



## Degradation of gaseous dioxin-like compounds with dielectric barrier discharges

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### ARTICLE INFO

#### Article history:

Received 21 January 2010

Received in revised form 3 June 2010

Accepted 7 June 2010

Available online 11 June 2010

#### Keywords:

PCDD/Fs

Dioxin-like PCBs

DBD plasma

OH radical

### 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<sub>WHO</sub> as the water vapor is incorporated into the gas stream.

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### 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 chlorophenoxy 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<sub>x</sub> are also effective in the decomposition of PCDD/Fs [10]. During the past decade, commercial SCR catalysts have been applied for combined dioxin/NO<sub>x</sub> 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<sub>x</sub>, SO<sub>x</sub>, 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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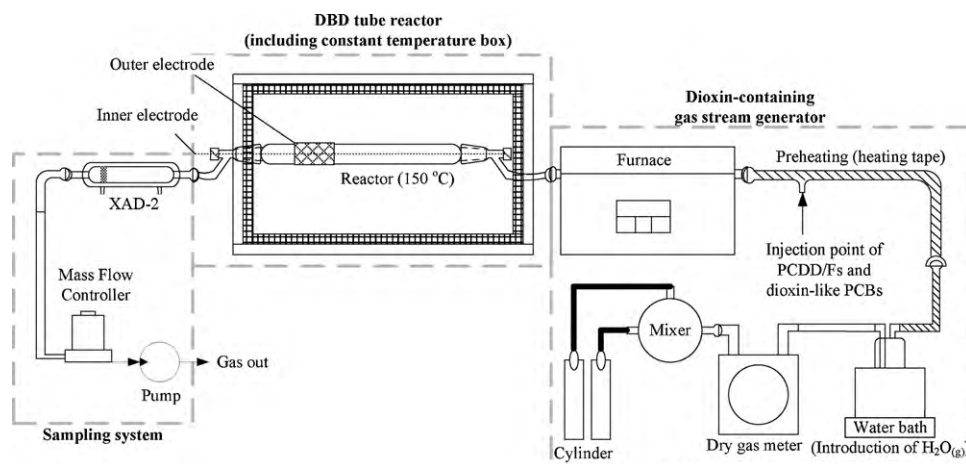


Fig. 1. Schematic diagram of the experimental setup.

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<sub>WHO</sub>/Nm<sup>3</sup>, 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<sup>3</sup> and 300 ng-TEQ<sub>WHO</sub>/Nm<sup>3</sup>, 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<sub>2</sub> with N<sub>2</sub>, through the reactor were set as 2.0 standard liters per minute (slpm) for the gas hourly space velocity (GHSV) of 2000 h<sup>-1</sup>. 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<sub>x</sub> or SO<sub>x</sub>. 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

spectrometer (HRMS) (JEOL JMS-700), which was equipped with a DB-5MS fused silica capillary column (60 m × 0.25 mm × 0.25 μm, J&W). The mean recoveries of the standards for all  $^{13}\text{C}_{12}$ -2,3,7,8-substituted PCDD/Fs and  $^{13}\text{C}_{12}$ -PCBs ranged from 53% to 106% and 47% to 102%, respectively. The recoveries were all within the acceptable 40–130% range set by the U.S. EPA in Method 23 and 1668A. For data analysis, toxic equivalent factors (TEFs) were adopted to compare the potential toxicity of each PCDD/F and PCB congener in a mixture to the well-studied and understood toxicity of 2,3,7,8-TCDD, which was assigned a TEF of unity (1.0). The TEF of each congener present in a mixture was multiplied by the respective mass concentration, and the products were summed to yield the 2,3,7,8-TCDD toxic equivalence (TEQ) of the mixture. In this study, the toxicity concentration of the PCDD/Fs and PCBs was calculated using WHO<sub>98</sub>-TEF values [23].

