Aerosol Formation and Decomposition of Benzene Derivatives by AC/DC Streamer Corona Discharge

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Abstract—This paper reports decomposition of three benzene derivatives (benzene, toluene and styrene) using a novel AC/DC streamer corona system. Experiments were carried out with individual compounds in air. It was found that in terms of the corona specific energy density, the removal processes of three benzene derivatives are different from each other. Except for styrene, the other two derivatives were significantly dominated by linear radical termination reactions. The produced aerosols were mainly with a diameter of 28-616 nm. At an energy density of 27-32 J/L, the number concentration of the produced aerosols from styrene was about $9\times10^5$/cm$^3$, which was a factor of 3-4 times more than that observed when processing benzene or toluene. Moreover, the AC/DC corona system can be used as a precipitator for the aerosol collection. Fourier transform infrared spectroscopy indicates that the non-volatile aerosol deposits contain the –COH and –COOH groups.

Keywords—Streamer corona, non-thermal plasma, aerosol, VOCs removal

I. INTRODUCTION

Over the last two decades, non-thermal plasma (NTP) induced volatile organic compounds (VOCs) emission control techniques are gaining considerable attention [1-3]. Urashima et al. consider that NTP technologies are useful for reducing a number of VOCs [4]. Streamer corona discharges are of interest because it can be used for large volume plasma generation [5, 6]. For industrial applications, two important issues are cost-effective corona discharge system and by-products emission control. The corona discharge can be generated by DC, pulse or AC/DC power sources. With regard to ultra-short pulsed corona, available heavy-duty pulsed power source relies on the complicated and expensive high-voltage components. The AC/DC corona system is one of the most cost-effective plasma systems. It has been used for NOx treatment and tar removal [7, 8]. Ariaans et al. reported that its productivity of O radicals is typically between 1-4 mole/kWh with a wire-plate reactor in air [9].

Ideal NTP process for VOCs emission control is to convert it to environmental-friendly compounds, such as CO$_2$ and H$_2$O. Unfortunately, by-products often include NOx, ozone, VOCs and aerosols. So far, very few works are available for discussing the aerosol formation. Yamamoto et al. reported that most of the generated aerosols have a diameter of less than 100 nm for CFC-113 decomposition with a packed-bed plasma reactor [10]. Borra et al. found that the maximum number concentration of the produced aerosol is about $10^6-10^7$/cm$^3$ and the corresponded diameter is 50 nm with dielectric barrier discharge reactor in air [11]. Kim et al. reported formation of aerosol from benzene removal in five different types of plasma reactors, the maximum number concentration was found in pulsed corona reactor with diameter of 39 nm [12].

This work aims to investigate the capability of the AC/DC corona system for benzene derivatives removal. The styrene, toluene and benzene rank form the major part of the total VOC emission in China. Experiments were mainly devoted to their individual removal efficiency and aerosol formation.

II. EXPERIMENTAL SETUP

A. Plasma System

The corona system consists of an AC/DC power source, a wire-plate type corona reactor, a circulation fan and gas pipes as shown in Fig. 1. The typical voltage waveforms are shown in Fig. 2. The DC level voltage and AC peak voltage are 27.1 and 40.8 kV, respectively. Size of the reactor plates were 850 × 850 mm$^2$. Length of 16 stainless steel pin electrodes was 650 mm. The distance between the two plates was 200 mm. The gap between each pin electrode was 44 mm. The reactor was placed in a closed flow system with a total gas volume of 780 L. The gas flow rate was 305 m$^3$/h in air.

B. Experimental Procedure

For each experiment, gas temperature and relative humidity were firstly measured, and then, a given amount of target component (in liquid phase, chemical pure) was injected into the closed flow system via an injection needle. At the same time, the circulation fan run for a sufficient time (typically 60-80 minutes) to get a stable VOCs concentration inside the system. In-situ gas chromatograph was used to monitor gaseous concentrations. Both gaseous compounds and generated aerosols were sampled for analyses.

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C. Gaseous and Aerosol Measurements

Concentrations of styrene, toluene and benzene were measured using a GC/FID (GC9750, Fuli) with a 30 m × 0.32 mm × 0.33 μm capillary column at various processing times. The gaseous by-products were also qualitatively analyzed by GC-MC (GC6890N-MS5973N, Agilent).

The size distribution, number concentration and collected charges on the aerosols were measured using a 13-stages electrical low pressure impactor (ELPI, Dekati) [13]. The FTIR spectra for non-volatile deposits were obtained within 400-4000 cm⁻¹ with the nicolet 560 spectrometer equipped with a mercury cadmium telluride (MCT) detector which accumulated 64 scans at a resolution of 4 cm⁻¹.

The removal efficiency was defined as follows:

$$\eta = \frac{C_o - C(t)}{C_o} \times 100\% \quad (1)$$

where $C_o$ is the initial VOC concentration, and $C(t)$ is its concentration after a certain processing time $t$.

