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Risø-R-1545(EN)

Emission reduction by means of low temperature plasma

Summary

Henrik Bindslev, Alexander Fateev, Yukihiro Kusano, Frank Leipold,
Bjarne Stenum, Helge Egsgaard, Per G. Kristensen, Niels B. K.
Rasmussen and Michael Ørtenblad

Author:

Henrik Bindslev*, Alexander Fateev*, Yukihiro Kusano*, Frank Leipold*, Bjarne Stenum* (*Optics and Plasma Research Department, Risø), Helge Egsgaard (Biosystems Department, Risø), Per G. Kristensen**, Niels B. K. Rasmussen** and Michael Ørtenblad** (**Danish Gas Technology Centre)

Title:

Emission reduction by means of low temperature plasma. Summary

Department:

Optics and Plasma Research Department

Abstract (max. 2000 char.):

The work performed during the project is summarised. In the project we focused on removal of nitrogen oxides NO_x (NO, NO₂) and, in particular, on removal of nitrogen monoxide (NO) by injection of plasma-produced reactive agents. As reactive agents we tested ozone (O₃), NH and NH₂ radicals from ammonia (NH₃) and nitrogen atoms (N) generated in dielectric barrier discharges (DBDs). Hydrazine (N₂H₄) as a reducing agent and direct plasma treatment of the entire exhaust gas was investigated as well. We performed laboratory experiments on synthetic exhaust gases, modelling of the mechanisms and a demonstration of the technique on a test engine, a 30 kW combustion engine fuelled with natural gas.

We achieved the best results with ozone injection into the exhaust gas. This technique is based on oxidation of NO to N₂O₅ that is subsequently removed from the exhaust gas by a scrubber. In the laboratory experiments we obtained complete removal of NO by injection of an ozone/oxygen mixture from an oxygen (O₂) DBD into synthetic exhaust gases with compositions close to those of real exhaust gases.

Ozone injection was chosen for demonstration of NO_x removal from the exhaust gas of the test engine. We achieved 95 % NO_x removal with an oxygen DBD and 70 % NO_x removal with an air DBD. The running costs relating to the demonstration were estimated to be approximately 30 DKK per kg removed NO_x for the oxygen DBD, and 25 DKK per kg removed NO_x for the air DBD.

For a commercially available ozone generator, the total costs of NO_x removal from a 3 MW power plant were estimated to 27 DKK per kg removed NO_x for oxygen as the feed gas, and 21 DKK per kg removed NO_x for air as the feed gas.

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Risø National Laboratory
Information Service Department
P.O.Box 49
DK-4000 Roskilde
Denmark
Telephone +45 46774004
bibl@risoe.dk
Fax +45 46774013
www.risoe.dk

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Preface

The PSO project no. FU3401 “Emission reduction from combustion engines by means of low temperature plasmas” was carried out as a collaborative project between Risø National Laboratory (Risø) and the Danish Gas Technology Centre (DGC) running from 1 June 2003 to 31 July 2005. The initial laboratory experiments were carried out at Risø. The demonstration of NO_x removal was performed at the test engine located at DGC.

Bjarne Sass, Martin Jessen and Søren Nimb from Risø and Johan G. Larsen from DGC are gratefully acknowledged for their technical assistance during the project. Bitten Skaarup from Risø and Conny R. Petersen from DGC are gratefully acknowledged for their editorial support.

Final report for PSO project no. FU3401

The work performed during the PSO project no. FU3401 “Emission reduction from combustion engines by means of low temperature plasmas” is summarised below. In this project we studied removal of toxic gaseous emission from combustion engines by mixing the exhaust gases with reactive agents generated in low temperature plasmas. We focused on removal of nitrogen oxides N_xO_y (NO, NO₂, NO₃, N₂O₅ and N₂O) and, in particular, on removal of nitrogen monoxide (NO).

The studies were carried out as laboratory studies, modelling of the chemical reaction paths and demonstration of NO_x removal from the exhaust gas of a test engine. For the laboratory experiments we established diagnostics and gas handling facilities for mixing of the synthetic exhaust gases and the gas mixtures fed to the plasma generators. For some of the initial laboratory studies we used a mixture of nitrogen (N₂) and NO (500 ppm) as a standard synthetic exhaust gas. This mixture was also used as the base for producing more realistic synthetic exhaust gases. Optical spectroscopy was used for diagnostics. A deuterium lamp with ultraviolet (UV) emission and a spectrometer equipped with a CCD camera were used for the UV absorption spectroscopy measurements. The spectrometer was also used for emission spectroscopy. Fourier transform infrared (FTIR) spectroscopy was employed for infrared (IR) absorption measurements. For the demonstration at the test engine, the NO_x concentration was measured with a calibrated chemiluminescence NO_x analyzer.

