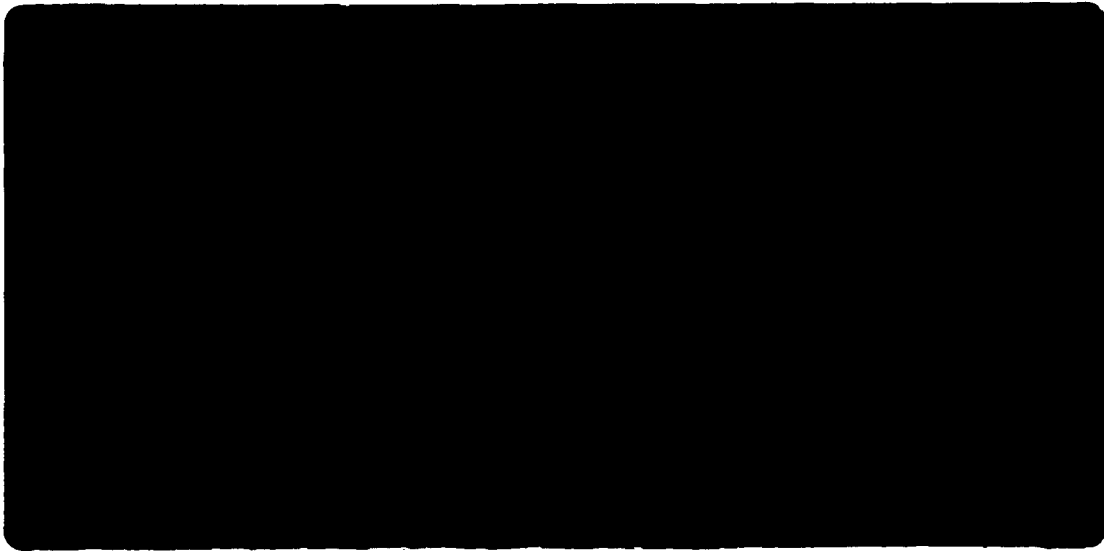*Institute of Paper Science and Technology*
Atlanta, Georgia

IPST TECHNICAL PAPER SERIES

NUMBER 404

INVESTIGATION OF FUME FORMATION DURING
PYROLYSIS OF BLACK LIQUOR DROPLETS

C.L. VERRILL AND K.M. NICHOLS

OCTOBER, 1991

INVESTIGATION OF FUME FORMATION DURING PYROLYSIS OF BLACK LIQUOR DROPLETS

by

Christopher L. Verrill and Kenneth M. Nichols
The Institute of Paper Science and Technology

ABSTRACT

Recent studies indicate that sodium evolution during devolatilization of black liquor may produce a significant amount of the fume in an operating recovery furnace. In this investigation, single droplets of industrial black liquor were exposed to a flowing gas stream of 95% N_2 with 5% CO or O_2 over a temperature range of 500 - 900°C. After 3 - 30 seconds in the pyrolytic environment, the char particles were withdrawn and quenched in a nitrogen stream. Sodium mass loss was determined from the measured amount of residual sodium in the char particles.

Approximately 10 - 20% of the sodium present in the black liquor solids is released during swelling and devolatilization of single droplets of black liquor. After swelling is complete, continued sodium release appears to occur only in non-oxidizing environments. The total amount of sodium release does not appear to be a strong function of temperature below 800°C; at higher temperatures, additional sodium may evolve as a result of thermal decomposition of Na_2CO_3. Aerosol formation during pyrolysis of individual droplets appears to be substantially less than during combustion.

Investigation of Fume Formation During Pyrolysis of Black Liquor Droplets

C.L. Verrill and K.M. Nichols

INTRODUCTION

The inorganic aerosol generated during kraft black liquor combustion is known as fume. The submicron-sized fume particles consist primarily of Na_2CO_3, with Na_2SO_4, $NaCl$, and the analogous potassium salts. Fume composition varies with location in the recovery furnace and is dependent on the conditions of combustion.[1,2] Furnace dust samples and equilibrium calculations indicate that about 10% of the sodium in the black liquor is vaporized and becomes fume.[3]

The principal benefit of fume formation is that the alkali aerosol reacts with environmentally undesirable sulfur gases in the flue gas; the resulting Na_2SO_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 boiler 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.[4] 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 atomic sodium decreases with increasing oxygen concentration.[5,6,7] 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.[8]

1

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.[9] Based on results from these studies, Cameron [10] 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.[11,12] 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.[13] Organic components of the black liquor solids begin to decompose at temperatures above 200°C and gas-phase volatiles are released.[14] 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.[13] In this report, the term **pyrolysis** refers specifically to black liquor 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.[12] 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.[14] 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 oxygen.[10]

Most previous researchers have studied fume formation only during char burning and smelt reactions. Experimental data indicate that sodium emission is continuous throughout combustion;[15,16,17] moreover, recent work has shown that sodium release during devolatilization may be a major contribution to overall fume formation.[17] 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.

