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Plasma Oxidation of Benzene Using DBD Corona Discharges

Bin Lu, Min Ji, Mengmeng Wang, and Jianbo Lü

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This study carried out application of dielectric barrier discharges driven by an AC power supply to benzene conversion in air. Only carbon dioxide and carbon monoxide was found as oxidation products. The effect of discharge space volume on benzene conversion, CO_2 selectivity, and energy efficiency were also investigated, resulting in the facts that the benzene conversion and energy efficiency can be improved obviously using a large EC tape width of a large discharge space volume. The energy efficiency is 1.246 mol-C_6H_6/kWh at an energy density of 31 J/L. The mechanism of benzene oxidation was also discussed.

Keywords benzene oxidation, corona discharges, DBD reactor, energy efficiency

1. Introduction

Plasma technologies have been widely studied for reducing hazardous air pollutants, such as volatile organic compounds (VOCs) that cause problems to human health and global warming. In 1997, Vercammen et al. suggested that plasma discharge technologies are useful for reducing VOCs at gas flow rates less than 1000 Nm^3/h and concentrations less than 10% (Ref 1). However, plasma discharge technologies have encountered site-specific constraints (e.g., economic considerations) that have limited their commercial availability, in comparison with conventional methods, such as adsorption and condensation (Ref 2). Recently, combination processes of plasma and catalysis have been investigated in order to improve plasma energy efficiency (Ref 3-5). Those studies suggested that the plasma technologies for VOCs removal still have potential to reduce the VOCs treatment cost.

In consideration of processes of plasma discharges in air, impacts of energized electrons with molecules in air result in the ionization and dissociation of N_2, O_2, and VOCs in air. O_2 is converted to O that reacts with O_2 to yield O_3. The O atoms in the discharge zone are the main reactants that can react with VOCs to convert them into CO and CO_2 (Ref 6, 7). This means that a large discharge space volume in which large amounts of O atoms are produced by discharges contributes to VOCs oxidation. This leads us to investigate experimentally the influence of the volume of discharge zone on benzene (C_6H_6) oxidation using a Dielectric Barrier Discharge (DBD) reactor.

2. Experimental Setup

Experiments were carried out using the DBD discharge system shown in Fig. 1. This system includes three mass flow meters (MF1-3), a C_6H_6 bubbling bottle hold in a water bath at 25 °C, a DBD reactor, and an alternative current (AC) power supply, and a discharge measuring system. A gas mixture of N_2, O_2, and C_6H_6 was used. N_2 was supplied at 200.59 mL/min, in which 0.59 mL/min was used for bubbling C_6H_6 (99.5%). O_2 was supplied at 50 mL/min. C_6H_6 concentration in the gas mixture was 358 ppm.

The DBD reactor consisted of a glass tube ($10.3OD\times 8.2ID\times 200\ mm^3$), a stainless steel rod ($6OD\times 130\ mm^2$), and an electric conductive (EC) tape. The EC tape was covered on the outer surface of the glass tube. The stainless steel rod was inserted in the glass tube and connected to the high-voltage output of the AC power supply. The discharge was limited in the space between the inside surface of the glass tube covered with the EC tape and the outside surface of the stainless steel rod. The discharge space volume was adjusted by using different widths (width 1, 10, or 100 mm) of the EC tape. The discharge voltage and current were measured with a voltage probe (V-P1, P6015A, Tektronix) and a current transformer (CT2, TCP202, Tektronix), respectively. A capacitor (C) of 450 μF in series with the reactor was used for collection of charges in circuit, which was from measuring the voltage of the capacitor with a low-voltage probe (V-P2, P6139A, Tektronix). The analog signals from the voltage probes and current transformers were recorded with a digital phosphor oscilloscope (TDS3054B, Tektronix).

C_6H_6 and its gaseous products from the outlet of the DBD reactor were analyzed online with a gas chromatograph (SP-3430, BFRL, Beijing) equipped with a 2 m Porapak-N and a methanizer prior to FID detector. C_6H_6 conversion was calculated using Eq 1. Carbon dioxide (CO_2) and carbon monoxide (CO) were found in this study. The carbon balance was >90%. The selectivity of CO_2 was calculated according to Eq 2.

$$\text{Bezene conversion} = \frac{C_0 - C}{C_0} \times 100\%, \qquad \text{(Eq 1)}$$

Bin Lu, Min Ji, Mengmeng Wang, and **Jianbo Lü**, School of Environment Science and Engineering, Tianjin University, Tianjin 300072, China. Contact e-mail: lubin7x@yahoo.com.

