Journal of KONES Powertrain and Transport, Vol.14, No. 3 2007

DEVELOPMENT OF LOW TEMPERATURE PLASMA NOX CONTROL SYSTEM FOR MARINE DIESEL ENGINE

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Abstract

The control of NO_x emissions from marine engines proves a challenge. Diesel engine manufacturers have been investigating a variety of methods with aim of reducing NO_x emissions. Currently, the plasma technology is undergoing rapid development in application to diesel engine exhausts. A combination of non-thermal plasma with catalysts can be referred to plasma assisted catalysts technology. This paper briefly describes research efforts aimed at non-thermal plasma reactor development for ship use with primary focus on NO oxidation condition. The part scale plasma reactor models have been designed and manufactured for the purpose of this trial. Exhaust emission plasma after-treatment module was fitted on exhaust outlet path of the marine test bed engine for fractional exhaust gas stream examination. Subsequently, the comprehensive series of trials were performed to assess the exhaust flow properties of the main exhaust channel and plasma reactor by-pass duct. Emission measurements were carried out on engine at steady-state operation. The NO reaction activity was a major task of the experiment and throughout the measurements, the engine outlet NO_x levels (NO and NO_2) were monitored with simultaneous NO, NO_2, N_2O level recording after NTP reactor.

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

1. Introduction

The International Maritime Organization (IMO) has recently adopted Annex VI to the International Convention for the Prevention of Pollution from Ships (MARPOL 73/78). The adoption of this new legislation has far reaching effects for all ship builders and ship operators. Diesel manufacturers and researchers have been investigating a variety of methods with aim of reducing diesel NO_x emission for reasonable extent considering the costs. These techniques have been divided into three areas of study: pre-treatment, primary (internal) and secondary (after-treatment) methods. All these systems provide different degree of effectiveness in reducing engine emissions. However, their adaptability to ship environment is to a degree restricted. Each of these categories, however, constitutes a trade-off with improving NO_x emissions and other emissions such as: hydrocarbons, particle matters and CO. The NO_x reduction technologies are part of after-treatment or secondary methods, which are fitted externally to the engine and are applied directly to the combustion gases. This experiment was set out to examine a promising approach to reduce NO_X and particulates from diesel exhaust that relies on application of plasma with catalyst.

The accepted model assumed that non-thermal plasma in the presence of water, oxygen and hydrocarbon will effectively convert NO to NO_2, while only partially oxidizing the hydrocarbons present in exhaust. Some catalysts can reduce NO_2 (but not necessarily NO) in the presence of excess oxygen, if specific hydrocarbons 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 successfully built-into a number of vessels. The SCR process uses urea, which is non-toxic and water-soluble, solution which is injected into the exhaust stream. It reacts with the NO_x over a catalyst bed. Comparison was made between the potential benefits of the non-thermal plasma and SCR systems for marine use [1]. A full scale of SCR system, which offers high removal of NOx (~90%), has significant disadvantage, especially when it is a need of carrying high amount of urea. The non-thermal plasma at atmospheric pressure systems has been developed, as an alternative solution, for incinerator flue gas clean-up. Currently, this technology is undergoing further development for diesel engine exhausts. Major task of the project was full scale NTP hybrid exhaust module for efficient NO_x reduction. The main participants of the project were: Maritime University and Technical University in Szczecin and Institute of Low Temperature and Plasma-Physics in Greifswald (Germany).

2. Application of NTP to marine diesel exhaust gases

Plasma is a partially ionised gas comprised of a charge of neutral mixture of atoms, molecules, free radicals, ions and electrons. Electrical current is converted into electron energy and the electrons create free radicals, which are capable of destructing pollutants in exhaust emissions. The plasma is generated using an alternating high voltage to break-down the gas flowing between two electrodes. The region between the two electrodes is filled with a material resulting in voltage breakdowns in the voids between the materials. The duration of the voltage breakdowns lies in the range of few nanoseconds. The system is compact and very flexible in terms of size and shape. In conventional application of plasma to the treatment systems of power plant flue gas, the plasma reactor is used to oxidize NO 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 combustion chamber and exhaust receiver, are 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. 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. A significant attempt to improve the NO removal at low exhaust gas temperatures (in modern marine diesel engines in range of 180-250°C) is to combine a non-thermal plasma process with a catalyst. In this joint process, the main role of the NTP 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 chemistry inside the plasma reactor is complex. 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 [3]. Modelling of the gas-phase chemical process indicates that these two processes are closely linked. The non-thermal plasma module for marine use requires: robust design, low voltage, minimum maintenance, and low energy consumption with easily scalable efficiency, as the rate of NO_x emission varies with engine load and external ship conditions. The expected high efficiency of this system must be achieved without generating significant amounts of other unwanted species. For the purpose of experiment DBD reactor was adopted. Dielectric barrier discharges plasma reactors (DBD) are compact and 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.

