NO_x reduction in black liquor combustion — reaction mechanisms reveal novel operational strategy options

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Abstract

Recovery boiler NO_x emissions originate mostly in the small amounts of nitrogen originally present in the black liquor. This paper summarizes recent research findings concerning the behavior of this black liquor nitrogen into an overall picture of the various NO formation paths in recovery furnaces. This overall description of the reactions of the fuel nitrogen reveals the key operating parameters by which NO emissions can be influenced. A major portion of recovery-boiler NO is formed from oxidation of the ammonia formed during devolatilization of the liquor droplets. Advanced kinetic modeling clearly shows that the efficiency of this oxidation is strongly dependent on the temperature and on the number of stages by which the air is mixed with the devolatilized gases. Formation of NO by this route can be minimized if the oxidation of the devolatilized gases takes place in several stages and at a relatively low temperature, preferably 850–900°C. In practice, this can be achieved by suitable adjustment of the air distribution and by introducing additional air feed levels in the upper furnace.

Another significant source for the final NO emission is the oxidation of nitrogen remaining in the char residue after the devolatilization stage. Laboratory devolatilization and combustion tests using single black-liquor droplets reveal that this char nitrogen readily oxidizes to NO if the droplets are allowed to completely burn out. However, in a recovery furnace, this complete burnout in flight typically happens only to the smallest droplets. Consequently, this NO from the char nitrogen can be minimized if the droplet size is large enough and spraying of the liquor is selected in such a way that most of the droplets reach the smelt surface before being fully burned out. In this case, the nitrogen in the char will be converted into an inorganic nitrogen compound that leaves the furnace along with the smelt.

INTRODUCTION

Nitrogen oxide emission (NO_x) from black liquor recovery boilers varies in the range of 30–120 ppm (8% O_2, dry). More than 95% of the NO_x emission is nitric oxide (NO), while nitrogen dioxide (NO_2) accounts for the rest *(1, 2, 3, 4, 5, 6, 7, 8)*. Previous recent research has indicated that a major part of the NO emission is "fuel NO," i.e., nitrogen oxide formed as a result of the oxidation of the organically bound nitrogen in the black liquor *(5, 9, 10)*. Only a minor part of the NO seems to be "thermal NO," i.e., nitrogen oxide formed by the oxidation of the molecular nitrogen in the combustion air. This is due to the relatively low temperatures in a recovery furnace *(11, 12, 13)*. Forssén *et al. (14)* have recently suggested the most important NO formation routes in black liquor combustion. The main source for the NO in the recovery furnace was suggested to be the oxidation of ammonia formed during devolatilization of the liquor droplets. Forssén *et al. (15)* also showed that a significant part of the original liquor nitrogen may leave the furnace as an inorganic compound in the smelt. The fate of this nitrogen has been a subject of recent studies reported elsewhere *(16, 17, 18, 19)*.

Very few studies have been reported concerning the influence of the various operating conditions on NO formation in the recovery furnace. Staged air supply has been referred to as one way of controlling NO emissions *(20)*. Contradicting observations have been reported for the influence of the liquor solids content. Firing higher dry-solids liquor has been reported to have both a positive *(4)* and a negative effect on the NO emission *(2, 3, 6)*.

The purpose of this paper is to summarize the research findings concerning black liquor nitrogen into an overall picture of the fuel-N behavior in recovery furnaces. This overall description of the reactions of the fuel nitrogen is then used to discuss the key operating parameters by which the NO emission can be influenced.

This paper is based on both laboratory experiments and kinetic modeling studies. Liquor pyrolysis (devolatilization) and combustion experiments were performed in a single-droplet tube reactor with a continuous gas analysis system. These studies have shed light on the influence of operating conditions on the release and conversion of black liquor nitrogen during the droplet burning process.

