



Destruction of PCDD/Fs by gliding arc discharges

YAN Jian-hua¹, PENG Zheng¹, LU Sheng-yong^{1,*}, DU Chang-ming², LI Xiao-dong¹,
CHEN Tong¹, NI Ming-jiang¹, CEN Ke-fa¹

1. State Key Laboratory of Clean Energy Utilization, Institute for Thermal Power Engineering, Zhejiang University,
Hangzhou 310027, China. E-mail: yanjh@cme.zju.edu.cn

2. Environmental Science and Engineering, Sun Yat-Sen University, Guangzhou 510275, China

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Abstract

PCDD/Fs have become a serious issue because of their toxicological effects and associated adverse health implications. In this study, the gliding arc plasma was tested for treatment of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), which were synthesized from pentachlorophenol in atmospheric condition at 350°C with or without the catalysis of CuCl₂. From the experiment, we found that the destruction efficiency of PCDD/F homologues after gliding arc discharge ranged from 25% to 79%. This result demonstrates that gliding arc plasma is an effective technology to decompose PCDDs/Fs in flue gas. A plausible degradation mechanism for PCDD/Fs by gliding arc was discussed. Finally, a multistage reactor structure of gliding arc was proposed to upgrade removal efficiency for PCDD/Fs.

Key words: PCDD/Fs; destruction; gliding arc discharges, multistage reactor

Introduction

Since polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) were discovered in the flue gases and fly ash of municipal solid waste incinerators (MSWIs) in 1977 (Olie *et al.*, 1977), PCDD/Fs have become a serious issue in many countries, because of their toxicological effects and associated adverse health implications. By means of upgraded air pollution control devices (APCDs) and using activated carbon injection (ACI) for removing PCDD/Fs, the PCDD/F emission from MSWIs would keep the emission limit of China (1 ng I-TEQ/Nm³). However, PCDD/Fs are merely transferred from flue gas to fly ash via the treatments of APCDs, which are still required further procedures to avoid the harmful effects on environment, such as safe landfill, melting, cement solidification and etc. In addition, the MSWIs adopted with ACI cannot effectively decrease the total PCDD/F emission (including those in stack gas and ash). Selective catalytic reduction (SCR) is another important method for the simultaneous reduction of both PCDD/Fs and NO_x from incineration processes with satisfied efficiency (Chang *et al.*, 2007). Generally, SCR device locates behind of particulates matter control device such as (ESP, bag filter, wet scrubber) to avoid poisoning caused by particulates, the clean flue gas then enter SCR

reactor after which is reheated to the SCR operational temperature range of 220–290°C. The defects of SCR are easy poisoning and high cost for catalysts.

Plasma technology is a new choice for decomposing PCDD/Fs, of which two very different kinds of plasma are generally used for PCDD/Fs disposal, i.e. thermal and non-thermal plasma. Thermal plasma was mainly adopted to melt fly ash into slag, which can be utilized as recycled construction material. The main drawbacks of thermal plasma are high energy consumption and complicated electrode structure, which are not suitable for flue gas treatment. An alternative for plasma processing is the non-thermal one. Silent, glow, corona, short pulse, electrical discharges are directly produced in the processed gas, mostly under low pressure. Gliding arc is a new technology of non-thermal plasma. In recent years, a number of researchers are paying increasing attention on this new technology for environmental protection. It was demonstrated that gliding arc plasma efficiently destructed volatile organic compounds (VOCs) (higher than 90%), NO_x, SO_x (Czernichowski *et al.*, 1995). The research of Yan *et al.* (2005, 2006) indicated that phenol in solution can be degraded by gas-liquid gliding arc discharge. Meanwhile, Du *et al.* (2006) found PAHs and soot in flue gas can be destructed by gliding arc discharge. As aromatic compound succeeded to degrade in aqueous or gas phase, PCDD/Fs are supposed to be decomposed by this technology. It was until now no reports on the application of treatment of PCDD/Fs by gliding arc discharge.

