NO_x reduction obtained by low-temperature plasma generated ozone

Main author
Torben Kvist Jensen
Danish Gas Technology Centre
Denmark
tkj@dcc.dk

Co-authors
Lars Jørgensen, Michael Ørtenblad
Danish Gas Technology Centre

Eugene Stamate
Risø-DTU

Peter Simonsen, Lasse Tobiassen
DONG Energy

IGRC2008@gasunie.nl

1. ABSTRACT

On large gas and coal fired power plants conventional deNO$_x$ equipment is installed but this is often not the case for smaller combined heat and power plants (CHP). Modern stationary natural gas engines for CHP generation are mostly operated at very lean conditions. One important reason is to obtain low NO$_x$ emissions. But is it not likely to reduce the NO$_x$ emissions significantly by leaning combustion conditions further. Another source for NO$_x$ emissions are smaller biomass fired CHP units. Today there is no NO$_x$ after treatment equipment installed on these plants.

One way of reducing NO$_x$ emissions is to add ozone to the flue gas just before it enters the chimney. The ozone will convert the NO$_x$ to dinitrogen pentoxide (N_2O_5). As the N_2O_5 is highly soluble in water it is easily removed from the flue gas by a scrubber. This technology has been tested in both laboratory experiments and pilot scale tests.

Laboratory experiments have been conducted in order examine the influence of different parameters as flue gas temperature, NO$_x$ and ozone concentrations. The experiments showed that it was possible to obtain a degree of reduction of up to 95 %. Furthermore, it was found that the compounds SO_2 and HCl which are present in flue gas from biomass combustion do not affect the deNO$_x$ chemistry negatively.

Beside laboratory measurements pilot-scale tests have been conducted on a CHP unit based on a natural gas fired engine and on a CHP unit based on a straw fired boiler. A part stream of 3-5 % of the flue gas was treated. It was found that it is possible to reduce the NO$_x$ emissions to a very low level on both units and that it requires approximately twice as much ozone on the straw fired unit compared to the gas engine unit.

C O N T E N T S

2. INTRODUCTION

Modern stationary natural gas engines for CHP generation are mostly operated at very lean conditions. One important reason is to obtain low NO_x emissions. By applying engines running very lean it is possible to reduce the NOx emissions. But is it not likely to reduce the NO_x emissions significantly by leaning combustion conditions further.
On smaller biomass fired CHP unit where the combustion takes place on a grate there is no NO_x after-treatment equipment installed. On these plants the only way of reducing NO_x emissions without changing the boiler design is by controlling and injecting the combustion air in an intelligent way.

In order to limit emissions of acidifying and eutrophying pollutants the European Parliament has launched the NEC directive. This directive implies a commitment to further reduce the emission of NO_x and, therefore, new means of reducing NO_x emissions from these smaller CHP units must be considered.

A common method to remove NO_x from flue gases is SCR catalysts. However, this technology requires a temperature higher than what is present in flue gas from gas engines. Another way of obtaining lower NO_x emissions is to add ozone to the flue gas. The ozone will convert the NO_x to dinitrogen pentoxide (N_2O_5). As the N_2O_5 is highly soluble in water it is easily removed from the flue gas by a scrubber.

A commercial system applying ozone injection has become available under the trademark LoTox [1].

The chemical reactions can take place at temperatures as low as room temperature. This is advantageous compared to other deNO_x techniques that require significantly higher temperatures. SCR catalysts are efficient at around 800 °C and reburning affects the primary combustion. Unlike these techniques, ozone based deNO_x can be installed as a retrofit unit at existing plants as a tail-end solution.

It is well known that traditional SCR catalysts for NO_x reduction are poisoned by alkali metals present in flue gas straw combustion. Therefore, ozone based deNO_x is an alternative solution as it is based on non-catalytic reactions.

