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Degradation of gaseous dioxin-like compounds with dielectric barrier discharges

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ABSTRACT

Developing effective technologies to reduce dioxin emissions has become an important issue in the research and industrial fields. In this study, a dioxin-containing gas stream generating system was applied to evaluate the effectiveness of dielectric barrier discharge (DBD) plasma technology for the destruction of dioxin-like compounds. The results indicate that the destruction efficiencies of dioxin-like compounds achieved with DBD plasma strongly depend on the composition of the simulated gas stream. As the DBD plasma is operated with the simulated gas stream containing 20% water vapor, around 74% PCDDs and 89% PCDFs can be destroyed by DBD plasma. UV, electrons, and OH radicals are generated via the DBD plasma process and react with the dioxin-like compounds in the gas stream. Dechlorination via UV and electrons and decomposition via OH radicals occur at the same time and significantly increase the destruction efficiency of PCDD/Fs in the presence of oxygen and water vapor. Additionally, the total toxicity destruction of dioxin-like compounds with the input energy of 1 kJ increases from 1.47 to 3.06 ng-TEQ_{WHO} as the water vapor is incorporated into the gas stream.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and coplanar polychlorinated biphenyls (co-PCBs) are commonly known as dioxin-like compounds that are listed as environmental hormones. PCDD/Fs and PCBs can be formed in combustion processes in the presence of carbon, chlorine, and catalysts [1,2]. Emission of PCBs originally present in combustion materials is also possible if the combustion temperature is not high enough (<800 °C) for complete destruction [3]. Operating temperature can affect the ratio of PCDD to PCDF formed with different precursors, such as chlorphenoxy radicals formed from chlorophenol [4,5]. In general, dioxin-like compounds are generated during the thermal process, which requires the installation of additional air pollution control devices (APCDs) to reduce emissions and meet regulations [6]. For an activated carbon injection (ACI) system, powder activated carbon (PAC) is injected upstream of the bag filter (BF) and accumulates on the filter bag surface, and flue gases are made to pass through the AC + residual dust layer. Without injecting PAC into the gas streams, most of PCDD/Fs in the vapor phase penetrated through the filter bag, while PCDD/Fs in the solid phase are effectively removed by the BF [7,8]. Although ACI + BF can effectively reduce PCDD/F emissions, Chi et al. [9] indicate it may actually increase the total PCDD/F discharge (including that in fly ash and flue gas) from municipal waste incinerators (MWIs). Another previous study indicates that selective catalytic reduction (SCR) catalysts currently applied to control NO_x are also effective in the decomposition of PCDD/Fs [10]. During the past decade, commercial SCR catalysts have been applied for combined dioxin/NO_x removal. For the effective destruction of PCDD/Fs, a temperature lower than 210 °C might be sufficient in pilot plants; however, flue gas temperatures of 240–260 °C are generally needed for effective PCDD/F destruction in field tests [11]. The flue gas reheating process consumes considerable amounts of energy. For end-of-pipe treatment, ACI + BF is predominantly used for reducing PCDD/F emissions from MWIs. In contrast to the SCR system, the ACI + BF process has some disadvantages. Activated carbon adsorbs PCDD/Fs but does not destroy them, and this physical process only transfers vapor-phase PCDD/Fs to solid-phase PCDD/Fs. Additionally, larger amounts of solid residue that are highly contaminated with PCDD/Fs have to be disposed of with the ACI system [12]. Although catalysts composed of noble metals (such as vanadium and titanium) can effectively decompose and remove PCDD/Fs from flue gas streams, the capital and operating costs of the SCR system are relatively high.

Nonthermal plasma technologies, which are mainly applied for ozone synthesis as firstly developed, have been under extensive investigation for the removal of a variety of pollutants, including NO_x, SO_x, VOCs, and dioxin from gas streams [13,14]. Dielectric barrier discharge (DBD), the mainstream nonthermal plasma used for ozone generation, can be divided into four types based on the reactor geometry: typical DBD, surface discharge, coplanar discharge,

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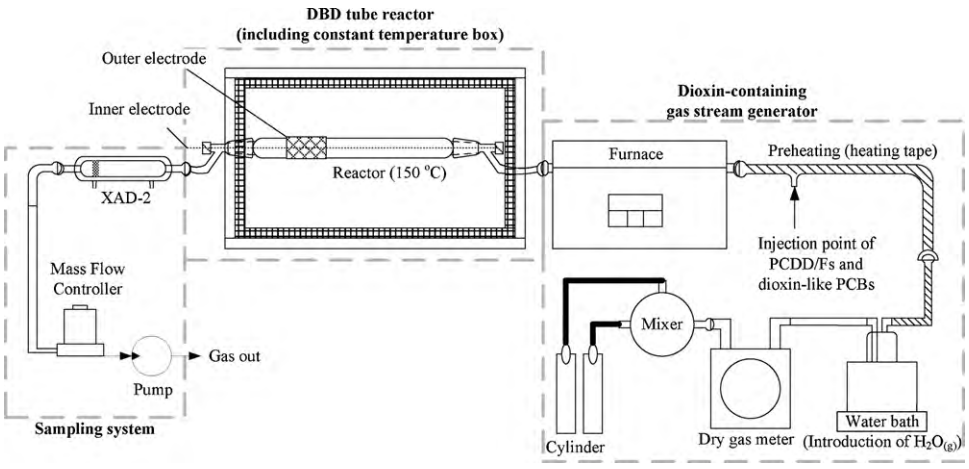

