

Recent Development of Technology in Scale-up of Plasma Reactors for Environmental and Energy Applications*

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Abstract To date, numerous studies have investigated the aftertreatment of exhaust gases from fossil-fueled combustors and combustion engines by plasmas as an environmental plasma application. Owing to the high power requirements of environmental plasma, it is difficult to use the plasma alone for aftertreatment; hence, a hybrid process that combines plasma processing with other techniques is required to reduce the overall power consumption. In developing countries, low-cost plasma hybrid processing has attracted considerable attention as an alternative to the selective catalytic reduction NO_x decomposition (De-NO_x) method and wet lime–gypsum SO_x decomposition method. Moreover, reduced catalytic activity can be enhanced by the plasma because of the decreased exhaust gas temperature, owing to the increased combustion efficiency. This paper reviews studies on successful air pollutant decomposition processes using the plasma chemical process with scale-up reactors. First, experimental techniques and block diagrams of various environmental plasma systems are presented. Subsequently, real-world systems of scale-up plasma reactors are described in detail. Several experimental results suggest that the hybrid treatment of particulate matter and dry De-NO_x is very promising from the viewpoint of energy consumption and material recycling. CO₂ treatment is a very important direction for future work in environmental plasma.

Keywords: Nonthermal plasma · Scale-up plasma reactor · Energy · Environment · Aftertreatment.

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Introduction

To date, many studies have investigated the aftertreatment of exhaust gases from fossil-fueled combustors and combustion engines by atmospheric-pressure nonthermal plasma (NTP) as an environmental application. However, few studies have investigated such an application with pilot and full-scale or scale-up plasma reactors in the real world. NTP used for emission aftertreatment is referred to as environmental plasma. As environmental plasma often requires a large amount of power, it is difficult to use it alone for aftertreatment; hence, a hybrid process that combines plasma processing with other techniques is required. A hybrid technology that uses concentration, adsorption, and chemicals for exhaust gas aftertreatment can reduce the plasma energy significantly, and circumvent the problems of the catalytic method. Moreover, hybrid technologies offer innovative global environmental protection solutions for boilers, furnaces, incinerators, diesel engines, and power generation plants.

This paper reviews experimental studies on environmental and energy plasma applications with scale-up plasma reactors, mainly conducted in Japan, especially at Osaka Prefecture University (OPU). Successful studies conducted at other institutions worldwide are also considered. The plasma process diagrams, reactor designs, plasma chemistry characteristics, performance test results, and energy efficiency evaluations are explained and compared. The compounds targeted for emission control treatment are nitrogen oxides (NO_x), sulfur oxides (SO_x), particulate matter (PM), carbon dioxide (CO_2), and dioxins. These pollutants contribute toward $\text{PM}_{2.5}$ issues, acid rain, smog, and health hazards; in particular, CO_2 emissions cause global warming.

Carbon (C), hydrogen (H), sulfur (S), and nitrogen (N) are the major components of fossil fuels. During combustion, fossil fuels release harmful components, such as NO_x (mainly NO and NO_2), SO_x (mainly SO_2 and SO_3), PM (mainly fly ash, soot, and dust), hydrocarbons (HC), CO_2 , and carbon monoxide (CO), as exhaust gases into the atmosphere, causing pollution. It is noted that thermal NO_x (Zeldovich NO and prompt NO) are generated while combustion reactions proceed, regardless of N contents of the fuel. These harmful components are targeted for the plasma treatment.

NTP can be generated easily by applying an alternating voltage or a high pulse voltage between electrodes that are coated with insulating materials such as ceramics. The exhaust gases can be treated by passing them between such electrodes or injecting a radical gas induced by the plasma. Recently, cooled ozone injection has emerged as a key technology for environmental plasma applications. It is suitable for scale-up plants because it can treat exhaust gases at higher flow rates by simply increasing the ozone gas injection rate. From the viewpoint of energy efficiency, as environmental plasma uses a large amount of electrical energy, it is disadvantageous for practical use. However, some applications have successfully reduced the energy consumption. In particular, the aftertreatment technology for glass melting furnace emission control can enhance the efficiency of combustors, while completely recycling the byproducts of the plasma hybrid process. This is a promising direction for future research. The overall plant design for this purpose, as well as other studies on economic analyses, is also reviewed in this paper.

Social Background of the Need for Environmental Plasma Treatment

Recent years have witnessed an increase in fossil fuel combustion, owing to unfavorable attitudes toward nuclear power generation. This has affected the balance of

energy supply, which may lead to changes in environmental protection measures and the global energy situation. Although new liquefied natural gas (LNG)-based power plants that incorporate a gas turbine combined cycle (GTCC) have higher thermal efficiency of more than 60%, there is a necessity for high-performance coal-fired power plants from the viewpoint of energy supply cost in Japan. For medium- and small-sized boilers used in regional heating and cooling systems, such as those in schools, hospitals, hotels, and factories, city natural gas is being increasingly used for power supply. Consequently, there has been a movement to tighten local regulations based on the Air Pollution Control Act.

Coal-fired power plants should be considered first as targets for environmental plasma treatment. A schematic diagram of an exhaust aftertreatment system for a coal-fired power plant, based on conventional technology, is shown in **Fig. 1(a)**. For comparison, another proposed system is shown in **Fig. 1(b)** [1]. **Fig. 1(a)** shows a typical example of the conventional system. Emission from the coal-fired boiler is treated continuously. NO_x is decomposed via selective catalytic reduction (SCR) of NO_x decomposition (De- NO_x). The electrostatic precipitator (Dry EP) removes the PM. SO_x is decomposed via the wet lime–gypsum method of SO_x decomposition (De- SO_x). Thus, the system comprehensively removes NO_x , SO_x , and PM from the exhaust gases of coal-fired boilers, although its configuration may vary. The above-mentioned methods are well-established technologies for preventing the release of these harmful components into the atmosphere. **Fig. 1(b)** shows the plasma system proposed by Yan et al. The plasma device charges the PM and oxidizes NO. The electrostatic precipitator (Dry EP) removes the PM. The De- SO_x and De- NO_x unit decomposes SO_x and NO_x via the NH_4OH method, followed by a second electrostatic precipitator (Wet EP). Although the wet lime–gypsum De- SO_x technology has been introduced in China, its use is limited; instead, the method of forming ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) byproducts through the discharge oxidation reaction of SO_x and NH_4OH is more popular. The EP is considered as a plasma reactor. Using a three-phase power supply increases the average voltage by 20–30%, resulting in the improved performance of the EPs [2]. The aftertreatment process shown in **Fig. 1(a)** is well established in Japan; hence, it is difficult to replace it with the plasma system. However, there is considerable scope for the development of the plasma system shown in **Fig. 1(b)** in China. The emission standards for air pollutants of thermal power plants that use coal boilers for power generation have been revised in China. Accordingly, the emission regulations for PM (soot and dust) have been tightened from 50 mg/Nm^3 to 30 mg/Nm^3 ; in certain large cities, it is less than 20 mg/Nm^3 (N = standard state, or 0°C and one atmosphere) [3]. The emission regulations for NO_x and SO_x have been also tightened. As environmental research is being actively conducted in all sectors, including industry, academia, and the government, the development of new environmental technologies, such as plasma treatment, has attracted considerable attention. Environmental plasma may be used as a finishing technology for exhaust gas treatment.

