THE EXPERIMENTAL ANALYSIS OF NON-THERMAL PLASMA REACTOR USE FOR MARINE DIESEL EXHAUST

Tadeusz Borkowski, Jarosław Myśków, Marcin Hołub*, Stanisław Kalisiak*
Siegfried Müller, Rolf-Jürgen Zahn****

Maritime University
ul. Wały Chrobrego 1/2, 70-500 Szczecin, Poland
tel.: +48 91 4809419, fax: +48 91 4809585
e-mail: tborkowski@am.szczecin.pl, jmyskow@am.szczecin.pl
*Technical University**
ul. Sikorskiego 37, 70-313 Szczecin, Poland
tel.: +48 91 4494129, fax: +48 91 4494561
e-mail: mholub@ps.pl, kal@ps.pl
*Institute of Low Temperature Plasma Physics***
Friedrich-Ludwig-Jahn-Str. 19,D-17489 Greiswald, Germany
tel.: +493834554448, fax: +49 3834554301
e-mail: mueller@inp-greiswald.de, zahn@inp-greiswald.de

Abstract

The control of NO_x (NO and NO_2) emissions from marine engines remains a challenge. In recent years, there have been a number of reports show that plasma device combined with a catalyst can reduce as high as 90% of NO_x in simulated diesel exhaust gas. In the case of real diesel exhaust, the beneficial role of a plasma treatment is now thought to be the oxidation of NO to NO_2, and the formation of partially oxidized hydrocarbons that are more active for the catalytic reduction of NO_2. This paper briefly describes research efforts aimed non-thermal plasma reactor development for ships use, and primary focused on NO oxidation conditions, functionally fitted to the engine mode of operation.

Keywords: marine diesel engine, exhaust emission gas treatment, low temperature plasma reactor

1. Introduction

There is no doubt that the contribution from ships to global gas emissions will increase, international shipping sharing about 7% of the total sulphur and 11% nitrogen discharge. The marine diesel engine is the prime mover for vast majority of merchant vessels and dominating as drives for electricity production on ships. Diesel manufacturers and researchers have been investigating a variety of techniques in the aim of reducing diesel emissions as far as reasonably practicable. These techniques have been divided into three areas of study: pre-treatment, primary (internal) and secondary (after-treatment) methods. All these systems have different extent of success in reducing engine emissions however, their effectiveness may not be adaptable for a given ship design. Each of these categories however, are a trade-off with improving NO_x emissions and other emissions such as: hydrocarbons, particle matters and CO. The NO_x reduction technologies called as after-treatment or secondary methods are fitted externally to the engine and are applied directly to the combustion gases. One promising approach to reducing NO_X and particulates from diesel exhaust is to use a combination of plasma with catalyst.

The presently accepted model is that, a non-thermal plasma in the presence of water, oxygen and hydrocarbon will efficiently convert NO to NO_2, while only partially oxidizing the

hydrocarbons present in exhaust. Some catalysts will reduce NO_2 (but not necessarily NO) in the presence of excess oxygen, if some hydrocarbon are present. In recent years selective catalytic reduction (SCR) has been promoted as a suitable after-treatment technology for the marine use. SCR is commercially available and it has been built-in to a number of vessels. The SCR process uses urea, which is water soluble and non-toxic, mixed into a solution and then injected into the exhaust stream. It reacts with the NO_x over a catalyst bed. Comparison made between the potential benefits of the non-thermal plasma and SCR systems for marine use[1]. A full scale SCR system that offers high NO_x removal (~90%), has significant disadvantages especially in the need to carry large amounts of urea solution. The non-thermal plasma at atmospheric pressure systems has been developed for incinerator flue gas clean-up. Currently, this technology is undergoing further development for diesel engine exhausts.

