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**FUME FORMATION DURING BLACK LIQUOR  
DROPLET COMBUSTION: THE IMPORTANCE OF  
SODIUM RELEASE DURING DEVOLATILIZATION**

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# Fume Formation During Black Liquor Droplet Combustion: The Importance of Sodium Release During Devolatilization

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# FUME FORMATION DURING BLACK LIQUOR DROPLET COMBUSTION: THE IMPORTANCE OF SODIUM RELEASE DURING DEVOLATILIZATION

by

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## ABSTRACT

Sodium release during black liquor drying and devolatilization may produce a significant amount of the fume in an operating recovery furnace. In order to investigate the mechanism of sodium release during these combustion stages, single droplets of industrial black liquor were exposed to pyrolytic environments at 500-900°C. Char particles were quenched after 3-30 seconds exposure.

Approximately 10-30% of the sodium present in the black liquor was released during drying and devolatilization. A likely mechanism of sodium loss during drying and devolatilization of black liquor is physical transport of alkali-containing material by eruptions of gases from rapidly heated droplets.

## KEYWORDS

Aerosols, Black Liquors, Combustion, Fumes, Particulate Emissions, Pyrolysis, Recovery  
Furnaces, Sodium Compounds

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## INTRODUCTION

The inorganic aerosol generated during kraft black liquor combustion is known as fume. The submicron-sized fume particles consist primarily of  $\text{Na}_2\text{CO}_3$ , with  $\text{Na}_2\text{SO}_4$ ,  $\text{NaCl}$ , and the analogous potassium salts. Fume composition varies with location in the recovery furnace and is dependent on the conditions of combustion.<sup>1,2</sup> Furnace dust samples and equilibrium calculations indicate that about 10% of the sodium in the black liquor becomes fume.<sup>3</sup> The principal benefit of fume formation is that the alkali aerosol reacts with environmentally undesirable sulfur gases in the flue gas; the resulting  $\text{Na}_2\text{SO}_4$  dust is removed by the electrostatic precipitator and returned to the system by mixing with the black liquor. Fume has detrimental effects on recovery furnace operation because it deposits on the heat transfer surfaces which reduces thermal efficiency, requires process steam to remove the deposits, and contributes to blockage of air passages.

Fume generation has historically been attributed to sodium vaporization from the high-temperature and strongly reducing environment of the char bed.<sup>4</sup> This hypothesis has been supported by chemical equilibrium calculations which show that the partial pressures of Na and NaOH increase with increasing temperature and that the partial pressure of Na decreases with increasing oxygen concentration.<sup>5,6,7</sup> It has been argued that equilibrium calculations overestimate the effect of temperature on fume formation as well as the enrichment of potassium and chloride in the fume.<sup>8</sup> Laboratory data from smelt pool reactor studies show that the rate of fume formation is an order of magnitude higher during sulfide oxidation than the rate under reducing conditions.<sup>9</sup> Based on results from these studies, Cameron<sup>10</sup> proposed a reaction-enhanced mechanism of fume formation, wherein rapid oxidation of sodium vapor near the smelt surface reduces the partial pressure of sodium in the boundary layer. The resulting increase in driving force enhances the rate of sodium vaporization.

Four distinct stages of black liquor droplet combustion have been identified: drying, devolatilization, char burning, and inorganic reactions of the residual smelt.<sup>11,12</sup> The extent to which these stages overlap depends on liquor properties and conditions of combustion. The

devolatilization stage of droplet combustion is characterized by a rapid expansion of particle volume and a continuous increase of particle temperature.<sup>13</sup> Organic components of the black liquor solids begin to decompose at temperatures above 200°C, and gas-phase volatiles are released.<sup>14</sup> Most of the gas evolution during devolatilization occurs as the particle temperature increases from 250 to 500°C; the period of rapid swelling occurs between 400 and 500°C.<sup>15</sup> If the temperature of the gaseous environment is above 550°C and the oxygen content is greater than 10%, burning volatiles form a visible flame around the swelling particle.<sup>13</sup> In this article, the term *pyrolysis* refers specifically to drying and devolatilization in conditions which do not support combustion. The porous, friable material remaining at the end of devolatilization is known as char.

Fume formation resulting from sulfide oxidation can occur during the char burning and inorganic reaction stages of black liquor combustion. Grace et al.<sup>12</sup> proposed a catalytic mechanism of char burning. Theoretically, this sulfate/sulfide cycle provides a high sodium partial pressure as long as there is organic carbon present in the char.<sup>14</sup> Once the organic carbon has been consumed, the reduction of carbonate by sulfide will maintain a sodium vapor pressure; therefore, the residual inorganics, in the form of entrained droplets or flowing smelt, will produce fume in the presence of air.<sup>10</sup>

This study was conducted to contribute to the understanding of the significance of sodium release prior to char burning and to the understanding of the mechanism of sodium release during devolatilization of black liquor. Most previous researchers have studied fume formation only during char burning and smelt reactions. Experimental data indicate that sodium emission is continuous throughout combustion;<sup>16,17,18,19</sup> moreover, recent work has shown that sodium release during devolatilization may be a major contribution to overall fume formation.<sup>18</sup>