Other disadvantages of SCR include the use of toxic gases such as ammonia and its relatively high operating cost. Moreover, an exhaust gas temperature of 300°C is required for catalyst activation. Usually, the exhaust gas temperatures of combustion furnaces in garbage treatment plants do not reach 300°C , and the temperature must be increased using heaters, resulting in additional energy consumption. The plasma process is suitable for this purpose because the treatment can be performed at atmospheric temperature. The typical energy supply apparatus for regional distribution constitutes small- and medium-

sized combustion boilers. It is widely used in industrial steam/warm water supply, district heating and cooling, hot water supply, etc., and has become indispensable in daily life. However, at present, it is nearly impossible to perform NO_x exhaust gas aftertreatment using ammonia, which is a hazardous substance.

The amount of energy used for exhaust gas treatment in the thermal power plant shown in **Fig. 1 (a)** is usually suppressed to a penalty of approximately 1% of the on-site electric power. It is difficult to realize this value via plasma processing. By contrast, for marine diesel engine aftertreatment such as urea SCR, this penalty is usually 10% calculated from data in references [4, 5]. Thus, there are many opportunities for using plasma technology to treat exhaust gases under more lenient restrictions compared with those for lean-burn-engine automobiles [6]. In such cases, a large- or pilot-scale experiment is crucial for the plasma chemistry, which plays an important role in the process.

Meanwhile, the concentration of NO_x and SO_x in the exhaust gases of thermal power plants and combustion furnaces of regional waste treatment plants is usually of the order of several tens to several hundred ppm. NO_x and SO_x are harmful components that must be treated first. However, it is difficult to treat a large amount of CO₂ emitted from thermal power stations, because its concentration in the exhaust gases is more than 10% (= 100,000 ppm or more) and it is a highly stable gas. To address this problem, many studies have reported the plasma decomposition of CO₂ and the reduction of fuel to CO and C. Recently, several studies have shown the economic benefits of plasma treatment with >55% energy efficiency, which leads to zero CO₂ emissions from thermal power plants incorporating GTCC [7]. Hence, this is a promising direction for future research. The rapid transfer of plasma technology from the laboratory to the industry is currently impeded by the high costs of high-voltage power sources and total power generation. Innovative nuclear power generation schemes can provide massive amounts of energy for combustion exhaust aftertreatment, and are thus considered to have immense potential.

Against the above-mentioned background, this paper explains the principle of air pollutant decomposition using the plasma chemical process with scale-up plasma reactors. First, experimental techniques and block diagrams of various environmental systems using NTP are described. Subsequently, real-world systems of scale-up plasma reactors are discussed.

Nitrogen Oxide Treatment

Plasma Chemical Hybrid Process (Wet De-NO_x Technology)

The plasma chemical hybrid process (PCHP) has been studied by several researchers [8–13]. Its principle is schematically shown in **Fig. 2**. The emission from the burners of the boiler is first treated by the injected ozone induced by the plasma ozonizer, and NO is oxidized to NO₂. Further, water-soluble NO₂ is treated with a chemical scrubber using sodium sulfite (Na₂SO₃) solution, which is a strong reducing agent, to yield N₂ and a clear and nontoxic solution of Na₂SO₄. Instead of Na₂SO₄, NaOH solution can be injected into the SO₂ environment. Na₂SO₃ is obtained via reaction (3) inside the scrubber. Finally, the cleaned gas is released from the stack.





As an early version of the PCHP, a pilot-scale coal-fired emission control method was reported in the Soviet Union [12]. Indirect plasma reactor ozone and activated radicals are injected into the exhaust pipe of the coal-fired boilers (experimental flow rate of the exhaust gas $\sim 10,000 \text{ m}^3/\text{h}$). The energy cost of the plasma reactor is high, i.e., approximately 5% of the thermal output of the boiler in an electrical power generation plant of 200 MW. The system involves ozone injection followed by the ammonia solution chemical scrubber. Recently, high-efficiency NO_x absorption in the water phase using the plasma ozonizer has been reported by Yasuda et al. [13] at OPU. For industrial applications, a high concentration of NO_x gas (=20.6%), produced by a metal dissolution process, has been successfully treated. The NO_x removal efficiency is as high as 97.6%. NO_x is not reduced to N_2 , but finally converted into HNO_3 , and can be recovered as a chemical solution.

In view of the issues discussed above, research was conducted on the full-scale operation of small- and medium-sized boilers with the PCHP, which had not been subjected to exhaust gas aftertreatment [8–11]. With cooperation from industry, academia (OPU), and the government, technology that can remove NO_x with nearly 100% efficiency by suppressing hazardous byproducts has been successfully developed, and is being commercialized as a plasma treatment for super-clean boilers. The details of the principle, product system, and performance test results are explained. An overall schematic view of the system is shown in Fig. 3. The device comprises a flue-tube boiler, an economizer (exhaust gas heat recovery system), a plasma ozone synchronizer, an Na_2SO_3 chemical scrubber, and a chimney where the exhaust gas is processed and NO_x is treated. By injecting ozone gas (O_3) formed by the plasma ozonizer in the middle of the flue gas, NO , which accounts for the major portion of NO_x in the exhaust gas at the boiler outlet, is completely oxidized to NO_2 and removed according to reaction (1). The NO_2 thus formed is a powerful and inexpensive reducing agent, and it is reduced to N_2 and non-toxic sodium sulfate (Na_2SO_4) waste fluid according to reaction (2) using Na_2SO_3 , which is available as chemical plant waste. The effluent may be diluted and released into the sewage.

The targeted boiler unit is designed for a boiler with a steam generation rate of 2.5 t/h and heat output of 1,570 kW. For greater steam generation, multiple systems may be required. To reduce CO_2 emissions in order to achieve carbon neutrality, attempts are being made to use bio-fuels (biodiesel, vegetable oil) or waste oil biomass (machine tool oil, automobile oil, food oil, rice bran oil, fish oil, glycerin) as boiler fuels. Depending on the fuel employed, a special burner (two-phase-flow low NO_x emission burner or rotary burner) can be used in this system to reduce CO_2 emissions and fuel costs. In the case of waste oil biomass, only approximately 20% of the total amount generated is used as fuel in Japan, whereas the rest is discarded. Thus, high processing costs are incurred. For example, if 20% biomass fuel is used in a 2.5 t/h steam generation boiler, CO_2 reduction of approximately 600 tons per year can be achieved, and the waste oil treatment cost can be reduced by around 6.8 million Japanese Yen (= 68,000 US\$). However, large amounts of harmful NO_x and PM may be produced by low-quality fuel or flame-retardant oil as a

result of combustion. The NO_x concentration can exceed 50 ppm, which is the regulated value of NO_x in cities under the Air Pollution Control Law. In such cases, a plasma treatment can be used to clean the exhaust gas to the maximum extent.

Figure 4 shows the structure of the electrical discharge section of the plasma reactor in the ozonizer. A coaxial NTP reactor or silent discharge-type reactor is used. O_3 gas is generated after O_2 gas by a pressure swing adsorption (PSA) passes through the 30 plasma reactors inside the ozonizer, and it is then injected into a flue gas duct for NO oxidation. The O_3 gas flow rate is constant, i.e., $0.9 \text{ Nm}^3/\text{h}$. When the discharge power is 1.5 kW and the PSA power is 1.6 kW, a maximum of 90 g/h of O_3 is generated with a concentration of 4.7% and plasma energy efficiency of 60 g/kWh. High-concentration O_3 gas is injected into the duct and diluted to oxidize nearly all of the NO to NO_2 according to reaction (1). Owing to the improved energy efficiency of the plasma ozonizer, the ratio of the plasma reactor energy cost to the thermal output decreases down to only 1% in our apparatus.

