Dust and flue gas chemistry during rapid changes in the operation of black liquor recovery boilers: Part 1—Dust formation

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ABSTRACT: This paper is the first part in a series of papers concerning dust and flue gas chemistry in kraft recovery boilers. For this study, we wanted to shed new light on the formation mechanism of fume and gaseous emissions measured during dynamic changes in boiler load at mills. This paper describes the test procedures and presents the results of dust formation. We paid special attention to the relative importance of the fume produced from the burning black liquor droplets versus the fume volatilized from the char bed. For the first time in this study, quantitative on-line data are available on the amount of particulate formed during char bed burning, as the liquor spraying was totally interrupted for a few minutes.

Application: The work adds insights on dust formation in kraft recovery boilers and demonstrates the possibility an on-line dust monitoring system.

Recovery boiler performance and flue gas chemistry have been widely studied by modeling the boiler operation [1-5] and by performing test runs in full-scale facilities [6-9]. These mill studies are usually performed in a steady state operation. The change in boiler operation is always a sum of changes of many operational parameters. In our full-scale studies, we managed to distinguish the effect of each parameter on boiler operation by changing rapidly only one or a few operating parameters while maintaining others constant. These transient tests give information on dynamic changes of a combustion process in a real boiler. We measured the effects of the rapid tests on flue gas composition with advanced on-line measurement techniques.

The current consensus of fume formation theories is that there is minimal vaporization of sodium during the pyrolysis and volatile burning stages of black liquor combustion, and that most of the sodium vaporization that leads to fume formation occurs during char burning [10-12]. The char burning can occur on the surface of the char bed or in the black liquor droplets that are burned in-flight [11, 13]. The proportion of fume formed from black liquor droplets or from the surface of the char bed is unknown.

This work describes full-scale measurements in two kraft recovery boilers during rapid changes in boiler load. The purpose of these studies was to shed new light on the formation mechanism of fume and gaseous emissions in recovery boilers. We used a novel on-line dust analyzer in these measurements to study dust behavior continuously during boiler operation. We were especially interested in the relative importance of the fume produced from the burning black liquor droplets versus the fume volatilized from the surface of the char bed. In a special test, we completely interrupted the liquor spraying for a few minutes in both boilers to study the formation of fume from the bed.

This paper is the first in a series of papers concerning dust and flue gas chemistry in kraft recovery boilers during dynamic changes in boiler load. This paper describes the test procedures in the mills and presents the results of dust formation. The second part will present dust composition results, and the third part will concentrate to gaseous emissions, especially NOx formation.

METHODS

Recovery boilers

For this study, we took measurements in two Finnish kraft recovery boilers. Both boilers have decanting floors, and the black liquor is sprayed to the furnace through splashplate nozzles. Combustion air is distributed through three air registers in boiler A (primary/secondary/tertiary). In boiler B, the secondary air is divided into two separate levels, so that there are four air registers (primary/lower secondary /upper secondary /tertiary).

Table I summarizes typical performance characteristics for these boilers. In these tests, the boilers were firing softwood liquors. **Table II** shows the elemental analysis of the black liquors.

Description of measurement systems

An on-line recovery boiler dust analyzer (RBD analyzer) measured the amount and composition of flue gas dust from kraft recovery boilers. We obtained measurements from the flue gas duct just before the flue gas enters the electrostatic precipitators. In that location, the dust in flue gases is mainly submicron fume.

The on-line dust analyzer operates by dissolving the flue gas dust sample in water and analyzing the flowing water sample potentiometrically for ion concentrations. The analyzer gives the total dust concentrations (g/Nm^3, dry gas) in the flue gases and the sodium, potassium, and chloride concentrations (as weight-%) in the dust. The operating principle of the analyzer is described in detail elsewhere [14, 15].

We measured gaseous emissions using standard on-line analyzers (see **Table III**) and collected dust samples with a 13-stage low-pressure impactor for chemical analysis in different particle size fractions. We also measured particle size distribution on-line with an ELPI-analyzer (electrical low-pressure impactor). All sampling probes of this on-line analyzing equipment were placed in the same flue gas duct, upstream from electrostatic precipitators.