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E-mail: lushy@zju.edu.cn

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In this article, gliding arc plasma is applied to process PCDD/Fs in flue gas, whereas PCDD/Fs is synthesized in atmospheric condition at 350°C with or without the catalysis of CuCl₂. The effectiveness of gliding arc plasma on the toxic substance is further confirmed. The basic knowledge in respect to the plasma evolution during gliding arc discharge and destruction mechanism for PCDDs/Fs was discussed in detail. Finally, a multistage reactor structure of gliding arc was proposed to upgrade removal efficiency for PCDD/Fs. The purpose of this work was to demonstrate the effectiveness of gliding arc plasma on the destruction of PCDD/Fs in simulated flue gas, which can be further applied in PCDD/F treatment in flue gas at an industrial scale.

1 Materials and methods

The schematic diagram of experimental setup is shown in Fig. 1. PCP (pentachlorophenol; China, analytical grade) powder mixed with CuCl₂ (China, purity > 98%) and sea sand were placed in a ceramic plug and covered with some quartz sand which has been baked for 2 h at 800°C. Then, the ceramic plug is pushed into the mid-place of the quartz tubular furnace, 50 cm in length and 2 cm in diameter. The dry air set at 300 ml/min induces into quartz tubular furnace. A proportional integral derivation (PID) temperature controller was employed to adjust the reacting zone temperature. XAD-2 resins and toluene in ice bath absorbed PCDD/Fs from the flue gas. The reactor system was rinsed with toluene and acetone to clean the inner surface of tube and pipeline, and the tube was heated at 600°C with dry air for 10 min between the individual runs.

All experimental reaction runs were conducted at 350°C for 30 min. There were a lot of researches on the optimum temperature of precursor formation due to the difference of precursors, reaction time or experiment apparatus (Stanmore, 2004; Altwicker, 1996); however, the general view for the temperature window is 300–400°C. Our previous experiments indicated that 350°C was the best temperature for the PCP catalyzed by CuCl₂ to produce PCDD/Fs.

The structure of gliding arc reactor is illustrated in Fig. 2. The interior pipe was made from a ceramic tube of inner

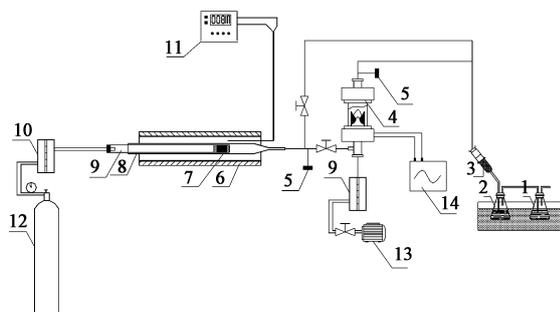


Fig. 1 Experimental setup of discharge on PCDD/Fs by gliding arc plasma (not to scale). (1, 2) toluene; (3) XAD-2 resin; (4) gliding arc reactor; (5) thermal couple; (6) tubular furnace; (7) ceramic-plug; (8) quartz tube; (9) handspike; (10) flow meter; (11) control panel; (12) dry air; (13) air compressor; (14) power supply of A.C.

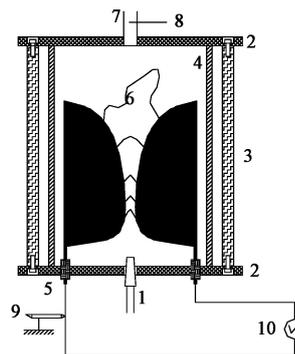


Fig. 2 Scheme of interior structure of gliding arc reactor. (1) nozzle; (2) flange; (3) stainless steel pipe; (4) ceramic pipe; (5) knife shape electrode; (6) discharging zone; (7) outlet; (8) thermal couple; (9) grounding; (10) power supply of A.C.