Figure 5 shows a test result of the aftertreatment. In the figure, the time-dependent NO and NO_x concentrations at MP1 (measurement point 1 at the exit of the boiler) and MP3 (measurement point 3 at the exit of the exhaust gas cleaning system) are shown, when city natural gas is used as fuel. The NO_x levels are measured using NO_x analyzers. The experiment is performed with a daily start and stop operation. The average flow rate of the city natural gas is $52 \text{ Nm}^3/\text{h}$, while that of the flue gas is $718 \text{ Nm}^3/\text{h}$ at an O_2 concentration of 3.3–4.0%. The average rates of O_3 injection and Na_2SO_3 supply are 86 g/h and 63 mol/h, respectively. The NO_x concentrations at MP1 are within 45–50 ppm. This small daily difference in NO_x is due to the difference in the O_2 concentrations at MP1 (between 3.3% and 4.0%). The NO_x concentrations at MP3 are within 5–8 ppm, which are equivalent to an NO_x removal efficiency of more than 85% over an operating time of 23 h. The achieved NO_x removal performance is satisfactory and stable.

Plasma Chemical Hybrid Process (Dry De- NO_x Technology)

Glass manufacturing systems or glass melting furnaces are suitable targets for nonthermal plasma aftertreatment [14, 15]. In the melting furnace system, for example, glass bottle melting furnace, glass raw materials, such as silica sand, are melted at approximately 1500°C by the heat produced by combustion burners fueled with either liquefied natural gas or heavy oil. Some furnaces also use electric joule heating or plasma heating for glass melting. However, such furnaces are relatively few because of their higher energy or operating costs; moreover, the flue gas from the burners contains environmental pollutants, such as NO_x (~600 ppm), SO_x (~600 ppm), and PM, including glass raw materials. To decrease the NO_x concentration in order to satisfy the NO_x regulation (< 450 ppm in Japan), a low fuel to air ratio of approximately 0.85 is employed for a low NO_x burner. Further, $\lambda = 1.2$ is suitable for complete combustion. If it is realized, approximately 30% of the fuel can be reduced compared with combustion with $\lambda = 0.8$. Therefore, highly efficient NO_x removal technology with low energy consumption is required for glass manufacturing.

Figure 6 shows a schematic diagram for the simultaneous removal of NO_x and SO_x from the exhaust gas of a glass manufacturing system via the PCHP. The following NO_x removal process is adopted. First, plasma-induced ozone gas is injected into the exhaust gas duct, and thermally decomposed into the oxygen radical. NO in the exhaust gas is

oxidized to water-soluble NO₂ with the oxygen radical. Na₂SO₃ is produced as a byproduct of the De-SO_x process using the NaOH solution; subsequently, NO₂ is reduced to N₂ gas by a chemical process with Na₂SO₄ as the byproduct. When the amount of injected water is reduced, this becomes a dry process, and solid Na₂SO₄ powder can be recovered by the EP. Na₂SO₄ is a typical raw material for glass, and it can be reused as a high-purity glass material. Through this procedure, NO_x is removed continuously. For effective NO_x removal, it is essential to oxidize NO to NO₂ sufficiently by water-cooled ozone gas injection. The present method is a highly suitable and self-consistent recycled De-NO_x process.

Figure 7 shows schematics and photographs of the plasma reactor used in the performance test [15]. Water-cooled ozone can be injected into the stabilizer at a generation rate of ~10 kg/h. A 6 kg and a 4kg ozonizer are used. The 4 kg/h plasma ozonizer is shown in **Fig. 7**. Its side view is shown in **Fig. 7(a)**. The ozonizer is composed of nonthermal plasma reactors and supplied with O₂ gas from a cold evaporator (CE) tank filled with liquid O₂. After adjusting its pressure from the CE tank to 0.13 MPa, oxygen is fed into the ozonizer at a flow rate of 26.7 Nm³/h. The ozone mass flow rate can be adjusted from 0 to 4 kg/h by changing the output of the high-voltage power supply unit. The ozonizer consists of 334 glass plasma reactors, as shown in **Fig. 7(b)** and **7(c)**. The glass plasma reactors are cooled with water at 15°C to maintain a constant ozone output even during long-term operation.

A detailed schematic of one of the glass plasma reactors in the ozonizer is shown in **Fig. 7**, along with a photograph of the arrangement of its various parts. The glass plasma reactor consists of a glass dielectric barrier electrode and a water-cooled ground electrode, and it can generate plasma via dielectric barrier discharge between the discharge gap. Further, the 1400-mm-long glass plasma reactors are installed by considering the point symmetry.

Thus far, simultaneous removal of NO_x and SO_x with an efficiency of 23 g/kWh at SE of Wh/m³ (NO_x removal efficiency = 39%, SO_x removal efficiency = 46%, and Q = 16,000 Nm³/h) has been achieved [15]. This process has considerable potential, and the technology can be used in existing aftertreatment systems of glass bottle manufacturing furnaces, which are widely used in developing countries, as well as for making plate glass for electric devices and windows.

Plasma-Adsorption Combined Process

The plasma-adsorption combined process for diesel engine exhaust NO_x treatment was first performed by the author's group [16]. Using the NO_x adsorption to the adsorbent, the oxygen-rich and oxygen-lean states are switched to reduce NO_x. **Figure 8** shows the principle for the treatment. The principle of De-NO_x of the plasma combined processing system is as follows. After NO_x is adsorbed in the O₂-rich normal operation condition with the exhaust gas path (a), it is subjected to high-concentration desorption by periodic adsorption through heating using waste heat under lean oxygen (O₂ < 2% is desirable) and CO- and HC- rich conditions with the exhaust gas path (b). The desorbed NO_x undergoes reduction to form N₂ by the N radical formed in the plasma. The reaction equation is as follows.



This reaction can be effectively implemented by supplying oxygen-lean gas through an oxygen penetrating membrane, or by controlling the engine operation mode with the fuel injection method. N₂ gas source was used in this experiment. In this system, plasma needs not be generated in the adsorption process. Further, the adsorption enriched NO_x is treated by plasma in a short time; hence, significant improvements in the energy efficiency of cleaning may be theoretically expected.

A pilot-scale aftertreatment for an actual marine diesel engine (output 1 MW class) was designed and manufactured based on laboratory-scale experiments, and an aftertreatment system was developed [16–18]. It was tested by alternately repeating (a) adsorption and (b) desorption with plasma treatment. The test was carried out using a marine diesel engine (**Fig. 9** for use in a marine sub-engine power generator, 6DK–20e, manufactured by Daihatsu Diesel MFG. Co., Ltd.; specifications: 4-cycle 6-cylinder, rotational speed: 900 rpm, maximum output: 1.04 MW, exhaust gas flow rate: 6815 Nm³/h (maximum output at 100% load)) with a scale-up adsorption tower, an NTP reactor with 48 surface discharge tubes with total power = 21.4 kW), a diesel particulate filter (DPF), and a gas cooler. A portion of the exhaust gas from the engine was branched, and exhaust gas with a flow rate of 800 Nm³/h was treated. The aftertreatment included (a) adsorption and (b) desorption processes. These processes were repeated alternately. In the desorption process (b), N₂ gas was passed through the adsorption tower at 12–24 m³/h. The discharged NO_x + N₂ gas was processed by the NTP reactor.

Figure 10 shows a surface discharge tube element of the NTP reactor used for NO_x reduction in the desorption process. The NTP reactor consists of a surface discharge element (ET-OC70G-C, Masuda Research Inc., Japan), air-cooling fins, and a flange to fix the discharge element to the frame. Tungsten discharge electrodes are arranged on the inner ceramic wall (alumina) of the discharge element. Two of these reactors are powered by a single-pulse high-voltage (maximum peak-to-peak voltage = 10 kV, frequency = 9.9 kHz, and maximum input power = 450 × 2 = 900 W) power supply (HCII-70/2, Masuda Research Inc.). A unit of the NTP generators (HCII-OC70 × 12) consists of 12 NTP reactors and 6 power supplies. The total input power of a unit is 900 W × 6 = 5.4 kW, and the discharge power is 5.0 kW. In the experiment, four NTP generator units (total input power is 5.4 × 4 = 21.6 kW) connected in three parallel separate flow lines are used. The flow rate of each line is 3.7–7.4 Nm³/h, and the total flow rate is 11.1–22.2 Nm³/h. When the high-concentration desorbed NO_x in N₂ enters through the inlet of the reactor, it is reduced by the NTP as a clean gaseous mixture of N₂ and O₂.

