

The influence of boron on the emission of sodium during black liquor combustion under oxidative conditions

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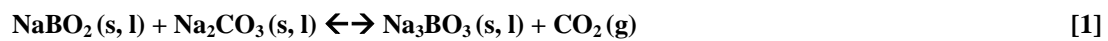
SUMMARY

The addition of boron to black liquor has the potential to reduce fume formation in a Kraft recovery boiler. Two Kraft black liquors, with and without boron, were analysed. Single 10 mg droplets were introduced into a furnace and were burned at temperatures of 900, 1000 and 1050°C with oxygen concentrations of 2, 5 and 10 (vol %). Under these conditions, the addition of boron to the black liquor is found to reduce both the extent of sodium emission and the combustion time. This shows that the boron reduced the sodium loss due to the lower amount of sodium carbonate available to be decomposed by the char. The char combustion time of the liquor with boron is found to be shorter because some of the char may be consumed by the borate. The added boron reduced the sodium loss mainly during the char combustion stage.

Keywords: Kraft pulping, chemical recovery, black liquor, sodium, boron.

INTRODUCTION

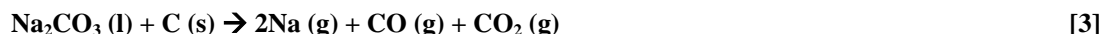
Many studies have been conducted on the effects of the addition of boron into the Kraft recovery cycle. In partial autocausticizing (ac) processes, boron added in small amounts is capable of debottlenecking the recausticizing plant by a reduction in lime usage (1, 2). This result promises cheaper alternatives than upgrading the existing plant, and even the potential elimination of the energy intensive lime making process. However, more information is needed on the role of boron to justify such actions. The reactions of boron take place in the recovery boiler, primarily in the smelt phase when sodium metaborate (NaBO_2) reacts with a part of the molten Na_2CO_3 to form trisodium borate (Na_3BO_3) and carbon dioxide (CO_2) as shown in Equation 1. The Na_3BO_3 then forms sodium hydroxide (NaOH), thereby regenerating the NaBO_2 as shown in Equation 2, when the smelt is dissolved into the green liquor (3). The residual Na_2CO_3 reacts with calcium oxide (CaO) in the causticizing process to form NaOH .



The addition of boron into the system however also influences the swelling characteristics of the black liquor and the melting temperature of the smelt. In one recent study, the characteristic swelling during the combustion of black liquor was shown to increase slightly at low boron additions (~10% ac), and to reduce at higher additions. The swelling influences the burning time, being slightly shorter at low additions and longer at high additions of boron when compared with black liquors without boron (4). The Na_3BO_3 is readily soluble in the smelt consisting of Na_2CO_3 , sodium sulphide (Na_2S) and sodium chloride (NaCl) and changes the overall melting properties of the salt mixtures (4).

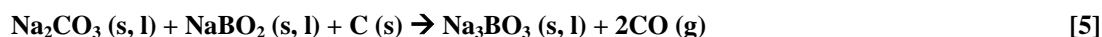
The release of sodium from the combustion of black liquor is one of the most important steps in fume formation in a recovery boiler. The sodium vapours released from a black liquor droplet react with combustion products, CO_2 and sulphur dioxide (SO_2), to form a fume, which mainly consists of Na_2CO_3 and sodium sulphate (Na_2SO_4) (5). This fume may subsequently, perhaps after being converted to other compounds (pyro or bisulphate), be deposited on the heat exchanger tubes or other surfaces of the flue gas duct, thus reducing the overall efficiency of a boiler. The combustion of a single droplet of black liquor is a process that can be divided into the four stages of drying, devolatilisation, char combustion and smelt oxidation (6). Frederick and Hupa (7) have suggested that a significant proportion of the sodium released from black liquor occurs during the devolatilisation stage. The sodium release mechanism could be due to the physical ejection of droplet fragments with the volatile gaseous from the black liquor (5) that would result in the generation of fine droplets. Li and van Heiningen (8) have suggested that sodium released during the char combustion stage under reducing conditions as shown in Equation 3, is the dominant cause of fume formation.