3. NO_X REMOVAL THEORY

Unlike must techniques for NO_x removal such as SCR, SNCR and reburning, NO_x removal by ozone does not occur by reducing but by oxidizing the NO_x compounds.
The NO and NO_2 are oxidized by O_3 to N_2O_5 in the following subsequent steps.

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$NO_2 + NO_3 \rightarrow N_2O_5$$

The oxidation from NO_2 to NO_3 is the slowest reaction in the chain. N_2O_5, which is the anhydride of nitric acid, can easily be removed from a flue gas by contact with water in a scrubber unit according to the following reaction to form Nitric acid (HNO_3).

$$N_2O_5(g) + H_2O \rightarrow 2\,HNO_3(aq)$$

The formed nitric acid can be used as acid or it can be neutralized and used as for instance as fertilizer.

Compared to other deNO$_x$ techniques the chemical reactions can take place at temperatures as low as room temperature.

4. LAB SCALE EXPRIMENT

4.1. Experimental setup

Laboratory experiments have been conducted in order to examine the influence of different parameters such as flue gas temperature, NO$_x$ and ozone concentration. The flue gas came from a 30 kW$_e$ natural gas fired turbocharged engine. The flue gas was cooled to the desired temperature. The experiments showed that it was possible to obtain a degree of reduction of up to 95 %.

The ozone was produced with a dielectric barrier discharge (DBD) unit in a low temperature atmospheric pressure plasma. The ozone concentration varies between 2 and 7 % (volume), depending on the discharge power and oxygen supply flow rate. The O_2/O_3 mixture was mixed with the experimental part of the exhaust. A mixing device was constructed for the best possible mixing at the mixing point.