Figure 11 shows the experimental result of the time-dependent change of the mass flow rate of untreated and treated NO_x exhaust. The white dots represent the mass flow rate of untreated NO_x, and the black dots represent the mass flow rate of treated NO_x. In the adsorption process of the ninth to twelves cycles, the values of the white dots of the untreated NO_x emitted from the engine decreased to those of the black dots. Meanwhile, the protrusion of the mass flow rate of untreated NO_x in the desorption process. When the high-concentration desorbed NO_x in N₂ enters through the inlet of the plasma reactor, the NO_x is reduced by the NTP through the reactor outlet.

As a result, a high-energy efficiency of 161 g (NO₂)/kWh was recorded. To the best of the author's knowledge, no other pilot-scale plasma cleaning test has been conducted for marine diesel NO_x. It is estimated that the demonstrated efficiency will require 4.3%

of the total engine output power to clear Tier III of International Maritime Organization (IMO), a performance that exceeds the urea SCR efficiency (by around 10%).

Plasma-assisted Selective Non-catalytic Reduction (SNCR) Process

Kambara et al. [19, 20] developed a new aftertreatment technology of SNCR for the combustion of NO_x in the exhaust gas of garbage incinerators. The method is characterized by the injection of the ammonia radical activated by atmospheric NTP. Although there have been several pilot-scale studies on ammonia radical shower technologies for NO_x reduction [21, 22], the plasma-assisted SNCR technology is promising because NO_x can be reduced without any toxic byproducts. No catalyst is required, and the operating cost of the apparatus is one-fifth of that of the SCR De- NO_x system. They attempted to carry out a pilot-scale test with an actual incinerator. The temperature range, in which NO removal takes place, is termed as the temperature window. Most waste incinerators use a rotary kiln for combusting solid waste. The distribution of the gas temperature in the kiln varies significantly because of the heterogeneous combustion of solid waste; hence, it is difficult for it to remain within the SNCR temperature window. The kiln exit is the most suitable location for installing an ammonia injector; however, the temperature at the kiln exit is between 700°C and 800°C , which is outside the temperature window. Therefore, it is essential for waste incinerators to shift the temperature window to allow for lower temperatures. To broaden and lower the narrow temperature window of the SNCR, a unique NO_x removal system involving activated ammonia injection using an intermittent dielectric barrier discharge (DBD) has been developed.

A test facility is shown in **Fig. 12**. It consists of the following parts: fuel feeder, combustor, heat exchanger, gas cooler, bag filter, induced draft fan, and stack. The flue gas flow rate was $4,000 \text{ Nm}^3/\text{h}$, and the NO_x concentration was around 200 ppm on a dry basis. Activated ammonia was injected into the combustor at a molar ratio (NH_3/NO) of 1.5. The gas temperature at the injection point was $700\text{--}750^\circ\text{C}$. Activated ammonia was generated by the pulsed DBD at an applied voltage of 15 kV and a repetition rate of 10 kHz using 100% ammonia (NH_3) gas. First, untreated ammonia gas was injected into an exit pipe from a pre-combustor at a molar ratio of 0.75, which is well known as the normal SNCR. In this condition, De- NO_x was 50% at a gas temperature of 800°C . When activated ammonia was injected into the combustor, De- NO_x attained 80% at a gas temperature of 730°C , which was similar to that obtained by lab-scale experimental tests. As a result, the gas-phase reactions in a $\text{NO}/\text{NH}_3/\text{O}_2$ system occur at temperatures between 730°C and 800°C . The maximum NO removal efficiency is around 80%. Note that SO_2 was also reduced by activated ammonia injection; however, the removal mechanisms of SO_2 are not elucidated.

Pulse Corona Plasma Treatment for Industry Plant Exhaust

In Korea, many studies on pilot-scale environmental plasma have been reported because environmental problems related to $\text{PM}_{2.5}$ have emerged as a social issue. Han et al. performed simultaneous removal of SO_x and NO_x using an advanced pulsed corona discharger with a thin water film, obtained from TiO_2 nanoparticles [23]. Dry-type pulse plasmas have been demonstrated for the removal of SO_2 and NO_x in practical applications, such as the treatment of flue gases from iron-ore sinter plants [24] and large-scale

industrial incinerators [25]. The removal of NO_x and SO_x using a pulsed corona discharger with a thin water-film electrode treated with a hydrophilic coating was evaluated in a sustainable and clean wet-type reactor. The maximum flow rate of the gas was $156 \text{ Nm}^3/\text{h}$. It was clarified that the addition of NH_3 (100 ppm) and C_3H_6 (200 ppm) is highly effective for NO_x removal. The removal efficiency of SO and NO is approximately 80% or higher.

Winands et al. reported a large-scale pulsed corona system, in which the pulse parameters, such as pulse rise time, peak voltage, pulse width, and energy per pulse, can be varied to realize a high-performance ozonizer [26]. The chemical efficiency of the system is determined by measuring the ozone production. The temporal and spatial development of the discharge streamers is recorded using an intensified charge-coupled device (ICCD) camera with a minimum exposure time of 5 ns. The camera can be triggered at any moment starting from the time the voltage pulse arrives at the reactor, with an accuracy of less than 1 ns. Measurements were performed on an industrial-size wire-plate reactor. The influence of the pulse parameters, such as pulse voltage, DC bias voltage, rise time, and pulse repetition rate, on the plasma generation was monitored. For higher peak voltages, an increase was observed in the primary streamer velocity, the primary streamer diameter, the light intensity, and the number of streamers per unit length of the corona wire. No significant separate influence of the DC bias voltage level was observed as long as the total reactor voltage (pulse + DC bias) remained constant and the DC bias voltage remained below the DC corona onset. For situations in which the plasma appearance changed (e.g., different streamer velocity, diameter, intensity), a change in ozone production was also observed. The best chemical yield (60 g/kWh) was obtained for low voltage (55 kV) and low-energy pulses (0.4 J/pulse). For high voltage (86 kV) and high-energy pulses (2.3 J/pulse), the yield decreased to approximately 45 g/kWh , which is still a high value for ozone production in ambient air (relative humidity = 42%). The pulse repetition rate has no influence on plasma generation and chemical efficiency up to 400 pulses per second (pps).

Direct Plasma Reduction of Marine Diesel NO_x and PM

A combined approach to reducing NO_x and PM emitted by medium-speed marine diesel engines using NTP reactors was studied by Hołub et al. [27]. **Figure 13** shows the experimental, analyzer, and acquisition system setup along with an NTP unit in an engine exhaust gas bypass. The marine diesel engine exhaust gas passes through a silencer via the inlet and outlet. A bypass channel is installed at the silencer. An NTP module is installed in the bypass channel (its flow rate is around 10% of that in the main duct) of the main exhaust system of a four-cycle marine diesel engine (6AL20/24, HCP Sulzer, Poland) for the main propulsion or generator sets of a small ship. The output power of the engine is 397 kW, and the rotating speed is 720 rpm. A test bench allows direct exhaust stream exposure using the main exhaust bypass to a plasma reactor without any additional components such as coolers or orifices that could alter the exhaust gas properties. The design of the employed reactor depends on the DBD comprising 36 parallel electrode rods positioned to allow movement of a gas stream through the assembly. The plasma is driven by a novel power supply based on a series-parallel resonance circuit topology, which allows high-voltage and frequency operations. The concentrations of the gas components, such as CO, CO_2 , NO, NO_2 , N_2O , NO_x , O_2 , soot, soluble organic fraction (SOF), adsorbed hydrocarbons, and total PM, are measured using gas analyzers.

