Ammonia preparation in the tailpipe: Spray/wall interaction and deposit formation

M. Börnhorst, C. Kuntz, S. Tischer, O. Deutschmann

Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS) Workshop, Sept. 18-20, 2018, Ann Arbor
Ammonia preparation in the tailpipe

Injection of a 32.5 wt.-% urea solution (AdBlue®) used as precursor for ammonia

Formation of liquid and solid deposits by incomplete evaporation and urea conversion

- Serious loss of NO\textsubscript{x} reduction efficiency

$$\text{(NH}_2\text{)}_2\text{CO (l)} \Rightarrow \text{NH}_3 (g) + \text{HNCO (g)}$$

$$\text{HNCO (g) + H}_2\text{O (g)} \Rightarrow \text{NH}_3 (g) + \text{CO}_2 (g)$$

SCR reaction

$$2 \text{NH}_3 + \text{NO} + \text{NO}_2 \rightarrow 2 \text{N}_2 + 3 \text{H}_2\text{O}$$

Endoscopic records from a hot gas test rig [1]

Liquid and solid deposits in SCR systems

Spray: $p_{\text{inj}}$, $T_{\text{inj}}$, $m_{\text{inj}}$

Drops: $u_d$, $d_d$, $T_d$

Gas: $T_g$, $p_g$, $u_g$

Wall: $\Theta$, $R_a$, $T_w$

Liquid Film: $A_f$, $h_f$, $T_f$

Solid deposit

Thermolysis & Hydrolysis

Evaporation

Solid by-products:
- Biuret
- Triuret
- Cyanuric acid
- Ammelide
- Ammeline
Outline

Urea decomposition
- Deposit formation at a hot gas test rig
- Deposit characterization

Kinetic modeling
- Kinetic measurements on urea decomposition
- DETCHEM\textsuperscript{MPTR} model

Integration to CFD
- Coupling of kinetic model with StarCCM+ simulation
Laboratory test rig

Hot gas test rig with integrated urea dosing system

Injection/measurement cell designed for undisturbed flow and optical access

Vertical compressor

TABELLE

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Operating range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas flow</td>
<td>L/min</td>
<td>50 - 3000</td>
</tr>
<tr>
<td>Gas velocity</td>
<td>m/s</td>
<td>0.5 - 25</td>
</tr>
<tr>
<td>Reynolds number</td>
<td>-</td>
<td>1200 - 50000</td>
</tr>
<tr>
<td>Gas temperature</td>
<td>°C</td>
<td>100 – 350</td>
</tr>
<tr>
<td>Injection mass flow</td>
<td>kg/h</td>
<td>0.03 – 5.3</td>
</tr>
<tr>
<td>Injection pressure</td>
<td>bar</td>
<td>5</td>
</tr>
<tr>
<td>Injection angle</td>
<td>°</td>
<td>33</td>
</tr>
</tbody>
</table>
Deposit formation in lab test bench

Film formation during injection

Evaporation leaves solid deposits

Dissolution of existing deposits

Deposit build-up over time

Injection

Flow direction

OP: \( T_{\text{gas}} = 300^\circ\text{C} \), \( V_{\text{gas}} = 1200 \text{ L/min} \), \( u_{\text{gas}} = 11 \text{ m/s} \), \( m_{\text{urea}} = 1 \text{ g/min} \), 3 x 40 min injection
### Deposit sampling

- Three injection periods of 40 min
- UWS mass flow of 1 g/min

<table>
<thead>
<tr>
<th>OP</th>
<th>$T_{\text{gas}}$ / °C</th>
<th>$V_{\text{gas}}$ / L/min</th>
<th>$u_{\text{gas}}$ / m/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>150</td>
<td>866</td>
<td>8.0</td>
</tr>
<tr>
<td>2</td>
<td>190</td>
<td>916</td>
<td>8.5</td>
</tr>
<tr>
<td>3</td>
<td>280</td>
<td>1030</td>
<td>9.5</td>
</tr>
<tr>
<td>4</td>
<td>320</td>
<td>870</td>
<td>8.0</td>
</tr>
</tbody>
</table>
Deposit Characterization