We tested two different techniques for NO_x removal by means of low temperature plasmas. In *remote treatment*, a reactive agent is generated in a low temperature plasma and injected into the exhaust gas. In *direct treatment*, the entire exhaust gas is exposed to the plasma. The plasmas were generated in dielectric barrier discharges (DBDs). Basically, a DBD consists of two metal electrodes covered with dielectric barriers, typically alumina (Al₂O₃). DBDs are AC powered, typically 10 – 20 kV at frequencies of 10 - 40 kHz. The input powers were determined by voltage and current measurements. At high power inputs the electrodes were water-cooled. During the project several DBDs with different geometries have been constructed and tested. Normally the DBDs were operated at atmospheric pressure. A DBD with parallel plate electrode geometry was placed in a sealed chamber equipped with optical windows for diagnostics of the plasma. In oxygen DBDs with coaxial electrodes, ozone could be produced in concentrations up to approximately 7 vol %.

As reactive agents we tested plasma-generated ozone (O₃), NH and NH₂ radicals from ammonia (NH₃) and nitrogen atoms (N). In addition, we investigated injection of hydrazine (N₂H₄) and direct plasma treatment. We used ozone injection into the exhaust gases for the demonstration at the test engine since the laboratory studies with ozone injection have given the most promising results.

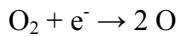
Recently, a commercial system applying ozone injection has become available under the trademark LoTOx (see, e.g., “Using Non-Thermal Plasma to Control Air Pollutants”, United States Environmental Protection Agency, EPA-456/R-05-001, February 2005, www.epa.gov/ttn/catc/dir1/fnonthrm.pdf).

1 Remote treatment

1.1 Injection of ozone

NO_x removal by ozone injection takes place as oxidation of NO_x to N₂O₅ and subsequent removal of N₂O₅ by a scrubber. In an O₂ DBD, ozone is formed according to the following reactions:

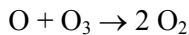
Dissociation by electron impact:



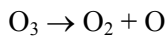
and a subsequent formation of ozone (where M is a third body):



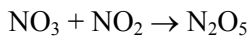
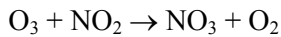
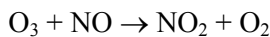
At steady state the ozone production is balanced by the decomposition reactions:



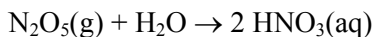
and thermal dissociation:



In, for example, an exhaust NO can be oxidized by O₃ to form NO₂, NO₃ and, subsequently, N₂O₅:



The oxidation of NO₂ to NO₃ is the slowest reaction in this chain. N₂O₅ can be efficiently removed from the exhaust by a washing bottle or a scrubber according to the following reaction forming nitric acid (HNO₃):



In humid exhaust gases, HNO₃ may be formed in the exhaust gas itself.

1.1.1 Laboratory experiments on ozone injection

In the laboratory studies we tested NO removal by injection of ozone into synthetic exhaust gases at various ozone concentrations and various temperatures of the exhaust gas. We used an atmospheric pressure O₂ DBD with parallel plate geometry for the ozone production. As synthetic exhaust gases we used N₂/O₂/NO/CH₄ mixtures with compositions close to those of real exhaust gases. Some experiments were carried out with water vapour in the exhaust gas as well. The water vapour was introduced by means of an electronically controlled evaporator.

The experiments were performed in a quartz tube in order to reduce the influence of surface reactions. The quartz tube with inlets for the synthetic exhaust gas and for the O₂/O₃ mixture from the DBD was placed in a furnace. The exhaust gases with and without passing the washing bottle were analysed by UV and IR absorption spectroscopy.

UV absorption spectroscopy showed that NO could be removed completely from the tested synthetic exhaust gases and that the final product in the washing bottle was HNO₃. This indicates that the oxidation from NO to N₂O₅ took place. When the O₃ supply was insufficient, the oxidation from NO to N₂O₅ could not be completed. It was found that the washing bottle could not trap NO₂ efficiently.

1.1.2 Ozone injection at the 30 kW test engine

The final stage of the project was a demonstration of NO_x removal from the exhaust gas from the test engine at DGC by ozone injection. The total exhaust gas flow rate from the engine was 2400 standard litre per minute (SLM). The NO_x concentration in the exhaust was normally between 300 and 700 ppm. A side tube with about 10 % of the total exhaust (250 SLM) was used for demonstration of NO_x removal. A prototype plasma source (a large coaxial DBD) for ozone generation was designed as well as a scrubber system for trapping N₂O₅ and HNO₃. The source was tested at Risø in advance in order to optimize the condition.

