

Borate Autocausticization of Black Liquor: A Potential Carbon Dioxide Mitigation Practice for the Pulping Industry

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[Summary]

The forest products industry based on renewable wood resources is intrinsically more environmentally benign and emits less amount of greenhouse gas than most other industries. There are still areas where further improvements can be made. One fossil fuel-intensive unit operation in pulping is the lime kiln, which provides slaked lime to recausticize the cooking liquor. In this study, we used liquors and wood chips from a local pulp mill to examine the feasibility of autocausticization by adding borate to the liquor cycle in the lab. Despite numerous difficulties encountered in trying to simulate the chemical recovery process in the pulp mill, autocausticization was achieved with calcined black liquor having 2 wt% borax to liquor solids which reached > 50% causticity and notably reduced sodium carbonate concentrations. Reductive transformation of sodium sulfate to sodium sulfide was not achieved in the simulation, however. Based on the results, substantial carbon dioxide emission reduction was deemed practical. Furthermore, the borate helped increase pulp yields slightly and improved pulp properties.

Key words: kraft pulping recovery cycle, causticization, greenhouse gas emissions, black liquor, lime kiln.

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研究報告

黑液硼酸鹽自動苛化—製漿工業二氧化碳 排放減量的潛在機會

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摘 要

基於再生木材資源之林產工業本質即屬對環境友善且比大多數其他工業排放較少溫室氣體。惟製程尚待進一步改善，其中化石燃料密集的單元操作為提供消石灰供蒸煮液再苛化之用的石灰窯。本研究中由本地漿廠獲取各種蒸煮液與木片並檢視於實驗室添加硼酸鹽至蒸煮液循環產生自動苛化反應之可行性。儘管於模擬漿廠化學回收循環中遭遇多項困難，但對蒸煮液固形分添加2%硼酸鹽之黑液於煅燒後達到高於50%之苛化度，且顯著減少綠液中之碳酸鈉濃度。惟實驗室條件下無法模擬硫酸鈉還原為硫化鈉的反應。基於試驗結果，大幅減少製程二氧化碳排放係具實用性，同時，添加硼酸鹽有助於增加紙張得率並稍微改善紙漿性質。

關鍵詞：硫酸鹽法製漿回收循環、苛化、溫室氣體排放、黑液、石灰窯。

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INTRODUCTION

Greenhouse gas emissions from anthropogenic activities are warming the earth and pose great threats to the continuing prosperity or even existence of civilization in the long run. In order to cope with the crisis, countries of the world have largely agreed upon the actions advocated by the Kyoto Protocol which took effect in February 2005. Among measures to mitigate greenhouse gas emissions, clean development mechanisms (CDMs) are pertinent to industrial processes, including the forest products sector. Based on carbon-neutral renewable resources, this sector is already much less harmful than metal smelting, cement, glass, and plastic industries. The predominant pulping method worldwide is the kraft process, which produces strong, bleachable pulps and has the advantage of pulping chemical recyclability. Recovery

boilers of kraft pulp mills are mostly powered by burning dissolved organic substances in the residual cooking liquor; thus are essentially free from the need for use of fossil fuels. The Achilles' heel of the industry is the need of a lime kiln to drive a cycle of limestone to slaked lime and back which requires external fuels. Modification of the practice would present a golden opportunity to reduce carbon dioxide (CO₂) emissions by the industry (Anon 2005).

Before discussing black liquor autocausticization, a brief description of the cooking liquor cycle in kraft pulping is warranted. In a typical kraft process, "white liquor" containing mostly sodium hydroxide (NaOH) and sodium sulfide (Na₂S) is fed to a digester to impregnate wood chips and then heated to ca. 170°C for bulk delignification to proceed.

Upon completion of digestion, the pulp is discharged with the entrained "black liquor," liquor containing dissolved wood organic substances, mostly lignin and carbohydrates, and residual chemicals, including weakened NaOH, sodium sulfate (Na_2SO_4) and sodium carbonate (Na_2CO_3). Upon separation of the pulp and black liquor, the latter is thickened by multi-effect evaporation to a high solids content of ca. 70%. The thick black liquor is sprayed into a boiler, called a recovery furnace (usually of the Tomlinson type) to be burned. The heat value of the dissolved organics is recovered and provides the necessary energy to drive most of the pulping cycle. The inorganic remains of the black liquor undergo a reductive reaction in the high-temperature (950°C) smelt bed of the boiler, where sodium sulfate is converted back to sodium sulfide. The smelt is subsequently dissolved in water to form a "green liquor", a greenish liquid mostly containing Na_2CO_3 and Na_2S . Sodium carbonate is not strong enough to cause delignification; hence it needs to be "causticized". Causticization of the green liquor requires using slaked calcium oxide (calcium hydroxide, $\text{Ca}(\text{OH})_2$), which reacts with Na_2CO_3 to form NaOH and calcium carbonate (CaCO_3), regenerating white liquor to complete the cycle. The latter, or limestone, is returned to a lime kiln and calcined again using external fossil fuel to regenerate calcium oxide and drive off CO_2 . The most carbon-intensive process in a typical pulp mill is judged by some to be the lime kiln, which generates CO_2 from both the fuel and limestone. It is, therefore, a high-priority process needing revamping to cut down on CO_2 emissions (Zao and Avedesian 1990, Thorp and Raymond 2004, Dahlquist and John 2005).