Throughout the measurement trials, the gas composition in the engine exhaust gas system is monitored using a gas analyzer before the gas passes through the NTP reactor, whereas two gas analyzers are fitted at the NTP reactor outlet. The gas component concentration and engine monitoring data are sent to the data server. A set of thermocouples is used to estimate the temperature in the NTP module. The trial schedule allows the reactor to heat up and reach adequately stable conditions for the engine exhaust system and outlet gas conditions. The NTP reactor temperature cannot be adjusted because it depends on the exhaust gas temperature of the engine. During the engine tests, this temperature varies from 150°C (idle) to 350°C (full engine load). This dependence is used to investigate the influence of the operating temperature on the related oxidation processes.

Results of the implementation of the NTP reactor in the exhaust duct of the test bench diesel engine demonstrate considerable improvements in the gas composition and PM emissions at extremely low energy densities (up to $16 \text{ J/dm}^3 = 4.4 \text{ Wh/m}^3$). Significant effects on the conversion of NO and PM under realistic engine exhaust conditions are observed. The removal rate of the unbalanced PM amount is determined. It reaches a maximum value of around 12% at 265 W. The total PM removal efficiency is 1.7 g/kWh at an active input power of 180 W. Partial oxidation of NO to higher nitride oxides such as NO₂ is observed, as is the conversion of PM particles into gaseous SOF and soot. Partial oxidation of NO is suggested as conditioning for NO_x catalyst-based reduction processes at temperatures below 200°C. These results suggest a two-stage process. i.e., the release of SOF by heat, followed by oxidation through the reactive oxygen species in the plasma, or through the direct decomposition of the polycyclic aromatic hydrocarbon in the SOF particles.

Microwave Plasma Reduction of Marine Diesel NO_x and PM

The reduction of NO_x and PM in the exhaust gas of a marine diesel engine using microwave NTP was studied by Balachandran et al. [28, 29]. Microwave plasma generation can remove the NO in a typical two-stroke marine diesel engine. A pilot-scale NTP reactor using two microwave generators has a multimode cavity, in which microwave energy is generated by stub tuners and waveguides. Passive electrodes are installed in the multimode cavity to generate microwave plasma. In the experiment [29], one magnetron is set-up at 1-kW power and has 0.2-kW reflected power, while the other magnetron is set-up at 0.6-kW power with a 0.1-kW reflected power. The reflected power varies slightly during the period of experiment, and matching the power source and the reactor is performed through the stub tuners on both magnetrons. Exhaust gas from an engine passes through the multimode cavity via the gas inlet/outlet. The passive electrodes, which consist of a needle electrode, a saw-tooth electrode, and cross-saw-tooth electrodes, are used to generate a high electric field region within a microwave environment, where high-energy electrons of 1–3 eV are produced for the generation of NTP. The generator-set diesel exhaust gas is used to test the pilot-scale microwave plasma reactor. The experimental setup used in the study includes a pilot-scale NTP reactor with two microwave generators, a 2-kW generator-set diesel generator, gas measurement systems, a high-voltage 30-kV supply, a gas flow rate meter, and a data-logging system. Two 2-kW microwave generators operating at 2.45 GHz are used to supply the required microwave energy into the microwave cavity, through two slotted waveguides. The exhaust gas from a generator-set diesel engine contains a higher percentage of NO than

NO₂; it is very similar to the exhaust from a typical two-cycle diesel marine engine.

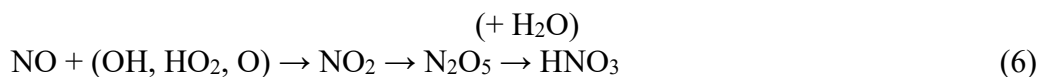
It was reported [30] that as a general rule, in DBD discharges the presence of oxygen tends to produce the oxidation of NO to NO₂, while in microwave discharges dissociation of NO into N₂ and O₂ usually occurs. The experimental results showed that nearly 100% removal of NO is possible for an exhaust gas flow rate of 60 L/s at an exhaust gas temperature of 40–70°C, which is obtained with a water-cooled reactor. They also showed that microwaves can significantly remove soot particles having a diameter of 10–365 nm, entrained in the exhaust gas of a 200-kW marine diesel engine with 40% engine load and a gas flow rate of 130 L/s. Microwaves irradiation demonstrated a PM reduction of up to 50% without the generation of plasma at the high temperature and up to 90% reduction with the generation of plasma. Because fine-tuning of the electrode position is necessary, the major challenge in these experiments is igniting the desired plasma and sustaining it using the passive electrodes for a long period, which is influenced by many factors such as the gas flow rate, geometry of the reactor, and microwave power applied.

Sulfur Oxide Treatment

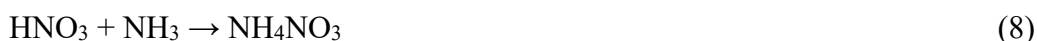
Pulse Corona Induced Plasma Chemical Process (PPCP)

SO_x reduction using plasma application is difficult because the chemical bond of S=O is extremely strong, although NO_x is partially decomposed into N₂ and O₂ by direct plasma application. Therefore, through plasma application, SO_x in the exhaust should be reduced either by oxidation followed by the wet process or by conversion to aerosol followed by the precipitation process. Examples of oxidation followed by the wet process have already been presented in the previous section. The PPCP method [25, 31–33] is a typical procedure for conversion into aerosol followed by the precipitation process. This method was proposed by Dr. Senichi Masuda.

The PPCP for boiler emissions is shown in **Fig. 14**. First, the gas passes through the air heater (AH) at a temperature of 200°C. The EP in the first stage can remove fly ash particles. Then, the gas is cooled down to 90°C, and NH₃ gas is injected. It is noted that the PCPP proceeds under the lower temperature condition and this is one of the critical conditions for the treatment. The gas is introduced to the PPCP reactor, which has a pair of high-voltage electrodes. Second, high-voltage pulse corona discharge is induced in the reactor. The reduction and oxidation reactions of NO and SO₂ proceed in the presence of radicals and ions.



Note that these industrial EPs are energized by the negative polarity pulse power supply, and the PPCP reactor is usually energized by the positive polarity pulse power supply. Finally, coexisting NH₃ reacts with HNO₃ and H₂SO₄.



The aerosols of NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ are captured by the EP, followed by the plasma reactor. The cleaned gas is released into the atmosphere. The NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ particles can be reused as fertilizer. $(\text{NH}_4)_2\text{SO}_4$ decomposition occurs at temperatures higher than 120°C . The following thermal reaction also occurs at temperatures lower than 80°C to enhance De- SO_x .



The PPCP method is a novel method for simultaneous NO_x and SO_x reduction, and it has the potential to replace ordinary wet gas treatment techniques; to this end, a large-scale test has been reported on an industrial incinerator [25]. The system was one of the world's largest-scale of PPCP for treating NO_x and SO_2 simultaneously. A PPCP unit equipped with an average 120 kW modulator has been installed and tested at an industrial incinerator with a gas flow rate of $42,000 \text{ m}^3/\text{h}$. In the experiment, the removal efficiency of SO_2 and NO_x were approximately 99 and 70%, respectively. However, the following problems for commercial applications should be noted: (1) high operating costs (approximately 5% of the power input) for the pulsed corona plasma discharge; (2) high NH_3 -associated costs (approximately one-third of the total cost); and (3) long residence time in the reactor ($>10 \text{ s}$).

