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Original Paper

Non-thermal plasma technology for abatement of pollutant emission from marine diesel engine

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Abstract: Plasma technology has long been regarded as a key essential tool in many industrial and technological sectors. However, the advancement of plasma technology in marine applications has not been fully realized yet. Herein, we present a short overview on the recent trends in utilization of plasma technology for air-pollution treatment in marine diesel exhaust. Four non-thermal plasma system, including electron beam dry scrubber (EBDS), dielectric barrier discharge (DBD), electron beam–microwave (EB–MW) plasma hybrid system, and plasma–catalytic hybrid system, are described with emphasis on their efficiency in removals of NO_x and SO_x gases. Non-thermal plasma has the great potential to be an efficient and environmentally compatible technique in simultaneous removals of NO_x and SO_x gases from the exhaust of marine diesel engine in the future.

Keywords: Plasma technology, Non-thermal plasma, Air-pollution treatment, Marine diesel engine

1. Introduction

Currently, plasma technology is extensively involved in various industrial manufacturing processes for high-tech electronic products, such as solar cells, chips, sensors, and semiconducting devices **[1]-[3]**. Plasma technology is not limited to electronic applications but is also applied in the automotive, steel, biomedical, textile, and paper industries **[4]-[6]**. Without plasma technology, the real-world practical use of many innovative and miniature products would not be realized.

Plasma is known as the fourth state of matter, accompanied by the three common states: solid, liquid, and gas. Plasma is an ionized gas that is comprised of electrons, negative and positive ions, excited species, and neutral molecules and atoms. Artificial plasma is usually generated in a vacuum chamber or an open system by applying a high voltage to a pair of electrodes (i.e., anode and cathode). Once the applied voltage reaches the breakdown point, plasma is generated through ionization, excitation, dissociation, attachment, and detachment. Overall, plasma is quasi-neutral, and its properties are dominated by the electric and magnetic fields. Fundamentally, plasma can be either non-thermal or thermal, according to the electron and ion temperatures generated in the plasma. Non-thermal plasma is in the non-equilibrium state, where the electron temperature is several orders of magnitude greater than the ion temperature ($T_e >> T_i$). Importantly, the occurrence of electron-collision reactions is dominant in non-equilibrium plasma, resulting in the dissociation of molecules into reactive and charged species. On the other hand, for thermal plasma, electrons and ions have almost the same temperature ($T_e \approx T_i$), yielding thermal equilibrium. The temperature is relatively homogeneous throughout the atoms, molecules, ions, and electrons in the system.

Most currently used plasma systems rely on non-thermal plasma owing to its advantages over other dry processing methods **[7]**. In particular, reactive species can accelerate the chemical reactions, allowing processing at low temperatures. High-energy ions are used for bombarding, cleaning, or etching material surfaces for specific applications **[8]**. Moreover, plas-

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Table 1: Type of plasmas

Type	Pressure		T_i		T_e		Typical applications
	High	Low	High	Low	High	Low	
Low-pressure plasma		✓		✓	✓		Semiconductor, lump and laser, display
Non-thermal plasma	✓			✓	✓		Air pollution control, waste treatment, polymer coating, polymer treatment
Thermal plasma	✓		✓		✓		Solid waste treatment, coating, ceramic processing, water treatments, cutting & welding
Nuclear fusion plasma		✓	✓		✓		Energy, military

ma can be used for surface modification **[9]**, thin-film fabrication **[10]**, and the synthesis of new materials with desired functionalities **[11]**. Various processing gases (e.g., Ar, O_2, H_2, NH_3, and air) can be employed for plasma generation under a wide range of pressure levels ranging from low to atmospheric, depending on the desired applications. Another important application of non-thermal plasma technology is sustainable pollution control, such as the decomposition of organic compounds in wastewater **[12]-[14]** and the abatement of toxic gas **[15]-[17]**. In the near future, non-thermal plasma is expected to be an efficient, sustainable, and eco-friendly method for solving environmental problems related to several industrial processes.

The environmental applications of non-thermal plasma technology have been extensively studied by researchers around the world, and this technology is already used in industrial processes. However, non-thermal plasma technology for marine pollution management has not yet been fully realized, and further development in this area is urgently required**[18]**. Herein, we present a short overview of the recent trends and possibilities of non-thermal plasma technology in marine pollution management.