Optimum reactor design delivers efficient oxidation rate from NO to NO_2 without increasing NO_x concentration (minimum reaction by-products) at least power consumption possible.

2.1. NTP reactor construction and exhaust gas assembly description

The part scale plasma reactor model has been designed and manufactured for the purpose of examination. Experimental NTP unit design included a modular DBD reactor for industrial exhaust gas cleaning purposes. Single module of the designed multiple–rod chamber is depicted in figure 1.

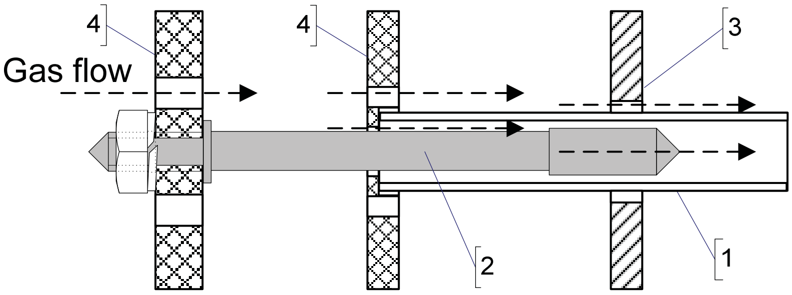

Fig. 1. Single module of the designed reactor chamber

Proposed construction consists of three plates (3 and 4 on Figure 1) that represent the construction basis for low voltage rods (2) and quartz-glass dielectric barriers (1). Plate 3 can be high-voltage supplied, however the polarity of the supplied power can be easily reversed. Dashed arrows represent gas movement through plates and tube volume. There are two discharge zones: between plate 3 and barrier 1 and between the steel rod 2 and the barrier glass tube. The chamber consists of a number of single tubes, which number (as well as shape and size), steel rods and plates can be application specific. Modularity and ease of problem driven optimization of the construction are biggest advantages of the reactor construction proposed. Reactor potential discharge volume is 7,524 cm^3. A resonant-type supply system was used. Advantages of electronic resonant power supplies are extensive, the most relevant include solid-state power transistor switching losses minimization and high-voltage transformer-less design. Typical overview of resonant high voltage alternating current power supply design is depicted in figure 2.

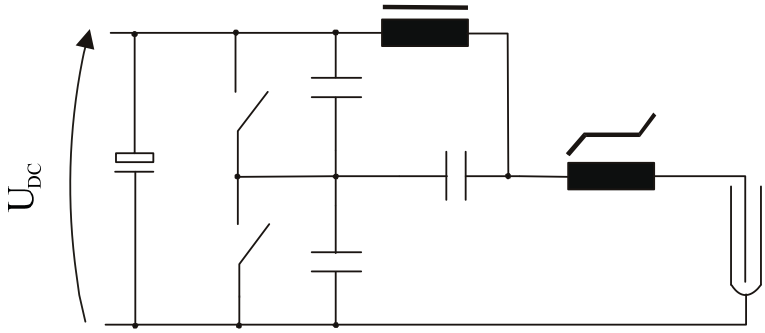

Fig. 2. Overview of an electronic resonant-type power supply

Power flow is controlled through the measures of the U_{DC} voltage of the DC-link. Power switches need to switch with the resonant frequency of the power supply – reactor system. Therefore 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 temperature change and occurring chemical processes. However, the control system actively maintains electrical resonance. Figure 3 a) presents typical voltage and current waveforms of power supply and b) reactor chamber while working. Resonant frequency of the system reached 5,9kHz, while output voltage can be adjusted up to $10kV_{p\text{-}p}$.

