CHEMICAL ENGINEERING TRANSACTIONS
VOL. 32, 2013
A publication of AIDIC
The Italian Association of Chemical Engineering
www.aidic.it/cet
Chief Editors: Sauro Pierucci, Jiří J. Klemeš

ISBN 978-88-95608-23-5; **ISSN** 1974-9791
DOI: 10.3303/CET1332061

New Technologies for Marine Diesel Engine Emission Control

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Atmospheric emissions of pollutants from marine diesel engines fuelled with heavy fuel oils contribute significantly to environmental pollution. To limit the presence of such pollutants in the environment, the International Maritime Organization recently introduced specific regulations to control SO_2, NO_x and particulate concentrations in exhaust gases. This paper is a short communication on two innovative techniques for marine diesel engine exhaust gas cleaning: the Electrostatic Seawater Scrubbing and the Electron Beam/Microwave Non-Thermal Plasma. These technologies are developed within the EFP7 DEECON (Innovative After-Treatment System for Marine Diesel Engines Emission Control) project and are able to provide State-of-the-Art removal of SO_2 and NO_x, together with a significant removal of Volatile Organic Compounds and Diesel Particulate Matter, which are among the most toxic pollutants emitted by ships and are currently excluded in the regulations due to the absence of reliable technologies for their removal. Preliminary experimental and modelling results on the treatment of model diesel exhaust gas are reported.

1. Introduction

Around 85% of worldwide trading goods are moved using maritime routes. In almost 70 % of the cases are within 400 km from the coastline, influencing the air quality within several hundreds of kilometers from the coast (Eyring et al., 2007). The most widely adopted systems for main ships propulsion are two or four strokes diesel engines. The most recent engines have specific fuel consumptions around 160 - 180 g/kWh, against the 200 - 220 g/kWh of gas turbines and 300 g/kWh of steam turbines. Typical specific exhaust gas flow rate is around 2.5 kg/s MW and installed power spans between 3 MW to over 80 MW. Diesel engines are also preferred to other kind of engines for their ability to work with relatively "inexpensive" fuels, commercially known as IFOs, which are blends of diesel and residual fuels with high viscosity and sulphur content larger than 2.7 % w/w on average. Recent estimation (World Energy Council, 2011; US Energy Information Administration, 2011) on the world energy consumption and on the use of crude oil fuels indicate that merchant navigation sector account for about 1.75 % of the total energy demand and about 5 % of the crude oil consumption (Figure 1).

Please cite this article as: Di Natale F., Carotenuto C., D Addio L., Lancia A., Antes T., Szudyga M., Jaworek A., Gregory D., Jackson M., Volpe P., Beleca B., Manivannan N., Abbod M., Balachandran W., 2013, Ebminew technologies for marine diesel engine emission control , Chemical Engineering Transactions, 32, 361-366 DOI: 10.3303/CET1332061

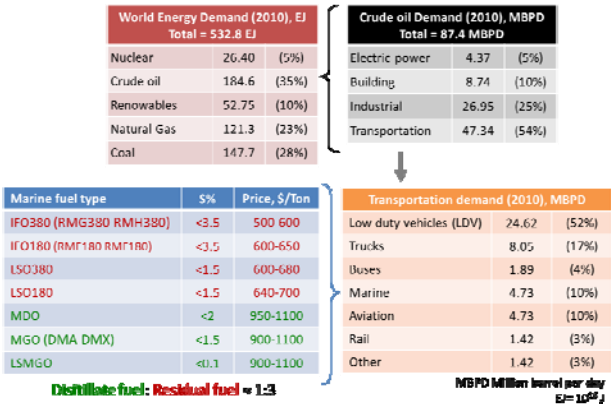


Figure 1: Breakdown of the worldwide energy consumption and of marine fuels cost indications.

Indications on fuel consumptions suggest that the overall impact of maritime sector on global atmospheric pollution should be limited within 5 % of the total emissions by fossil fuel combustion. However, two factors strongly influence the actual environmental footprint of maritime sector. Firstly, the use of IFOs leads to substantial emission of pollutants in the exhaust. A typical composition of an IFO fuelled large 2-strokes engine exhausts is: 13 % O_2; 75.8 % N_2; 5.2 % CO_2; 5.35 % H_2O; 1,500 ppm_v NO_x, 600 ppm_v SO_x; 60 ppm CO; 180 ppm VOC (Volatile Organic Carbon); 120 mg/Nm^3 Diesel Particulate Matter (DPM).

