Effect of Gas Liquid Two Phase Flow on VOCs Degradation by Atmospheric Low Temperature Plasma

ChangLin Liu*, Xi Ren and MingHui Zeng

School of Electronic Information and Engineering, Shanghai JiaoTong University, Shanghai, China

*Corresponding author: liuchanglin@sjtu.edu.cn

Abstract. This paper proposes a combination of barrier dielectric discharge (DBD) and saturated sodium bicarbonate solution boiling tube to generate a gas-liquid two-phase flow containing plasma, and through characterization methods to study the solution in the boiling tube under the action of DBD discharge the law of boiling evolution. Then, by designing the cavity, the gas-liquid two-phase flow mixture produced by the boiling tube was sprayed into the needle electrode discharge area of the reaction chamber, and the influence of the gas-liquid two-phase flow on the plasma treatment of VOCs was explored. Spectral diagnosis proved that after the introduction of gas-liquid two-phase flow, the plasma concentration in the discharge area increased significantly, and the removal rate of VOCs was effectively increased from 32% to 55% in the decontamination experiment. It is proved that the introduction of gas-liquid two-phase flow can improve the effect of plasma degradation of VOCs.

Keywords: Plasma, gas-liquid two-phase flow, volatile organic compounds.

1. Introduction

In recent years, atmospheric pressure discharge plasma has gradually been applied to the field of decontamination of VOCs due to its large number of chemically active active molecules and easy preparation [1, 2]. However, while achieving better results, there are also some limitations, such as the low concentration of active groups in the plasma. In order to overcome these problems, some scholars have increased the discharge power [1], changed the discharge method [3, 4], and designed a suitable cavity [5]. To improve the effect of the treatment, some scholars have adopted the method of combining with other treatment methods. At present, the method of combining with the photocatalytic method is more popular [6-8]. The catalyst is placed in the discharge area or after the discharge area, and the synergistic effect is used to enhance the oxidation effect. It has a very good degradation effect, but the disadvantage is that the catalyst is easily deactivated quickly due to contamination.

This study tried to put forward a new idea to improve the removal rate of VOCs. In the experiment of plasma treatment of VOCs, gas-liquid two-phase flow was introduced to explore the influence of gas-liquid two-phase flow on plasma treatment of VOCs.
2. Experiment
As shown in the figure, the plasma decontamination system for VOCs is mainly composed of a gas distribution system, a reaction chamber, a power supply, and a gas chromatograph. The gas distribution system includes gas cylinders, mass flow meters, bubbling bottles, thermostats and gas mixing bottles. There are two types of gas cylinders, one is compressed air, which flows directly through the pipeline through the flow meter into the gas mixing cylinder; the other is pure nitrogen (Shanghai Weichuang Company, the concentration is 99.999%), which is fed with ethyl acetate In the bubbling bottle (this experiment uses ethyl acetate as the target VOCs), under the action of bubbling and gas flow, ethyl acetate quickly volatilizes, flows out of the bubbling bottle with nitrogen, and enters the gas mixing bottle after mixing with air Outflow.

VOCs flow out from the gas mixing bottle into the reaction chamber. The main structure above is cylindrical (50mm in diameter, 150mm in total length) quartz. There are two needle-shaped metal electrodes facing each other along the cross section at 100mm. The end is connected to the power supply, the electrode tip is 10mm apart, and the middle area of the electrode is the discharge area; 20mm directly below the discharge area is the nozzle of the boiling tube, the boiling tube is fixed by the bracket and placed vertically, and the model is CTP-2000K Suman Power connection; one end of the cylindrical quartz tube of the main body is the entrance of the VOCs to be processed, and the other end is sealed; in addition, there is a branch pipe at the sealed end, which is connected to the gas chromatograph through a pipe. The model gas chromatograph characterizes the changes in the concentration of VOCs before and after being processed; the bottom of the reflecting cavity is that the boiling tube is a device for generating gas-liquid two-phase flow, which is composed of a graduated sharp-nosed quartz glass tube, and At 50mm and 100mm from the top of the nozzle, a copper foil with a width of 5mm is respectively pasted as the DBD discharge electrode, and it is led out by a high-voltage wire, which is hereinafter called the upper electrode and the lower electrode. The following text refers to the boiling tube area between the two electrodes as the C zone. Since the C zone is the area where the reaction occurs, it is mainly for the observation and data collection of the C zone. During the experiment, a high-speed camera model i-SPEED 716 was used to take pictures of the discharge phenomenon; an infrared thermal imager model FLIR A655sc produced by American Filial Company was used to collect temperature change pictures of various areas.

