurized reactor. In these experiments, the original black liquor at 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 plus sodium metaborate samples used in these experiments are shown in Table 2.

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*.<sup>8</sup> 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; 5400 psi 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 were obtained. To ensure that all air was removed from the vessel before the temperature-pressure

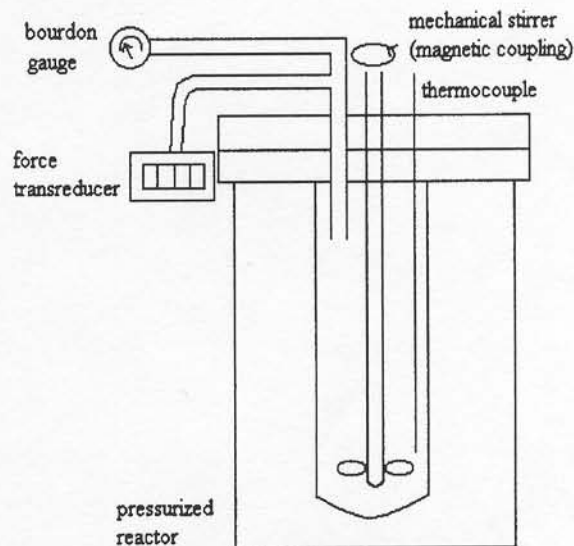


Figure 1. Apparatus for vapor pressure-temperature measurements.

measurements were made, similar experiments were conducted using distilled water. At pressures from 100 to 400 kPa, the corresponding temperatures of the distilled water agreed with the literature values to within ±0.2 K. Figure 1 shows the pressurized reactor used in these experiments.

**BPR 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 also shown in Table 2.

The BPR for these samples were determined by the method described by Frederick et al.<sup>5</sup> The apparatus for the BPR measurements is shown in Figure 2. The corresponding boiling point of water was also measured several times during the course of this work.

This technique is a multistage 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.

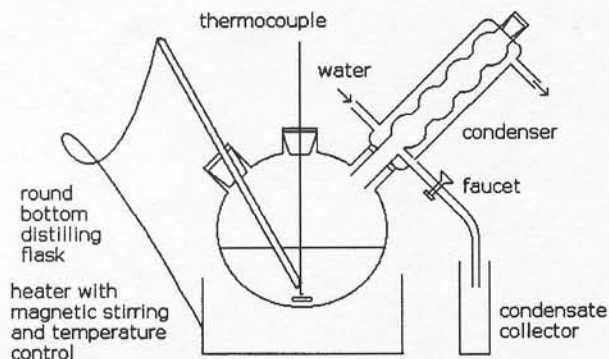


Figure 2. Apparatus for measurement of the BPR at atmospheric pressure.

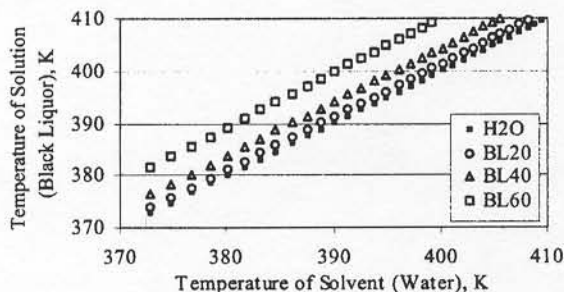


Figure 3. Dühring's lines for the slash pine black liquor at different solids levels.

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.

The obtained data were analyzed in the accordance to the models developed by Frederick et al.<sup>5</sup> and Zaman et al.,<sup>6</sup> eqs 4 and 5. The results obtained in the evaporation and dilution series were treated separately, and two curves were obtained for each sample. The SLs during evaporation and dilution were also calculated.

## Results

### BPR at Elevated Pressures and Temperatures.

Figure 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 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.

**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 5 compares the BPR measured in this study with those

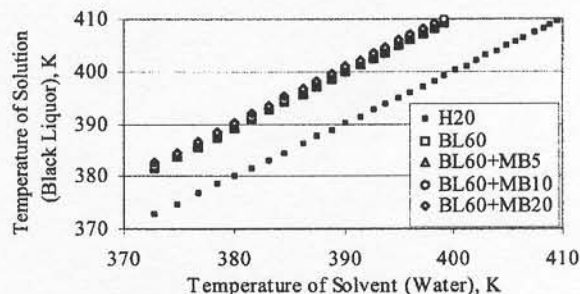


Figure 4. Dühring's lines for 60% solids slash pine black liquor with different  $\text{NaBO}_2$  levels.

