

The Technology of Non-thermal Plasma Assisted NH₃-SCR Reduce Marine Diesel Emission and Aldehydes Byproducts Formation

^{1,2}Lei Jiang, ²Yixi Cai and ³Yong Luo

¹School of Energy and Power Engineering, Jiangsu University of Science and Technology, Zhenjiang Jiangsu 212003, China

²School of Automotive and Traffic Engineering, Jiangsu University, Zhenjiang 212013, China

³Nantong Rainbow Offshore and Engineer Equipment Co., Ltd, Nantong, 226300, China

Abstract: This study describes briefly various after-treatment technologies in marine diesel engines and application difficulties of DPF and SCR are included. An experiment has been conducted using non-thermal plasma generated by Dielectric Barrier Discharge (DBD) process assisted NH₃-SCR catalyst to reduce the nitrogen oxides (NO_x) from diesel engine exhaust. The formation mechanism of byproducts-type such as HCHO and CH₃CHO in the non-thermal plasma assisted NH₃-SCR hybrid system.

Keywords: Marine diesel, after-treatment technology, selective catalytic reduction, non-thermal plasma, aldehydes byproducts

INTRODUCTION

The high efficiency of the diesel engine has made it the primary propulsion source for marine applications worldwide (Müller *et al.*, 2003). For the marine engine, the International Maritime Organization (IMO) issued the stringent Tier III standards requiring that by 2016 the NO_x emissions from marines entering Emission Control Area (ECA) must be lower than 3.49 g/kWh, which is 80% less than that of Tier I in 2000. Among lots of techniques for the marine engine NO_x abating, SCR is the most promising one for Tier III showed in Fig. 1 (Lei and Jun, 2013; Bin *et al.*, 2011b).

Selective Catalytic Reduction (SCR), using urea as a reductant in the exhaust over a catalyst, can produce NO_x reduction of ~90% or more. One alternative to SCR under consideration is Non-Thermal Plasma (NTP) and catalyst hybrid system where the reductant is a hydrocarbon-designated Plasma Assisted Catalytic Reduction (PACR). One potential advantage of the PACR approach is that the diesel fuel itself can be the reductant thus removing the need for a urea infrastructure (McAdams *et al.*, 2008).

CURRENT TECHNOLOGY

SCR technology: One of the solutions is Selective Catalytic Reduction (SCR)-an emissions-reduction technology with the ability to deliver near-zero emissions of nitrogen oxides (NO_x), a smog-causing pollutant and greenhouse gas. SCR's performance has

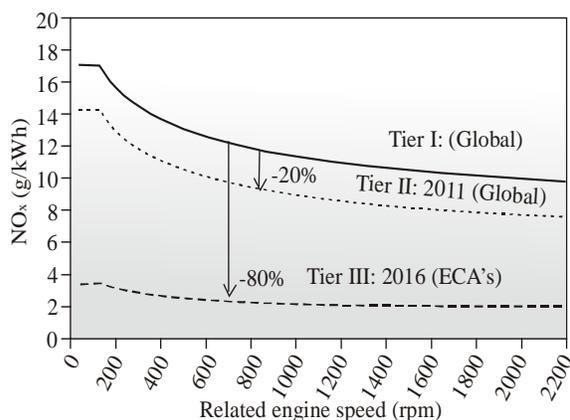


Fig. 1: NO_x Emissions in MARPOL annex VI

been proved in millions of miles of real-world truck operations in other countries, as well as in long-term field tests in the U.S. SCR reduces NO_x emissions to very low levels, while at the same time delivering excellent fuel economy and reliability. The system doesn't change the basic design or operation of the engine (Müller *et al.*, 2003). The overview of SCR systems is shown in Fig. 2.

NO_x in diesel exhaust is usually composed of >90% NO. Therefore, the main reaction of SCR (Koebel *et al.*, 2000) with ammonia will be:



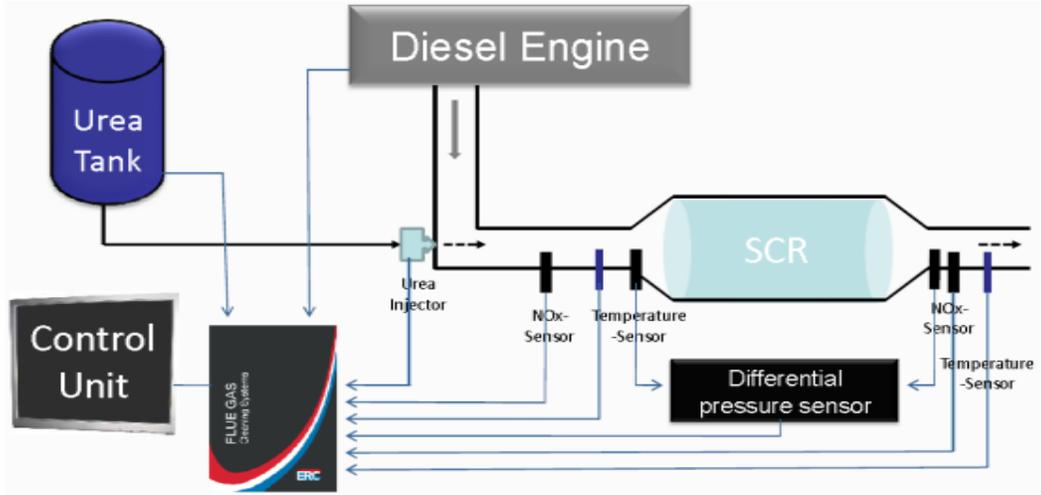
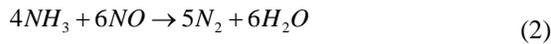
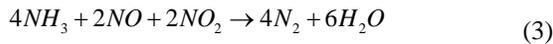


Fig. 2: Overview of SCR systems

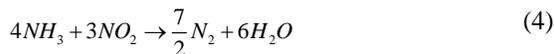
This reaction implies a 1:1 stoichiometry for NH_3 and NO and the consumption of some oxygen. The reaction consuming no oxygen is much slower and is therefore not relevant in lean combustion gases:



On the other hand, the reaction rate with equimolar amounts of NO and NO_2 is much faster than that of the main reaction (1):



It should be mentioned that the reaction with pure NO_2 is again slower than reactions (1) and (3):



At high temperatures ($>400\text{ }^\circ\text{C}$) the commonly used catalysts based on $\text{TiO}_2\text{-WO}_3\text{-V}_2\text{O}_5$ tend to form nitrous oxide. One of the possible reactions leading to nitrous oxide is:



At still higher temperatures, ammonia may be oxidized to NO , thus limiting the maximum NO_x conversion:



However, fuel sulfur content seems to be a major issue common to all emissions after-treatment systems. The SCR technology may not be significantly damaged by higher than regulated sulfur fuel levels but the PM



Fig. 3: Drawback factors for SCR systems

emission limits would not be achieved. Especially when an oxidation catalyst or a particulate trap is used, increasing the fuel sulfur level results in progressively increased PM mass fraction (Müller *et al.*, 2003). The drawback factors for SCR systems is shown in Fig. 3.

NTP technology: Plasma is called the forth form of material besides solid, liquid and gas. According to the particle temperature, it can be divided into thermal Plasma and Non-Thermal Plasma (NTP). Non-thermal plasma is mainly produced by gas discharge, discharge gas electronic temperature typically up to tens of kelvin, while the other particle temperature is 300~500 K. Non-thermal plasma reactors can be used as a particulate trap or as a NO_x converter. The effective oxidation of NO to NO_2 is produced by active compounds, which are generated in plasma. Particulate trapping in a plasma reactor can be accomplished by electrostatic precipitation. The oxidation of the carbon fraction by NO_2 can be used to decrease the concentration of particulate matter. The general gas discharge generation of plasma belongs to low temperature plasma (Chae, 2003).

Dielectric Barrier Discharge (DBD) is one of non-thermal plasma techniques and it offers the advantage to excite molecules for reaction processes on a low temperature level in the near-atmospheric pressure range (Lee *et al.*, 2004) NO_x is reduced at low temperature when NO_2 is involved in the reaction

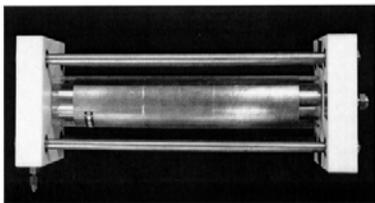


Fig. 4: Dielectric barrier discharge reactor

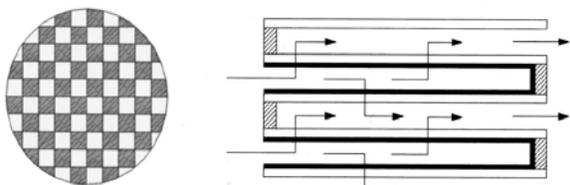
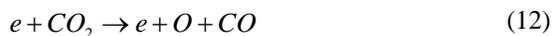
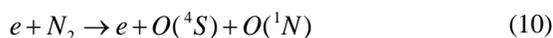
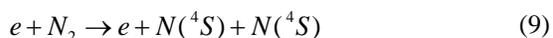
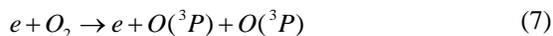


Fig. 5: Wall flow monolith for diesel filter

mechanism. Therefore, if non-thermal plasma converts NO to NO₂, the reduction rate of NO_x will be greatly enhanced in the catalytic process even at a low temperature.