	BOILER A	BOILER B
Load [tons ds/day]	2100-2200	3200-3300
BL dry solids [%]	71-74	78-80
Steam production [kg/s]	71	118
Temperature [°C]	480	490
Pressure [bar]	80	92
BL spraying conditions		
Temperature [°C]	124	135
Pressure [bar]	1.3	1.1
Residual O_2 before precipitator full load [% O_2]	4-6	2.5
Air distribution [%] [primary/secondary/tertiary]	30/44/26	21/49/30
NOx emissions [mg NO_2/Nm^3]	230-250	150-180
Black liquor	hardwood/softwood	softwood
BL Spray nozzles	splashplate	splashplate
Floor	decanting	decanting

I. General information of recovery boilers.

ON-LINE MEASUREMENT	METHOD
Total dust and dust composition (Na,K,Cl)	Dekati Recovery Boiler Dust-analyzer (RBDA)
Particle size distribution of dust	Dekati Electrical Low Pressure Impactor (ELPI)
O_2-concentration	H&B Magnos 16-paramagnetic O_2 analyzer
CO	H&B Uras 3 G -IR-analyzer
SO_2	Monitor Labs Model 8850-fluorescence analyzer
TRS	Monitor Labs Model 8850-fluorescence analyzer
	Monitor Labs Oxycon 8875 A TRS ⇒ SO_2 convert.
NOx	Monitor Labs Model 8840-chemiluminesence-analyzer
HCl	GASMET -FTIR-analyzer

III. On-line flue gas analyzers

The automatic data collection systems of the mills continuously collected the process data of the boilers during the tests. The collected process variables were one minute's average values, whereas the on-line analyzers saved the measured values every 10 seconds.

Table III shows the on-line analyzing equipment used in this work.

EXPERIMENTAL

Boiler and data treatment tests

To reduce the boiler load, we removed liquor guns; to increase the load, we replaced liquor guns. The spraying of black liquors remained constant during each test. In other words, we changed the load by changing the number of black liquor droplets introduced to the boiler. In a special test, we completely interrupted the liquor spraying for a few minutes in both boilers. The sootblowing was not operating and the boilers were controlled manually during the tests. **Table IV** summarizes the test procedures in the mills.

The purpose of these dynamic tests in boiler operation was to learn more about the relationships between operating parameters and formation of fume and gaseous emissions. In addition, for the first time, the dust amount and composition were measured continuously and in real time.

Test 3 (total interruption of black liquor spraying) included firing 4-5 oil-burners before the liquor stop to ensure proper start up after the test and to maintain the temperature in the furnace. We stopped the black liquor flow suddenly for a few minutes by taking out the rest of the black liquor guns at the same time. After the test, we replaced the liquor guns. **Figure 1** shows an example of the initial measurement data of the on-line dust analyzer during test 3 in boiler A.

	BOILER A	BOILER B
Dry solids %	71.0	79.0
C %	31.8	31.0
H %	3.3	3.1
N %	0.067	0.056
Na %	20.8	20.6
K %	2.4	2.8
S %	6.1	6.3
Cl %	0.4	0.2
HHV calorimetric MJ/kg	12.65	12.67

II. The elemental analysis of the black liquors.

Normally, the combustion air was adjusted to the load during the load changes, but during the total interruption of black liquor flow the combustion air remained at the same level as with part load operation. This was for safety, to ensure the proper restart of black liquor burning after the interruption. To compare dust formation results we calculated the mass flows of dust (kg/s) during the tests in both boilers (**Fig. 2**).

These dust curves (Figs. 1 and 2) included a time lag due to the dynamics of the on-line dust-analyzer. They were treated mathematically (deconvolution) to clean the measured signal from this time lag of the analyzing system. We used the data from the step response tests of the analyzer in the calculations. These mathematical tests showed the reduction in dust concentration was extremely rapid ($\tau < 20$ s) when the liquor spraying was interrupted.