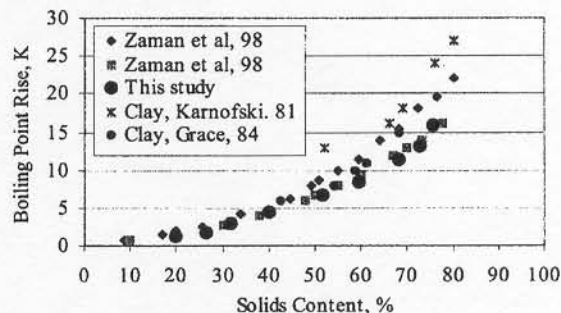


Figure 5. Black liquor BPR: comparative results.

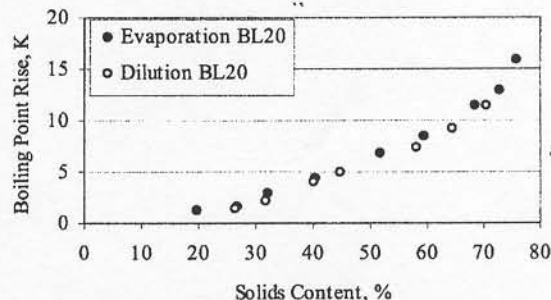


Figure 6. BPR of the slash pine black liquor.

measured in studies using either boiling temperature measurements<sup>6</sup> or oil dispersion codistillation techniques.<sup>9,10</sup>

The BPR results shown in Figure 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 65% solids with this technique,<sup>7</sup> 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 6 shows the BPR 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 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.

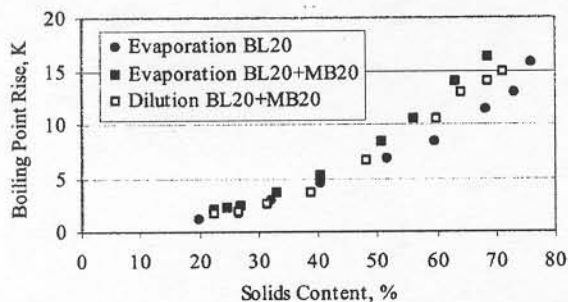


Figure 7. BPR of the slash pine black liquor with 20%  $\text{NaBO}_2$ .

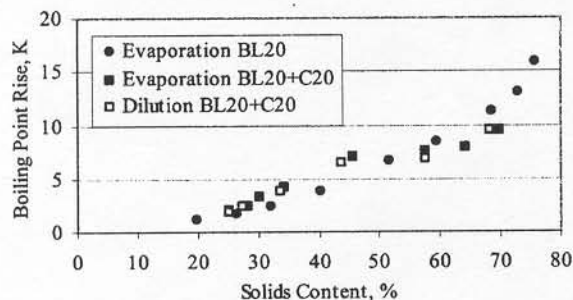


Figure 8. BPR of the slash pine black liquor with 20%  $\text{Na}_2\text{CO}_3$ .

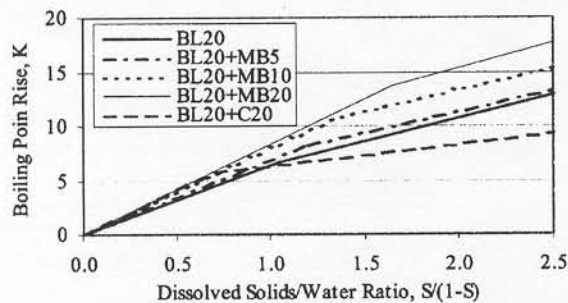


Figure 9. BPR during evaporation of the slash pine black liquor with/without  $\text{NaBO}_2/\text{Na}_2\text{CO}_3$ .

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 8 and 9.

Comparing Figure 7 to Figure 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 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<sup>5,6</sup> described in eqs 4 and 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.