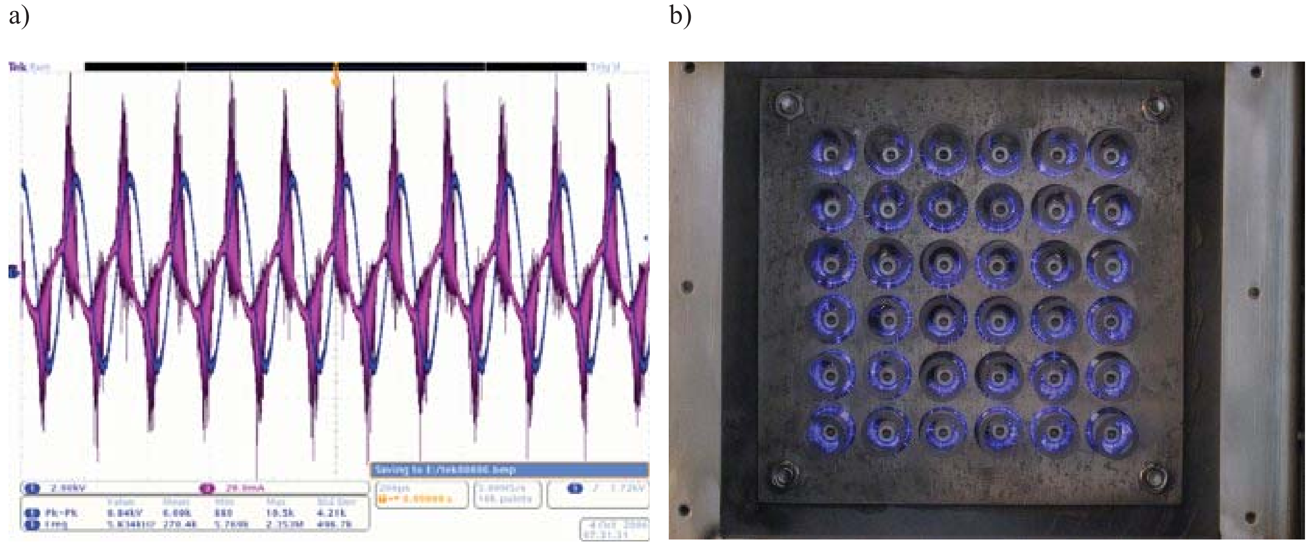

Fig. 3. a) – output voltage and current of the supply system under load, b) – working reactor elements

Exhaust emission plasma assisted after-treatment module is fitted on an exhaust outlet path of the marine test bed engine. Figure 4 presents an outline of a laboratory plasma system that includes non-thermal plasma (DBD) reactor and apparatus setup for fractional exhaust gas stream examination. The design of the exhaust system allows full scale after-treatment module located along with the silencer. The bypass setup enables a variety of fits to accommodate optional modules by altering their number and size. A design concept allows adopting a number of NTP modules to minimise development risk, before building a full-capacity reactor.

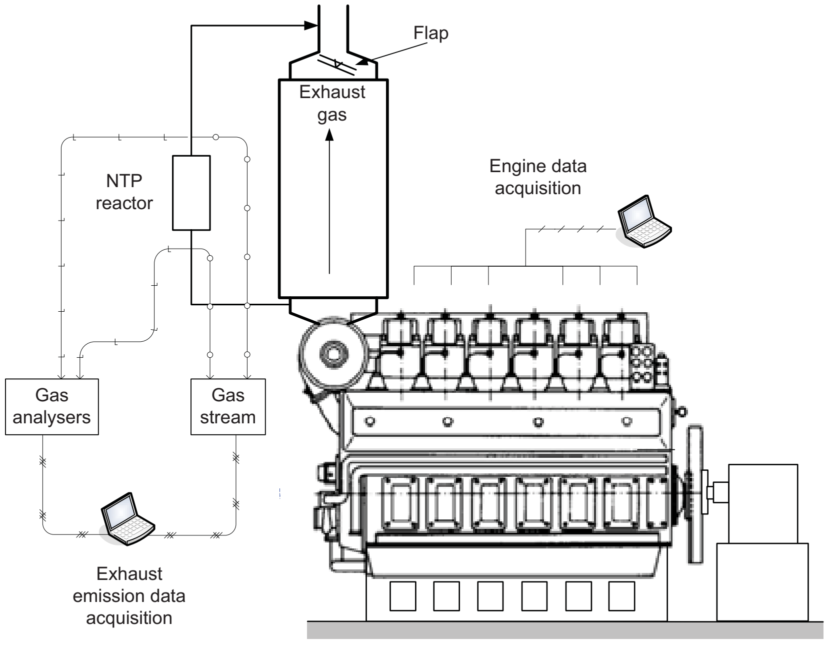

Fig. 4. Non-thermal (DBD) plasma reactor „by-pass" arrangement and measurement equipment setup

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. The total exhaust gas flow rate corresponded to engine effective load. The exhaust flow through the plasma reactor can be controlled by restriction flap, mounted upstream the main silencer. Reactor part gas stream parameters are presented in figure 5.

