Non-Thermal Plasma Technology for the Abatement of NOx and SOx from the Exhaust of Marine Diesel Engine

N. Manivannan, W. Balachandran, R. Beleca, and M. Abbod

***Abstract*—Non-thermal plasma based technology is proposed to the abatement of NOx and SOx of the exhaust gas from marine diesel engine. Proposed technology uses electron gun and microwave energy to generate the plasma. Fundamentals of non-thermal plasma and chemistry are presented with a set of simulation results of the reduction of NOx and SO_2 for a typical two stoke marine diesel exhaust engine which is supported by an experimental results obtained with microwave plasma. A new scheme is also proposed in this paper to generate required plasma for the treatment of NOx and SOx form high exhaust flow rate.**

***Index Terms*—Abatement of NOx and SOx, non-thermal plasma, marine diesel emission control, electron beam plasma and Microwave plasma.**

I. Introduction

Non-thermal plasma technology for the abatement of NOx (NO + NO_2) and SOx from marine diesel engine exhaust gas is addressed in this paper. The toxic gases (NOx and SOx) are harmful to human health (cancer, respiratory irritation, nervous system problems, and birth defects) and environment (acid rain, ozone production, eutrophication, acidification of lakes and streams, accelerated corrosion of buildings and monuments, and reduced visibility) [1], [2]. IMO's MARPOL Annex VI, regulation 13 and regulation 14 defines the emission limits of NOx and SOx from marine exhaust [3], [4].

There are number of technologies those have been implemented on board to reduce the level of NOx and SOx from marine diesel engine [5]. Though these technologies can remove 99% of SOx and 90% of NOx, they possess number of drawbacks; two separate technologies for removal of NOx and SOx, requires high installation cost as well as maintenance cost, the installation takes large space on the ship and requires large storage of ammonia is required for the removal of NOx [5], [6]. On other hand, it has been proved and utilized that Non-Thermal Plasma (NTP) technology has number advantages in depollution in power plant such as simultaneous removal of NOx and SOx and reduced energy requirements [7].

There are a number of ways non-thermal plasma can be generated; Dielectric Barrier Discharge (DBD), Corona Discharge (CD), Electron Beam Generated Plasma (EBGP) and Microwave Plasma (MP). Out of these ENGP has been implemented for high throughput applications such as power plants to control the pollutions [8]. Electron beam can generate high density of electrons with high energy as required to generate high energy plasma. However non-of these NTP technologies have been studied or used in the marine industry in any form to remove NOx and SOx.

In this paper, we propose Electron Beam (EB) + Microwave Wave (MW) based NTP scheme to reduce NOx and SOx from the marine diesel engine. The major idea behind the combination of EB and MW is that, while EB can produce enough electrons to generate plasma, MW would maintain the energy of those electrons by re-energizing them. This combination would reduce the energy requirements that of using EB alone to generate same energy of plasma. Furthermore, since EB+MW plasma is electrode-less system, it avoids the problem of contamination.

The paper is structured in the following ways; Section I presents the basics of physics and chemistry NTP, in particular, for the typical gas composition of marine exhaust and Section II presents a set-of simulation result of reduction efficiency of NOx and SOx for a typical two-stroke marine diesel engine along with experimental results obtained with MP. The proposed new scheme, combination of MW and EB, is presented in the section III and finally conclusions are drawn in the Section IV.

II. Non-Thermal Plasma Chemistry and Physics

The basic principle of non-thermal plasma is that electron temperature (Te) and gas temperature (Tg) is greatly differ such that $T_e >> T_g$. High energy electrons impact with gas molecules and produce various radicals and ions. In the case of exhaust gas of marine diesel engine which composes of high concentration of CO_2, H_2O, N_2 and low concentrations of NOx, and SO_2, particulate matters (PM), hydro carbon(HC), volatile organic compounds (VOC) and soot particles, the major radicals produced will be $OH\cdot$, $O\cdot$, $N\cdot$ and $H\cdot$. When these radicals interact with NOx and SOx, they will be turned into H_2SO_4 and HNO_3 respectively. These acids can be dissolved into sea water after adjusting the pH levels.