Aftertreatment for Power Generation Plant Emission

Yan et al. reviewed the history of the fundamentals and environmental applications of nonthermal plasmas, especially for multiple emissions such as NO_x , SO_x , PM, VOC, and mercury, from coal-fired boilers [34]. Coal is a fossil fuel with the longest global lifespan (the ratio of resource to production is approximately 800). Therefore, it can be used conveniently for electrical power generation at low costs. However, large amounts of NO_x , SO_x , PM, and mercury are contained in the untreated emission from pulverized coal-fired boilers. Therefore, aftertreatment has been proposed with a highly developed system. SCR-EP-FGD (FGD: flue gas desulfurization) is a typical configuration currently used for coal-fired boilers in advanced countries. EP is an apparatus for high-voltage electrical discharge. However, because DC corona discharge is used, the plasma is induced near the wire discharge; therefore, the gaseous removal efficiency is not sufficiently high. Some pilot-scale tests have plotted the annual exhaust gas flow rates. The highest flow rate was achieved by ENEL [35], i.e., $\sim 10^6 \text{ Nm}^3/\text{h}$.

Mercury, which is a well-known hazardous substance, is present in coal-fired flue gas in the form of elementary mercury (Hg^0), oxidized mercury (Hg^{2+}), and particle-bound mercury (Hg^p) [34]. Existing air pollution control devices in coal-fired boilers can capture mercury. For existing well-equipped coal-fired boilers in Japan, the concentration of mercury near the stack is nearly at the background level. If untreated, it can reach $100 \mu\text{g}/\text{Nm}^3$. It is reported that pulsed EP, similar to plasma treatment, can effectively remove trace elemental mercury from flue gas.

Considering flue gases, NTP direct induced chemical processes are much more

complicated, such as conversions of VOCs to aerosols and CO oxidation. Several references [36–38] are added on the topics.

PM Treatment

Marine Diesel Electrostatic Precipitation

A system for the simultaneous removal of SO_x and PM from marine diesel engines using EP is reviewed [1]. Owing to recent tight regulations related to MARPOL convention Annex VI, which is a regulation determined by the IMO, newly manufactured marine diesel engines should use either low-sulfur fuel or an exhaust gas cleaning system (EGCS), which can reduce the SO_x emission. Most EGCSs use a wet chemical scrubber as the main apparatus. Treatment of a large amount of exhaust gas emitted from marine diesel engines requires extremely large apparatus. For newly manufactured ships, NO_x treatment should also be considered along with SO_x and PM treatment. Fuji Electric Co. has developed an EGCS capable of the simultaneous removal of SO_x and PM.

Figure 15 shows a conceptual diagram of a developed EGCS [39]. One of its characteristics is the EP followed by the seawater scrubber for SO_x removal. The volume of the waste solution of the scrubber can be reduced to avoid the use of an excessively large wastewater treatment system inside the ship. In the system, the flue gas emitted by the diesel engines passes through the EP for dust removal. The EP is energized by a high-voltage power supply with control panels, and the treated flue gas passes through the economizer, where heat exchange between water and gas occurs. Subsequently, the gas is introduced into the SO_x scrubber using seawater to remove SO_x. The SO_x scrubber has a shower-type structure, and the seawater is circulated using pumps. The wastewater is treated using the wastewater treatment apparatus. The seawater is supplied through filters using pumps. The exhaust gas is continuously monitored using gas sensors. A pilot-scale test has been carried out on the basis of this concept.

Plasma Regeneration of DPF for PM Removal

With the recent tightening of IMO environmental regulations [1], there is a growing demand for effective reduction technology for PM, NO_x, and SO_x in the exhaust gas of marine diesel engines. A honeycomb ceramic DPF has been used in diesel vehicles. Although a continuous regeneration system has been realized using oxidation catalysts (that carry out continuous combustion removal of the collected PM while driving the engine), it is challenging to use it in S-containing marine diesel engines because of S poisoning; hence, there is a need to develop new methods.

To establish a DPF regeneration method for marine diesel engines without S poisoning, the results of actual pilot-scale engine bench tests of the nonthermal plasma radical injection method have been reported [18, 40–42].

Pilot-scale plasma regeneration of the DPF for diesel PM removal is reviewed [41]. **Figure 16** shows the experimental device, method, and schematic diagram of the test apparatus, and photograph of the apparatus. The tested engine is a marine diesel generator (Daihatsu Diesel Co., Ltd., Model 5DK–20, 5-cylinder, maximum output = 800 kW), multiple units of which are installed in car carrier vessels, passenger ships, tankers, etc.; it is an auxiliary device that supplies inboard power. Marine diesel oil (MDO, S = 0.075%, amount of heat = 45.4 MJ/kg) is used as the fuel. The exhaust gas flow rate is 1,460 Nm³/h for 25% engine load and 2,530 Nm³/h for 50% engine load.

In **Fig. 16 (a)**, the exhaust gas from the marine diesel engine is branched into two pipes, and around 5% of the total flow is made to pass through the honeycomb-shaped wall-flow type ceramic DPF, whereas the rest is bypassed. The branch flow rate is adjusted using butterfly valves A and B. More than 95% of the PM is trapped by the DPF. The PM trapped in the DPF is burned (DPF regeneration) by injecting O_3 , formed by the plasma ozone synchronizer. The exhaust gas temperature is measured using a temperature sensor, and the upstream and downstream pressure difference of the DPF is measured using pressure sensors, respectively. The reduction in pressure loss, while injecting O_3 , indicates the burning of PM, which is collected in the DPF.

A silent-discharge-type ozonizer ($O_3 = 90$ g/h) is used as the plasma apparatus, and O_3 with a concentration of 4.7% is injected into the upstream DPF. The collected PM is burned by the oxidation of active species, such as O and NO_2 . The device has 10 inbuilt concentric cylindrical silent discharge reactors, and achieves high O_3 concentration by separating oxygen from the atmosphere using PSA equipment and passing it into the reactor.

The experimental results of processing PM are explained. The pressure difference before and after DPF and an example of the time-dependent change of the exhaust gas flow rate during DPF regeneration are shown in **Fig. 17**. The initial flow rate of the exhaust gas branch is set at around 100–200 Nm^3/h . The plasma is turned on while injecting O_3 . The engine load (output) is 50% in the range of 0–300 min, and the exhaust gas temperature is 300°C. The output is 25% in the range of 300–410 min, and the exhaust gas temperature is 320°C. In the range of 410–600 min, the output is 50%, and the exhaust gas temperature is 320°C. According to the experimental results, when the PM collection of plasma is turned off, the pressure difference increases, and the flow rate decreases. However, both are restored by applying plasma and injecting O_3 . Hence, the continuous regeneration of the DPF for marine diesel engines has been successfully accomplished for the first time and various basic reproduction characteristics have been revealed. Under the present conditions, the ozonizer power consumption for the total process is around 5% of the engine power.

Plasma Burner for Diesel PM Removal

Lee et al. reported a DPF regeneration system for diesel engine PM emission using a plasma burner system for actual automobiles [43]. The active regeneration of the DPF is possible using this system. In general, the DPF should be periodically burned (regenerated) to remove PM. In the proposed system, a plasma burner is used for filter regeneration. There are two methods for DPF regeneration: electric-heater and full-flow type diesel burner methods. The plasma burner system avoids the drawbacks of these methods by successively discharging and partially oxidizing the fuel, which produces hydrogen for flame stabilization. The author carried out field tests for over 20,000 km with actual automobiles, and verified the validity of this method. The system comprises a plasma burner followed by diesel oxidation catalysts (DOC) and DPF. The proposed plasma burner was shown to be successful, and is the world's first plasma device that is applicable to commercialized automobile systems. The plasma research group of Korea Institute of Machinery and Materials (KIMM) has contributed toward combustion improvement as well as aftertreatment significantly in the field of plasma application to industries in terms of NO_x treatment for diesel engines, plasma-combined catalyst

treatment, and application to power generation plants with large-scale plasma apparatus.