D. Electrical Measurements

The applied voltage waveform on the reactor was measured using a 5000:1 voltage probe (P150-GL, Finechem Co., Ltd.). The discharge current was measured using a current transformer (CT-4, Tektronix). Their waveforms were recorded with a four-channel digital oscilloscope (DPO7054, Tektronix). The discharge power ($p$) was calculated as follows:

$$p = f \cdot \int_0^{t_0} V(t) \cdot I(t) \cdot dt \quad (2)$$

The specific plasma energy density in J/L was calculated as:

$$\varepsilon = \frac{p \cdot \Delta t}{V} \cdot \frac{T}{T_s} \quad (3)$$

where $t_0$ is the voltage pulse duration as shown in Fig. 2. $V(t)$ and $I(t)$ are the applied voltage and discharge current, respectively. $f$ refers to the pulse repetition rate in pps (pulse per second), $\Delta t$ is the processing time in seconds, $V$ is the total gas volume of the system (780 L), $T_s = 298$ K, $T$ is the gas temperature in Kelvin.

III. RESULTS AND DISCUSSION

A. Removal Efficiency

Fig. 3 illustrates removal efficiencies of three benzene derivatives as a function of the specific plasma energy density. At a certain level of energy density, the
removal efficiency decreases in the order of styrene > toluene > benzene.

Considering their simplified global reactions [1], styrene is a zero-order, and toluene and benzene are first-order kinetics. For styrene removal, radical termination reactions are not very significant. For toluene and benzene, however, O radical termination reaction to form O3 significantly affects the process. The reaction rates between those compounds and O radicals contribute to the observations [14].

In order to compare the system efficiency, the energy constant $\beta$ value ($\beta = C(t)/C_0 = \exp\left(-\frac{\varepsilon}{\beta}\right)$) was used [15-17].

In this study, typical $\beta$ values for styrene, toluene and benzene are 16-60, 277 and 500 J/L, respectively. They are comparable with many previous works (Fig. 4). As for the costs, AC/DC power source is about 3 US dollar/W, which is 8-10 times less than the ultra-short pulsed power source. As for plasma generation, large volume of corona discharge can be generated as comparing to DBD and packed bed reactor. Thus, we conclude that the AC/DC corona system is one of the most cost-effective plasma systems for VOCs removal.

B. Aerosol Byproducts

Fig. 5 shows typical aerosol distribution under an energy density of around 27-32 J/L with and without VOCs in air. The number concentrations decrease with increase of the aerosol diameter. For a certain particle diameter, the aerosol concentration decreases in the order of styrene > toluene > benzene > air discharge with RH = 87% > air discharge with RH = 32% > without discharge.

The generation of aerosol in air is due to water clusters as suggested by Hakoda et al. [18]. However, the pathways of aerosol formation from VOCs removal are still poorly understood. One of possible ways for its formation is that the plasma polymerization occurred during VOC removal. The olefinic bond in styrene makes it has largest trend for polymerization.

Moreover, besides polymerization, the oxidation process may also contribute to aerosol formation. For instance, some oxidation products are non-volatile compounds in ambient temperature and pressure, e.g. acetoephene, benzoic acid and phenylacetic acid from styrene, benzoic acid and 4-methyl-2-nitrophenol from toluene, and 2-nitro-phenol, 3-nitro-phenol and 4-nitrocatecho from benzene removal.

Fig. 6 shows the effects of the specific energy density on the total aerosol concentrations. It drops with increasing the energy density because of their electrostatic precipitation inside the reactor. This
argument is in agreement with the observations that the low AC/DC repetition rate (frequency) inhibits the aerosol number concentration at a certain level of energy density. Considering the conversion of styrene to aerosol and the decomposition of aerosol are dependent on energy density rather than treatment time, whereas the aerosol precipitation efficiency closely relates to the residence time or treatment time. For a certain energy density, a low frequency corresponds to a long treatment time, resulting more aerosol to be collected by electrostatic precipitation.

Fig. 7 shows the collected charge on the generated aerosols. Comparing experimentally obtained and theoretically derived charge values [19], one can see that the aerosols are sufficiently charged in the reactor, useful for electrostatic precipitation.

C. Analysis of Non-volatile Deposits

As an example, the non-volatile deposit from styrene removal is collected for FTIR analysis. As shown in Fig. 8, the spectrum is similar to that obtained by Luo et al. for preparing polystyrene films on glass substrates [20]. The two bands at 1280 and 1060 cm$^{-1}$ are, however, only observed within this work, indicating the formation of -COOH and -COH.

IV. CONCLUSION

This paper studied the aerosol formation and decomposition of three benzene derivatives by a homemade AC/DC streamer corona system. The main conclusions can be summarized as follows:

1. Present AC/DC plasma system is not only cost-effective way for benzene derivatives removal, but also is very efficient for byproduct aerosols collection.

2. For a given corona specific energy density, styrene leads to the largest amount of aerosol generation, and then toluene and benzene. Oxygen-containing groups (-COH and -COOH) are also observed on the non-volatile deposits.

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