Cameron (9), however, has suggested that the release of sodium from the smelt under oxidation conditions (13% O₂), as shown in Equation 4 is greater than under reducing conditions.



Droplet burning in a recovery furnace takes place in both oxidising and reducing environments. For the devolatilisation stage the external gas environment does not significantly influence the behaviour of the droplet, as the droplet creates a gas environment of its own. Char burning is naturally strongly dependent on the oxygen concentration surrounding the particle. Tamminen *et al* (10) showed that most of the fuming occurs when the liquor droplets are in flight and in contact with oxygen, and only a small part of the fuming originates in the strongly reducing smelt bed surface. Previous studies by Cameron (9) also indicate that fuming is significantly stronger in gases containing oxygen than under reducing conditions.

During the combustion of black liquor containing boron in a recovery boiler, a fraction of the Na₂CO₃ is converted into Na₃BO₃ as shown in Equation 1. The percentage of metaborate conversion through the decarbonisation reactions between NaBO₂ and Na₂CO₃ increases as the temperature is increased (11). Tran *et al* (11) have suggested that the decarbonation of Na₂CO₃ can be enhanced by the presence of char carbon as shown in their complicated combined reaction Equation 5.



The carbonate content can be expected to affect the release of sodium from the decomposition of Na₂CO₃ shown in Equation 3. In addition a study based on thermogravimetric measurements conducted by Janson (12) has suggested that decomposition of sodium pyroborate (Na₄B₂O₅) to NaBO₂, boron trioxide (B₂O₃), sodium vapour and oxygen might occur at temperatures above 1000-1100°C. However, the volatilisation or decomposition of Na₄B₂O₅ or Na₃BO₃ is presently not well understood.

Reports from two mill trials showed that boron addition caused less fume formation and no increase of corrosion or fouling in the recovery boilers. This was evidenced by the electrostatic precipitators being found to be cleaner than when burning black liquor without boron (1, 2). While this suggests that the addition of boron may influence the release of sodium during black liquor combustion, no systematic study has been conducted on the influence of boron on sodium emission. To address these issues, the aim of this study is to investigate the influence of boron on sodium emissions during the combustion of a black liquor droplet under oxidative conditions.

EXPERIMENTAL

Two samples of black liquor, one with and one without boron, were used in this experiment as shown in Table 1. A consistent quantity of black liquor (10 mg) was applied to a platinum hook. The black liquor droplet was introduced into a furnace that was electrically heated to maintain a uniform temperature of 900, 1000 or 1050°C. These temperatures were chosen to be representative of those in a black liquor boiler based on the measurement of Borg *et al* (13) and Tavares *et al* (14). The gaseous environment within the furnace was N₂ with oxygen added at a concentration of 2, 5 or 10 vol %.

A brief description of the reactor is provided here, whereas full details of the experimental facilities are described elsewhere (15). The reactor is made of quartz glass and placed within a muffle furnace (Fig. 1). The reaction chamber itself is spherical and is 0.08 m in diameter. The incoming gases are pre-heated in the furnace prior to entering the reaction chamber. They are fed into the reactor bulb through a 0.026 m diameter quartz tube (gas inlet). An optical window is installed at the opposite end of this tube to allow the combustion process to be recorded with a video camera (VCR). This arrangement prevents any sodium vapour from condensing on the window. The sample is inserted into the reaction chamber at the end of a rod through a 0.026 m tube (sample inlet tube) directed upwards from the chamber.

Table 1: Elemental composition of the black liquors (WBL= Wet black liquor, DS= Dry solids)

	weight-% of WBL	
Dry solids	74.0	73.9
Chemical analysis	weight-% of DS	
C	30.3	30.0
H	3.5	3.4
N	0.20	0.34
S	3.74	4.07
Na	22.0	22.2
K	1.59	1.69
Cl	0.05	0.05
B	0	0.373
O (by balance)	38.6	38.2

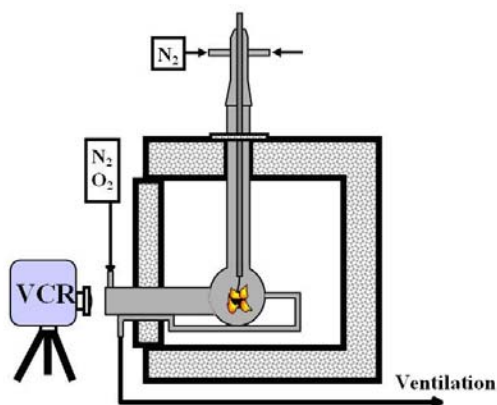


Fig. 1: A schematic diagram of the experimental apparatus.

