

Decomposition of Dilute VOCs in Air by a Streamer Discharge

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Abstract—The efficiencies and products of VOCs decomposition by positive DC streamer discharge were comparatively investigated in a link tooth wheel-cylinder plasma reactor. The VOCs studied include formaldehyde, benzene, toluene and p-xylene. The results indicate that the order of the total decomposition rate for these VOCs is formaldehyde>p-xylene>toluene>benzene under the same reaction conditions. The constitution of decomposition products depends on the chemical structure of the VOCs. Compared with Benzene hydrocarbons, formaldehyde more easily converted to CO₂, instead of other products. The rate of benzene conversion to CO₂ is the highest among three benzene hydrocarbons. Humidity had a negative effect on VOCs decomposition. The byproducts, such as O₃ and NO_x, induced by gas discharge were detected, being about 400 ppm O₃ and 10ppm NO_x, respectively. And the specific energy density and the energy efficiency for the four VOCs were also considered in the study.

Keywords—Streamer discharge, VOCs, products

I. INTRODUCTION

Many studies have found that typical VOCs, such as formaldehyde, benzene, toluene and xylene represent hazards to human health through chronic exposure. Conventional techniques in use for the removal of VOCs mainly include adsorption, thermal oxidation, catalytic oxidation, and condensation. Recently, non-thermal plasma technology is a very hot topic because of its high removal efficiency, wide applicability, and good economy [1-3]. Many researchers have reported that non-thermal plasma chemical reactions are an effective method for the destruction of VOCs [4-15]. The plasma process is expected to convert the organic compounds into harmless compounds, such as water and carbon dioxide. However, it is found that the plasma treatment leads to formation of various byproducts because of incomplete oxidation. In this study, decomposition rate, decomposition products and the energy efficiency for formaldehyde, benzene, toluene and p-xylene decomposition by positive DC streamer discharge are comparatively investigated.

II. EXPERIMENTAL METHOD

The apparatus used in this study consists of a reaction gas mixture preparation unit, a non-thermal plasma discharge reactor, a high-DC power supply and a gas analysis unit, as shown in Fig.1.

A gas mixture containing 41 ppm formaldehyde or 175 ppm benzene or 171 ppm toluene or 165 ppm p-xylene, 0 or 2.5% H₂O in cleaned air was fed to the link tooth wheel-cylinder discharge reactor at a rate of 3

L/min. VOCs and H₂O were introduced into the system

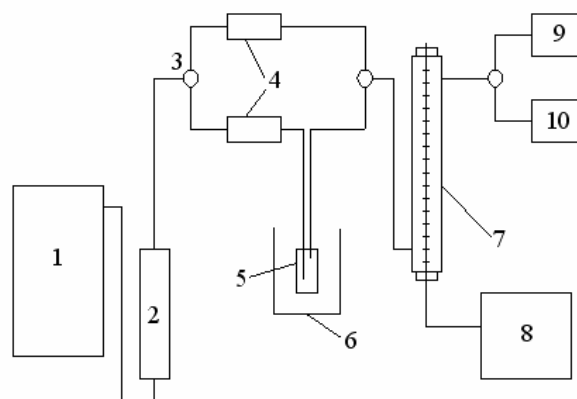


Fig. 1. Schematic diagram of the experimental apparatus

1. air compressor; 2. air cleaning tube; 3. tee fitting; 4. flow rate controller; 5. bubble tower; 6. temperature-controlled water bath; 7. plasma reactor; 8. power supply; 9. MS analyzer; 10. GC analyzer.

with temperature-controlled bubble towers. The total gas flow rate was controlled using mass flow controllers.

The measurement of VOCs was carried out using a gas chromatograph with a flame ionization detector (Agilent HP-6890). A quadrupole mass spectrometer (AVI QuadStar 422), a gas filter correlation CO analyzer (Thermo Electron model 48) and a chemiluminescent NO-NO_x analyzer (Thermo Electron model 44) were used to detect CO₂, CO, and NO/NO_x, respectively. Formaldehyde and ozone were measured by chemical spectrophotometric method.

The products of VOCs decomposition are mainly CO₂, CO and other organic compounds. The total VOC decomposition rate (R_{total}) can be expressed as

$$R_{total} = \frac{[\text{VOC}]_{in} - [\text{VOC}]_{out}}{[\text{VOC}]_{in}} \times 100\% \quad (1)$$

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Received; November 9, 2006, Revised; August 29, 2007,
Accepted; September 10, 2007

where, $[\text{VOC}]_{\text{in}}$ and $[\text{VOC}]_{\text{out}}$ are the inlet and outlet VOC concentrations of the plasma reactor, in ppm.

