Dust and flue gas chemistry during rapid changes in the operation of black liquor recovery boilers—Part 3: Gaseous emissions

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ABSTRACT: This is the third of three papers concerning dust and flue gas chemistry of kraft recovery boilers during rapid changes in boiler dynamics. This paper presents the results of the formation of gaseous emissions, especially NOx, during the full-scale mill trials. The purpose of these studies was to find out how the changes in boiler load effect emission formation in the two kraft recovery boilers. We were especially interested in the share of NOx produced from black liquor droplet burning in-flight versus the NOx formed by surface reactions from the char bed.

These dynamic tests indicate that all—or an absolute majority—of the NOx emissions originated in the black liquor droplets during in-flight burning. The surface reactions of the char bed played little or no role in NOx formation. NOx emissions increased linearly as nitrogen input (i.e., dry solids load) to the boiler increased. The black liquor nitrogen conversion to NOx in the flue gases was 25%–30% of the total nitrogen in black liquor solids.

Sulfur emissions (SO_2, TRS) were low or zero during full load operation of these boilers. In boiler A, sulfur emissions were sensitive to rapid changes in boiler load.

Application: The tests confirmed that NOx originate in the nitrogen of black liquor droplets burning in-flight. NOx emissions of different black liquors can thus be estimated from pyrolysis-NO in single droplet combustion tests.

Nichols et al. (1993) reported that NOx emissions in kraft recovery boilers originate almost exclusively in the fuel nitrogen [1, 2]. A minor portion can also form via prompt-NOx mechanism in the early stages of black liquor pyrolysis [3, 4]. Most of the NOx forms in the black liquor volatilization stage via ammonia (NH_3) which is oxidized to NO, and a minor part comes from the char burning stage if oxygen is in contact with the char surface [3, 5]. The char burning stage may start when the black liquor droplets are burning in-flight. It also may occur on the surface of the char bed, when droplets are forced to the bed before reaching the final burning stage. The relative share of NOx produced from in-flight burning of liquor droplets and from reactions on the surface of the char bed is not known.

SO_2 emissions are formed mainly through the oxidation of H_2S and COS in the lower furnace. The source of gaseous sulfur compounds is obviously the fuel, black liquor. High sulfidity liquors may produce higher concentrations of gaseous sulfur compounds. Temperature in the lower part of the furnace also affects the release of sulfur. If the boiler is operating at a low furnace temperature, the flue gases contain higher concentrations of sulfur gases. [6, 7]. The low temperature may be due to the low heating value of black liquor. By increasing the temperature, for example, by increasing the dry solids (ds) content of the black liquor, sulfur emissions usually decrease. When boilers are burning black liquors with high dry solids content (about 80%), SO_2 emissions are very low or even zero [8]. The SO_2 produced in the furnace reacts with sodium compounds to produce sodium sulfate (i.e. condensed fume). With high solids firing, there is enough sodium to bind all the sulfur dioxide. That is why, in a modern kraft recovery boiler SO_2 emissions are low when the boiler is running in a steady state.

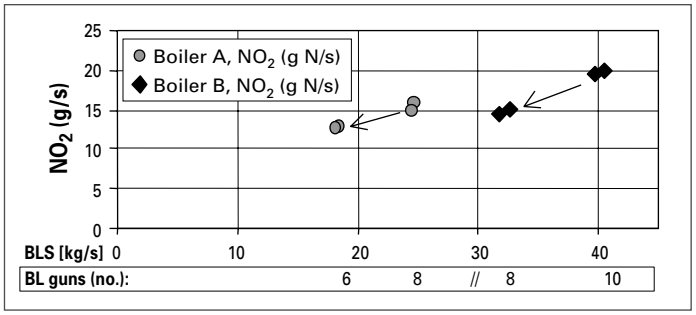
Part 1 of this series of papers presented results for dust formation during rapid changes in boiler load and described the mill test procedures [9]. Part 2 presented the results of dust composition and particle size distribution [10].