Kinetic modeling was used to study the influence of temperature, stoichiometry, and mixing mode on the conversion of the gas-phase nitrogen species. This model is based on a database of some 300 elementary reactions describing the conversion and oxidation of hydrocarbons in the presence of reactive nitrogen species.

In this paper, we first introduce the main reactions and routes for the conversion of the liquor nitrogen in recovery furnaces. Next, we discuss each of the key reactions separately in detail. In particular, we study the influence of various operating conditions on the yields of each of the reaction paths. Finally, we compare the nitrogen conversion and overall NO formation for four modes of furnace operation.

In this paper, we use the terms pyrolysis and devolatilization interchangeably with no difference in their meaning.

PROPOSED OVERALL PICTURE OF FUEL-NITROGEN REACTION PATHWAYS IN RECOVERY BOILERS

We will start by introducing the main reactions and routes of the conversion of black liquor nitrogen in recovery furnaces. These reaction pathways are based on recent research work at our laboratory and elsewhere. Each of the reaction pathways are then discussed in greater detail.

The significance of the different routes changes, depending on the operating conditions. Four cases are summarized in **Figs. 1–4**. In this short introductory paragraph, we only discuss the base case (Case I) in Fig. 1. Later in the discussion, we compare the four cases with each other.

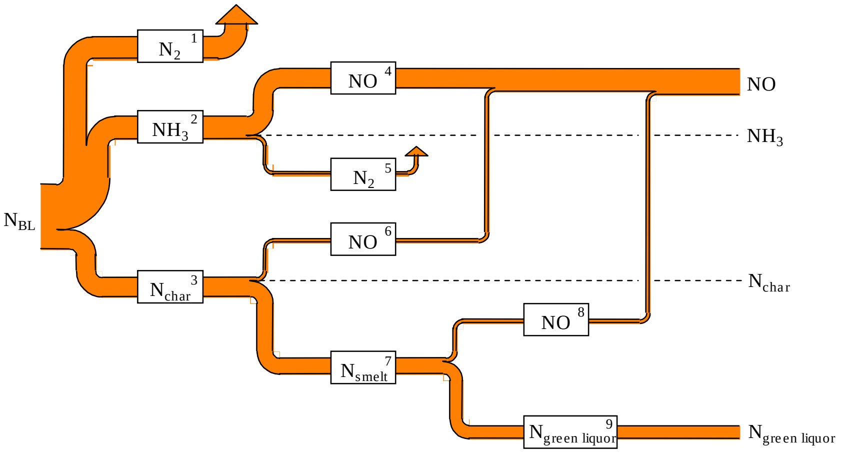

Figure 1. Proposed overall picture of fuel-nitrogen reaction routes in recovery boilers. Case I: no air staging, coarse droplets.

Figures 1–4 show the conversion of black liquor nitrogen (left) into various compounds that leave the furnace either along with the flue gases or with the smelt (right). The boxes represent the various conversion reactions. The chemical symbols on each of the boxes indicate the product of the reaction taking place in the box. The nitrogenous reactant enters the boxes from the left, and the product indicated on the box leaves the box to the right. The width of each of the lines indicates the importance of that particular route. If the reaction product is molecular nitrogen, we have "removed" it from the figure as an unreactive species (Boxes 1 and 5). The design principles of these types of reaction and flow diagrams have been previously discussed by Kilpinen and Hupa *(21, 22)*.