### 3. Results

To evaluate the effectiveness of DBD plasma in destroying dioxin-like compounds, experimental tests were conducted with a lab-scale reactor to avoid the influence of real complex flue gas composition. The PCDD, PCDF, and PCB destruction efficiencies based on mass and toxicity achieved with DBD plasma are presented in Fig. 2. As the oxygen and water vapor content were controlled at 0% (100% N<sub>2</sub>), the destruction efficiencies of dioxin-like compounds achieved with DBD ranged from 17% to 61% on mass basis and from 22% to 54% on toxicity basis. The toxicity destruction efficiencies of PCDD/Fs were lower than their mass destruction efficiencies. That may be caused by the lower destruction efficiency (34–50%) of lowly chlorinated PCDD/F congeners (higher toxicity) compared with highly chlorinated congeners (55–85%). The destruction efficiencies of PCBs achieved with DBD plasma were significantly lower than those of PCDD/Fs. We considered that dioxin-like PCBs may be generated from deoxygenation of PCDFs or via other reaction paths of PCDD/Fs. Interestingly, the toxicity destruction efficiency of PCDDs was significantly lower than that of PCDFs. This may be attributed to the destruction efficiency of high-toxicity PCDDs (34–35%) being considerably lower than that of high-toxicity PCDFs (41–53%). The toxicity destruction efficiency of dioxin-like PCBs was higher than their mass destruction efficiency because the TEF values of dioxin-like PCBs were irregular with the numbers of chlorine of dioxin-like PCBs. The highest TEF value of the PCBs was 0.1 of 3,3',4,4',5-P5CB, and the second was

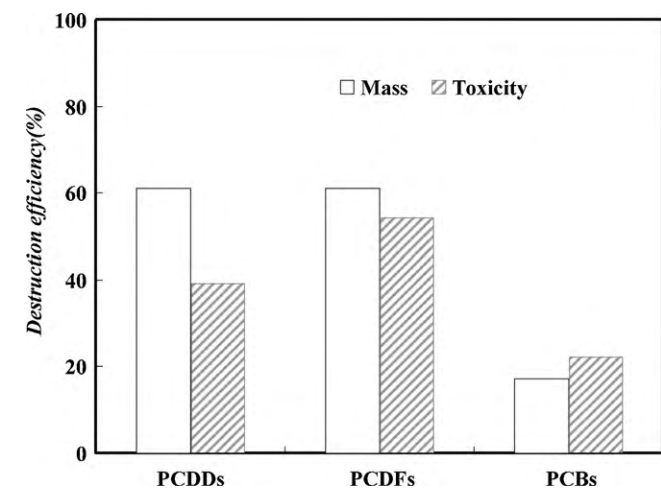


Fig. 2. Destruction efficiency of dioxin-like compounds achieved with DBD plasma [inlet concentration of dioxin-like compounds: 2980 ng/Nm<sup>3</sup> (300 ng-TEQ<sub>WHO</sub>/Nm<sup>3</sup>); SV=2000 h<sup>-1</sup>, testing duration=120 min; operating temperature: 150 °C, carrier gas = N<sub>2</sub>].

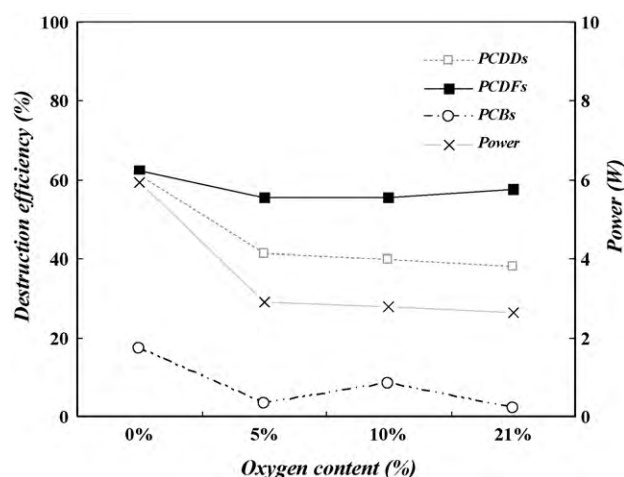


Fig. 3. Destruction efficiencies of dioxin-like compounds achieved with DBD plasma and discharge power at different oxygen contents (inlet concentration of dioxin-like compounds: 2980 ng/Nm<sup>3</sup>; SV = 2000 h<sup>-1</sup>; testing duration = 120 min; operating temperature: 150 °C; carrier gas = N<sub>2</sub>).