RESULTS

Dust formation vs. boiler load

Figure 3 shows the results of dust load in the flue gases against the number of black liquor guns operating and the dry solids load [BLS kg/s] of boiler A and B. In the full load (boiler A: 2100 metric ton BLS/day and boiler B: 3300 metric tons BLS /day) the amount of fume in the flue gases was 6-8 wt-% of the black liquor dry solids load (60-80 g dust/kg BLS). The zero point [BLS kg/s=0] shows the formation of fume from the surface of the char bed during the total interruption of black liquor flow.

Figure 4 shows the combined data

TEST	BOILER A	BOILER B
Test 1 - Full load→Part load	8 BL guns→6 BL guns	10 BL guns→8 BL guns
Test 2 - Repetition of Test 1	8 BL guns→6 BL guns	10 BL guns→8 BL guns
Test 3 - Stepwise reduction Full load→part load→full stop	8 BL guns→5 (+4 oils)→0 BL guns	10 BL guns→8 (+5 oils)→0 BL guns
Test 4 - Start up after a shutdown	—	1 BL gun→2→4 BL guns

IV. Test procedures in different tests were boiler load was changed.

from both boilers and dust formation trendlines as a function of boiler load. The amounts of dust in flue gases and the boiler load showed clear dependency. The more liquor droplets introduced to the furnace, the more dust was formed. The equations of the trendlines are second order polynomial.

Figure 5 shows the results when the mass flow of dust and the BLS flow are normalized against the floor area of the boiler (boiler A: 104 m^2, boiler B: 164 m^2). Due to normalization, the furnace liquor loading (BLS g/s per m^2) of both boilers are now relative to each other and the dust formation is comparable. Although the boilers were different sizes, the dust formation per square meter of floor had exactly the same trend. At the full load (240 g BLS/s per floor m^2) the dust formation averaged 15 g/s per square meter of floor.

During the rapid interruption of black liquor flow (BLS=0 in Figs. 4 and 5) the fume release from the char bed was 100 g/s in boiler A and 200 g/s in boiler B. The fume release per floor square meter was aproximately 1 g/s per floor m^2 (960-1200 mg/s m^2)(**Fig. 6**).

DISCUSSION

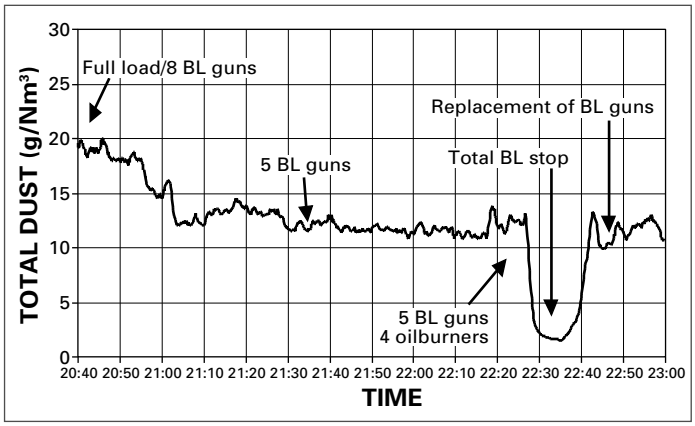
We found it interesting that in these tests the formation of fine dust behaved in such a similar way in both boilers.

One reason for the similar formation of dust may be the way in which the load changes were made: the number of black liquor guns operating was changed and the particle size distribution of liquor drops was kept constant. Both boilers were firing softwood liquor with similar composition in these tests, and the liquors were sprayed through splashplate nozzles. Although the dry solids concentrations of the black liquors were different (in boiler A: 71%-74% and boiler B: 78%-80%), we operated both boilers so that the liquor drops were sprayed into the furnace as quite coarse droplets falling directly on the bed surface and not on the walls.

