# Evidence of sodium fuming during pyrolysis of black liquor

**William J. Frederick and Mikko M. Hupa**

Dept. of Chemical Engineering, Abo Akademi University, SF-20100 Turku, Finland

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Small, submicron (0.1–1 $\mu$m) particles of sodium salts, generally referred to as "fume," play an important role in kraft recovery boilers by acting as a trap for sulfur dioxide. Fume also contributes to the formation of deposits, particularly in the cold end of the boiler bank and the economizer section. Neither the mechanism of fume formation nor the relative amount formed during the various stages of black liquor combustion is well understood.

Various researchers have attempted to predict the amount of fume formed or to describe the mechanism of sodium volatilization that leads to fume formation. Borg *et al.* (*1*) and Pejryd and Hupa (*2*) used a chemical equilibrium approach to estimate the fume content of gases in the lower furnace. Cameron (*3*) showed that sodium can be volatilized by a mechanism involving the oxidation of $Na_2S$ in the smelt.

A critical observation regarding the fume content of the gases in recovery boilers is the fume's relatively low sensitivity to temperature (*4*). This lack of temperature sensitivity is not consistent with any of the mechanisms proposed for fume formation. On the basis of thermodynamic equilibrium, for example, one would predict a nearly exponential increase in fume content with increasing temperature (*1, 2*). The data of Cameron indicate that the rate of fume formation doubles with a temperature increase of 110°C for smelt temperatures near 1000°C (*5*). Both the equilibrium approach and Cameron's results point to a higher increase in fume content than observed with an increase in temperature in recovery boilers.

Nearly all of the experimental work on fume formation has been focused on sodium release from smelt or sodium release during char burning. There has been relatively little consideration given to sodium release during devolatilization of black liquor prior to char combustion. In those studies in which measurements were made during devolatilization, there is evidence that some sodium may be released during devolatilization (*6, 7*).

Here, we present new experimental findings which indicate that sodium release during black liquor devolatilization is an important and perhaps the dominant mechanism of sodium fume formation.

## Experimental procedures

Sodium loss from black liquor during pyrolysis was measured using a single droplet technique (*8*). Droplets of black liquor weighing from 8 mg to 20 mg were pyrolyzed in a laboratory muffle furnace. The furnace was enclosed in a container to isolate it from the ambient gas environment. The container was purged with 95% $N_2$ and 5% CO during the experiments.

The droplets were suspended on a platinum hook, lowered into the furnace, and allowed to remain there for 5–60 s. The pyrolyzed droplets were removed, were cooled in a nitrogen purge, and were weighed and analyzed for sodium content. The experiments were recorded videographically to obtain the elapsed time for devolatilization.

The experiments were conducted at furnace temperatures of 700°C and 800°C with seven different liquors. The initial dry solids content of the liquors was adjusted to 60% prior to pyrolysis.

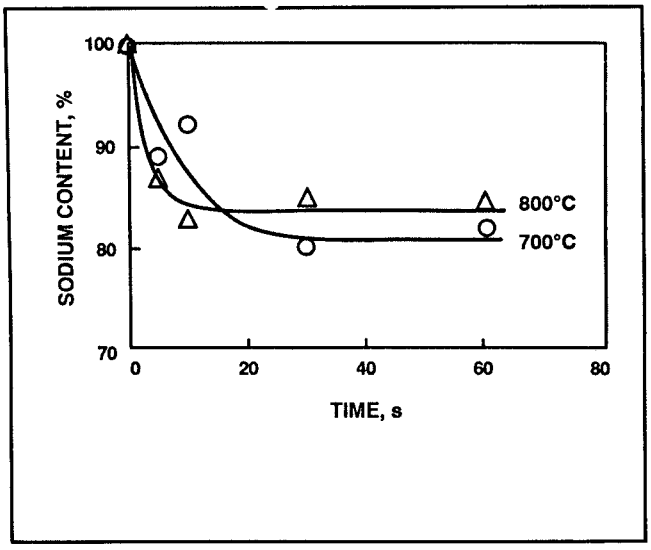
## Results

**Figure 1** shows how the sodium content in the char residue varied with exposure time for the pyrolyzed droplets. At both temperatures, the sodium content, expressed as a percentage of the initial sodium mass of the droplet, decreases to 80–85% of the initial sodium content and then becomes constant after pyrolysis is complete.