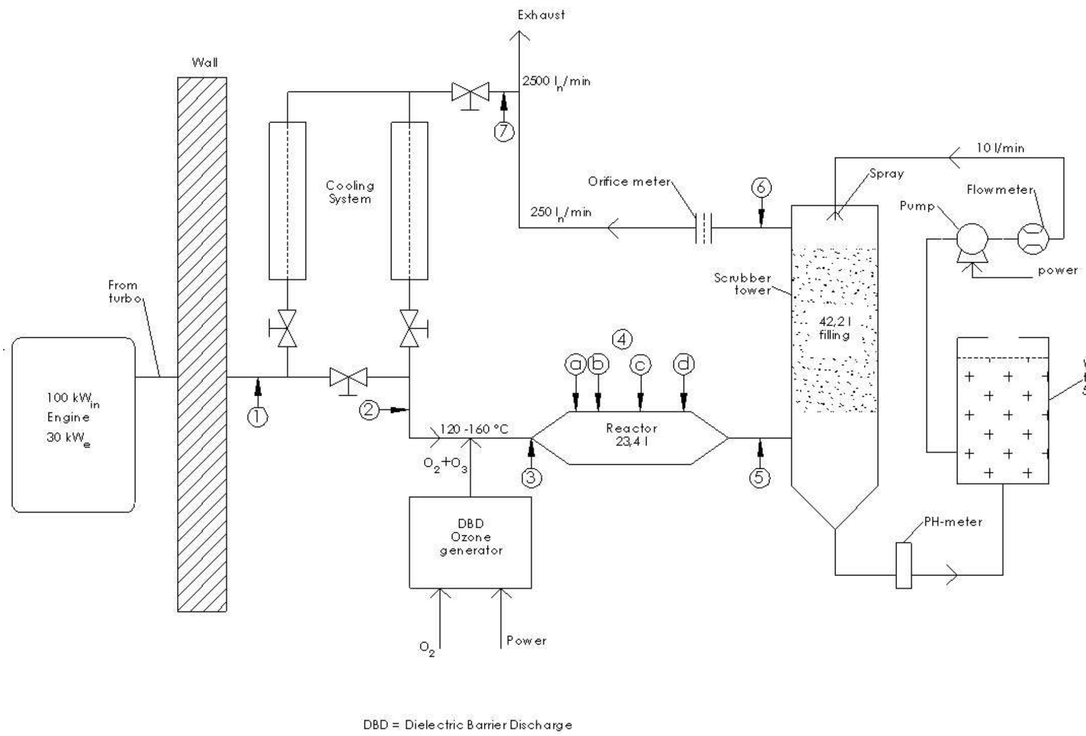

Figure 1. Scematic drawing of the setup for lab scale experiments

4.2. Results of lab scale experiments

The DBD effect was stepwise variable from 0-500 W resulting in increasing ozone formation. Similarly, the oxygen flow was stepwise variable from 1.4-6 normal litres per minute. Variation of these two parameters results in varied ozone formation and thus various levels of NO_x reduction. The conducted test matrix is given in Table 1.

Table 1. Parameters from selected test series

Effect	Oxygen flow	Temperature	Ozone media
W	l_n/min	°C	
0 – 500	1,4 - 6	160	Pure O_2
		110	Pure O_2
		140	Air

The figures below show the NO_x reduction level as a function of the DBD effect and the oxygen/pressurized air flow during tests. Figure 2 and Figure 3 illustrate that it is easier to achieve higher reduction levels at a process temperature of 110 °C than at a temperature of 160 °C. Both tests used pure oxygen as ozone medium.

From Figure 2 it appears that more than 5 normal litres oxygen/min. and min. 400 W in the DBD unit at a flue gas temperature of 160 °C are necessary to achieve reduction levels at approx. 95 %. Increases in both parameters will only increase the reduction level marginally. Figure 3 shows that reduction levels of around 95 % at a flue gas temperature of 110 °C can be achieved already at an oxygen flow of 3 normal litres oxygen/min. and a DBD effect of 250 W. It is, obviously, easier to reach high reduction levels at that temperature than at 160 °C, which results in lower operating costs.

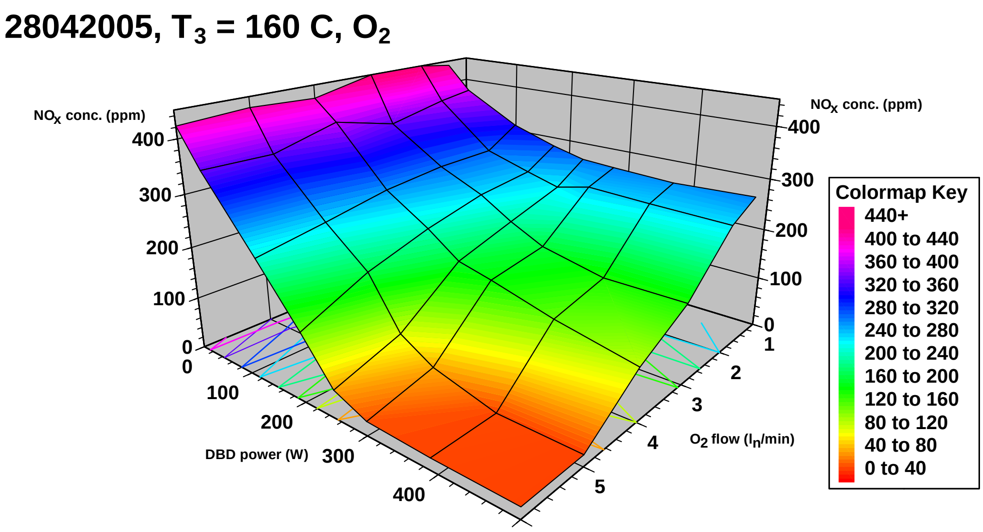

Figure 2. NO_x reduction as a function of DBD effect and oxygen flow at 160 °C and with pure O_2 as ozone medium