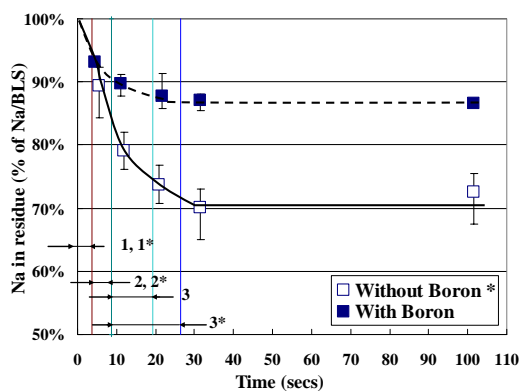
Three experimental runs were repeated for each exposure time (4, 10, 20, 30 and 100 s) and for each set of furnace conditions. A video recording was used to identify the stages of black liquor combustion and the combustion time for each stage. After the droplet was burned for a given exposure time, the hook was raised and quenched in a nitrogen purge for 10 s before it was removed from the furnace. The weight of the hook, together with the residue, was measured and the weight of the residue was determined by subtraction. The hook was transferred to a container filled with 10 ml of distilled water and rinsed for 90 mins to ensure that all sodium salts are dissolved. The sodium concentration of each solution was then analysed using Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). The loss of sodium was measured for mill black liquors with boron and without boron for combustion at 900, 1000 and 1050°C in the range 2 to 10% O₂, at distinct times by analysing the sodium remaining in the residues. These temperatures are considered to be representative of those in a black liquor boiler (13, 14).

Data Analysis

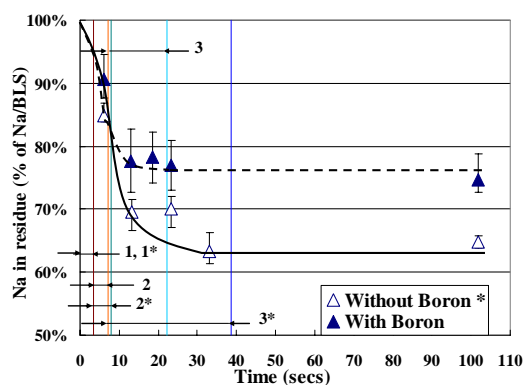
The average time for each of the combustion stages was determined by examining the video footage. Using this technique, the quenching time is too long to allow the drying phase to be resolved separately. Hence, the drying and devolatilisation stages were measured combined. The time required to raise the hook from the reactor to the purge (approximately 1 s) was not included in the measured time.

RESULTS AND DISCUSSION

Typical results for the sodium content in the black liquor residue, as a function of time, are shown in Figure 2 for both black liquors (with and without boron) at 10% O₂ for 900 and 1000°C. Each of the points in Figure 2 represents an average of 3 measurements. The percentage of sodium loss during each stage was determined by the line of best fit over time (Fig. 2). As expected, the sodium content of the residue reduces during each of the stages of combustion and reaches a constant value at the completion of the smelt oxidation stage.



a)



b)

Fig. 2: The mass fraction of sodium remaining in the residue for both liquors over time. a) 900°C at 10% O₂, and b) 1000°C at 10% O₂, where the range marked 1 represents the drying and devolatilisation stage, the range marked 2, the char combustion stage, and that marked 3, the smelt oxidation stage.

Combustion Time

Drying and Devolatilisation Stage

The time for drying and devolatilisation for the 2% O₂ cases was determined from the moment at which the droplet was introduced into furnace until the time at which it swells to its maximum size. For 5 and 10% O₂ cases, this time was determined when the visible diffusion flame disappeared. The average time of 15 determinations for the 3 different oxygen concentrations (2, 5 and 10%) at 3 different temperatures (900, 1000 and 1050°C) for both liquors was approximately 3.5 s for 900°C and 3.2 s for 1000 and 1050°C (Fig. 3a).