Radical formations and radical + molecule reactions are very fast and highly depend on the reaction rates. While reaction rate of electron impact depends on the electron energy and cross-section of impact, reaction rate of radical + molecules depend on the chemistry and temperature of the gas. The reactions given Table I play dominant role in the formation of radicals and conversion of NOx and SOx into H_2SO_4 and HNO_3;

Manuscript received April 22, 2013; revised July 16, 2013. This work has been supported by the DEECON project, grant number 284745 funded by the EC Seventh Framework Programme theme FP7-SST-2011-RTD-1.

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TABLE I: PLASMA CHEMISTRY AND ASSOCIATED REACTIONS RATE CONSTANTS OF THE CONVERSION OF NOX AND SO_2 INTO H_2SO_4 AND HNO_3. TREPRESENTS TEMPERATURE OF GAS.

Reactions	Reaction Rate [9], [10]		Index
	Symbols	Value ($cm^3 molecule^{-1} s^{-1}$)	
$e + H_2O \rightarrow OH^{\cdot} + H^{\cdot} + e$	k_{d1}	**See Fig. 1**	(R1)
$e + O_2 \rightarrow O^{\cdot} + O^{\cdot} + e$	k_{d2}		(R2)
$e + O_2 \rightarrow O + O^* + e$	k_{d3}		(R3)
$e + N_2 \rightarrow N^{\cdot} + N^{\cdot} + e$	k_{d4}		(R4)
$O^* + H_2O \rightarrow OH^{\cdot} + OH^{\cdot}$	k_{e1}	2.2×10^{-10}	(R5)
$NO + O^{\cdot} + M \rightarrow NO_2 + M$	k_1	$3.0\times10^{-11}(T/300)^{0.3}$	(R6)
$NO + OH^{\cdot} + M \rightarrow HNO_2 + M$	k_2	$2.5\times10^{-12}\exp(260/T)$	(R7)
$HNO_2 + OH^{\cdot} \rightarrow NO_2 + H_2O$	k_3	$3.3\times10^{-11}(T/300)^{-0.3}$	(R8)
$NO_2 + OH^{\cdot} + M \rightarrow HNO_3 + M$	k_4	4.1×10^{-11}	(R9)
$SO_2 + OH^{\cdot} + M \rightarrow HSO_3 + M$	k_5	$1.3\times10^{-12}(T/300)^{-0.7}$	(R10)
$HSO_3 + O_2 \rightarrow SO_3 + HO_2$	k_6	$1.1\times10^{-13}\exp(-1200/T)$	(R11)
$SO_3 + H_2O \rightarrow H_2SO_4$	k_7	$3.9\times10^{-41}\exp(6830/T)[H_2O]^2$	(R12)
$N^{\cdot} + OH^{\cdot} \rightarrow NO^{\cdot} + H^{\cdot}$	k_8	$3.8\times10^{-11}\exp(85/T)$	(R13)
$N^{\cdot} + NO \rightarrow N_2 + O^{\cdot}$	k_9	3.1×10^{-11}	(R14)
$N^{\cdot} + NO_2 \rightarrow N_2O + O^{\cdot}$	k_{10}	3.0×10^{-12}	(R15)

Table I also gives associated reaction rate constants of the radical + gas reactions and reactions rate constants of the electron impact reactions (k_{d1}, k_{d2}, k_{d3} and k_{d4}) are calculated using the following equations (1) and (2);

$$kd_j = \sqrt{\frac{2q}{m_e}} \int_0^{\infty} \varepsilon \sigma_j(\varepsilon) f(\varepsilon) d\varepsilon \qquad (1)$$

where, q - charge of the electron, e; m_e - mass of the electron; ε - electron energy (V), σ_j collision cross section area (m^2) of j^{th} electron impact reaction; $f(\varepsilon)$ = electron energy distribution function (EEDF) and $j \in (1, 2, 3, 4)$.

In many cases, either the Maxwellian EEDF (MEEDF) or the Druyvestein EEDF have been used; for low mean electron energy (<16.6eV) there is no significant difference between these two distributions [11]. In this work, the Maxwellian EEDF is used since the mean electron energy in the plasma is expected to be low [12]. The Maxwellian EEDF can be expressed as;

$$\mathrm{f}(\varepsilon) = \gamma^{-1.5} \mathrm{b}_1 \mathrm{e}^{\left(-\frac{\varepsilon \mathrm{b}_2}{\gamma}\right)} \qquad (2)$$

where γ – mean electron energy of a single electron

$$b_1 = G(2.5)^{1.5} G(1.5)^{-2.5}$$

$$b2 = G(1.25) G(0.75)^{-1}$$

and $G(x)$ is known as Gamma function and given by the following integral;

$$G(\mathrm{x}) = \int_0^{\infty} \mathrm{e}^{-\mathrm{v}} \mathrm{v}^{\mathrm{x}-1} \mathrm{dv} \qquad (3)$$

where v is a dummy variable and used to evaluate the integral.