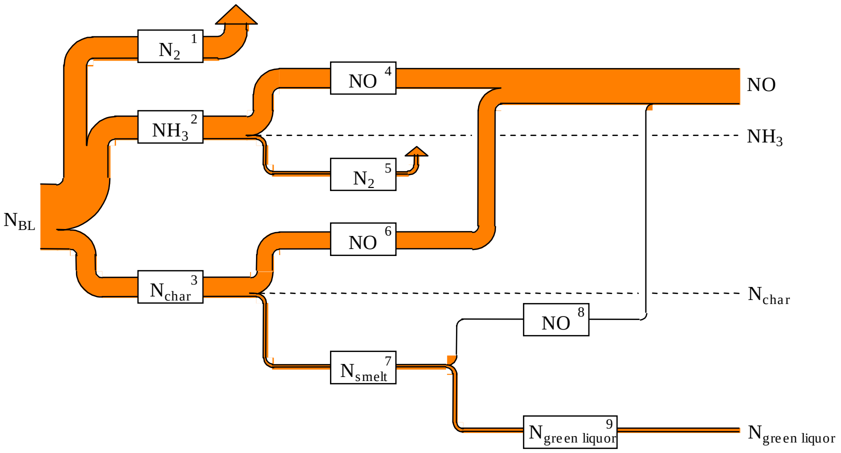

Figure 2. Nitrogen species pathway in black liquor combustion. Case II: no air-staging, fine droplets.

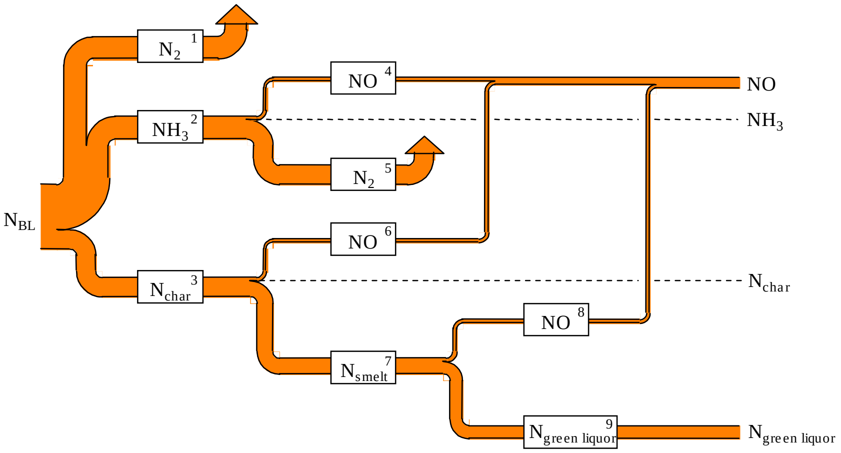

Figure 3. Nitrogen species pathway in black liquor combustion. Case III: air-staging, coarse droplets.

The first step in the burning process, the devolatilization, yields three different nitrogenous products (Boxes 1, 2, and 3). Some two-thirds of the nitrogen is released as volatile nitrogen compounds, either N_2 (Box 1) or ammonia (Box 2). The rest, roughly one-third, remains as organic nitrogen bound in the char carbon matrix (Box 3).

The ammonia formed during the devolatilization is readily oxidized to NO when the pyrolysis gases are burnt with the combustion air (Box 4). However, under certain conditions, part of this ammonia can also be converted to molecular nitrogen (Box 5). The ratio between the products NO and N_2 is dependent on the conditions under which the oxidation of the pyrolysis gases takes place. This will be discussed more quantitatively in the following paragraphs by using detailed chemical kinetic modeling.

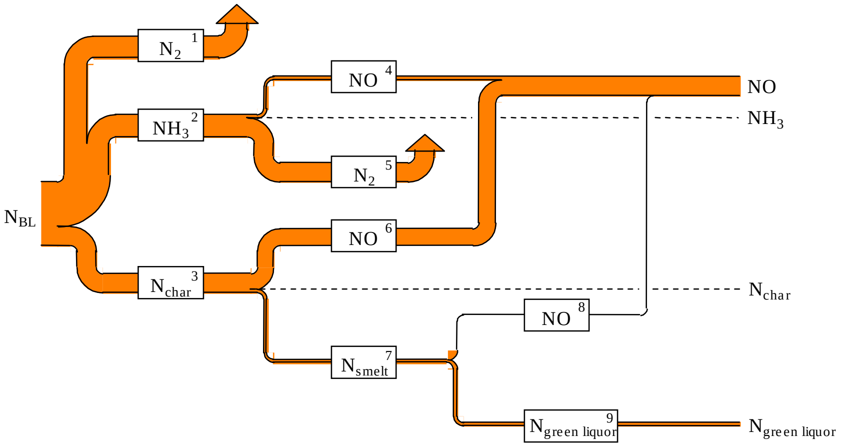

Figure 4. Nitrogen species pathway in black liquor combustion. Case IV: air-staging, fine droplets.