Fig. 1. Schematic diagram of the experimental setup.

and packed-bed discharge. In general, the plasma technology developed for PCDD/F removal is thermal plasma, such as a plasma torch. Fly ash containing high PCDD/F concentration can be melted and decomposed by thermal plasma [15,16]. More recently, a combination of plasma and catalysis has been proposed, and research on this topic has been continuously reported. This approach has the following advantages. Firstly, the working temperature of the catalyst can be substantially reduced as compared to the SCR system. Short-lived (electrons, radicals, and excited species) and long-lived (mainly ozone) active species are beneficial for pollutant removal. Secondly, some unwanted or unfavorable by-products generated from plasma treatment can be converted into less harmful species through catalysis. Based on the above-mentioned viewpoints, a typical DBD reactor was constructed in the present study. In the lab-scale experiment, a gas stream containing stable PCDD/F concentration is needed to evaluate the PCDD/F removal efficiency achieved with the specific control technology. However, PCDD/F-containing gas stored in steel cylinders is not available so far. In this study, an innovative PCDD/F gas stream generating system is adopted for this purpose. Additionally, the influences of oxygen and water vapor contents of the gas streams on PCDD/F and PCB destruction achieved with DBD plasma in a lab-scale reactor are experimentally evaluated.

2. Materials and methods

2.1. Dioxin-containing gas stream generating system

A dioxin-containing gas stream generating system was developed to investigate the effectiveness of the DBD process for dioxin removal. The dioxin-containing gas stream generating system developed consists of a dioxin stock solution injector, a temperature controller, an evaporator, and gas flow rate controllers [17]. The system constructed can stably generate a gas stream with the dioxin concentration ranging from 1.0 to 500 ng-TEQ_{WHO}/Nm^3, while reproducibility tests indicate that the PCDD/F recovery efficiencies are between 93% and 112% [17]. The experimental setup is schematically shown in Fig. 1. With different types of dioxin stock solutions being injected into the system, the distributions of dioxin congeners in the gas stream can be varied. The dioxin stock solution used in this study was prepared by the extraction of fly ash sampled from the bag filter of a Waelz plant [18]. The injected stock solution contained relatively high concentrations of seventeen 2,3,7,8-substituted PCDD/F congeners and twelve toxic dioxin-like PCB congeners. The total mass and toxicity concentration of the dioxin-like compounds, including 29 toxic congeners of PCDD/Fs and PCBs in simulated gas stream, are controlled at 2980 ng/Nm^3 and 300 ng-TEQ_{WHO}/Nm^3, respectively, with a gas flow rate of 2 lpm. The major congeners based on toxicity include 1,2,3,7,8-PeCDD (25%) and 2,3,4,7,8-PeCDF (24%) of PCDD/Fs and 3,3′,4,4′,5-PeCB (1.85%) of PCBs.

2.2. Lab-scale DBD reactor system

Fig. 1 shows the schematic diagram of the lab-scale experimental system developed in this study. It consisted of a dioxin-containing gas stream generator, a DBD reactor, and a sampling system. The inner electrode and outer electrode of the DBD system were made of stainless steel and connected with a power supply. The applied voltage and frequency were controlled at 12 kV and 100 Hz, respectively. The reactor was installed in a cyclic oven to keep it in isothermal condition, and the temperature was controlled by a regulator. To prevent interference caused by plasma reaction, the temperature of the DBD reactor was monitored with an alcohol-in-glass thermometer located at the middle of the reactor. The material of the dielectric was borosilicate glass, and the dielectric constant was 4.0–4.1 [19]. The inner diameter and thickness of the glass tube were 26.8 and 1.6 mm, respectively. The length of the gap was 13.2 mm, and the effective discharge length was fixed at 11.8 cm. Based on the real flue gas condition observed in the Waelz plant, the gas flow rates of the carrier gas, comprising 15% O_2 with N_2, through the reactor were set as 2.0 standard liters per minute (slpm) for the gas hourly space velocity (GHSV) of 2000 h^{-1}. In general, the operating temperature of the DBD reactor is usually set as ambient temperature for ozone generation. Relevant studies [20–22] indicate that DBD reactors could also be operated at a high temperature for the removal of NO_x or SO_x. Destruction of dioxin-like compounds was carried out with a dioxin-containing gas stream generating system, with DBD being operated at atmospheric pressure and 150 °C based on the real flue gas condition observed in the Waelz plant [18].

2.3. Dioxin-like compound collection and analysis

In this study, gaseous PCDD/F and PCB samples were collected by XAD-2 (Fig. 1). For PCDD/F and PCB analysis, the samples were spiked with known amounts of Method 23 (for the PCDD/F samples) and Method 1668A (for the PCB samples) internal standards, respectively, following internal quantification standards. After clean-up procedures, 17 2,3,7,8-substituted PCDD/F and 12 toxic PCB congeners were analyzed with high resolution gas chromatography (HRGC) (Hewlett Packard 6890 plus)/high resolution mass