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Short communication

Advanced VOCs decomposition method by gliding arc plasma

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Abstract

The decomposition of a series of volatile organic compounds (VOCs) has been carried out by gliding arc, a new-interest type of plasma technology in our laboratory. The operation of gliding arc was done at ambient temperature and normal pressure. Feed compositions were containing 0.1–0.5% of aromatic VOCs and 1–8% of chlorinated VOCs diluted in atmospheric air and total flow rates were varied from 3 to 5 L/min. Significant conversions (>50%) of VOCs with high destruction efficiency have been achieved in gliding arc plasma.

Keywords: Plasma; Gliding arc; Decomposition reaction; Aromatic VOCs; Chlorinated VOCs

1. Introduction

Many processes in industry cause pollution via the generation of volatile organic compounds (VOCs). Potential deleterious effects of the release of these compounds include: acute (e.g. respiratory and nervous system) and chronic (carcinogenic and mutagenic) health effects, soil and ground-water contamination and ozone depletion [1].

As awareness of these issues increases, government legislation is continually introduced and upgraded. Therefore, industries all over the world are being forced to dramatically reduce or eliminate VOC emissions, or stop production altogether. The conventional methods used to treat pollutants are carbon adsorption and incineration. Carbon adsorption has significant power requirements and typically only removes 40–50% of the pollutant. Incineration (thermal or catalytic) provides very high removal efficiencies through relatively simple means. It can also treat any pollutant and can cope with varying VOC concentrations and compositions as well as variations in the volume of the stream. However, additional fuel must be added when treating dilute VOC streams, making the process extremely energy intensive. The other major disadvantage of incineration is the formation of more damaging pollutants, such as dioxins and furans.

During the last decade, the potential for plasma-assisted technologies to treat dilute VOC streams has been recognized and investigated [2]. This process is similar to incineration in that non-thermal plasmas are capable of very high destruction efficiencies. However, by definition the bulk of a non-thermal plasma is much cooler than the electrons (which are eventually responsible for the VOCs destruction). Therefore, the energy can be thought of as targeting the pollutants, resulting in much lower power requirements than in conventional incineration.

Gliding arc plasma can be easily characterized by the presence of burn-like flames between two metal electrodes. This flame is created as an effect of arcs movement on the surface of electrodes (sliding) caused by high velocity of penetrated gas. This type of plasma has received attention from many scientists for the application in chemical reactions, such as pollutant decomposition [3]. Although gliding plasma is classified as cold plasma, some characteristics of thermal plasma are existed. Song et al. mentioned the plasma and thermal combustion process which are simultaneously occurred in gliding arc plasma [4]. This characteristic becomes one of the advantages of this plasma to decompose toxic and dangerous gases which usually have strong chemical structure. Gliding arc plasma is able to produce energetic radical species, more active compared to the other types of non-thermal plasmas. Capability to enhance high emission flow rates and concentrations has opened the possibility to apply gliding plasma to decompose VOCs in the real industrial scales of process.

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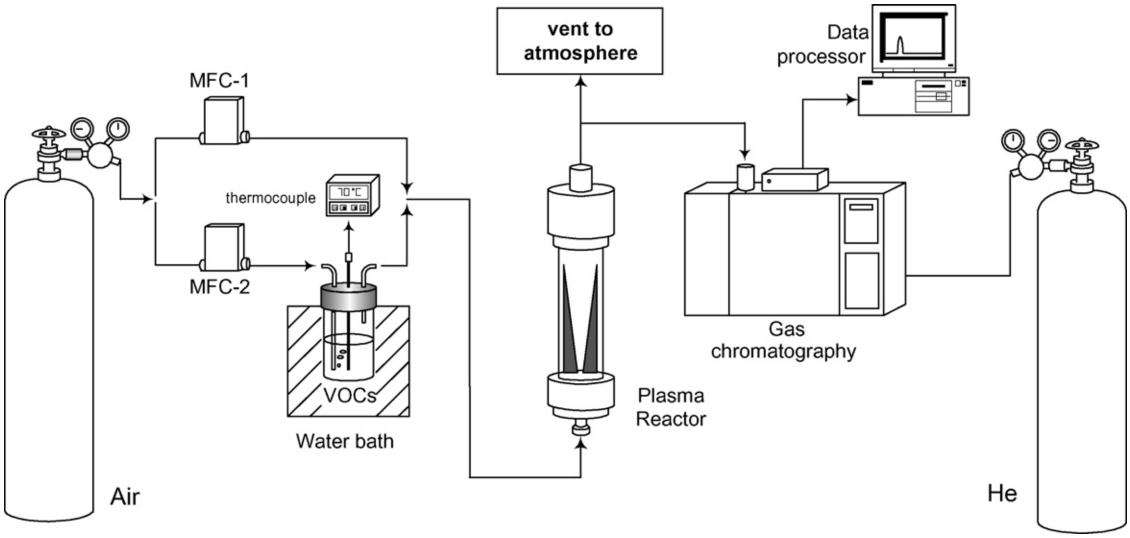

Fig. 1. Schematic diagram of experimental setup.