High Performance Liquid Chromatography (HPLC)
- Deposit composition

Thermogravimetric analysis (TGA)
- Decomposition kinetics

3D-Structure analysis
- Surface profile of deposits
Deposit analysis by HPLC

- Method development for qualitative and quantitative deposit analysis based on Koebel et al. (1995) and Bernhard et al. (2011)
- Separation and quantification of components by adsorption potential
  - Na$_2$HPO$_4$ buffer as solvent and eluent
  - Anion exchange column
  - Photodiode-array detector (UV/VIS)
- Method validation and calibration by standard solutions
- Strong pH sensitivity affects measurement accuracy
TGA procedure

- Thermogravimetric analysis of decomposition kinetics
- Grinded, representative sample of deposit
- TG Setup: Netzsch STA 409, TASC 414/2
- Initial sample mass of 15 – 20 mg
- Gas flow of 100 ml/min synthetic air
- Temperature program: heating rate of 2K/min, from 40 to 700°C
TGA of urea and by-product decomposition

![Graph showing the TGA of urea and by-products]

Sample mass [%] vs Temperature [°C]

1. Urea
2. Biuret
3. Cyanuric acid
4. Ammelide
Characterization of OP 1 deposit

<table>
<thead>
<tr>
<th>OP</th>
<th>$T_{\text{gas}}$ / °C</th>
<th>$V_{\text{gas}}$ / L/min</th>
<th>$u_{\text{gas}}$ / m/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>150</td>
<td>866</td>
<td>8.0</td>
</tr>
</tbody>
</table>

Deposit volume: cm³ 16.87
Max. height: mm 19.25
Mean height: mm 5.24

<table>
<thead>
<tr>
<th>Substance</th>
<th>Urea</th>
<th>Biu</th>
<th>Triu</th>
<th>CyA</th>
<th>Amd</th>
<th>Amn</th>
<th>Mel</th>
<th>Rest</th>
</tr>
</thead>
<tbody>
<tr>
<td>Portion [wt.-%]</td>
<td>65.6</td>
<td>0.2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>34.2</td>
</tr>
</tbody>
</table>

Characterization of solid deposits from urea water solution injected into a hot gas test rig, Börnhorst et al. (2018)
Characterization of OP 2 deposit

<table>
<thead>
<tr>
<th>OP</th>
<th>(T_\text{gas} / ^\circ\text{C})</th>
<th>(V_\text{gas} / \text{L/min})</th>
<th>(u_\text{gas} / \text{m/s})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>190</td>
<td>916</td>
<td>8.5</td>
</tr>
</tbody>
</table>

- Deposit volume: \(0.13 \text{ cm}^3\)
- Max. height: \(0.80 \text{ mm}\)
- Mean height: \(0.47 \text{ mm}\)

### Substance Portion [wt.-%]

<table>
<thead>
<tr>
<th>Substance</th>
<th>Urea</th>
<th>Biu</th>
<th>Triu</th>
<th>CyA</th>
<th>Amd</th>
<th>Amn</th>
<th>Mel</th>
<th>Rest</th>
</tr>
</thead>
<tbody>
<tr>
<td>Portion</td>
<td>57.0</td>
<td>9.7</td>
<td>2.2</td>
<td>0.4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>30.7</td>
</tr>
</tbody>
</table>

Characterization of solid deposits from urea water solution injected into a hot gas test rig, Börnhorst et al. (2018)
Characterization of OP 3 deposit

<table>
<thead>
<tr>
<th>OP</th>
<th>T_{gas} / °C</th>
<th>V_{gas} / L/min</th>
<th>u_{gas} / m/s</th>
<th>Deposit volume</th>
<th>cm³</th>
<th>0.83</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>280</td>
<td>1030</td>
<td>9.5</td>
<td>Max. height</td>
<td>mm</td>
<td>2.55</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mean height</td>
<td>mm</td>
<td>0.57</td>
</tr>
</tbody>
</table>

Characterization of solid deposits from urea water solution injected into a hot gas test rig, Börnhorst et al. (2018)
Characterization of OP 4 deposit

<table>
<thead>
<tr>
<th>OP</th>
<th>T&lt;sub&gt;gas&lt;/sub&gt; / °C</th>
<th>V&lt;sub&gt;gas&lt;/sub&gt; / L/min</th>
<th>u&lt;sub&gt;gas&lt;/sub&gt; / m/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>320</td>
<td>870</td>
<td>8.0</td>
</tr>
</tbody>
</table>