A previous study conducted by Forssén *et al* (16), comparing the combustion times of a liquor with and without boron in 21% O₂ at 800°C is included in Figure 3a. The times for the combined drying and devolatilisation stage of the liquor with boron were approximately 3 to 10% longer than for the liquor without boron except for the cases at 1000°C and 5% O₂ and 1050°C. The addition of boron in the liquor may influence the devolatilisation time due to the effect of boron on the dissociation of the organic bonds during thermal treatment. The drying and devolatilisation time was found to be weakly dependent on the oxygen concentration and furnace temperature. This can be explained by considering the two stages within this measurement. The drying process is controlled mainly by the heat transfer. However, the drying rate has been previously found to be constant when the furnace temperature is above 900°C (6). The present finding therefore suggests that the rate of devolatilisation is almost independent of the furnace temperature, being dominated instead by the heat generated by the combustion of the droplet itself. The oxidation process is, of course, influenced by the oxygen concentration of the surrounding gas (6).

Char Combustion Stage

The oxygen concentration has a significant influence on the char combustion time for both liquors (Fig. 3b). The combustion time for both liquors decreases as oxygen concentration is increased. From the video footage, the intensity of the glowing char was also observed to increase as oxygen concentration was increased. The dependence of the combustion time on the furnace temperature decreases as oxygen concentration is increased from 2 to 10%. The average char combustion time for the liquor with boron was typically 5 to 15% less than for the liquor without boron (Fig. 3b), agreeing with the observations of Forssén *et al* (16). Many tiny glowing particles were observed (from the video) to be ejected at the end of this stage, from both liquors and at all furnace temperatures for 5% and 10% O₂. This is consistent with the observations of Volkov *et al* (17) during the char combustion stage at the oxygen concentration of 3 to 7%.

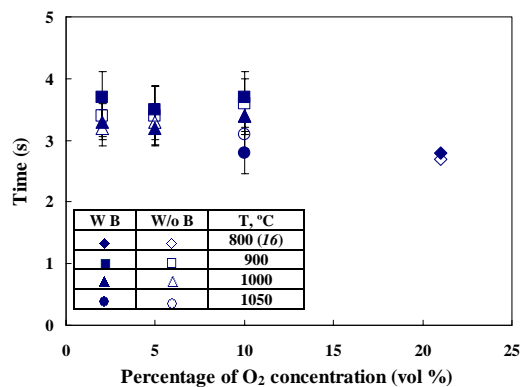
At lower oxygen concentrations, oxygen does not reach the particle surface because it is consumed by hydrogen (H₂) and carbon monoxide (CO) outside the particle to produce CO₂ and H₂O. The CO₂ and H₂O then diffuse into the particle and react with the carbon via gasification reactions, which are endothermic. At higher oxygen concentrations, more oxygen can reach the particle surface and react with the char directly via an exothermic oxidation reaction (18). At higher oxygen concentrations, the surface temperature of the liquor is also higher (19). A study conducted by Frederick *et al* (19) shows that a temperature difference between the surface of a black liquor particle and its surroundings at 800°C and 10% O₂ is 85°C higher than at 800°C and 2% O₂. Thus, increase of temperature increases the char consumption due to the carbon consuming reactions, such as those with carbonate and sulphate (18). Hence, the increase of decomposition of Na₂CO₃ may increase the sodium loss as shown in Equation 3. The increase in char combustion time may lead to the vaporisation of Na₂CO₃ (20), which could also further increase the sodium loss. With addition of boron to the liquor, the char combustion time was found to be shorter than that of the liquor without boron. This could be due to additional char consumption by the borate as suggested by Tran *et al* (11) (Eq. 5).

