DEGRADATION OF HCB IN SIMULATED FLY ASH BY GLIDING ARC PLASMA

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Introduction

Hexachlorobenzene (HCB) as one persistent organic pollutants (POPs) regulated by the Stockholm Convention has been used in many fields in the past, such as solvents in chemical industry and agricultural chemical pesticides, and proved harmful to human health[1]. Although the production and use of HCB has been banned by many countries, HCB still existes in the environment because of its long half-life period in real environment[2]. Therefore, some disposal technologies of HCB have been utilized including thermal treatment, catalyst degradation and advanced oxidation methods[3-5] etc. Especially, HCB can be almost completely destroyed by incineration, but some more harmful by-products can be easily generated such as PCDD/Fs and PCBs[6, 7].

Plasma technology as high-efficiency chemical treatment method can be utilized to degrade chlorinated organic compounds like VOCs, CBs and PCDD/Fs. Gliding arc(GA) plasma as non-thermal plasma owns the characteristics of lower gas temperature, abundant active species and high chemical selectivity[8]. So it utilization field contains organic compounds destruction, hydrogen production, and surface treatment. Especially, degradation of chlorobenzenes (CBs) in aqueous solution by contact glow discharge electrolysis and destruction of CB in waste gas by dielectric barrier discharge(DBD) was investigated[9, 10].

Gliding arc in tornado (GAT) plasma as a novel GA plasma reactor has larger plasma region and longer reaction time than traditional GA plasma and has the application of fuel conversion[11]. The three-dimensional (3D) geometry structure using a reverse vortex flow (RVF)[12] expends field of application and offer the possibility to treat simulated fly ash containing HCB. In this study, degradation effects of HCB in simulated fly ash under different conditions by GAT plasma are investigated in detail. By analyzing the end products of treatment process and comparing with previous researches, possible degradation mechanism is proposed.

Materials and methods

Schematic diagram of experimental system is shown in Fig 1. Experimental gas is divided into tangential carrier gas and vertical drive gas from cylinder and controlled by independent mass flowmeters. Carrier gas is utilized to carry fly ash into GAT plasma reactor and drive gas is to drive and stabilize GAT plasma. A screw feeder is used as fly ash feeder with stable and controllable speed. The key part of experimental system is GAT plasma reactor shown in Fig 2 and its main body is a hollow cylinder made by quartz. Inner GAT reactor, spiral anode and cathode are supplied by DC high voltage power (10 KV). After discharging in the gap between anode and cathode, the arc is derived along spiral anode up to top circular part and stable plasma region is obtained in the central region of GAT plasma reactor. Flow of drive gas is set as 7-11 L/min with inlet diameter of 2 mm, and varied flow of drive gas leads different working patterns of GAT plasma[13]. After passing GAT reactor, simulated fly ash and exhaust gas are separated by glass filtering cartridge and HCB in exhaust gas is absorbed by hexane. And then the gas after absorption is collected by air pocket. At last, collected HCB and exhaust gas samples are used to detection. And detection device contains HP Agilent 6890 Gas Chromatograph(GC) with ECD detector carried out on a 60-m DB-5 silicafused capillary column with internal diameter of 0.25 mm and a stationary phase film thickness of 0.25 μm and Gasmet Portable FT-IR Gas Analyzer DX4000 (Gasmet Technologies Inc.).

