Nitrogen oxide emission formation in a black liquor boiler

BY ANDERS BRINK, MARKUS ENGBLOM, AND MIKKO HUPA

ABSTRACT: This study of nitrogen oxide (NO_x) formation in a recovery boiler uses computational fluid dynamics (CFD) combined with a detailed reaction mechanism. The model is used to reveal where NO_x is formed in the recovery boiler and how different process parameters affect the emission. The CFD investigation includes a detailed model for black liquor droplet conversion and a model for the char bed behavior. The gas phase reactions are described using a reaction mechanism consisting of 21 species involved in 54 reactions.

Application: A CFD model including a detailed description of the gas phase chemistry helps in understanding the origin of nitrogen oxide emissions and tuning the recovery boiler.

BACKGROUND

Emissions of nitrogen-containing species from the black liquor recovery boiler originate mainly from nitrogen in the black liquor, but atmospheric nitrogen also can react in the boiler. Today, the nitrogen chemistry in recovery boilers is mostly well understood. Nevertheless, CFD modeling can still help provide an even more detailed picture of the chemistry.

A number of groups [1-4] have performed CFD studies of black liquor recovery boilers, and CFD calculations have been established as a standard tool used by boiler manufacturers. Still, predicting NO_x emission from black liquor recovery boilers is an evolving field, and only a few attempts have been made [5,6]. Challenges that must be solved include, for example, the description of release of nitrogen-containing species from the black liquor, as well as coupling a sufficiently complex reaction scheme. The large size of modern recovery boilers and the large number of air ports for introducing combustion air also contribute to the computational challenges.

In our study, we carried out the CFD analysis of a black liquor boiler using a highly detailed model to investigate the origin of the nitrogen emissions. We studied both the gas phase chemistry and the release of nitrogen-containing species from the black liquor droplets. For the gas phase part, our specific goal was to investigate the importance of thermal-NO formation. We carried out this part of the study using two different gas phase reaction mechanisms, one including the extended Zeldovich mechanism and another in which these reactions are excluded. In focusing on the release of nitrogen containing species from the black liquor droplets, we investigated the influence of droplet size.

MODEL DESCRIPTION

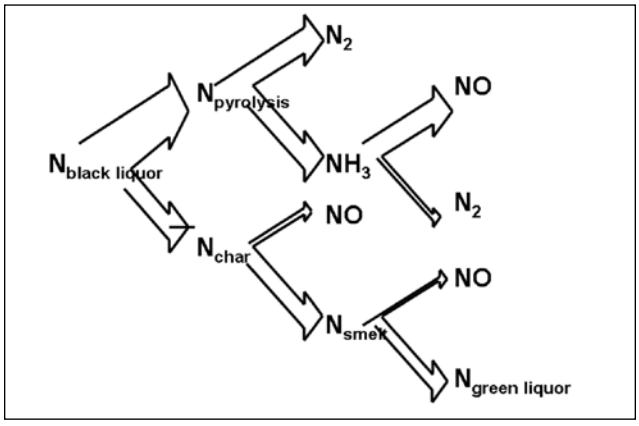
The overall Åbo Akademi furnace model comprises a number of application-specific sub-models mainly for black liquor recovery boilers and biomass-fired bubbling beds. For modeling the black liquor recovery boiler, the most important submodels are the black liquor droplet model, the char bed model, and the gas phase chemistry model. Here, we present only the most relevant sub-models. Description of the Åbo Akademi furnace model can be found elsewhere [4,6-10].

We modeled black liquor droplets in a Lagrangian reference frame, tracking individual particles that represent a certain fraction of the spray. We took into account the size distribution of the droplets, as well as the influence of the turbulent field on the black liquor trajectories. By tracking a sufficiently large number of droplets, we obtained a statistically accurate description of the spraying process. We modeled the black liquor droplet conversion using four steps: drying, devolatilization, char-carbon conversion, and smelt bead formation.