The char nitrogen may be oxidized to NO during the oxidation of the char residue (Box 6). However, at normal lower furnace operating conditions, a significant part of the char nitrogen will not be oxidized to NO. Rather, it will be converted from the organic carbon matrix to an inorganic salt and remain in the smelt residue (Box 7).

This smelt nitrogen can then be partly oxidized to NO if the smelt residue has contact with oxygen (Box 8). However, if the smelt is maintained under reducing conditions, this smelt will be removed from the recovery furnace along the smelt spout into the dissolving tank and the green liquor (Box 9).

For the base case described in Fig. 1, the main part of the NO in the final flue gases will originate in the ammonia released from the liquor droplets during the devolatilization stage. Some minor contribution comes from the oxidation of the char residues or the smelt. A significant fraction of the original liquor nitrogen will leave the furnace along with the smelt.

Liquor nitrogen release during devolatilization (Boxes 1, 2, and 3)

Black liquors contain typically around 0.1 wt.% nitrogen, which is an order of magnitude less than the nitrogen content in conventional fuels, such as coals. The nitrogen is mainly in an organic form *(23, 24)*. Accurate liquor nitrogen analysis has proved to be difficult to perform because of the constraints in the commonly used fuel-nitrogen analysis methods. Our recent comparisons using three different methods indicated that the traditional Kjeldahl nitrogen analysis showed that the level of nitrogen for most kraft liquors varies between 0.05 and 0.15 wt.% of dry solids *(14, 25, 26)*. These differences will have an effect on the formation of recovery boiler NO_x emission.

During the devolatilization stage (pyrolysis stage), the organic matrix of the black liquor is thermally degraded, and a significant fraction of the organic nitrogen is released as gaseous species (Boxes 1 and 2). The first studies by Aho *et al. (9, 10)* indicated that 60–80% of the black liquor nitrogen is devolatilized in single-droplet devolatilization experiments using similar droplet sizes as in real recovery boiler operation (2–3 mm). Approximately equal shares of NH_3 and N_2 were found in their pyrolysis gases. They sampled also for HCN in the pyrolysis experiments but could not find detectable amounts in the pyrolysis gases.

Iisa *et al. (27)* have reported 30–60% of fuel nitrogen found in char when analyzing pyrolysis residues of very small liquor particles (100 µm) in a laminar entrained flow reactor.

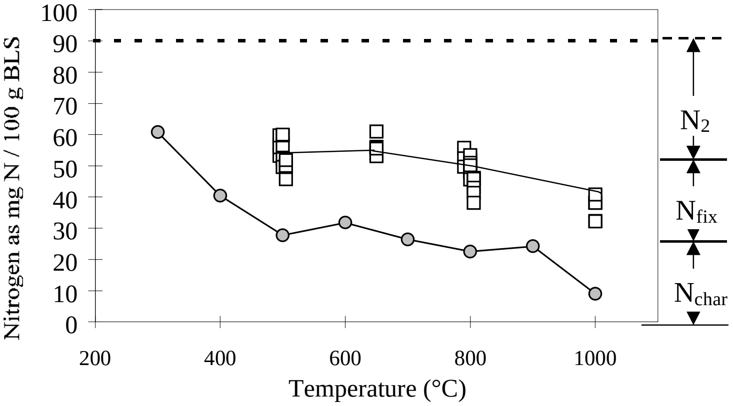

Figure 5. Nitrogen distribution during pyrolysis of single black liquor droplets in nitrogen atmosphere; pine kraft liquor. Nitrogen as N_{char}, N_{fix} and N_2.