0.01 of 3,3',4,4',5,5'-H6CB. Others were lower than 0.001. Therefore, the TEQ concentrations of dioxin-like PCBs were significantly affected by the amount of 3,3',4,4',5-P5CB and 3,3',4,4',5,5'-H6CB. In this case, the destruction efficiencies of 3,3',4,4',5-P5CB and 3,3',4,4',5,5'-H6CB were 22% and 43%, respectively, and the toxicity destruction efficiency of dioxin-like PCBs was higher than their mass destruction efficiency. To promote the destruction efficiency of dioxin-like compounds and to better understand the major pathways leading to the destruction, the compositions of the simulated flue gases were adjusted. Moreover, mass destruction efficiency is used in subsequent discussions and figures because the toxicity destruction efficiency affected with the TEF value was too complex to clearly understand changes in dioxin-like compounds achieved with DBD plasma.

Fig. 3 shows the comparison of dioxin-like compound destruction efficiency achieved with DBD plasma and power consumption at different oxygen contents, with N<sub>2</sub> as the carrier gas. As the oxygen content of the gas stream was increased from 0% to 21%, the discharge power of the DBD plasma system decreased from 5.9 to 2.6 W. This trend is similar to that reported by McLarnon and Penetrante [24]. The destruction efficiencies of dioxin-like compounds decreased from 61% to 38% of PCDDs, from 62% to 58% of PCDFs, and from 17% to 2% of dioxin-like PCBs with an increase in oxygen content. The destruction efficiencies of dioxin-like PCBs achieved with DBD plasma are significantly lower than those of PCDD/Fs and even lower than 3% as the oxygen content was controlled at 21%. The decreasing trends of the destruction efficiencies of dioxin-like compounds may have been affected by the lower discharge power with the increase in oxygen content within the DBD plasma system. Fig. 4 presents the destruction efficiencies of the PCDD/F congeners achieved with DBD plasma at different oxygen contents. As the oxygen content of the gas stream was controlled at 0%, there was no significant variation in the destruction efficiencies between PCDD and PCDF congeners achieved with DBD plasma. However, a significantly decreasing trend in the PCDF destruction efficiency was observed with an increase in oxygen content. Relevant studies [25,26] indicate that the major mechanism leading to PCDD/F destruction with a catalyst is dechlorination. Along with the destruction of PCDD/Fs with DBD plasma, highly chlorinated PCDD/F congeners are transformed to lowly chlorinated PCDD/F congeners. A previous study [27] indicates that lowly chlorinated PCDD/F congeners are presumably formed via successive dechlorination of highly chlorinated congeners. Therefore, the destruction

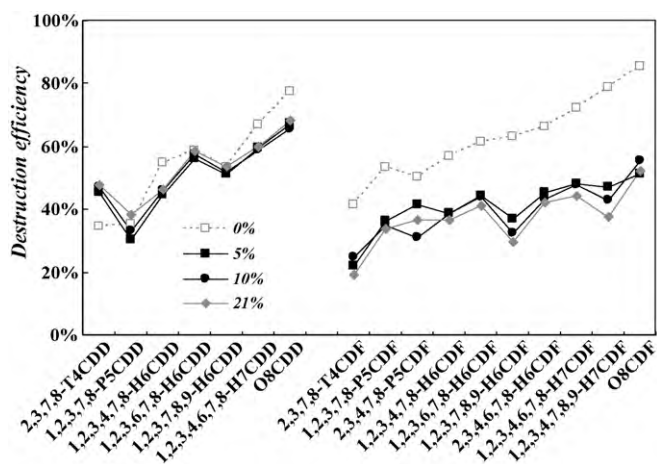


Fig. 4. Destruction efficiency of PCDD/F congeners achieved with DBD plasma at different oxygen contents.

efficiency of PCDD/Fs achieved with DBD plasma increases with an increase in the chlorination level of the congeners.

