NON-THERMAL PLASMA REACTOR USE IN MARINE DIESEL ENGINE EXHAUST SYSTEM

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Abstract

Large seagoing vessels are one of the largest pollution sources in the sea environment world. Marine engines operate with extremely low quality fuels contaminated by sulfur and aromatic compounds. Vessels are responsible for an estimated 14% total nitrogen oxide emission and 16% sulfur oxide, respectively. Nitrogen oxides emissions cause serious problems including acid rain in local areas such as harbors' vicinity. All diesel engine manufacturers have been working on reducing on NO_x from ships. This paper describes one of the experimental methods - using non-thermal plasma reactor. NTP reactor was built as the after-treatment module in exhaust gas system in marine diesel engine. Emission measurements were carried out on the engine with and without demonstrator NTP module. The main aim was to analyze exhaust gas compounds during real engine operation, in accordance with test cycles procedureD-2 and E-2 (ISO-8178 rules). The experiment test bench gives the innovative role in the development exhaust gas after-treatment technology for marine systems. One of the most promising method to decrease the number of toxic compounds from exhaust gas is implementing of NTP reactor as after main treatment module. As the next step is proposed a two-stage plasma-chemical process for the control of harmful compounds: non-thermal plasma reactor and catalyst. This combination should be more effective and probably gives reduction with more efficiency of harmful exhaust gas compounds.

Keywords: *marine diesel engine, exhaust emission gas treatment, non-thermal plasma reactor*

1. Introduction

Nitrogen oxide emissions from ships are estimated around 5 million tons per year. The study shows that the sulfur content of marine fuel is far greater than in diesel fuel used for trucks, buses and cars [1, 3, 4]. Globally, ships use fuel with an average sulfur content of 2.7% compared to 10 to 15 ppm contents for road transport fuels. Worldwide ocean-going vessels according to more recent estimates, can contribute more than 25% of total NO_x emission in some port cities and coastal areas. The study also finds that international ships release more carbon dioxide, the primary greenhouse gas responsible for global warming, than many of the industrialized nations listed in the Kyoto Protocol.

Marpol Annex VI is an international agreement for limiting air pollution from ships, especially harmful compounds like NO_x and SO_2. The operation of a diesel engine with a power output of more than 130 kW is prohibited unless the engine has been certified by survey authority in order to meet emission standards. For international trading vessels, these requirements have been in place, as the regulation effectively applies to engines installed after 1 January 2000, and does not apply to engines installed before that date. Diesel engine must have an exhaust gas emission technical file prepared by the manufacturer and approved by the relevant survey authority.

This technical file is required to accompany an engine throughout its life on board of the ship. The operation of a diesel engine is also permitted when an exhaust gas cleaning system or any other equivalent method is applied to reduce onboard nitrogen oxides emissions at least to the previous specified limits.

Air pollutants, such as sulphur dioxide and nitrogen dioxides, accelerate the rate of deterioration of a large number of various materials, metals become corroded more quickly in an acid environment. Exhaust gas emissions from ships also contribute to global warming. For these reasons, the diesel manufacturers and researchers have been investigating a variety of techniques which aim at the reduction of diesel exhausts harmful emissions. There are various methods for reducing NO_x emissions, differing somewhat in cost and effectiveness. These techniques have been divided into three areas: pre-treatment, primary (internal) and secondary (after-treatment) methods. One of the after-treatment method of reducing NO_X and particulates from diesel exhaust is to use a non-thermal plasma reactor located in exhaust line from engine.

2. Proposed NTP exhaust after-treatment system

The plasma is an ionized gas. The basic part of reactor consist of two electrodes separated by a void space that is lined with a dielectric material and is filled with quartz-glass; one electrode is a high-voltage electrode, and another one is of low voltage. The used type of reactor is called dielectric barrier discharge - DBD. Gas flows inside and outside of the quartz pipes - construction details and gas flow are shown on Fig. 1 and Fig. 2.