## EXPERIMENTAL

### Dynamic Aerosol Collection

At the Institute of Paper Science and Technology (IPST), a droplet furnace has been constructed for the collection of aerosol throughout the respective stages of black liquor combustion.<sup>20</sup> During aerosol collection experiments, individual droplets of industrial kraft black liquor were formed on nichrome wires and inserted into the quartz reaction chamber of the furnace. At the moment the droplet entered the reaction chamber, a remote switch activated the fume capturing apparatus. A digitally-controlled drive system moved an aerosol collection medium over the furnace exit at a constant linear speed. The combustion environment was 7.5% O<sub>2</sub> in 97.5% N<sub>2</sub> at 750°C with an average gas velocity in the quartz reaction chamber of 0.61 m/sec. This condition is the midpoint of the desired range of gas composition, temperature, and flow rate.

In a typical experiment, 15-25 cm of the aerosol collection medium were exposed to the products of combustion. The greatest retention of fume particles was obtained when the aerosol was collected primarily by impaction rather than filtration. Fume component assays and Scanning Electron Microscopy (SEM) have been utilized for locating the aerosol deposits on the collection media. For fume component assays, the media were carefully divided into sections; each section was then agitated in purified water to dissolve the captured material. Ion Chromatography (IC) was used to measure the amounts of CO<sub>3</sub><sup>=</sup> and SO<sub>4</sub><sup>=</sup> in each sample. The sodium concentration of the samples was determined by Inductively Coupled Plasma spectroscopy (ICP). Sections were cut from precise locations on some media and investigated by SEM. This visual observation provided valuable qualitative information about the morphology, size distribution, and density of the collected aerosol.

### Mass Loss Determination

For the investigation of sodium loss during droplet pyrolysis, the equipment was modified to prevent air infiltration and to allow the char residue from individual droplets to be extracted through a quench stream of nitrogen. Black liquor droplets, weighing 2 to 10 mg, were formed on

nichrome wires and inserted into the reaction chamber. After 3 to 30 seconds, the char was withdrawn from the pyrolytic environment into the quench stream and allowed to cool. Five experiments were conducted: three at 600°C in 95% N<sub>2</sub> with 5% CO, one at 900°C in 95% N<sub>2</sub> with 5% CO, and one at 500°C in 95% N<sub>2</sub> with 5% O<sub>2</sub>. A constant average gas velocity in the quartz reaction chamber of 0.61 m/sec was maintained by adjusting the gas flow rate. The conditions were chosen to extend the temperature range that has been used in previous sodium loss studies. Replications of the first experiment at 600°C were conducted to quantify the precision of the experimental technique and to identify sources of error.

Each experiment consisted of 6-10 determinations of char mass loss and sodium mass loss; a typical experiment was comprised of two replicates of three exposure times. Composite samples of 5-20 fully-intact char particles were accumulated for each determination. Control of the exposure time was very good; for a given determination, the standard deviation of the average exposure time ranged from 0.1 to 0.3 seconds. ICP was used to measure the amount of sodium in acid-digested char and black liquor samples.

#### Droplet Observation

Observations of droplet combustion and pyrolysis in the furnace were recorded on videotape. Times for each stage of droplet combustion were calculated from the elapsed time indicated on the video images. The first appearance of the droplet in the field of view was used to denote the start of drying; the first sign of swelling or ignition indicated the onset of devolatilization; the maximum swollen volume of the char particle was taken as the start of char burning; coalescence of a smelt bead denoted the start of the inorganic reactions; visible cooling of the smelt was taken as the end of droplet combustion. These definitions imply that drying, devolatilization, char burning, and inorganic reactions are distinct and sequential stages of combustion; note, however, that there is always some overlapping of the physical processes occurring during droplet combustion.<sup>13</sup>