Fig. 5 compares the dioxin-like compound destruction efficiency and discharge power achieved with DBD plasma at different water vapor contents, with air as the carrier gas. As the water vapor content was increased from 0% to 20%, the discharge power of the DBD plasma system was observed between 2.4 and 3.7 W. With the existence of water vapor, the discharge power of DBD was slightly lower than the results obtained with different oxygen contents (2.6–5.9 W). However, the PCDD/F destruction efficiencies achieved with DBD plasma in the presence of water vapor were significantly higher compared with the case without water vapor. As the water vapor content was increased from 0% to 20%, the PCDD and PCDF destruction efficiencies based on mass concentration increased from 38% to 74% and 58% to 89%, respectively. Although the PCDD and PCDF destruction efficiencies achieved with DBD plasma at 20% water vapor were significantly increased, the PCB destruction efficiencies achieved with DBD plasma were still low ( $\leq 25\%$ ). Especially, the PCB destruction efficiency was 1.5% as the water vapor content was 10%. Fig. 6 shows the destruction efficiencies of the PCDD/F congeners achieved with DBD plasma at different water vapor contents. In the absence of water vapor, the destruction efficiencies of the PCDD/F congeners achieved with

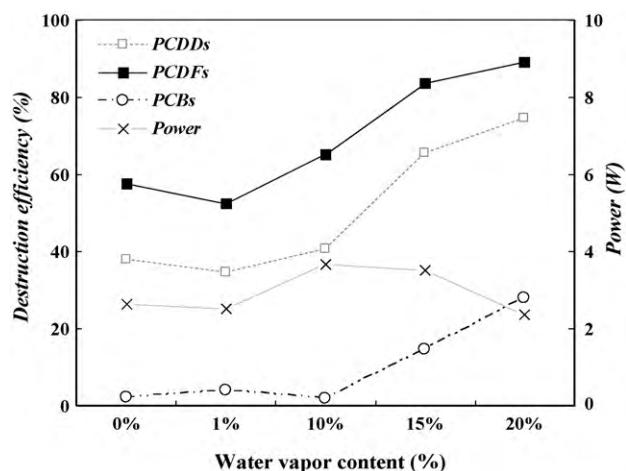


Fig. 5. Destruction efficiencies of dioxin-like compounds achieved with DBD plasma and discharge power at different water vapor contents (gas stream:  $O_2 = 21\%$ ; inlet concentration of dioxin-like compounds:  $2980 \text{ ng/Nm}^3$ ;  $SV = 2000 \text{ h}^{-1}$ ; testing duration = 120 min; operating temperature:  $150^\circ\text{C}$ ).

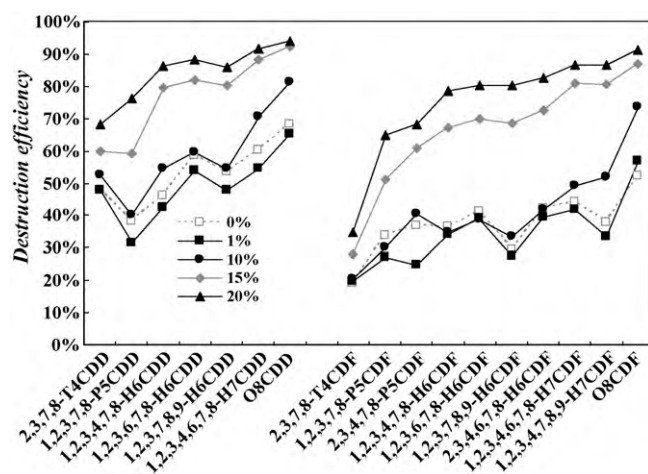


Fig. 6. Destruction efficiency of PCDD/F congeners achieved with DBD plasma at different water vapor contents.