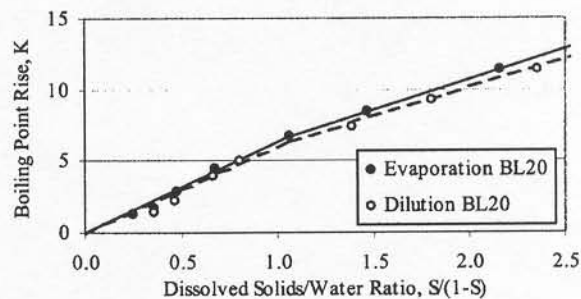


Figure 10. BPR for the slash pine black liquor during evaporation and dilution.

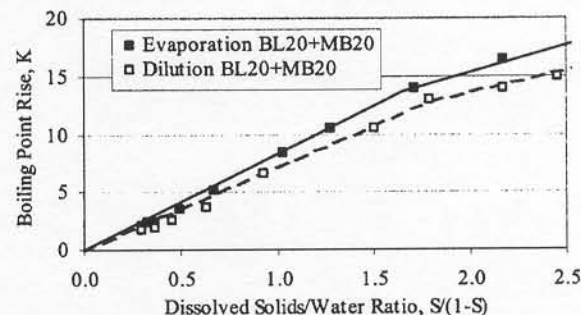


Figure 11. BPR for the slash pine black liquor with 20%  $\text{NaBO}_2$  during evaporation and dilution.

In Figure 10 the BPR is plotted versus the dissolved solids/water ratio, using the linear models<sup>5,6</sup> for the slash pine black liquor without sodium metaborate during evaporation and dilution.

In Figure 11 the BPR of the slash pine black liquor with 20% sodium metaborate added, using the linear models<sup>5,6</sup> 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 of the borate-treated black liquors but not for the untreated or sodium carbonate treated black liquors.

**Effect of the Inorganic Portion of the Black Liquor on the BPR.** As will be discussed later, the hysteresis in the BPR with borate is believed to be due to a known reaction between lignin and borate. 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 12.

As shown in Figure 12, the inorganic portion of the black liquor with the addition of  $\text{NaBO}_2$  does not have the hysteresis associated with the addition of  $\text{NaBO}_2$  to the black liquor.

**Linear Equations Model.** From the data obtained during evaporation and dilution of the different black liquors, parameters of eqs 4 and 5 that describe the BPR were determined. These parameters and the SLs are shown in Tables 3 and 4 for evaporation and dilution, respectively.

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

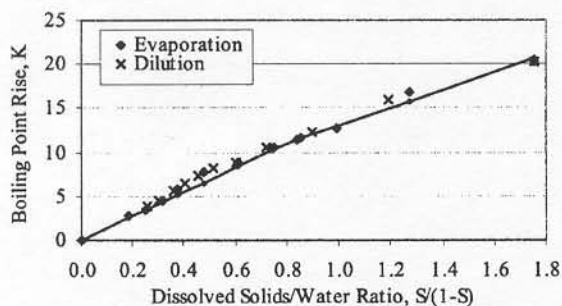


Figure 12. BPR of a NaOH + Na<sub>2</sub>CO<sub>3</sub> + Na<sub>2</sub>SO<sub>4</sub> + NaBO<sub>2</sub> water solution during evaporation and dilution.

Table 3. Parameters of Linear Equations of BPR versus the Dissolved Solids Water Ratio for Evaporation<sup>a</sup>

sample	parameter					SL		
	<i>a</i>	<i>r</i> <sup>2</sup>	<i>a'</i>	<i>b'</i>	<i>r</i> <sup>2</sup>	<i>S</i> (1 - <i>S</i> )	<i>S</i> , %	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	34.49

<sup>a</sup> *S* (%) = total solids in the black liquor (solids originating from black liquor plus added salt). SBL (%) = black liquor originating solids in the black liquor. *r*<sup>2</sup> = statistical indication of the ability of a straight line to fit data.

Table 4. Parameters of Linear Equations of BPR versus the Dissolved Solids Water Ratio for Dilution<sup>a</sup>

sample	parameter					SL		
	<i>a</i>	<i>r</i> <sup>2</sup>	<i>a'</i>	<i>b'</i>	<i>r</i> <sup>2</sup>	<i>S</i> (1 - <i>S</i> )	<i>S</i> , %	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

<sup>a</sup> *S* (%) = total solids in the black liquor (solids originating from black liquor plus added salt). SBL (%) = black liquor originating solids in the black liquor. *r*<sup>2</sup> = statistical indication of the ability of the straight line to fit data.

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 Tables 3 and 4.

