The Technology of Non-thermal Plasma Assisted NH$_3$-SCR Reduce Marine Diesel Emission and Aldehydes Byproducts Formation

1, 2Lei 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 (NOx) from diesel engine exhaust. The formation mechanism of byproducts-type such as HCHO and CH$_3$CHO 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 NOx 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 NOx 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 NOx 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 (NOx), a smog-causing pollutant and greenhouse gas. SCR's performance has 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 NOx 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.

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

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$$ (1)
This reaction implies a 1:1 stoichiometry for NH3 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:

\[ 4\text{NH}_3 + 6\text{NO} \rightarrow 5\text{N}_2 + 6\text{H}_2\text{O} \]  

(2)

On the other hand, the reaction rate with equimolar amounts of NO and NO2 is much faster than that of the main reaction (1):

\[ 4\text{NH}_3 + 2\text{NO} + 2\text{NO}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \]  

(3)

It should be mentioned that the reaction with pure NO2 is again slower than reactions (1) and (3):

\[ 4\text{NH}_3 + 3\text{NO}_2 \rightarrow \frac{7}{2}\text{N}_2 + 6\text{H}_2\text{O} \]  

(4)

At high temperatures (>400 °C) the commonly used catalysts based on TiO2–WO3–V2O5 tend to form nitrous oxide. One of the possible reactions leading to nitrous oxide is:

\[ 4\text{NH}_3 + 4\text{NO} + 3\text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \]  

(5)

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

\[ 4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O} \]  

(6)

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 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 NOx converter. The effective oxidation of NO to NO2 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 NO2 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) NOx is reduced at low temperature when NO2 is involved in the reaction.
mechanism. Therefore, if non-thermal plasma converts NO to NO₂, the reduction rate of NOₓ 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 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:

\[ e + O_2 \rightarrow e + O(^3P) + O(^1P) \] (7)
\[ e + O_2 \rightarrow e + O(^3P) + O(^1D) \] (8)
\[ e + N_2 \rightarrow e + N(^4S) + N(^4S) \] (9)
\[ e + N_2 \rightarrow e + O(^4S) + O(^1N) \] (10)
\[ e + H_2O \rightarrow e + O + OH \] (11)
\[ e + CO_2 \rightarrow e + O + CO \] (12)

OH radicals can be formed more efficient in reaction:

\[ O(^1D) + H_2O \rightarrow OH + OH \] (13)

**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 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 NOₓ, also found that the energy density has a significant effect on the NOₓ 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 (CH₂CHO), 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 NOₓ (active) and resistance to SO₂ but also to monitor, whole process of produce by-products such as CO, N₂O, HCHO, CH₂CHO.

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 NH₃-SCR hybrid system

Table 1: Mechanisms of HCHO and CH₃CHO formation at 1 ATM

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Reaction number</th>
<th>Reactions</th>
<th>Reaction number</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCO + HCO → HCHO + CO</td>
<td>(14)</td>
<td>CH₃CHO + O₂ → HCHO + CO + OH</td>
<td>(19)</td>
</tr>
<tr>
<td>CH₂OH + O₂ → HCHO + HO₂</td>
<td>(15)</td>
<td>CH₃CH(OH)CH₂O → CH₃CHOH + HCHO</td>
<td>(20)</td>
</tr>
<tr>
<td>CH₁O + CH₃O → CH₂OH + CHO</td>
<td>(16)</td>
<td>C₂H₅ + O → CH₃CHO + H</td>
<td>(21)</td>
</tr>
<tr>
<td>C₂H₅ + O → HCHO + CH₃</td>
<td>(17)</td>
<td>CH₃CH₂O + O₂ → CH₃CHO + HO₂</td>
<td>(22)</td>
</tr>
<tr>
<td>C₂H₃ + O → HCHO + CH₃</td>
<td>(18)</td>
<td>HOC₃H₆O₂ + NO → CH₂OH + CH₃CHO + NO₂</td>
<td>(23)</td>
</tr>
</tbody>
</table>

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 (CH₃CHO) are determined as the major aldehydes-type unregulated byproduct constituents of partial oxidation of C₃H₆ in the plasma process according to the selective absorption of gas on FTIR spectra. Using C₃H₆ as an additive generating HCHO and CH₃CHO in the DBD reactor and this can be explained from two aspects: the first is that C₃H₆ can directly react with O radicals to produce HCHO via reaction (14) and the second is that several intermediate species of C₃H₆ decomposition and fragments can further form HCHO and CH₃-CHO easily via the following reactions (14)-(23) listed in Table 1.

As shown in Fig. 7 is the Concentration of HCHO and CH₃CHO formation at the outlet the DBD reactor as a function of energy density at different concentration of C₃H₆. It is observed from Fig. 7 that the generation amount of HCHO and CH₃CHO with the increase of the input energy density and the added C₃H₆ concentration increased, especially in the case of high energy density input and the high concentration of C₃H₆. Since the decomposition of C₃H₆, a large amount of HCHO and CH₃CHO was emitted form the DBD reactor.

Reaction (23) for CH₃CHO formation reaction, the reaction rate is proportional to the temperature, but as a
result of the reaction of reactant CH$_3$CH$_2$O generation rate and temperature is inversely proportional, eventually leading to generate CH$_3$CHO general rate and temperature is inversely proportional. Also, because the CH$_3$CHO SCR reactor in NO, NO$_2$, NH$_3$ reaction, cause only a small amount of CH$_3$CHO 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 NOx 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 CH$_3$CHO increases with the growing of energy density as well as the C$_3$H$_6$ addition increases and decreases with the reaction temperatures increasing. HCHO and CH$_3$CHO are almost completely removed when the feed gas is processed in the catalytic reactor, i.e., the concentration of HCHO and CH$_3$CHO at the outlet of the plasma catalytic reactor is only a few ppm, indicating that HCHO and CH$_3$CHO can make a difference to the NOx removal in the NH$_3$-SCR reactions.

ACKNOWLEDGMENT

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

REFERENCES


Bin, G., L. He, Z. Lin and H. Zhen, 2011a. Selective catalytic reduction of NOx with NH3 over Mn, Ce substitution Ti$_{0.9}$V$_{0.05}$O$_{2+\delta}$nanocomposites catalysts prepared by self-propagating high-temperature synthesis method. J. Phys.Chem., 115(26): 12850-12863.


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 NOx with NH$_3$ over Ti$_{0.9}$Ce$_{0.05}$V$_{0.05}$O$_{2+\delta}$nanocomposites catalysts prepared by solution combustion route. Chem. Eng. J., 181-182: 307-322.