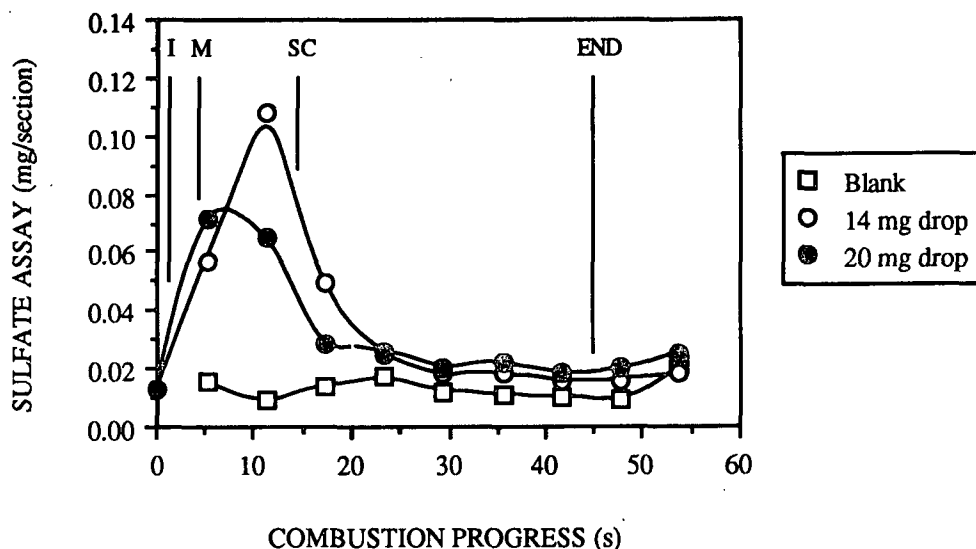
## RESULTS AND DISCUSSION

### Aerosol Collection During Droplet Combustion

During the first aerosol collection experiment, borosilicate glass fiber (BGF) filters were used as the aerosol collection medium. Three filters were analyzed for typical fume components: two that had been exposed to droplet combustion products and one "blank" that had been exposed to combustion gases without burning liquor. Each filter was carefully divided into nine sections, then the amounts of  $\text{CO}_3^-$ ,  $\text{SO}_4^-$ , and sodium were measured in the dissolved samples.

An unfortunate oversight in the selection of BGF filters was that sodium oxide is a significant component of borosilicate glass. The soluble quantity of sodium in the glass fibers is both non-uniformly distributed and as much as 100 times higher than that contained in the collected aerosol. Analytical determination of the amount of captured sodium was therefore impossible. The average background level of carbonate in the filters was approximately 25 times greater than the amount expected to be formed during combustion. Fortunately, the amount of background  $\text{SO}_4^-$  in the BGF filters was very low, which allowed accurate sulfate concentration measurements to be made. An interesting result was obtained when the sulfate assays were plotted against combustion progress, as shown in Figure 1. Granted that  $\text{Na}_2\text{SO}_4$  does not account for a majority of the total sodium in the liquor, these data nonetheless suggest that an appreciable fraction of sodium evolution occurred during drying and devolatilization.

The times during combustion when the sulfate-containing aerosol was formed were calculated from the locations of the filter sections, the speed of the filter drive mechanism, and an estimated average residence time between droplet and filter. These data represent total amounts of material collected over discrete time intervals; the actual transient behavior of sulfate formation during combustion may not be accurately represented by the continuous lines drawn in Figure 1.



**Figure 1.** Total mass of  $\text{SO}_4^{=}$  per section of filter as a function of estimated combustion progress. Furnace environment: 7.5%  $\text{O}_2$  in 92.5%  $\text{N}_2$  at 750°C; liquor #2 dry solids content: 71%; combustion events indicated: ignition (I), max. swollen volume (M), smelt coalescence (SC), cooling of residue (END).

After the first aerosol collection experiment, the BGF filters were deemed inappropriate for further quantitative investigations. Silver membranes were found to be a more suitable aerosol collection medium. This material combines the desirable characteristics of high purity and surface capture of polymeric screen membranes with the superior strength and thermal stability of the BGF filters. Quantitative determinations of fume formation during droplet combustion will be possible with silver membranes as the aerosol collection medium because there are negligible amounts of soluble contaminants in the membranes. The only disadvantage of silver membranes is their extremely high cost.

In a recent experiment, the combustion products from a single droplet were impacted on a moving silver membrane. Combustion conditions were identical to those described above. Eight consecutive samples were cut from the center line of the membrane and investigated by SEM; each section represented approximately 2.5 seconds of combustion progress. Submicron-sized aerosol (0.10-0.25  $\mu\text{m}$ ) was present on all samples. The fine material was similar to that observed on stationary BGF filters that had been used to collect droplet combustion aerosol under various

conditions. There were no large spheres (1-30  $\mu\text{m}$ ) on silver membrane samples, which is consistent with the absence of visible spark formation during char burning in less than 10%  $\text{O}_2$ .<sup>20</sup> The amount of collected material increased over the first six samples and then remained constant.

An important conclusion that can be inferred from the sulfate assays in Figure 1 and the SEM analysis of the silver membrane is that a substantial amount of inorganic aerosol is formed during the first seconds of black liquor droplet combustion, presumably before char burning has begun.