Various methods have been proposed to reduce or eliminate the need for lime kilns in pulp processes. Among these, 2 methods

have dominated and received the most attention. One involves adding sodium borate to black liquor; and the change in boron valence during the cycle causes auto-causticization to some extent. The other is adding titanate salt. There are numerous research papers examining the influence of borate auto-causticization on the pulping process within the last few years. These reports variously focused investigations on the effects of borate addition on causticization, pulp yields, fiber quality, and kinetics (Prihoda et al. 1996, Tran et al. 1999, 2001, 2003, Hunter et al. 2001, Genco et al. 2002, Hoddenbagh et al. 2002, Hupa et al. 2002, Kochesfahani and Bair 2002, Bujanovic et al. 2004, Cameron et al. 2004, Forssén et al. 2004a, b, Gershon 2004, Lien et al. 2004, Lindberg et al. 2004, Mao et al. 2004, Sinquefield et al. 2004, Wintoko and Richards 2004). Eckert et al. (2005) arrived at a positive evaluation of the practicality and functionality of the process, and concluded that the method will be applied to several pulp mills within years. The effects of titanate on auto-causticization were mostly studied by Nohlgren's group; they and others explored aspects of titanate addition on causticization, pulp yields, fiber quality, and kinetics (Nohlgren et al. 1998, 2003a, b, 2004a, b, Zhung et al. 1998, Zeng and Heiningen 2002, Wintoko and Richards 2004, Chen et al. 2005).

In this study, we examined the feasibility of borate auto-causticization in the lab. Since most of the experimental materials, from wood chips to the various cooking liquors, were directly obtained from a certain operating pulp mill in southern Taiwan, the study fulfills the "local context" scenario, and the experimental results may constitute viable reference information for mills to consider taking up the practice and thus help abate greenhouse gas emission problems in this country.

MATERIALS AND METHODS

Materials

In order to produce accurate and comparable results, we collected black liquor, white liquor, and green liquor samples, together with wood chips (mostly eucalypts) from a pulp mill in southern Taiwan. The liquor containers were filled with nitrogen and kept under refrigeration (4°C) to prevent modification of their chemical compositions. Industrial grade sodium tetraborate decahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), or borax, and quicklime (CaO) were obtained from Xuangjian Co., Taipei, Taiwan.

In order to simulate the recovery cycle of black liquor, containers such as crucibles (ca. 50 mL) made of various materials were purchased. Porcelain and nickel crucibles failed under the highly caustic and extreme heating conditions used. Eventually crucibles made of aluminum oxide were found to perform satisfactorily under the severe conditions required.

A conventional oven was generally satisfactory for drying the green and white liquors. Black liquor, highly viscous with dissolved organic substances, however, tended to splatter when being directly dried at a higher temperature (105°C). Reduced-pressure drying at a more-moderate temperature was necessary to achieve a constant mass. For calcining of the liquors, a Nabertherm C-6 muffle furnace (Lilienthal, Germany) capable of reaching 1100°C was used. In order to achieve a reductive condition in the smelt which facilitates the reduction of Na_2SO_4 to Na_2S , a glass tube oven (Kuozhou, Taipei, Taiwan) capable of operation at 1000°C with an external gas feed capability was used.

Methods

Characterization of cooking liquors

The active alkali and its components were determined in accordance with a mill lab method. In the procedure, 5 mL liquor specimen was diluted, excess barium chloride was added to precipitate sodium sulfate, then the liquor was titrated with 0.5 N HCl to a phenol phthalate end point (aliquot A). Then 5 mL of a 37% formaldehyde solution was added and the pink color reappeared. This was further titrated with the HCl solution until the pink color again disappeared (aliquot B), and it was titrated to the methyl orange end point (aliquot C). From the 3 titers, the concentrations of sodium hydroxide, sodium sulfide, and sodium carbonate were estimated, and the total alkali and active alkali values determined according to the following relationships:

A is equivalent to the charge of $\text{NaOH} + 1/2 \text{Na}_2\text{S}$;

B is equivalent to the charge of $\text{NaOH} + \text{Na}_2\text{S}$;

$2(B - A)$ is equivalent to the charge of Na_2S ; and

C is equivalent to the charge of total alkali, or $\text{NaOH} + \text{Na}_2\text{S} + \text{Na}_2\text{CO}_3$.

After the addition of borate, the total alkali titration results were found to be influenced by the presence of boron. A calibration curve was constructed and the alkali components adjusted accordingly.