When we suddenly interrupted the black liquor flow, the fume formation decreased rapidly (in about 20 s). The release of fume from the char bed was 100 g/s in boiler A and 200 g/s in boiler B. This was 1 g/s per square meter of floor area in both of the boilers and 5%-10% of the total dust formed during full load operation (see Figs. 4 and 5).

The fume formation results from rapid load changes and liquor interruption tests indicate that most of the fume (about 90%-95%) was formed from in-flight burning of black liquor droplets. Only a small part (about 5%-10%) originated in the char bed.

Temperature plays an important role in the chemistry of fume formation. Sodium volatilization (which leads to fume formation) rises with temperature on the char bed surface, or in the lower part of the furnace [16]. Tavares et al., for example, reported problems with interpreting char bed temperatures in their laboratory tests [17].



1. Dust concentration (g/Nm³) in the flue gases as a function of time during the stepwise reduction in boiler load and a total interruption of liquor flow (test 3) in Boiler A.

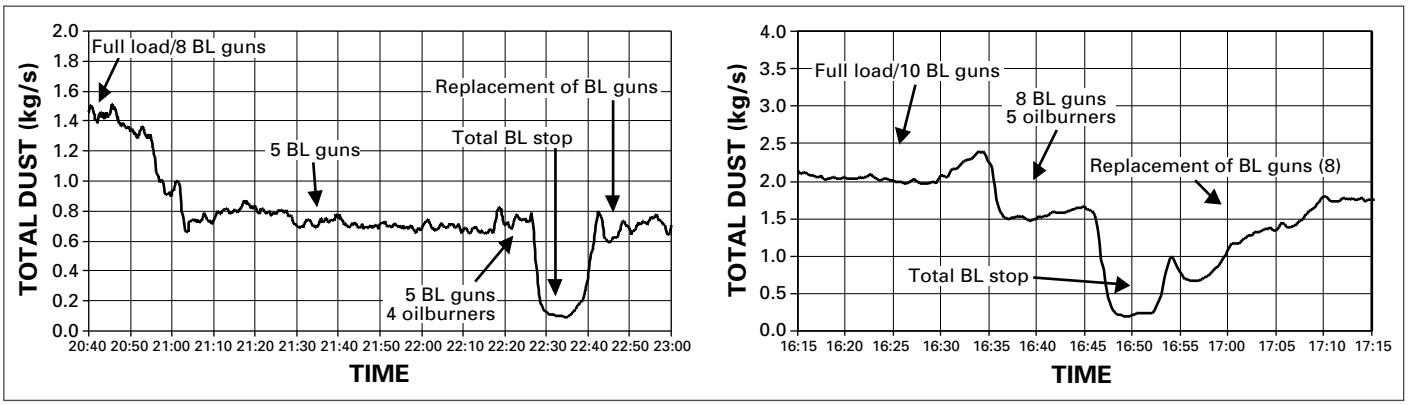
In these measurements, a reliable temperature measurement of the bed surface would have been important in estimating the role of bed temperature changes for the fuming phenomenon. We conducted the liquor interruption tests as rapidly as possible, so that the temperature of the bed surface would not have had time to decrease. We also noticed that the smelt flow continued during the interruption tests. However, we could not reliably measure the temperature of the bed surface. That is why we cannot be sure whether the fume formation from the char bed surface during liquor spraying is the same (1 g/s m^2) as obtained during the liquor stop test. However, due to a very short interruption of liquor spraying, we believe that the release of fume from the char bed surface is about the same order also with full load operation."