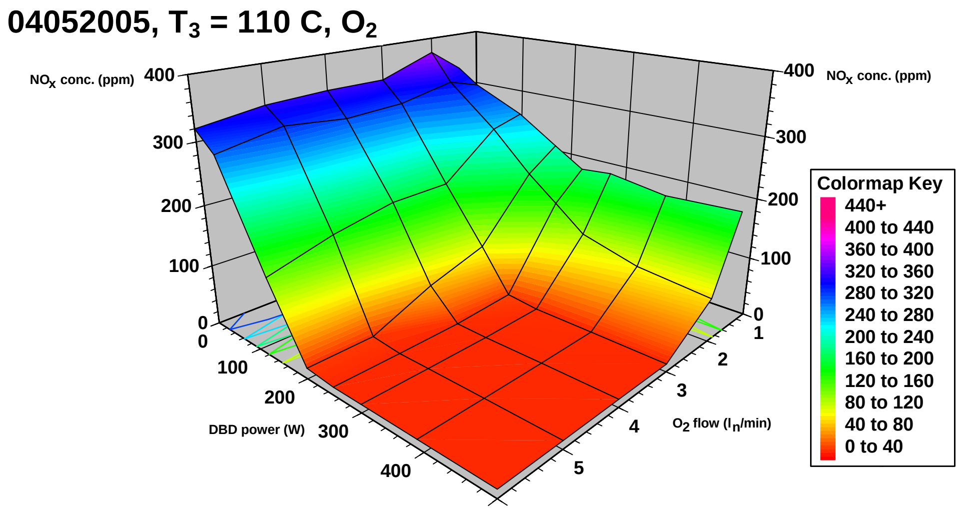

Figure 3. NO_x reduction as a function of DBD effect and oxygen flow at 110 °C and with pure O_2 as ozone medium

Figure 4 shows that dry pressurized air results in lower reduction levels. This is due to the fact that the lower oxygen content results in a smaller amount of ozone, which - in turn - results in less conversion of NO_x. The figure shows that under the given circumstances reduction levels of approx. 75 % can be achieved.

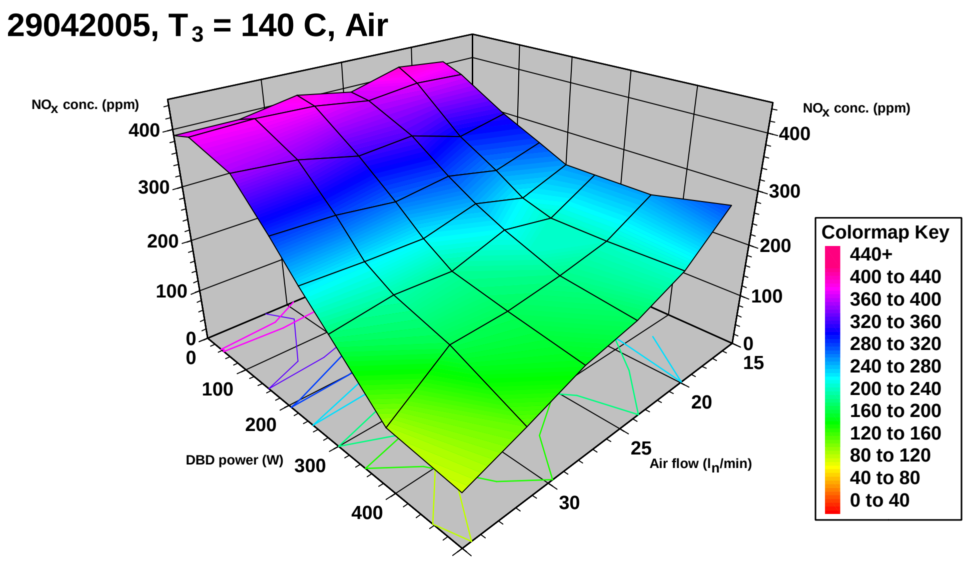

Figure 4. NO_x reduction as a function of DBD effect and oxygen flow at 140 °C and with pressurized air as ozone medium

4.2.1. *Influence of HCl and SO_2 on the deNO$_x$ reactions*

The technology might also be applicable for NO_x removal from flue gas from biofuel fired boilers. Flue gas from biomass combustion often contains SO_2 and HCl, which might affect the chemistry of the deNO$_x$ processes negatively. In order to examine that tests were conducted on "synthetic" flue gas from biofuel combustion. The synthetic flue gas was combustion products from a natural gas burner and varying amounts of SO_2 and gaseous HCl (1% in N_2) were added. The experiments showed no negative effect on the NOx removal due the SO_2 and HCl.