The calculated rate constants of electron impacts are shown in Fig. 1. The cross-section data for the electron impact reactions {(1) to (4)} was obtained from [13], [14]. As can be seen there is a significant variation in the way electron impact rate constant varies against the mean electron energy of the plasma. This variation plays a vital role in the NOx and SOx conversion.

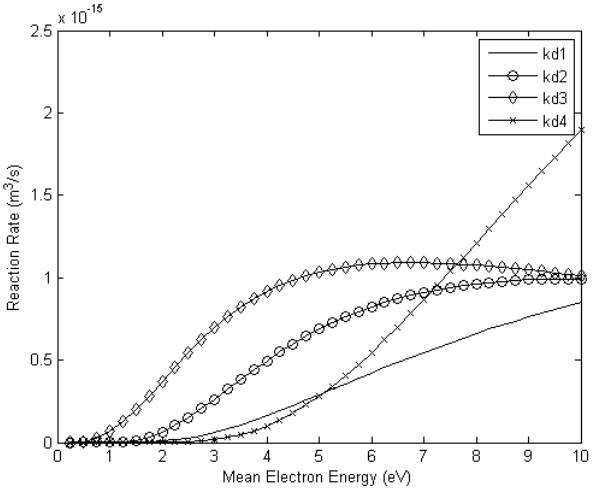


Fig. 1. Electron impact reaction rates for mean electron energies up to 10 eV

III. RESULTS

The differential equations of concentration change of each species involved in the reactions (Table I) is derived using mass balanced equations and solved using MATLAB solver ode15s. The key results are shown in Fig. 2. These results were obtained for a typical exhaust composition of a two stroke marine diesel engine; O_2 (13.0%), N_2 (75.8%), CO_2 (5.2%), H_2O (5.35%), NOx (1500 vppm) SOx (600 vppm) and CO (60 ppm) and HC (180ppm).

One of our initial experimental results suggests that MP alone can abate NOx and SOx by 60% and 80% respectively from the exhaust of a diesel car engine. The improved MP (so to generate high and more uniform electron density and high dosage of microwave energy) and pre-processed

exhaust gas (i.e.: temperature controlled and oil particles removed) can increase the abatement proportion greatly.

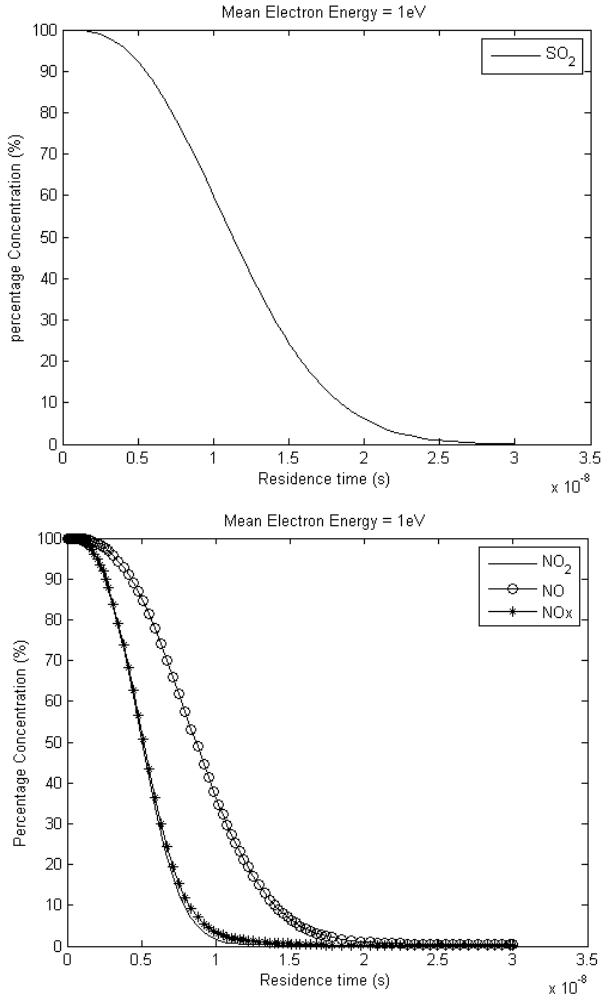
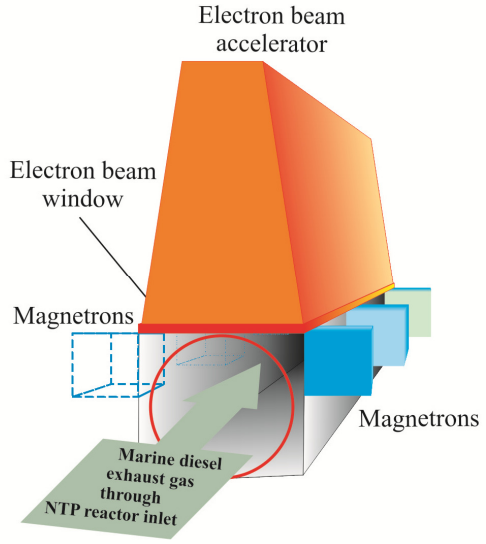