In addition, in the last forty years, the car transportation industry and electric power generation were subjected to restrictive environmental regulations that have strongly reduced their environmental footprint, while the maritime sector was largely unregulated until the middle of nineties. It was recently estimated (Neef, 2009) that ships produce at least 15 % of the world's NO_x (more than all of the world's cars, busses and trucks combined), between 2.5 - 4% of greenhouse gases, and between 3 - 7 % of global SO_x output and 5 % of black carbon emission. Estimation of contribution of maritime shipping to global emissions of VOC and CO is not available at the present time.

Due consideration must be given to the emission of particulate matter from cooled exhaust gases of IFO fuelled marine diesel engines. The emitted particles are represented by elemental carbon (~5% w/w), organic carbon (~ 10 % w/w), ash (~ 5 % w/w), sulphate (~ 40% w/w) and water associated with the sulphur (~ 35 % w/w) (IMO, 2009). Specific DPM emissions are generally higher for IFO than for Marine Gas Oil due to the presence of fine particulates, which are harmful to health. According to Winnes and Fridell (2009) “this finding emphasizes that to minimize negative health effects of particles from ships, further regulation may be needed to reduce small-sized particles; a fuel shift to low sulphur fuel alone does not seem to accomplish this reduction”.

In order to reduce the environmental footprint of ships, the International Maritime Organization (IMO) recently issued the legislation of Marpol Annex VI guidelines to be enforced in 2012 for the Emission Control Areas on sulphur fuel content (1 %) and NO_x emissions based on ship engine speed. Facing this legislation, ship owners have the alternative, either to operate ships with costly low-sulphur fuels, or to keep burning heavy fuel oils but adopting proper retrofitting devices, such as scrubbers and selective catalytic reactors. These technologies allow a reliable reduction of SO_2 and NO_x, but suffer the drawbacks of large footprints, significant pressure drops and additional fuel consumption. At present, fuel switching is still the most adopted option followed by ship-owners to comply with environmental legislations. There are only about 30 scrubbers in operation or under commissioning (Gregory, 2013). The existing scrubber models are based on three different concepts: open-loop seawater scrubbers; closed-loop (chemical absorption with freshwater) scrubbers and dry-scrubbers. The SCR units are usually used for high dust configurations and hence more effective when coupled with fuel switching. Although very effective in removing SO_2 and NO_x, all these solutions are largely ineffective towards submicron particles ($DPM_{<1}$) and VOC emission control.

Pertinent literature reveals that the potentialities of two alternative solutions for gas cleaning: the wet electrostatic scrubbing and the non-thermal plasma process. The first can be considered as a modified scrubber aimed to remove both SO_2 and $DPM_{<1}$; the second is an alternative method for NO_x, SO_2 and VOC removal from gas, and is sometimes coupled with a SCR unit to have a high performance hybrid system. The DEECON consortium is currently developing and optimizing these two processes for marine application by integrating both processes in order to create a novel on-board after-treatment unit more advanced than any currently available. In this paper, the two after-treatment systems are introduced, and

preliminary experimental and modelling results are presented. The paper is structured into two separate sections; one focused on the wet electrostatic scrubbing system and the other on the non termal plasma system.

2. Experiments and modelling of submicron particle removal by wet electrostatic scrubbing

The wet electrostatic scrubber adopted here considers the use of seawater as scrubbing liquid in order to simultaneously accomplish $DPM_{<1}$ and SO_2 removal. For this reason, it was called Electrostatic Sea-Water Scrubber (ESWS). The most comprehensive reviews on the wet electrostatic scrubbing is those reported by n Jaworek et al. (2006), which was recently updated by Jaworek et al. (2013) in terms of fundamental physics on the particle capture mechanisms. To the best of our knowledge, only one paper on electrified seawater scrubber for particle removal is available in the open literature (Ha et al., 2010). The main parameter needed to design a wet electrostatic scrubber is the scavenging coefficient, Λ, which takes into account for all the main features of particles and droplets interactions; in terms of droplet-particle relative velocity, numerical concentration, size and charge distribution etc., and represents the inverse of the characteristic scavenging time. Although expressions for the scavenging coefficient are reported in literature, they were not developed for the specific case of interest (charged submicron particles and a spray of charged droplets). To fill this gap, lab-scale tests on submicron particle (100 - 750 nm) capture were carried out with the experimental protocol shown in D'Addio et al. (2012).