### Droplet Pyrolysis Behavior

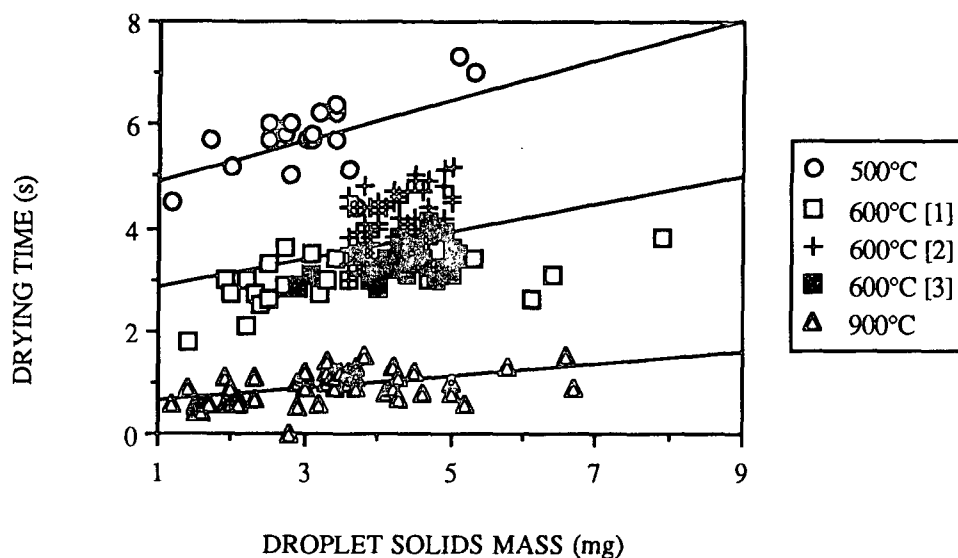
Drying and swelling times and droplet mass data, corresponding to the char particles that were accumulated for sodium mass loss determination, were extracted from a database of information from more than 450 individual droplet devolatilizations. A summary of the furnace conditions and average pyrolysis behavior of the 261 selected char particles is presented in Table I. Reduced droplet mass variability in the second and third experiments at 600°C indicates improvement in experimental technique.

TABLE I. Droplet Pyrolysis Conditions.

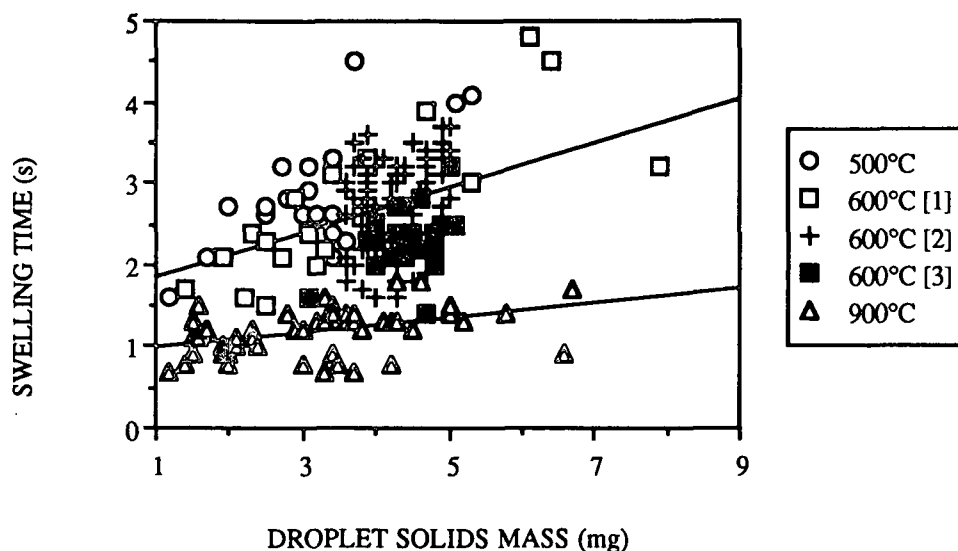
Furnace Temperature (°C)	Gas Composition (% in $\text{N}_2$ )	Number of Droplets	Droplet Solids Mass (mg)	Drying Time (s)	Swelling Time (s)
500	5% $\text{O}_2$	30	$3.5 \pm 1.3$	$5.8 \pm 0.7$	$2.8 \pm 0.7$
600 [1]	5% CO	30	$3.7 \pm 1.9$	$3.0 \pm 0.5$	$2.8 \pm 0.9$
600 [2]	5% CO	121	$4.2 \pm 0.5$	$4.0 \pm 0.6$	$2.7 \pm 0.6$
600 [3]	5% CO	30	$4.4 \pm 0.5$	$3.4 \pm 0.4$	$2.3 \pm 0.4$
900	5% CO	50	$3.2 \pm 1.3$	$0.9 \pm 0.3$	$1.2 \pm 0.3$

The effect of furnace temperature on drying and swelling time is apparent in Table I. The behavior of the drying time corresponds to the change in heat transfer mechanisms from convection to radiation.<sup>14</sup> Because there was no luminous flame surrounding the particles, the effect of furnace temperature on swelling time in the pyrolytic environment of this study is greater than that reported for devolatilization in a combustive environment.<sup>11</sup> The swelling time data agree with other indications that devolatilization time is a weak function of temperature over a wide range of conditions.<sup>14</sup>

Drying times versus the calculated mass of droplet solids are shown in Figure 2; Figure 3 is a plot of swelling time data. At very short exposure times, many of the droplets had not reached maximum swollen volume before extraction; thus, there are fewer points on the graphs than there are reported in Table I. Simple linear regression models were used to group the data in Figures 2 and 3; these lines do not imply that statistical correlations exist between the variables. The mean liquor solids content during the second experiment at 600°C was somewhat lower than in the other experiments; accordingly, the mean drying times were longer, as indicated in Figure 2 and Table I.



