Direct and Indirect Plasma Technologies for NOx/SOx reduction

E. Stamate

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Outline and motivation

- Introduction
- NOx reduction mechanism and gas kinetic model
- Experimental setup – power-plant-scale reactor
- Correlation of IR and UV measurements with simulations
- Effect of water droplets, temperature profile and temperature gradient
- Biomass power plants
- Conclusions

**MOTIVATION**

Evaluate and optimize the low temperature oxidation in real experimental conditions including complex measurements and cost estimations
**Introduction**

Ozone

- NOx → O₃ → N₂O₅

**High temperature burner**

- Power plants, gas turbines, incinerators, boilers, diesel, etc.

**NOx**

- 95% NO (0.063 g/l)
- 5% NO₂ (1.260 g/l)

**Strong negative effects on the quality of air, soil and human health**

Use the same principle to reduce the NOx under controllable conditions

- NO + O₃ → NO₂ + O₂
- 2NO₂ + O₃ → N₂O₅ + O₂
- N₂O₅ + H₂O → 2HNO₃

**HNO₃ (aid rain)**
NOx reduction technologies:

- Selective catalytic reduction [Chen, 1992],
- Selective non-catalytic reduction [Lyon, 1975, Nam, 2000];
- Low-temperature oxidation by ozone [Jarvis, 2003];
- Non-thermal plasma [Mukkavilli, 1988], [Dinelli, 1990], [Chakrabarti, 1995], [Yamamoto, 2000];
- Electron beam irradiation and several hybrid techniques [Chang, 1997], [Martin, 2004].

None of these methods is free of trade-offs and limitations.

Advantages of low temperature oxidation:

- The discharge device is kept clean (the exhaust gas does not pass through the discharge reactor);
- The removal rate of NO is higher comparing with direct oxidation methods which has discharge poisoning problem (occurrence of reverse reactions reforming NO and NO$_2$ by O radical) [Yoshioka, 2003; Elisasson, 1991].
Chemical reaction model

Nitrogen network

NO \rightarrow NO_2 \rightarrow NO_3 \rightarrow N_2O_3

HNO_2 \rightarrow HNO_3

N_2O_4 \rightarrow N_2O_5

Loss channels:
- O_3 decays in gas and at walls
- O^{(3P)} recombination at walls
### Chemical kinetics model