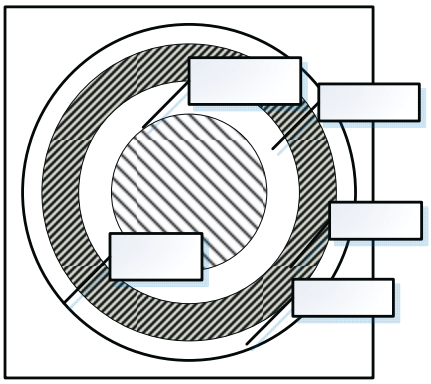

Fig. 1. The basic-single electrode of Dielectric Barrier Discharge reactor

The phenomenon of discharge occurs when the voltage through the plate exceeds the insulating effect of the quartz tube. The duration of these discharges is measured in nano-seconds. In a DBD field, the oxygen molecules split into two atoms of oxygen O^+ and O^+. The elemental oxygen radical, being very reactive, will form ozone - O_3. Oxygen radicals react with carbon monoxide (CO) to form carbon dioxide (CO_2), sulfur dioxide (SO_2) and nitrogen oxide (NO_x) to form nitric acid (HNO_3) in the presence of moisture. The two most important processes initiated by the plasma are the partial conversion of NO into NO_2, and the partial oxidation of unburned hydrocarbons in the exhaust gas [2, 3, 5].

Generally, ozone is an unwanted by-product of after-treatment systems. However, it is possible to use a certain concentrations of ozone as a chemical oxidizer, resulting in the removal of SO_2 and NO_x. In lower temperature conditions, a substantial enhancement in ozone generation can be expected because the ozone losing processes are enhanced by the increase of gas temperature. Ozone decomposes when the temperature of flue gas is higher than 80°C. NO can be oxidized to NO_2 by free oxygen and ozone. The reactions of NO oxidation by ozone are presented below:

$$NO + O \rightarrow NO_2, \tag{1}$$

$$NO + O_3 \rightarrow NO_2 + O_2. \tag{2}$$

Ozone oxidizes NO_x into other forms of nitrogen oxides, such as nitrogen trioxide and dinitrogen pentoxide through the following reactions:

$$NO_2 + O_3 \rightarrow NO_3 + O_2, \quad (3)$$

$$2NO + 3O_3 \rightarrow N_2O_5 + 3O_2. \quad (4)$$

When a plasma discharge is applied to a flue gas, energetic electrons are created, transferring energy to the dominant gas molecules (N_2, O_2, H_2O, CO_2) by collisions. These collisions result in the formation of primary radicals ($O^{\cdot}$, $N^{\cdot}$, $OH^{\cdot}$, etc.), positive and negative ions and excited molecules. After the formation of primary radicals, the electron-ion, ion-ion reactions, and electron detachments create more secondary radicals ($O_2^{\cdot}$, $HO_2^{\cdot}$, etc). Substantial amount of $O^{\cdot}$, $O_2^{\cdot}$, $OH^{\cdot}$, and $H^{\cdot}$ radicals are easily generated in NTP. In flue gas applications, these radicals may oxidize SO_2 and NO, or react with them to form aerosols. Since the formation energy of the radicals is on the order of 10 eV, the energy of the electrons in a NTP discharge is approximately equal to the energy needed for radical formation. NO can be oxidized to NO_2 and N_2O_5 when the plasma field exceeds the ordinary level of operation, E = 5.0 ~ 8.0 kV/cm, with the existence of O_2 and H_2O. Plasma oxidation of NO have a high technical potential, but would require a high energy consumption, in a low oxygen stream NO can be reduced to N_2 by reducing radicals such as $N^{\cdot}$ in plasma discharge.

$$N^{\cdot} + NO \rightarrow N_2 + O. \quad (5)$$

However, increasing O_2 concentration may reduce reduction efficiency, which is not practical in the diesel engine application, where excess air usually exists. The oxidation of NO to NO_2 in the gas phase occurs in the presence of O_2.

$$2NO + O_2 \rightarrow 2\,NO_2 \quad k=1.4\cdot10^{-38}\ cm^6/s, \quad (6)$$

$$NO + O_2 \rightarrow NO_2 + O. \quad (7)$$

With the presence of water vapor or oxygen, the formation reaction of nitric acid in thegas phase might take place in the gas phase.