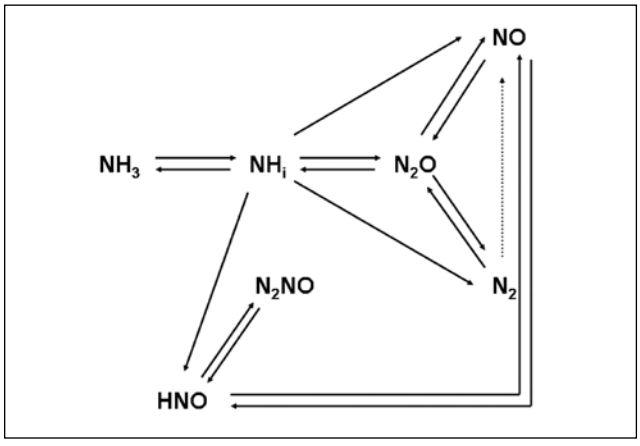
The drying stage is assumed to be heat-transfer limited. During the drying stage there is an initial swelling. When 90% of the water content has been dried off, the devolatilization step begins and the main swelling occurs. During the devolatilization step the rest of the water is dried off at a rate proportional to the release of volatiles. We described the devolatilization rate using a single rate expression of the Arrhenius type. When all volatiles have been released, the char-carbon conversion step begins. We modeled the char-carbon conversion by taking both oxidation and gasification reactions into account. After the carbon has been consumed, a smelt bead is formed. The smelt bead is modeled as an inert particle.

Most of the droplets will hit either the char bed or the walls before combustion is completed. Upon landing, particles are assumed to release their volatile components, whereas the char-carbon and the inorganic materials enter the char bed. The char-bed model builds on the model by Frederick and Hupa [11]. It includes a full coupling between the char bed and the gas phase. A detailed description of the char bed model has been presented by Bergroth *et al.* [10] and recent updates to the model by Engblom *et al.* [12]. **Figure 1** summarizes the fate of the nitrogen entering the recovery boiler. The split between the different paths is liquor-dependent.

The CFD model assumes that 35 wt% of the nitrogen forms NH_3 and another 35 wt% forms N_2 during the devolatilization step. It further assumes that the nitrogen release is proportional to the carbon release. The remaining 30 wt% nitrogen



***1. Nitrogen pathways in black liquor combustion according to Forssén* et al. [13].**



2. Schematic picture of the nitrogen chemistry described by the augmented reaction mechanism.

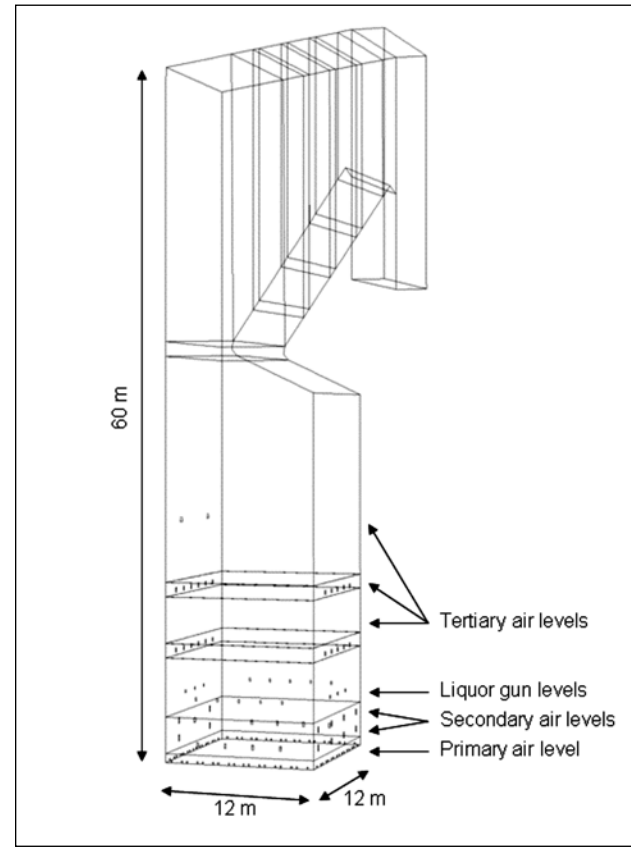
is assumed to go into the char residue. During the char-carbon conversion stage it is assumed that the nitrogen is released at the same rate as the carbon, if the char conversion occurs during oxidizing conditions. If the char conversion occurs during reducing conditions, the nitrogen is assumed to accumulate in the char particle, resulting in an increased N/C ratio. If the final burn out of the particle takes place at oxidizing conditions, the accumulated nitrogen will be released.