2. Application of NTP to marine diesel exhaust after-treatment

In conventional application of plasma to the treatment systems of power plant flue gas, the plasma reactor is used to oxidize NO_x to nitric acid [2]. A combination of non-thermal plasma (NTP) with catalysts can be referred to plasma assisted catalysts technology. The NO_x in engine exhausts – close to exhaust receiver, is composed primarily of NO. Consequently, present after-treatment schemes have focused on the reduction of NO. Recent developments in catalytic control of NO_x are revealing the significance of NO_2 as an intermediary stage for achieving higher NO_x removal efficiencies [3] [4]. This implies that the conversion of NO to NO_2 is an important intermediate step in the final reduction of NO_x to N_2 Oxidation is the dominant process for exhausts, containing NO in mixtures of N_2, O_2 and H_2O, particularly when O_2 concentration is 5% or higher. There are two removal possibilities of NO pathways from exhaust gas:

1. oxidation $\qquad O + NO \leftrightarrow NO_2$, $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (1)

$\qquad\qquad\qquad\qquad OH + NO_2 \leftrightarrow HNO_3$, $\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (2)

2. reduction $\qquad N + NO \leftrightarrow N_2 + O$, $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (3)

Reaction rate coefficients for these and other main processes are listed in table 1.

Tab.1. Basic reactions and rate coefficients of NO_x

Reaction	Rate coefficient	Reference
$NO + O + N_2 \rightarrow NO_2 + N_2$	$9,1 \cdot 10^{-28} T^{-1.6}$	[5]
$NO_2 + OH + M \rightarrow HNO_3 + M$	$2,2 \cdot 10^{-30} (T/300)^{-2.9}$	[5]
$N + NO \rightarrow N_2 + O$	$3,1 \cdot 10^{-11}$	[6]
$N + OH \rightarrow NO + H$	$3,8 \cdot 10^{-11} \exp(85/T)$	[5]
$N + O_2 \rightarrow NO + O$	$4,4 \cdot 10^{-12} \exp(-3220/T)$	[5]
$NO + O_3 \rightarrow NO_2 + O_2$	$2,0 \cdot 10^{-12} \exp(-1400/T)$	[7]

As mentioned before, in diesel engine exhaust gases, NO_x consists mainly of NO. A significant attempt to improve the NO removal at lower temperatures (modern marine diesel engines; 180-250°C) is to combine a non-thermal plasma process with the catalyst. In this kind of joint process, the main role of the non-thermal plasma is to convert NO into NO_2. It was found that the rate of NO oxidation to NO_2 by the non-thermal plasma significantly decreases with the increase in reaction temperature [2].

The alternative method capable of oxidizing NO to NO_2 is to use ozone, which can be efficiently produced by dielectric barrier discharge (DBD), externally. When ozone is mixed with

the exhaust gas, NO can be easily oxidized to NO_2 without producing any by-products. Then, the oxidation of NO by mixed ozone and exhaust is efficient, and the reduction of NO_2 back to NO does not occur. Anyhow, more attractive and preferred pathway over oxidation, for marine diesel engine would be reduction (eq. 3), since the end products N_2 and O could be exhausted to the ambient atmosphere. The simulated NO removal possibility in DBD plasma reactor presented in [3]. During the current pulse, the primary radicals N, OH, O and H are produced by electro-impact dissociation feed gas. Primarily they are produced by the following reactions:

$$e + N_2 \rightarrow N + N + e, \qquad k = 9 \cdot 10^{-10} \; [cm^3 \, s^{-1}] \tag{4}$$

$$e + H_2O \rightarrow H + OH + e, \qquad k = 6 \cdot 10^{-11} \; [cm^3 \, s^{-1}] \tag{5}$$

$$e + O_2 \rightarrow O + O + e, \qquad k = 1 \cdot 10^{-9} \; [cm^3 \, s^{-1}] \tag{6}$$