EXPERIMENTAL METHODS

At the Institute of Paper Science and Technology, (IPST) a droplet furnace has been constructed to allow the dynamic collection of aerosol throughout the respective stages of black liquor combustion. Droplet combustion events are recorded by a video camera while a moving filter system simultaneously captures any generated particulate.[18] In this investigation, the equipment was modified to allow the char residue from individual droplets to be extracted though a quench stream of nitrogen. Stationary filters were used to capture the total particulate generated during pyrolysis.

Individual droplets of an industrial kraft black liquor, weighing 2 to 10 mg, were formed on nichrome wire hooks and inserted into the furnace. Three sets of pyrolytic conditions were used: 600°C and 900°C in 95% N_2 with 5% CO and 500°C in 95% N_2 with 5% O_2. The conditions were chosen to extend the temperature range that has been used in previous sodium loss studies. A constant average gas velocity in the quartz reaction chamber of 0.61 m/sec was maintained by adjusting the gas flow rate. Observation of droplet pyrolysis in the furnace was recorded on video tape.

After 3 to 30 seconds exposure to the pyrolytic environment, the char was withdrawn into the quench stream and allowed to cool. The time required to fully withdraw a droplet from the center of the reaction chamber to the quench zone was approximately 0.2 seconds. A composite sample of five fully-intact char particles was accumulated for each experiment. Each composite sample was treated by acid digestion, and inductively coupled plasma spectroscopy was used to measure the amount of sodium in the digested samples.

RESULTS AND DISCUSSION

Droplet Pyrolysis Behavior

In Figure 1, exposure time is plotted against droplet mass for a majority of the char particles formed; data from pyrolysis times of 7, 15, and 20 seconds are omitted for clarity. The maximum variation in dry solids mass for all 110 char particles falls within the range of the 30 second data. Dry solids mass was calculated from the

4

measured droplet mass and the liquor solids. To account for evaporative losses, the
solids content of the black liquor was determined periodically during the investigation.
The maximum variation in exposure time is exhibited by the scatter of the 10 second
data about the mean exposure time line.
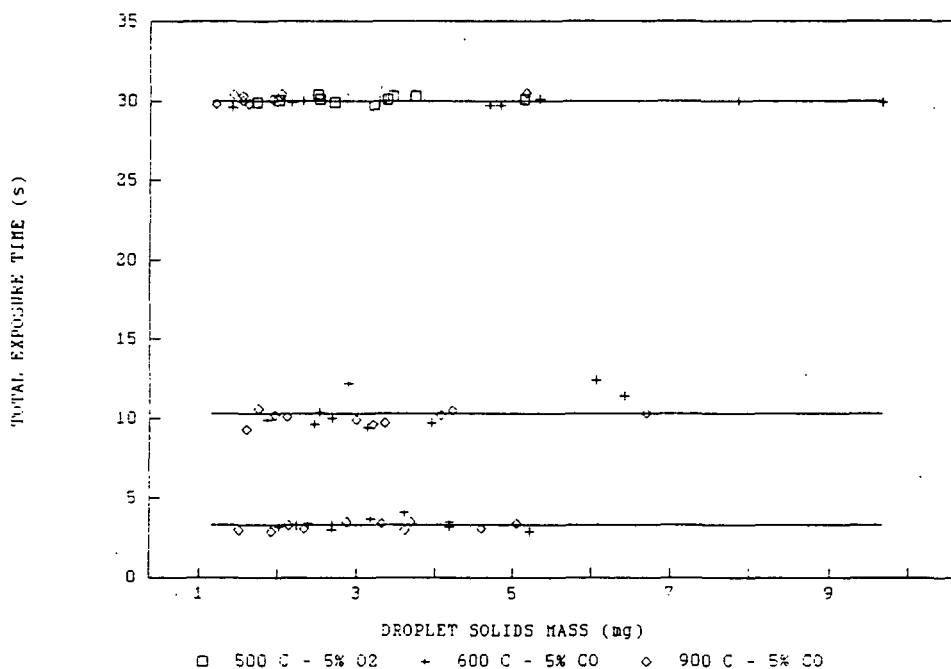
Figure 1. Control of droplet mass and exposure time