Black liquor, because of its viscous opaque nature, was not amenable to the above procedures. In order to characterize its salt content, it was first dried and ashed to remove all organic substances leaving only salts. Then the salts were dissolved in deionized water. Through a trial and error process, we found that for every 50 mL of black liquor, adding 20 mL of water appeared to give a consistent total salt content with the green and white liquors. In a subsequent analysis, all black liquor characterizations were based on this make-up ratio.

Pulping conditions

In order to compare the effects of the borated cooking liquor on the pulp yield and pulp strength properties, a standard set of pulping conditions was adopted. Cooking was carried out using an electrically heated 20-L rotating digester fitted with 4×2-L digester canisters (Erst Haage, D-45476, Mülheim, Germany). A standard cooking routine entailed the following: 200 g of wood chips (o.d. weight); 18% active alkali charge; 25% sulfidity; a 4:1 liquor to wood ratio; a maximum cooking temperature of 170°C; a maximum pressure of 8 kgf cm⁻²; time to temperature of 90 min; time at temperature of 90 min; and the H-factor of the cooking of 1576.

Following digestion, the wood pulp was removed and washed over a 200 mesh screen to obtain the pulp and shives yields.

Handsheets preparation and evaluation

Handsheets from the wood pulp were prepared in accordance with TAPPI Standard T205m-58 using a standard circular sheet mold of 200-cm² area. The handsheets thus prepared were conditioned overnight in an atmosphere of 20°C and 65% relative humidity (RH). Then test specimens were cut and measured according to TAPPI T220 om-83 for tensile, tear, bursting, and folding endurance of the pulp.

Borate addition to black liquor and calcination

Initially, sodium borate at a modest dosages (1400 mg L⁻¹) was added to the black liquor, and the black liquor was dried, ashed, and calcined at 700~850°C for 1~5 h. The steps were thought to generate a smelt resembling the one at the mill.

As mentioned above, however, certain difficulties were encountered in drying the black liquor, which thickened to very high

viscosity and splattered with the evolving vapor. Subsequently, the crucible materials became a problem as the high temperature and high alkalinity rendered the system overly corrosive to porcelain and nickel crucibles. Although a platinum crucible could withstand the rigor, they were too expensive. Finally, aluminum oxide crucibles were found to perform well under the conditions employed.

Intermediate results suggested that no appreciable sulfate reduction took place during calcination. We tried using reducing gases such as carbon monoxide to convert the salt in the smelt. The gas was fed to a glass oven containing a black liquor specimen heated to 800°C. Despite many attempts, no significant sulfide formation was observed.

The black liquor splatter problem was resolved using a reduced temperature vacuum oven (20 mmHg, 50°C over diphosphorus pentoxide as an auxiliary desiccant) to dry the liquor, and we then conducted a separate ashing step at 525°C in a muffle furnace to remove all organic carbon.

Upon checking with the mill manager, we opted to use a calcination temperature at 950°C for 1 h to match the on-site conditions. A much better autocausticization efficacy was observed. Yet, sulfate reduction to sulfide was only marginally improved, and full reduction was still beyond the ability of our laboratory setup.

Borate addition to green liquor and reverse calcination

As the initial borate addition to the black liquor did not provide the expected results, we tried to reverse the process and added sodium borate to the green liquor. The liquor was dried and calcined to 800°C for 1~3 h. Then the smelt was dissolved with distilled water and the alkali of the reconstituted green liquor was titrated to provide information on

the change in the degree of causticization.

We noted in the cooking liquor titration that when borax was added to the green liquor, the titrated total alkali values changed. The same was occurring with the white liquor titration. Thus, we established calibration curves for the titration values based on the quantities of borate added. All titration values were then corrected for this effect.

Cooking cycles with borate added to the reconstituted white liquor

Essentially no appreciable amount of sulfate reduction to sulfide was achieved in our lab setup. In order to examine the effect of using the borate-containing white liquor on cooking the wood chips, we use either direct doping of the white liquor or recausticized green liquor from our black liquor calcination with sodium sulfide added.

Both liquors were separately used to cook wood chips in the standard mode. The resulting pulp yields and pulp properties were evaluated according the conditions described above.

RESULTS AND DISCUSSION

Characterization of the cooking liquors

The mill white, green, and black liquors were titrated for their active and total alkali charges as well as their causticity. The results are shown in Table 1. Periodic rechecking was carried out and the liquors remained stable under the storage conditions.

The results indicated that the black liquor had a much depleted Na_2S content,

whereas its Na_2CO_3 content was the highest. The green liquor, meanwhile, had the highest sulfidity and least amount of NaOH. The white liquor, despite its high causticity, had a relatively lower total alkali content compared to the other liquors.

Initial trials of black liquor autoausticization by borax addition

In a series of initial trials, borax at 1000 mg L^{-1} (w/v black liquor) was added, and the quasi-dried liquor was calcined at 700~800°C to observe whether there was any increase in the NaOH content of the resulting smelt. The results are shown in Table 2.