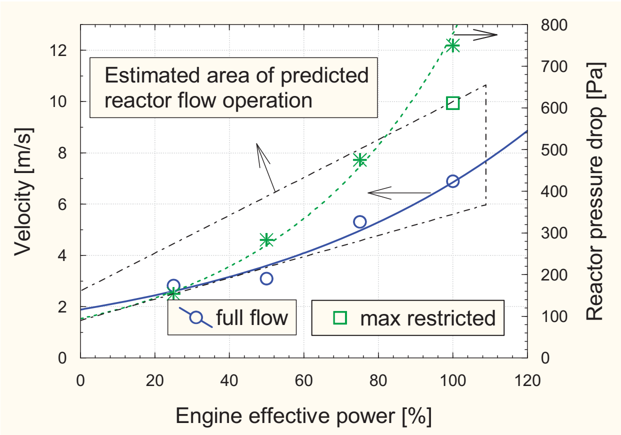

Fig. 5. Exhaust gas flow through the plasma reactor within the engine load range

2.2. Test bed experimental setup and operation details

Measurements were carried out on a test-bed for ship propulsion engine, operating at steady speed and load. Engine specification is shown in Table 1.

Tab.1. 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

All tests were carried out in accordance with test-cycles procedure D-2 and E-2 (ISO-8178), which include generator and pitch propeller drive. All engine performances, together with exhaust gas components concentration, were continuously recorded by means of measurement assembly presented in figures 4 and 6.

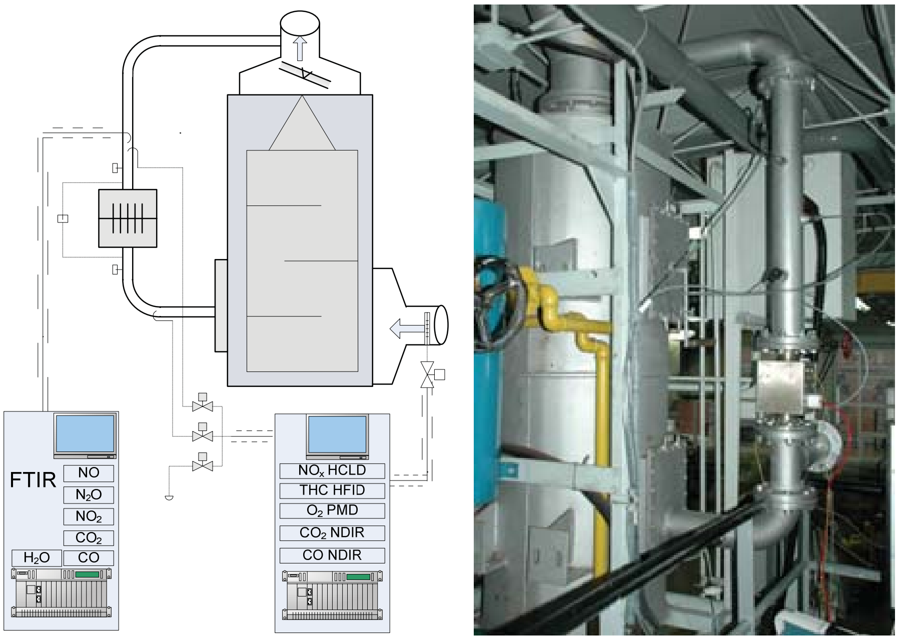

Fig. 6. Measurement equipment setup and NTP reactor assembly

The engine test trial and basic performance measurement procedure conducted in accordance to ISO standards provided important engine operating data. Amongst these variables the most significant were: effective load, speed, fuel consumption, exhausts temperature, turbo-blowers performance, and ambient condition parameters. Equally essential, the exhaust gas emission components were registered. To reduce emissions variability due to fuel influence, all tests were performed with the selected marine distillate fuel - DMX adhering to ISO-8217 standard.

3. Results and discussion

The NO_x reaction rate was measured behind one-stage non-thermal plasma reactor system. 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 unconverted NO_2. During the tests, the reactor process temperature has risen approximately 30 K at flow condition. Also, 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 indicate the state of plasma processor temperature. The processor temperature could not be adjusted, as it depended on engine exhaust gas temperature. During tests it raised from room temperature up to 350°C. This has been used to investigate the influence of operating temperature on oxidation process.