diameter 100 mm and total volume 2.35 L. The upper and bottom flange of the reactor made with Teflon, where two knife electrodes made of stainless steel were symmetrically disposed on the bottom flange. The flue gas discharged from tubular furnace joint with carrying gas was injected into the discharging zone of reactor through a nozzle of inner diameter 1 mm. The temperature of flue gas before and after gliding arc discharging was measured by thermal couple (Fig. 2). The operational condition of gliding arc reactor is given in Table 1. When the electrodes are raised to the assigned voltage (10 kV), an arc form between the electrodes. The airflow blows this arc, which glides along the electrodes until it is remaining.

Table 1 Operational conditions of gliding arc reactor

Parameter	Value
Power frequency (Hz)	50
Carrier gas flow rate (L/min)	2.2 (air)
Narrowest electrode gap (mm)	2.0
Length of electrode (mm)	150
Maximum voltage (kV)	10

Each sample was spiked by 10 µl five ¹³C isotope internal standards (¹³C-2,3,7,8-TCDD, ¹³C-2,3,7,8-TCDF, ¹³C-1,2,3,6,7,8-HxCDD, ¹³C-1,2,3,4,6,7,8-HpCDF, ¹³C-OCDD) and then extracted by 250 ml toluene for 24 h (4–5 circulations per hour). The extract was concentrated to 1–2 ml by rotary evaporation. The concentrated solution, which has to be purified by multistage chromatography columns, i.e. acidic/alkaline silica gel column, acidic alumina column and another small acidic alumina column. The cleaned-up elute was kept in clean beaker and concentrated to 1–2 ml, then transferred into a centrifugal tube and gently blown to dry by high purity nitrogen. Added 10 µl recovery standards (¹³C-1,2,3,4-TCDD; ¹³C-1,2,3,7,8,9-HxCDD) to the dry centrifugal tube and vibrated the tube using ultrasonic equipment for 15 min. ¹³C-1,2,3,4-TCDD is used to calculate the amount of tetra-penta CDD/Fs, ¹³C-1,2,3,7,8,9-HxCDD for hexa-octa CDD/Fs.

All analyses were performed on a low resolution Finnigan Voyager mass spectrometer (LRMS) with a trace 2000 high resolution gas chromatograph (HRGC). Chro-

matographic separations were carried out on a 60-m DB-5 silica-fused capillary column with internal diameter of 0.25 mm and a stationary phase film thickness of 0.25 μm . The temperature program for GC oven was: initial temperature 100°C, held for 2 min; 100–200°C at 25°C/min; 200–280°C at 3°C/min; 280°C held for 20 min. Carrier gas: Helium (99.999%), 1 ml/min. Splitless sample injection. Mass spectrum condition: electron impact ionization 70 eV; electron multiplier voltage 420 V; ion source temperature 220°C; interface temperature 250°C; SIM (selected ion monitoring mode). All the isotope standards were purchased from Wellington laboratories, Canada or Cambridge Isotope Laboratory, USA. The toxicity of the sample is presented in terms of PCP weight using TEF in USEPA method 8280B (USEPA method 8280B, 1998).

2 Results and discussion

Isotope standards including sample, internal and recovery standards were added in all experiment samples. The recovery ratio of isotope standards varied from 60%–120%, which showed acceptable reliability of the series of experiments according to USEPA Method 8280B. The formation of PCDD and PCDF without and with gliding arc discharge is shown in Table 2.

T1 was conducted as a blank experiment for reference, which indicated: (1) the process of gliding arc discharge is PCDD/Fs free; (2) the existing PCDD/Fs in background do not interfere the conclusion drawn by following experiments.