Frederick and Hupa [19] recently reported that the surface temperature of a
17 mg droplet, pyrolyzed at 800°C in 95% N_2 with 5% CO, increased from 500°C to
800°C during an elapsed devolatilization time of three seconds. Due to temperature
gradients within the droplet, the internal temperature should have increased from
approximately 200°C to about 700°C during swelling. [19] It is therefore expected that the
heating rate of a fully dried droplet in this investigation was 100 - 200°C/sec. It is
assumed that the quench procedure quickly cooled the char to below 200°C; the actual

5

heating and cooling history of liquor droplets during the pyrolysis experiments was not determined.

The elapsed times for drying and devolatilization during droplet pyrolysis, presented in Table I and Figures 2 and 3, were calculated from the elapsed time indicated on the videotapes. The first appearance of the droplet in the field of view was used to denote the start of drying; the first sign of swelling indicated the onset of devolatilization; the maximum swollen volume of the char particle marked the end of devolatilization. Simple linear regression models were used to correlate the data in Figures 2 and 3.

TABLE I. Droplet Behavior during Pyrolysis

Temperature (°C)	Gas Comp. (in N2)	Number of Droplets	Mass Solids (mg)	Drying Time (s)	Devol. Time (s)
500	5% O2	30	3.5 ± 1.3	5.8 ± 0.7	2.8 ± 0.7
600	5% CO	30	3.7 ± 1.9	3.0 ± 0.5	2.8 ± 0.9
900	5% CO	50	3.2 ± 1.3	0.9 ± 0.3	1.2 ± 0.3

The drying times, shown in Figure 2, are more dependent on furnace temperature than the swelling times plotted in Figure 3; similar results have been reported for combustion of black liquor droplets.[11] The mean swelling time for the liquor at 500°C in an oxidizing atmosphere and at 600°C in an inert atmosphere is nearly the same, as shown in Figure 3 and Table I. The effect of furnace temperature on devolatilization time in the flowing pyrolytic environment of this study is greater than
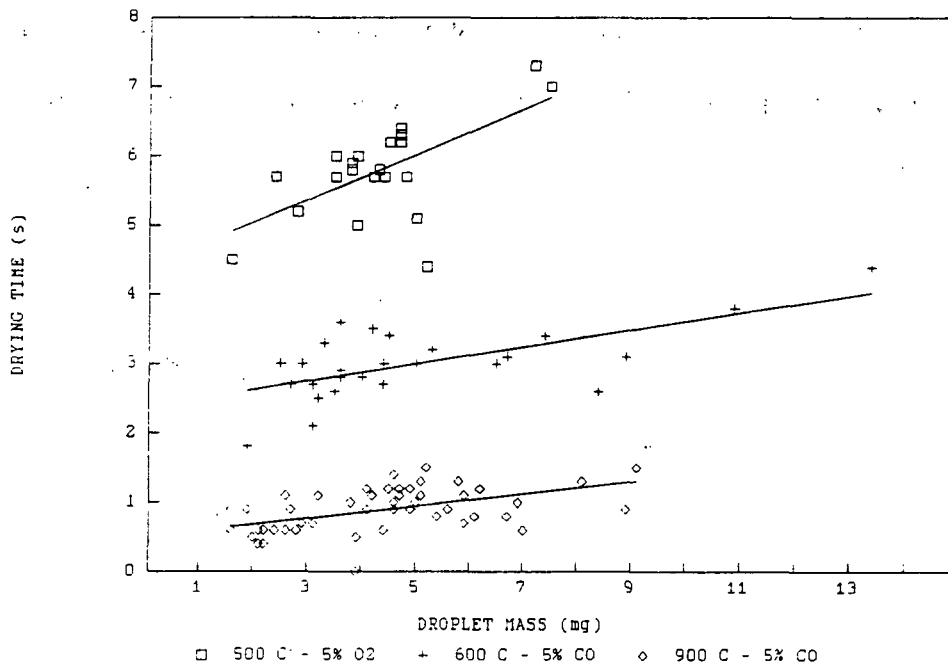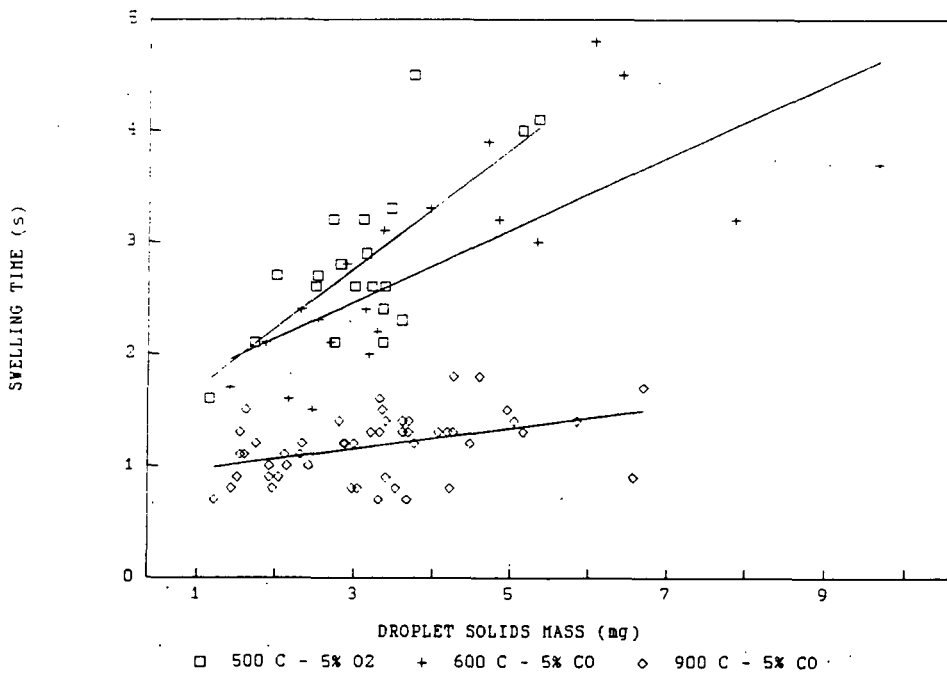
Figure 2. Drying time during droplet pyrolysis

