A Computationally Efficient Approach for Predicting NO$_x$ Emission Trends from Black Liquor Recovery Boilers

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Outline

• Objective
• Background
• New NO$_x$ model
• Results
• Conclusions
• Acknowledgements
Objective

• A fast, reliable method for NO\textsubscript{x} emission prediction
• Use the fast Eddy Dissipation Combustion Model
• Utilized previously developed 2-step nitrogen chemistry
Background

Black Liquor (BL) Combustion

Stages of BL Combustion

- **Drying**
- **Pyrolysis/devolatilisation and gas combustion**
- **Char combustion**
- **Smelt**

Chemical reactions:

- $\text{O}_2 + \text{H}_2\text{O}$
- $\text{CO}_2 + \text{H}_2\text{O}$
- $\text{NH}_3$
- $\text{N}_2$
- $\text{CO}_2$
- $\text{NO}$
- $\text{N}_2$
- $\text{H}_2\text{O}$

**NdM 2003**
Background

Single droplet furnace example of experimental results

- CO₂ and NO linear dependent during devolatilization step
- NO release stop during char oxidation step
- NO released again during smelt oxidation
- Only 20-50% of N detected during experiments
Nitrogen release from droplet

- **NH$_3$**
- **N$_2$**
- **NO**

**Background**

- Fuel-N
- Char-N
- Small-N

- 35%
- 30%
- Ox
- Red
Nitrogen reactions at biomass firing conditions

Background

Coda Zabetta et al 2000
Background

Standard NO\textsubscript{x} model

2-step nitrogen chemistry

\[
\begin{align*}
\text{NH}_3 + \text{O}_2 & \rightarrow \text{NO} + \text{H}_2\text{O} + \frac{1}{2}\text{H}_2 \\
\text{NH}_3 + \text{NO} & \rightarrow \text{N}_2 + \text{H}_2\text{O} + \frac{1}{2}\text{H}_2
\end{align*}
\]

\[
\begin{align*}
r_1 &= 1.21 \cdot 10^8 T^2 e^{-8000/T} \left[ \text{NH}_3 \right]^{0.5} \left[ \text{O}_2 \right]^{0.5} \\
r_2 &= 8.73 \cdot 10^{17} T^{-1} e^{-8000/T} \left[ \text{NH}_3 \right] \left[ \text{NO} \right]
\end{align*}
\]

Standard EDCM

\[
\begin{align*}
\tilde{\omega}_1 &= \min \left[ A \frac{\varepsilon}{k} \min \left[ \frac{\tilde{Y}_{\text{NH}_3}}{r_{\text{NH}_3,R1}}, \frac{\tilde{Y}_{\text{O}_2}}{r_{\text{O}_2,R1}} \right] , \tilde{\omega}_{1,\text{chem}} \right] \\
\tilde{\omega}_2 &= \min \left[ A \frac{\varepsilon}{k} \min \left[ \frac{\tilde{Y}_{\text{NH}_3}}{r_{\text{NH}_3,R1}}, \frac{\tilde{Y}_{\text{NO}}}{r_{\text{NO,R1}}} \right] , \tilde{\omega}_{2,\text{chem}} \right]
\end{align*}
\]
Background

Test case
Joutseno boiler

• The mill has a pulp capacity of 600 000 ADt/year

• Recovery boiler – 3150 t/d (dry solids). Height 79 m.

• Strong and weak odorous gases (NCGs) burnt in recovery boiler
Reaction rate terms in the EDCM for \( \text{NH}_3 + \text{O}_2 \)

**Background**

EDCM  
Turbulent mixing  
Chemistry

![Graph showing reaction rate terms in the EDCM for \( \text{NH}_3 + \text{O}_2 \).](image)
New NO\textsubscript{x} model

• Mixing rate of NH\textsubscript{3} usually limiting

• Chemistry determines selectivity in NH\textsubscript{3} conversion

• Partly same (elementary) reactions
**New NO\textsubscript{x} model**

2-step nitrogen chemistry

\[
\begin{align*}
NH_3 + O_2 &\rightarrow NO + H_2O + \frac{1}{2}H_2 \\
NH_3 + NO &\rightarrow N_2 + H_2O + \frac{1}{2}H_2
\end{align*}
\]

\[r_1 = 1.21 \cdot 10^8 T^2 e^{-8000/T} [NH_3][O_2]^{0.5}[H_2]^{0.5}\]

\[r_2 = 8.73 \cdot 10^{17} T^{-1} e^{-8000/T} [NH_3][NO]\]

Modified EDCM

\[
\tilde{\omega}_1 = \min \left[ A \frac{\tilde{\varepsilon}}{k} \min \left[ \frac{\tilde{Y}_{NH_3}}{r_{NH_3,R1}}, \frac{\tilde{Y}_{O_2}}{r_{O_2,R1}} \right] \frac{r_1}{r_1 + r_2}, \tilde{\omega}_{1,\text{chem}} \right]
\]

\[
\tilde{\omega}_2 = \min \left[ A \frac{\tilde{\varepsilon}}{k} \min \left[ \frac{\tilde{Y}_{NH_3}}{r_{NH_3,R1}}, \frac{\tilde{Y}_{O_2}}{r_{O_2,R1}} \right] \frac{r_2}{r_1 + r_2}, \tilde{\omega}_{2,\text{chem}} \right]
\]
Results

NO mole fraction fields

<table>
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<tr>
<th></th>
<th>Standard EDCM</th>
<th>Modified EDCM</th>
<th>EDC</th>
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<tbody>
<tr>
<td>25 ppm</td>
<td>0.000300</td>
<td>0.000285</td>
<td>0.000270</td>
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<tr>
<td>122 ppm</td>
<td>0.000265</td>
<td>0.000255</td>
<td>0.000240</td>
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<tr>
<td>120 ppm</td>
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<td>0.000210</td>
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25 ppm  122 ppm  120 ppm
Results

Reaction rate in the EDCM for NH$_3$ + NO

Standard EDCM  Modified EDCM
Results

Reaction rate in the EDCM for NH$_3$ + NO

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<thead>
<tr>
<th>Standard EDCM</th>
<th>Modified EDCM</th>
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<tbody>
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<td>kmol/m$^3$s</td>
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<td>0.00003</td>
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<td>0.0001</td>
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</tr>
<tr>
<td>$1 \times 10^{-8}$</td>
<td></td>
</tr>
</tbody>
</table>
Results

Fraction of NH₃ consumed by the reaction between NH₃ and O₂.

\[ f = \frac{\tilde{\omega}_{R1}}{\tilde{\omega}_{R1} + \tilde{\omega}_{R2}} \]
Results

NO mole fraction fields, modified EDCM

\( d_p = 4.5 \text{mm} \)

\( d_p = 3.5 \text{mm} \)

30% more \( \text{NH}_3 \) release in flight

122 ppm

131 ppm
Conclusions

Model overcomes severe shortcoming of standards
EDCM (Magnussen-Hjertager Model):

• Unreasonable situations where part of the chemistry is mixing limited and part chemically limited avoided

• Chemistry always influences results

• Do not provide a full nitrogen chemistry model

• Predicted temperature field favors NO formation
Acknowledgement

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