5. *PILOT SCALE TESTS*

In addition to laboratory measurements pilot scale tests were conducted. This was done in order to test the deNO_x concept on flue gases from heat and power producing units in operation. For that purpose a semi-mobile test unit was built.

The pilot scale test unit consists of

- an ozone generator based on oxygen as supply gas
- a unit mixing the ozone and flue gas
- a reactor where the deNO_x chemistry processes occurs
- a water scrubber removing the produced N_2O_5
- a catalyst for removing any ozone that might be present in the cleaned flue gas

These components were built into two 20-feet containers.

The unit was tested on two different CHP plants. The first plant is based on 5,5 MW_e natural gas fired engine located at Ringsted Combined Heat and Power. The temperature of the exhaust gas just before it is led to the chimney was around 70 °C. The other plant was Haslev Combined Heat and Power, a 5 MW_e unit consisting of a straw fired boiler and a steam turbine. The flue gas temperature just upstream from the chimney is around 120 °C. In both cases a part stream of the flue gas was sampled just before it is led to the chimney and subsequently treated by the test unit. Both plants are owned and operated by DONG Energy, a Danish power utility company.

5.1. *Results of pilot-scale tests*

The concentration of NO_x in the flue gas from the gas engine unit was rather constant as shown in *Figure 5*. From the straw fired boiler the NO_x emissions varied, both on a shorter and a longer time scale as shown in *Figure 5*. A reason for the fluctuations on the shorter time scale is that the boiler is a so-called cigar fired boiler where the main combustion takes place at the edge of an in coming straw bale. When partially burned straw falls from the edge of the bale and down on the grate below it affects the combustion significantly and thereby also the NO_x formation [2]. The variation on the longer time scale is probably due to variation in the fuelling.

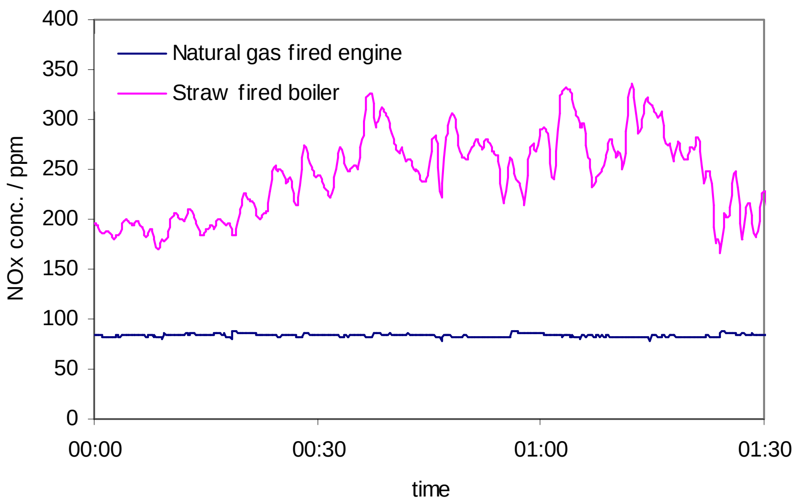

Figure 5. NO_x emissions from the two plants that the deNO_x unit was test on

At each condition given below the amount of ozone injected was constant. No control system was used to control the O_3 flow to follow the variation in the NO_x concentration.