Figure 3. Devolatilization time during droplet pyrolysis

7

that reported by Hupa et al.[11] for devolatilization in a stagnant combustive environment. In these trials, there was no combustion of volatiles surrounding the particle; therefore, there is likely to be a greater effect of the furnace temperature on the rate of devolatilization.[14]

Mass Loss During Pyrolysis

Black liquor mass loss results for the low and high temperature conditions are plotted against exposure time in Figures 4 and 5. The lines shown in these figures are not based on statistical regression. No mass loss is expected to occur until the particles are fully dry; accordingly, average drying times from Table I were used as origins of the curves presented in these figures. The apparent increase in mass during pyrolysis at 900°C (see Figure 5) is a result of partial oxidization 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 shapes of the curves for the low temperature trials, shown in Figure 4, 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_2 with 5% O_2 at 500°C was like that
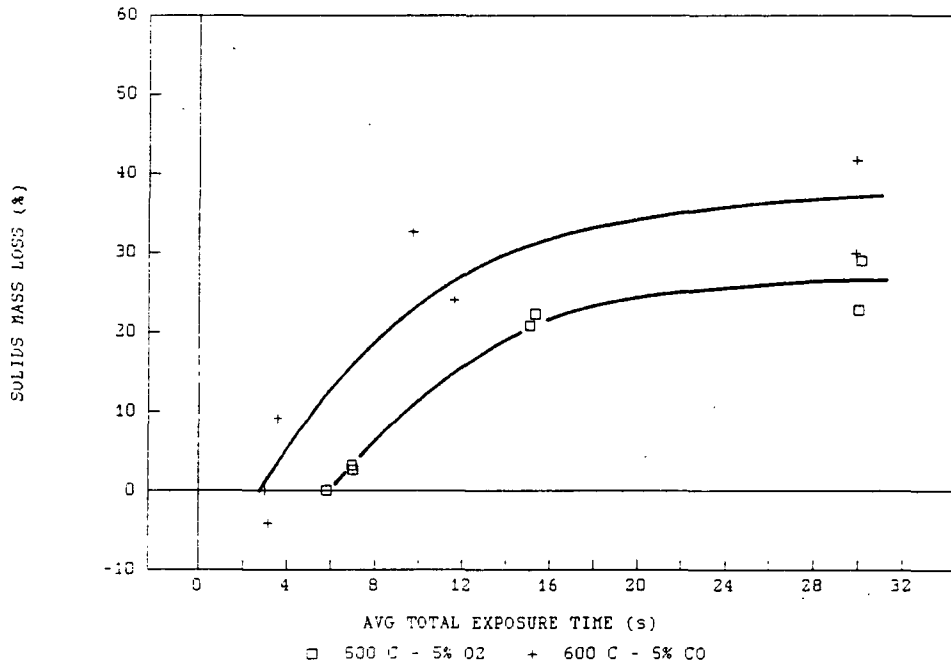
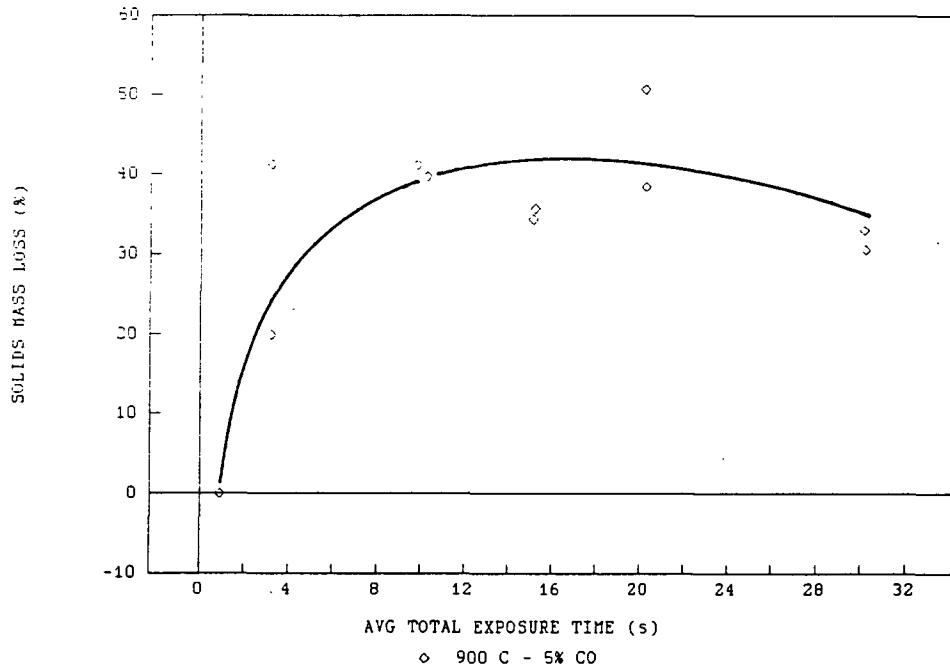**Figure 4.** Mass loss during low temperature pyrolysis

Figure 5. Mass loss during high temperature pyrolysis

9

observed during combustion at higher temperatures and oxygen concentrations.[18] These droplets underwent random serpentine expansion and formed hollow char particles with delicate but resilient external films. Particles produced in 95% N_2 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