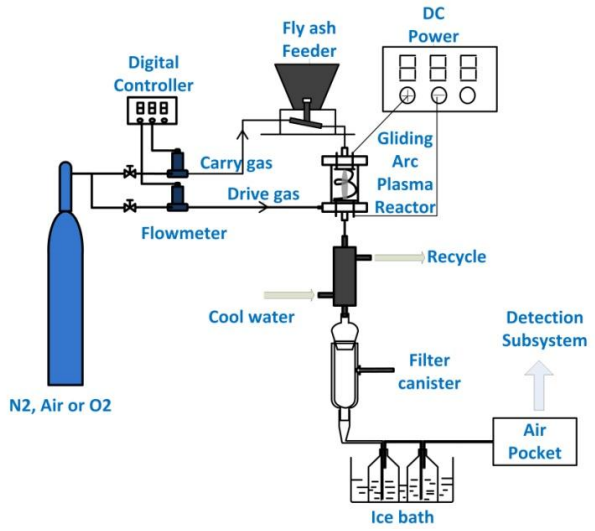

Fig 1 Schematic diagram of experimental system

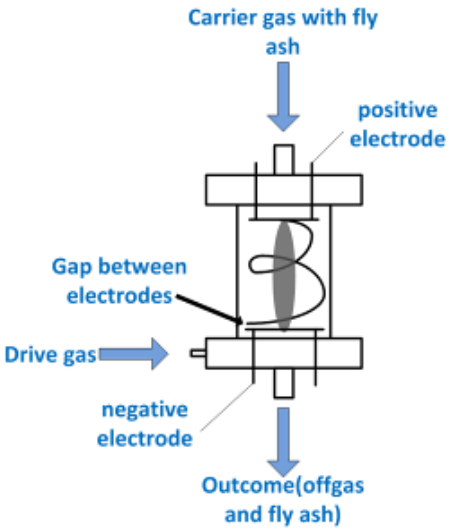

Fig 2 Schematic diagram of GAT plasma reactor

Simulated fly ash samples based on quartz sand sifted by 100 meshes. After mixture of quartz sand and HCB/hexane solution and dried by rotary evaporator, simulated fly ash containing HCB is obtained with average concentration of 8.25 ug/g. All solvents used in experiment are purchased from Mallinckrodt Baker, Inc. USA with pesticide residue analysis grade. HCB is detected by GC-ECD and exhaust gas is detected by Gasmat DX4000.

Degradation rate and remove efficiency of HCB are respectively calculated by subsequent formulas:

$$\eta_{\mathrm{deg}radation} = \frac{(m_{origin-solid} - m_{left-solid} - m_{left-gas})}{m_{origin-solid}} \times 100\% \qquad \eta_{remove} = \frac{(m_{origin-solid} - m_{left-solid})}{m_{origin-solid}} \times 100\%$$

In order to facilitate the calculation, ug/g and ug/L are utilized as calculation units.

Results and discussion

The experimental operating condition is set as 11 L/min drive gas, 2 L/min carrier gas and 40 KΩ external resistance.

Effects of different feeder speeds and different experimental atmospheres

Different feeder speeds are set as 0.9 g/min, 1.9 g/min and 3.3g/min by adjusting rotary speed of screw. Under above-mentioned operating condition, degradation effects with different feeder speeds are listed in Table1.

Table 1 Degradation effects of HCB by GAT plasma under different feeder speed conditions.

Feeder speed(g/min)	3.3	1.9	0.9
HCB left in simulated fly ash(μg/g)	0.752	0.724	0.628
HCB in exhaust gas(μg/L)	0.519	0.242	0.124
Degradation rate of HCB (%)	66.1	71.3	70.3
Remove efficiency (%)	90.9	91.2	92.4

It is investigated in Table 1 that remove efficiencies are generally beyond 90% and degradation rates of HCB are 66.1-70.3%. So it is indicated that GAT plasma may degrade HCB in simulated fly ash, not just make HCB transfer from solid phase to exhaust gas. The highest degradation rate (71.3%) is obtained under 1.9 g/min

condition, but the highest remove efficiency (92.4%) is obtained under 0.9g/min condition. Under 3.3 g/min condition, simulated fly ash particles cannot come into enough contact with active species existing in plasma region. On the other hand, low feeder speed(0.9 g/min) means full mixture and highest remove efficiency but it also means a waste of energy. Overall, feeder speed of 1.9 g/min is the optimum operating condition under which the best degradation effect is obtained.

Experimental atmosphere of plasma system has a strong influence on degradation of HCB, so three different atmospheres(N_2, air and O_2) are chosen as experimental atmosphere. The degradation effects under different experimental atmosphere conditions are listed in Table 2.