**CHEMSIMUL (Risø DTU)**

<table>
<thead>
<tr>
<th>ID</th>
<th>Reaction</th>
<th>$A$ (cm$^3$ molecule$^{-1}$s$^{-1}$)</th>
<th>$-E_a$(kcal/mol)</th>
<th>$\beta$</th>
<th>$T$(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NO + O$_3$ → NO$_2$ + O$_2$;</td>
<td>$3.16 \times 10^{-12}$</td>
<td>3.1</td>
<td>0</td>
<td>212-422</td>
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<tr>
<td>2</td>
<td>NO$_2$ + O$_3$ → NO$_3$ + O$_2$;</td>
<td>$1.20 \times 10^{-13}$</td>
<td>4.87</td>
<td>0</td>
<td>230-600</td>
</tr>
<tr>
<td>3</td>
<td>NO$_2$ + NO$_3$ → N$_2$O$_5$;</td>
<td>$9.42 \times 10^{-9}$</td>
<td>0</td>
<td>-4.5</td>
<td>236-538</td>
</tr>
<tr>
<td>4</td>
<td>O$_3$ + N$_2$ → O$_2$ + O$^{(3)}$P + N$_2$;</td>
<td>$7.16 \times 10^{-10}$</td>
<td>22.26</td>
<td>0</td>
<td>300-3000</td>
</tr>
<tr>
<td>5</td>
<td>O$^{(3)}$P + O$_3$ → 2 O$_2$;</td>
<td>$3.11 \times 10^{-14}$</td>
<td>3.14</td>
<td>0.75</td>
<td>250-2000</td>
</tr>
<tr>
<td>6</td>
<td>O$^{(3)}$P + O$_2$ → O$_3$;</td>
<td>$2.32 \times 10^{-9}$</td>
<td>0</td>
<td>-2.2</td>
<td>200-1000</td>
</tr>
<tr>
<td>7</td>
<td>N$_2$O$_5$ + N$_2$ → NO$_2$ + NO$_3$ + N$_2$;</td>
<td>$4.57 \times 10^{5}$</td>
<td>21.86</td>
<td>-3.5</td>
<td>200-400</td>
</tr>
<tr>
<td>8</td>
<td>NO$_3$ → NO + O$_2$;</td>
<td>$2.50 \times 10^{6}$</td>
<td>12.12</td>
<td>0</td>
<td>298-934</td>
</tr>
<tr>
<td>9</td>
<td>NO + O$^{(3)}$P → NO$_2$;</td>
<td>$1.51 \times 10^{-6}$</td>
<td>0</td>
<td>-2.41</td>
<td>300-1340</td>
</tr>
<tr>
<td>10</td>
<td>NO$_2$ + O$^{(3)}$P → NO$_3$;</td>
<td>$271 \times 10^{-9}$</td>
<td>2.29</td>
<td>-4.94</td>
<td>200-2500</td>
</tr>
<tr>
<td>11</td>
<td>NO$_2$ + O$^{(3)}$P → O$_2$ + NO$_2$; 1.00 × 10$^{-11}$</td>
<td>0</td>
<td>0</td>
<td>298-329</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>2 NO$_2$ → O$_2$ + 2 NO$_2$;</td>
<td>$8.50 \times 10^{-13}$</td>
<td>4.87</td>
<td>0</td>
<td>298-329</td>
</tr>
<tr>
<td>13</td>
<td>NO$_2$ + NO$_3$ → O$_2$ + NO + NO$_2$;</td>
<td>$5.40 \times 10^{-14}$</td>
<td>2.96</td>
<td>0</td>
<td>298-332</td>
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<tr>
<td>14</td>
<td>2 NO$_2$ → O$_2$ + 2 NO;</td>
<td>$2.71 \times 10^{-12}$</td>
<td>26.03</td>
<td>0</td>
<td>300-2500</td>
</tr>
<tr>
<td>15</td>
<td>2 NO$_2$ → NO + NO$_3$;</td>
<td>$1.59 \times 10^{-14}$</td>
<td>20.87</td>
<td>0.73</td>
<td>300-2500</td>
</tr>
<tr>
<td>16</td>
<td>2 NO$_2$ → N$_2$O$_4$;</td>
<td>$0.0259$</td>
<td>0</td>
<td>-4.8</td>
<td>300-500</td>
</tr>
<tr>
<td>17</td>
<td>N$_2$O$_4$ + H$_2$O → HNO$_3$ + HNO$_2$;</td>
<td>$4.18 \times 10^{-10}$</td>
<td>11.59</td>
<td>0</td>
<td>298-323</td>
</tr>
<tr>
<td>18</td>
<td>N$_2$O$_4$ + N$_2$ → 2 NO$_2$ + N$_2$;</td>
<td>$3.28 \times 10^{4}$</td>
<td>12.72</td>
<td>-3.8</td>
<td>300-500</td>
</tr>
<tr>
<td>19</td>
<td>N$_2$O$_5$ + H$_2$O → 2 HNO$_3$;</td>
<td>$2.51 \times 10^{-22}$</td>
<td>0</td>
<td>0</td>
<td>290-293</td>
</tr>
<tr>
<td>20</td>
<td>HNO$_2$ + NO$_3$ → HNO$_3$ + NO$_2$;</td>
<td>$1.00 \times 10^{-15}$</td>
<td>0</td>
<td>0</td>
<td>298</td>
</tr>
<tr>
<td>21</td>
<td>NO$_3$ + NO → 2 NO$_2$;</td>
<td>$1.80 \times 10^{-11}$</td>
<td>0</td>
<td>-0.22</td>
<td>0</td>
</tr>
<tr>
<td>22</td>
<td>O$_3$ + NO$_2$ → NO + 2 O$_2$;</td>
<td>$1.00 \times 10^{-18}$</td>
<td>0</td>
<td>0</td>
<td>298</td>
</tr>
<tr>
<td>23</td>
<td>O$_3$ + NO$_3$ → NO$_2$ + 2 O$_2$;</td>
<td>$1.00 \times 10^{-17}$</td>
<td>0</td>
<td>0</td>
<td>298</td>
</tr>
<tr>
<td>24</td>
<td>NO + NO$_3$ → 2 NO + O$_2$;</td>
<td>$2.71 \times 10^{-11}$</td>
<td>1.882</td>
<td>-0.23</td>
<td>0</td>
</tr>
<tr>
<td>25</td>
<td>2 O$^{(3)}$P → O$_3$;</td>
<td>$3.82 \times 10^{-13}$</td>
<td>-1.79</td>
<td>-1</td>
<td>200-4000</td>
</tr>
<tr>
<td>26</td>
<td>O$^{(3)}$P + NO$_2$ → O$_2$ + NO;</td>
<td>$5.5 \times 10^{-12}$</td>
<td>0.3736</td>
<td>-0.179</td>
<td>220-420</td>
</tr>
<tr>
<td>29+30</td>
<td>2 NO + O$_2$ → 2 NO$_2$;</td>
<td>$5.61 \times 10^{-21}$</td>
<td>1.053</td>
<td>1.053</td>
<td>270-600</td>
</tr>
<tr>
<td>27</td>
<td>NO + NO$_2$ → N$_2$O$_3$;</td>
<td>$2.70 \times 10^{7}$</td>
<td>0</td>
<td>-8.7</td>
<td>200-300</td>
</tr>
<tr>
<td>28</td>
<td>N$_2$O$_3$ + N$_2$ → NO + NO$_2$ + N$_2$;</td>
<td>$6.76 \times 10^{14}$</td>
<td>9.7</td>
<td>-8.7</td>
<td>225-300</td>
</tr>
<tr>
<td>29</td>
<td>N$_2$O$_5$ + 2 H$_2$O → 2 HNO$_3$ + H$_2$O;</td>
<td>$4.4 \times 10^{-21}$</td>
<td>0</td>
<td>-8.7</td>
<td>225-300</td>
</tr>
<tr>
<td>30</td>
<td>N$_2$O$_5$ + 3 H$_2$O → 2 HNO$_3$ + 2 H$_2$O;</td>
<td>$8 \times 10^{-20}$</td>
<td>0</td>
<td>-8.7</td>
<td>225-300</td>
</tr>
</tbody>
</table>
Heterophase reactions