The calcination temperature of 700°C was obviously insufficient, as indicated by the presence of black specks in the ash. Inadequacy of black liquor oven-drying caused the splattering problem and uneven ashing. As the reaction temperature was too low, reductive conditions for sulfide formation were not present and the green liquor formed by dissolving the smelt contained a minimal amount of sulfide. At the borax dosage used, there was no significant difference between the treatment and control group with regard to the NaOH content for treatment at 800°C.

In a bid to counter the loss of sulfide in the green liquor, a reducing gas of carbon monoxide (CO) was fed to a calcination tube containing black liquor solids with borax. Different borax dosages were also used (1400, 2800, 4200, and 5600 mg L^{-1} of liquor). Calcination time at 800°C of 1, 2 and 3 h were carried out. The results are shown in Table 3.

Table 3 shows that CO was unable to

Table 1. Mill cooking liquor characteristics

Item	Na_2S (g L^{-1})	NaOH (g L^{-1})	Na_2CO_3 (g L^{-1})	Total alkali	Causticity (%)
Mill green liquor	26.9	20.2	79.2	126.3	20.4
Mill white liquor	25.0	77.4	12.6	115.0	86.0
Mill black liquor	3.2	30.6	87.4	121.2	25.9

Table 2. Results of the initial black liquor autocausticization trial with 1000 mg L⁻¹ (w/v) borax addition at different calcination temperatures and times

Calcination conditions			Na ₂ S (g L ⁻¹)	NaOH (g L ⁻¹)	Na ₂ CO ₃ (g L ⁻¹)	Total alkali	Causticity (%)
Borax dosage (mg L ⁻¹)	Temp (°C)	Time (h)					
0*	700	3	--	--	--	--	--
0	800	2	1.5	30.5	92.5	124.4	24.8
0	800	5	1.7	32.9	101.8	136.4	24.4
0	850	2	1.6	32.1	100.4	134.1	24.2
1000*	700	3	--	--	--	--	--
1000	800	2	2.2	31.9	88.0	122.1	26.6
1000	800	5	2.7	34.2	96.7	133.6	26.1
1000	850	2	2.2	33.7	96.1	132.0	26.0

* Incomplete ashing.

Table 3. Autocausticization trials of adding different dosages of borax to black liquor and using carbon monoxide as a reducing gas to enhance sulfate reduction to sulfide

Calcination conditions			Na ₂ S (g L ⁻¹)	NaOH (g L ⁻¹)	Na ₂ CO ₃ (g L ⁻¹)	Total alkali	Causticity (%)
Borax dosage (mg L ⁻¹)	Temp (°C)	Time (h)					
1400	800	1	3.4	11.5	85.9	100.8	11.8
1400	800	2	4.5	10.2	87.2	102.1	10.5
2800	800	1	4.8	12.9	88.2	105.9	12.8
2800	800	2	3.6	10.7	89.5	103.7	10.6
4200	800	1	5.8	12.6	83.8	102.2	13.1
4200	800	2	4.0	11.8	91.2	107.0	11.4
5600	800	1	3.9	12.4	94.3	110.6	11.6
5600	800	2	4.9	13.0	95.4	113.3	12.0

reduce the sulfate to sulfide. Instead, it contributed to a near doubling of the sodium carbonate. In spite of the increased difficulty of conducting the reactions in a muffled furnace (for ashing) and then in a reducing furnace (calcination), the results were disappointing.

Autocausticization of the green liquor

Effects of the presence of borax in the green liquor on its causticization efficiency were examined by adding 1400, 2800, 4200, and 5600 mg L⁻¹ of borax, and then various amounts of slaked lime was added at 100°C. The results are shown in Table 4.

Under suitable conditions, the mill green liquor was capable of turning into a white liquor similar in characteristics to that at the mill. The presence of borax had no apparent causticization function under the lime causticization conditions, as the reaction requires high-temperature calcination of the smelt. An excess amount of lime caused the Na₂CO₃ to be adsorbed onto the lime mud, and this was harmful to the efficiency of the operation.

The possible presence of residual organic or interfering substances in the black liquor salts may have led to the poor results for our initial black liquor autocausticization trials.

Table 4. Mill green liquor containing various amounts of borax causticized at 100°C with Ca (OH)₂ and subsequently analyzed for chemical compositions

Borax dosage (mg L ⁻¹)	CaO (g)	Na ₂ S (g L ⁻¹)	NaOH (g L ⁻¹)	Na ₂ CO ₃ (g L ⁻¹)	Total alkali	Causticity (%)
0	0	26.9	20.2	79.2	126.3	20.4
0	5	26.1	64.9	28.2	119.1	69.7
	10	23.7	77.1	13.2	113.9	85.4
	15	18.4	66.4	14.5	99.3	82.1
	1400	5	26.7	66.4	29.9	123.0
2800	10	27.3	74.7	18.1	120.0	80.5
	15	21.9	67.3	15.4	104.6	81.4
	5	24.9	68.2	30.8	123.9	68.9
4200	10	24.9	70.2	16.6	111.7	80.9
	15	20.8	63.1	14.8	98.7	81.0
	5	25.8	66.1	32.3	124.2	67.2
5600	10	19.3	82.2	17.0	118.5	82.8
	15	17.2	71.7	16.3	105.2	81.5
	5	27.3	68.8	32.9	128.9	67.6
	10	27.3	78.2	19.3	124.8	80.2
	15	22.5	67.6	16.0	106.1	80.9