$$\rightarrow O + O(^1D) + e, \qquad k = 3 \cdot 10^{-9} \; [cm^3 \, s^{-1}] \tag{7}$$
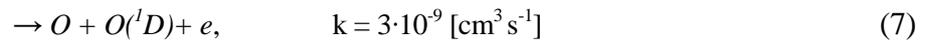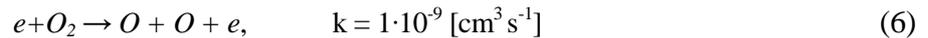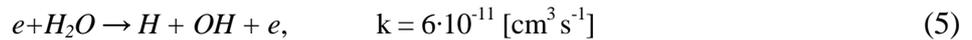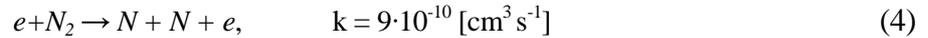
O atoms created during the current pulse are basically produced in their ground state – $O(^4S)$ and in the first excited state $O(^1D)$, latter with water, produce OH radicals:

$$O(^1D) + H_2O \rightarrow OH + OH, \tag{8}$$

Due to the likelihood that restricted species will be produced in NO plasma removal process after the NO is depleted, the DBD power level should be adjusted to current NO concentrations, and prevent O_3 formation and NO as well.

The non-thermal plasma module for marine use requires: robust design, low voltage, minimum maintenance, process with easily scaleable efficiency, as the rate of NO_x emission varies with engine load and other conditions. The efficiencies required for cleaning devices are also quite tough. This efficiency must be realized without generating significant amounts of other unwanted species. Dielectric barrier discharges plasma reactors (DBD) are compact – efficient plasma sources, commonly used as ozonizers and are attractive due to their ability to operate in a stable mode at low pressures, with high average power compared to corona-beam reactors. The oxidation from NO to NO_2 without decreasing NO_x concentration (minimum reaction byproducts) and with least power consumption is the key for the optimum reactor design.

3. Engine test bed operation and apparatus setup description

Exhaust emission plasma assisted after-treatment module is fitted on a exhaust outlet path of the marine test bed engine, with specification engine given in Table 2. Engine could be operated at steady speed and load conditions, over a range of power settings. The mode of operation is determined using the relevant for ship propulsion engines ISO test cycles [9]. In proposed solution the non-thermal plasma reactor is inserted between the engine turbocharger outlet and catalyst.

Tab. 2. Test-bed engine specification

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

Figure 1 presents an outline of a laboratory plasma-catalyst system that includes non-thermal plasma (DBD) reactor, for fractional exhaust gas stream examination. The part scale plasma reactor models have been designed and were being manufactured [10]. The design of the exhaust

system is suitable for the full scale concept, where it takes the place along with silencer. The approach will enable other fits, to be more suitable accommodate modules, by altering their number and length. Based on the concept that utilises a number of modules and it will minimise development risk, before going in to full scale.
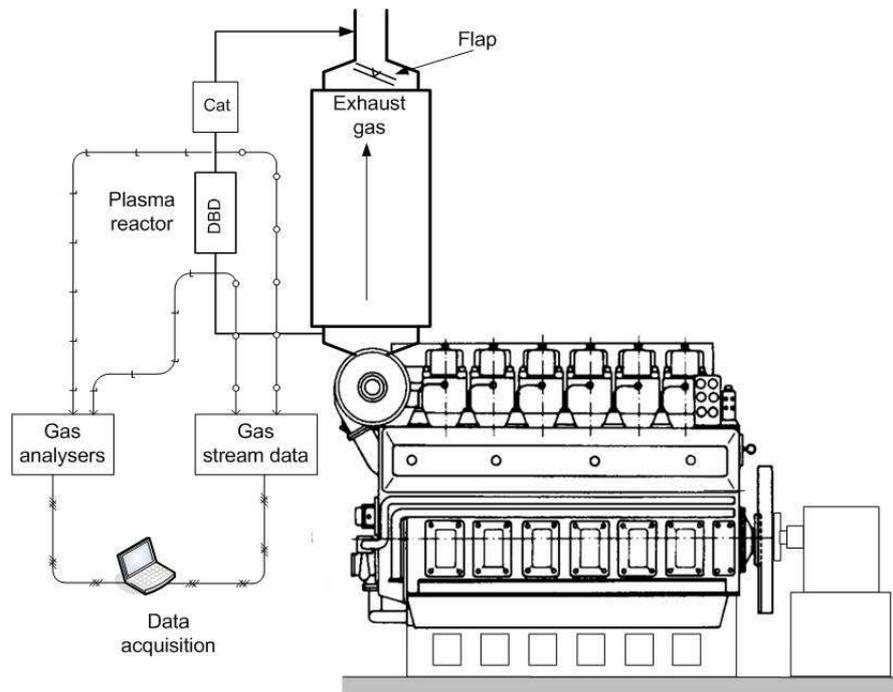
Fig. 1. Non-thermal (DBD) plasma reactor „by-pass" arrangement