The nitrogen conversion in the gas phase is described using the Eddy Dissipation Concept [14]. In this concept the fluid is split into reacting and non-reacting parts. The reacting part is modeled as a perfectly stirred reactor that is fed with fluid from the non-reacting part. Equation 1 shows the expression used for calculating the chemical reaction rate of a species *i*.

$$\tilde{\dot{\omega}}_i = \frac{\gamma^3 \chi}{\tau^*}\left(Y_i^o - Y_i^*\right) \quad (1)$$

In the equation, $\gamma^3\chi$ is the mass of turbulent fine structures that can react; τ^* is the residence time in the reacting structures; Y_i is the mass fraction of species *i*; the superscript *o* refers to the feed stream to the reactor, and the superscript * to the stream leaving the reactor.

The Eddy Dissipation Concept is combined with a reaction scheme consisting of 21 species [7]. The reaction scheme



3. Technical sketch of the recovery furnace.

contains two global reactions for methane conversion to CO and H_2 followed by 52 elementary reactions describing the CO/H_2 and NH_3/NO chemistry. The first two reactions were taken from the four-step mechanism for hydrocarbon combustion put forth by Jones and Lindstedt [15], while the second part is a skeletal mechanism. The skeletal mechanism has been developed for fuel-nitrogen oxidation in biomass combustion [16]. **Figure 2** shows a schematic picture of the reaction paths included in the mechanism. The mechanism describes only a part of the nitrogen chemistry; for example, reaction paths describing reburning are not included. In the figure, the path representing the three reactions describing the extended Zeldovich mechanism – i.e., thermal-NO formation – is shown with a dotted arrow.

The detailed gas-phase chemistry requires significant computational resources. To reduce the computational times to a reasonable level, we used the following procedure. First, we computed an initial solution using the four-step reaction mechanism of Jones and Lindstedt [15]. During this stage, particle calculations were performed for every 10th iteration. After the converged solution was obtained, we switched to the detailed description. Then we converged the solution again, but froze the source terms from the particle calculations. In this way, we could investigate the effect of the chemistry without the influence of other process parameters. We used a similar concept when investigating the influence of the spray characteristics. In this case, we performed droplet cal-

culations in a "post-processing" mode, assuming that they did not influence the gas flow.

TEST CASE

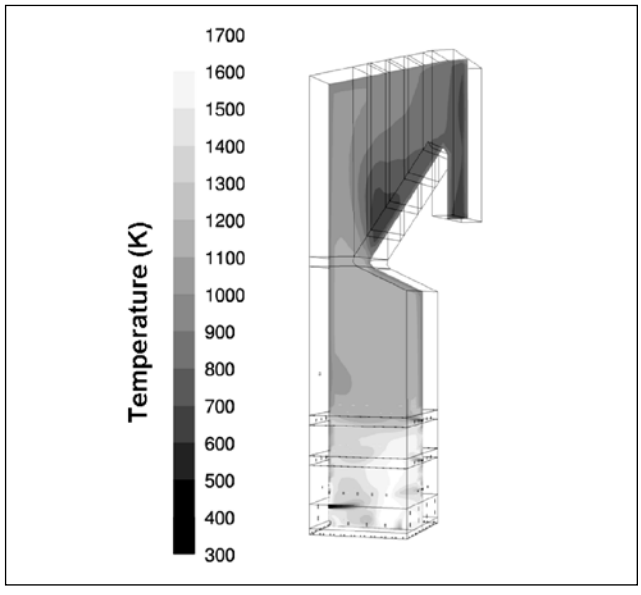
As a test case, we used a full scale recovery boiler. The computational domain representing the simulated recovery furnace is shown in **Fig. 3**. The furnace is about 60 m high, with a nose level at about 30 m and a 12 × 12 m cross-section. The recovery boiler has a capacity of 3150 t DS/day and fires black liquor at a dry solid content of about 80%. In the modeling we assumed that the nitrogen content of the dry solid was 0.8%.

To describe the spray characteristics, we used the Rosin-Ramler distribution. The average droplet diameter has been set to 6.3 mm and the spread parameter to 2.9 mm. The spray characteristics have not been measured, but the size distribution has been estimated based on the black liquor properties and the dimensions of the liquor guns.