$$NO + NO_2 + H_2O \leftrightarrow 2HNO_2. \quad (8)$$

Some reactions lead to the formation of NO_3 and N_2O_5, both are very soluble.

$$2NO_2 \rightarrow NO_3 + NO, \quad (9)$$

$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M, \quad (10)$$

$$N_2O_5 + H_2O \leftrightarrow 2HNO_3. \quad (11)$$

This most possible reaction paths of NO_x removal, when NO_2 dissolves into water and it is somewhat impairing the efficiency of NO_x removal. Test stand design includes a modular DBD reactor construction used for industrial exhaust gas cleaning purposes. The prototype reactor construction was designed at the Szczecin University of Technology, Electrical Engineering Department. A simplified cross-section of the designed NTP reactor - rod chamber is depicted in Fig. 2. Proposed construction consists of three plates (numbered 1 to 3 on Fig. 2) that represent the construction basis for low voltage rods (E) and quartz-glass dielectric barriers (I1). Plate 3 can be high-voltage supplied, however the polarity of the supplied power can be easily reversed. Plates 2 and 3 are separated by dielectric I2. Arrows represent the gas flow through the single tube. There are two discharge zones: between plate 3 and barrier I1 and between the steel rod E and the barrier glass tube.

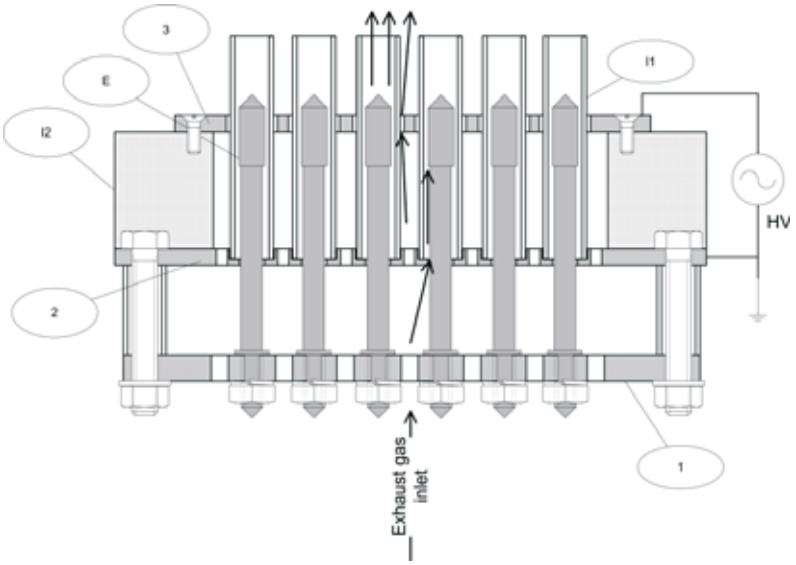

Fig. 2. Simplified cross-section of the designed reactor chamber

The overall chamber consists of 36 single tubes, however the number of tubes (as well as shape and size) of steel rods and plates can be application specific. A resonant-type power electronic supply system was used. Advantages of resonant power electronic supplies are well known, the most relevant include solid-state power transistor switching losses minimization and high-voltage transformer-less design. Overview of the resonant, high voltage alternating current power supply design used is depicted in Fig. 3.