Hence, we retro-calcined the dried green liquor with borax addition to examine whether autoausticization took place. At a borax dosage of 5600 mg L⁻¹ of the original green liquor, the dried liquor solids were calcined at 500, 650, and 800°C for 1, 2, and 3 h. The results are shown in Table 5.

Under an adequate calcination temperature and duration (3 h), autoausticization apparently took place, with reduced carbonate and increased hydroxide concentrations. The same problem beset our green liquor trials, i.e., loss of sulfide also occurred in these cases, suggesting that retro-calcination of the

Table 5. Retro-autoausticization of the green liquor (Gr. liq.) at different temperatures and times with 5600 mg L⁻¹ (w/v green liquor) borax

Calcination conditions		Na ₂ S (g L ⁻¹)	NaOH (g L ⁻¹)	Na ₂ CO ₃ (g L ⁻¹)	Total Alkali	Causticity (%)
Mill white liquor		25.0	77.4	12.6	115.0	86.0
Mill green liquor		26.9	20.2	79.2	126.3	20.4
Gr. liq. + borax	500°C 1 h	10.3	17.4	95.6	123.3	15.4
	500°C 2 h	9.7	22.3	92.8	124.8	19.4
	500°C 3 h	9.1	25.1	86.1	120.3	22.6
	650°C 1 h	11.5	19.2	97.9	128.6	16.4
	650°C 2 h	8.3	27.3	92.3	127.9	22.8
	650°C 3 h	9.3	36.8	76.6	122.7	32.5
	800°C 1 h	11.9	18.7	99.1	129.7	15.9
	800°C 2 h	10.2	53.2	57.4	120.8	48.1
	800°C 3 h	8.3	64.2	55.5	128.0	53.6

green liquor resulted in oxidative conditions at the temperature tested and the sulfide in the liquor reverted back to sulfate as a result.

The effects of borax on liquor titration were examined. Calibration curves for the titrated concentrations of NaOH, Na₂CO₃, and Na₂S with increasing borax charges are shown in Figs. 1 and 2. Sodium hydroxide and Na₂S were least affected, while both carbonate and total alkali concentrations apparently increased with an increasing borax charge. The curves were used for correcting all liquor titration results.

Effect of adding borax on pulping and pulp properties

In order to understand the effects of borax on wood pulp digestion, different amounts of borax were added to the mill white liquor, and mill wood chip pulping was carried out using these liquors. All cooking conditions were the same as those described above. The results of the digestions are shown in Fig. 3. The pulps thus obtained were made into handsheets, and their properties evaluated as shown in Table 6.

Adding borax, especially at higher charges, tended to improve pulp yields. The

difference could be as high as 3%. The presence of borate also caused a reduction in the kappa number of the pulps, meaning less residual lignin existed in the resulting pulps.

As for the handsheet properties of the pulp, there were also noticeable improvements in tensile and bursting strengths.

In order to establish whether the beneficial effects exerted by the presence of borate were proportional to the amount of its dosage, we increased the dosage and did a further series of pulping trials using the same conditions. The results are shown in Fig. 4, and the

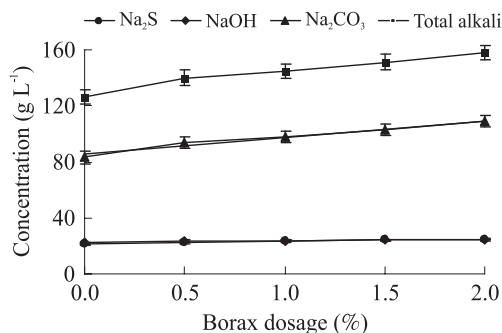


Fig. 2. Calibration curves for sodium sulfide, sodium hydroxide, sodium carbonate, and total alkali in green liquor with different dosages of borax.