## Discussion

**Effect of Metaborate on the BPR.** As shown by the Dühring plot in Figure 4, where the effect of sodium borate tetrahydrate on the BPR was measured, the BPR increased by only 2 K with the addition of 20 g of sodium borate tetrahydrate/100 g of black liquor solids to a 60% solids 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 2). If we consider Figure 7, the addition of 20 g of sodium metaborate/100 g of black liquor solids (MB20) to a 60% solids liquor increases the solids concentration to 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 liquor, the expected autoausticizing is about 120%. Because this is a higher addition level than what would be used even at full autoausticizing, the expected increase in the BPR for commercial autoausticizing 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<sup>11</sup> and Lundquist et al.,<sup>12</sup> who found that borate forms a complex with lignin and also with the lignin transformation products formed during kraft pulping. In accordance to the results of these authors, lignin alkali transformation products characterized by 1,2-diol and 1,3-diol including the β-O-4 structure react with borate, forming five- and six-membered rings, respectively. The arylglycerol β-aryl ether structure represents the dominant lignin bond in wood and is the most reactive structure during kraft pulping.<sup>13</sup> However, the β-O-4 structure is still present in lignin dissolved during kraft pulping.<sup>14</sup> 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 at a 120% autoausticizing level to a 60% solids liquor increases the solids concentration to 64% and increases the boiling point by about 5 K. At less than 120% autoausticizing, the increase in 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.

### Literature Cited

- (1) Grace, T. M. Pulp and Paper Manufacture. In *Alkaline Pulping*, Grace, T. M., Malcolm, E. W., Eds.; Joint Textbook Committee of the Paper Industry; CPPA/TAPPI: Montreal/Atlanta, 1989; Vol. 5.
- (2) Janson, J. Pulping processes based on autocausticizable borate. *Svensk Papperstidn.* **1980**, *63*, 392.
- (3) Tran, H.; Mao, X.; Cameron, J.; Bair, C. M. Autocausticizing of Smelt with sodium borates. *Pulp Pap. Can.* **1999**, *100* (9), 35.
- (4) Peters, M. S. *Elementary Chemical Engineering*, McGraw-Hill: Boston, 1984.
- (5) Frederick, W. J.; Sachs, D. G.; Grady, H. J.; Grace, T. M. Boiling Point Elevation and Solubility Limit for Black Liquors. *Tappi* **1980**, *63* (4), 151.
- (6) Zaman, A. A.; McNally, T. W.; Fricke, A. L. Vapor Pressure and Boiling Point Elevation of Slash Pine Black Liquors: Predictive Models with Statistical Approach. *Ind. Eng. Chem. Res.* **1998**, *37*, 275.
- (7) Adams, T. N.; Frederick, W. J. *Kraft recovery boiler physical and chemical processes*; The American Paper Institute, Inc.: New York, 1988.
- (8) *PC Measurement News*; ComputerBoards, Inc.: Middleboro, MA, Spring 1998; Vol. 1, No. 1.
- (9) Clay, D. T.; Karnofski, M. A. Black liquor solid formation during oil-flash evaporation. *Tappi* **1981**, *64* (12), 4.
- (10) Clay, D. T.; Grace, T. M. Measurements of high-solids black liquor boiling point rise. *Tappi* **1984**, *67* (2), 92.
- (11) Gierer, J.; Norén, I. Zur Spaltung von  $\beta$ -Hydroxy-alkyl-aryläthern durch Alkali. II. Der Stereochemische Verlauf. *Acta Chem. Scand.* **1962**, *16*, 1976.
- (12) Lundquist, K.; Li, S.; Stomberg, R. Stereochemistry of lignin structures of the arylglycerol  $\beta$ -aryl ether type. *Nord. Pulp. Pap. Res. J.* **1996**, *11* (1), 45.
- (13) Argyropoulos, D. S.; Menachem, S. B. In *Advances in Biochemical Engineering Biotechnology*; Scheper, T., Ed.; Springer-Verlag: Berlin, 1997.
- (14) Froass, P. M.; Ragauskas, A. J.; Jiang, J.-E. NMR Studies Part 3: Analysis of Lignins from Modern Kraft Pulping Technologies. *Holzforschung* **1998**, *52* (4), 385.

Received for review July 18, 2000

Revised manuscript received January 2, 2001

Accepted March 19, 2001

IE000675A