**Figure 2.** Drying time during pyrolysis as a function of droplet size and furnace temperature. Gas composition at 500°C: 5% O<sub>2</sub> in 95% N<sub>2</sub>; others: 5% CO in 95% N<sub>2</sub>; liquor #3 dry solids content: 71-74%.



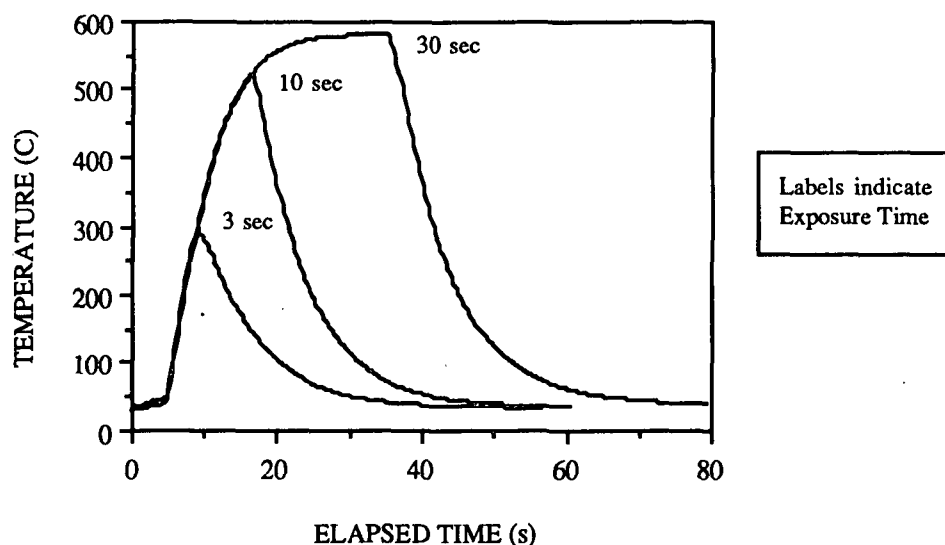
**Figure 3.** Devolatilization time during pyrolysis as a function of droplet size and furnace temperature. Same conditions as Figure 2.

#### Droplet Thermal History

A 0.81 mm diameter thermocouple was used to investigate the heating and cooling history of a liquor droplet in the laboratory furnace. The thermocouple, mounted in the droplet insertion hardware, was inserted into the reaction chamber for a given exposure time and then withdrawn to cool in the quench stream. Figure 4 is a typical plot of thermocouple response as a function of exposure time. Heat transfer to a swelling black liquor droplet may be substantially different than to a thermocouple junction; however, this technique does provide a valid approximate thermal history for a droplet. An important interpretation of this experiment is that the droplets only reached the furnace temperature during the longest exposure times.

Droplet heating rates were estimated from the elapsed time required for the thermocouple temperature to increase from 100°C to 80% of the maximum (ultimate) temperature; this corresponds to the nearly linear region of the curves in Figure 4. This “average linear heating rate” ranged from 36°C/sec at 500°C to 106°C/sec at 900°C. In a similar experimental system, Frederick and Hupa<sup>21</sup> measured the surface temperature of liquor droplets during pyrolysis and combustion.

For a 17 mg droplet, pyrolyzed at 800°C in 95% N<sub>2</sub> with 5% CO, the surface temperature increased at a rate of approximately 100°C/sec during devolatilization.



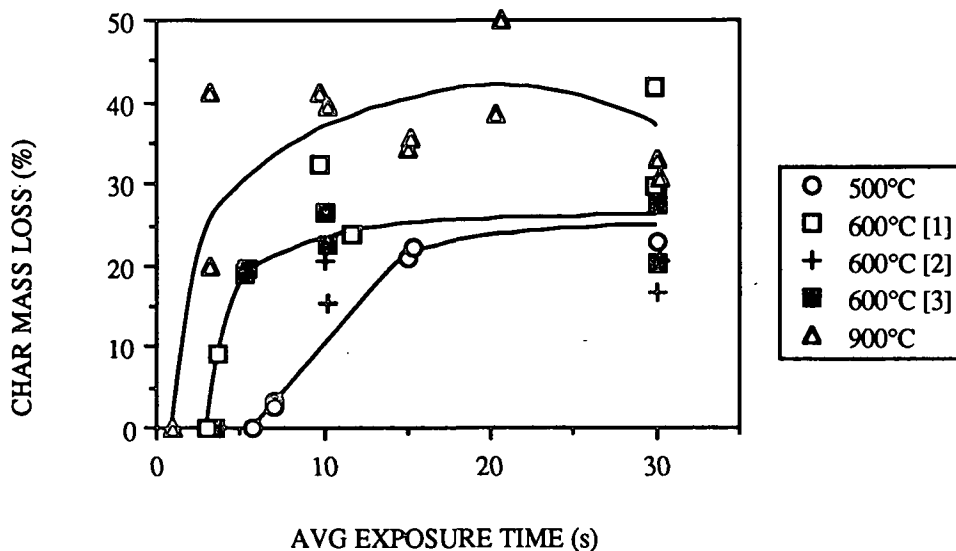
**Figure 4.** Thermocouple response as a function of exposure time. Furnace conditions: air at 600°C; avg. gas velocity: 0.61 m/s; quench flow: 5 slpm N<sub>2</sub>.