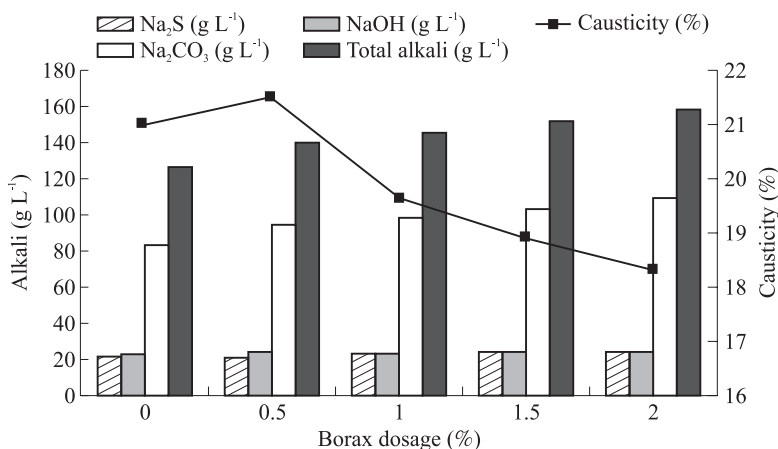


Fig. 1. Effects of adding various amounts of borax to green liquor (w/v) on the titration results of the total alkali component concentrations.

corresponding handsheet properties are shown in Table 7. The same was done using the lab-made white liquor. The results of pulping and

handsheet properties are shown in Fig. 5 and Table 8, respectively.

Overall, adding borate contributed to

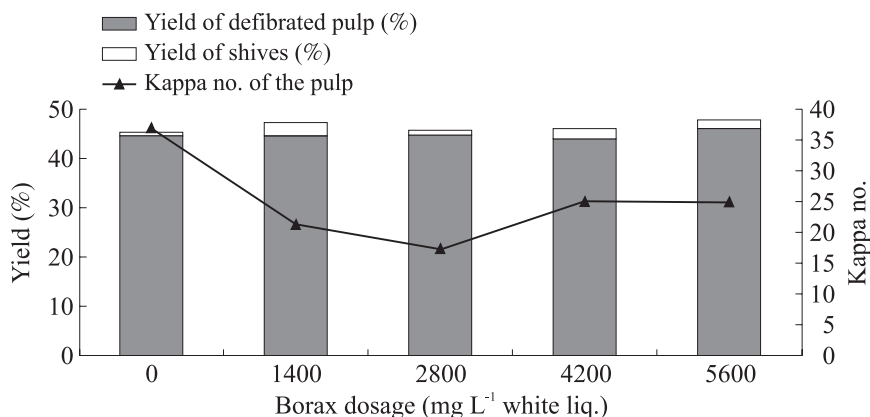


Fig. 3. Effects of adding various amounts of borax on the pulping results of 200 g of mill wood chips at a H-factor of 1576 using the lab-prepared white liquor.

Table 6. Handsheet properties made from the pulp obtained from the borax-containing lab-prepared white liquor (Fig. 2)

Borax dosage (mg L ⁻¹)	Tensile index (N·m ⁻² g ⁻¹)	Breaking length (km)	Tear index (mN·m ⁻² g ⁻¹)	Bursting index (kPa·m ⁻² g ⁻¹)	Folding endurance (dbl. fold)	Surface strength (A)	Air permeance (s 100 mL ⁻¹)	Smoothness (s)
0	21.2	2.16	4.55	0.89	2	2	0.5	3.3
1400	25.4	2.59	4.53	1.04	2	< 2	0.6	4
2800	27.3	2.78	4.94	1.23	3	2	0.7	5
4200	26.2	2.67	4.95	1.00	2	2	0.7	5
5600	24.4	2.49	4.52	1.08	2	2	0.7	5

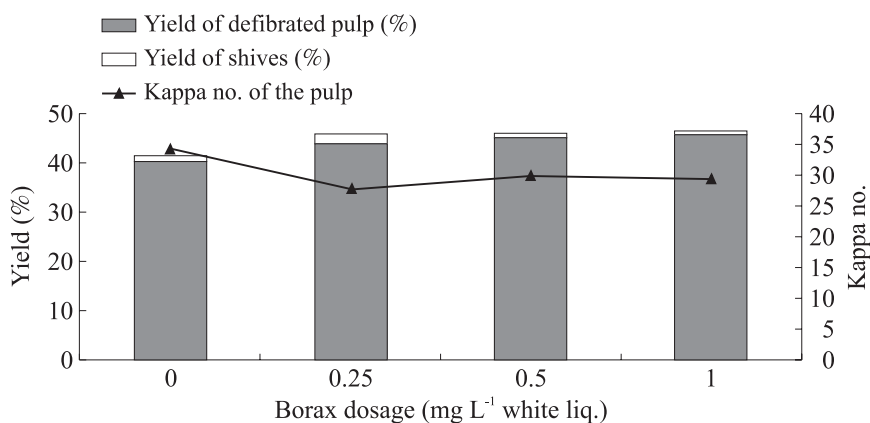
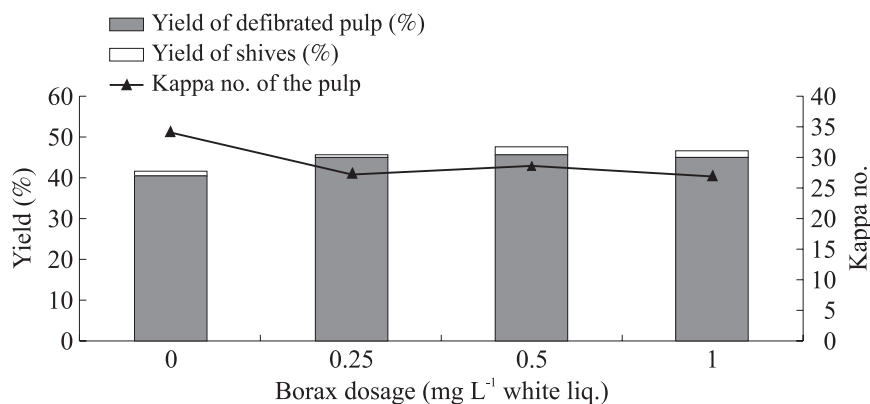