Figure 5 shows data for a pine kraft liquor devolatilized 300 seconds in a laboratory furnace at different temperatures. In the figure, the NH_3 released is referred to as N_{fix}, and it was measured after oxidation to NO. The char was analyzed for nitrogen by the high-temperature combustion (HTC) method *(14)*, and the rest was assumed to be N_2. The figure shows the almost equal split between these three forms of nitrogen, as already suggested by Aho *et al. (9)*. Quite interestingly, for these relatively large particles, the devolatilization reactions for nitrogen seem to be quite insensitive to the furnace temperature between 500 and 900°C. Similar results has been reported earlier by Aho *et al. (9, 10)*, where the amount of released NH_3 during pyrolysis was almost constant at temperatures between 600 and 800°C for several liquors. Obviously, the treatment of the liquor particles at 1000°C in an inert gas for 300 seconds was long enough to release the nitrogen completely. However, this condition is probably not very relevant for real-world recovery furnace operation, although it should be taken into account if performing small-scale laboratory experiments.

Forssén *et al.* have recently studied NO formation in droplet burning tests for 17 different liquors originating from kraft, soda, anthraquinone pulps of pine, birch, eucalyptus, straw, and bagasse *(15)*. The percent split between “pyrolysis NO” and “char NO” was surprisingly constant, roughly 60/40, and did not vary much. On the other hand, the total amount of NO formed varied a lot and was almost directly proportional to the liquor nitrogen content.

In summary, the devolatilization stage seems to result in an almost equal split into molecular nitrogen, ammonia, and char nitrogen. The split seems to be almost independent of liquor type and nitrogen content. Moreover, the split is independent of temperature (500–900°C) for typical droplet sizes found in recovery boilers.

Conversion of volatile nitrogen (Boxes 4 and 5)

About a third of the fuel nitrogen is released as ammonia during devolatilization. Ammonia reacts readily with oxygen, forming either NO or N_2 (Boxes 4 and 5). Which of these two products dominate is strongly dependent on the specific conditions at which the devolatilized gases containing the ammonia are oxidized.

We have studied these reactions by using detailed kinetic modeling. The kinetic model assumes that the devolatilization gases—released when black liquor is sprayed into the hot furnace environment—flow through a plug flow reactor into which air is added in several stages, varying from one up to six stages.

The detailed reaction mechanism was taken from Kilpinen *et al. (24)*, and it consists of around 300 reversible elementary reactions between 55 chemical species, with the reaction rate data taken from a number of independent laboratory experiments. The mechanism includes the oxidation reactions of hydrocarbons, NH_3, HCN, and N_2 (“thermal NO,” “N_2O–NO intermediate”) as well as the interaction reactions between hydrocarbon and nitrogen species (“reburning,” “prompt NO”). A more detailed discussion of the elementary reaction modeling approach, computer codes used, etc., is given by Kilpinen *(28)*.