As mentioned above the NO_x oxidation occurs in steps. First NO is oxidised to NO_2, which subsequently is oxidised to NO_3 and later to N_2O_5. That is clearly illustrated in *Figure 6*, which shows the concentration of NO_x in the raw flue and in the treated flue together with NO concentration in the treated flue gas versus the amount of ozone supplied. For smaller amounts of ozone the ozone is used for oxidizing NO to NO_2 leading only to a very modest NO_x decrease. By increasing the ozone addition the formed NO_2 will be oxidised. It is also shown that for both the natural gas fired engine and for the straw fired boiler it is possible to reduce the NO_x emission to practically nothing. The odd shape of NO-NO_x curves for the treated straw flue gas is probably due to variation of the NO_x concentration of the raw incoming flue gas.

Using a too low amount of ozone will lead to inefficient use of the ozone as the amount of NO_x removed is low compared to the amount of ozone used. But on the other hand, it is ozone-costly to aim for a total NO_x removal. This is illustrated in *Figure 7* that shows the specific ozone consumption given as a relation between the amount of ozone consumed and the amount of NO_x removed. For the gas engine unit the optimal ozone utilization is obtained by injecting ozone so a NO_x reduction on 65-90 % is reached. For the straw fired boiler the best ozone exploitation was obtained at a NOx removal at around 70 %. Apparently the window for optimal ozone application is narrower and located at lower degrees of reduction for the straw fired unit than for the gas engine unit. This is probably due to the fact that the NO_x concentration in the raw flue gas varies while the injected amount of ozone is constant. This means that each at any given measurement which is an average of 20 minutes of measurement there will be periods where the ratio between NOx in the flue gas and ozone injection is not optimal.

At conditions where the exploitation of injected ozone is best, the price paid for the NO_x removal given as ozone consumption was found to be around twice as high for NO_x removal from the flue gas from the straw fired boiler unit compared to the gas engine unit. The lower ozone efficiency for the straw fired boiler is probably due to both the variations in NO_x concentration in the raw flue gas and higher flue gas temperature compared to gas engine. The effect of temperature was illustrated in *Figure 2* and *Figure 3*.

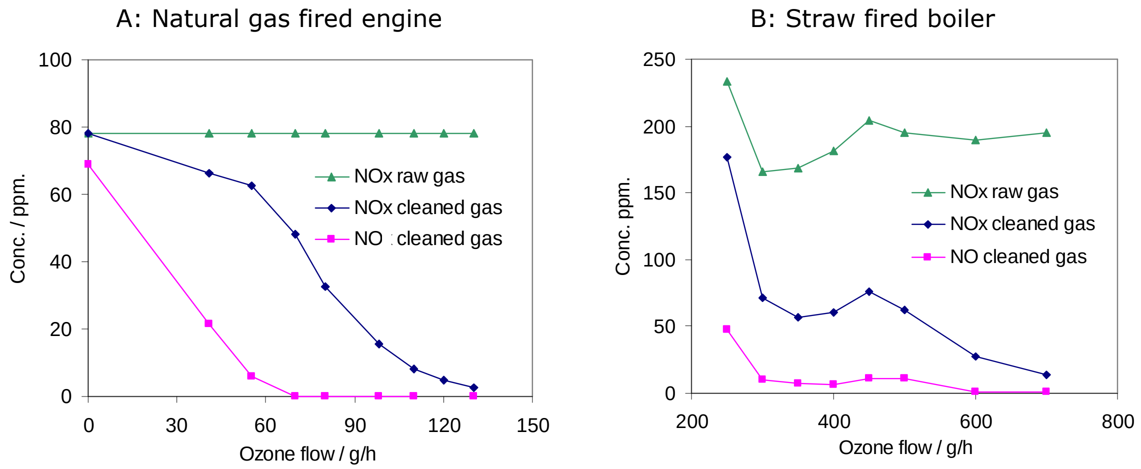

Figure 6. Concentration of NOx in the raw flue and in the treated flue gas together with the NO concentration in the treated flue gas versus the amount of ozone supplied. Each mark for the straw fired unit represents an average value of 20 minutes of continuous measurements.