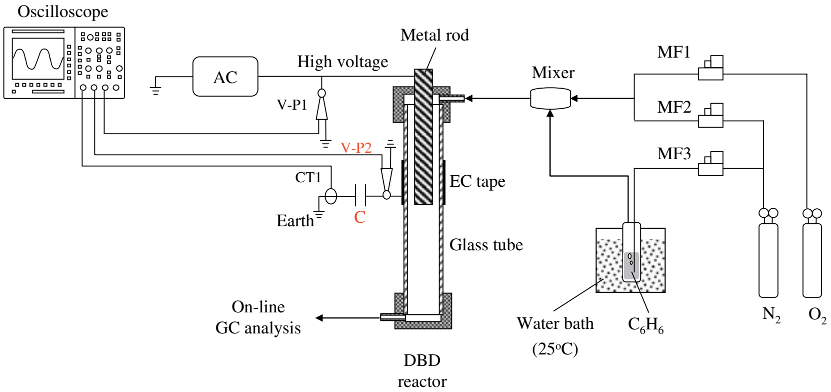

Fig. 1 Schematic diagram of DBD discharge system for C_6H_6 oxidation

where C_0 and C are C_6H_6 concentrations in ppm at inlet and outlet of the DBD reactor, respectively.

$$CO_2 \text{ selectivity} = \frac{\text{moles of } CO_2 \text{ formed}}{6 \times \text{moles of } C_6H_6 \text{ converted}} \times 100\%. \qquad \text{(Eq 2)}$$

The energy injection density in J/L is defined as the energy injection (P) used for discharges in the DBD reactor per unit gas volume treated over 1 s. The energy efficiency in mol-C_6H_6/kWh is defined as Eq 3.

$$\text{Cumulative Exhausted Energy} = \sum_{i=1}^{N}\left\{\frac{U_i + U_{i+1}}{2} \times \frac{[C(u_{i+1} - u_i)]}{t_{i+1} - t_i}\right\}, \qquad \text{(Eq 3)}$$

where U_i is the discharge voltage of the reactor, u_i is the voltage of the capacitor, C is the number of the capacitor, and N is the number of samples gathered by the digital oscilloscope.

$$\text{Energy efficiency} = \frac{C_6H_6 \text{ conversion} \times C_0 \times F}{P \times 0.082 \times T} \times 3.6, \qquad \text{(Eq 4)}$$

where F is the flow rate of the gas mixture (250.68 mL/min). T is the gas temperature (298 K) at the inlet of the DBD reactor. P in watts is calculated according to Eq 5.

$$P = \frac{\text{Cumulative Exhausted Energy}}{t_{N+1} - t_1} \qquad \text{(Eq 5)}$$

3. Results and Discussions

Figure 2 shows the time dependence of cumulative exhausted energy in the circuit system, according Eq 3. During the 0.5 T, the cumulative exhausted energy in circuit first increases and then decreases with time, owing to the fact that the capacitor stores energy over the first 0.25 T and discharges energy over the next 0.25 T. If the DBD reactor does not produce gas discharges, i.e., no energy exhausted, the cumulative exhausted energy in 0.5 T will be zero. Therefore, as shown in Fig. 2, the cumulative exhausted energy at 0, 0.5, 1, 1.5, and 2 T gradually increase when discharges occur.