This paper (Part 3) concentrates on the formation of gaseous emissions (NOx, SO_2, TRS, and HCl) during rapid changes in boiler operation. The transient tests made in this study give information how dynamic changes that are typical in the normal operation of a kraft recovery boiler affect the formation of gaseous pollutants (NOx, SO_2, TRS, and HCl). A special issue we looked at was the relative share of NOx formed from black liquor droplets versus the NOx formed through reactions on the surface of the char bed. We investigated that when the black liquor flow was totally interrupted for a few minutes in both boilers.

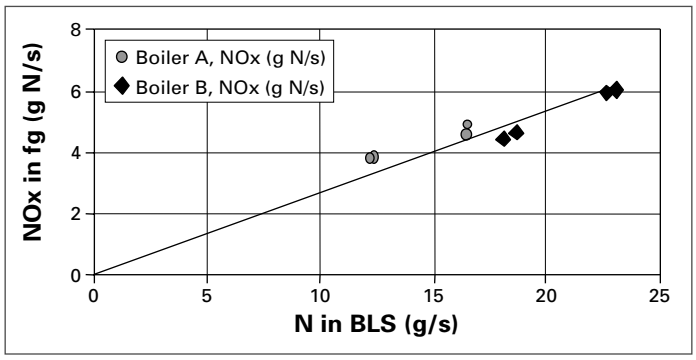
FLUE GAS MEASUREMENTS AND THE BOILERS

The flue gas composition (particulate, NOx, SO_2, TRS, and HCl emissions) was measured on-line in two Finnish kraft recovery boilers. Part I of the papers describes in detail the test procedures and the measurements.

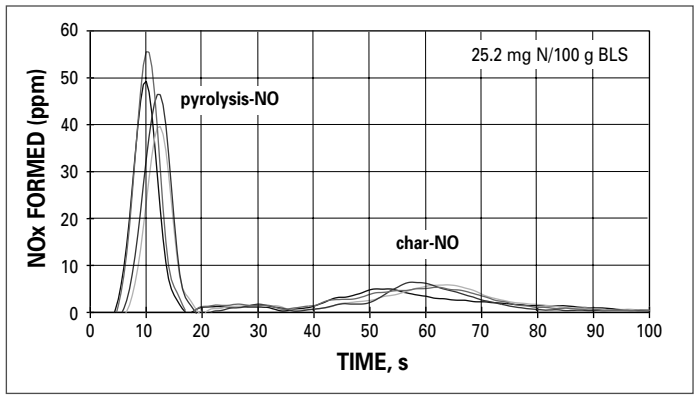
The two recovery boilers differed in size, the floor area being 104 m^2 in boiler A and 164 m^2 in boiler B. The maximum load of boiler A is 2200 metric tons black liquor solids (BLS)/day; and for boiler B is 3300 metric tons BLS/day. The black liquor burned in these tests was softwood liquor. The nitrogen content of the liquor was 0.067% N in dry solids in boiler A and 0.056% N in dry solids in boiler B, respectively. The dry solids content of the liquor was 71%-74% in boiler A and 78%-80% in boiler B.



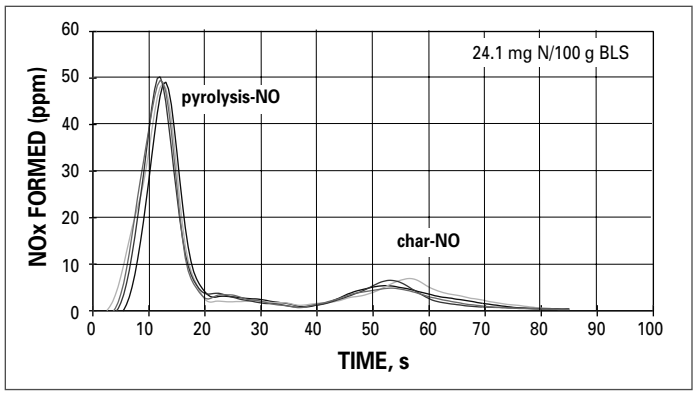
1. NOx in flue gases [g NO_2/s] as a function of boiler load.



2. NOx in flue gases [g N/s] as a function of nitrogen in black liquor dry solids (BLS).



3. Pyrolysis-NO and Char-NO formed during the single droplet combustion test. Liquor A, (4 runs).



4. Pyrolysis-NO and Char-NO formed during the single droplet combustion test. Liquor B (4 runs).

Combustion air was distributed through three air registers in boiler A (primary, secondary, and tertiary). In boiler B, the secondary air was divided into two separate levels, so that there is actually four air registers in the furnace (primary, lower secondary, upper secondary, and tertiary).