\[ k = AT^\beta \exp\left(\frac{E_a}{RT}\right) \]

- Recombination of oxygen
- Decomposition of ozone on the reactor wall

\[
\frac{d[O(3\,P)]}{dt} = -[O(3\,P)] \left\{ \frac{(30\,\text{cm})^2}{5.78 \times 0.292\,\text{cm}^2\,\text{s}^{-1}\,C/273\,\text{K}^{\text{h}5}} + \frac{2 \times 30\,\text{cm}}{9.9 \times 10^{-3}\,\sqrt{2} \times 4.25 \times 10^4\,\text{cm}\,\text{s}^{-1}\,\sqrt{T/273\,\text{K}}} \right\}^{-1}
\]

\[
\frac{d[O_3]}{dt} = -[O_3] \left\{ \frac{(30\,\text{cm})^2}{5.78 \times 0.208\,\text{cm}^2\,\text{s}^{-1}\,C/273\,\text{K}^{\text{h}5}} + \frac{2 \times 30\,\text{cm}}{2 \times 10^{-6}\,\sqrt{2} \times 3.47 \times 10^4\,\text{cm}\,\text{s}^{-1}\,\sqrt{T/273\,\text{K}}} \right\}^{-1}
\]

Rec #7: \( N_2O_5 \rightarrow NO_2 + NO_3 \) can be quenched if \( N_2O_5 \) absorbed by water droplets

\[ J = n_g c_{\gamma_{\text{obs}}} / 4 \]

- \( n_g \) is the gas density ([\( N_2O_5 \)]) and
- \( c \) is the root mean square thermal velocity of the \( N_2O_5 \) molecules

\[ n_c = x \cdot [H_2O] = x \cdot C_{H_2O} \cdot \frac{p}{k_B T} \]

\[ N_d = \frac{N_A m_d}{M_{H_2O}} = \frac{4N_A \rho \pi r^3}{3M_{H_2O}} \]

\[ A = 4\pi r^2 n_d = \frac{3 \cdot C_{H_2O} \cdot \rho M_{H_2O}}{\rho r RT} \]
Radicals concentrations at different ozone input, 60 °C

Most of NO is converted into NO$_2$ within 0.3 second after ozone injection at high ozone input case.
NOx reduction setup

1. Flue gas flow
2. NOx concentration
3. Inlet flue gas temperature
4. Electric power to ozone generator
5. Oxygen production
6. Oxygen consumption
7. Ozone production
8. Reactor temperature
9. pH in scrubber media
10. Temperature of scrubber media
11. Ozone concentration after scrubber
12. Temperature after scrubber
13. NOx after scrubber
Details on experimental set-up

UV measurement

UV lamp

Lens

Detector

IR measurement

NOx

Reactor

20 cm

35 cm

200 cm

10 cm

ϕ = 60 cm

50 cm

Spectrometer

CCD camera

120 cm

IR measurement

80 cm

80 cm
Ringsted and Haslev power plants in Denmark

**Key figures from Ringsted CHP and Haslev CHP**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Ringsted CHP</th>
<th>Haslev CHP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power</td>
<td>MW&lt;sub&gt;el&lt;/sub&gt;</td>
<td>2 x 5.5</td>
<td>5</td>
</tr>
<tr>
<td>Heat</td>
<td>MJ / s</td>
<td>2 x 6.5</td>
<td>13</td>
</tr>
<tr>
<td>Flue gas flow</td>
<td>std. m&lt;sup&gt;3&lt;/sup&gt; / h, dry</td>
<td>49,000</td>
<td>31,000</td>
</tr>
<tr>
<td>Flue gas temperature</td>
<td>°C</td>
<td>65</td>
<td>105 – 115</td>
</tr>
<tr>
<td>O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>vol. %</td>
<td>11</td>
<td>8 – 10</td>
</tr>
<tr>
<td>NO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>ppm</td>
<td>90 – 100</td>
<td>150 – 300</td>
</tr>
</tbody>
</table>
Two container arrangement