2. Non-Thermal Plasma Technology for Marine Pollution Management

Marine diesel engines emit several gas pollutants into the environment, such as CO, CO_2, NO_x, and SO_x **[19]**. The amount of these gas pollutants normally varies according to the engine type, engine power, operating conditions, fuel and lubricating-oil type, and emission-control system. Among the gas pollutants, NO_x and SO_x, which are emitted without proper management, are the most harmful toxic gases and have local and global impacts on the environment and human health. Therefore, marine exhaust emissions are regulated according to the International Marine Organization (IMO) ship-pollution rules in order to reduce the level of toxic NO_x and SO_x gases released into the marine environment **[20]**. Several methods have been used to reduce the level of NO_x and SO_x emission from marine diesel engines, such as engine modification, water-based control, exhaust-gas recirculation, selective catalytic reduction, and alternative fuels with low sulfur content. The amount of NO_x and SO_x can be reduced by up to 99% and 90%, respectively, using these methods. However, two separate systems are needed for NO_x and SO_x removal in conventional processes, which incurs significant installation and maintenance costs, a large installation space on ships, and the storage of large amounts of ammonia for NO_x removal **[21]**.

The non-thermal plasma process has recently emerged as an eco-friendly and effective method for the simultaneous removal of NO_x and SO_x gases from diesel engine exhaust **[22]**. One characteristic of non-thermal plasma is that the electron temperature is substantially higher than the gas temperature. The occurrence of electron-collision reactions is dominant in non-equilibrium plasma, resulting in the dissociation of molecules into several reactive and free-radical species (e.g., OH, O, N, H). These reactive species can not only lead to the oxidation of SO_x and NO_x gases **[23]** but also dissociate various volatile organic compounds into CO and CO_2. In this section, four non-thermal plasma systems—(i) the electron-beam dry scrubber (EBDS), (ii) dielectric-barrier discharge (DBD), (iii) the electron beam–microwave (EB–MW) plasma hybrid system, and (iv) the plasma-catalytic hybrid system—are described, with emphasis on their effectiveness for the abatement of NO_x and SO_x gases.

2.1 Electron beam dry scrubber (EBDS)

Electrons generated in a vacuum tube are accelerated by a high voltage into a gas-processing chamber through a small window. The electron-beam irradiation can dissociate and ionize the O_2 and H_2O in exhaust gas, forming oxidative radicals (e.g., O, OH, HO_2) **[24][25]**. These oxidative species can turn NO_x and SO_x into HNO_3 and H_2SO_4, respectively. Subsequently, ammonia (NH_3) is added to the treated combustion flue to convert HNO_3 and H_2SO_4 into ammonium nitrate (NH_4NO_3) and ammonium sulfate ($(NH_4)_2SO_4$), respectively. These products can be repurposed to make fertilizer. The EBDS system shows potential applicability to simultaneously treat both NO_x and SO_x gases with a high efficiency **[24]**. However, this method has not yet been fully developed for practical use, owing to its high cost and large energy loss at the vacuum interface.

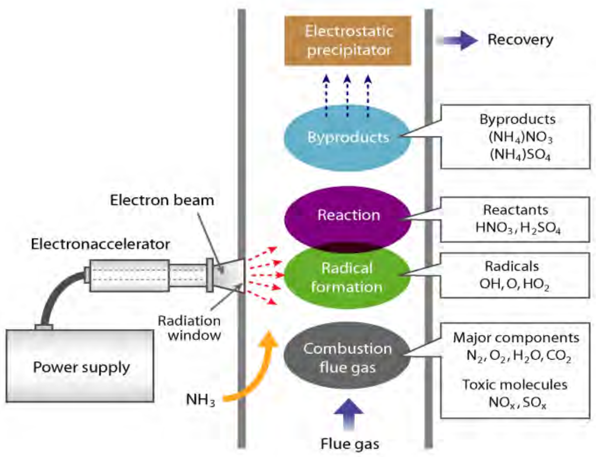

Figure 1: Flue gas treatment by electron beam dry scrubber (EBDS) **[24]**.

2.2 Dielectric barrier discharge (DBD)

DBD is composed of a small pulsed micro discharge generated between electrodes covered with thin dielectric layers by a high alternating-current voltage (**Figure 2**) **[26]**. DBD is the most common technique for producing ozone. Ozone is applied for various cleaning processes such as sterilization **[27]**, deodorization **[28]**, and decolorization **[29]** owing to its strong oxidation. DBD with the ozone production is considered as an efficient technique for flue-gas cleaning and toxic-gas decomposition in diesel gas exhaust **[30][31]**. However, the efficiency of DBD for the removal of toxic gas is low at present, and the removal of NOx by DBD is currently under investigation in laboratory and pilot plants. The main obstacles hindering the application of DBD to large-scale processes are the need for an external cooling system, the high operation cost, and the incomplete removal of toxic gas. Therefore, the rational development and design of DBD systems are important tasks for improving the efficiency of DBD for practical use.

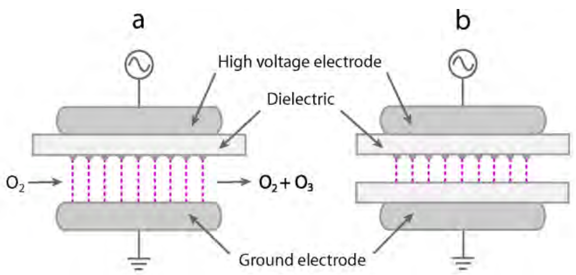

Figure 2: Dielectric barrier discharge (DBD): (a) one dielectric layer and (b) both dielectric layers **[24]**.