SINGLE DROPLET COMBUSTION TESTS IN LABORATORY

We also conducted laboratory studies of the NOx formation tendencies of the black liquors burned in the mill tests. In the single droplet combustion test, we burned weighted liquor droplets in a tube furnace under controlled conditions. The NO formed during combustion was measured with an on-line NO-analyzer based on chemiluminescence. The test system is described in more detail elsewhere [13, 15].

The laboratory tests compared the calculated NOx formation tendencies of the liquors to the measured NOx emissions in boiler conditions.

The single droplet combustion tests for black liquors have been developed within the Combustion and Materials Chemistry Team at Åbo Akademi University, beginning in the early 1990s [e.g. 11-14].

RESULTS AND DISCUSSION

NOx formation from droplets

In the mill tests, we changed the boiler by changing the number of black liquor guns operating and by keeping the spraying pressure constant. In that way, we changed the number of black liquor droplets introduced to the furnace, but the droplet size remained unchanged. When looking at the nitrogen chemistry, the main variable was the organic nitrogen input in the black liquor droplets.

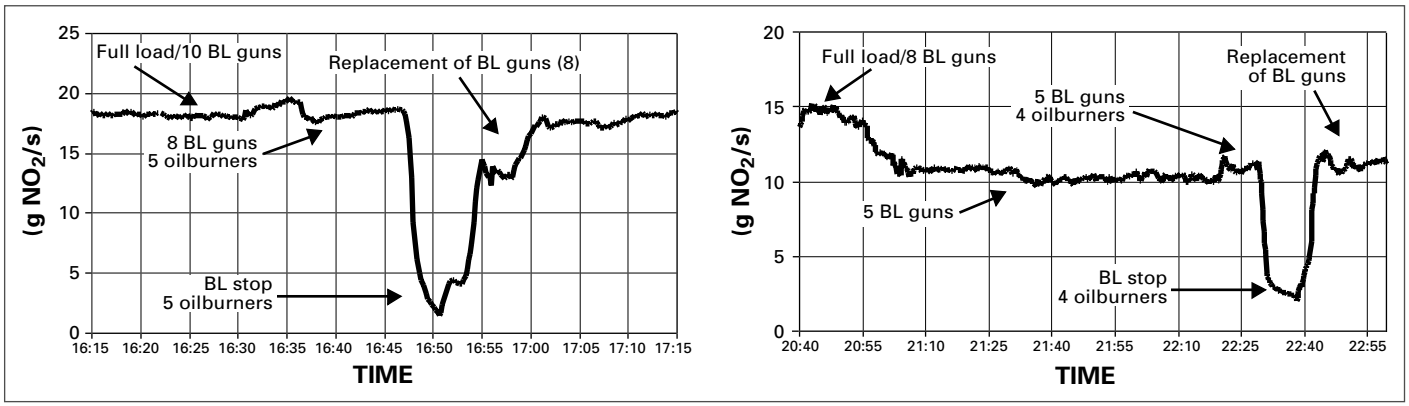
Figure 1 shows how NOx formation decreased as the boiler load was reduced by taking off black liquor guns. There was a linear dependency between the formation of NOx emissions and the nitrogen input in BLS. **Figure 2** shows how NOx emissions increased linearly with the nitrogen input in black liquor.

The results show that conversion of the black liquor nitrogen to NOx in the flue gases was 25%–30% of the total nitrogen in BLS. This is consistent with the earlier finding of Kymäläinen et al. (1999) that the total formation of NO corresponds to about one-third of the black liquor nitrogen [15].

Figures 3 and 4 show the NO formation curves of the liquors when burned in single droplet combustion tests in the laboratory. The first peak is the NO formed during the pyrolysis of the liquor (pyrolysis-NO). The second, lower peak is the NO formed during char burning (char-NO). To validate the laboratory results, we compared the NOx formation tendencies of the liquors calculated from pyrolysis-NO to the measured NOx emission.