Table 2 Degradation effects of HCB by GAT plasma under different conditions

Feeder speed(g/min)	N_2	Air	O_2
HCB left in simulated fly ash(μg/g)	0.704	0.577	0.453
HCB in exhaust gas(μg/L)	0.202	0.200	0.161
Degradation rate of HCB (%)	70.5	70.9	75.5
Remove efficiency (%)	91.5	93.0	94.5

It is investigated in Table 2 that degradation rate and remove efficiency decrease gradually with the increase of O_2 content, and the highest degradation rate and remove efficiency are simultaneously obtained under O_2 condition which are respectively 75.5% and 94.5%. That can be explained that more active species such as O_3 and OH radicals may be produced with the increase of O_2 content for stronger excitation, ionization and dissociation reactions in plasma region[14]. Those active species may destroy HCB molecules. So O_2 atmosphere is the optimum experimental atmosphere. In summary, appropriate feeder speed (about 2.0 g/min) and O_2 atmosphere are two optimum operating conditions and best degradation effect (degradation rate of 75.5% and remove efficiency of 94.5%) is obtained under the optimum condition.

Degradation mechanism of HCB by GAT plasma by analyzing exhaust gas components

Due to former studies, UV illumination in plasma region is benefit of the brokendown of C-Cl bonds and formation of C-H bonds[15], so it is supposed that collected end-product possibility contains HCl and low chlorinated CBs. However, almost no HCl and low chlorinated CBs are detected and major component of exhaust gas is proved CO_2, CO and CH_4. So it is supposed that although HCB may take dechlorination reaction, Cl atoms can fully react with some chemical groups like CH_x^- and CO^-[16] and form some chlorinated organic compounds because Cl atoms take up a relatively small proportion of whole reaction system.

Destruction process is regarded as oxidation process by some strong oxidability molecules, active ion and free radicals produced by GAT plasma performing the brokendown of C-C or C=C bonds in benzene ring structure. And O_3 is special in this process because of not only its strong oxidation ability but also its synergistic reaction ability with UV illumination[17]. GAT plasma simultaneously supplying O_3[18] and UV illumination can promote HCB synergistic destruction reaction.

The plasma processing under N_2/O_2 condition can produce significant yields of nitrogen oxides(NO_x)[16] and NO_x is proved an important component in exhaust gas presented in Fig 3. It is investigated in Fig 3 that concentration of NO_2 decrease with the increase of N_2O and NO concentrations after adding simulated fly ash containing HCB into GAT plasma reactor. It indicates NO_2 may transform to NO and N_2O after HCB added into reaction system in plasma treatment process, but N_2O occupy a very small proportion because of the existence of oxygen. So it is

supposed that NO_3 radicals from NO_2 oxidation degrade HCB to CO_2, CO and CH_4, and simultaneously NO_3 radical is reduced to NO and N_2O[4].

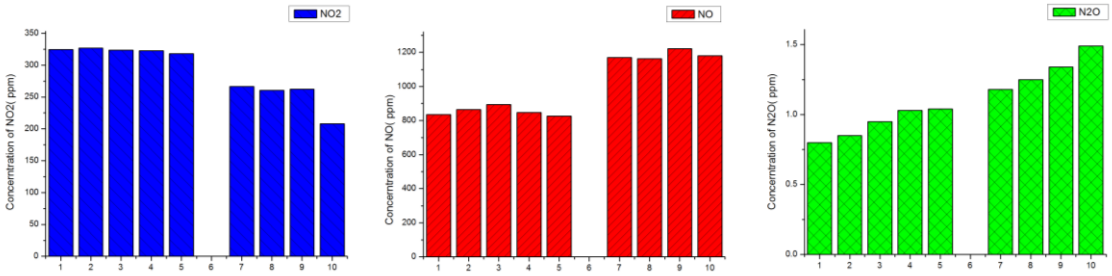

Fig 3 Some end-products in exhaust gas treating by GAT plasma (period 1-5# stand for discharge with no simulated fly ash injected; period7-10# stand for discharge with simulated fly ash)

In summary, GAT plasma make not only parts of HCB in simulated fly ash transfer to exhaust gas but also degraded in GAT plasma region. It is supposed that degradation mechanism contains two parts: dechlorination and oxidation. And UV may mainly lead the former and the latter may be leaded by some active strong oxidizability species produced by GAT plasma, such as O_3 and NO_3 radical. Degradation end products of HCB consist of CO_2, CO and CH_4 etc. and some undetected samll molecule organic compounds.

Acknowledgements

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