Exit gases from the IPST droplet furnace were impacted on borosilicate glass fiber filters. Investigation of the filters from the 900°C trials by Scanning Electron Microscopy (SEM) revealed a few 10 - 15 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 products from combustion of the same liquor in air at 750°C, were not observed.[18] Due to equipment difficulties, it was not possible to determine the composition of the particulate formed during pyrolysis by energy dispersive x-ray spectroscopy; however, the SEM images provide qualitative evidence that there is less aerosol captured during droplet pyrolysis than during combustion.

Sodium Mass Loss in N_2 with 5% CO

The amounts of sodium remaining in the char during pyrolysis in N_2 and

10

CO, as a percentage of the initial black liquor solids, are plotted in Figure 6. No sodium mass loss is expected to occur during drying; therefore, origins of the curves were determined from the amounts of sodium in the dry black liquor solids and the average drying times taken from Table I. For both temperatures, there is a rapid initial loss of approximately 10 - 20% of the sodium in the black liquor solids. Frederick and Hupa[18] presented curves of similar shape in their study of sodium loss during pyrolysis of black liquor droplets in 95% N_2 with 5% CO at 700 - 800°C. An unexpected increase in the mass of sodium after long exposure to the inert environment is indicated in Figure 6. Additional experiments are needed to determine if this is a repeatable trend or an artifact of the scatter in the data.