Fig. 4. Effects of adding borax to the mill white liquor (w/v) on the pulping of mill wood chips (pulping conditions stipulated in “Methods”).

Table 7. Effects of adding various amounts of borax to mill white liquor on the resulting pulp properties ($n = 10$, t -test results; probabilities shown in parentheses)

Borax dosage (%)	Tensile index ($N \cdot m^2 g^{-1}$)	Breaking length (km)	Tear index ($mN \cdot m^2 g^{-1}$)	Bursting index ($kPa \cdot m^2 g^{-1}$)	Folding endurance (dbl. fold)	Surface strength (A)	Air permeance ($s 100 mL^{-1}$)	Smoothness (s)
0	21.2	2.2	4.55	0.89	2	2	0.5	3.3
0.25	25.3	2.58	4.21	1.01	2	2	0.6	4
	(1.2E-04)		(0.14)	(7.1E-04)				
0.5	26.5	2.70	4.49	1.06	2	3	0.7	5
	(2.0E-07)		(0.80)	(8.3E-04)				
1	30.	3.15	5.74	1.40	3	4	1.1	8
	(6.6E-11)		(0.003)	(3.4E-10)				

**Fig. 5. Effects of adding various amounts of borax to the lab-prepared white liquor (w/v) on the pulping of 200 g (oven-dried) mill wood chips.****Table 8. Effects of adding various amounts of borax to the lab-prepared white liquor (w/v) on the resulting pulp properties ($n = 10$, t -test results; probabilities shown in parentheses)**

Borax charge (%)	Tensile index ($N \cdot m^2 g^{-1}$)	Breaking length (km)	Tear index ($mN \cdot m^2 g^{-1}$)	Bursting index ($kPa \cdot m^2 g^{-1}$)	Folding endurance (dbl. fold)	Surface strength (A)	Air permeance ($s 100 mL^{-1}$)	Smoothness (s)
0	21.2	2.2	4.55	0.89	2	2	0.5	3.3
0.25	29.7	3.0	4.97	1.17	3	5	0.8	5
	(4.5E-09)		(0.06)	(7.1E-05)				
0.5	28.8	2.9	4.99	1.15	2	4	0.7	5
	(3.7E-08)		(0.13)	(1.4E-08)				
1	28.3	2.9	4.99	1.18	3	4	0.8	6
	(9.7E-09)		(0.05)	(4.7E-08)				

higher pulp yields and caused the pulps to have a lower residual lignin content (kappa number). Beneficial effects were notable. The same was true for handsheets made from

those pulps which had slightly improved properties. Thus, adding borate to kraft cooking liquor appears to contribute positively to both pulp yields and paper strength.

Black liquor autoausticization

After the initial failed black liquor autoausticization experiments, we carefully reviewed the process steps and decided that proper black liquor drying was critical. The black liquor was dried in a reduced pressure oven over 6 d. Results of water removal are shown in Fig. 6.

The results indicated that the black liquor with its highly viscous and crust-forming tendency was rather recalcitrant to proper drying. Once dried, however, there were few subsequent problems in the 2-stage ashing and calcining processes. An autoausticization effect was finally taking place. Fig. 7 shows the results of borate autoausticization at the lower-temperature (800°C) conditions. The results indicated that when 2 wt% of borax to dried black liquor solids was added, calcination at 800°C for 2~4 h achieved autoausticization with a reduced Na₂CO₃ content and increased NaOH content. The 4-h results

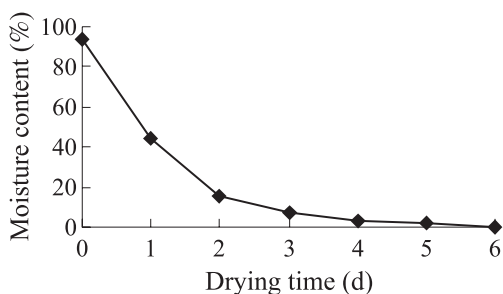


Fig. 6. Black liquor drying results in a reduced-pressure oven over diphosphorus pentoxide.

showed a greater loss of Na₂S and an inferior causticization rate; hence, the 3 h maximum should be adopted.

Table 9 shows the effects of repeated autoausticization tests ($n = 3$) at 800°C and 3 h. Sulfide losses were notable, but the causticity consistently reached a 50% level.