The rates of VOC conversion to CO, CO_2 and other HCs (R_{CO} , R_{CO_2} and R_{HC}) are given as

$$R_{\text{CO}} = \frac{[\text{CO}]_{\text{out}}}{n \times [\text{VOC}]_{\text{in}}} \times 100\% \quad (2)$$

$$R_{\text{CO}_2} = \frac{[\text{CO}_2]_{\text{out}}}{n \times [\text{VOC}]_{\text{in}}} \times 100\% \quad (3)$$

$$R_{\text{HC}} = R_{\text{total}} - R_{\text{CO}} - R_{\text{CO}_2} \quad (4)$$

where $[\text{CO}]_{\text{out}}$ and $[\text{CO}_2]_{\text{out}}$ are the concentrations of CO and CO_2 of the plasma reactor outlet, in ppm. n is carbon atom number of VOC.

The specific energy density (SED, $\text{kW}\cdot\text{h}/\text{m}^3$) and the energy efficiency (ξ , $\text{g}/\text{kW}\cdot\text{h}$) for the four contaminations can be calculated by the following expressions

$$\text{SED} = \frac{U \cdot I}{60Q} \quad (5)$$

$$\xi = \frac{60Q \cdot [\text{VOC}]_{\text{in}} \cdot M \cdot R_{\text{total}} \cdot 10^{-3}}{22.4 \cdot U \cdot I} \quad (6)$$

where U (kV) and I (mA) are the applied voltage and the current of the reactor, Q (L/min) is the flow rate of the system, M (g/mol) is the molar mass of the inlet VOC. Assume that the study is under the standard condition.

III. RESULTS AND DISCUSSION

A. Product Analysis for VOCs Decomposition

a) Formaldehyde decomposition

The formaldehyde decomposition as a function of the applied voltage is shown in Fig.2. R_{total} was up to 97% and a large proportion of decomposed formaldehyde converted to CO_2 in the dry air (Fig.2a). R_{total} dropped to 74% and R_{CO} also obviously reduced when H_2O was added to the feed gas (Fig.2b).

Comparing Fig.2a with Fig.2b, the humidity had a negative effect on R_{total} . The formation of other HCs was negligible in both cases.

b) Benzene Hydrocarbons decomposition

The benzene hydrocarbons decomposition as a function of the applied voltage was given in Fig.3, Fig.4 and Fig.5, respectively.

In dry air, maximum benzene decomposition rate was only 36%, and R_{CO_2} was higher than R_{CO} , as shown in Fig.3a. Fig.3b shows that benzene decomposition rate dropped to 31%, and R_{CO_2} reduced while R_{CO} increased, R_{HC} also had a visible reduction with the addition of 2.5% H_2O .

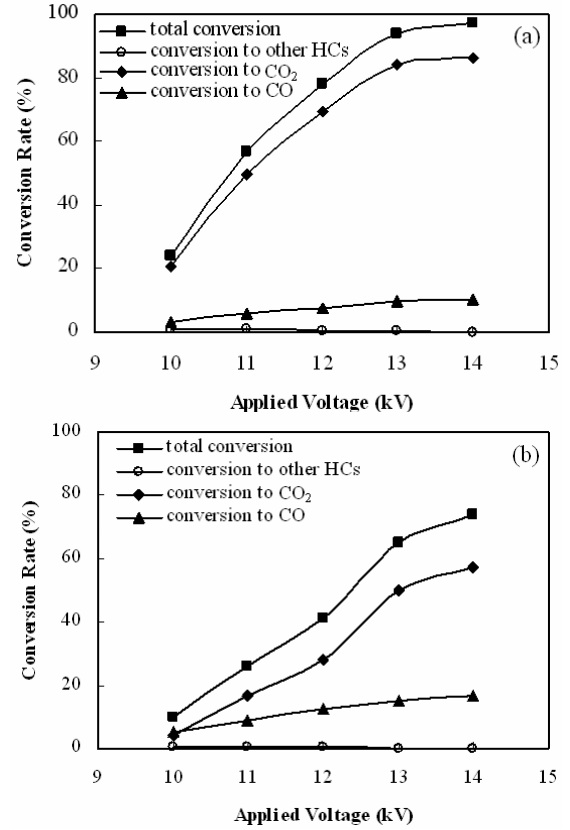


Fig. 2. Formaldehyde decomposition as a function of applied voltage at room temperature. (a) 41 ppm HCHO + dry air (b) 41 ppm HCHO + air with 2.5% H_2O