The time required to fully withdraw a droplet from the center of the reaction chamber to the quench zone was approximately 0.2 seconds. Assuming that pyrolysis reactions are quenched at temperatures below 200°C, a cooling time can be defined as the elapsed time between the maximum temperature measured by the thermocouple and 200°C. The average of 24 determinations of cooling rate (taken from eight measurements at each furnace temperature) was  $11.2 \pm 2.0$  seconds. Additional mass loss could have occurred during the quench period; therefore, the actual pyrolysis time is greater than the reported droplet exposure time.

#### Mass Loss During Pyrolysis

Total char mass losses for all five experiments are plotted against exposure time in Figure 5. Char mass loss is defined as the percent difference between the initial mass of liquor solids and the mass of the accumulated char sample for each determination. The initial mass of liquor solids was calculated from the sum of the droplet masses and the solids content of the black liquor. To account for evaporation loss, solids content was periodically determined during each experiment.

No significant char mass loss is expected to occur until the particles begin to swell; accordingly, average drying times from Table I are used as origins of the curves in Figure 5. Lines are shown in the figure to group the data; these lines are not based on statistical regression.



**Figure 5.** Char mass loss during pyrolysis as a function of exposure time and furnace temperature. Quench flow: 2 slpm N<sub>2</sub> at 500°C, 5 slpm N<sub>2</sub> at 600-900°C.

During three of the shortest exposure time determinations at 600°C, the char was withdrawn from the furnace before drying was complete. The resulting negative values of char mass loss are not shown in Figure 5. To prevent this error in subsequent experiments, the minimum exposure time was taken as 1.25 times the average drying time, as determined from several video sequences of droplet pyrolysis. Improvements in experimental technique are evident as reduced scatter of char mass loss values from the third experiment at 600°C.

The apparent increase in mass during pyrolysis at 900°C is a result of partial oxidation of highly reduced char immediately upon removal from the quench stream. This conclusion is supported by the observation of spontaneous combustion exhibited by many of these char particles when they were removed from the nitrogen quench and exposed to ambient laboratory air. Micrographs of several intact char particles, pyrolyzed at 900°C for 30 seconds, reveal changes in morphology that

indicate that all highly reduced particles underwent rapid oxidation after being removed from the furnace.

It is interesting that the ultimate mass losses for the low temperature trials, shown in Figure 5, are very similar despite the difference in gas composition. There were, however, substantial differences in char formation observed at the two conditions. The swelling behavior of droplets exposed to 95% N<sub>2</sub> with 5% O<sub>2</sub> at 500°C was like that observed during combustion at higher temperatures and oxygen concentrations.<sup>19</sup> These droplets underwent random serpentine expansion and formed hollow char particles with delicate but resilient external films. Particles produced in 95% N<sub>2</sub> with 5% CO at 600°C were porous and brittle with more internal structure. The swelling of these particles during devolatilization was uniform and spherical.

#### Aerosol Formation During Pyrolysis

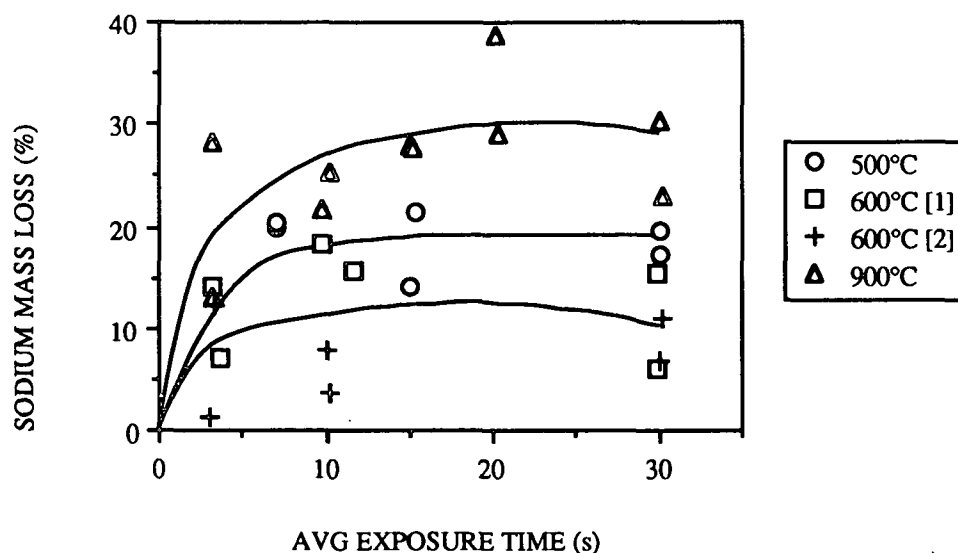
During several of the char mass loss determinations, exit gases from the IPST droplet furnace were impacted on stationary BGF filters. Investigation of the filters from the 900°C trials by SEM revealed a few 10-20 μm smooth-surfaced spheres and numerous 1-2 μm plate-like deposits and submicron-sized globular deposits on the fiber surfaces. There were fewer and less substantial deposits on the filters from pyrolysis at 600°C; a few large (25 μm) smooth spheres and some irregular agglomerated deposits were observed on some regions of these filters. The copious quantities of sodium and sulfur containing particulate, present on filter samples produced by impaction of combustion products of the same liquor in air at 750°C, were not observed.<sup>20</sup> However, the SEM images provide qualitative evidence that aerosol is formed during pyrolysis.