![Schematic diagram of decontamination system.](image)
3. Results and discussion

3.1. Evolution of boiling experiment
This paper mainly discusses the influence of the introduction of gas-liquid two-phase flow on plasma, so it is very important to study the evolution law of boiling experiment which produces gas-liquid two-phase flow. At the beginning of the experiment, saturated sodium bicarbonate solution was injected into the boiling tube to make the liquid level exceed the upper electrode by 10 mm. Then, the working voltage of the power supply was adjusted to 11 kV and the working frequency was adjusted to 50 kHz. From the connection of the power supply to the liquid level in the boiling tube falling to the lower electrode position, the heating process was captured by high-speed camera. It can be divided into three typical stages. The physical process of each stage is briefly described below. The first stage is the transverse heat transfer process, which is characterized by the formation and aggregation of small bubbles; the second stage is the bubble dominated heat transfer stage, which is characterized by the bubble clusters breaking up and forming large bubbles, and the solution is periodically upwelling and disappearing with the continuous fluctuation of the liquid surface after being heated; the third stage is the boiling climax stage, which is also the stage of generating a large number of gas-liquid two-phase flow bubbles. At this time, the formed large bubbles do not continue to expand and break, but continue to form at the bottom of the lower electrode and move upward, ejecting from the nozzle of the boiling tube. This stage continues until the solution level drops to the lower electrode. At this time, there is no solution in the boiling tube in Zone C, and the discharge filament disappears.

In the third stage, a large number of experimental data are required to monitor the thermal evolution of the gas-liquid boiling. In the third stage, a large number of experimental data are used to monitor the boiling process. The temperature distribution and change period during the experiment were tested, and the temperature data were processed by FLIR software. The temperature change period of multi group boiling experiment is shown in the figure below. This result is consistent with the result obtained from image data taken by a high-speed camera.

3.2. Decontamination results
The concentration of VOCs was measured by gas chromatograph before and after the introduction of gas-liquid two-phase flow. The initial ventilation speed was set at 2L/min, and after the experimental system was balanced (VOCs to be detected filled the chamber and pipeline of the experimental system and kept stable), the two needle shaped metal electrodes were powered by the excitation power supply. The working voltage was 5kV and the working frequency was 70kHz. There is a bright arc current between the two electrodes. After the discharge phenomenon is stable, the concentration of VOCs passing through the plasma area is measured by gas chromatograph; then the boiling experiment is carried out, and the gas-liquid two-phase flow is injected into the discharge area of needle electrode in the cavity by boiling tube, and the concentration of VOCs is measured by gas chromatograph. From the above experimental data, it is concluded that the removal rate of VOCs is stable at about 32% when the needle electrode is used for discharge degradation, and the removal rate increases to 55% after the introduction of gas-liquid two-phase flow. The experimental results show that the introduction of gas-liquid two-phase flow significantly increases the removal rate of VOCs.

3.3. Analysis of decontamination mechanism
Firstly, in order to verify the effect of introducing gas-liquid two-phase flow on plasma treatment of VOCs, three groups of plasma diagnosis were carried out successively. The first group diagnosed the gas-liquid two-phase flow mixture ejected from the boiling tube; the second group diagnosed the needle electrode discharge area without introducing the gas-liquid two-phase flow mixture; and the third group diagnosed the discharge area under the condition of introducing gas-liquid two-phase flow mixing. The emission spectrum intensity data of the three groups of experiments, including visible light, were collected from 300 nm to 800 nm. The results are shown in the figure below.
Figure 2. The third stage jet gas-liquid two-phase flow cycle.

Figure 3. 4 randomly selected experimental temperature change cycles.

The black curve below is the emission spectrum of the first group, the blue curve is the emission spectrum of the second group, and the red curve is the emission spectrum of the second group. It can be seen from the figure that the introduction of a gas-liquid two-phase mixture has a great influence on the emission spectrum measurement results. The emission intensity of sodium ions at 589.6 nm is as high as 19077, which is much higher than the measured value before adding the introduction. At the same time, we noticed that after the introduction of gas-liquid two-phase flow, the emission intensity levels of some key species components such as active oxygen (O2+, O) and N2+ have been greatly improved compared to before the introduction, especially the level of atomic oxygen has been greatly improved. The spectral emission intensity is 17750, and the test result of OH after introduction is
about twice higher than before introduction. In addition, we can find that the plasma concentration 
after introducing the gas-liquid two-phase flow is greater than the sum of the gas-liquid two-phase 
flow and the needle electrode discharge. Therefore, by introducing the sodium bicarbonate aqueous 
product produced by DBD discharge heating under atmospheric pressure, the content of hydroxyl 
radicals and active particles O2+, O, N2+ can be increased. The existence of atomic oxygen and 
excited nitrogen can greatly enhance the reaction efficiency, and then achieve the removal effect we 
expected.

