Decomposition of $N_2O$ catalyzed by the bed material from co-combustion of sewage sludge and wood pellets in CFB boiler

Vesna Barišić
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Kinetics of Catalytic Nitrogen Oxide Reactions in Multifuel CFB Conditions

Vesna Barišić

Dr. Fredrik Klingstedt, Dr. Pia Kilpinen, Prof. Mikko Hupa
**Introduction**

The decomposition of $\text{N}_2\text{O}$ catalyzed by the bed material from co-combustion of sewage sludge and wood pellets in CFB boiler.

\[ \text{N}_2\text{O} \rightarrow \text{N}_2 + \frac{1}{2}\text{O}_2 \]

- Solids from CFB boiler:
  - char
  - lime
  - ash
  - bed material

Lack of data in the literature regarding the catalytic activity of solids from fluidized bed during combustion of biomass fuels and wastes.

Catalytic activity affected by flue gases, especially water vapor.

**Objective.** Catalytic activity of bed material from co-combustion of biomass fuels and wastes towards $\text{N}_2\text{O}$ decomposition was studied as a function of:
- fuel type,
- particle size,
- and presence of water vapor.

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**Experimental**

**Tested solids**

Bed material from the bottom bed of a 12 MW\textsubscript{th} CFB boiler:

- **Ch1** – wood pellets
- **Ch2** – wood pellets & sludge A
- **Ch3** – wood pellets & sludge B
  - mixture of sand & ash
  - char burned off before testing

<table>
<thead>
<tr>
<th></th>
<th>Wood pellets</th>
<th>Sludge A</th>
<th>Sludge B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry mat., wt-% a.r.</td>
<td>99.6</td>
<td>98.0</td>
<td>97.2</td>
</tr>
<tr>
<td>Ash, wt-%, dry</td>
<td>0.4</td>
<td>46.8</td>
<td>42.1</td>
</tr>
<tr>
<td>Volatiles, wt-%, dry</td>
<td>84.3</td>
<td>52.4</td>
<td>59.5</td>
</tr>
<tr>
<td>Nitrogen, wt-% dry</td>
<td>&lt;0.1</td>
<td>2.8</td>
<td>2.8</td>
</tr>
<tr>
<td>SiO\textsubscript{2}, wt-% of ash</td>
<td>12.8</td>
<td>27.4</td>
<td>21.8</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}, wt-% of ash</td>
<td>2.4</td>
<td>14.5</td>
<td>36.8</td>
</tr>
<tr>
<td>Fe\textsubscript{2}O\textsubscript{3}, wt-% of ash</td>
<td>1.7</td>
<td>22.3</td>
<td>5.8</td>
</tr>
<tr>
<td>CaO, wt-% of ash</td>
<td>32.5</td>
<td>5.7</td>
<td>5.3</td>
</tr>
<tr>
<td>MgO, wt-% of ash</td>
<td>5.4</td>
<td>1.2</td>
<td>1.1</td>
</tr>
<tr>
<td>P\textsubscript{2}O\textsubscript{5}, wt-% of ash</td>
<td>2.8</td>
<td>15.7</td>
<td>13.6</td>
</tr>
<tr>
<td>Na\textsubscript{2}O, wt-% of ash</td>
<td>0.7</td>
<td>0.14</td>
<td>0.1</td>
</tr>
<tr>
<td>K\textsubscript{2}O, wt-% of ash</td>
<td>12.9</td>
<td>1.65</td>
<td>1.2</td>
</tr>
<tr>
<td>SO\textsubscript{3}, wt-% of ash</td>
<td>3.8</td>
<td>5.0</td>
<td>3.8</td>
</tr>
<tr>
<td>Cl\textsuperscript{-}, wt-% of ash</td>
<td>1.0</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>CO\textsubscript{3} , wt-% of ash</td>
<td>~24</td>
<td>3.9</td>
<td>1.7</td>
</tr>
</tbody>
</table>
Experimental Bed material characterization

- **Elemental composition** – X-ray fluorescence (XRF)
- **Total BET surface area** – N$_2$-physisorption
- **Morphology and elemental composition of the particle’s surface** – Scanning electron microscope combined with an energy dispersive X-ray analyzer (SEM/EDX)
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**Experimental Setup**

