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Decomposition of benzene in a corona discharge at atmospheric pressure

Kohki Satoh [a,b,*], Toshiharu Matsuzawa [a], Hidenori Itoh [a]

[a] Department of Electrical and Electronic Engineering, Muroran Institute of Technology, 27-1 Mizumoto, Muroran 050-8585, Japan
[b] Centre of Environmental Science and Disaster Mitigation for Advanced Research, Muroran Institute of Technology, 27-1 Mizumoto, Muroran 050-8585, Japan

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Abstract

We investigated the decomposition characteristics of benzene in a positive DC corona discharge between multineedle and plane electrodes with a background gas of nitrogen–oxygen mixture at atmospheric pressure. We obtained C_2H_2, HCN, HCOOH, CO and CO_2 as benzene fragments and by-products, and C_2H_2 and HCN as minor intermediate products. Benzene was primarily converted into CO_2 via CO at low oxygen concentrations (0.2%) and via CO and HCOOH at the atmospheric oxygen concentration (20%). Further, 57% and 24% of carbon atoms were deposited on the plane electrode and the discharge chamber at oxygen concentrations of 0.2% and 20%, respectively.

Keywords: Benzene; Corona discharge; Decomposition characteristics; Infrared absorption spectroscopy; Hazardous air pollutants

1. Introduction

Environmental contamination by hazardous air pollutants (HAPs), which can potentially affect human health even in low concentrations if the exposure time is sufficiently large, has become the centre of public interest. Benzene, present in exhaust fumes, is considered to be an HAP, and many techniques have been developed for removing it [1]. The use of discharge plasma for benzene removal has recently attracted attentions. This is because charged particles, chemically active species and UV radiation (produced in discharge plasmas [2]) potentially initiate and assist the decomposition and conversion of benzene in exhaust fumes. Further, a plasma reactor is a simple device and its size can be less than that of conventional reactors such as catalytic and thermal oxidation reactors [1]. Therefore, benzene emitted from automobiles (reportedly one of the major sources of HAPs) can be effectively removed by a plasma reactor installed in them.

Recently, some techniques for decomposing benzene using discharge plasmas have been investigated, and the decomposition characteristics of benzene in such plasmas have been reported. Goto et al. [3] have decomposed benzene at a low concentration in a nitrogen–oxygen mixture by using a barrier discharge and reported that the nitrogen atoms may contribute to the decomposition of benzene. Ogata et al. [4] have used a packed-bed discharge to decompose benzene in a nitrogen–oxygen mixture and reported that benzene is destroyed by the short-lived nitrogen and oxygen species and electron impacts; however, O_3 does not contribute in this decomposition process. These results suggest that the type of discharge can influence the decomposition characteristics of benzene. Further, the conclusions regarding the influence of oxygen on the benzene decomposition process do not conform to each other. Therefore, detailed experiments are required to clarify the decomposition characteristics and role of oxygen in the discharge.

In this study, we investigate the fragments and by-products produced in a DC corona discharge in a nitrogen–oxygen mixture containing benzene at atmospheric pressure and examine the decomposition characteristics of benzene. First, we clarify the types and quantities of the fragments and by-products in the discharge, which are essential parameters in the discharge plasma treatment of HAPs in addition to the decomposition rate and efficiency, and focus on the influence of oxygen in the background gas on the decomposition characteristics. Since the DC corona discharge has a large

* Corresponding author. Department of Electrical and Electronic Engineering, Muroran Institute of Technology, 27-1 Mizumoto, Muroran 050-8585, Japan.

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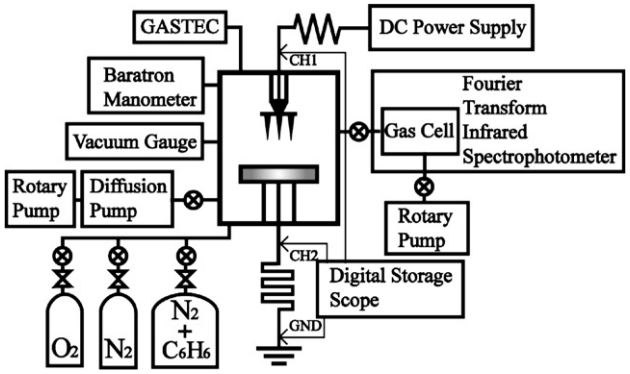

Fig. 1. Schematic diagram of the experimental apparatus.

discharge volume, the flue gas can be effectively exposed to the discharge. Further, the discharge can be generated in the flue without inducing exhalation breathing resistance [5]. Therefore, the DC corona discharge is suitable for flue gas treatment. Further, the decomposition characteristics of benzene clarified in this study can be used as fundamental data for gases (whose molecules contain an aromatic ring) used to fabricate new materials.