The 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. The trial schedule allowed the reactor heating-up to reach stable state before turning on the plasma, adequately to exhaust gas condition. Upon reaching stable gas pressure and temperature level and as soon as the NO_x levels stabilized, the plasma supply unit was turned on at a fixed power stage. The example of plasma operation process on engine exhaust gas is shown in the Figure 7. It was observed that when power supply of plasma reactor was turned off, the NO and NO_2 outlet concentration in gas passing through the reactor correlated to total NO_x level recorded at the reactor inlet.

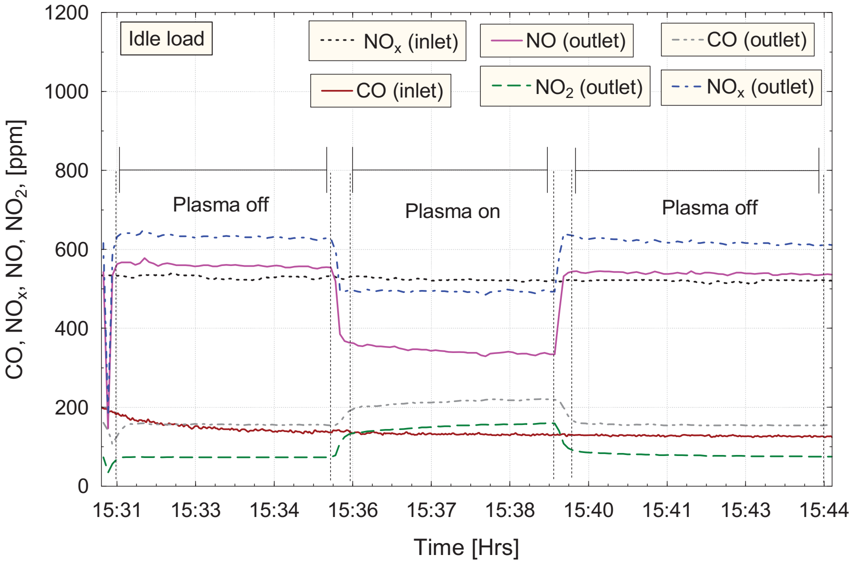

Fig. 7. An example of NTP reactor operation

When plasma reactor was under operation, NO oxidation to NO_2 proved quite stable and efficient. The oxidation at low temperature and low gas flow condition was quite effective (idle engine load). Presumably, the significant presence of liquid-phase hydrocarbons and propane was responsible for high efficiency of NO oxidation. The experimental measurements under low engine load demonstrated particularly efficient and significant oxidation process. Throughout this paper all the results are presented in terms of constant specific energy density supplied to plasma reactor.

In the setup the NTP reactor was used mainly as a means to oxidize NO. Oxidation is the dominant process in exhausts containing dilute concentrations of NO, even if there is insufficient amount of ozone. Oxidation process develops also during the normal exhaust gas flow – without plasma operation, which is shown on figure 8.

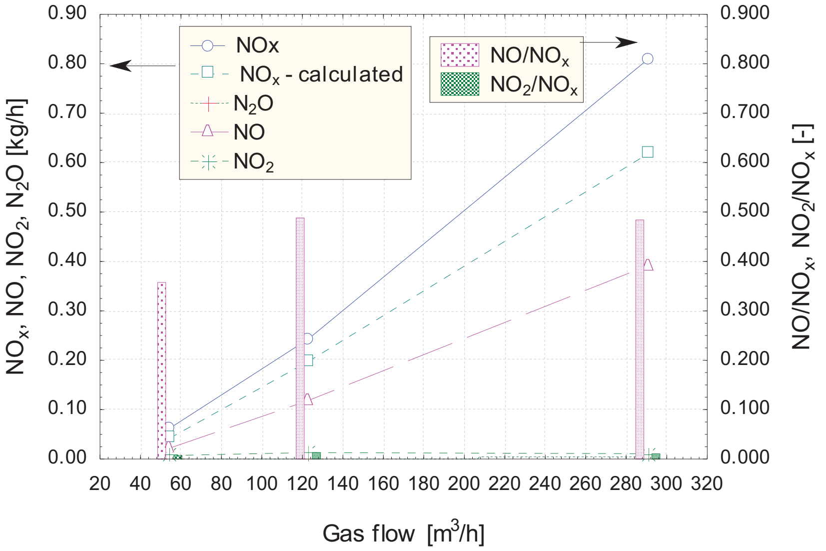

Fig. 8. Untreated exhaust gas and NO oxidation process

The kinetic energy of the electrons deposits primarily on major gas components, N_2 and O_2. The most useful deposition of energy is associated with the formation of N and O radicals through electron-impact dissociation. The NTP reactor gas components measured during engine tests (idle load - example) are presented in table 2.