Fig. 2. Abatement of SO_2 (top) and NOx (bottom) with NTP : mean electron energy is 1eV

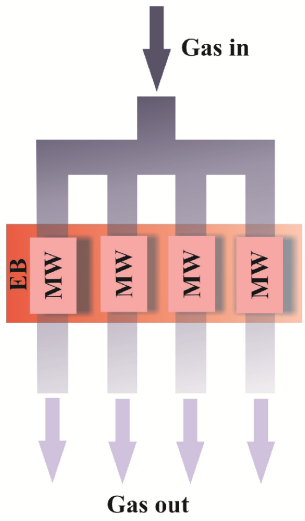
IV. Proposed Electron Beam + Microwave Integrated NTP

In addition to MWP, use of electron beam can give a great deal of flexibility in both of the plasma parameters (electron density and mean electron energy) and ability to generate high dosage of plasma energy (i.e.: 9kGy) [8]; making it possible to approach results obtained our numerical prediction. The proposed MP and EB integrated NTPR is shown in Fig. 3. As shown in this figure, single unit NTPR contains a multiple set of magnetrons and a single electron beam for lab scale testing, where flow rate of exhaust gas is very low (up to 200 l/s) and the second figure shows the multiple parallel arrange of a single units to handle large flow rates (up to 800 l/s).

The Non-thermal plasma based power plant deNOx and deSO_2 uses energy dosage of up to 9kGy [8]. Based on this dosage, the power required for various exhaust flow rate of marine diesel engine is calculated and plotted in Fig. 4. There will be a significant power difference at high flow rates between low dosage and high dosage; this implies huge energy saving can be achieved when NTP efficient enough to uses low dosage. This will be the focus of our next stage of research.



(a) Single unit of NTPR for labs scale testing {Typical size - 0.5m (length) × 0.5m (width) × 1.5m (height)}



(b) Multiple unit NTPR for the pilot scale testing

Fig. 3. Proposed integrated (MWI and EB) NTPR

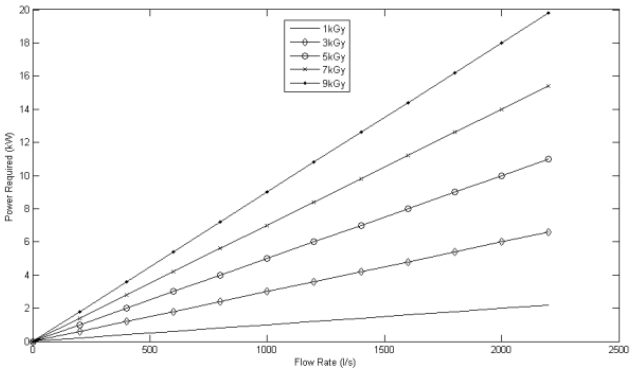


Fig. 4. Power requirement for various exhaust flow rate

V. Conclusions

Abatement of NOx and SOx from exhaust gas of marine engine can be performed with the use of non-thermal plasma. The numerical studies predict that 100 % removal of NOx and SOx is possible. Our initial non-thermal plasma, which was generated by microwave radiation, shows very promising results with 60% reduction of NOx

and 80% SOx. We propose a scheme based on microwave-electron beam integrated non-thermal plasma to generate required electron energy density and electron energy for both lab-scale testing and pilot scale testing.

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