From Figure 6, it is seen that about 18% of the sodium was evolved during the first 10 seconds of pyrolysis at 600°C, and about 24% of the sodium was evolved during the first 10 seconds at 900°C. Frederick and Hupa[18] 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[16] 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.[16] These values agree remarkably well with those of both droplet studies despite two orders of magnitude difference in the heating rates.
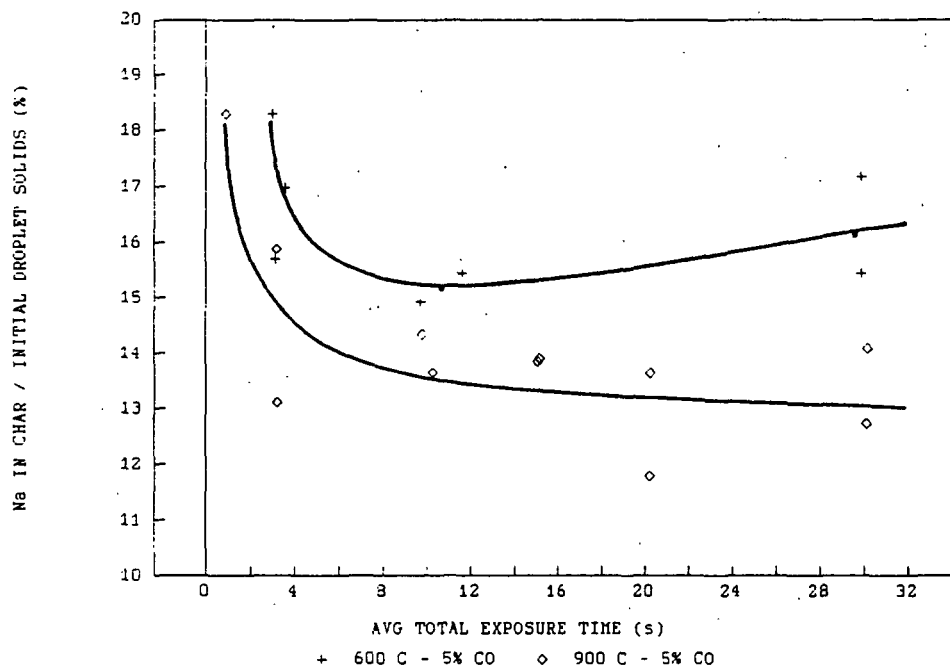
11
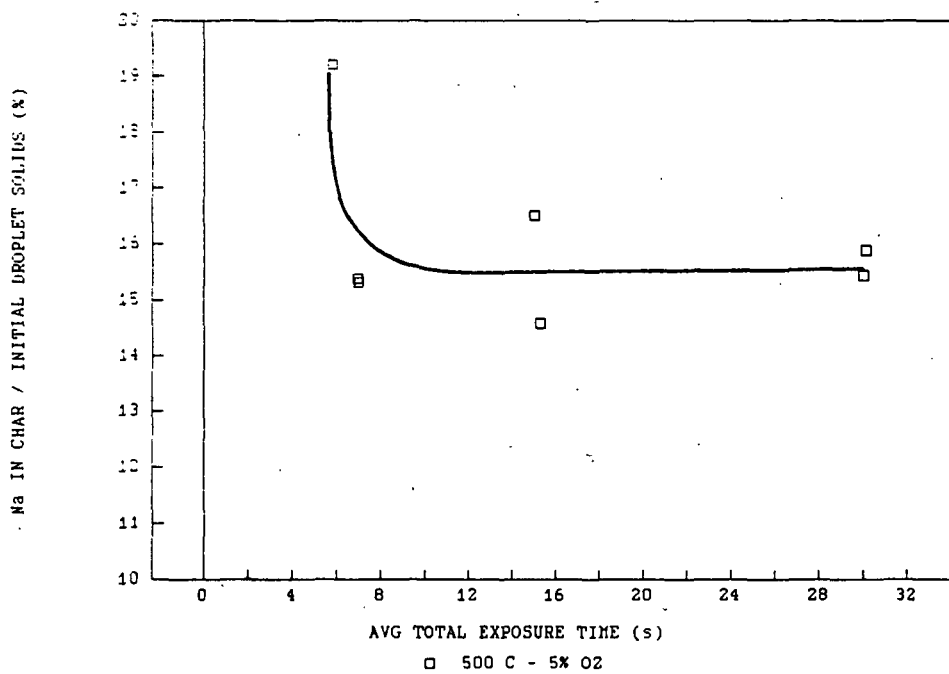
Figure 6. Sodium mass loss during pyrolysis in 95% N_2 + 5% CO

Figure 7. Sodium mass loss during pyrolysis in 95% N_2 + 5% O_2

12

Sodium Mass Loss in N_2 with 5% O_2

The amount of sodium remaining in the char during exposure to the environment of 95% N_2 with 5% O_2 at 500°C is shown in Figure 7. The sodium mass loss was approximately 20% for all char samples. This mass loss occurred abruptly, at very short exposure times; further sodium mass loss did not occur with additional exposure time. A comparison with the low-temperature data in Figure 6 reveals significant differences in sodium emission during devolatilization between inert and oxidative environments. After exposure to the low temperature oxidative atmosphere for 7 seconds, approximately 20% of the sodium had evolved from the partially swollen char. Char particles withdrawn from the inert environment at 600°C after 3 seconds had swollen to approximately the same extent, but the mass of sodium had only decreased by 11%. Within the experimental error associated with the data plotted in Figure 7, there is no significant change in sodium mass after swelling is complete.