In our study, two sets of experiments were designed to synthesis of PCDD/Fs, in which T2 and T3 were catalyzed with CuCl_2 , in comparing to T4 and T5 without catalysis of CuCl_2 . From T2 to T5, generally, the yield of PCDDs was much higher than that of PCDFs, and the yield of higher chlorinated homolog (OCDD) was more than lower chlorinated ones, and PCDD/F yield of T2 and T3 under catalysis was considerably higher than that of T4 and T5 without catalysis. Specially, T2 and T3 were characterized that tetra-octaCDD/F homologues were all detected, while, TCDD, PeCDD, PeCDF, HxCDF and HpCDF were not detected in both T4 and T5 without catalysis of CuCl_2 . Similar result for generation of PCDD/Fs by PCP were also reported in the research of Chen *et al.* (2004). The previous studies (Altwicker, 1996; Hell *et al.*, 2000) generally agreed with the formation mechanism of PCDD/Fs that the PCDDs are more preferred to be generated from precursors than PCDFs.

2.1 Degradation of PCDD/F homologue

The content of PCDD/Fs under no discharge and discharge have been summarized in Table 2. From both types of experiment, we found that all PCDD/F homologues were degraded in different extent by gliding arc discharge ranged from 25% to 79% (Table 3). Generally, the degradation efficiencies of T3 for overall homologues were observed slightly higher than that of T5, and the degradation efficiencies for OCDD and OCDF were significantly higher than the other lower chlorinated homolog in both T3 and T5. For T3, the degradation efficiency of 64% and 62% were obtained in respect to the reduction of total concentration and TEQ concentration, in comparing to 62% and 61% for T5.

Table 3 Comparison of PCDD/F homolog yield (ng) without and with gliding arc discharge

	T1	T2	T3	T4	T5
TCDF	0.08	133.54	63.07	22.80	17.05
PeCDF	ND	35.71	14.53	ND	ND
HxCDF	ND	6.94	ND	ND	ND
HpCDF	ND	113.40	49.15	ND	ND
OCDF	4.12	3372.96	699.57	334.62	152.43
TCDD	ND	32.51	17.92	ND	ND
PeCDD	ND	41.82	13.89	ND	ND
HxCDD	ND	213.24	64.76	12.14	8.45
HpCDD	3.99	641.85	359.49	127.72	90.81
OCDD	0.78	38816.51	14134.39	17128.11	6356.71

ND: no detected; T1: blank test; T2, T3: PCDD/F synthesized with CuCl_2 and T4, T5: without CuCl_2 .

2.2 Gliding arc discharge in the geometry

The process of gliding arc discharge in two knife electrode geometry is shown in Fig.3, which is mainly consisted of three phases (Alexander *et al.*, 1999) as: the high voltage electric field initially break down the flue gas and air between the two electrodes, which begins the cycle of the gliding arc evolution in first stage; then the equilibrium stage as phase B takes place after formation of a stable plasma channel, the final stage of non-equilibrium begins when the length of gliding arc exceeds its critical value, as a result, the discharge plasma rapidly cools down and there is stepwise ionization; after the decay of the non-equilibrium discharge, there is new break-down at the shortest distance between electrodes and cycle repeats.

In this process, free electrons, UV, O_3 , H_2O_2 and radicals (O, OH, etc.) are generated and accelerated by gliding arc plasma and obtain enough energy to cause inelastic collision, they will transfer all or part of its kinetic energy to PCDD/F molecules with which they have collided,

Table 2 PCDD/F yield without and with gliding arc discharge

No.	Reactant	Gliding arc discharge	Σ PCDD (ng)	Σ PCDF (ng)	I-TEQ (ng)	Chlorine degree
T1	Sea sand + $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	Yes	1.70	4.23	0.006	7.42
T2	Sea sand + PCP+ $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	No	39713.43	3662.54	49.79	7.95
T3	Sea sand + PCP+ $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	Yes	14590.46	826.32	18.80	7.94
T4	Sea sand + PCP	No	17267.98	357.42	19.06	7.98
T5	Sea sand + PCP	Yes	6455.96	169.48	7.44	7.68

For T1–T5, sea sand: 1.0 g; for T2–T5, PCP: 70 mg; for T1–T3, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$: 1.0 g.