#### Sodium Mass Loss During Pyrolysis

The amounts of sodium remaining in the char are plotted versus exposure time in Figure 6. Note that the experiments at 600°C and 900°C were conducted in an atmosphere of 5% CO in 95% N<sub>2</sub>; the carrier gas contained 5% O<sub>2</sub> during the 500°C experiment. Because there was significant sodium loss at the shortest exposure times in all experiments, the origin of the curves in Figure 6 are not assumed to be at the average drying times, as in Figure 5. The moisture content of the char



samples would not affect the accuracy of these results because the amount of sodium was determined from the concentration of a dissolved sample.



**Figure 6.** Sodium mass loss during pyrolysis as a function of exposure time and furnace temperature. Same conditions as Figure 5.

The data in Figure 6 indicate that, for all conditions, there is a rapid initial loss of 10-30% of the sodium in the black liquor solids. The significant change in sodium mass at the shortest exposure times suggests that sodium evolution may occur during drying. After swelling is complete, sodium loss appears to continue only during pyrolysis at 900°C. Frederick and Hupa<sup>18</sup> presented curves which indicate similar behavior of sodium loss during pyrolysis of black liquor droplets in 95% N<sub>2</sub> with 5% CO at 700-800°C.

From Figure 6, it is apparent that about 10% of the sodium was evolved during the first 10 seconds of pyrolysis at 600°C, and about 25% of the sodium was evolved during the first 10 seconds at 900°C. Frederick and Hupa<sup>18</sup> reported average sodium mass losses of 23-33% during pyrolysis of 8-20 mg droplets of five kraft liquors for 10 seconds at 800°C. Within experimental error, good agreement exists between their data and the sodium losses indicated in Figure 6. Li and van Heiningen<sup>17</sup> conducted a thermogravimetric study of sodium evolution during kraft liquor char pyrolysis at a heating rate of 20°C/min. They reported 18% sodium mass losses after

exposure to 88% He with 12% CO at 750-800°C for 30 minutes.<sup>17</sup> These values agree remarkably well with those of both droplet studies despite two orders of magnitude difference in the heating rates.

A comparison of the sodium mass loss in the environment of 95% N<sub>2</sub> with 5% O<sub>2</sub> at 500°C and the 600°C data reveals a significant effect of gas composition on sodium emission during devolatilization. After exposure to the low temperature 5% O<sub>2</sub> atmosphere for 7 seconds, approximately 19% of the sodium had evolved from the partially swollen char. Char particles withdrawn from the oxygen-free environment at 600°C after 3 seconds had swollen to approximately the same extent, but the mass of sodium had only decreased by 9%.

In a related combustion study, Volkov et al.<sup>16</sup> exposed droplets of kraft black liquor to oxidizing conditions over a temperature range of 900-1100°C. Char residue was extracted through a nitrogen quench after a fixed exposure time. The total sodium evolved during combustion ranged from 30-50% of the sodium present in the liquor. At the minimum exposure time of three seconds, they reported a 20% sodium loss for 2 mm diameter droplets burnt in air at 900°C.<sup>16</sup> Model predictions indicate that drying and devolatilization of similar-sized droplets in air at 800°C would be complete in about three seconds;<sup>14</sup> therefore, it is likely that part or all of the initial sodium loss reported by Volkov occurred before char combustion commenced.

### The Fate of Sodium During Pyrolysis

According to Grace et al.,<sup>22</sup> approximately two-thirds of the total sodium present in black liquor is associated with ionized organic liquor components. This "organically bound" sodium typically accounts for 12% of the mass of dry liquor solids.<sup>22,23</sup> Thermogravimetric studies of kraft liquor char and coal model compounds indicate that organic alkalis form alkali carbonate, organics, and CO<sub>2</sub> during pyrolysis at temperatures between 450°C and 675°C.<sup>17,24</sup> The carbonate subsequently decomposes by reaction with carbon to form atomic alkali and CO; this reaction starts at temperatures between 675°C and 800°C.<sup>17,24,25</sup> It has been demonstrated that the alkali carbonate catalyzes the gasification of residual carbon as long as reactive species (CO, CO<sub>2</sub>, O<sub>2</sub>) are present

in the gas phase and that no atomic sodium is evolved until the carbon is depleted and the temperature exceeds 800°C.<sup>17,24</sup>