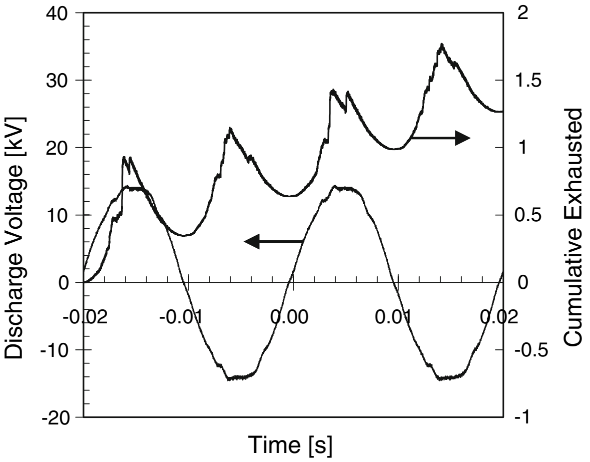

Fig. 2 Time dependence of cumulative exhausted energy (2 T, 10.3 kV of RMS discharge voltage, 1 mm of width of the EC tape)

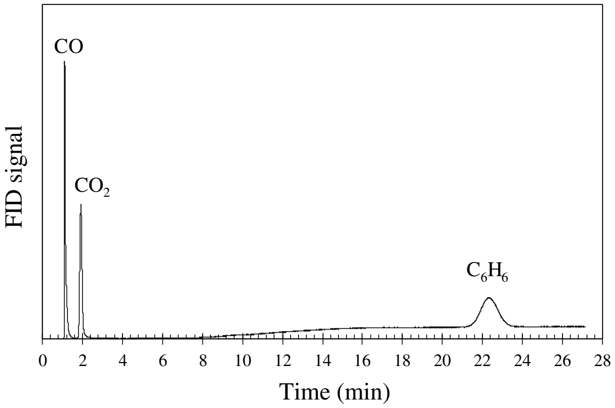

Fig. 3 Typical gas chromatogram of products of C_6H_6 oxidation (EC tape width 100 mm)

Figure 3 shows the gas chromatogram of products of C_6H_6 oxidation using the EC tape of 100 mm width. Only CO and CO_2 were detected out as oxidation products.

C_6H_6 conversion as a function of energy density using various widths of the EC tape is shown in Fig. 4. C_6H_6 conversion increases with increasing energy density linearly.

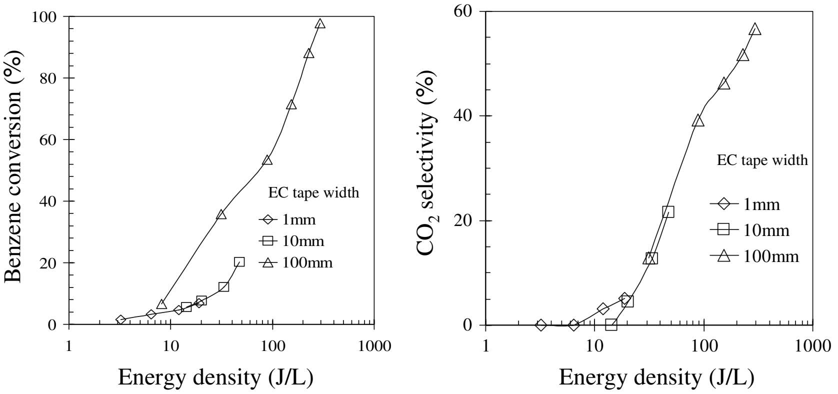

Fig. 4 C_6H_6 conversion and CO_2 selectivity as a function of energy density

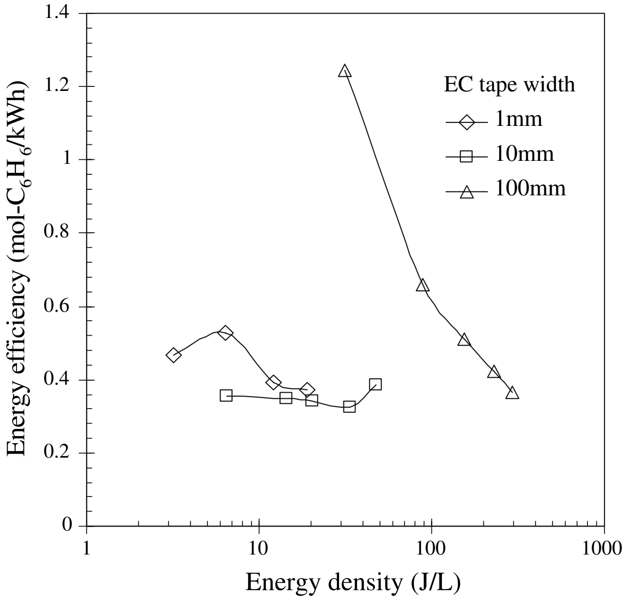

Fig. 5 Energy efficiency as a function of energy density

C_6H_6 conversion using EC tapes of 1 and 10 mm width is less than 20% at an energy density less than 47 J/L. However, C_6H_6 conversion increases from 36% to 98% as the energy density increases from 31 to 293 J/L.