In a similar study, Volkov et al.[15] exposed droplets of kraft black liquor to oxidizing conditions over a temperature range of 900 to 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. Depending on initial droplet diameter, 5 - 20% of the sodium mass evolved during the minimum exposure time of 3 to 6 seconds in air at 900°C.[15] This agreement with the initial sodium loss in 95% N_2 with 5% O_2 at 500°C suggests that there is little temperature effect on sodium release during devolatilization in combustive environments.

The Fate of Sodium During Devolatilization

According to Grace et al.[20] 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.[20,21] Thermogravimetric studies of kraft liquor char and model coal compounds indicate that organic alkali compounds decompose to alkali carbonate, organics, and CO_2 during pyrolysis at temperatures below 675°C.[16,22]

Based on the results of thermogravimetric analysis of sodium and potassium benzoate heated at 25°C/min in argon, Stewart et al.[22] proposed that the carbonate subsequently decomposes by reacting with carbon to form atomic alkali and CO at temperatures above 700°C. Li and van Heiningen[16] found that sodium emission from kraft liquor char started below 675°C and increased with temperature during pyrolysis in helium at a heating rate of 20°C/min. Srinivasachar et al.[23] studied sodium release from pulverized and devolatilized coal samples with atomic absorption spectroscopy; during pyrolysis at high heating rates (250°C/sec) in argon atmospheres, sodium vapor first appeared at 800°C and peaked at 1000°C.

Stewart et al.[22] reported that vaporization of alkali, in oxidizing atmospheres containing CO_2 or O_2, only occurred after all the carbon had been consumed and a temperature of 1200°C was reached. During kraft liquor char pyrolysis, the addition of CO or CO_2 to the helium environment suppressed Na_2CO_3 decomposition up to about 800°C.[16] It has been concluded that the alkali carbonate catalyzes the

gasification of residual carbon as long as reactive species are present in the gas phase.[22]

Sodium release during black liquor devolatilization is significant under a wide range of conditions. The recent findings of Frederick[17] and those presented in this report indicate there is a 10 - 20% initial loss of sodium mass during pyrolysis in non-combustive environments with either CO or oxygen present. At the minimum exposure time of three seconds, Volkov et al.[15] reported a 20% sodium loss for 2 mm diameter droplets burnt in air at 900°C. Model predictions indicate that drying and devolatilization of similar-sized droplets in air at 800°C would be complete in about three seconds;[14] therefore, it is likely that part or all of the initial sodium loss reported by Volkov occurred during devolatilization.

Based on the thermogravimetric studies, sodium emission during devolatilization must occur before all the organically bound sodium is converted to Na_2CO_3, otherwise the reactive gases will suppress carbonate decomposition until high temperatures are reached. Atomic sodium is the only inorganic species with an appreciable vapor pressure at temperatures of 450 - 700°C;[14] therefore, the sodium released during the initial period of devolatilization and swelling is likely to be in the form of atomic alkali or volatile organic-alkali compounds. In order to understand the nature of the volatile sodium compounds and the mechanism by which they evolve, additional experiments must be performed to determine the effect of liquor composition, heating rate, and other process variables on sodium mass loss during pyrolysis and devolatilization.

CONCLUSIONS

Approximately 10 - 20% of the sodium present in the black liquor solids is released during swelling and devolatilization of single droplets of black liquor. After swelling is complete, continued sodium release appears to occur only in non-oxidizing environments. The total amount of sodium release does not appear to be a strong function of temperature below 800°C; at higher temperatures, additional sodium may evolve as a result of thermal decomposition of Na_2CO_3.

Total mass loss of char during pyrolysis in non-combustive environments is a strong function of furnace temperature; the gas composition does not appear to have a significant effect. The sodium mass loss and physical behavior of char during pyrolysis is greatly affected by the gas composition. The char used for experimental studies of black liquor combustion is commonly produced by devolatilization of black liquor droplets in a high temperature stream of nitrogen and carbon monoxide. Videographic observation of liquor swelling behavior indicates that the char produced at low temperature and low oxygen conditions may be more representative of the char that remains at the end of devolatilization during combustion of black liquor droplets in a recovery furnace.