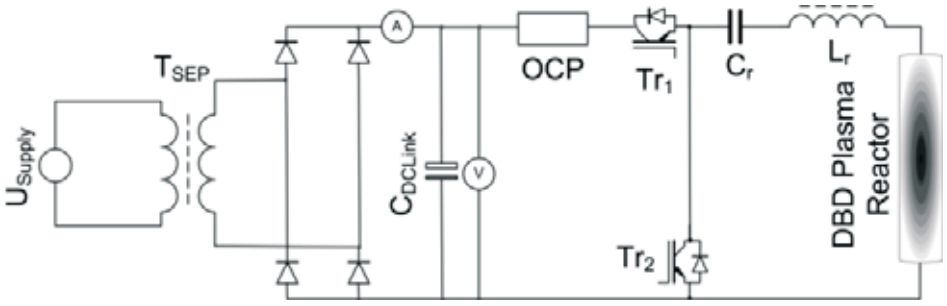

Fig. 3. Overview of the resonant-type power electronic supply construction

Power flow is controlled with the measures of the U_{DC} voltage over the DC-link capacitor C_{DCLink}. Power switches Tr_1 and Tr_2 (in the case of the supply presented IGBT transistors) need to switch with the resonant frequency of the power supply - reactor system. DBD reactor's parasitic capacitance together with C_r - L_r resonant passive components represent a classical, serial resonant circuit. Power across the DC-Link can be measured with the means of current and voltage measurement as represented in Fig. 3. It is a non-direct measurement method as losses across power transistors and additional, passive components losses of the resonant circuit are neglected. Empirically these losses however do not exceed 5% of the measured power. Because of safety issues separating transformer T_{SEP} was used between the single-phase power grid U_{Supply} and the high-voltage resonant circuit, additionally a fast response over-current-protection (OCP) circuitry was used.

A control system was implemented searching the resonant frequency of the reactor-power supply and maintaining it while working, a ZCS (zero-current switching) method was implemented. Some minor resonant frequency changes occur due to reactor parasitic capacitance change together with all time, temperature and chemical processes occurring however the control system actively maintains an electrical resonance.

3. Test bed and apparatus set-up

The preliminary stage of the NTP application to after-treatment exhaust gas revealed the NO_x reaction trends. Throughout the measurements, the engine outlet (after turbocharger) NO_x levels (NO, and NO_2) were monitored with simultaneous NO, NO_2, N_2O measurement after plasma reactor, allowing to estimate the quantities of converted NO_2. NTP module was built on a by-pass system - a part of real exhaust system from marine diesel engine which specification data shown in Tab. 1. During the tests, set of thermocouples were used to indicate the state of plasma processor temperature. The processor temperature could not be adjusted, as it depended on engine exhaust gas temperature. During the engine tests it raised from room temperature up to 350°C. This has been used to investigate the influence of operating temperature on oxidation process.

Tab. 1. Test engine specification

Engine		Nominal rate	
Designation	Maker, type	Power [kW]	Speed [revs/min]
Small ship propulsion Generator sets	SULZER 6AL20/24	397	720

Emission measurements were carried out on engine at steady-state operation. Sampling gas was distributed to all analysers. The performance measurement procedure of marine engines on test beds, performed in accordance to Annex VI of Marpol 73/78 convention - with the specification given in the IMO NO_x Technical Code and ISO-8178 standard. All tests were covered by test-cycles procedure D-2 and E-2. The test performed with the selected marine distillate fuel DMX in accordance to ISO-8217 standard. All engine performances were carried out continuously and simultaneously together with exhaust gas components concentration recorded by means of measurement assemble presented in Fig. 4. The engine test was provided in two stages: idle and part engine load (25% of the of nominal). On each measurement stage, the engine was in steady state of operation and all parameters were examined without NTP plasma operation (plasma off) and with NTP plasma operation (plasma on). The crucial gas components concentrations such as: CO, CO_2, NO, NO_2, N_2O, NO_x, O_2, Soot, SOF, Total PM were measured using set of state of art gas analyzers: MIR FT - Fourier Transform Infrared spectroscopy multigaz analyzer, HORIBA MEXA-1230PM and AVL-Pierburg CEB II Combustion Emission Bench. The trial schedule allowed the reactor heating-up to reach stable condition, adequately to engine exhaust system and outlet gas condition.