The NOx formation tendency of liquor A (from boiler A) was 86 ppm NO (3% O_2, dry flue gas) calculated from the pyrolysis NO. The NOx formation tendency of liquor B (boiler B) was 95 ppm NO. These were compared to the measured NOx concentrations with full load operation of the boilers (boiler A: 105 ppm, and boiler B: 80 ppm, 3% O_2, dry). **Table I** summarizes the results of single droplet combustion tests.

The results show that the pyrolysis-NO in the single droplet combustion test gives a good approximation of the NOx



5. NOx emissions (g NO2/s) during load reduction and the black liquor interruption test. Small amount of oil was burned during the liquor stop tests. Boiler A (left), boiler B (right).

formation tendency of the black liquor. The calculated NOx emissions (from the pyrolysis NO) were ±20% of the measured NOx emissions. This indicates that the char-NO in the single droplet combustion test can be neglected when NOx formation tendencies of different black liquors are compared. The char-NO in boiler conditions usually ends up with the smelt as the liquor droplets fall down to the char bed before reaching the final combustion step (char combustion).

The difference in the measured and calculated NOx emissions may be due to the operating conditions of the boilers (e.g. air distribution, droplet spraying etc.). In the laboratory test, the conditions are equal for each black liquor droplet.

NOx FORMATION FROM CHAR BED SURFACE

The share of NOx produced from the surface reactions of the char bed was studied in a test where the black liquor flow was totally interrupted for a few minutes. Before the interruption, 4-5 oil burners were fired to ensure a proper restart of the black liquor firing after the test. We measured the NOx formed during the test and estimated the share of NOx produced from oil burning and from the surface of the char bed.

Figure 5 shows the NOx formation as a function of time during load reduction, followed by the total interruption of black liquor flow in both boilers. In boiler A, NOx emissions in the flue gases were 2.6 g NO_2/s, and in boiler B, 1.8 g NO_2/s as the liquor spraying was completely interrupted.

We estimated NOx emissions from oil burning from the amount and composition of oil burned and compared that to the measured NOx emissions during the tests. In boiler B, five oilburners were burning oil (four in the secondary air level and one in the tertiary level) during the liquor stop. The amount of oil burned was 4.1 metric tons/h (1.14 kg/s), and the nitrogen content of the oil was 0.3 wt-%. The measured NOx emissions (1.8 g NO_2/s) were 16% of the maximum fuel-NOx, if all the nitrogen in oil would have converted to NO_2. Expressed per energy unit of burned oil, the NOx emissions would have been 38 mg NO_2/MJ oil. This is far too low specific NOx emission for heavy oil, if burned at a normal air ratio (normally at least 100-150 mg NO_2/MJ) [16]. As the oil was burned under huge excess air (airflow was constant and adjusted to full BLS load during the test), the combustion of oil can be considered to be incomplete and only a part of oil nitrogen was oxidized to NOx.

The results indicate that all the NOx emissions originated in oil burning, and not from the surface reactions of char bed during the rapid test of liquor flow interruption. Correspondingly, the trendline in Fig. 2 is drawn through origin, indicating that the amount of NOx formed on the surface of the char bed was very small or even zero.

		LIQUOR A	LIQUOR B
Pyrolysis-NO	mgN/100g BLS	15.1	16.5
Char NO	mgN/100g BLS	10.1	7.5
NOx formation tendency (pyrolysis NO)	ppm (3% O_2, dry flue gas)	86.0	95.0
Comparison:			
NOx measured with full load	ppm (3% O_2, dry flue gas)	105.0	80.0

I. Results from single droplet combustion test.

The results also confirm that the share of black liquor nitrogen that ends up to the char bed during black liquor combustion will continue its way along with the smelt (smelt-N), as already concluded by Forssén et al. (1997), based on single droplet combustion tests in laboratory [5].

OTHER GASEOUS EMISSIONS SO_2, TRS AND HCL EMISSIONS

Sulfur emissions (SO_2 and TRS, total reduced sulfur) were low or nonexistent during full load, stable operation of the boilers. Due to high dry solids firing (boiler A 71%-74% ds., boiler B 78%-80% ds.) there was enough sodium in flue gases to bind all the SO_2 formed in black liquor combustion.