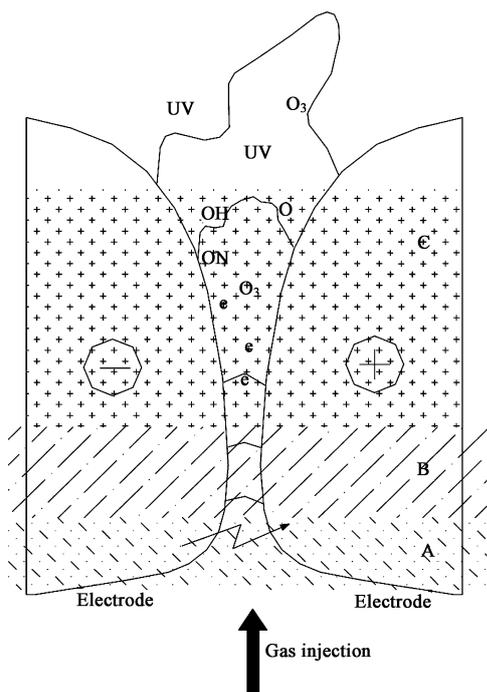


Fig. 3 Gliding arc discharge. A: flue gas and air break-down phase; B: equilibrium heating phase; C: non-equilibrium reaction phase (Alexander *et al.*, 1999).

resulting in a change to the PCDD/F molecules such as ionization, dissociation or excitation. Gliding arc plasma simultaneously discharges UV ray to dissociate the C-Cl bond in PCDD/F molecule. Thus, both above electrical destruction and photoelectric effect jointly decompose PCDD/Fs.

2.3 PCDD/F destruction mechanism

As air in atmospheric condition is utilized in this study, moderate level of moisture is contained in it. Major composition of carrier gas is given as: O₂, N₂, H₂O. Electron and its collision with broad energy distribution are generated in plasma condition, consequently, the energy transfer and various types of elementary reactions such as excitation, ionization, dissociation and etc. (Pignolet *et al.*, 1990; Peyrous *et al.*, 1989) will occur to induce a series of chemical oxidizing reaction in multiphase. Major reactions occurring in gliding arc discharge are given in Fig.4.

PCDD/F molecular exposed in strong oxidized atmosphere in discharging field can be destroyed by UV

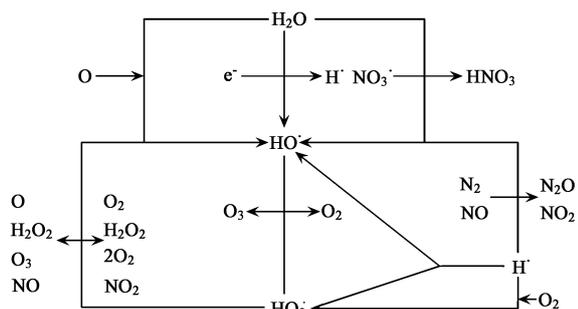


Fig. 4 Reaction circulation of gliding arc discharge.

illumination and radical attack as shown in Fig.5, which may finally be oxidized to CO₂, CO, H₂O, HCl, etc. Photolysis by UV is generally considered to benefit to the break of the C-Cl bond, and instead the formation of C-H bond occurs. This reaction process may finally cause the PCDD/F molecular transfer to non-chlorine structure (Fig.5). In gliding arc discharge, both of the electrical destruction and photoelectric effect simultaneous exist. When applied with enough electrical energy, a further destruction with radicals will no doubt occur on the non-chlorine benzene rings as shown in Fig.6, and form CO₂ or CO as mentioned by Zhou *et al.* (2003).