DBD plasma ranged from 19% to 68%. As the water vapor content was increased to greater than 10%, a significant increase in the destruction efficiency of the PCDD/Fs was observed. The OCDD and OCDF destruction efficiencies achieved with DBD plasma were even higher than 90% as the water vapor content was controlled at 20%. However, the destruction efficiency of lowly chlorinated congeners (especially TCDF) was still low ( $\leq 35\%$ ). Similar to the results presented in Fig. 4, the destruction efficiencies of the PCDD/F congeners achieved with DBD plasma increased with an increase of chlorination in the presence of water vapor.

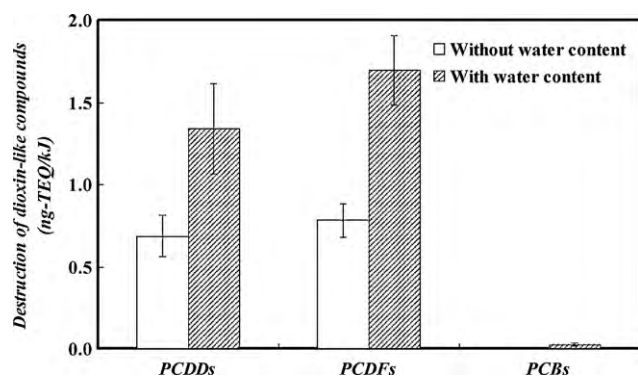
#### 4. Discussion

The results obtained from the lab-scale experiment indicate that the destruction efficiencies of dioxin-like compounds achieved with DBD plasma strongly depend on the gas composition of the simulated gas stream. Without the existence of oxygen and water vapor in the gas stream, the destruction efficiencies of dioxin-like compounds achieved with DBD plasma ranged from 17% to 61%. As the oxygen content was increased from 0% to 21%, the destruction efficiencies of dioxin-like compounds were even reduced to 3–58%. Compared with other dioxin control technologies [16], the destruction efficiencies of dioxin-like compounds achieved with DBD plasma were relatively lower than those achieved with activated carbon adsorption or catalytic decomposition. The significantly lower destruction efficiency of dioxin-like PCBs achieved with DBD plasma may be attributed to the fact that PCBs were probably regenerated from the dechlorination of non-toxic congeners of highly chlorinated PCBs or the deoxygenation of PCDFs [28]. In a DBD reactor, UV, electrons ( $e^-$ ), and free radicals (such as OH radicals) are generated and react with dioxin-like compounds. For the oxygen reaction,  $O(^3p)$  and  $O(^1D)$  are the dominant species. For water vapor reaction,  $OH^\bullet$ , H, and O are the dominant species, and  $O(^1D)$  can react with  $H_2$  or  $H_2O(g)$  to form OH radicals [29]. Previous studies indicate that OH radicals are more reactive than H radicals in reacting with chlorophenol [30,31]. Therefore, the PCDD/F destruction efficiency achieved with DBD in the presence of water and oxygen was higher than in the case without water vapor. Around 74% PCDDs and 89% PCDFs based on mass can be destroyed as the water vapor content was 20%. In general, highly chlorinated PCDD/F congeners are of more stable structures compared with lowly chlorinated congeners [32,33]. However, from the results presented in Figs. 4 and 6, the PCDD/F destruction efficiencies achieved with DBD plasma increased with increasing chlorination. This result can be explained by different

**Table 1**  
Total PCDD/F destruction efficiencies with different gas parameter.

Oxygen content	Destruction efficiency (%)		Water content	Destruction efficiency (%)	
	Mass	Toxicity		Mass	Toxicity
0%	61.2	47.9	0%	43.1	39.0
5%	44.9	38.9	1%	39.3	33.3
10%	43.9	37.1	10%	47.0	40.9
21%	43.1	39.0	15%	70.1	61.9
			20%	78.1	72.6