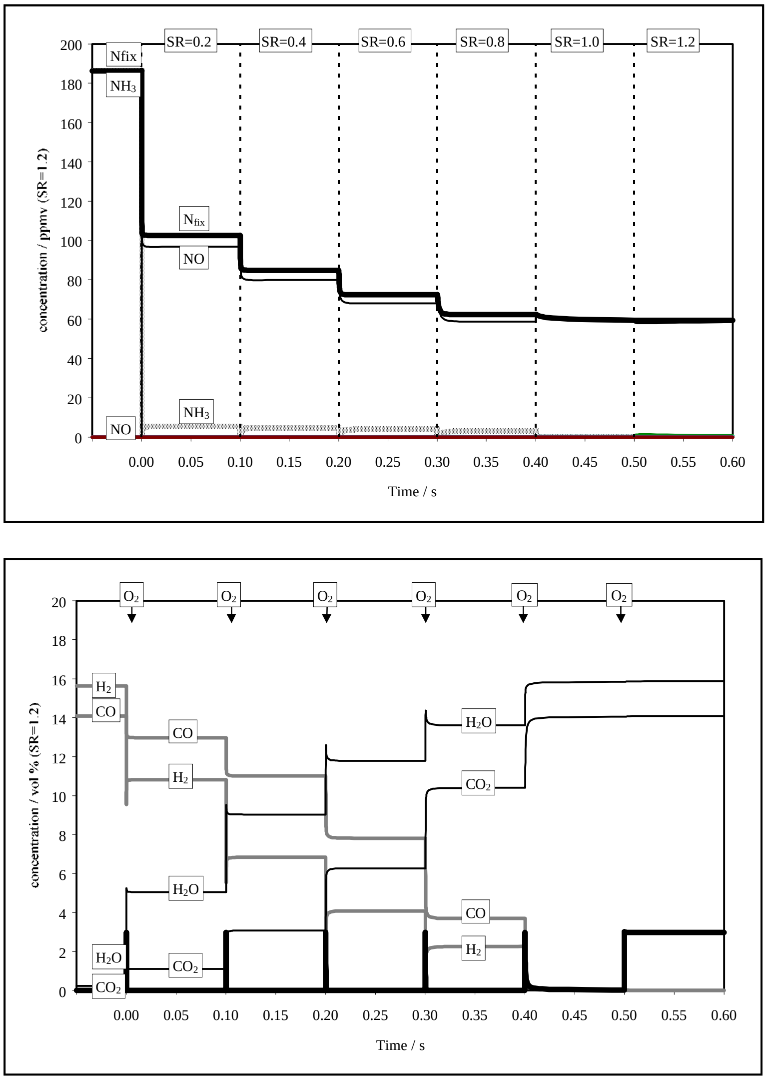

Figure 6. Distribution of minor (upper) and major (lower) components in model calculations of black liquor combustion; calculations for 900°C with air addition in six steps.

Figure 6 is an example of the calculations. The upper portion of the figure shows the concentration of minor, nitrogen-containing species as a function of reaction time. The lower part shows the concentration of main species. The normalized concentration (in ppm) of all relevant fixed-nitrogen species and their sum, referred to as N_{fix}, are given as a function of time. Since the concentrations are normalized, the amount of initial NH_3 that has been converted to N_2 can be seen as a reduction, i.e., a decrease in the N_{fix} concentration. We see that during the first stage, about 50% of the ammonia will be rapidly oxidized to mainly NO, but at the same time, almost 50% of NH_3 has been converted to N_2. After the rapid oxidation, when all O_2 has been consumed by the main species, the reaction speed of the NH_3 conversion decreases, and no further reactions occur before the second air introduction. A small amount, less than 10%, of the devolatilized NH_3 will remain to the second stage. In the second stage, a part of the remaining NH_3 and the NO produced in the first stage will react to N_2 again. The modeling results showed that additional N_2 is also formed via reduction of NO with other reducing species, such as the H radical originating from H_2. At the end—after all air has been added in six stages—the final NO_x emission predicted is about 60 ppm (3% O_2), which means that about 70% of the initial NH_3 has formed N_2 under these conditions.

The predicted N_{fix} concentrations are summarized in **Fig. 7** for various temperatures and air additions. N_{fix} emission (that will be NO in most cases) decreases in general with increasing number of air addition stages at a constant temperature. Low temperatures favor low N_{fix} emission. Additional model calculations showed that the presence of hydrocarbons significantly reduces the efficiency of air staging due to the formation of cyanide and cyano compounds. Still, for the best case, a N_{fix} emission reduction of about 30% was found to be possible when hydrocarbon content was 4%. The concentration of hydrocarbons was assumed to be above 4 vol.%, which should represent an upper limit that can be expected to exist in practical recovery furnaces.