In Figure 2 shows experimental results and theoretical model predictions of the ratio Λ / q, where q is the droplet charge, as a function of the numerical concentration of sprayed droplets, N, for selected particle sizes (150, 250 and 350 nm) and for different temperatures (between 25 and 65 °C). The results show similar linear trends of the ratio Λ / q as a function of N. The data range varied from $1.5 \cdot 10^{-5}$ $pC^{-1}s^{-1}$ up to about $8 \cdot 10^{-5}$ $pC^{-1}s^{-1}$ and the scavenging rate is more than one order of magnitude higher than that of a conventional scrubber. Moreover, the experiments were successfully compared with the scavenging model discussed by Di Natale et al. (2008) and Carotenuto et al. (2010).

This model was used to calculate the particle size distribution at the exit of a co-current flow wet electrostatic scrubber operated with different values of the important process parameters: liquid to gas mass flow ratio (L/G), droplets size and charge distributions and residence time in the scrubbing column. The combustion off-gas considered (T = 50 °C, relative humidity = 100%, P = 1 bar) has the typical particle size distribution of a diesel engine (D'Addio et al., 2011). For the sake of simplicity, the particles charge is modelled by considering the passage of the gas through a region of free-ions generated by a corona source similar to that adopted in D'Addio et al. (2012) experiments. The residence time in this charging unit, t_r, and ionic current, N^*_i, are estimated to be 0.7 ms and $1.5 \cdot 10^{14}$ ions/m^3, respectively. Particle charges are calculated according to classical equations of field and diffusion charging mechanisms (e.g. Hinds, 1999).

With respect to the charged spray droplets, the size distribution is modelled according to Rosin-Rammler function, assuming a shape factor equal to 3 and numerical mean droplet sizes equal to 100, 200 and 300 μm. At the nozzle exit, two droplet charge levels of 5 and 10% of the Rayleigh limit were used. These values are assumed to be the droplet charge levels close to the nozzle exit. These data are consistent with the typical performances of Air-Atomizing/Induction Charging nozzles (Jaworek et al., 2006). The L/G is varied from 0.5 to 2 kg/kg. Droplet evaporation was taken into account according to D'Addio et al. (2011).

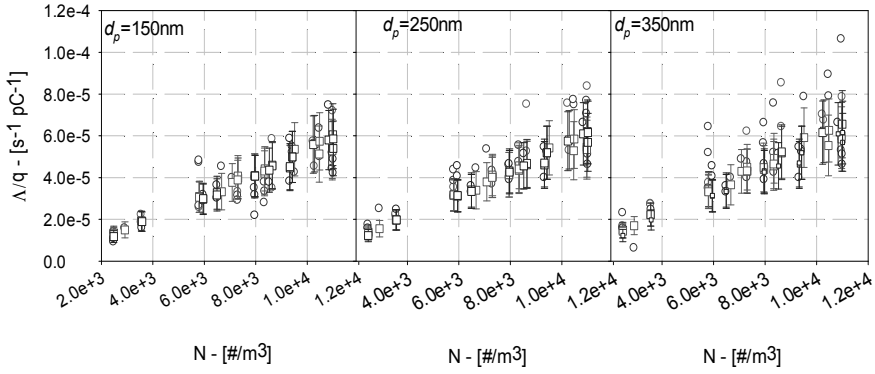


Figure 2: Comparison between experimental analysis and modeling predictions for tests at temperature from 25 to 65°C. ○: Experiments; □: Model (Carotenuto et al., 2010).