Direct Plasma for Diesel PM Reduction

Soot elimination and simultaneous NO_x and SO_x reduction in the diesel engine exhaust can be achieved by a combination of discharge plasma and flowing oil film for aftertreatment [44]. The Yao group reported some experimental results on diesel PM removal using uneven DBD reactors [45]. The schematics of the plasma reactor for PM removal are shown in **Fig. 18**. The structure of the uneven DBD reactor has been described; uneven SUS plasma and uneven alumina plates are stacked inside the reactor, and multiple layers are constructed. Experiments were carried out with an actual diesel engine of 3.0 kW. The experimental results of a PM monitor show that the PM from diesel engines can be removed efficiently using the reactor. The energy efficiency was high, typically in the range of 3–10.6 g/kWh at an energy density of 2–16 J/L. Note that this study was carried out through a collaboration with Daihatsu Motor Company, and the plasma treatment was carried out with an actual diesel engine bench.

Carbon Dioxide Treatment

Microwave Plasma Process

Although few large-scale tests have been performed, plasma application has considerable potential for the treatment of CO₂. CO₂ is easily converted into CO, a type of fuel gas. Spencer et al. treated CO₂ dissociation with a 1-kW radio-frequency (RF) plasma source using low-pressure ($\sim 10^{-9}$ Torr) plasma [7]. The apparatus has a double helix antenna electrode driven by 13.56-MHz RF power supply magnetic coils, which enhance the plasma owing to the magnetic field. The concentrations of CO₂ and CO are measured using a residual gas analyzer. Although the maximum volumetric flow rate was 100 sccm (standard cc per minute) in the experiment, scale-up should be considered. The conversion energy efficiency η is the ratio of CO₂ dissociation enthalpy per molecule (= 2.9 eV/molecule) to the actual plasma electrical power density of the plasma. In the experiment, η reached 3%. If η reaches 52% for the aftertreatment of a GTCC electrical power generation plant, the plasma treatment of CO₂ would pay or CO₂ could be recycled with the electrical power generated from the station. Thus, zero CO₂ emission from the GTCC thermal power plant will be theoretically possible and yield significant results. In another study, Rusanov et al. [46] reported a high-efficiency CO₂ conversion experiment with a 2.4-GHz microwave plasma system, operating at a moderate pressure of 50–200 Torr. According to their analysis, the energy efficiency was $\eta = 80\%$, which is an excellent value, confirming the feasibility of the technology.

Gliding Arc Process

Gliding arc discharge can be operated under atmospheric pressure, and higher energy efficiency is achieved for CO₂ conversion. A reactor called GAP (**Fig. 19 (a), (b)**) is tested for CO₂ reduction [47]. The gas flow rates were in the range of 14–40 L/min at 100% CO₂ concentration. The maximum energy efficiency occurred at an *SE* of 0.31 eV/molecule and a flow rate of 27.0 L/min. The results of the GAP can be compared with other discharges. An energy efficiency of 43% for CO₂ dissociation has been achieved experimentally in the GAP reactor at atmospheric pressure.

Surface Discharge Plasma Process Combined with Adsorbent

We present a highly efficient CO₂ reduction technique using an adsorbent and nonthermal plasma flow at the bench scale [48]. The plasma reactor consists of 12 surface discharge elements, which are energized by a 10-kHz bipolar pulsed high-voltage power supply. Molecular sieve zeolite 13X is used as an adsorbent, and placed downstream of the plasma reactor. In the physical adsorption process, approximately 10% CO₂ gas with a flow rate 10 L/min is prepared using a 99.5% CO₂/N₂ cylinder and nitrogen cylinder. It is then introduced into the flow channel, and CO₂ is adsorbed by the adsorbent. After the adsorption process, the circulation flow channel is set, and N₂ plasma flow is generated with a blower. Consequently, CO₂ adsorbed by the adsorbent is desorbed with a higher concentration (currently ~20%) and reduced to CO with high efficiency. The generated CO can be reused as fuel. We evaluate the experimental results by calculating the conversion efficiency of CO₂ to CO and the energy efficiency of the plasma. When the number of experimental repetitions is 5, a maximum CO concentration of 5% and a maximum CO₂ concentration of 20% are achieved. The energy efficiency associated with the conversion of desorbed CO₂ to CO reaches 14% with a plasma power of 300 W. Discussions are carried out by comparing the values with those obtained in other studies on the plasma reduction of CO₂. In the experimental results, a high-energy efficiency of $\eta = 19\%$ is achieved with atmospheric-pressure treatment. The original concentration of CO₂ in the exhaust gas is typically 10%. However, the concentration is increased up to approximately 16% by repeated adsorption/desorption via zeolite adsorbents. As a result, the conversion efficiency increases, and η becomes higher. Combinations of other processes are very promising in terms of improving the energy efficiency, because, in the case of CO₂ concentration using a honeycomb rotor-type adsorbent [49], the CO₂ concentration can be increased from 13.5% up to more than 90%. Future pilot-scale tests are desired with scale-up adsorbent and plasma apparatus.

Dioxin Treatment

Reduction with Pulse Corona Discharge

Dioxins are among the most toxic substances known to human beings. Therefore, it is important to prevent them from diffusing into the environment. Accordingly, the treatment of dioxins has attracted considerable attention. Although particulate dioxins can be removed using a bag filter and an EP, the removal of gas-phase dioxins is difficult. Plasma application is suitable for this purpose. We performed a pilot-scale test for dioxin removal with pulsed corona discharge-induced plasma [50].

Figure 20 shows a schematic diagram of the experimental setup for the pilot plant test. After the flue gas from the garbage incinerator is treated by an EP, a part of the gas—at a maximum flow rate of 5000 Nm³/h—is introduced into the exhaust gas treatment line. After the gas is cooled down to 160–190°C by a gas-gas heat exchanger, it passes through a bag filter. The concentration of PM in the flue gas is reduced to <5 mg/Nm³. In the experiment, NO_x treatment was carried out with PCHP. The gas passes through an NTP reactor, which oxidizes NO to NO₂ and decomposes dioxins simultaneously. Subsequently, the channel is divided, and a sample of the gas at a rate of 50 Nm³/h passes through a Na₂SO₃ chemical reactor in which NO₂ is reduced. The flow rate of the sample gas is controlled with an inverter-controlled fan. The treated gas is released from the stack.

Figure 21 shows the details of the bag filter preceding the NTP reactor. The NTP

reactor is often called a PPCP reactor. The pulsed corona discharge is induced by a nanosecond pulse with a high-voltage power supply (maximum power consumption = 50 kW, electrical efficiency = 80%). There are 22 PPCP reactors located in two rows. Each plasma reactor is of coaxial type, and consists of a stainless cylindrical coil electrode (length = 2 m and diameter = 15 cm) and centered stainless positive wire electrode.

In the waveforms of the pulse high voltage and induced discharge current applied to the NTP reactor, the peak voltage is 110 kV, and the width is 375–1,300 ns. A DC bias voltage of 35 kV is added. The maximum pulse repetition frequency is 1000 pps.