Smelt Oxidation Stage

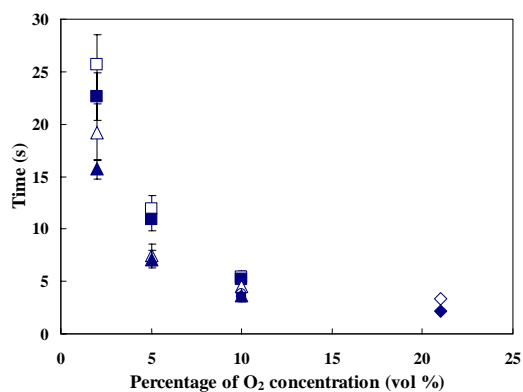
The smelt oxidation stage is identified here by a change in the intensity of the glowing of the smelt residue. The glowing is produced by the heat release from the oxidation of Na₂S to Na₂SO₄ (6). The smelt oxidation starts when the porous char collapses and the molten smelt coalesces into a small bead of residue on the hook. The end of this stage is denoted by the end of the intense glowing. The smelt oxidation was not included in our finding for 2% O₂ because the glowing smelt could not be detected from the recorded video.

An unusual phenomenon was observed for 10% O₂ at 1000°C. The smelt glowed intensely for an average time of 3 s and then ceased, consistent with that seen in the smelt oxidation at 900°C. Then, an average of 4 s later, the smelt started to glow again and this lasted for an average of 14 s. The reason for this observation is not clear at present. However, it could be caused by a delay in the oxidation of Na₂S due to the presence of small quantities of carbon retained inside the smelt, keeping the Na₂S in a reduced form. This phenomenon was not observed in the liquor with boron.

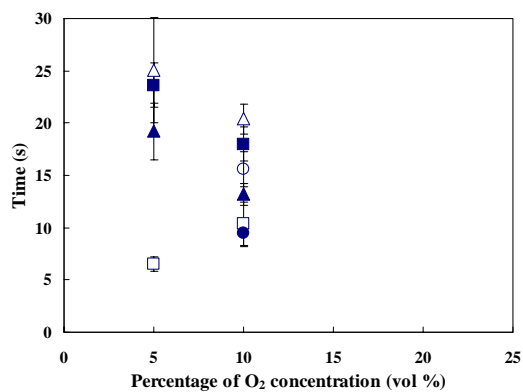
At 900°C, the smelt oxidation time for the liquor with boron was found to be 40 to 70% longer than for the liquor without boron, at both 5 and 10% O₂, (Fig. 3c). However, somewhat surprisingly, at 1000°C and 1050°C, the smelt oxidation time for the liquor without boron was found to be 35 to 40% longer than for the liquor with boron. The manner in which the borate in the smelt interacts with the sulphide oxidation chemistry obviously requires further studies.



a)



b)



c)

Fig. 3: The average combustion time for the black liquor droplet with boron and without boron. a) the drying and devolatilisation stage, b) the char combustion stage, and c) the smelt oxidation stage.

Sodium release

Drying and Devolatilisation Stage

The loss of sodium from both liquors after the drying and devolatilisation stages was approximately 5% of the total sodium in the black liquor solids (BLS). The sodium loss from the liquor with boron was approximately 10 to 30% lower than the liquor without boron. The sodium loss for both liquors was found to be independent of the oxygen concentration and furnace temperature (Fig. 3a). This suggests that the sodium loss is mainly due to the physical ejection of droplet fragments with the volatile gaseous (5) rather than vaporisation. It is important to note that such fragments are likely to be small, which suggests that a significant number of fine droplets could be generated by this mechanism.

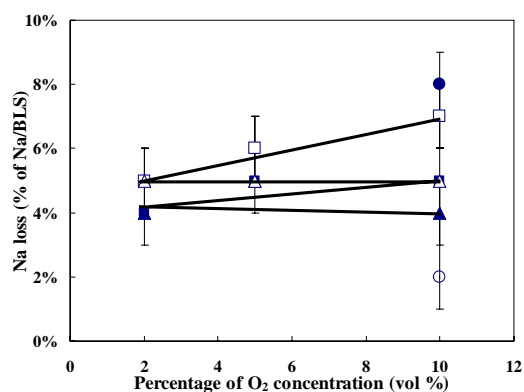
Char Combustion Stage

Significant loss of sodium from both liquors was observed during the char combustion stage. The sodium loss at this stage was found to be dependent on oxygen concentration and furnace temperature. At 900°C, the sodium loss during this stage for the liquor without boron, especially at 10% and 5% O₂, was 50% higher than the liquor with boron (Fig. 4b). At 1000°C, the sodium loss from both liquors increases as oxygen concentration is decreased.