Tab. 2. NTP reactor of exhaust gas flow components contribution

Air	Dynamic pressure		Pa	99840	Measurement concentration	NO_x	mg/m^3	1066,29
	Air temp.		°C	22,3		CO	mg/m^3	159,68
Exhaust gas Duct	Diameter		m	0.108		N_2O	mg/m^3	8,66
	Area		m^2	0,009		NO	mg/m^3	404,16
	Temperature		K	416,2		NO_2	mg/m^3	124,23
	Static pressure		Pa	0		NO_x*	mg/m^3	761,58
	Dynamic Pressure		Pa	1,70		THC	mg/m^3	66,50
	Wet degree		%	2,7	Emission	NO_x	kg/h	0,07115
	Average velocity		m/s	2,02		CO	kg/h	0,01066
	Concentration	O_2	%	15,63		N_2O	kg/h	0,00058
		CO_2	%	3,9		NO	kg/h	0,02697
	Gas density		kg/m^3	1,31		NO_2	kg/h	0,00829
	Flow		m^3/h	66.7		NO_x*	kg/h	0,05082
	Flow - dry		kg/m^3	42.4		THC	kg/h	0,00444

* calculated

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. In the exhausts containing both O_2 and H_2O, plasma produces not only O radicals but also OH radicals, while only O radical can be effective in oxidizing NO to NO_2. However, the OH radicals can further oxidize NO_2 to nitric acid. The acid formation is not a desired part of the plasma process. The presence of the hydrocarbon prevents the formation of acid products and increases the efficiency for NO to NO_2 oxidation. Figure 9 shows effect of rising exhaust flow and gas temperature on NO oxidation efficiency resulting from NTP reactor operation. It was observed that with higher gas flow and temperature, at fixed reactor energy density, NO oxidation decreases. The decrease in NO oxidation efficiency was associated with the following: the decreased coefficient rate of oxidation resulting from gas temperature increase, which reduced the efficiency of NO conversion to NO_2; weakened hydrocarbons influence caused by temperature rise and reduction of ozone presence, which plays a significant function in NO oxidation. Figure 9 shows the exhaust gas composition against mass flow nitrogen oxides allocation, caused by plasma stroke. For a given electric field, the ratio of reacted NO and NO_2 – indicated higher value under part and medium engine load than under idle engine running.