The amount of aerosols captured during pyrolysis of individual droplets appears to be substantially less than during combustion. Additional work is needed to determine the chemical composition of the particulate.

ACKNOWLEDGEMENTS

REFERENCES

1. Tran, H. How does a kraft recovery boiler become plugged? Tappi Kraft Recovery Operations Seminar Notes. Orlando, FL, January 22-27, 1989:183-191.

2. Rizhinshvili, G.V.; Kaplun, L.V. Bumazh. Prom. (1):26-28(1983).

3. Borg, A.; Teder, A.; Warnqvist, B. Tappi 57(1):126-129(1974).

4. Lang, C.J.; DeHaas, G.G.; Gommi, J.V.; Nelson, W. Tappi 56(6):115-119(1973).

5. Bauer, T.W.; Doorland, R.M. Can. J. of Tech. 32(3):91-101(1954).

6. Pejryd, L.; Hupa, M. Bed and furnace gas compositions in recovery boilers - advanced equilibrium calculations. Proceedings of the Tappi Pulping Conference. San Francisco, CA, November 12-14, 1984:579-590.

7. Shiang, N.; Edwards, L. Understanding and controlling fireside deposits in kraft recovery furnaces. Chemical Engineering Technology in Forest Products Processing, Volume 2, Crowell, B. (ed.), AIChE Forest Products Division, 1988:105-114.

8. Cameron, J.H. J. Pulp Paper Sci. 14:J76-J81(1988).

9.   Clay, D.T.; Grace, T.M.; Kapheim, R.J. Fume formation from synthetic sodium salt melts and commercial kraft smelts. AIChE Symposium Series 80(239):99-106(1984).

10.   Cameron, J.H. Chem. Eng. Comm. 59:243-257(1987).

11.   Hupa, M.; Solin, P.; Hyöty, P. Combustion behavior of black liquor droplets. Proceedings of the TAPPI/CPPA International Chemical Recovery Conference. New Orleans, LA, April, 1985:335-344.

12.   Grace, T.M.; Cameron, J.H.; Clay, D.T. Char Burning, Project 3473-6 Summary Technical Report. Appleton, WI, The Institute of Paper Chemistry, 1985.

13.   Frederick, W.J. Combustion Processes in Black Liquor Recovery: Analysis and Interpretation of Combustion Rate Data and an Engineering Design Model. Report No. One for U.S. Dept. of Energy, DOE/CE/40637-T8 (DE90012712), March, 1990.

14.   Adams, T.N.; Frederick, W.J Kraft Recovery Boiler Physical and Chemical Processes. The American Paper Institute, New York, 1988.

15.   Volkov, A.D.; Evseev, O.D.; Ibatullina, R.I.; Dravolina, E.I. Mezhuz. Sb. Nauchn. Tr. Ser. Khim. Tekhol. Tsellyul. (7):72-75(1980).

16.   Li, J.; van Heiningen, A.R.P. Tappi 73(12):213-219(1990).

17.   Frederick, W.J.; Hupa, M. Tappi, in press (1991).

18.   Verrill, C.L. Inorganic Aerosol Formation During Kraft Black Liquor Droplet Combustion. Ph.D. thesis in progress. Atlanta, GA, The Institute of Paper Science and Technology, 1991.

19.   Frederick, W.J.; Hupa, M. Combustion characteristics of spent pulping liquors: recent experimental findings. Presentation at the Nordic Workshop on Combustion of Biomass, Trondheim, Norway, February 27, 1991.

20.   Grace, T.M.; Sachs, D.G.; Grady, H.J. Tappi 60(4):122-125(1977).

21.   Alén, R.; Sjöström, E. Utilization of black liquor organics as chemical feedstocks. Proceedings of the 6th Annual International Symposium on Wood and Pulping Chemistry. Melbourne, Australia, April, 1991:357-360.

22. Stewart, G.W.; Chakrabarti, A.; Moore, W.R. Reactions of alkali containing species in combustion streams. USDOE Proceedings: High-Temperature, High-Pressure Particulate and Alkali Control in Coal Combustion Process Streams. Science Applications, Inc., McLean, VA, 1981:275-300.

23. Srinivasachar, S.; Helble, J.J.; Ham, D.O.; Domazetis, G. Prog. Energy Combust. Sci. 16:303-309(1990).