Figure 4 shows the plasma reactor used in the experiments. The reactor geometry was a concentric cylinder. The stainless steel discharge electrode has a smooth surface. Cylindrical dielectric barriers made of pyrex was wrapped with a copper film tape serving as a grounded electrode. Generally there are two kinds of DBD reactors. One is a single dielectric barrier discharge reactor that uses only one dielectric material around the internal or external electrodes. The other is a double DBD reactor that uses a dielectric material around both of electrodes. We used a single DBD type reactor.

Formation of active components as radical is induced by electron impacts with the main components of the exhaust gas: nitrogen, oxygen, water and carbon dioxide:



OH radicals can be formed more efficient in reaction:



DPF technology: A Diesel Particulate Filter (DPF) is a device designed to remove diesel particulate matter or soot from the exhaust gas of a diesel engine. The regeneration of a diesel filter is characterized by a dynamic equilibrium between the PM being captured in the filter and the PM being oxidized Chae *et al.* (2003). The rate of PM oxidation depends on the filter exhaust temperature. At temperatures typically found in diesel exhaust gases, the rate of PM oxidation is small. Therefore, to facilitate filter regeneration, either the exhaust gas temperature has to be increased or a catalyst has to be applied. The catalyst can be applied directly onto the filter media or dissolved in fuel as a fuel additive.

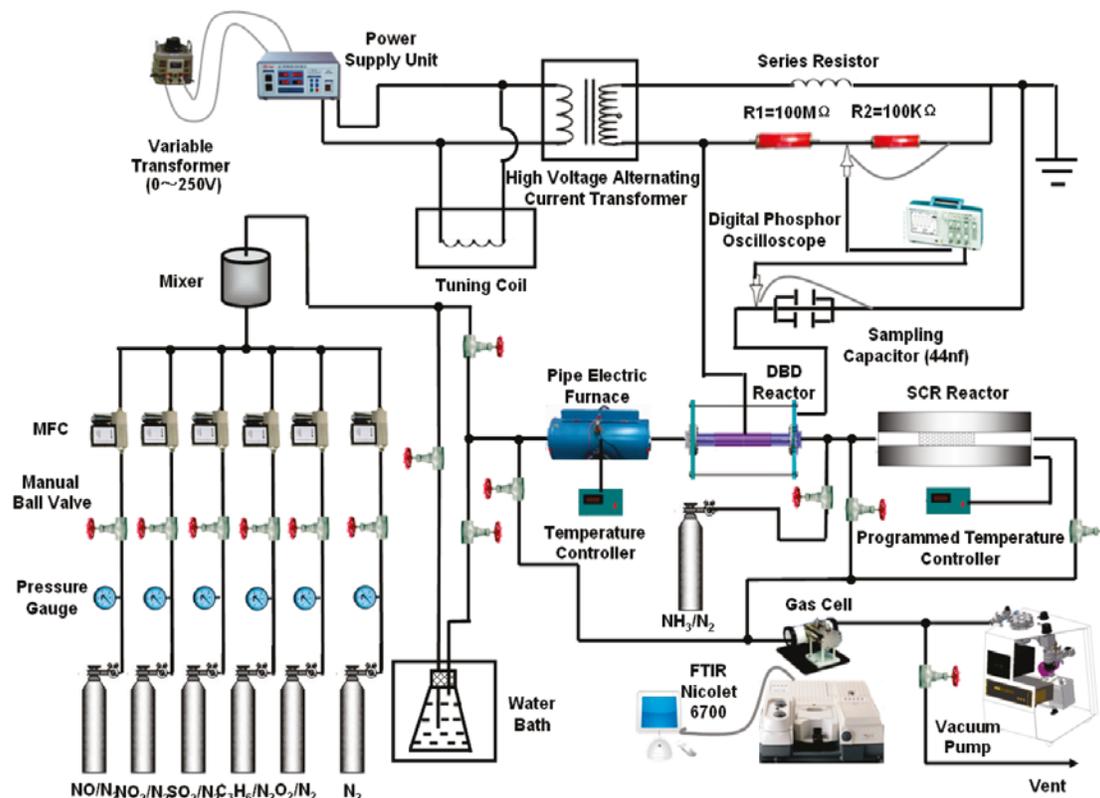
Figure 5 shows a typical wall flow monolith for Diesel Engine Particulate Filter (DPF). Most catalyzed diesel traps utilize monolithic wall flow substrates coated with a catalyst. The catalyst lowers the PM combustion temperature, allowing the filter to self-regenerate during periods of high exhaust gas temperature. A number of diesel filter catalysts have been developed, increasing both noble and base metal formulations. Bickel and Majewski (1993) and Hartwig (1985) suggested that a catalyzed ceramic traps exhibit very good diesel particulate matter filtration efficiencies, but were characterized by relatively high exhaust gas pressure drop.