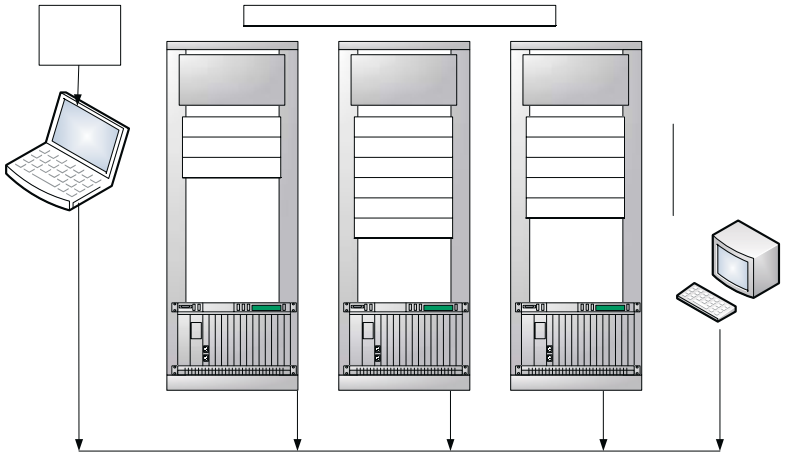

Fig. 4. Analyzers and acquisition system set up

4. Experiment results and discussion

The preliminary engine trial confirmed that the two most important processes initiated by plasma are the partial conversion of NO into NO_2, and partial oxidation of unburned hydrocarbons in the exhaust gas. Diesel engine exhaust contains few gaseous hydrocarbons. However, under engine load transient conditions a significant amount of liquid-phase hydrocarbons VOC (volatile organic fraction) can build up in form of particulates. The hydrocarbons promote the oxidation of NO to NO_2, but have no effect on reduction of NO to N_2. The oxidation of NO to NO_2 is strongly coupled with hydrocarbon oxidation chemistry.

The plasma process does not always guarantee the efficient oxidation of NO to NO_2. The presence of the hydrocarbon prevents the formation of acid products and increases the efficiency for NO to NO_2 oxidation. The table below shows main gas compounds concentrations during the test (ambient conditions: P_a = 1017.88 hPa, T_a = 25.92ºC, H_a = 31.12%).

Tab. 2 Compounds concentration recorded during test

Engine load	NTP reactor	CO_2 [%]	CO [ppm]	N_2O [ppm]	NO [ppm]	NO_2 [ppm]	NO_x [ppm]	Soot [mg/m^3]	SOF [mg/m^3]	PM [mg/m^3]
Idle T_{exh}=158 [ºC]	OFF	3.00	168.78	0.45	449.76	101.68	551.45	2.70	25.50	28.20
	ON	2.81	175.47	1.18	371.04	107.00	478.04	3.44	24.96	28.40
25% T_{exh}=220 [ºC]	OFF	4.14	86.58	0.22	754.42	103.84	858.27	2.11	37.44	39.55
	ON	4.14	95.74	0.96	704.96	115.09	820.05	1.97	27.60	29.57

Some fluctuation of PM concentration were recorded - to establish the reason for these cause the engine operational parameters were investigated. It has been found strong influence of temperature of charging air on simultaneous PM concentration changes. The charge air temperature is controlled by means of external water cooling system with thermostatic valve with single value set-point. The engine charge air temperature records presents Fig. 5.

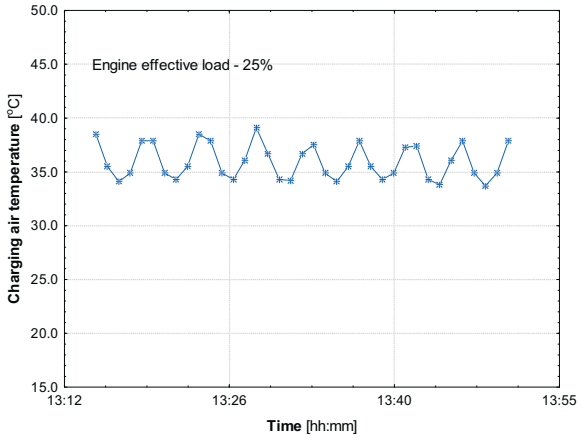

Fig. 5. Engine charging air temperature at 25% engine load

Fig. 6 shows the effect of unstable charge air temperature transferred on PM concentration resulting from NTP reactor operation. It was observed that with higher gas flow and temperature (part engine load), at fixed reactor energy density, PM reduction increases. The increase in PM efficiency removal was associated with the main PM component - SOF. The other PM constituent - soot reduction degree was much slower and weaker. The increased coefficient rate of PM oxidation resulting from exhaust gas temperature increase, has additional influence on CO concentration rise. The CO concentration rise was noticed in both engine loads, average CO values are shown in Tab. 2, while raw data trends can be observed in Fig. 8.