The recent findings of Frederick and Hupa<sup>18</sup> and those presented in this report indicate there is a 10-30% loss of sodium mass during drying and devolatilization in noncombustive environments with either CO or oxygen present. Based on thermogravimetric studies, sodium emission during devolatilization must occur either before all the organically bound sodium is converted to Na<sub>2</sub>CO<sub>3</sub> or after sufficiently high particle temperatures have been reached for Na<sub>2</sub>CO<sub>3</sub> to decompose. Two mechanisms are being considered to explain the sodium loss before black liquor char combustion begins: vaporization of volatile alkali compounds and physical transport of alkali-containing material.

Elemental sodium is one of the most volatile inorganic species present in black liquor; the vapor pressures of sodium salts are very low, even at 900°C.<sup>14</sup> The particle temperature may be high enough to produce a vapor pressure of elemental sodium during the swelling period of devolatilization; however, this would not explain sodium loss during drying. It is proposed that, if vaporization is the mechanism of sodium loss, the fugitive sodium must be associated with volatile organic compounds. These compounds must not decompose at the temperatures of droplet drying and devolatilization. If a relatively low molecular weight organic sodium compound had a substantial vapor pressure at 200°C, then it could easily be swept from the boundary layer surrounding the devolatilizing particle into the bulk phase, where it would be decomposed to pyrolysis gases and volatile sodium (Na or NaOH).

During the first observations of spent pulping liquor droplet combustion in laboratory furnaces, researchers noted that the droplets bubbled violently during drying as water vapor erupted through a surface film.<sup>11,26</sup> Bubble formation and erupting jets of gases were also observed in high-speed photographic images of pyrolyzing coal particles.<sup>27</sup> When Miller<sup>15</sup> investigated the swelling of kraft black liquor, he found behavior similar to that of coal; bubbles began to form when the liquor

solids were heated to 250°C. Smith et al.<sup>28</sup> proposed that bursting fly ash particles are responsible for a large fraction of the submicron-sized aerosol formed during pulverized coal combustion.

They explained that gas evolution during rapid heating causes the slag films surrounding fly ash particles to burst which liberates volatile substances that subsequently condense as fume.<sup>28</sup>

Raask<sup>29</sup> observed that some particles were ejected during slag film rupture but indicated that very few submicron-sized particles were formed as a result of these gas explosions.

The physical transport of sodium-containing material explains sodium loss during both drying and devolatilization. The eruptions of water vapor and pyrolysis gases from the surface film of the liquor droplets eject tiny droplets of liquor into the gas phase surrounding the particle. Under non-combustive conditions, the organic alkali compounds in the ejecta would be rapidly decomposed to low molecular weight gases and sodium carbonate aerosol. If the gaseous environment supports combustion, then the mechanisms of char burning and sulfide oxidation, discussed in the introduction, would produce sodium vapor from the burning bits of ejected liquor. The sodium vapor would further react and condense as submicron-sized fume.

In order to understand the nature of sodium evolution during drying and devolatilization, future experiments are planned to investigate the effects of process variables on the rate of sodium loss. If alkali release is a result of physical ejection of sodium-containing material, then the particle heating rate should affect the extent of sodium loss. Liquor composition should have a similar effect if vaporization of sodium compounds is responsible for fume formation during the initial stages of black liquor droplet combustion.

## CONCLUSIONS

Sodium release during the drying and devolatilization stages of kraft black liquor droplet combustion may be a significant source of fume in recovery furnaces. Approximately 10-30% of the sodium present in the black liquor solids is released during pyrolysis of single droplets of black

liquor. After swelling is complete, continued sodium release appears to occur only at higher temperatures above 800°C; additional sodium may then evolve as a result of thermal decomposition of Na<sub>2</sub>CO<sub>3</sub>.

Sodium mass loss during pyrolysis in 95% N<sub>2</sub> with 5% CO is a strong function of furnace temperature. The remarkable agreement between data for combustion in air at 900°C and the sodium loss results from an experiment at 500°C in 95% N<sub>2</sub> with 5% O<sub>2</sub> suggests that the effect of temperature on sodium release during devolatilization is attenuated by the presence of oxygen. The physical behavior of char during pyrolysis is also greatly affected by gas composition. Total char mass loss during pyrolysis in noncombustive environments is a strong function of furnace temperature; gas composition does not appear to have a significant effect.

Sodium loss during black liquor drying and devolatilization is probably a result of the physical transport of alkali-containing material by eruptions of water vapor and pyrolysis gases through the surface film of rapidly heated droplets. Vaporization of organo-alkali compounds may also be a source of sodium at relatively low particle temperatures.

The aerosol collected from droplet pyrolysis is similar to that formed during combustion. There also appears to be a substantial amount of particulate matter generated during the first seconds of droplet combustion.

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