The targeted dioxins to be removed are polychlorinated dibenzo-p-dioxins (PCDDs), polychloride dibenzofurans (PCDFs), and coplanar polychloride bisphenols (PCBs) with chlorine degrees (the number of chlorine atoms in a molecule) of 1–8. Because their concentrations are extremely low (less than 100 ng/Nm³) and difficult to detect, each sampling lasts for 4 h. The dioxins are trapped and concentrated with an adsorbent, the main component of which is a copolymer of styrene and divinylbenzene. The concentrated dioxins are analyzed using a high-resolution gas chromatograph-mass spectrometer. The concentration of the particulate dioxins trapped by the bag filter is analyzed separately and known to be <1 pg-TEQ/Nm³ (TEQ: toxic equivalent). This is a negligible value compared to the dioxins in the exhaust gas. The dioxin removal achieved with this system is the sum of the removals due to the plasma and bag filter. With an applied plasma energy density of 2.9–6.1 Wh/Nm³, the decomposition efficiency for dioxins is 75–84% based on TEQ; the maximum conversion efficiency of NO to NO₂ is 93%.

Reduction with Gliding Arc Discharge

Various dioxin removal techniques have been developed. PCDD/Fs in fly ash from municipal solid waste incinerators can be decomposed in nonthermal plasma in a vortex-shaped gliding arc reactor [51]. The typical operating conditions are voltage of 10 kV, the tangential gas flow rate of 11 L/min, and axial carrier gas flow rate of 2 L/min inside the reactor. The degradation efficiencies of PCDD/Fs are 54.9%, 61.7%, and 66.8% on a mass basis and 60.7%, 73.3%, and 70.1% on a toxicity basis under N₂, air, and O₂ conditions, respectively. After treatment, the morphology of fly ash changes: needle-shaped crystals increase, pores and fragments appear, and high-temperature melting occurs, owing to direct contact with the high-temperature core of the arc. The results are explained tentatively by the creation of reactive intermediates, leading to dechlorination and oxidation of PCDD/Fs, finally producing end products such as CO₂, CO, HCl, and CH₄.

Summary of Updated Energy Efficiency Achievement

Table 1 summarizes the performances of the technologies reviewed in this paper. For the treatment, the energy efficiency defined as a quantity of treated mass per unit of plasma energy in g/kWh of the process should be increased. In general, the energy efficiency decreases as the decomposition efficiency of pollutants increases and increases as the concentration of pollutants increases. Therefore, the target energy efficiency value differs depending on the target pollutant. For the treatment to be commercialized, a minimum treatment efficiency of 1 g(PM)/kWh for PM and 50 g(NO₂)/kWh for NO_x reduction is desired. Accordingly, in our process, i.e., the plasma-combined process, the exhaust gas has not been treated directly. Instead, PM and NO_x are concentrated by

accumulation on a filter or an adsorbent; subsequently, the concentrated pollutants are treated with higher energy efficiency. This method is based on the chemical principle that polluting substances with higher concentrations can be treated with higher energy efficiencies.

Among the test results with scale-up environmental plasma, it is clarified that the following four points are important from the perspectives of commercialization and energy efficiency.

(1) The use of plasma independently in NO_x aftertreatment is not energy efficient, as it requires a large amount of power; achieving energy efficiency in practical terms is difficult, and hybrid processing with catalysts, adsorption, and other chemicals is essential.

(2) The energy efficiency in PM aftertreatment is higher than that in NO_x processing as the initial concentration of PM is high; if the processing is performed by collecting with the DPF or EP, it may be possible to achieve practical energy efficiency.

(3) SO_x removal can be relatively easily performed by spraying an alkaline solution in a scrubber. Although processing only with plasma is difficult, the PPCP is a promising plasma hybrid processing technology.

(4) Because CO₂ treatment has a relatively high concentration in the exhaust gas, the energy efficiency becomes high. Thus, CO₂ removal is very promising for power generation with zero CO₂ emission at an energy efficiency of >55%. Because dioxins have a relatively low concentration in exhaust gases, the energy efficiency becomes low. However, plasma treatment can effectively remove them with high removal efficiency.

Conclusions

This paper reviewed recent studies on the application of scale-up plasma hybrid-exhaust gas treatment technologies. The current performance of the hybrid plasma clean boiler was discussed. Subsequently, a test of marine diesel exhaust gas treatment using radical injection and low-oxygen plasma was demonstrated. The application of this system will influence global environment protection strategies (for automobiles and ships) and promote related research in the future.

Several experimental results suggest that the hybrid treatment of PM is very promising from the viewpoint of energy consumption; currently, other commercial applications for NO_x, SO_x, and CO₂ are somewhat limited. However, the availability of dry De-NO_x for glass melting furnaces is very promising for energy saving, with complete recycling of the glass materials. Other processes can reduce the energy consumption for commercial use.

To continue the use of fossil fuel and biofuel combustors as full-fledged energy sources, there is a growing demand for low-cost, energy-saving exhaust gas treatment of NO_x, SO_x, PM, and CO₂. Plasma technology has considerable potential for cleaning the exhaust gases of coal-fired boilers, where the traditional non-plasma procedure (SCR-EP-FGD) is not adequate. Further CO₂ treatment is an important direction for future work.

In this paper, selected results of technologies in scale-up of plasma reactors for environmental and energy applications are reviewed from the viewpoint of industry applications. References [1, 21, 34] could give complete lists of papers in this research field.

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Figure and Table Captions

Fig. 1 Schematic diagram of an exhaust aftertreatment system for (a) coal-fired power plant with conventional technology along with (b) the comparison under investigation

Fig. 2 Diagram of PCHP for NO_x reduction

Fig. 3 Overall schematic view of the PCHP system with a boiler

Fig. 4 Structure of the electrical discharge section of the plasma reactor in the ozonizer [8]

Fig. 5 Test result of time-dependent NO and NO_x concentrations at MP1 (boiler exit) and MP3 (exit of aftertreatment) during four successive days of operation in firing city natural gas [8]

Fig. 6 Schematic diagram for the simultaneous removal of NO_x and SO_x from the exhaust gas of a glass manufacturing system via PCHP

Fig. 7 4 kg/h plasma ozonizer. (a) Side view of the plasma ozonizer. (b) Plasma reactors. (c) Cross section of plasma reactor

Fig. 8 Principle of the plasma-adsorption combined process

Fig. 9 Photograph of the experimental setup for exhaust-gas De-NO_x aftertreatment with the marine diesel engine system

Fig. 10 Surface discharge tube element of the NTP reactor used for NO_x reduction in the desorption process

Fig. 11 Result of time-dependent NO_x emissions before and after the gas passes through the aftertreatment system for operating cycles 9–12 [16]

Fig. 12 Schematic diagrams of the small-scale test facility for incinerator NO_x emission [19]

Fig. 13 Marine diesel emission control. Experimental, analyzer, and acquisition system setup along with nonthermal plasma unit in engine exhaust gas bypass [27]

Fig. 14 Diagram of pulse corona induced plasma chemical process. EP: electrostatic precipitator; AH: air heater

Fig. 15 Concept of developed marine diesel exhaust gas cleaning system developed inside a ship [39]

Fig. 16 Experimental device, method, and a schematic diagram of the test apparatus for marine DPF regeneration [41]

Fig. 17 Time-dependent change of the exhaust gas flow rate during DPF regeneration [41]

Fig. 18 Structure of the full-scale uneven DBD plasma reactor for diesel PM removal [45]

Fig. 19 High-performance CO₂ reduction plasma reactor (GAP reactor). (a) Side view and (b) GAP discharge in air at atmospheric pressure with exhaust temperature measurement by thermocouple [47]

Fig. 20 Schematic diagram of the pilot-scale experiment for the simultaneous removal of dioxins and NO_x

Fig. 21 Plasma reactor for dioxin control (PPCP reactor)

Table 1 Performance comparisons of the technologies reviewed in the paper