However, in boiler A, SO_2 emissions were sensitive to changes in load. During a part load operation SO_2 was purged to the flue gases. SO_2 emissions increased by the factor of 4-7 (6-13 g SO_2/s full load → 40-55 g SO_2/s part load) when the boiler load was decreased about 25% of the full load (24.5 kgBLS/s → 18.5 kgBLS/s). At the same time some momentary peaks of TRS emissions were detected, although no high, continuous TRS emissions were formed.

The result is consistent with the $S/(Na+K)_2$ mole ratio in dust which increased from 0.8 to almost unity during part load operation in the boiler A. At the same time, the carbonate content of the dust fell to almost zero. These results indicate that the operating conditions in boiler A were very near those where there is not enough sodium to bind all the sulfur and SO_2 emissions are purged. Part 2 of this series of papers discusses dust composition more fully [10].

In boiler B, no SO_2 or TRS emissions were present in the flue gases during changes in boiler load. Also, during the total interruption of black liquor flow no SO_2 or TRS emissions were found in either of these boilers. During the liquor interruption the carbonate content in dust doubled in boiler A compared to full load operation. This indicates that the in-flight release (from liquor droplets or char particles) dominates also the volatilization of sulfur.

The FTIR-analyzer provided continuous measurement of hydrogen chloride gas (HCl). We wanted to measure HCl because of the possibility that it could interfere with dust composition measurements (Cl content in dust) performed with the new on-line dust analyzer (see Parts 1 and 2 of this series of papers). As HCl is a water-soluble gas, a part or all of it can dissolve in water in the sample-taking probe of the on-line dust analyzer, together with the chloride in dust. If found in high concentrations, it affects the chloride results in dust.

In these measurements, we did not detect HCl in either boiler. The detection limit for HCl was 20 ppm (FTIR). Hydrogen chloride (HCl) emissions could not be detected even when SO_2 was present in the flue gases during part load operation in boiler A. In that situation, a part of the chloride could have formed HCl in the presence of SO_2.

CONCLUSIONS

The purpose of these studies concerning dust and flue gas chemistry during rapid changes in boiler dynamics was to find out how rapidly the changes in boiler dynamics affect emissions formation in two modern kraft recovery boilers. A further interest was the share of NOx produced from burning black liquor droplets, and from the surface reactions of the char bed.

These dynamic tests in two kraft recovery boilers indicated that all—or an absolute majority—of the NOx emissions originate in black liquor droplets during in-flight burning. The surface reactions of the char bed played little or no role in NOx formation. NOx emissions measured during the liquor stop test formed from oil burning.

NOx emissions increased linearly and simultaneously as the nitrogen input increased (i.e., as the dry solids load increased). The black liquor nitrogen conversion to NOx in flue gases was about 25%–30% of the total nitrogen in BLS, which is consistent with laboratory studies with a single droplet combustion system in Åbo Akademi University [15]. These NOx results are in agreement with the earlier findings that the liquor nitrogen content determines mostly the NOx emission levels in kraft recovery boilers [1, 2].

The single droplet combustion test with the liquors showed that the pyrolysis-NO gives a good approximation of the NOx formation tendency of the black liquor. The calculated NOx emissions (from the pyrolysis-NO) were ±20% of the measured NOx emissions. This indicates that the char-NO in single droplet combustion test can be neglected when NOx formation tendencies of different black liquors are compared. The results confirmed that the share of black liquor nitrogen that ends up to the char bed during black liquor combustion would continue its way along with the smelt (smelt-N).

Sulfur emissions (SO_2 and TRS) were low or zero in both of the boilers during stable, full load operation. The boilers burned softwood liquor with high dry solids. Especially in boiler B, sulfur emissions did not react on load changes due to very high dry solids (ds.) content in the liquor (78%-80% ds.). In boiler A, sulfur emissions were more sensitive to changes in boiler load; SO_2 emissions increased simultaneously as the boiler load was reduced. The dry solids content of the black liquor was lower than in boiler B (72%-74% ds.). Evidently, the overall conditions in the furnace (i.e., temperature, dry solids load, and air distribution) affect the sulfur and dust chemistry.

The liquor flow interruption test indicated that the in-flight release also dominates volatilization of sulfur, while the release of sulfur from the char bed plays only a minor role. **TJ**

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