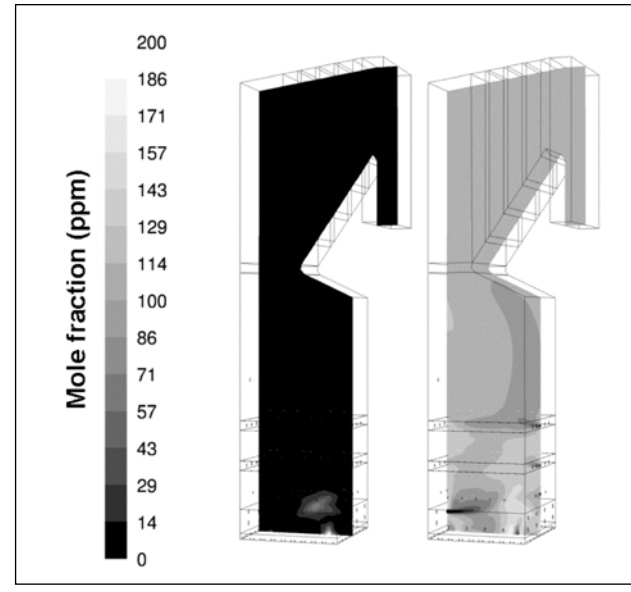
RESULTS AND DISCUSSION

The temperatures prevailing in the boiler have a strong impact on the nitrogen chemistry. **Figure 4** shows the calculated temperature field at a plane in the center of the boiler. It shows that the temperature in the lower part of the boiler is high, with temperatures up to 1700 K commonly prevailing. According to the CFD calculations, there are local hot spots with still higher temperatures. The maximum temperature found in the CFD calculations is around 1850 K.

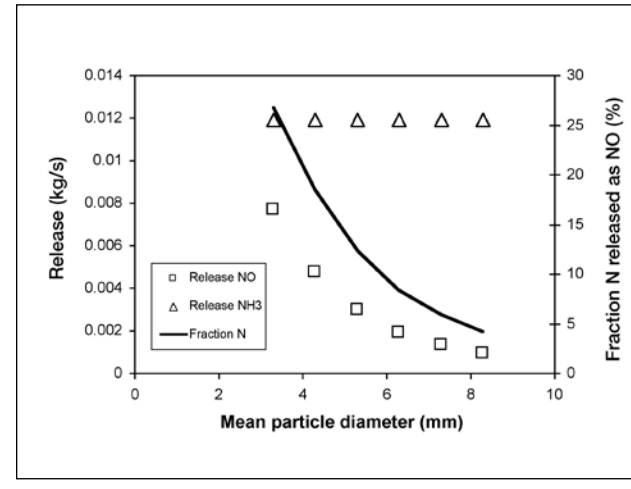
Figure 5 shows the NH_3 and NO mole fraction fields in the boiler. NH_3 reacts immediately, except in some regions close to the bed. Studying these regions in more detail revealed that the oxygen content is very low, preventing NH_3 from being oxidized. The NO field shows that the highest NO concentration is found in the lower part of the boilers. The mole fraction NO at the outlet in the calculation is 110 ppm if



4. Temperature (in Kelvin) drawn at a plane cutting through the center of the boiler.



5. Left NH_3 mole fraction field. Right, NO mole fraction field.



6. Nitrogen release as function of droplet diameter.

the thermal-NO formation mechanism is included in the reaction scheme and 116 ppm in the case where it is excluded. This result is surprising, but investigating the concentrations of other nitrogen-containing species reveals that excluding the three reactions describing thermal-NO formation also influences some other species. Without the thermal-NO mechanism, the N-radicals build up in the hot regions in the bottom of the boiler, and are later converted to NO.

Comparing the amounts of fuel-nitrogen released to the nitrogen in NO at the outlet reveals an almost perfect match. A mole fraction of 110 ppm and 116 ppm at the outlet corresponds to 95% and 99% conversions of the fuel nitrogen, respectively. This indicates that almost all NH_3 is oxidized to NO in the lower part of the boiler and that the nitrogen released as NO is left unreacted.

The results indicate that the dominant source for the nitrogen emission is the fuel-nitrogen. In the CFD model, fuel-ni-

trogen can be released during two of the stages in the particle conversion: as NH_3 during the pyrolysis stage and as NO during the char oxidation stage. During the char oxidation stage the nitrogen can also be released as N_2 if the oxidation takes place in oxygen-lean conditions. To investigate the source of the fuel-nitrogen, the release of NH_3 and NO were integrated in the boiler. The results are summarized in **Fig. 6.** In the CFD calculations an average droplet diameter of 6.3 mm has been assumed. Fig. 6 shows that at these conditions approximately 90 percent of the nitrogen is released as NH_3 and less than 10 percent as NO.