Subsequently the comprehensive series of trials were performed to assess the exhaust flow properties through the main exhaust channel and plasma reactor by-pass pipe, within the engine operation effective load and consequent emission profiles achieved. Emission measurements were carried out on engine at steady-state operation. All engine performances were continuously, together with exhaust gas components concentration recorded by means of measurement assemble presented in figure 2. During the engine trials the exhaust gas flows from the engine exhaust receiver after turbocharger, via a by-pass line and main duct – exhaust gas silencer. Proportional amount of gas stream is controlled through restriction flap. The sampling unit consists two probes situated below and above the plasma reactor. Sampling gas is distributed to all analysers. The upper end of the sampling probes – a sintered ceramic filter, the probe itself, sample line, transfer pump and distribution box, are heated by means of separate temperature controlled units. Exhaust emission is subsequently recorded at intervals over a measurement period of 15 minutes on every engine load. For each of the test levels, engine performance data are recorded in as much detail as test bed equipment. In addition to the exhaust emission, some essential operating engines data are measured to asses, the respective engine operating conditions – in accordance to ISO-3046 standard. Amongst other variables, this included: effective load, speed, and fuel consumption, exhaust temperature, performance of the turbo-blowers, together with the ambient conditions prevailing at the time of the measurement 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, which include generator and pitch propeller drive. To reduce emissions variability due to fuel variables, all tests performed with the selected marine distillate fuel DMX in accordance to ISO-8217 standard.
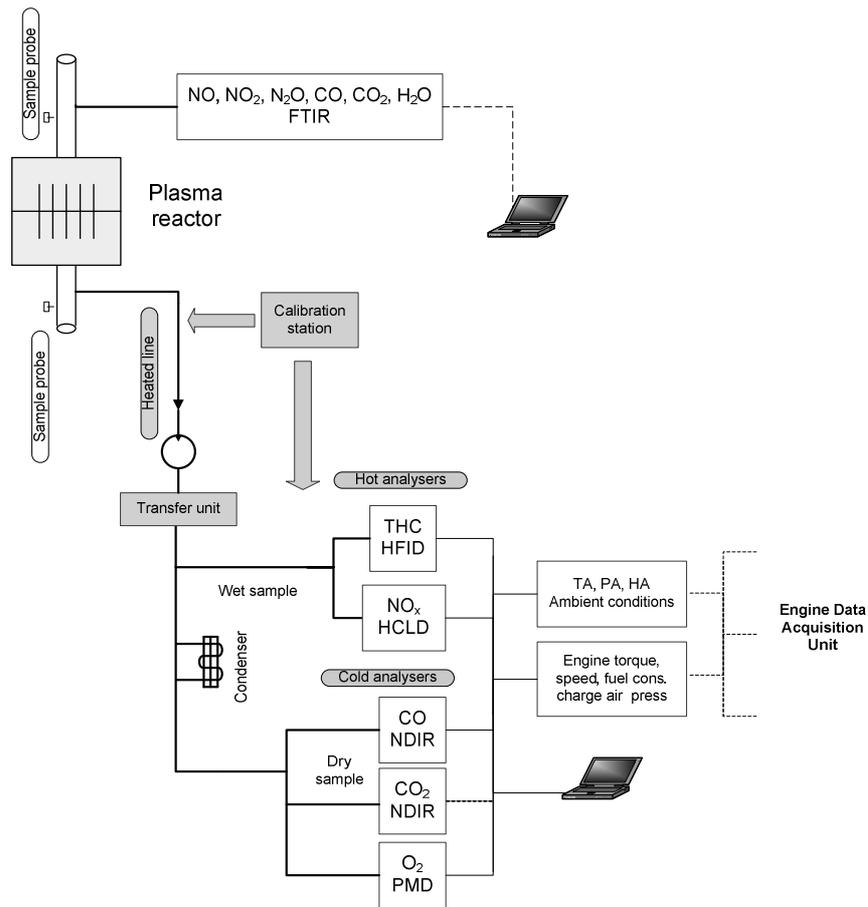
Fig. 2. Measurement equipment setup

