Strategies for NOx / SOx reduction at biogas power plants using pellets

E. Stamate

Department of Energy Conversion and Storage

Technical University of Denmark
MOTIVATION

Address the particularities of NOx/SOx reduction in biomass power plants
"Estimates show that it is possible to raise Danish agricultural production of biomass for bioenergy 4-5 times through greater exploitation of straw at CHP plants, slurry for biogas, animal fat for biodiesel and by using perennial energy crops as well as grass from low-lying areas. [http://en.fvm.dk/focus-on/bioenergy/biomass-in-denmark/](http://en.fvm.dk/focus-on/bioenergy/biomass-in-denmark/) (Ministry of Food, Agriculture and Fisheries of Denmark)

NO\textsubscript{x} and SO\textsubscript{2}

Combustion of fossil fuels and biomass produces other gases besides greenhouse gases, including nitrogen oxides (NO\textsubscript{x}) and sulphur dioxide (SO\textsubscript{2}), which also have significant environmental impacts. NO\textsubscript{x} contributes to photochemical smog, which is harmful to human health, while SO\textsubscript{2} reacts in the atmosphere to become sulphuric acid and contributes to acidification. The effects of NO\textsubscript{x} and SO\textsubscript{2} are primarily regional, while CO\textsubscript{2} is a global issue.

DONG Energy has a target of reducing the NO\textsubscript{x} and SO\textsubscript{2} emissions from its power stations by 90\% and 95\% respectively by 2020 compared with 1990. For NO\textsubscript{x}, this means that emissions must have fallen to 0.33 g/kWh by 2020, as they were 3.30 g/kWh in 1990.

For SO\textsubscript{2}, the target for 2020 is 0.24 g/kWh, as emissions from power stations were 4.80 g/kWh in 1990. The table on the next page shows that the target for SO\textsubscript{2} has been met, as emissions have been reduced to 0.07 g/kWh, equivalent to a 99\% reduction compared with 1990.

For NO\textsubscript{x}, emissions have to be reduced further, as they are currently 0.39 g/kWh, equivalent to a reduction of 88\% compared with 1990. Analyses show that reduction of NO\textsubscript{x} emissions from power stations does not necessarily require new expensive plants. In fact, in some cases it pays not to invest in new expensive deNO\textsubscript{x} plants that capture nitrogen oxides and prevent them from being emitted. Instead, DONG Energy’s business unit Thermal Power focuses on making a number of small investments and improving operation and maintenance at the power stations, both those with and those without deNO\textsubscript{x} plants.

Biomass in electricity and heat generation at thermal power stations in Denmark, %

Introduction

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

High temperature burner

NOx + O3 → NO2 + O2
2NO2 + O3 → N2O5 + O2
N2O5 + H2O → 2HNO3

HNO3 (aid rain)

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

Use the same principle to reduce the NOx under controllable conditions

NOx

95% NO (0.063 g/l)
5% NO2 (1.260 g/l)
NOx reduction technologies:

- Selective catalytic reduction
- Selective non-catalytic reduction
- Low-temperature oxidation by ozone
- Non-thermal plasma
- Electron beam irradiation and several hybrid techniques

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 NO₂ by O radical)
Typical 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
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. m³ / 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>O₂</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%
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 °C

Over 95% NOx reduction at 150 ppm O\textsubscript{3} at molar ratio O\textsubscript{3}/NO\textsubscript{x} = 1.875
<table>
<thead>
<tr>
<th>Ringsted</th>
<th>Haslev</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diesel gas fueled;</td>
<td>Straw fueled;</td>
</tr>
<tr>
<td>60 °C flue gas;</td>
<td>115 °C flue gas;</td>
</tr>
<tr>
<td>Negative pressure in the reactor;</td>
<td>Positive pressure in the reactor;</td>
</tr>
<tr>
<td>No big particles in the flue gas;</td>
<td>Big residual particles (deposited on the observation windows and mesh);</td>
</tr>
<tr>
<td>Stable flue gas composition;</td>
<td>High fluctuations of NO\textsubscript{x} level in flue gas;</td>
</tr>
<tr>
<td>Ozone input higher than 75 g/h leads to high NO\textsubscript{x} reduction.</td>
<td>Higher humidity in the reactor;</td>
</tr>
<tr>
<td></td>
<td>Higher ozone flow input needed (over 300 g/h) for high NO\textsubscript{x} reduction;</td>
</tr>
<tr>
<td></td>
<td>Additional problems related to water cooling, sensors, alarms, contamination.</td>
</tr>
</tbody>
</table>
Time dependence of NOx levels

![Graph showing the time dependence of NOx levels with traces for different concentrations and time intervals.]

- Trace 1
- Trace 2
- Trace 3

**Time [sec]**

**Concentration [ppm]**

**NOx [ppm]**

- NOx SL1
- NOx SL2

\[ \Delta T_{NOx} = 37 \text{ sec} \]
Ozone generator reaction time

- $t_{ox_{on}} = 21$ sec
- $t_{ox_{off}} = 21$ sec
- $t_{ox} = 42$ sec

Ozone level [ppm] vs. Time [sec]

Concentration [ppm] vs. Time [sec]

- NOx_In
- NOx_Out
- Ozone_Out
Delay compensated NOx removal - biomass

<table>
<thead>
<tr>
<th>Time [sec]</th>
<th>NOx_In</th>
<th>Nox_Out</th>
<th>Ozone_Out</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>180</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>360</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>540</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>720</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>900</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Ozone consumption and cost

![Graph showing specific ozone consumption in kg O₃ per kg NOx removed vs. degree of reduction. Different symbols represent straw-fired boiler and natural gas-fired engine.]

![Graph showing cost in DKK per kg NOx vs. annual operating time in hours. Lines represent LOX, PSA, and AIR systems.]
NOX/SOx PlasTEP reactor built at DTU

- 6 m long reactor
- up to 250 SLM flue gas
- up to 100 g/h O$_3$ (air, O$_2$)
- NO, NO$_2$, O$_3$ sensors
- 7 sampling ports
- Controlled gas flows
- Gas and reactor heating
- Wet scrubber
- O$_3$ destroyer
- NOx up to 10000 ppm
- PC control
NOX/SOx PlasTEP reactor built at DTU
NO\textsubscript{2} and O\textsubscript{3}\textsuperscript{R} as a function of O\textsubscript{3}\textsuperscript{IN} at P\textsubscript{1} for all four mixing schemes for an air flow of 40 slm, ozonized air of 10 slm, 0.027 slm of NO and initial values of NO=316 ppm and NO\textsubscript{2}=104 ppm (O\textsubscript{3}\textsuperscript{IN}=0 ppm).
Constant $O_3^{IN}$, “on-off” NO, $NO_x$ at $P_1$ and $P_5$ for 50 slm dry air, 0.21 slm NO, $NO_x$-on= 411 ppm, NO-on= 304 ppm. $O_3^{IN}$=1900 ppm, Power ozone generator = 256 W.
DTU - pentagon DBD structure

- Quick coupling for cooling (6 mm or ¾ inch tube)
- DBD plate (reed)
- Mounting ring
- High voltage
- Water or air cooling
- Thermal conductive paste (green)
- Cooling block (Copper or Aluminium)
- Ground connection
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.
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
Conclusions

- NOx reduction by Ozone can be done with an efficiency higher than 95%
- NOx reduction in biomass power plants needs additional settings to compensate delays in ozone delivery
- A small size reactor for NOx/SOx reduction is available within the PlasTEP and PlasTEP+ projects