Ozone generator
SMO 300 S (WEDECO): 2.64 kg O$_3$ controllable from 10% up to 100%
FTIR spectra for different $O_3$ concentrations

Port 2, 60 °C

- 25 g/h
- 100 g/h
- 150 g/h

Wavenumber (cm$^{-1}$)
NO\textsubscript{x} reduction efficiency at different O\textsubscript{3} input

Ringsted power plant (4 MW, natural gas fueled)
80 ppm NO\textsubscript{x} for the untreated flue gas, 60 \degree C

Over 95% NO\textsubscript{x} reduction at 150 ppm O\textsubscript{3} at molar ratio O\textsubscript{3}/NO\textsubscript{x} = 1.875
Ozone measurements by both FTIR and UV are consistent with simulation.
Simulated NO$_2$ and N$_2$O$_5$ concentration at different ozone input, 60 °C

No effect on NO$_2$

Strong effect on N$_2$O$_5$

10 μm H$_2$O
NO$_2$ and N$_2$O$_5$ at different ozone input, 60 °C

100 µm H$_2$O

100 µm water droplets simulation in the reactor shows best fitting with measurement
(a) no water

(b) 100 μm water

(c) 10 μm water

At 100 °C, the 10 μm water droplets in the reactor, the NO₂ reduction rate is optimum.
**Effect of temperature gradient**

NO: 73 ppm  
NO$_2$: 7 ppm  
ozone input: 150 ppm  
ozone/NO$_x$: 1.875  
T: 113 – 63 ºC  
Radius of reactor: 30 cm

NO: 554.5 ppm  
NO$_2$: 5.45 ppm  
ozone input: 1763 ppm  
ozone/NO$_x$: 3.15  
T: 113 – 63 ºC  
Radius of reactor: 2.5 cm

Higher temperature in the entrance: rapid initial removal of NO$_2$  
Lower temperature: reduce the subsequent decay of O$_3$
Ringsted
- Diesel gas fueled;
- 60 °C flue gas;
- Negative pressure in the reactor;
- No big particles in the flue gas;
- Stable flue gas composition;
- Ozone input higher than 75 g/h leads to high NO\textsubscript{x} reduction.

Haslev
- Straw fueled;
- 115 °C flue gas;
- Positive pressure in the reactor;
- Big residual particles (deposited on the observation windows and mesh);
- High fluctuations of NO\textsubscript{x} level in flue gas;
- Higher humidity in the reactor;
- Higher ozone flow input needed (over 300 g/h) for high NO\textsubscript{x} reduction;
- Additional problems related to water cooling, sensors, alarms, contamination.
Time dependence of NOx levels
Time delays in NOx reduction - biomass
Ozone generator reaction time

- Ox_on = 21 sec
- Ox_off = 21 sec
- Ox = 42 sec

Ozone level [ppm] vs. Time [sec]

Concentration [ppm] vs. Time [sec]
Delay compensated NOx removal - biomass
Ozone consumption and cost

![Graph showing specific ozone consumption and cost](image-url)

- **Specific ozone consumption / kg Cr / kg NOx removed**
  - Degree of reduction: 0 to 1
  - Data points for Straw fired boiler and Natural gas fired engine

- **Cost (DKK/kg NOx)**
  - Annual operating time: 2000 to 7000 hours
  - Lines for LOX, PSA, and AIR
Conclusions

- NOx reduction by Ozone can be done with an efficiency higher than 95%
- Water droplets can improve the removal efficiency but result in N₂O₅ capture in the reactor
- NOx reduction in biomass power plants needs additional settings to compensate delays in ozone delivery
Disadvantages NOx versus catalytic reduction

- More complicated physical design
- Need for pH regulating chemicals
- Waste water issues
- Space requirements
- Environmental and safety aspects of producing and using ozone
Advantages for ozone injection method

- Positive income from fertilizer or hydrochloric acid production.
- The plasma deNOx process also removes formaldehyde and SO$_2$, so reduces the need for an oxidation catalyst on gas engine plants and reduces SO$_2$ taxes on biomass plants.
- On biomass plants with bag filters, e.g. straw fired plants, the scrubber can utilize the latent heat in the flue gas by cooling the flue gas from e.g. 120 °C to 70 °C and increasing the efficiency of the CHP plant.
- Some CHP or district heating plants operate with a very cold temperature of the return water, around 45 °C, from the district heating system, which permits the deNOx plant to operate as part of a condensation step utilizing even more energy from the flue gas.
- No need for storage and handling of ammonia as needed with the SCR technology.