2.3 Electron beam–microwave (EB–MW) plasma hybrid system

Figure 3 (a) shows a schematic of a single unit of an EB–MW plasma hybrid system **[32]**. It comprises multiple sets of magnetrons and a single EB. In this system, EB produces a high density of electrons with high energy to generate plasma. Additionally, MW irradiation helps to maintain the energy of generated electrons by re-energizing them. By combining EB and MW irradiation, the plasma energy can be maintained at a high level while the energy required for EB is reduced. In addition, contamination can be avoided owing to the absence of electrodes in the EB–MW hybrid system **[32][33]**. In a laboratory-scale experiment, the levels of NO_x and SO_x were reduced by up to 60% and 80%, respectively. This hybrid system can potentially be developed for handling larger gas volumes with a higher flow rate by constructing multiple parallel arrangements of a single hybrid system, as schematically shown in **Figure 3 (b)**.

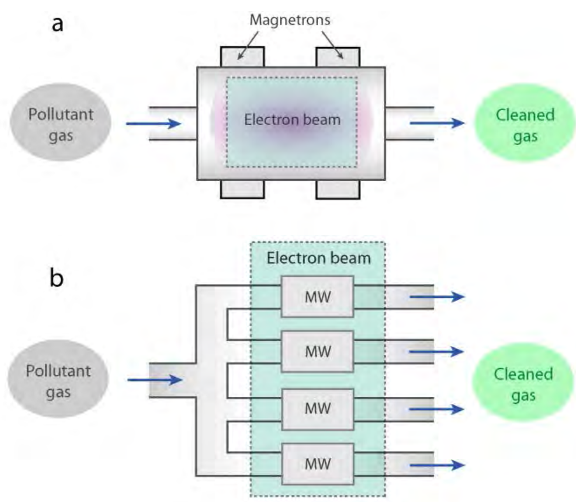

Figure 3: Electron beam–microwave (EB–MW) plasma hybrid system: (a) single unit and (b) multiple MW units with single EB **[32]**.

2.4 Plasma–catalytic hybrid system

The combination of non-thermal plasma and the high reaction selectivity of catalysts can lead to an improvement in the removal efficiencies of toxic gases **[34]-[36]**. There are two types of this hybrid system. The first type is called in-plasma catalysis (IPC). Here, the catalysts are introduced into the plasma discharge (**Figure 3 (a)**), and toxic gas can be decomposed by the plasma. Simultaneously, the catalysts become activated under plasma exposure to react with the toxic gas for treatment. The second type is post-plasma catalysis (PPC). In the PPC system, the catalysts are placed in a zone separated from the plasma reactor. As shown in **Figure 3 (b)**, the toxic gas is first decomposed by the plasma. Then, the residual contaminants that cannot be decomposed by the plasma, as well as byproducts, are transferred to the next reactor and removed by catalysts. The combination of plasma and catalysis in the treatment process can increase the reaction rate, extend the lifetime of the catalyst, and reduce the onset temperature of the catalytic reaction.

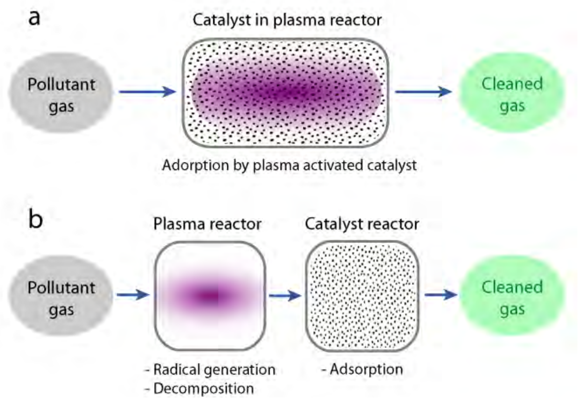

Figure 4: Two types of plasma-catalytic hybrid system: (a) In plasma catalysis (IPC) and (b) Post plasma catalysis (PPC) systems.

3. Conclusions

Non-thermal plasmas generated by different types of systems show great potential for the treatment of toxic gases emitted from marine diesel engines. Non-thermal plasma offers several advantages over conventional processes, such as operation at an ambient temperature, no need for external combustion devices, and the flexible treatment of various harmful gases. However, the practical use of non-thermal plasma in marine diesel engines has not been realized, owing to its high cost and low efficiency for large-scale processes. To realize its practical use, further intense development and design of non-thermal plasma systems are required. We believe that non-thermal plasma technology is a promising, efficient, ecological, and sustainable long-term solution for the abatement of NO_x and SO_x emitted from marine diesel engines in future smart ships.

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