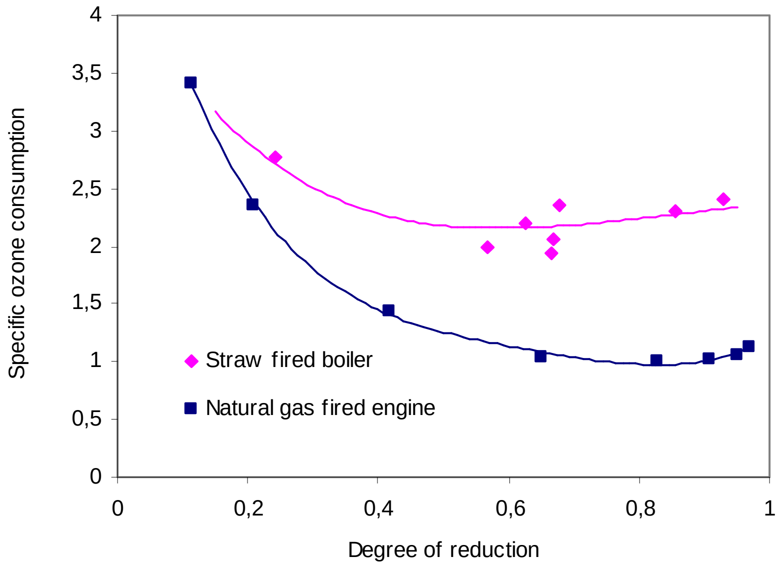

Figure 7. Specific ozone consumption versus degree of NO_x reduction. The values shown are normalised to the specific ozone consumption (kg O_3 / kg NO_x removed) for the gas engine unit at a degree of NO_x reduction of 0,8. Each mark for the straw fired unit represents an average value of 20 minutes of continuous measurements.

6. CONCLUSIONS

A technique for NO_x reduction for combustion processes was examined. The technique is based on injecting ozone into the NO_x containing flue gas where it will react with NO_x forming an anhydride of nitric acid, N_2O_5. N_2O_5 is easily removed later using a water scrubber. Lab-scale experiments were conducted as well as pilot tests at two different power plants. One of the plants was a gas engine based CHP unit and the other was a CHP unit based on a straw fired boiler and a steam turbine.

It was found that

- NO_x emissions can be reduced by more than 95 % by addition of ozone to the flue gas
- The reduction of NO_x emission is more efficient at lower temperature (110 °C) than at higher temperature (160 °C).
- O_2 is more efficient than air as ozone agent.
- The technique is applicable on flue gas from biomass combustion despite the presence of compounds such as SO_2 and HCl.
- Reduction of NO_x emissions requires approximately half as much O_3 when it is applied to the natural gas fired engine unit compared to the straw fired boiler unit.
- The higher O_3 consumption on straw fired units is due to both higher flue gas temperature and larger NO_x fluctuations in the flue gas compared to the gas engine unit.

7. ACKNOWLEDGEMENT

The work presented is financially supported by the Danish natural gas distribution companies, DONG Gas Distribution A/S, HNG I/S, Naturgas Midt-Nord I/S, KE Bygas, A/S Naturgas Fyn A/S and energinet.dk (former Eltra) as a part the PSO programme. DONG Energy A/S is acknowledged for making the CHP units available for the project.

8. REFERENCES

[1] Using Non-Thermal Plasma to control Air pollutants”, United States Environmental Protection Agency, EPA-456/R-05-001, Feb. 2005, www.epa.gov/ttn/catc/dir1/fnonthrm.pdf.

[2] Jensen T.K., Nihøj, J., Fenger L.D. (2005): Development of biomass combustion technology. 14th European Biomass Conference and Exhibition: Biomass for Energy, Industry and Climate Protection.

[3] Bindslev, H. et al. Emission reduction by means of low temperature plasma PSO project no. FU3401. Final report. Risø-I- 2380(EN). 2005.