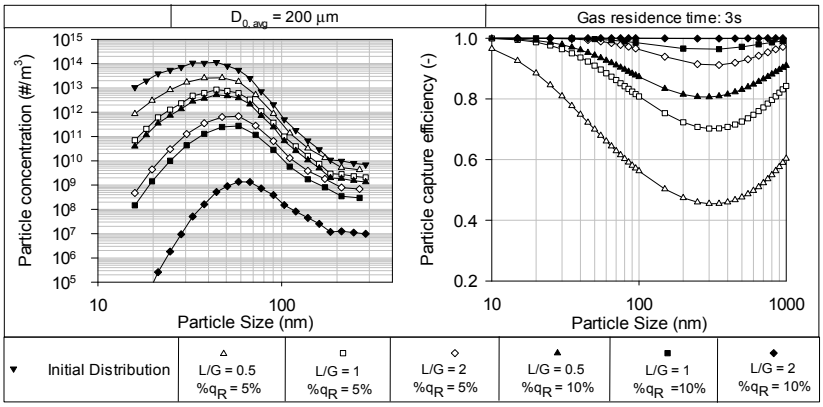


Figure 3: Model predictions on the particle concentration at the exit of the scrubbing column. T=50 °C, Relative humidity 100%, P = 1 bar. Curves are parametric with the L/G ratio and with the droplet charge.

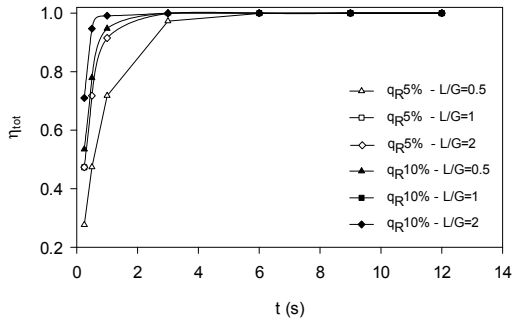


Figure 4: Removal efficiency as a function of particles residence time for different droplet charges and liquid to gas ratio, for 100 µm mean droplet size.

Figure 3 shows the particle concentration at the exit of the scrubber column and the corresponding particle capture efficiency as a function of particle size, for the case of 200 µm droplets and for different values of droplet charge and L/G ratios. Figure 4 shows the overall particle removal efficiency as a function of the residence time for a droplet size average diameter of 100 µm. The particle concentration largely decreases by increasing the droplets charge and the L/G ratio, mirroring the corresponding increases of particles abatement efficiency. An increase of particle residence time and a decrease in average droplet size causes significant reduction of the particle concentration and a correspondent increase of the capture efficiency.

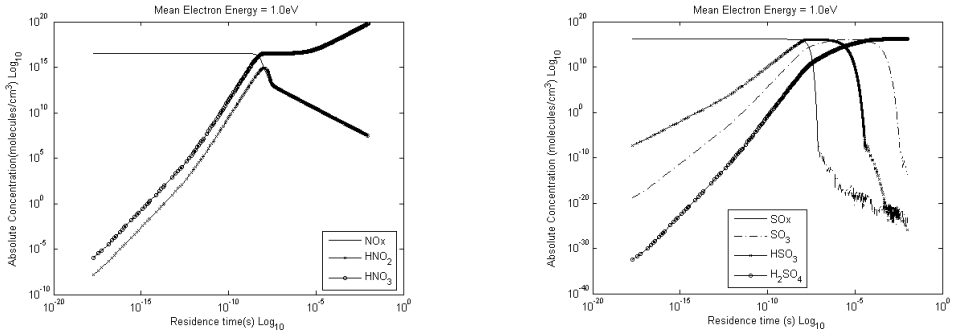
3. Non thermal plasma for marine diesel engine applications