Deposit volume: cm³, 0.35
Max. height: mm, 2.46
Mean height: mm, 0.99

<table>
<thead>
<tr>
<th>Substance</th>
<th>Urea</th>
<th>Biu</th>
<th>Triu</th>
<th>CyA</th>
<th>Amd</th>
<th>Amn</th>
<th>Mel</th>
<th>Rest</th>
</tr>
</thead>
<tbody>
<tr>
<td>Portion [wt.-%]</td>
<td>1.6</td>
<td>0</td>
<td>0</td>
<td>68.1</td>
<td>5.9</td>
<td>1.2</td>
<td>0</td>
<td>23.2</td>
</tr>
</tbody>
</table>

Characterization of solid deposits from urea water solution injected into a hot gas test rig, Börnhorst et al. (2018)
Deposit composition

- Similar deposit composition for similar operating temperatures
- Prediction of deposit composition by characteristic urea decomposition kinetics
**DETCHEM**

- Multiple Phase Tank Reactor
- 0D batch type reactor model
- Solves for species balances in multiple phases and heat balance
- Homogeneous and inter-phase reactions

\[
\frac{dn_i}{dt} = \sum_{\text{phases}} V_{\text{phase}} \cdot \dot{\omega}_i + A_{\text{interface}} \cdot \dot{s}_i
\]

\[
\frac{dH}{dt} = k_W \cdot (T^{\text{extern}} - T) + Q_{\text{const}}
\]

\[
c_i = n_i \cdot \left( \sum_{i \in \text{phase}} n_i \cdot v_i \right)^{-1}
\]

\[
v_i = \begin{cases} 
\frac{M_i}{\rho_i} & \text{condensed} \\
\frac{RT}{p} & \text{gas phase}
\end{cases}
\]
**Kinetic model**

Reactions described with $k = A \cdot T^\beta \cdot \exp \left( \frac{E_A}{RT} \right)$:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$n$</th>
<th>$A$ (SI units)</th>
<th>$\beta$</th>
<th>$E_A$ (kJ/mol)</th>
<th>No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>cya(s) → 3 HNCO(l)</td>
<td>0.5</td>
<td>$1.000 \cdot 10^{12}$</td>
<td>0</td>
<td>150.42</td>
<td>[R01]</td>
</tr>
<tr>
<td>biu(l) → urea(l) + HNCO(l)</td>
<td>1</td>
<td>$1.107 \cdot 10^{20}$</td>
<td>0</td>
<td>208.23</td>
<td>[R02]</td>
</tr>
<tr>
<td>urea(l) + HNCO(l) → biu(l)</td>
<td>1 + 1</td>
<td>$6.517 \cdot 10^{7}$</td>
<td>0</td>
<td>93.45</td>
<td>[R03]</td>
</tr>
<tr>
<td>urea(l) → NH$_3$(g) + HNCO(l)</td>
<td>0.5</td>
<td>$9.500 \cdot 10^{9}$</td>
<td>0</td>
<td>95.50</td>
<td>[R04]</td>
</tr>
<tr>
<td>2 biu(l) → ammd(s) + HNCO(l) + H$_2$O(g) + NH$_3$(g)</td>
<td>2</td>
<td>$2.337 \cdot 10^{20}$</td>
<td>0</td>
<td>250.76</td>
<td>[R05]</td>
</tr>
<tr>
<td>biu(l) + HNCO(l) → cya(s) + NH$_3$(g)</td>
<td>1 + 1</td>
<td>$3.397 \cdot 10^{11}$</td>
<td>0</td>
<td>143.68</td>
<td>[R06]</td>
</tr>
<tr>
<td>biu(l) + HNCO(l) → triu(s)</td>
<td>1 + 1</td>
<td>$9.091 \cdot 10^{10}$</td>
<td>0</td>
<td>150.97</td>
<td>[R07]</td>
</tr>
<tr>
<td>triu(s) → cya(s) + NH$_3$(g)</td>
<td>1</td>
<td>$1.238 \cdot 10^{18}$</td>
<td>0</td>
<td>194.94</td>
<td>[R08]</td>
</tr>
<tr>
<td>urea(l) + 2 HNCO(l) → ammd(s) + H$_2$O(g)</td>
<td>1 + 2</td>
<td>$1.274 \cdot 10^{8}$</td>
<td>0</td>
<td>110.40</td>
<td>[R09]</td>
</tr>
<tr>
<td>biu(l) → biu(m)</td>
<td>1</td>
<td>$7.193 \cdot 10^{15}$</td>
<td>0</td>
<td>171.50</td>
<td>[R10]</td>
</tr>
<tr>
<td>biu(m) → biu(l)</td>
<td>1</td>
<td>$3.162 \cdot 10^{9}$</td>
<td>0</td>
<td>192.00</td>
<td>[R11]</td>
</tr>
<tr>
<td>bin(m) → 2 HNCO(g) + NH$_3$(g)</td>
<td>1</td>
<td>$2.626 \cdot 10^{25}$</td>
<td>0</td>
<td>271.38</td>
<td>[R12]</td>
</tr>
<tr>
<td>HNCO(aq) + H$_2$O(l) → CO$_2$(g) + NH$_3$(g)</td>
<td>1 + 1</td>
<td>$4.703 \cdot 10^{2}$</td>
<td>0</td>
<td>87.01</td>
<td>[R13]</td>
</tr>
</tbody>
</table>