2. Experimental

The schematic diagram of the experimental setup is shown in Fig. 1. The VOCs were injected to the reactor by flowing a portion of air to the liquid VOCs chamber. The chamber was immersed inside the water bath to maintain the chamber temperature by controlling the water bath temperature. The concentration of VOCs was calculated based on the vapor pressure property. The flow of air from gas cylinder was controlled by two mass flow rate controllers (Tylan, FC-280S) and the gas mixture composition of the outlet of the reactor was analyzed before and after plasma process.

The reactor was consisted of a quartz-glass tube with inner diameter of 45 mm and length of 250 mm. One pair of electrodes stuck on the bottom part of the reactor. The electrode has a triangular shape and made from stainless steel. The length of the electrodes was 150 mm and the electrode gap was only 1 mm. High velocity gas was introduced in-between the electrodes by a capillary tube with inner diameter of 0.3 mm. The total volumetric flow of gas was varied from 3 to 5 L/min.

To produce arc plasmas, a high frequency alternating current (AC) power supply (Auto electric, A1831) was connected to the electrodes. The maximum voltage and current were 10 kV and 100 mA, respectively. Fig. 2 shows the waveform pattern of voltage and current used in this experiment. It shows that waveform transformation was occurred during the plasma process. At the equilibrium plasma condition, after the breakdown, the voltage decreased to the equilibrium voltage. However, the average currents increased as an effect of sudden elevation of current during arcs production.

The concentration of VOCs and gaseous products in the outlet of the reactor was determined by gas chromatography with thermal conductivity detector (YoungLin M600D, Column: Chromosorb 101). Qualitative and quantitative analysis were also done by quadruple mass spectroscopy (QMS, Balzers QMS 200).

Destruction efficiency terminology was used as the way to measure the system efficiency and calculated as:

$$\text{Conversion} = \frac{\text{converted mol of VOCs}}{\text{initial mol of VOCs}} \tag{1}$$

$$\text{Destruction efficiency} = \frac{\text{converted mol of VOCs}}{\text{supplied power}} \tag{2}$$

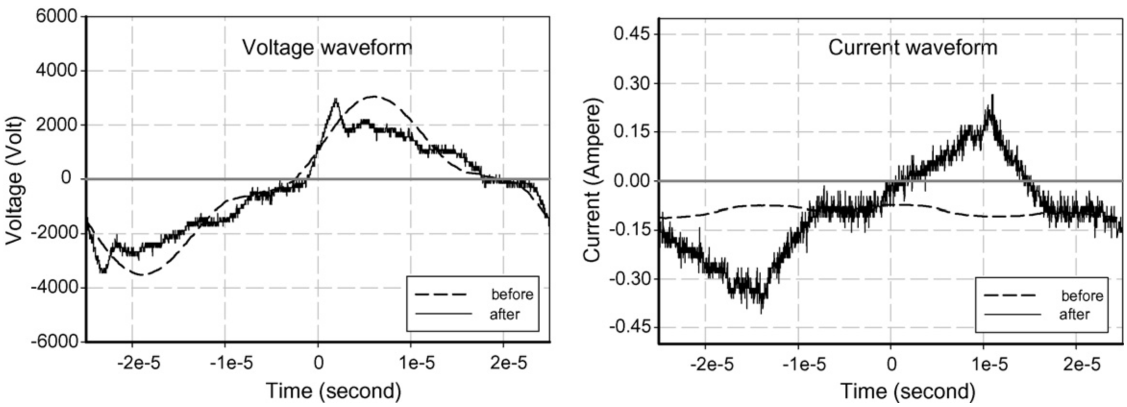

Fig. 2. AC voltage and current waveform of the before and after plasma breakdown.