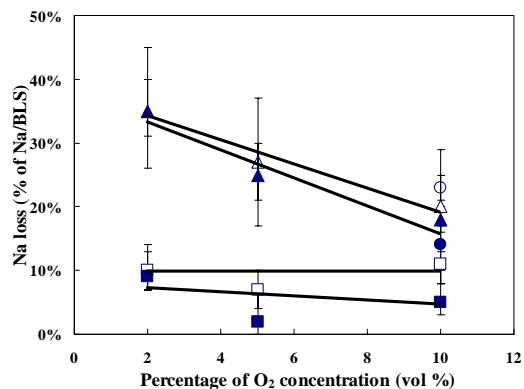
The study conducted by Forssén *et al* (16) suggested that decarbonation by boron can occur during the char combustion stage where small amounts of Na₂CO₃ in the droplet are converted into Na₃BO₃ according to the percentage of autocausticizing by the boron. This suggests that the boron may reduce the sodium loss due to the smaller amount of carbonate in the particle (Fig. 3b). Under this scenario, the sodium loss from the liquor with boron would be lower than the liquor without boron, and this is seen when the furnace temperature is at 900°C. At 1000°C however, the percentage of sodium loss for both liquors was fairly similar. This suggests either that the reaction rates of Na₂CO₃ decomposition are dominant at the higher temperature or that some of the sodium loss is due to the decomposition of the sodium borate

Smelt Oxidation stage

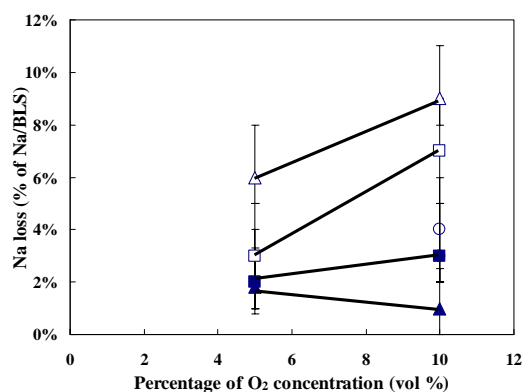
In this stage the sodium loss from the liquor without boron was found to be higher than that from the liquor with boron and the loss increases gradually as oxygen concentration is increased (Fig. 4c). A similar finding was observed the study by Clay *et al* (21), in which fuming increased as oxygen concentration increased. The present result partially agrees with the study of Cameron (9), implying that the loss of sodium from the smelt may be through the mechanism shown in Equation 4. However, the total sodium loss during the smelt oxidation stage is found not to be as significant as that during the char combustion stage.



a)



b)



c)

Fig. 4: The mass fraction of sodium loss from the black liquor solid (BLS) with boron and without boron. a) the drying and devolatilisation stage, b) the char combustion stage, and c) the smelt oxidation stage. Symbols as per Fig. 3.

The rate of sodium loss

The rate of sodium loss during the different stages of black liquor combustion is shown in Figure 5. This was estimated from the sodium loss (Fig. 4) and the time taken for each combustion stage (Fig. 3). The average rate of the sodium loss at the end of the drying and devolatilisation stage was found to be independent of the oxygen concentration and furnace temperature (Fig. 5a). Figure 5b clearly shows however, that the rate of sodium loss during the char combustion stage is dependent on oxygen concentration and furnace temperature. The rate of sodium loss increases as both oxygen concentration and furnace temperature are increased. Interestingly, the rate of sodium loss for the liquor without boron at 900°C at 10% O₂ and 1000°C at 2% O₂ were

fairly similar. The presence of boron influences the average rate of sodium loss during the smelt oxidation stage (Fig. 5c). However, this rate is small compared to that during the char combustion stage.