EXPERIMENTAL SECTION AND ALDEHYDES BYPRODUCTS EVOLVEMENT RULES

Guan *et al.* (2012), He *et al.* (2010), Bin *et al.* (2011a), Gregorio *et al.* (2004), Koebel *et al.* (2001), Hammer *et al.* (2004), Young *et al.* (2003), Stefan and Thomas (2000) and Takayuki *et al.* (2010) had researched Non-thermal plasma assisted NH₃-SCR hybrid system to reduce NO_x, also found that the energy density has a significant effect on the NO_x removal efficiency at low reaction temperatures (<250°C) and the effect almost disappears at higher temperatures in the range of 300-450°C (He *et al.*, 2010).

Because the non-thermal plasma assisted NH₃-SCR coupling system with all kinds of by-products, such as C₃H₆ incomplete oxidation produce CO, formaldehyde (HCHO), acetaldehyde (CH₃CHO), ozone (O₃) and nitro methyl ester (CH₃ONO₂), formic acid (CH₂O₂), nitrous acid (HONO) and so on, also may with N species nonselective reaction generated HCN, N₂O, N₂O₅, N₂O₃ species, etc. For the non-thermal plasma assisted NH₃-SCR coupling system, it is important not only to evaluate the efficiency of conversion of NO_x (active) and resistance to SO₂, but also to monitor, whole process of produce by-products such as CO, N₂O, HCHO, CH₃CHO.

The schematic diagram of the DBD facilitated NH₃-SCR hybrid system is presented in Fig. 6 (Bin *et al.*, 2011a). The reaction system by DBD reactor and

Fig. 6: Schematic diagram of the experimental setup for DBD assisted NH_3 -SCR hybrid systemTable 1: Mechanisms of HCHO and CH_3CHO formation at 1 ATM

Reactions	Reaction number	Reactions	Reaction number
$\text{HCO} + \text{HCO} \rightarrow \text{HCHO} + \text{CO}$	(14)	$\text{CH}_2\text{CHO} + \text{O}_2 \rightarrow \text{HCHO} + \text{CO} + \text{OH}$	(19)
$\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2$	(15)	$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{O} \rightarrow \text{CH}_3\text{CHOH} + \text{HCHO}$	(20)
$\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2$	(16)	$\text{C}_2\text{H}_5 + \text{O} \rightarrow \text{CH}_3\text{CHO} + \text{H}$	(21)
$\text{CH}_3\text{O} + \text{CH}_3\text{O} \rightarrow \text{CH}_3\text{OH} + \text{HCHO}$	(17)	$\text{CH}_3\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CH}_3\text{CHO} + \text{HO}_2$	(22)
$\text{C}_2\text{H}_5 + \text{O} \rightarrow \text{HCHO} + \text{CH}_3$	(18)	$\text{HOC}_3\text{H}_6\text{O}_2 + \text{NO} \rightarrow \text{CH}_2\text{OH} + \text{CH}_3\text{CHO} + \text{NO}_2$	(23)

SCR will reactor in series composition. A corundum tube with 20 mm internal diameter and 25 mm external diameter were used as the dielectric. A diameter 14 mm screw stainless steel placed on corundum tube's axis as a grounding electrode.

The outer surface of the corundum tube was wrapped with stainless steel net and linked to the high voltage which frequency is 50 Hz. The effective length of plasma discharge area is from 0 to 150 mm by changing the length of the stainless steel net. The SCR reactor is an inner diameter of 16 mm and a length of 800 mm quartz tube, which loaded the catalyst. And placed it into a tubular resistance furnace equipped with a temperature-programmed temperature controller. The DBD reactor was placed downstream of an electric tubular resistance furnace, in which the reacting gases can be heated up before entering the DBD reactor. Results and discussion are showed in article (Bin *et al.*, 2011a).