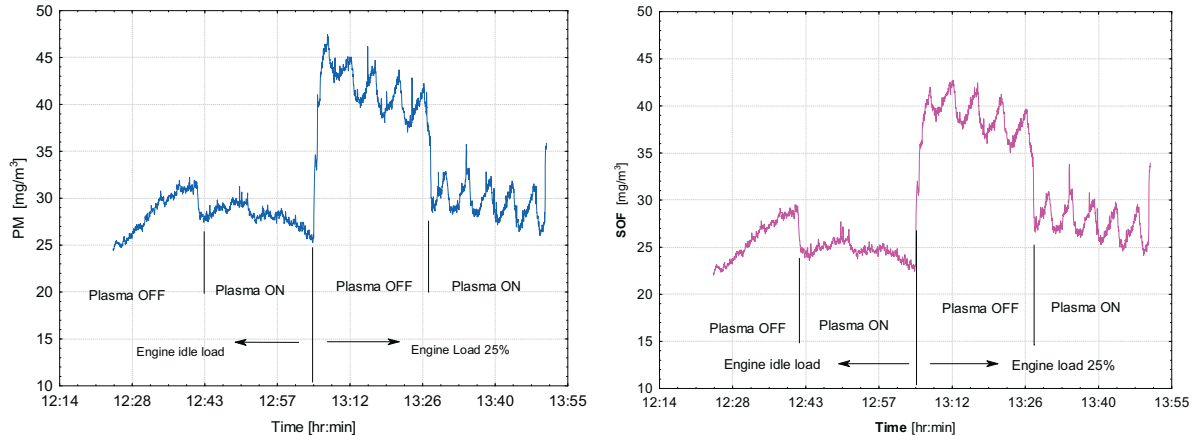

Fig. 6. PM and SOF concentration under the idle and 25% of engine load

Fig. 7 shows the nitrogen oxides allocation, caused by plasma stroke. For a given electric field, the ratio of reacted NO and NO_2 - indicated similar value under idle and part engine load. The main aim of the experiment involved basic NO oxidation trends was confirmed [6]. For a fixed NTP reactor energy level density, the plasma-associated process exhibited NO oxidation characteristics variable for specific exhaust gas states and flows. The idle engine load revealed higher NO conversion efficiency.

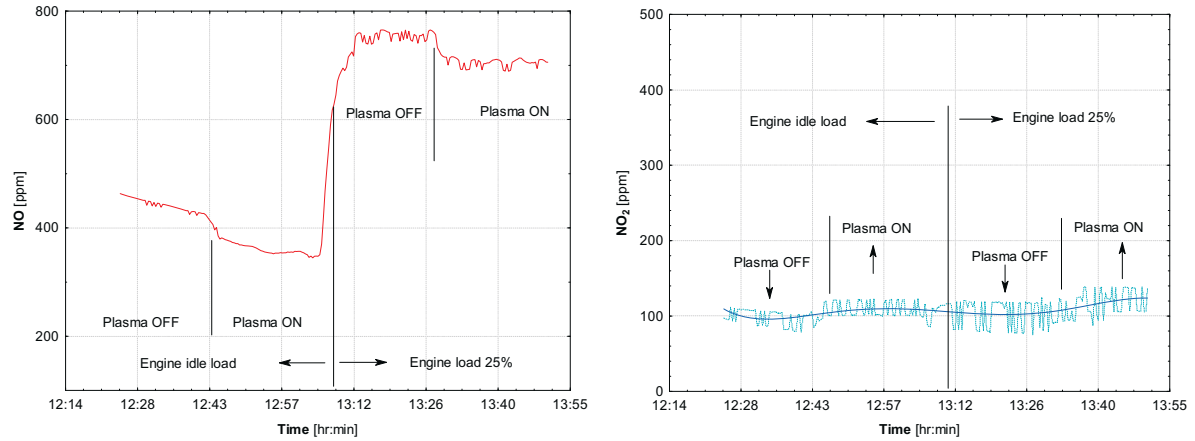

Fig. 7. NO and NO_2 concentration during test under the idle and 25% of engine load

Preliminary tests were conducted in the exhaust gas stream to determine the effect of oxidation on NO removal. These results suggest that NO has to be oxidized into NO_2 (or other more soluble nitrogen oxides) before any significant removal could take place.