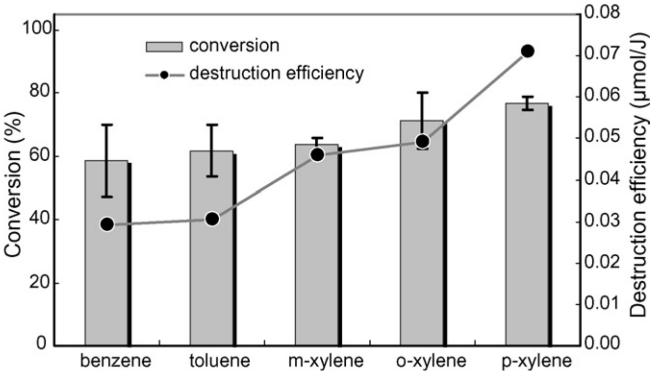

Fig. 3. Aromatic VOCs conversion and destruction efficiency. The experiment was conducted at flow rates of 5 L/min and VOCs concentration of 0.1–0.5%. The total consumed energy and frequency were 270 W and 20 kHz, respectively.

The supplied power was calculated by integrating the voltage and current waves captured by oscilloscope (Agilent 54641A).

$$\text{Supplied power} = \text{freq} \times \int_{t_1}^{t_2} [V(t) \times I(t)]\ \mathrm{d}t \qquad (3)$$

3. Results and discussion

3.1. Decomposition of aromatic VOCs

The aromatics were injected separately to the reactor at the concentrations of 0.1–0.5% by volume and the total flow rate of 5 L/min. Fig. 3 shows the experimental results for decomposition of aromatic VOCs (benzene, toluene, *meta*-, *ortho*-, and *para*-xylene) by gliding arc plasma. High destruction rates of target material, which are more than 50%, were achieved with the supplied power of ∼270 W. By comparing the destruction efficiency of VOCs which refers to the converted VOCs per supplied power, it shows that xylene is the easiest compound to be destructed among other chlorinated VOCs. On the other hand, benzene shows the lowest destruction efficiency means that it is difficult to be decomposed. The chemical bond strength and molecule stability are the main factor which can determine the decomposition rates in the plasma process. The order of aromatic VOCs destruction efficiency in gliding arc follows (Fig. 3):

benzene < toluene < xylene

The energy efficiencies in gliding arc show that those are much higher than other type of non-thermal plasmas. Fig. 4 shows the energy efficiency comparison between gliding arc and other non-thermal plasmas. The existence of plasma-combustion process by arcs formation can enhance the ability to decompose the target material in higher flow rates with higher conversion values. Higher energy capacity ions and radicals are required to break the chemical bond of stable compounds, e.g. aromatic VOCs. The energy density of gliding arc is higher than other types of non-thermal plasmas. This can be the answer why the destruction efficiency in gliding arc is better than other non-thermal plasma to decompose aromatic VOCs.

In our experiment, VOCs decomposition efficiency increases with increment of field strength. At fixed VOCs concentrations, the lower flow rate, the higher VOCs decomposition efficiency. An interesting finding is that at the same flow rate, the higher VOCs decomposition efficiencies were obtained at the higher VOCs concentrations. Similar trend is found for decompositions of benzene, toluene, and xylene by other plasma methods [5,6].

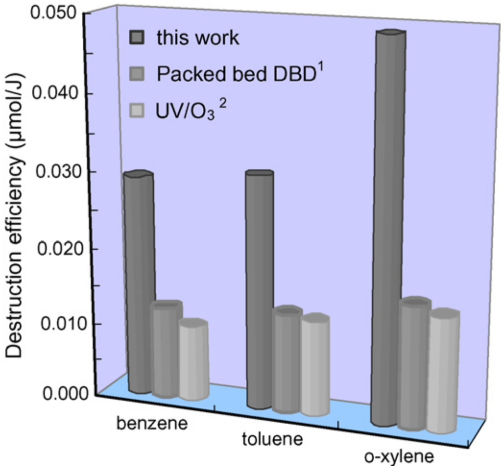

Fig. 4. Destruction efficiency comparison between gliding arc plasma and other non-thermal plasmas. 1, See ref. [4]; 2, see ref. [5].

The formation of carbon monoxide, carbon dioxide, and water in the outlet gas after reaction were detected by GC. Small amount of acetylene, C_2H_2, was found as single significant compound of hydrocarbon. The transformation from toluene and xylene into benzene was found in a significant amount (>10%) for the toluene and xylene decomposition, but the most products were dominated by carbon monoxide, carbon dioxide, and water. The total calculated carbon atom from carbon monoxide and carbon dioxide reached more than 80%. Based on the results that higher energy efficiency of decomposition with less toxic outlet and also the capability to handle higher concentration of target compounds (>1000 ppm) and flow rates (∼5 L/min), it can be proposed that gliding arc is a proper tool to decompose aromatic VOCs in industrial level.