In conclusion, the ammonia formed during devolatilization of the liquor droplets in the lower furnace is readily, and in practice almost quantitatively, oxidized to NO if mixed with the combustion air at high temperatures. However, if the oxidation with air takes place in several stages and at a moderate temperature, the conversion to NO is less efficient. Up to two-thirds of the ammonia can be converted to N_2 at optimum staged oxidation conditions.

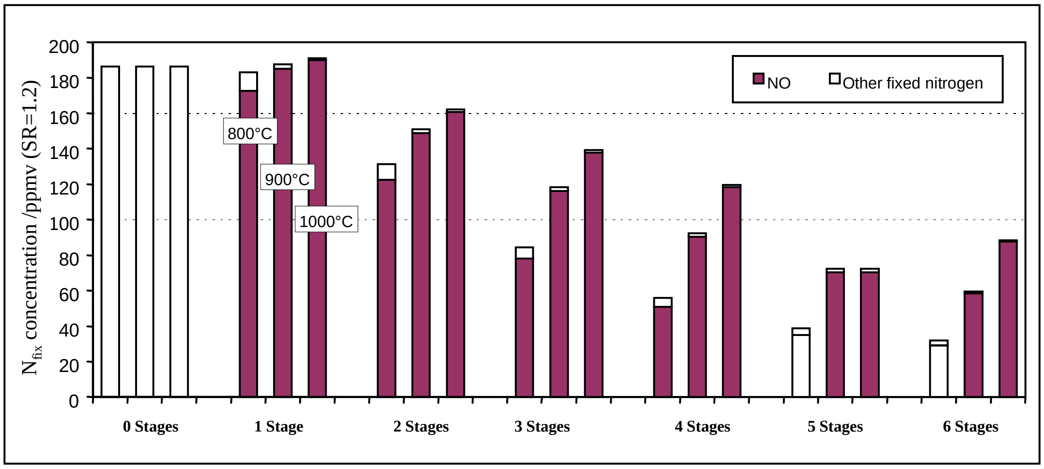

Figure 7. Amount of total fixed nitrogen (N_{fix}) in model calculations of black liquor combustion; calculations for 800, 900 and 1000°C with air addition in six stages.

Char nitrogen conversion (Boxes 6 and 7)

The char residue after devolatilization typically contains 30–40% of the liquor nitrogen. This nitrogen can, depending on conditions, either be oxidized into NO (Box 6) or converted into an inorganic nitrogen compound that remains in the salt residue of the droplet (Box 7).

If the char is burned at high temperature in an atmosphere with a high oxygen content, the nitrogen in the char will be readily oxidized into NO *(15)*. Under these conditions, the conversion of the char nitrogen is almost quantitative.

However, if the oxidation of the char occurs at a lower temperature and with a lower level of oxygen or using a “milder” oxidizer such as CO_2, the result is different. A “mild” oxidation by CO_2 at 750°C results in an almost quantitative conversion of the char nitrogen into the “smelt nitrogen” *(15)*. The smelt nitrogen forms NO immediately when the smelt residue of the char particle is oxidized with oxygen (Box 8). A similar result was achieved when burning the char with a few percent oxygen at temperatures 700–900°C *(14)*. At a higher temperature, some oxidation of char nitrogen will occur during the char gasification in CO_2.

Our earlier work has shown that the nitrogen in the char residue, just after the devolatilization stage, is completely insoluble in water, thus indicating that the nitrogen is bound in the organic structure of the char. However, the nitrogen will form NO after all free carbon has been consumed, indicating that it is remaining in the inorganic salts and that the nitrogen is in the inorganic form *(28)*. Obviously, during a slow oxidation of the char by CO_2 there is a gradual conversion of the carbon-bound nitrogen into an inorganic nitrogen compound.