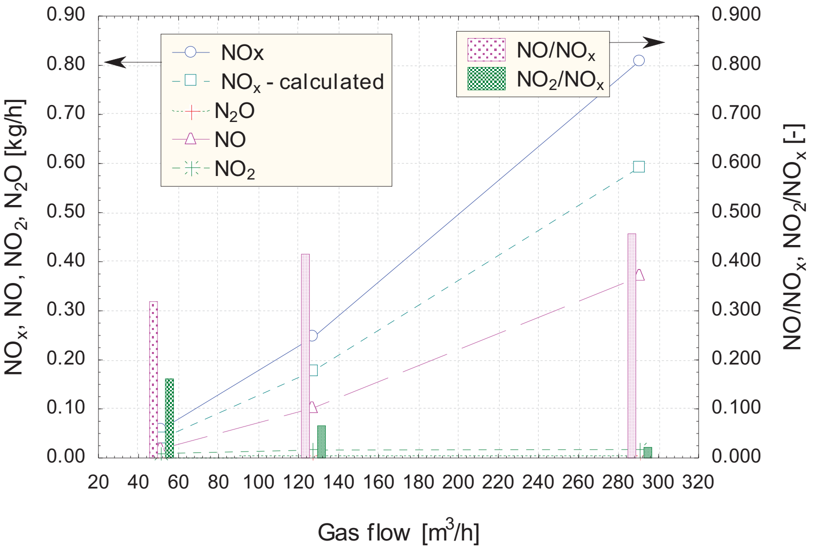

Fig. 9. NTP reactor operation and NO oxidation process

4. Conclusions

Experimental study involving a NTP reactor operation with realistic exhaust gas of marine engine was performed. Technical condition of the reactor after experimental trials (approximately 150 running hours) was excellent – figure 10. The primary aim of the experiment involved basic NO oxidation trends under variable engine modes of operation. For a fixed reactor energy level density, the plasma-associated process exhibited NO oxidation characteristics variable for specific exhaust gas states and flows – figure 11. The idle engine load revealed higher NO conversion efficiency – close to 15 %, while under part and medium engine load it gradually decreased to 4% value. For that reason NTP reactor operation under nominal engine load was not undertaken. The NO oxidation process obtained under different load conditions was influenced by exhaust gas flow, elevated temperature and gas components share. Different NTP reactor construction exhibits much higher NO conversion efficiency at similar flow and engine running condition [4]. Following the evaluation stage, programme now undergoes a re-design to build and test a part scale NTP reactor with catalyst model to capture 1/10th of the experimental engine exhaust gas flow range. This will give the possibility to increase experimental engine effective load up to nominal level.

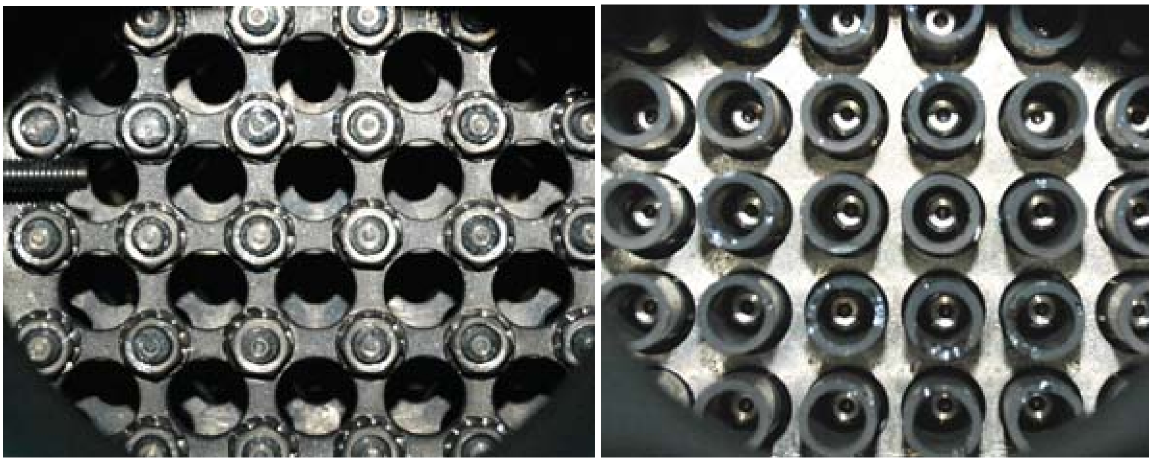

Fig. 10. NTP reactor inlet and outlet view after experimental trials

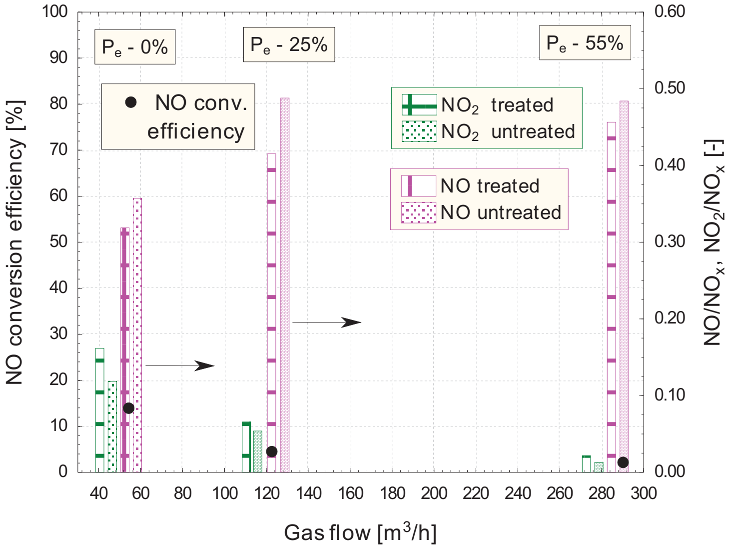

Fig.11. Plasma NO_x reaction – oxidation efficiency process under ascending engine loads

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