4. Results and discussion

The NO_x reaction activities were measured in a one-stage non-thermal plasma reactor system. An marine engine functional exhaust gas was used in the plasma reactors tests. The total exhaust gas flow rate was corresponding to an engine effective load. Effectively, the exhaust flow through the plasma reactor path can be controlled by restriction flap, mounted upstream the main silencer. Equivalent reactor proportional part gas stream parameters are presented in figure 3. The total exhaust gas amount and attribute components during the engine tests presented in table 3. Typically, the reactor was heated up to reach stable temperature, adequately with exhaust gas condition without turning on the plasma. Upon reaching the exhaust gas pressure and temperature level, and as soon as the NO_x levels stabilized, the plasma was turned on at a typical power stage. Throughout the measurements, the engine outlet NO_x levels (NO and NO_2) were monitored with simultaneous NO, NO_2, N_2O measurement, allowing to estimate the quantities of unconverted NO_2. During the tests, the reaction temperature was raised usually approximately 30 K. At each temperature, sufficient time was allowed to reach steady state (or near steady state) to assure that the NO_x loss was not due to storage effects. Set of thermocouples were used to provide reference state of the plasma processor temperature. The processor temperature can not adjusted as is dependent to engine exhaust gas temperature and during test raised from room temperature up to 350°C. This has been used to investigate the operating temperature of the process. The chemistry inside the plasma reactor is complex. It is concluded that the two most important processes initiated by the plasma are the partial conversion of NO into NO2, and the partial oxidation of unburned hydrocarbons in the exhaust gas. In fact, modeling of the gas-phase chemistry indicates that these two chemical processes are closely linked [3].
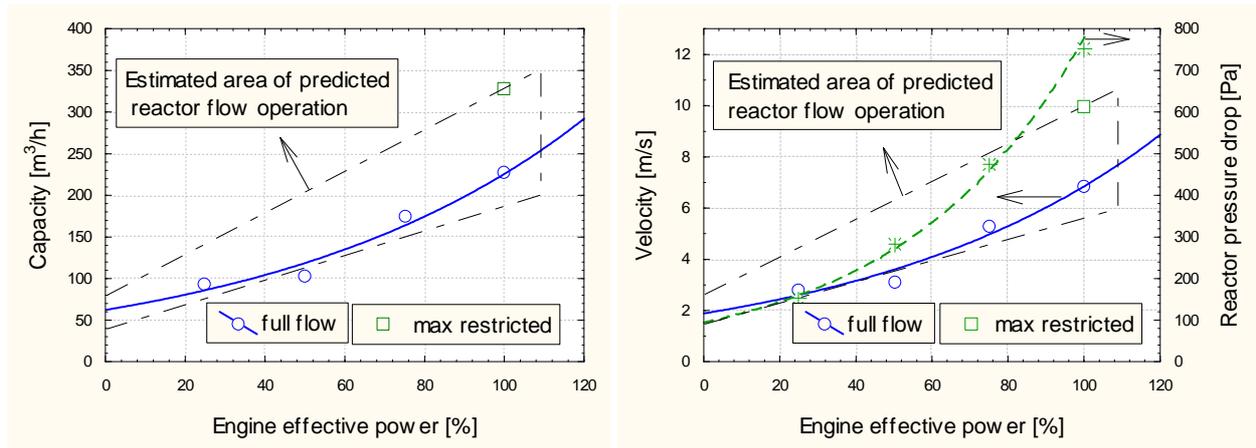
Fig. 3. Exhaust gas flow through the plasma reactor within the engine load range and