CO_2 selectivity at various energy densities is illustrated in Fig. 4. CO_2 selectivity increases with increasing energy density. CO_2 selectivity using the EC tape of 100 mm width is a little higher than those using EC tapes of 1 and 10 mm width. The energy efficiencies at various energy densities are shown in Fig. 5. The energy efficiencies of EC tapes of 1 and 10 mm width are 0.372 mol-C_6H_6/kWh at 19 J/L and 0.326 mol-C_6H_6/kWh at 33 J/L, respectively. Although the energy efficiency using the EC tape of 100 mm width decreases from 1.246 to 0.365 mol-C_6H_6/kWh when the energy density increases from 31 to 292 J/L, such an energy efficiency is at least three times higher at 31 J/L than those using EC tapes of 1 and 10 mm width at 19 J/L and 33 J/L, respectively.

The energy efficiency for C_6H_6 oxidation using plasma discharges is an important figure for the practical use of the plasma technologies. Figure 6 shows energy efficiencies using plasma discharges with or without catalysts as a function of initial VOCs concentrations. The energy efficiency can be improved using plasma discharges and catalysts, such as Pt and MnO_2 (Ref 3, 10, 11). The energy efficiency at maximum using the EC tape of 100 mm width is 1.246 mol-C_6H_6/kWh, the highest level in all VOCs removal processes using plasma discharges.

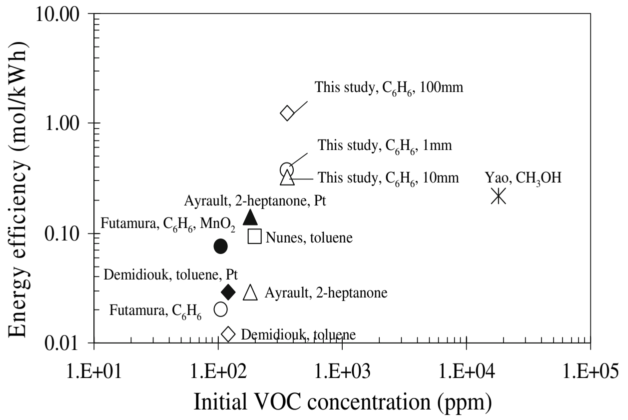

Fig. 6 Energy efficiency of plasma VOCs removal at various initial concentrations (Ref 8, 9)

The mechanism of C_6H_6 oxidation in air plasma discharges is not clear. From the facts that oxidation products are CO and CO_2, and carbon balance is higher than 90%, the cleavage of C–C bonds in C_6H_6 rings occurs, which is obviously due to the discharges. The cleavage of C–C bonds in C_6H_6 rings is possible (1) by impact with energized electrons to intermediates (M) and finally to CO and CO_2 (Eq 6) and (2) by reaction of activated oxygen species (such as O) to intermediates (M′) and finally to CO and CO_2 (Eq 7). These reactions cannot occur in the gases downstream of the discharge zone because of the very fast decay of the activated oxygen species. The large discharge space volume may enhance the first step of C_6H_6 oxidation to intermediates (M and M′), which results in an obvious improvement of energy efficiency.

$$C_6H_6 \xrightarrow{\text{energized electrons}} M \xrightarrow{\text{oxidation}} CO, CO_2 \qquad \text{(Eq 6)}$$

$$C_6H_6 \xrightarrow{\text{activated oxygen}} M' \xrightarrow{\text{oxidation}} CO, CO_2 \qquad \text{(Eq 7)}$$

In conclusion, a DBD reactor driven by AC power was used to evaluate the effect of discharge space volume on C_6H_6 oxidation. The energy efficiency can be improved obviously using a large EC tape width of a large discharge space volume. The energy efficiency is 1.246 mol-C_6H_6/kWh at an energy density of 31 J/L. This energy efficiency figure is highest in all plasma oxidation of VOCs.

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