CONCLUSIONS

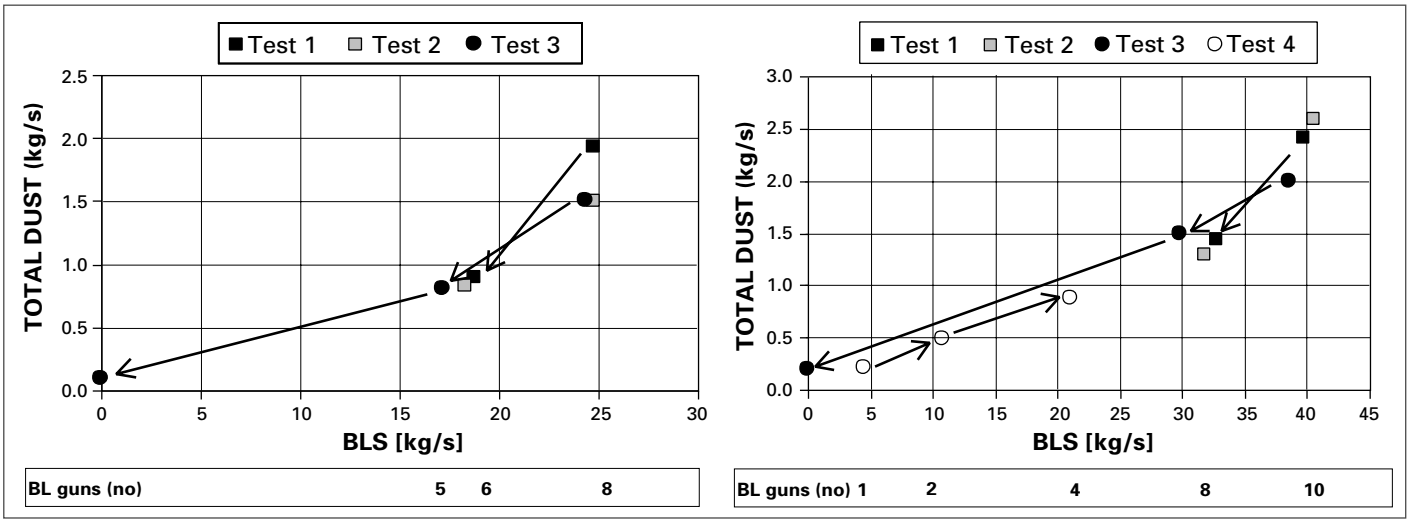
In these full scale kraft recovery boiler tests, we focused especially on the relative importance of the fume produced from the burning black liquor droplets versus the fume volatilized from the char bed. For the first time the fume released from char bed was measured on-line during the total interruption of black liquor spraying.

The amounts of dust in flue gases and the boiler load showed clear dependency. For this study, we kept the spraying pressure and the droplet size of the black liquor constant. We altered the load by changing the number of liquor guns operating. The more liquor droplets introduced to the furnace, the more dust was formed.

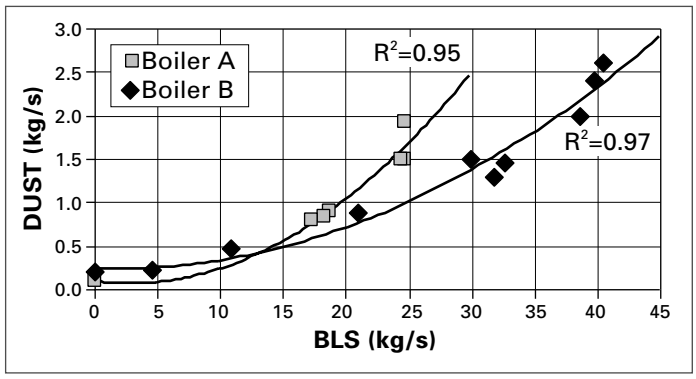
The dust formation behaved in a similar way in both boilers during the tests. The boilers were burning similar kind of softwood liquors, although the dry solids contents of the black liquors were different (boiler A: 71%-74 %, boiler B: 78%-80%).