Table 10 shows the effects of dried mill black liquor calcined at 950°C for 1 h with 2 wt% borax to liquor solids ($n = 4$) on the causticity and s Na₂S loss. Enhanced causticity, a reduced Na₂CO₃ content, and a lesser loss of Na₂S were achieved. The causticity of the resulting products showed a reasonable stability among the replications, indicating the feasibility of the methodology. Despite improving the pulp washing efficiency (Table 9), certain amounts of chemical losses were unavoidable. Nevertheless, a stable autoaus-

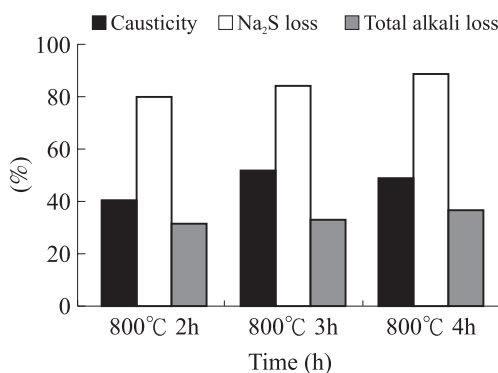


Fig. 7. Effect of dried black liquor on borate autoausticization at 800°C and 2~4 h calcination conditions.

Table 9. Effect of borax of dried mill black liquor at 800°C and 3 h on the causticity and sodium sulfide loss

Calcination conditions	Na ₂ S (g L ⁻¹)	Total alkali	Na ₂ S loss (%)	Total alkali loss (%)	Causticity (%)
Mill green liquor	26.9	126.3	--	--	20.4
Mill white liquor	25	114.99	--	--	86.0
Black liquor + 2% borax and calcined at 800°C for 3 h	3.67 ± 0.78	102.16 ± 1.04	86.36 ± 2.91	19.12 ± 0.82	50.57 ± 0.67

Table 10. Effects of the lab-generated black liquor (Bl. liq.) from pulping experiments after flash-drying and calcining at 600°C for 3 h and 950°C for 1 h on liquor causticity

Calcination conditions	Na ₂ S (g L ⁻¹)	NaOH (g L ⁻¹)	Na ₂ CO ₃ (g L ⁻¹)	Na ₂ SO ₄ (g L ⁻¹)	Na ₂ S loss (%)	Total alkali	Total salts	Causticity (%)
Mill green liquor	26.9	20.24	79.16	175.6	--	126.3	301.9	20.4
Mill white liquor	25	77.38	12.62	22.8	--	114.99	137.8	86.0
Bl. liq. 600°C 3 h	3.2	30.6	82.2	182	88.1	116.0	298	27.1
Bl. liq. 950°C 1 h	5.3	31.3	82.8	216.1	80.3	119.4	335.5	27.4
Bl. liq. + 2% borax 600°C 3 h	4.7	30.2	73.9	188.3	82.5	108.8	297.1	29.0
Bl. liq. + 2% borax 950°C 1 h	8.19	61.24	61.30	224.9	69.55	130.73	355.62	49.95
	±0.75	±2.48	±2.29	±3.8	±2.77	±3.18	±5.76	±1.14

ticization efficiency at ca. 50% causticity was consistently achieved. The table also shows that calcination at a lower temperature had practically no effect even with the same borax charge. Calcining black liquor salts at 950°C for 1 h with conditions akin to the smelt trough of the mill recovery boiler apparently gave results comparable to those of the borax-added black liquor salt calcined at 800°C for 3 h (Fig. 7).

The loss of the Na₂S charge, however, suggested that our lab calcination conditions were unable to adequately reduce sodium sulfate in the smelt to sulfide, which is routinely achieved in the mill recovery boiler, and should pose no problem with or without borax addition. In other words, borate autocausticization can be a practical, viable process as indicated by several studies (Kilponen et al. 2001, Möllersten et al. 2003).

CONCLUSIONS

We carried out a series of experiments examining the effects of adding borax to kraft black liquor on the subsequent causticization performance. Retro-introduction of borax to the green liquor first proved the transformation of carbonate to hydroxide, and the subsequent improvement in black liquor drying and a more-optimal calcination temperature

range led to successful causticization at about 50% efficiency. The white liquor generated from the reclaimed black liquor containing borax and the mill white liquor with borax added both suggested that the chemical might improve pulp yields and enhance pulp strength to some extent. Thus, the practice might curtail the need for full-scale lime-kiln operations and lead to mitigation of CO₂ emissions from external fuel used for producing calcium oxide from limestone. Based on the 50% causticization efficiency achieved in our study, the lime-kiln output could be reduced to ca. 40%, suggesting a greenhouse gas emission abatement of 60% from the operation, which translates to a 0.16-ton carbon dioxide reduction per ton of pulp production. Based on a 400,000 metric ton total pulp production of Taiwan's 2 pulp mills, an annual carbon dioxide emission reduction of 64,000 tons could be achieved, turning the pulping industry greener.

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