Formaldehyde (HCHO) and acetaldehyde (CH_3CHO) are determined as the major aldehydes-type unregulated byproduct constituents of partial oxidation of C_3H_6 in the plasma process according to the

selective absorption of gas on FTIR spectra. Using C_3H_6 as an additive generating HCHO and CH_3CHO in the DBD reactor and this can be explained from two aspects: the first is that C_3H_6 can directly react with O radicals to produce HCHO via reaction (14) and the second is that several intermediate species of C_3H_6 decomposition and fragments can further form HCHO and $\text{CH}_3\text{-CHO}$ easily via the following reactions (14)-(23) listed in Table 1.

As shown in Fig. 7 is the Concentration of HCHO and CH_3CHO formation at the outlet the DBD reactor as a function of energy density at different concentration of C_3H_6 . It is observed from Fig. 7 that the generation amount of HCHO and CH_3CHO with the increase of the input energy density and the added C_3H_6 concentration increased, especially in the case of high energy density input and the high concentration of C_3H_6 . Since the decomposition of C_3H_6 , a large amount of HCHO and CH_3CHO was emitted from the DBD reactor.

Reaction (23) for CH_3CHO formation reaction, the reaction rate is proportional to the temperature, but as a

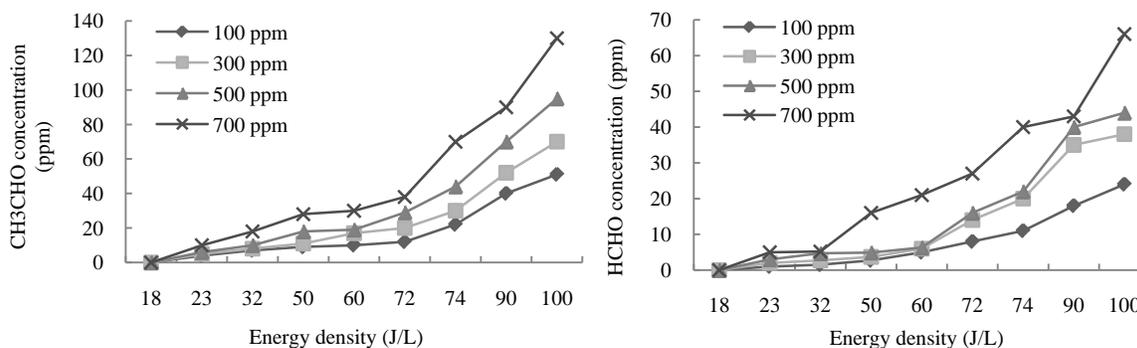


Fig. 7: Concentration of HCHO and CH₃CHO formation at the outlet the DBD reactor as a function of energy density at different concentration of C₃H₆

result of the reaction of reactant CH₃CH₂O generation rate and temperature is inversely proportional, eventually leading to generate CH₃CHO general rate and temperature is inversely proportional. Also, because the CH₃CHO SCR reactor in NO, NO₂, NH₃ reaction, cause only a small amount of CH₃CHO can be detected by DBD-SCR outlet.

CONCLUSION

- It have been confirmed that after-treatments device must be used in order to meet the more stringent emission regulations in the future. The technology which could remove oxide of NO_x and PM from diesel exhaust simultaneously will have greater development potential and will become the focus of future research. The technology of non-thermal plasma assisted SCR is a very promising technique.
- The concentration of HCHO and CH₃CHO increases with the growing of energy density as well as the C₃H₆ addition increases and decreases with the reaction temperatures increasing. HCHO and CH₃CHO are almost completely removed when the feed gas is processed in the catalytic reactor, i.e., the concentration of HCHO and CH₃CHO at the outlet of the plasma catalytic reactor is only a few ppm, indicating that HCHO and CH₃CHO can make a difference to the NO_x removal in the NH₃-SCR reactions.

ACKNOWLEDGMENT

This study was financially supported by the advantages of Jiangsu province college preponderant discipline (Naval Architecture and Marine Engineering).

REFERENCES

Bickel, K. and W.A. Majewski, 1993. Evaluation of a Catalyzed Ceramic Diesel Particulate Filter and Catalytic Convert on an Underground Mine Vehicle. SAE Technical Paper 932493.