![Figure 4. Plasma diagnosis result graph.](image)

Under normal temperature and atmospheric pressure, when a voltage is applied to the needle-
shaped metal electrode, the high-energy electrons and the gas molecules between the electrodes 
produce inelastic collisions, resulting in a large number of active particles. It mainly includes the 
collision and interaction between electrons and oxygen molecules and nitrogen molecules. The 
following is the main reaction between high-energy electrons and oxygen molecules and nitrogen 
molecules in general.

\[
e + O_2 \rightarrow O_2^+(X^2\pi_g) + 2e \quad (1)
\]

\[
e + O_2 \rightarrow O_2^+(A^4\pi_g) + 2e \quad (2)
\]

\[
e + O_2 \rightarrow O(\tilde{3}P) + O(\tilde{1}D) + e \quad (3)
\]

\[
e + O_2 \rightarrow O(\tilde{3}P) + O(\tilde{1}D) + e \quad (4)
\]
$$e + N_2 \rightarrow N_2^+(X^2\sum_p^+)+2e$$  (5)

$$e + N_2 \rightarrow N_2^+(B^2\sum_g^+)+2e$$  (6)

$$e + N_2 \rightarrow N(^4S)+N(^2D)+e$$  (7)

$$e + N_2 \rightarrow N(^4S)+N(^2D)+e$$  (8)

In addition, when DBD discharge is carried out in the boiling tube, on the one hand, the discharge is carried out in the C region of the boiling tube to generate active ions, and the gas-liquid two-phase flow ejects into the discharge area of the reflecting cavity. On the other hand, after the gas-liquid two-phase flow enters the discharge area, part of the water vapor reacts with the high-energy electrons in the region to generate more hydroxyl radicals:

$$N_2^+ + O_2 \rightarrow N_2 + 2O$$  (9)

$$O_2 + e \rightarrow O + O + e$$  (10)

$$H_2O + e \rightarrow H + OH + e$$  (11)

$$H_2O + O \rightarrow 2OH$$  (12)

When a voltage is applied between the electrodes, the electrons between the electrodes gain energy and start to accelerate their movement. During the movement, some of them collide with gas molecules to ionize them, forming active particles such as oxygen, hydrogen, nitrogen and hydroxyl radicals (especially after introducing the mixture of gas-liquid two-phase flow), and some directly collide with ethyl acetate to dissociate them into smaller organic compounds. These smaller organic molecules either directly collide with active particles to produce oxidation reactions, or continue to be bombarded by other high-energy electrons to produce inelastic collisions, dissociate into smaller organic molecules, and then react with active particles. From the experimental results, consistent with the spectral diagnosis results in the previous section, the introduction of gas-liquid two-phase flow effectively increased the number of oxygen atoms and hydroxyl radicals, and effectively improved the removal effect of VOCs by plasma degradation.

4. Conclusions
This chapter focuses on the study of plasma treatment of VOCs. In order to effectively improve the limitation of plasma degradation of VOCs, a new method is proposed, that is, by introducing gas-liquid two-phase flow, the electron density of plasma is effectively increased. The gas-liquid two-phase flow was characterized by the gas-liquid two-phase flow imaging instrument. The diagnosis results show that the gas-liquid two-phase flow significantly increases the concentration of active groups such as OH and O in the plasma, and increases the removal efficiency of VOCs from 32% to 55%. Finally, the mechanism of plasma treatment of ethyl acetate is discussed and analyzed.

References
[1] Mustafa MF et al., Volatile organic compounds (VOCs) removal in non-thermal plasma double dielectric barrier discharge reactor. J Hazard Mater 2018; 347: 317-324.
[2] Futamura S, Zhang AH, Yamamoto T, The dependence of nonthermal plasma behavior of
VOCs on their chemical structures. J Electrostat 1997; 42: 51-62.

[3] Huang L, Nakajo K, Ozawa S, Matsuda H, Decomposition of Dichloromethane in a Wire-in-Tube Pulsed Corona Reactor. Environmental ence & Technology 2001; 35: 1276-81.

[4] Norberg A, Modeling current pulse shape and energy in surface discharges. Ieee T Ind Appl 1992; 28: 498-503.

[5] Karatum O, Deshusses MA, A comparative study of dilute VOCs treatment in a non-thermal plasma reactor. Chem Eng J 2016; 294: 308-315.

[6] Li Y, Fan Z, Shi J, Liu Z, Shangguan W, Post plasma-catalysis for VOCs degradation over different phase structure MnO2 catalysts. Chem Eng J 2014.

[7] Chang T et al., Post-plasma-catalytic removal of toluene using MnO2–Co3O4 catalysts and their synergistic mechanism. Chem Eng J 2018; 348: 15-25.

[8] Bahri M, Haghighat F, Rohani S, Kazemian H, Metal organic frameworks for gas-phase VOCs removal in a NTP-catalytic reactor. Chem Eng J 2017; 320: 308 - 318.