Phase transitions with $s_0^0 = 0.01$:

<table>
<thead>
<tr>
<th>Phase transition</th>
<th>$s_0^0$</th>
<th>$k$</th>
<th>$T$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O(g) ⇌ H$_2$O(l)</td>
<td>1</td>
<td>0.086</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>NH$_3$(g) ⇌ NH$_3$(l)</td>
<td>1</td>
<td>0.088</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>NH$_3$(aq) ⇌ NH$_3$(l)</td>
<td>1</td>
<td>0.088</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>NH$_3$(aq) ⇌ NH$_3$(l)</td>
<td>1</td>
<td>0.088</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>urea(l) ⇌ urea(s)</td>
<td>1</td>
<td>0.047</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>urea(aq) ⇌ urea(l)</td>
<td>1</td>
<td>0.047</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>urea(aq) ⇌ urea(l)</td>
<td>1</td>
<td>0.047</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>HNCO(g) ⇌ HNCO(l)</td>
<td>1</td>
<td>0.055</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>HNCO(g) ⇌ HNCO(aq)</td>
<td>1</td>
<td>0.055</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>HNCO(aq) ⇌ HNCO(l)</td>
<td>1</td>
<td>0.055</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>ammd(s) → ammd(g)</td>
<td>1</td>
<td>$1.000 \cdot 10^{11}$</td>
<td>0</td>
<td>245.67</td>
</tr>
</tbody>
</table>
Decomposition of urea in DETCHEM\textsuperscript{MPTR}

- Validation of overall mass loss by experimental data
- Evolution of different species in liquid and solid phase during decomposition
Simulation of chemical decomposition

- Urea
- Biuret
- Cyanuric acid
- Triuret
CFD-Simulation of thermogravimetric decomposition in StarCCM+

- Mesh with ~30000 cells
- Timestep of 20 ms
- Segregated flow model
- k-ε-turbulence model
- Evaporation/condensation model
- Rohsenow boiling model
- Complex Chemistry CVODE model

MPTR algorithm → C-code → Implementation by user coding
Coupling of DETCHEM<sup>MPTR</sup> with Star-CCM+

- **StarCCM+**: (g) and (l)
- **User Code MPTR**: (aq), (l), (s)

### Calculation of reaction rates in different phases (aq, l, s) and at interfaces

- **Calculation of concentrations in gas phase and liquid film, gas-liquid equilibrium, heat balance**
- **Input parameters**: $r_i$, $c_{i,\text{film}}$, $T_{\text{film}}$, $\Delta t$
Simulation of by-product decomposition

- Excellent agreement with simulation in DETCHEM^{MPTR}

- Continuous improvement of kinetic model for better agreement with experiments
Conclusion

- Systematic study on deposit formation in a hot gas test rig
- Characterization of derived solid deposits
- Kinetic modeling of urea decomposition and simulation in DETCHEMMPT
- Integration of DETCHEMMPT algorithm into a CFD simulation by user coding

Outlook

Comprehensive simulation of entire test rig
- Flow field
- Spray injection
- Spray/wall interaction
- Wall heat transfer
- Liquid film formation and flow
- Urea decomposition and by-product formation

Sept. 20, 2018  Marion Börnhorst
We acknowledge financial support by

Research Association for Combustion Engines

Thank you for your attention.

Contact: marion.boernhorst@kit.edu