mechanisms of reactions via electrons, OH radicals, and UV. For OH radicals, Sun et al. [34] indicate “adducting and ring-opening” and “ring-opening and adducting” as the two main mechanisms of PCDD degradation. Mhin and Balasubramanian [35] indicate that addition is more significant than substitution on account of higher energy degrees calculated by the density functional theory. On the other hand, the path of “adducting and ring-opening” which has less reaction energy and transition state than “ring-opening and adducting” was also proven [34]. Katsumata et al. [36] also propose the mechanism of PCDD/Fs reacting with OH radicals. With UV and electrons, the C–Cl bond was subject to destruction and formation of the C–H bond (dechlorination) [14,37]. These reactions compete with each other, resulting in a specific destruction efficiency. The reactions leading to PCDD/F destruction were significant because the mass destruction efficiency of the PCDD/Fs was greater than 70% with 20% water content. However, the destruction efficiencies of lowly chlorinated congeners were lower than those of highly chlorinated congeners because the former were formed by dechlorination of highly chlorinated congeners. This result is better explained by the difference between total mass and toxicity destruction efficiencies. Table 1 indicates that the total PCDD/F destruction efficiencies based on mass were always higher than those based on toxicity because lowly chlorinated congeners were of higher TEF values. The PCDD/F destruction efficiency was significantly increased with an increase in water content. Therefore, “adducting and ring-opening” with OH radicals for PCDD/Fs may be more significant than dechlorination with UV and electrons. To better investigate the effect of water vapor on PCDD/F destruction achieved with DBD plasma, Fig. 7 presents the toxicity destruction of dioxin-like compounds based on the energy consumption of DBD plasma as the water vapor contents were controlled at 0% and 20%, respectively. Based on 1 kJ energy input, 0.69 ng-TEQ<sub>WHO</sub> PCDDs, 0.78 ng-TEQ<sub>WHO</sub> PCDFs, and 0.001 ng-TEQ<sub>WHO</sub> PCBs can be decomposed by DBD plasma in the absence of water vapor. As 20% water vapor was incorporated into the DBD plasma system, 1.34 ng-TEQ<sub>WHO</sub> PCDDs, 1.69 ng-TEQ<sub>WHO</sub> PCDFs, and 0.03 ng-TEQ<sub>WHO</sub> PCBs can be decomposed for the same amount of energy input. The total toxicity destruction of dioxin-like compounds with the input



**Fig. 7.** Destruction of dioxin-like compounds achieved with DBD plasma based on energy consumption [water vapor contents were 0% (without) and 20% (with)].

energy of 1 kJ increased from 1.47 to 3.06 ng-TEQ<sub>WHO</sub> as water vapor was incorporated into the gas stream. The existence of water vapor in the DBD reactor significantly enhanced the destruction efficiencies of dioxin-like compounds. The water vapor contents in real flue gases of MSWIs range from 15% to 20% and OH radicals can be easily generated with DBD plasma. Effective OH• generation is favorable for removing dioxin-like compounds via DBD reactor. However, the composition of real flue gas is more complex than simulating gas in the laboratory scale model and other components, such as HCl, SO<sub>2</sub>, NO<sub>x</sub>, particle, hydrocarbons may exist. Their influences on the formation of highly active species, are unknown, and need to more study for understanding step by step.

## 5. Conclusions

Previous study indicates that activated carbon injection only transfers gaseous PCDD/Fs to fly ash and would make ash disposal even more complicated. In addition, decomposition of dioxins by a catalyst should be operated with a gas temperature above 200 °C for effective gaseous PCDD/F removal. The flue gas reheating process consumes a considerable amount of energy. Therefore, developing effective techniques for controlling PCDD/F emission have become an important issue in the research and industrial fields. In this study, the destruction efficiency of PCDD/F compounds achieved with DBD plasma reached 70% as the water vapor content in simulated gas was controlled at 20%. Additionally, the operating temperature of the DBD plasma system applied in this study was controlled at 150 °C. This temperature window was close to the real flue gas temperature measured at the end-of-pipe of various APCDs. Existence of water vapor in a DBD reactor significantly improves the energy utilization efficiency in destruction of dioxin-like compounds. DBD plasma system may serve as an alternative technology for PCDD/F removal after the particle removing devices in the MWIs.

## Acknowledgements

The authors gratefully acknowledge the financial supports provided by the National Science Council (NSC-94-2211-E-008-040). The authors also greatly appreciate Dr. H.M. Lee (Physics Division, Institute of Nuclear Energy Research) for valuable discussion.

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