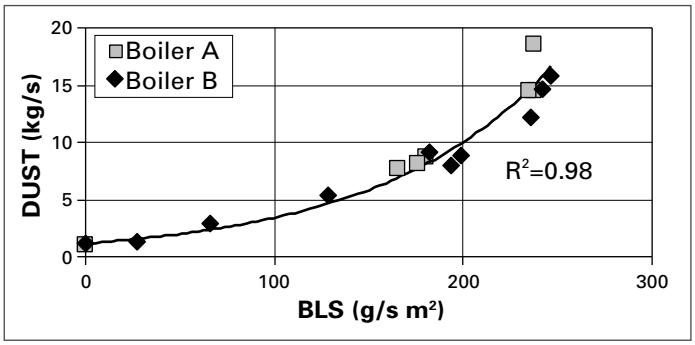
2. The mass flow of dust (kg/s) during load changes and the black liquor interruption test in boiler A (left) and boiler B (right).



3. Mass flow of dust [kg/s] against the number of black liquor guns and BLS load [kg/s]. Left: boiler A. Right: boiler B.



4. The trendlines of dust formation [kg/s] against the BLS load [kg/s] in boiler A and boiler B.



5. Dust formation per floor m² as a function of normalized BLS input (g/s per floor m²) in boiler A and boiler B.

The amount of fume formed was 6-8 wt-% of the BLS load of the boiler during full load operation of the two boilers.

The release of fume during the total interruption of black liquor flow was about 1 g/s per floor square meter of the two boilers. However, the temperature effect on fuming phenomenon is difficult to interpret in these rapid tests. Based on a very short interruption in liquor spraying, we believe the release of fume from the surface of the char bed is about the same order during full load operation. Thus, we can say that the major amount of dust (90%-95%) in the flue gases originated in black liquor droplets and only 5%-10% released from the surface of the char bed in these two boilers.

ACKNOWLEDGEMENTS

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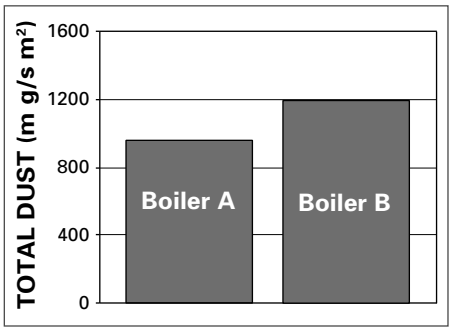
involved in boiler operation during the test runs. The National Technology Agency of Finland (TEKES), Oy Metsä-Rauma Ab, Oy Metsä-Botnia Ab, Kvaerner Pulping Oy, and Dekati Oy provided financial support.

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6. Fume release (mg/s per floor square meter) from the char bed surface during the total interruption of black liquor flow.

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INSIGHTS FROM THE AUTHORS

Recovery boiler technology requires good knowledge of dust behavior. The real time and on-line data of the amount and composition of dust in different operational conditions of a recovery boiler have been missing. Previous analysis of dust has been based on time consuming sampling and chemical analysis of dust samples in a laboratory. For the first time, we were able to monitor dust amount and composition in a continuous basis and during transients in boiler operation.

One of the challenging aspects of this research was to convince the operators to do the difficult tests (e.g., total interruption of black liquor flow), but with good collaboration and many fruitful meetings, we managed to get the best result. The collaboration with the mill operators was essential for the work.

The test where the black liquor flow was totally interrupted for a few minutes gave interesting smelt bed results. We were fortunate to have lots of on-line data from the mill operation, including files

from different air emissions, dust and its composition, and process data, but it was a challenge to work with and find the essential details from all that data. We also were surprised at how useful the on-line monitoring device could be in monitoring sootblowing [see *TAPPI JOURNAL*, 84(5): 74(2001)]. This was a new area for application of this on-line system.

The on-line dust analyzer might be a useful tool to monitor potassium and chloride behavior in individual boilers. Hopefully researchers who model recovery boiler operations and dust formation and composition find these measurement results from real kraft recovery boilers useful. The on-line signal of dust analyzer can be very helpful in monitoring and optimizing sootblowing operations.

It would be interesting to use the on-line measurement system in mills burning highly potassium and chloride rich liquors (e.g. U.S. mills) and to compare the results to those from the mills described in the papers with relatively small amounts of potassium and chloride in the liquors (Finnish mills).

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