3.2. Decomposition of chlorinated VOCs

Chlorinated hydrocarbons are classified as VOCs with high toxic level and very dangerous if exhalant by human body. High potential ozone destruction compounds are also the environmental issues that address us to decompose the chlorinated VOCs [1]. Three main chlorinated VOCs, dichloromethane, chloroform, and tetrachlorocarbon, were chosen as the target compounds. These compounds are mostly used as solvents and reactants in the industries and have big probabilities to be released as gas pollutants. Fig. 5 shows the degree of conversion of chlorinated VOCs by gliding arc at normal pressure and room temperature. The efficiency process and conversion rate show higher than that of aromatic VOCs. Dichloromethane can be destructed perfectly when the concentration was lower than 3% at 5 L/min. In gliding arc, the decomposition efficiency for chlorinated VOCs follows:

dichloromethane > chloroform > tetrachlorocarbon

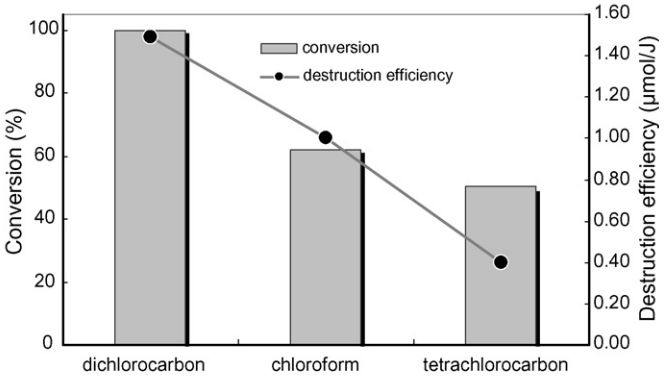

Fig. 5. Chlorinated VOCs conversion and destruction efficiency. The experiment was conducted at flow rates of 5 L/min and VOCs concentration of 3%. The total consumed energy and frequency were 270 W and 20 kHz, respectively.

Comparison among the other non-thermal plasmas shows that gliding arc is more efficient to handle the decomposition of chlorinated VOCs (Fig. 6). For dichloromethane case, the efficiency can be 10 times higher than dielectric barrier discharge (DBD) and radio frequency discharge. Our system has slightly better performance compared to the previous experiment using gliding arc. However, previous results also support that gliding arc is much better than other non-thermal plasmas, e.g. DBD and radio frequency, and even thermal plasma. Although thermal plasma can decompose chlorinated VOCs perfectly, e.g. chloroform [9] and tetrachlorocarbon [11], the destruction efficiency of the process was lower than gliding arc or non-thermal plasmas.

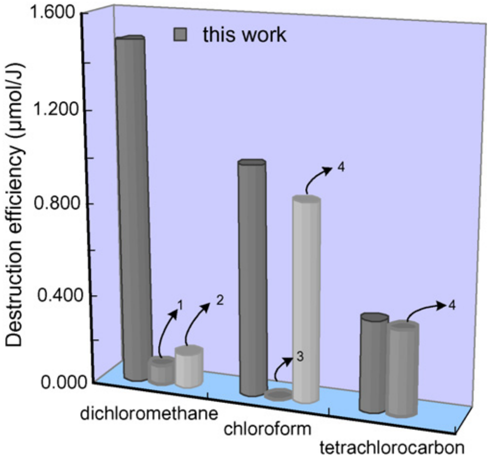

Fig. 6. Destruction efficiency comparison between gliding arc plasma and other non-thermal plasmas for chlorinated VOCs. 1, Glow discharge, see ref. [7]; 2, radio frequency, see ref. [8]; 3, silent discharge, see ref. [9]; 4, gliding arc, see ref. [10].

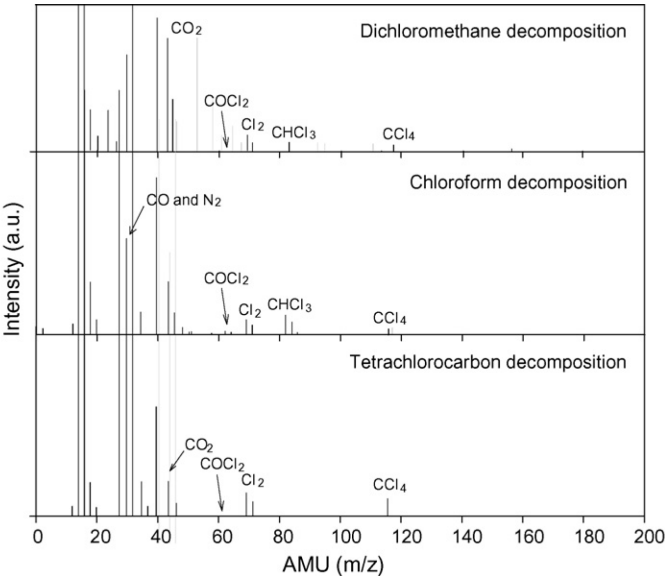

Fig. 7. QMS spectra of chlorinated VOCs decomposition by gliding arc plasma. The data were obtained at 1% of VOCs in gas flow rate of 3 L/min.