- Bin, G., L. He, Z. Lin and H. Zhen, 2011a. Selective catalytic reduction of No_x with NH₃ over Mn, Ce substitution Ti_{0.9}V_{0.1}O_{2.8}nanocomposites catalysts prepared by self-propagating high-temperature synthesis method. *J. Phys.Chem.*, 115(26): 12850-12863.
- Bin, G., L. He, Z. Lin and H. Zhen, 2011b. Removal of NO_x with selective catalytic reduction based on non-thermal plasma pre-oxidation. *Ind. Eng. Chem. Res.*, 50(9): 5401-5413.
- Chae, J.O., 2003. Non-thermal plasma for diesel exhausts treatment. *J. Electrostat.*, 57: 251-262.
- Chae, J.O., J.W. Hwang, J.Y. Jung, J.H. Han, H.J. Hwang and S. Kim, 2003. Reduction of the particulate and nitric oxide from the diesel engine using a plasma chemical hybrid system. *Phys. Plasmas*, 8(4): 1403-1410.
- Guan, B., L. He, Z. Lin, T. Bo and H. Zhen, 2012. Effect of ignition temperature for combustion synthesis on the selective catalytic reduction of NO_x with NH₃ over Ti_{0.9}Ce_{0.05}V_{0.05}O_{2.8}nanocomposites catalysts prepared by solution combustion route. *Chem. Eng. J.*, 181-182: 307-322.
- Gregorio, M., V.S. Teresa and B.F. Antonio, 2004. Mechanism of low-temperature selective catalytic reduction of NO with NH₃ over carbon-supported Mn₃O₄ role of surface NH₃ species: SCR mechanism. *J. Catal.*, 226(1): 138-155.
- Hammer, T., K. Th. and M. Baldauf, 2004. Plasma catalytic hybrid processes: Gas discharge initiation and plasma activation of catalytic processes. *Catal. Today*, 89(1-2): 5-14.
- Hartwig, M.M., 1985. Platinum/Silver Vanadate Catalyzed Diesel Exhaust Particulate Filter. US Patent 4510265, Engelhard Corporation.
- He, L., G. Bin, C. Qi and H. Zhen, 2010. An investigation on the principal paths to plasma oxidation of propylene and NO. *Energy Fuels*, 24(10): 5418-5425.
- Koebel, M., M. Elsener and G. Madia, 2001. Reaction Pathways in the selective catalytic reduction process with NO and NO₂ at low temperatures. *Ind. Eng. Chem. Res.*, 40(1): 52-59.

- Koebel, M., M. Elsener and M. Kleemann, 2000. Urea-SCR: A promising technique to reduce NOx emissions from automotive diesel engines. *Catal. Today*, 59(3-4): 335-345.
- Lee, Y.H., J.W. Chung, Y.R. Choi, J.S. Chung, M.H. Cho and W. Namkung, 2004. NOx removal characteristics in plasma plus catalyst hybrid process. *Plasma Chem. Plasma Process.*, 24(2): 137-154.
- Lei, J. and H. Jun, 2013. Design and experimental study on the Urea-SCR converter exhaust system of the marine diesel engine. *Appl. Mech. Mater.*, 291-294: 1889-1894.
- McAdams, R., P. Beech and J.T. Shawcross, 2008. Low temperature plasma assisted catalytic reduction of NOx in simulated marine diesel exhaust. *Plasma Chem. Plasma Process.*, 28(2): 159-171.
- Müller, W., H. Ölschlegel, A. Schäfer, N. Hakim and K. Binder, 2003. Selective catalytic reduction-Europe's Nox reduction technology. *Proceeding of the Future Transportation Technology Conference*. Costa Mesa, California.
- Stefan B. and H. Thomas, 2000. Selective catalytic reduction of nitrogen oxides by combining a non-thermal plasma and a V₂O₅-WO₃/TiO₂ catalyst. *Appl. Catal. B-Environ.*, 28(2): 101-111.
- Takayuki, O., T. Kondo, N. Kitajima and M.Sato, 2010. Adsorption and plasma decomposition of gaseous acetaldehyde on fibrous activated carbon. *IEEE T. Ind. Appl.*, 46(1): 23-28.
- Young, S.M., J.K. Dong, T.K. Kyong and N. In-Sik, 2003. Nonthermal plasma-enhanced catalytic removal of nitrogen oxides over V₂O₅/TiO₂ and Cr₂O₃/TiO₂. *Ind. Eng. Chem. Res.*, 42(13): 2960-2967.