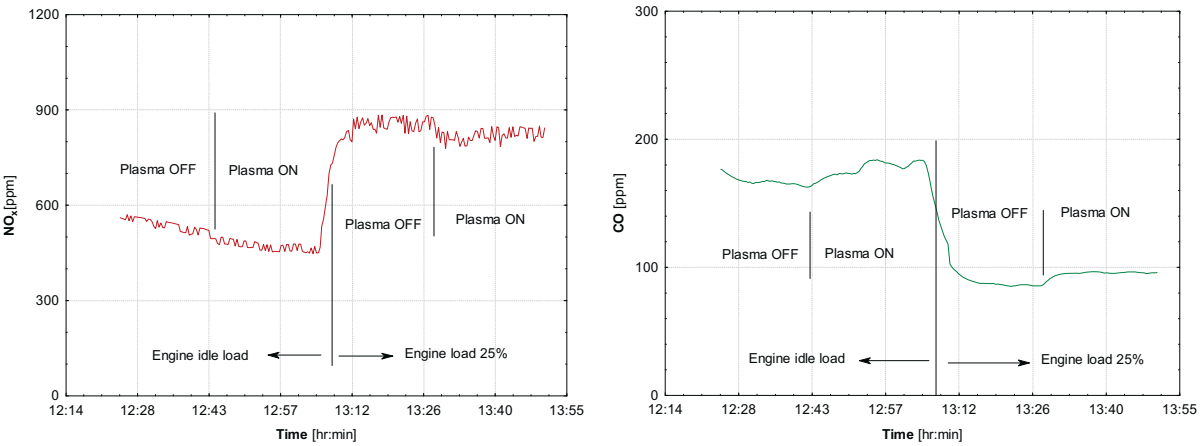

Fig. 8. NO_x and CO concentration during test under the idle and 25% of engine load

5. Conclusions

Experimental study involving a NTP reactor operation with realistic exhaust gas of marine engine was performed. It was observed that the in-situ ozone concentration increased as the NTP reactor power Increased. It was also found experimentally that the concentration of O_3 produced in-situ varied directly with the power level, but did not exceed 2 ppm at the maximum voltage level in low gas temperature condition. Since the reaction between ozone and NO_x is a constant molar ratio, there is not enough in-situ ozone present to remove a significant amount of NO_x. Therefore, it was concluded that the amount of in-situ ozone formed was not sufficient to be considered a major removal mechanism. Therefore, NO_x removal can only be initiated after NO was oxidized either by O_2 or the oxidizing radicals developed from O_2 under the NTP plasma discharge. In conclusion, the maximum NO_x removal efficiency was less 13% when the gas residence time was less than few mili-seconds. Longer residence times also lead to higher removal efficiencies.

The main important effects were observed as follows:

1. the reduction of PM concentration - approximately 25% (at 25% of engine load),
2. the reduction of NO concentration - roughly 13% and 7%, with simultaneous increase of NO_2 about 5% and 11% (at 0% and 25% of engine load),
3. the total NO_x removal - approximately 13% and 5% (at 0% and 25% of engine load),
4. the increase concentration of CO - about 10% and 4% (at 0% and 25% of engine load).

There was significant amount of NO removal in hot gas stream. NO_x removal efficiency increased with inlet NO_x concentration, and applied NTP power. In real gas stream, 13% de-NOx efficiency was the maximum limit.

Through the present pilot-scale test, it was found that the present planar type DBD reactor can be effective to decrease the PM emission. The experiment test bench gives the innovative role in the development exhaust gas after-treatment technology for marine systems.One of the most promising method to decrease the number of toxic compounds from exhaust gas is implementing of NTP reactor as after main treatment module. As the next step is proposed a two-stage plasma-chemical process for the control of harmful compounds: non-thermal plasma reactor and catalyst. This combination should be more effective and probably gives reduction with more efficiency of harmful exhaust gas compounds.

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