2.4 Multistage reactor of gliding arc

The effectiveness of destruction of PCDD/Fs by gliding arc discharge is confirmed in our work, however, the destruction efficiency is not yet satisfied to meet require-

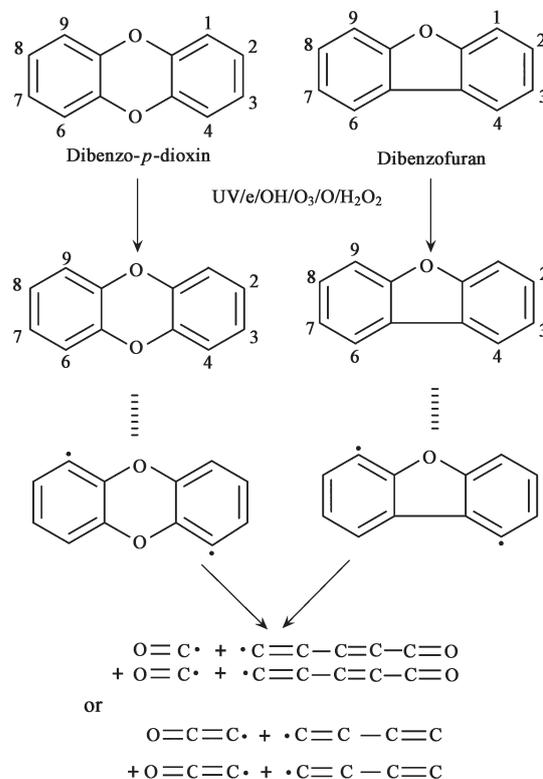


Fig. 5 Typical destruction of PCDD/F molecule due to UV and radical attack.

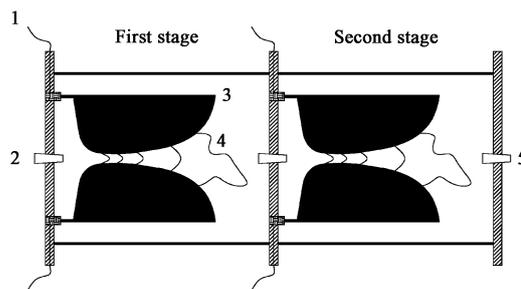


Fig. 6 Schematic of a multistage reactor of gliding arc. (1) power supply of A.C; (2) nozzle and flange; (3) knife shape electrode; (4) discharging field; (5) outlet.

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ment in industrial application. This technology can be optimized in many aspects such as the structure of reactor and operational parameter as (types of carrier gas, power supply, etc.). The tentative plan of multistage reactor is initially proposed by Du (2006) as Fig.6, which can be a feasible way to upgrade the destruction efficiency.

3 Conclusions

The PCDD/Fs in simulated flue gas of bench scale has been treated by gliding arc discharge. The effect of gliding arc discharge on the destruction of PCDDs/Fs as well as destruction mechanism can be summarized as follows.

Destruction efficiencies of PCDD/F homologues via gliding arc discharge ranged from 25%–79%, generally, 64%, 62% in regard to the reduction of total concentration and 62%, 61% in regard to TEQ concentration were obtained in gliding arc treatment.

The destruction mechanism described in this paper provides a reasonable explanation for the process, including: chemical kinetic model of reactants and intermediates in gliding arc discharge; destruction pathway of the PCDD/Fs.

Finally, a multistage reactor of gliding arc was proposed to upgrade the destruction efficiency for PCDD/Fs.