From Fig. 6 it can be seen that the amount of NH_3 released is independent of the mean particle diameter. This originates in the assumption that all pyrolysis gases are released upon hitting the char bed or the boiler wall. The nitrogen released as NO, on the other hand, is highly dependent on the droplet size. In the model the nitrogen is released as NO if the char oxidation occurs during oxidizing conditions. Such conditions are encountered only by small entrained particles. The volume where this occurs is mainly located between the liquor guns and the tertiary air.

Figure 6 shows that increasing the mean particle diameter from 6.3 mm to 8.3 mm approximately halves the NO release. Similarly, decreasing the mean diameter from 6.3 mm to 4.3 mm almost doubles the release. The smallest mean particle value that was used in the CFD calculations was 3.3 mm. In this case more than 25 percent of the nitrogen is released as NO. If all char-N would be released at oxidizing condition this would result in approximately 46 percent of the total nitrogen release being NO. Based on these calculations it is possible to estimate the NO concentration in the flue gas as a function of the mean particle diameter, assuming that all nitrogen released as NH_3 or NO will form NO. Using these assumptions, increasing the mean droplet diameter to 8.3 mm from 6.3 mm would decrease the NO from 110 ppm to 105 ppm. Using a mean droplet of 3.3 mm would result in an increase of NO to 137 ppm.

FUTURE INVESTIGATIONS

Changing only the spray characteristics without updating the flow field is a somewhat speculative approach. However, it is likely that the changes on the flow pattern itself are not the main concern associated with this approach. For example, it is not possible to spray large wet droplets to the bed without severely influencing the boiler operation. In addition, at reducing conditions, the gas phase chemistry cannot be described fully with the reaction scheme used in this study. Still, it would be interesting to investigate whether air staging changes the temperature field in the boiler so that temperature favoring the reduction of NH_3 with NO to N_2 is obtained, or if other reactions paths including HCN-chemistry are of greater importance. In addition, the assumption that all nitrogen associated with the volatiles are released as NH_3 at the bed surface should be further investigated.

CONCLUSIONS

We used a comprehensive CFD model to study the NO formation mechanisms in a modern recovery boiler. The modeling revealed that excluding the thermal-NO reaction path from the gas phase chemistry had only a minor influence.

1 The temperature field in the boiler is such that almost all nitrogen released from the black liquor droplets in flight is oxidized to NO.
2 Black liquor spray characteristics play an important role. Decreasing the average droplet diameter leads to a high-

INSIGHTS FROM THE AUTHORS

We chose this topic because understanding nitrogen oxide formation mechanisms is essential for meeting today's environmental regulations. We chose our methodology because with today's computer tools it is possible to answer questions that purely experimental work cannot. Our findings can be used to tune the recovery boiler.

In earlier research, the complexity of nitrogen oxide formation in a recovery boiler has been addressed by studying specific parts of the formation and destruction process. In our work, we combined a comprehensive description of the gas-phase chemistry with a detailed black liquor particle and char bed model.

The most difficult aspect of our research was to ensure a correct description of the release process of nitrogen-containing species from the black liquor droplets at conditions prevailing in the recovery boiler. This is critical. In our modeling we used the best information obtainable from experimental laboratory-scale research.

The most surprising aspect of our findings was the great sensitivity of nitrogen emissions to the black liquor spraying. It will be essential for mills to have good data and use it when modeling.

For future research, some improvements to black liquor droplet modeling still need to be undertaken. The fate of droplets hitting the boiler walls should especially be investigated.


Brink


Engblom


Hupa

Anders Brink is a senior researcher, Markus Engblom is a post-graduate student, and Mikko Hupa is a professor, all at Abo Akademi University, Turku, Finland. Email contact author Brink at anders.brink@abo.fi.

er amount of char burnout in flight at oxygen rich conditions above the black liquor guns. This is likely to lead to increased NO emission. In contrast, increasing the average particle diameter has an opposite effect. **TJ**

ACKNOWLEDGEMENTS

This work has been part of the activities of the Åbo Akademi Process Chemistry Centre, funded by the Academy of Finland in the Centres of Excellence Program. Additional support obtained from our industrial partners Andritz Oy, Foster Wheeler Energia Oy, International Paper, Metso Power Oy, Oy Metsä-Botnia Ab and Vattenfall Utveckling AB and by the National Technology Agency of Finland in the research project ChemCom is gratefully acknowledged.

Received: October 21, 2007
Accepted: February 7, 2008

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