Tab. 3. Total engine exhaust gas flow and components contribution

Operation mode	D2	1	2	3	4
Engine power	[kW]	400	300	200	100
Engine speed	[rpm]	720	720	720	720
Exhaust flow	kg/h	2 690	2 229	1 675	1 040
NO_x	kg/h	5,62	4,48	2,95	1,49
CO	kg/h	0,25	0,17	0,12	0,08
CO_2	kg/h	273	210	144	76
O_2	kg/h	299	267	216	150
HC	kg/h	0,42	0,34	0,26	0,14
SO_2	kg/h	1,41	1,08	0,74	0,39

The experimental measurements demonstrate particularly significant oxidation process. In the present paper, all the results were presented in terms of constant specific energy density supplied to plasma reactor. In this application the plasma is used to oxidize NO to NO_2. Oxidation is the dominant process for exhausts containing dilute concentrations of NO. The kinetic energy of the electrons is deposited primarily into the major gas components, N_2 and O_2. The most useful deposition of energy is associated with the production of N and O radicals through electron-impact dissociation. Diesel engine exhausts contain little gaseous hydrocarbon, and under some load transient conditions a significant amount of liquid-phase hydrocarbons VOC (volatile organic fraction) in the particulates. The hydrocarbons promote the oxidation of NO to NO_2, but not the reduction of NO to N_2. The oxidation of NO to NO_2 is strongly coupled with the hydrocarbon oxidation chemistry. The plasma operation process results with the exhaust gas is shown in the Figure 4. When the electrical power to the plasma reactor is turned off and gas is passed through the reactor, the NO and NO_2 outlet concentration basically correlates to total NO_x level recorded at the reactor inlet. When the electrical power to the plasma reactor is turned on, the NO is oxidized to NO_2. The oxidation at this temperature and gas flow conditions is quite effective (idle engine load). Presumably the presence of liquid-phase hydrocarbons and propane could improve the efficiency of NO oxidation. The plasma process does not repeatedly guarantee the efficient oxidation of NO to NO_2. In the exhausts containing both O_2 and H_2O, plasma produces not only O radicals but also OH radicals, only O radical can be effective in oxidizing NO to NO_2. However, the OH radical can further oxidize NO_2 to nitric acid. This acid formation is not a desired part of the plasma process and the presence of the hydrocarbon prevents the formation of an acid products and increases the efficiency for NO to NO_2 oxidation.
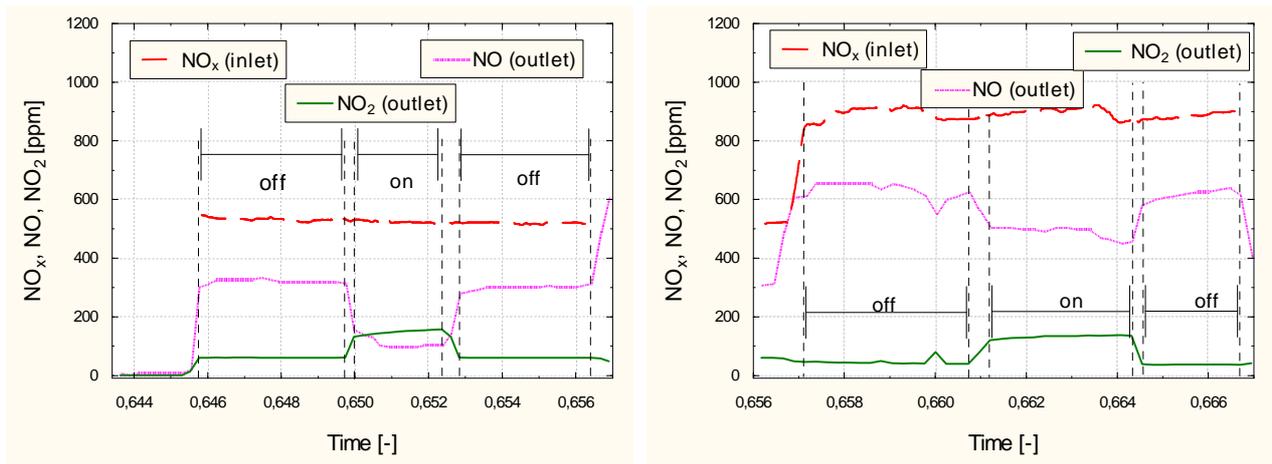
Fig. 4. Plasma reactor NO$_x$ concentration record under two ascending engine loads