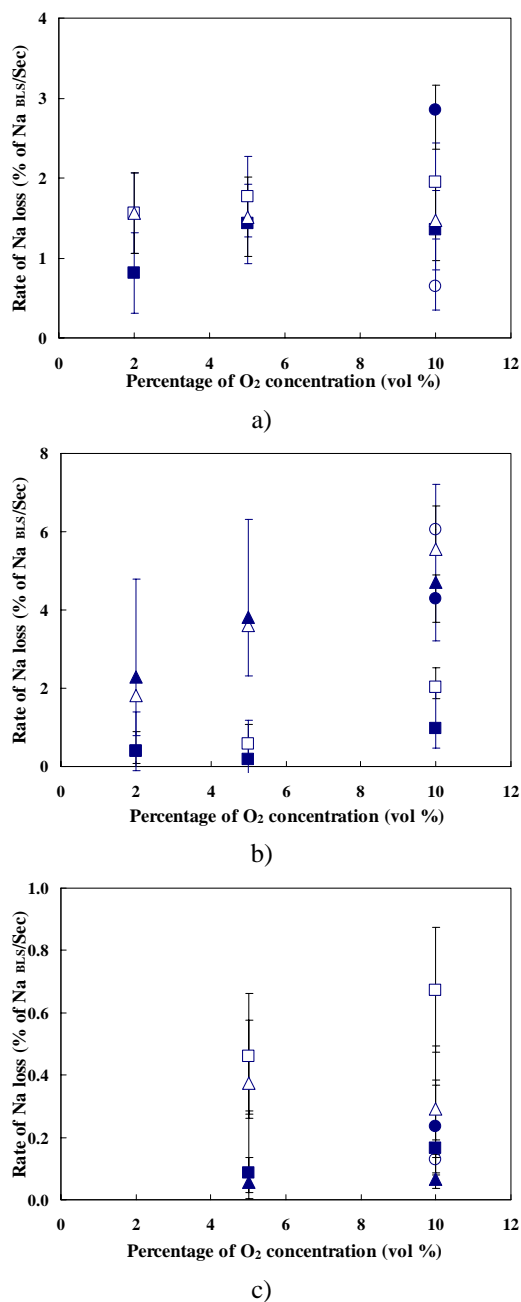


Fig. 5: The rate of sodium loss for the liquor with boron and without boron. a) the drying and devolatilisation, b) the char combustion stage, and c) the smelt oxidation stage. Symbols as per Fig. 3.

Further Discussion

Oxidation of the residue after the char combustion stage is completed, probably only occurs for a small percentage of droplets in a recover boiler, since the bulk of the inorganic material falls to the bed under reducing conditions. Nevertheless, it could still be significant in fume formation. The results from the drying and devolatilisation stage suggest that the formation of

fine droplets by the physical ejection of liquor fragments is likely to be significant. While such fine droplets may constitute a small mass fraction of the liquor flux, they can result in a large number of fine particles. Such particles are flow tracers and a percentage is likely to be entrained into the oxygen rich air ports.

The addition of boron to the black liquor reduced the overall sodium loss (% of Na/BLS), and this agrees with the results of the two mills trials of boron addition that showed less fume formation - as evidenced by the electrostatic precipitators being found to be cleaner when burning black liquor with boron (1, 2). Recently, a study on the release of elemental sodium during the combustion of black liquor was conducted using a laser diagnostic technique, Planar Laser-Induced Fluorescence (PLIF) (22). It is proposed that the release of atomic sodium from these two liquors will be studied using this laser measurement technique.

CONCLUSIONS

1. Addition of boron not only causes autocausticizing but also influences the liquor burning behaviour as measured by single droplet measurements.
2. The overall sodium release from the burning droplet is altered, particularly at 5 and 10% O₂. At 900°C, the sodium release for the liquor with boron at 2, 5 and 10% O₂ was 2%, 7% and 14% (of Na/BLS) lower, respectively, than the sodium release for the liquor without boron. At 1000°C, the sodium release for the liquor with boron at 2, 5 and 10% O₂ was 1%, 6% and 9% (of Na/BLS) lower, respectively, than the liquor without boron. This finding of decreasing sodium emission may have major practical significance and requires more work.
3. The characteristic combustion times were also influenced by the boron, but no simple pattern of the changes could be concluded.

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