UV/IR absorption spectroscopy and the chemiluminescence NO_x analyzer available at DGC were used for detection of nitrogen oxides after ozone injection, after mixing and at the exhaust. The ozone concentration in the outlet of the DBD was measured by means of laser absorption at 634.7 nm, while ozone at the scrubber outlet was detected by UV absorption.

Pure oxygen, air and synthetic air (80 % N₂ + 20 % O₂) were used as feed gases for the DBD. The NO_x concentration in the exhaust after the scrubber outlet was measured with the chemiluminescence NO_x analyzer. The NO_x emission decreased with increasing DBD power input and oxygen flow rate. This is a result of a higher ozone production rate at high DBD powers and oxygen flow rates. 95 % NO_x removal was obtained at an oxygen flow rate of 3 SLM and a power of 250 W. The experiments performed with compressed air showed maximum NO_x removal efficiency of about 70 % at a flow rate of 35 SLM and a DBD power of 500 W. Humidity is known to reduce the O₃ production and synthetic air was found to be more efficient and showed NO_x removal efficiency up to 90 %.

It should be noted that nitrogen oxides may be produced in an air DBD and that N₂O produced in the DBD cannot be removed at a later stage. It was found that the emission of N₂O was of the order of 2 – 5 ppm at the scrubber outlet. There is no production of nitrogen oxides in oxygen DBDs.

Measurements of the ozone concentration in the injected O₂/O₃ mixture showed that the O₃ consumption for the NO_x removal was comparable with that expected from the stoichiometry of the oxidation of NO to N₂O₅, and it is unlikely that the ozone consumption can be reduced significantly. However, compared with the energy required to dissociate the oxygen molecules, the energy consumption for the ozone production is large indicating that the power consumption may be reduced. The total power consumption at 95 % NO_x removal corresponds to about 15 % of the total power from the engine for ozone generation from oxygen and to about 30 % for ozone generation from air with 70 % NO_x removal.

For oxygen as feed gas, the running costs of the demonstration were estimated to be about 30 DKK per kg removed NO_x at a removal efficiency of 95 %. The running costs are dominated by the costs of the oxygen consumption of about 20 DKK per kg removed NO_x. For air as DBD feed gas, the running costs were estimated to be about 25 DKK per kg removed NO_x at a removal efficiency of 70 %. (For the cost estimations the NO_x emission is considered as NO₂ emission, and an oxygen price of 1.20 DKK/Nm³, a compressed air price of 0.03 DKK/Nm³ and a local price for the power of 0.20 DKK/kWh have been assumed).

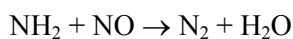
The DBD ozone generator used for the test engine was not optimized with respect to costs and energy efficiency. For a commercially available ozone generator the power consumption corresponds to 8 % of the power of the power plant (3 MW) for 95 % NO_x removal with oxygen as feed gas or for 70 % NO_x removal with air as feed gas.

For the commercially ozone generator the total costs incl. the capital costs were estimated to

- 27 DKK per kg removed NO_x for 95 % removal for ozone generation from oxygen
- 21 DKK per kg removed NO_x for 70 % removal for ozone generation from air (8 DKK per kg removed NO_x for the air consumption). For ozone generation from air the capital costs are a factor of two larger than for ozone generation from oxygen.

1.2 Injection of NH₂ radicals

Initially, we studied reduction of NO in exhaust gases by injection of NH₂ radicals produced in argon/ammonia (Ar/NH₃) DBDs according to the reaction:



Several DBD geometries were tested with powers up to several hundreds of watts and with ammonia concentrations up to about 10 %. The plasma and the reactive species were analysed with emission and absorption spectroscopy. Strong emission from NH radicals was observed, but NH₂ radicals could not be detected by emission spectroscopy most likely due to strong quenching of the excited level of the NH₂ radicals. Ground state NH₂ radicals were detected by laser absorption spectroscopy. The highest NH₂ concentration was found for an NH₃/Ar concentration between 6 % and 8 %, but absolute NH₂ concentrations could not be measured with this technique. Modelling indicates that the main stable products of an Ar/NH₃ plasma are nitrogen molecules (N₂), hydrogen molecules (H₂) and hydrazine (N₂H₄) and that the concentration of NH₂ is low due to a short lifetime (0.3 ns). NH₂ is expected to recombine to N₂H₄ which was detected by UV absorption spectroscopy in the plasma as well as in the exhaust gas.

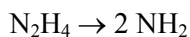
Injection from an Ar/NH₃ (6 %) plasma into synthetic exhaust gas (standard N₂/NO mixture) showed a small NO reduction at room temperatures. At 340 °C the NO reduction was more efficient than at room temperature. This may be assigned to thermal decomposition of N₂H₄ or catalytic reactions on heated stainless steel surface (see below).