Figure 4 (second diagram) shows effect of rising exhaust flow and gas temperature on NO oxidation efficiency under engine part load condition. With higher gas flow and temperature, at given reactor energy density NO oxidation decreases. The decrease in NO oxidation efficiency could be recognized with the following reasons: the rate coefficient of oxidation reaction decreases with gas temperature increase, thus reducing the efficiency of NO conversion to NO$_2$, hydrocarbons influence was weakened with temperature rise and reduction of ozone which plays an significant function in NO oxidation. Figure 5 shows the exhaust gas composition regarding mass flow nitrogen oxides allocation, caused by plasma stroke. For a given electric field, the ratio of reacted NO and NO$_2$ – resulted was higher under engine part load than idle.
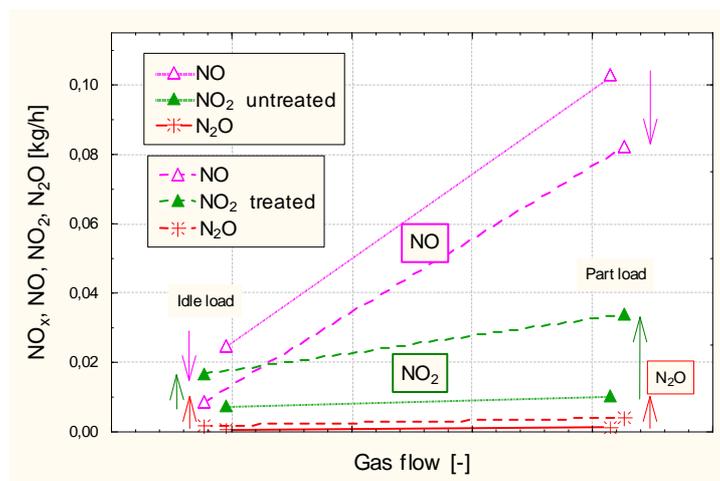
Fig. 5. Nitrogen oxides flow trends in plasma reactor operation under two ascending engine loads