Non-thermal plasma (NTP) is an emerging technology for a feasible VOC and NO_x emission control with low power consumption. The non-thermal plasma reactor (Jaworek et al., 1996) is a system in which electric fields are used to generate a plasma with electron temperature much higher than that of the gas temperature, including vibration and rotational temperature of molecules. There are three promising methods for generating non-thermal plasmas in atmospheric gas pressure containing the pollutants, namely electron beam (EB) irradiation, microwave (MW) irradiation and electrical discharge (DC, AC and pulsed fields) techniques. High energetic electrons induce molecular excitation, ionization and dissociation and, at the same time, the attachment of lower energy electrons that form negative ions in the discharge area. Secondary plasma reactions will be initiated by dissociated molecules, radicals and ions by radical–molecule reactions and ion–molecule reactions in the downstream afterglow discharge region. Highly oxidising radicals as O and OH·can be produced to produce an effective oxidation of air pollutants.
Recently, two types non-thermal plasma units for heavy-duty diesel engine and boilers have been proposed (e.g. Yamamoto et al., 2010; Yoshida et al., 2008). The first type is a *wet process* which controls the oxidation process to convert NO_x to N_2O_3 and N_2O_5 that are both highly water soluble and may be easily removed with the wet scrubbing process. A similar system was patented and commercialized, for example, by Dupont. This system achieved removal efficiencies as high as 90 %. The second type of

NTPR is a *dry process*, which makes use of EB irradiation, specifically developed to allow the parallel removal of up to 90 % of NO_x and 80 % of SO_2 in flue gases by oxidation to nitrate and sulphates and formation of ammonia salts, which can be removed by means of an electrostatic precipitator and used as fertilizers in agriculture, provided NH_3 is supplied to the system. Furthermore, the radicals break VOC bonds promoting their conversion to CO and CO_2 (Inghineanu et al. 2005; Calinescu et al, 2008).
The DEECON project is focused on the use of a combined electron beam and microwave non thermal plasma system, which may overcome some of the main concerns of conventional plasma reactors.
Modelling work, based on the non-thermal plasma kinetics predicts that more than 99 % of NOx and SOx can be converted into HNO_3 and H_2SO_4 when electron energy in the non-thermal plasma is in the range of 0.5eV to 3.5eV. Modelling results presented in Figure 5a and 5b clearly shows how concentrations of NOx and SOx decrease with residence time when mean electron energy is 1eV. These graphs also show the concentrations of intermediate products HNO_2, SO_3, HSO_3 and the concentrations of the final products HNO_3 and H_2SO_4 (Manivannan et al., 2012).
Early preliminary experiments on MW irradiation combined with AC corona on diesel exhaust gases (90 °C) in a laboratory scale non thermal plasma reactor were made using a Ford Duratorq (Puma) diesel engine (High Speed Direct Injection, 4 cylinder, 2 litre) fuelled with ultra-low sulphur diesel. Results shown in Figure 6 demonstrate that NO_x can be reduced by about 90 %, while SO_2 can be reduced to 100 %.

4. Conclusions

In order to reduce the environmental footprint of marine diesel engines, new technological solutions are needed to overcome intrinsic drawbacks of existing emission control strategies. Among the most relevant issues to face, it should be considered that: *i*) both fuel switching and scrubbers are not able to reduce submicron particulate emissions, that is a relevant environmental threat; *ii*) the capital and operating costs of SCR unit for NO_x removal is relatively high and the retrofit is not easy due to space limitations.



(a) (b)

Figure 5: Conversion of NOx and SOx into HNO_3 and H_2SO_4 through non-thermal plasma when mean electron energy is 1eV. (a) Absolute concentrations of NOx and HNO_2 and HNO_3 and (b) Absolute concentrations of SOx (SO_2), SO_3, HSO_3 and H_2SO_4

Figure 6: Simultaneous removal of SO_2 100 % and NO_x 90 % from a diesel engine exhaust using a combination of microwave and AC corona based non thermal plasma.

The DEECON projects aims to develop a new integrated unit aimed to reduce SO_2, NO_x, VOC and DPM in marine diesel exhaust gases. The main processes, involved in the DEECON unit, are new concepts of

electrified seawater scrubber (ESWS) and Electron Beam/Microwave induced non-thermal plasma system (EBMW-NTPR). Preliminary experimental and modelling analyses showed that the two processes may be suitably used to achieve the project objectives:the ESWS unit is able to remove SO_2 with an overall efficiency above 98 % (data not shown), while DPM levels can be reduced by more than 90 % in terms of numerical concentration; the EBMW-NTPR is very promising in terms of NO_x and SO_2 removal, and pertinent literature indicates that they may be suitable for a reduction of VOC compounds as well. These technologies are new for the maritime sector and represent a breakthrough in the greening of maritime pollution, anticipating the adoption of future and tighter regulatory requirements.

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