Kymäläinen *et al.* have shown that the nitrogen in the smelt residue is in a readily soluble form, and this soluble nitrogen species will, in an alkaline solution, gradually form ammonia *(16, 17)* (Box 9). Despite the fact that the main reactions involved in the char nitrogen seem to be well identified, more work is required to study the details of this conversion. In particular, the influence of temperature needs further study.

In conclusion, if the char particle is completely oxidized (burned out), the char nitrogen will mostly form NO. However, if the char is oxidized at “mild” conditions, such as probably those prevailing on the bed surface, the char nitrogen may be almost quantitatively converted into smelt nitrogen. Consequently, it is probable that the smaller droplets, which tend to burn out in flight, may contribute to NO formation. On the other hand, larger particles that are not burned out in flight—but are instead gradually oxidized on the smelt bed surface—probably release their nitrogen into the smelt. However, as mentioned, more work is required to reveal more accurately the influence of the furnace temperature and gas composition on the char nitrogen conversion.

CONCLUSIONS AND IMPLICATIONS

Figures 1–4 summarize the NO formation trends for four essentially different operating modes. These figures are based on the findings discussed in the previous paragraphs, and they are aimed at demonstrating the principle changes to be expected in the recovery furnace nitrogen chemistry when the two most important operating parameters—the liquor spray or air distribution—are altered.

Figure 1 represents a base case, an example of a typical operating mode. In this operation, the air distribution is conventional, with no explicit air staging. The liquor spray is coarse, so that most of the droplets reach the bed while still containing char.

In this case, the majority of the volatile ammonia is efficiently mixed with large amounts of air at high temperatures and converted to NO. Further, in this case the char nitrogen is well preserved and leaves the furnace along with the smelt. Consequently, practically all of the NO emission originates in the volatile nitrogen.

Figure 2 (Case II) shows the changes to Case I when the liquor spray is changed to produce finer droplets. The air distribution as compared with Case I remains unchanged. In this case, the volatile NO remains the same as in Case I. However, since a larger share of the liquor droplets will have time to burn out before reaching the bed surface, a major part of the char nitrogen will also be oxidized into NO. This Case II gives a clearly higher NO emission than the base case. Moreover, the flow of nitrogen being fed into the dissolving tank along with the smelt will be significantly smaller than in the base case.

Figure 3 (Case III) shows how efficient air staging can influence the NO formation. In this case, the droplet spray is assumed to be the same as in the base case (coarse), and the air staging is able to decrease the volatile ammonia oxidation to only a fraction of that in the base case. An NO reduction of up to 70–80% is theoretically possible at ideal staging conditions. However, in practice it will be very difficult to realize such ideal conditions, and the reduction will be less efficient under actual boiler operating conditions.

Finally, Fig. 4 shows the case with strong air staging but very fine liquor spray. In this case, the volatile NO is well controlled, but the char nitrogen will be efficiently oxidized to NO, thus increasing emission of NO.

These four cases clearly show the complexity of how changes in operating conditions can affect the final NO emission. Any major changes in operating strategy simultaneously affect both the droplet size distribution and air distribution, so the net result may be a combination of several effects.

A change to higher liquor solids content is a good example of a major change that can affect NO emission in several ways, depending on the detailed operating strategy selected. The higher solids content allows the liquor droplets to be larger and more efficiently fed down to the bed surface. If this is done, the char NO formation (Box 6) can be efficiently kept under control. The volatile NO may change too, because the temperature distribution in the furnace will change. But the air distribution is also likely to change, which will influence the volatile NO formation even more. An increase in furnace temperature may also directly influence some of the reactions, but more work is needed to allow an accurate prediction of these changes.

Consequently, no general conclusions can be drawn as to the effect of the change in the high-solids firing on NO emissions. The conflicting experiences reported in the literature *(2, 4)* can probably be explained by the fact that the increase in the solids content has resulted in other changes in the operation. These other changes have probably been different in the different cases, and thus they have influenced the final NO emission in different ways.

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