Ar is costly and not very efficient as carrier gas and nitrogen (N₂) was tested instead. Comparisons of Ar and N₂ as carrier gases indicated that the production rate of NH₂

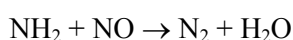
radicals in an N₂/NH₃ plasma was comparable with that in the Ar/NH₃ plasma. Injection from N₂/NH₃ plasmas into synthetic exhaust gas (standard N₂/NO mixture) showed some NO reduction. However, the most efficient reduction was observed with injection from pure N₂ plasmas. This reduction is assigned to injection of N atoms (see below).

1.3 Injection of hydrazine

As mentioned in the previous section one of the products in Ar/NH₃ and N₂/NH₃ DBDs is N₂H₄. Thermal dissociation of N₂H₄ into NH₂ radicals takes place at temperatures above 300 °C:



The NH₂ radicals may promote NO reduction:



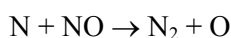
At room temperature N₂H₄ is stable and can therefore be injected into the hot exhaust gas.

Tests with injection of hydrazine into heated synthetic exhaust gas (standard N₂/NO mixture) were performed in order to investigate the applicability of N₂H₄ as a reducing agent. The experiments were performed in a quartz tube placed in a furnace. No significant NO reduction was observed at exhaust gas temperatures below 700 °C while hydrazine decomposes at temperatures above 300 °C. Ammonia was found to be the main product of the decomposition. Experiments with a heated stainless steel tube suggested that catalytic surface reactions significantly interfere with gas phase reactions.

It was concluded that N₂H₄ cannot be used for NO reduction at temperatures below 700 °C.

1.4 Injection of nitrogen atoms

N atoms generated in N₂ DBDs have shown to reduce NO according to the reaction:



However, the lifetime of the N atoms is short. Different DBDs have been designed in order to reduce the transportation time of the N atoms from the plasma to the exhaust. The NO reduction in synthetic exhaust gases (standard N₂/NO mixture) was monitored by means of UV absorption spectroscopy and FTIR spectroscopy. The strongest NO reduction was observed with short distances from the DBD to the mixing volume and high injection flow rates. At an injection, a flow rate 6 times the flow rate of the synthetic exhaust gas up to 75 % NO reduction was observed. For an N₂ flow rate equal to the flow rate of the exhaust, a maximum reduction of 28 % was achieved. The high injection flow rate is required due to a low concentration of nitrogen atoms in the mixing volume between the injected plume and the exhaust gas. The recombination of N atoms is so fast that it seems unrealistic to achieve high concentration of N atoms in the mixing volume.

It was concluded that the technique is too expensive, although NO reduction as the result of injection of nitrogen atoms was observed.

2 Direct treatment

Some tests of direct treatment of the synthetic exhaust gases were performed in order to investigate whether N atoms generated from the N_2 in the exhaust gas could reduce NO. In the first tests with the standard exhaust gas fed to a coaxial DBD, the NO concentration was reduced 93 %. However, the total N_xO_y concentration was 14 % of the initial NO concentration indicating that both reduction and oxidation of NO took place. In synthetic exhaust gas mixtures of O_2 (7 %), N_2 and NO (465 ppm), the NO concentration could be reduced slightly, but the total concentration of N_xO_y increased with power up to a maximum of about 850 ppm. Even in the absence of NO in the synthetic exhaust gas, considerable amounts of N_2O were detected after plasma treatment. Experiments performed using humid exhaust gases (the exhaust gas passed a washing bottle with water before treatment) showed that humidity promotes the N_xO_y production even in the absence of O_2 in the synthetic exhaust gases. The total N_xO_y concentration was found to increase slightly by adding NH_3 to the exhaust gas. The experiments with the coaxial DBD were performed without preheating of the exhaust gases. However, the gases were heated in the DBD.

Some experiments were performed with humid (about 1 %) synthetic exhaust gases (N_2/O_2 (7 %)/NO) preheated to about 40 °C. The gases were fed to the DBD with parallel plate electrodes, and minor additional plasma heating of about 10 °C could be expected. Although humidity was found to promote NO production, a complete NO removal was obtained by adding methane CH_4 (6 %) to the synthetic exhaust gas. However, if methane (or other hydrocarbons) is present in the discharge, production of toxic compounds for example CN compounds is possible.

Although direct treatment of the exhaust is being used and high energy efficiency has been reported, we have concluded that direct treatment of the exhaust gas is not suitable for this project. At our experimental conditions we did not observe efficient N_xO_y reduction at low methane concentration.

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