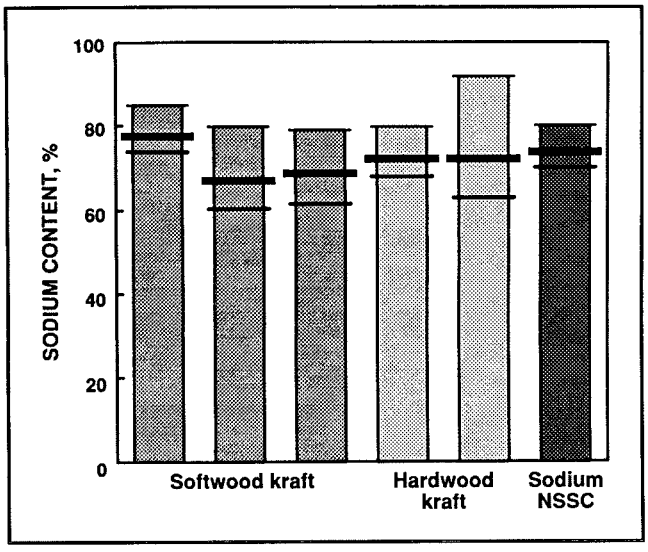
We measured the time to complete devolatilization in these experiments by observing the time to maximum swelling of the droplets in the furnace. Devolatilization was complete in 6–11 s for droplets pyrolyzed at 700°C and was complete in 4–8 s at 800°C. The time depended primarily on the droplet mass. In a gas environment of $N_2$ and CO, pyrolysis occurs, but further combustion reactions, such as char burning and smelt reactions, do not occur. Therefore, these data indicate that 15–20% of the sodium is lost during pyrolysis of this liquor at these conditions.

The sodium loss during pyrolysis is similar for the seven liquors of three different types that we tested. For the other six liquors, **Fig. 2** shows the residual sodium content after 10 s of exposure at 800°C in the $N_2$ and CO atmosphere. The data are averages for 4–5 droplets per liquor. The heavy horizontal lines indicate average values, and the light lines indicate the ranges of values obtained. For the six liquors shown, the average sodium loss during pyrolysis is 23–33% and is not strongly dependent on the liquor type. There is no correlation between

1. The amount of sodium retained in the char residue over time, expressed as a percentage of the initial sodium mass of the droplet, or of the sodium initially in the black liquor solids




2. The amount of sodium retained in the char residue after 10 s, expressed as a percentage of initial sodium. (Sodium-NSSC denotes a sodium-base neutral sulfite semichemical liquor.)




I. Sodium fume yield in kg of black liquor solids during pyrolysis, char combustion, and gasification

| | *Sodium fume yield, g Na/kg* | *Temp., °C* | *Gas composition* |
|---|---|---|---|
| Pyrolysis | | | |
| Fast | 30-60 | 800 | 95% $N_2$, 5% CO |
| Slow | 33 | 800 | Helium |
| Char burning | 0.01 | 954 | 13% $O_2$ |
| Char gasification | 3 | 750 | 20% $CO_2$, 10% CO, 70% He |

the sodium loss during pyrolysis and the total sodium content of the liquor.

## Discussion

The data show that a substantial amount of sodium is lost from black liquor during pyrolysis. The sodium loss during pyrolysis is enough to account for all of the precipitator catch in recovery boilers. This finding does not mean that fuming cannot occur during the other stages of combustion but only that the rates may be lower during those stages.

The leveling off of sodium content with time (Fig. 1) is also seen in the data of Li and van Heiningen (*6*). In their nonisothermal, slow-pyrolysis data, the sodium in the liquor residue decreases as pyrolysis proceeds, remains constant between 725° and 750°C, and finally begins to decrease rapidly at higher temperatures. The plateau in the amount of sodium retained probably occurs because pyrolysis is complete by the time it reaches 725°C; this temperature is consistent with measured droplet temperatures during devolatilization (*9*). The increasing sodium loss above 750°C may arise from $Na_2CO_3$ decomposition after pyrolysis is complete (*6*).

**Table I** shows the yield of sodium fume during different stages of combustion as taken from published data. The sodium fume yield during fast pyrolysis is based on our results in this study. The yield during slow pyrolysis is based on the data of Li and van Heiningen (*6*) over temperatures ranging from 200°C to 725°C, at which pyrolysis is expected to be complete (*9*). The sodium fume yield during slow pyrolysis is about the same as our observed yield during devolatilization.

The sodium fume yield during char burning is based on Cameron's work, in which small quantities of char were burned in a large molten salt pool. The yield may be low because of mass transfer limitations in the experimental system. The yield during char gasification is based on Li and van Heiningen's data; it may be high because of the extended duration of the experiment (35 min). The results in Table I indicate that at least ten times more sodium fume is formed during devolatilization than during the other stages of combustion.

The amount of sodium released during pyrolysis in our experiments is not strongly dependent on temperature, as indicated by the data in Fig. 1. This finding is consistent with the relationship between fume yield and temperature as observed in operating recovery boilers.

A recent study on the release of mineral matter during coal devolatilization (*10*) provides additional support that substantial metal release occurs during devolatilization of carbonaceous fuels. The work indicates that organically bound metals are carried away with the pyrolysis products during devolatilization and that the rate of metal release increases with increasing heating rate. The amount of sodium released in our study is perhaps by coincidence similar to the results of Baxter *et al.* (*10*), who found that up to 17% of the titanium in coal was released during rapid devolatilization.

The mechanism of metal release

during devolatilization is not understood. We are continuing our research to elucidate the mechanism.

## Conclusions

A substantial quantity of sodium fume is formed from black liquor during pyrolysis. The amount is enough to account for the sodium in the precipitator catch in recovery boilers. Based on the limited data available, the total fume yield during devolatilization is at least ten times higher than during other stages of combustion.□

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