2. Experimental apparatus and conditions

Fig. 1 shows a schematic diagram of the experimental apparatus. A multineedle electrode and a plane electrode are placed in a cylindrical stainless steel chamber, which has an inner diameter of 197 mm and a height of 300 mm. Thirteen stainless steel needles with a length of 55 mm and a diameter of 4 mm are mounted on a metal disc holder (diameter: 50 mm) at equal intervals to form the multineedle electrode. The plane electrode is made of stainless steel and has a diameter of 80 mm; the distance between the needles and the plane electrode is fixed at 30 mm. The plane electrode and the discharge chamber are earthed, and a high positive DC voltage (approximately 22 kV) is applied to the multineedle electrode to generate a streamer corona discharge. A resistance of 1 − MΩ is inserted between the DC power supply (Max-Electronics Co., Ltd., LS40-10) and the multineedle electrode to stabilise the corona discharge; it also protects the multineedle electrode when the corona discharge changes into a spark discharge. The applied voltage is measured by using a high-voltage probe (Tektronix P6015A), and the discharge current is measured every second through the monitor output of the DC power supply. The electrical energy input to the corona discharge is calculated from the applied voltage and discharge current.

Nitrogen gas containing 766 ppm of benzene is used as the benzene source, and a mixture of nitrogen and oxygen with purities of 99.999% and 99.5%, respectively, is used as the background gas. First, 300 ppm of benzene is introduced into the evacuated discharge chamber; then, the background gas is added to increase the total gas pressure in the discharge chamber up to 1013 hPa. The mixture ratios (%) of the background gas are N_2/O_2 = 99.8/0.2, 99/2, 95/5 and 80/20. These gases are sealed in the chamber and then the DC voltage is applied. Gas samples are obtained from the discharge chamber before and after the discharge, and the benzene concentration and gaseous products in the corona discharge are measured by using a Fourier transform infrared spectrophotometer (Shimadzu, FTIR-8900) equipped with a gas cell (Infrared Analysis Inc., 10PA), which has an optical path length of 10 m. Silicon wafer chips with dimensions of 4 mm × 4 mm × 0.5 mm are placed on the plane electrode. After the corona discharge, the deposit on the chips is analysed by infrared absorption spectroscopy.

3. Results and discussion

Fig. 2 shows the temporal variations in the applied voltage, discharge current and input power in the nitrogen–oxygen mixture containing 300 ppm of benzene. The current and the power do not change significantly with time; however, they rapidly decrease at the beginning of the discharge. Similar tendencies are observed at the different mixture ratios of the background gas; however, the magnitudes of the discharge current and the input power depend on the mixture ratios of the background gas.

Fig. 3 shows the infrared absorbance spectra of a gas sampled before and after a 30-min discharge, and the observed spectra are listed in Table 1. The absorbance spectra of benzene, such as those of CH bend (673 cm^{-1}, 1038 cm^{-1}) and CH str (3068 cm^{-1}), decrease after the 30-min discharge; Simultaneously, the absorbance spectra of C_2H_2 (CH bend: 730 cm^{-1}, CH str: 3289 cm^{-1}), HCN (bend: 712 cm^{-1}), HCOOH (C–O: 1105 cm^{-1}, C═O: 1770 cm^{-1}), CO (2050–2220 cm^{-1}), CO_2 (anti str: 2349 cm^{-1}), O_3 (anti str: 1042 cm^{-1}) and N_2O (2170~2260 cm^{-1}) are observed. Therefore, it is inferred that C_2H_2, HCN, HCOOH, CO and CO_2 are produced from benzene and its fragments in the corona discharge. On the basis of these absorbance spectra, the concentration of these molecules can be deduced assuming that Lambert–Beer's law holds.

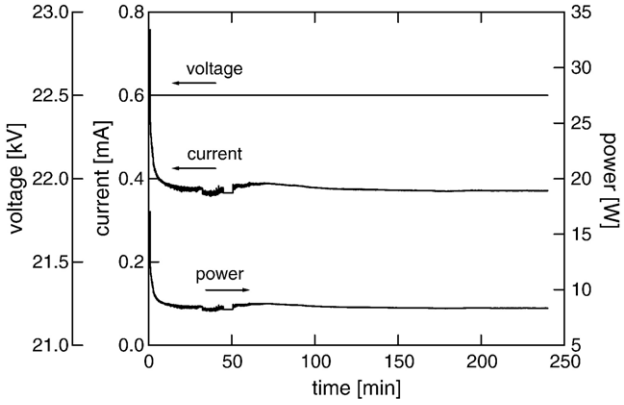

Fig. 2. Temporal variations in the applied voltage, discharge current and input power to the corona discharge in N_2–O_2 (80%–20%) mixtures containing 300 ppm of benzene.