As seen in Fig. 7 of the QMS spectra, CO and CO_2 come as the most dominant products of the decomposition reaction. CO was mostly produced when tetrachlorocarbon was decomposed. The total calculated carbon atom from CO and CO_2 reached around 70%. When tetrachlorocarbon was destructed into two Cl_2 molecules, C radical remained as intermediate species. This heightens the chance for C radicals to collide with other compounds, thus raising the possibility of C radicals to collide with oxygen. This idea is supported by our finding of consumed oxygen calculation. The processing of the QMS spectra of oxygen has shown that the concentration of oxygen in the output product (after treatment with plasma) was 5–10% lower than its concentration in inlet stream (before treatment with plasma). It matches which the fact of consumed oxygen for the reactions associated with CO and CO_2 formation. The rate of CO_2 production was about 1/10–1/5 lower than that of CO in the output. CO_2 was produced by reaction of CO and single O or radical ($O^\bullet$)

$$CO + O \rightarrow CO_2 \tag{4}$$

At the decomposition of dichloromethane and chloroform, minor transformation reaction into tetrachlorocarbon was occurred and the selectivity was less than 12%. Traces of other chlorinated compounds, e.g. $COCl_2$ and HCl, were also detected. Gaseous state of $COCl_2$ was detected by our QMS where HCl was measured analytically by iodometry titration. Yellow-greenest liquid was also produced that might be considered as remaining species of C and Cl which form liquid chlorinated compounds, e.g. HCl and $COCl_2$. The amount of liquid production was not significant and can only be detected after long period of operation, i.e. 2 h.

Fig. 8 shows that the conversion gradually increases when the frequency of power rose. Frequency has an important factor than can change the number of waveform pulse which can effect on supplied power to the reactor. The increment of frequency shows no-effect on the products distribution which dominated by CO, CO_2, and Cl_2. Chlorinated VOCs conversion decreases with the increase in total gas flow rates. The maximum conversion of tetrachlorocarbon could reach 80% at a concentration of 1% and a total air flow rate of 3 L/min. At the same conditions, the conversion of chloroform can reach higher value (>97%). Similar to the aromatic VOCs decomposition, the removal efficiency increased with rise of initial concentration. Some references

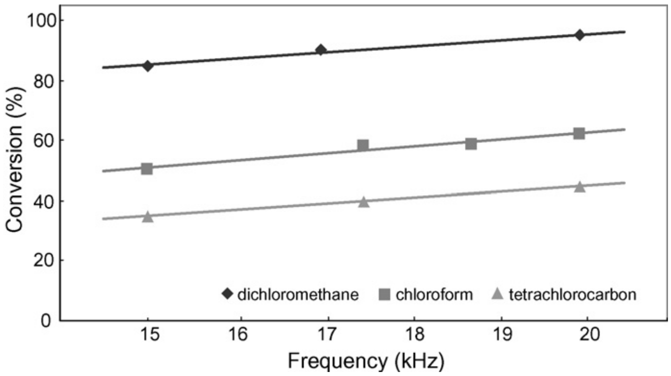

Fig. 8. Effects of frequency variation on the conversion of chlorinated VOCs. The experiment was conducted at fixed flow rate of 5 L/min.

proposed that radical Cl, produced by fragmentation reactions of chlorinated VOCs, can give a positive effect and help the decomposition process.

4. Conclusion

The VOCs decomposition in gliding arc plasma at atmospheric pressure was performed and studied. The significant conversion of VOCs, both aromatic and chlorinated VOCs, has been achieved for the decomposition using gliding arc. The results show better energy efficiency compared to other non-thermal plasmas. The products were dominated by CO, CO_2, and water for aromatic VOCs, where CO, CO_2, and Cl_2 for chlorinated VOCs. Based on these result, the gliding arc has a bright future to be applied as an alternative tool to decompose gaseous toxic compounds. The capability to handle high flow rates (∼5 L/min) with high concentration (>1000 ppm) can be other supporting factor to use in industrial level.

Acknowledgements

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