Appendix

Abbreviate	Full name
PCDDs	Polychlorinated dibenzo- <i>p</i> -dioxins
PCDFs	Polychlorinated dibenzofurans
TCDD	Tetrachlorinated dibenzo- <i>p</i> -dioxins
PeCDD	Penta-chlorinated dibenzo- <i>p</i> -dioxins
HxCDD	Hexa- chlorinated dibenzo- <i>p</i> -dioxins
HpCDD	Hepta- chlorinated dibenzo- <i>p</i> -dioxins
OCDD	Octa- chlorinated dibenzo- <i>p</i> -dioxins
TeCDF	Tetra-chlorinated dibenzofurans
PeCDF	Penta-chlorinated dibenzofurans
HxCDF	Hexa-chlorinated dibenzofurans
HpCDF	Hepta-chlorinated dibenzofurans
OCDF	Octa-chlorinated dibenzofurans
APCDs	Air pollution control devices
ACI	Activated carbon injection
SCR	Selective catalytic reduction
VOCs	Volatile organic compounds
PCP	Pentachlorophenol
PID	Proportional integral derivation
MSWIs	Municipal solid waste incinerators
LRMS	Low resolution mass spectrometer
HRGC	High resolution gas chromatograph
I-TEQ	International toxicity equivalent quantity

References

- Alexander F, Sergei N, Lawrence A K *et al.*, 1999. Gliding arc discharge[J]. *Progress in Energy and Combustion Science*, 25: 211–231.
- Altwickler E R, 1996. Relative rates of formation of polychlorinated dioxins and furans from precursor and De novo reactions[J]. *Chemosphere*, 33: 1897–1904.
- Chang M B, Chi K H, Chang S H *et al.*, 2007. Destruction of PCDD/Fs by SCR from flue gases of municipal waste incinerator and metal smelting plant[J]. *Chemosphere*, 66: 1114–1122.
- Chen T, Li X D, Yan J H *et al.*, 2004. Formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans from pentachlorophenol on fly ash surface[J]. *Journal of Chemical Industry and Engineering*, 55: 1696–1701.
- Czernichowski A, Labbe P, Laval F, 1995. Lesueur emerging technologies in hazardous waste management[M]. U.S. ACS Symp Series.
- Du C M, Yan J H, Li X D *et al.*, 2006. Removal of PAH and soot in flue gas by gliding arc discharge[J]. *Journal of the Chinese Society for Electrical Engineering*, 26(1): 77–81.
- Du C M, 2006. Degradation of organic contaminations from gas and liquid phase using gliding arc discharge plasma[D]. Ph. D Thesis. Zhejiang University.
- Hell K, Altwickler E R, Stieglitz L *et al.*, 2000. Comparison of 2,4,6-trichlorophenol conversion to PCDD/PCDF on a MSWI-fly ash and a model fly ash[J]. *Chemosphere*, 30: 995–1001.
- Olie K, Vermeulen P L, Hutzting O, 1977. Chlorodibenzo-*p*-dioxins and chlorodibenzofurans are trace components of fly ash and flue gas of some municipal incinerators in the Netherlands[J]. *Chemosphere*, 6: 455–459.
- Peyrou R, Pignolet P, Held B, 1989. Kinetic simulation of gaseous species generated by an electrical discharge in dry or humid oxygen[J]. *J Phys D: Appl Phys*, 22: 1658–1667.
- Pignolet P, Hadj-Ziane S, Held B *et al.*, 1990. Ozone generation by point to plane corona discharge[J]. *J Phys D: Appl Phys*, 23: 1069–1072.
- Stanmore B R, 2004. The formation of dioxins in combustion systems[J]. *Combustion and Flame*, 136: 398–427.
- USEPA method 8280B[EB], 1998. <http://www.epa.gov/SW-846/8280b.pdf>.
- Yan J H, Du C M, Li X D *et al.*, 2005. Plasma chemical degradation of phenol in solution by gas-liquid gliding arc discharge[J]. *Plasma Source Science and Technology*, 14: 1–8.
- Yan J H, Du C M, Li X D *et al.*, 2006. Degradation of phenol in aqueous solutions by gas-liquid gliding arc discharges[J]. *Plasma Chemistry and Plasma Processing*, 26(1): 31–41.
- Zhou Y X, Yan P, Cheng Z X *et al.*, 2003. Application of non-thermal plasma on toxic removal of dioxin-contained fly ash[J]. *Powder Technology*, 136: 345–353.