- **Secondary inlet**
- **Sample**
- **Quartz wool**
- **Quartz plate**
- **Thermocouple**

**Primary inlet**

**Outlet**

**Experimental**

- **Data acquisition**
- **T indicator**
- **Gas Chromatograph**

**Setup**

- **Evaporator**
- **\(\text{H}_2\text{O}\) pump**
- **\(\text{N}_2\text{O}\)**
- **He-II**
- **He-I**

1: Mass flow controllers  
2: Tube furnace  
3: Fixed bed reactor  
4: Thermocouple  
5: Condenser  
6: Calibration gas  
7: Pump

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**Results**

**Effect of fuel type**

Sample particle size: 125-710, pressure 1 atm, residence time: 0.4 s, N₂Oₜₐₐₚ: 500 ppmv in He, total gas flow 1800 ml/min.

<table>
<thead>
<tr>
<th>Bed material</th>
<th>Ch1</th>
<th>Ch2</th>
<th>Ch3</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>93.7</td>
<td>95.0</td>
<td>86.9</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.6</td>
<td>1.0</td>
<td>5.4</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.6</td>
<td>1.1</td>
<td>1.5</td>
</tr>
<tr>
<td>CaO</td>
<td>2.6</td>
<td>1.0</td>
<td>2.3</td>
</tr>
<tr>
<td>MgO</td>
<td>0.6</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.6</td>
<td>0.8</td>
<td>2.2</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.1</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.8</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>sum</td>
<td>99.6</td>
<td>99.5</td>
<td>99.3</td>
</tr>
</tbody>
</table>

Bet surface area, m²/g

<table>
<thead>
<tr>
<th>Ch1</th>
<th>Ch2</th>
<th>Ch3</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.44</td>
<td>2.72</td>
<td>2.85</td>
</tr>
</tbody>
</table>
Results

Effect of fuel type

Ch3 (wood pellets & sludge B), 125-710 µm

a group of particles

ash particle

sand particles

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Results

Effect of particle size

Decomposition of N$_2$O catalyzed by the bed material from co-combustion of sewage sludge and wood pellets in CFB boiler

**Ch1** (wood pellets)

- 125-297 µm
- 355-500 µm
- 125-710 µm

**Ch2** (wood pellets & sludge A)

- 125-297 µm
- 355-500 µm
- 125-710 µm

Fraction 125-297 µm: ~8 wt-%; 355-500 µm: ~48 wt-%; 125-710 µm: ~97 wt-% of original sample

Pressure 1 atm, residence time: 0.4 s, N$_2$O$_{in}$: 500 ppm$_v$ in He, total gas flow 1800 ml/min.
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**Results**

**Effect of water vapor**

Sample particle size: 125-710, pressure 1 atm, temperature 850°C, mass of sample ~3 g, residence time: 0.4 s, N$_2$O$_{in}$: 500 ppm$_v$ in He, total gas flow 1800 ml/min.

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Conclusions

- All investigated materials act as a catalyst, in the temperature range 800-910°C, and their activities were affected by fuel type.

- The elemental composition of the bed material, mostly sand particles, gave good correlation with the activity. The measured catalytic activity of the bed material samples increased with the amount of the catalytically active oxides (CaO, MgO, Fe₂O₃, Al₂O₃).

- The elemental composition of the coating layer of the sand particles changed according to the composition of the ash from the parent fuel.
Conclusions

• In case of the bed material sampled while burning wood pellets with small amount of ash, different size fractions of bed material had similar activities.

• In case of the bed material sampled while burning wood pellets and sludge with high amount of ash, the activity of different size fractions of bed material decreased when particle size increased from 125-297 to 355-500\(\mu\)m.

• The higher activity of 125-297 \(\mu\)m fraction was attributed to a higher content of particles of ash (sludge), which are more porous and have a higher amount of catalytically active oxides.
Conclusions

• Increase of water up to 15 vol-% caused a significant decrease in the activity of bed materials, but from 15 vol-% to 30 vol-% there was only a minor further decrease.

• The decrease of activity was attributed to both sintering and coverage of active sites by H₂O molecules.
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