5. Conclusions

Experimental studies involving a plasma reactor operation with sensible exhaust gas from marine engine performed. The primary aim of the experiment involved basic NO oxidation trends under engine characteristic mode of operation. For a given reactor energy level density, the plasma-associated process exhibits NO oxidation characteristics different for two exhaust gas states and flows – figure 6. The idle engine load reveal higher NO conversion efficiency – close to 50 %, while part load of the engine decreased final efficiency to 26%. The NO oxidation process obtained under different load conditions is characterized by: exhaust gas flow where capacity increased twice, elevated temperature and gas components share.
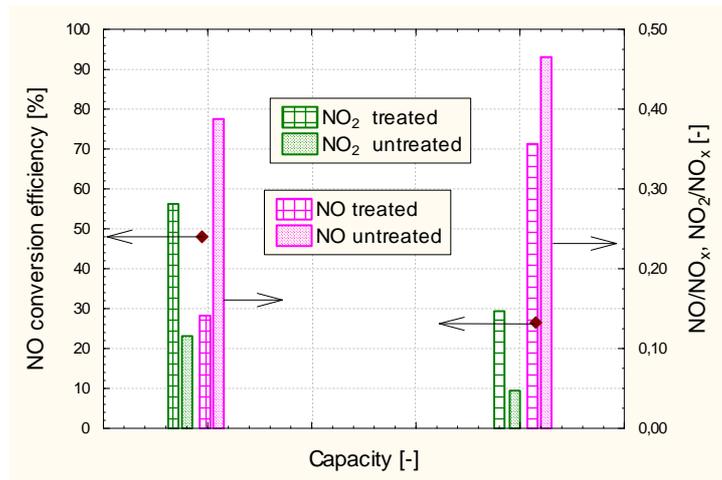
Fig.6. Plasma NO_x reaction – oxidation efficiency process under two ascending engine loads

Following the evaluation stage a programme is now underway to design, build and test a part scale reactor model to develop $1/10^{th}$ range of the exhaust gas flow. It will give the possibility to increase experimental engine effective load up to nominal level. The plasma-associated technique, exhibiting a high NO oxidation level, can be a viable alternative after treatment system.

References

[1] Hughes D. E., McAdams R., *Non-thermal plasma for marine diesel*, International Council on Combustion Engines CIMAC Congress 2004, 7-11 June, Kyoto (Japan) 2004, Paper No. 231, p. 15.

[2] Penetrante B., Schultheis S. E., *Non-Thermal Plasma Techniques for Pollution Control: Part B - Electron Beam and Electrical Discharge Processing*, Springer-Verlag, Berlin Heidelberg New York, 1993.

[3] Gentile A. C., Kuschner M. J., *Reaction chemistry and optimization of plasma remediation of N_xO_y from gas streams*, Journal Appl. Phys. 78(3) 1 August 1995.

[4] Penetrante B.M., Vogtlin G.E., Merritt B.T., Brusasco R.M., *Plasma Technology for Tail Pipe Reduction of NO_x in Diesel Exhaust*, South Coast Air Quality Management District,Symposium on Air Pollution Health Impacts, Recent Findings, Implications, Dieselization and Policy Initiatives, Diamond Car, CA November 20-21, 1997.

[5] Atkinson R., Baluch D.L., Cox R. A., Hampson R.F., Kerr J.A., Kuschner J., Troe J., Journal of Phys. *Chemical Reference Data*, 18 881, 1989.

[6] Person J. C., Ham D.O., Radiat. Phys. Chem. 31, 1, 1998.

[7] jorth J., Notholt J., Restelli G., Int. J. Chem. Kin. 24, 51, 1992.

[8] Mok Y. S., *Application of dielectric barrier discharge to selective catalytic reduction of nitrogen oxide*, Journal Chem. Eng., Japan 37, 1337, 2004.

[9] International Maritime Organisation, *Draft technical code on emission of nitrogen oxides from marine diesel engines*, 1997.

[10] Kalisiak S., Paterkowski W., *The semiconductor corona generator for cleaning gas pollution*, 4th International Conference on Unconvencional Electromechanical and Electrical Systems (UEES) St. Petersburg, Russia, June 21-24 1999.

[11] Shelef M., *Selective Catalytic Reduction of NOx with N-Free Reductants*, Chemical Reviews 95, 1995.