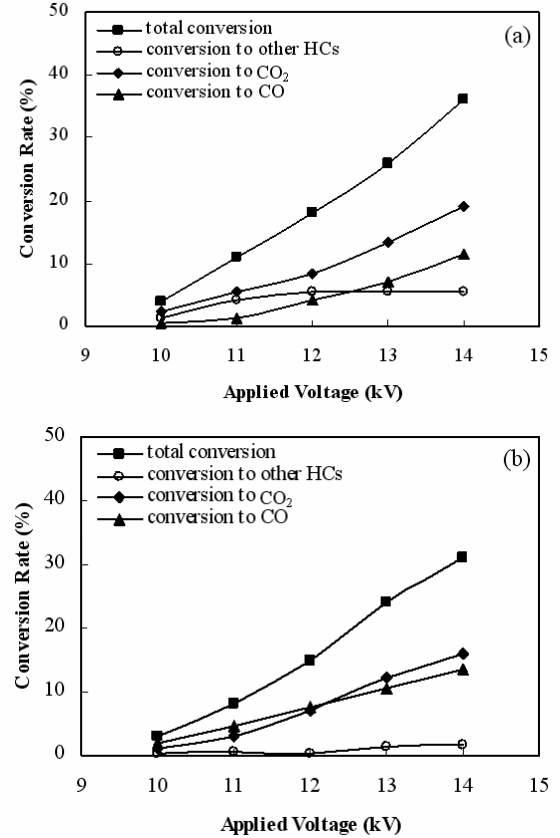


Fig. 3. Benzene decomposition as a function of applied voltage at room temperature. (a) 175 ppm C_6H_6 + dry air (b) 175 ppm C_6H_6 + air with 2.5% H_2O

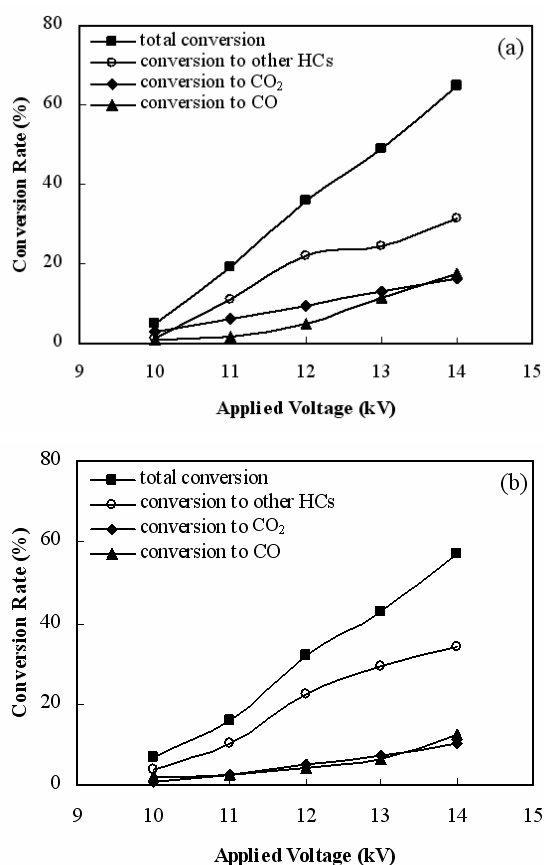


Fig. 4. Toluene decomposition as a function of applied voltage at room temperature. (a) 171 ppm C_7H_8 + dry air (b) 171 ppm C_7H_8 + air with 2.5% H_2O

From Fig.4a, it can be seen that the maximum toluene decomposition rate was 65%, R_{CO_2} was a little more than R_{CO} , and toluene of more than 30% was decomposed into other HCs in the dry air. The addition of water resulted in a decrease of R_{total} , R_{CO_2} and R_{CO} , but a small increase of R_{HC} (Fig.4b).

R_{total} of p-xylene decomposition was up to 82%, R_{CO_2} was lower than R_{CO} in the dry air (Fig.5a). Like toluene, H_2O had a negative effect on R_{total} , R_{CO_2} and R_{CO} except R_{HC} (Fig.5b).

The comparison of the decomposition products for different VOCs at the same voltage of 14 kV was shown in table 1. Whether in the dry air or in the humid air, R_{CO_2} of formaldehyde was highest among the four VOCs and R_{HC} of formaldehyde was close to zero, which can be attributed to the structure of formaldehyde having no ring and only one carbon atom. So, formaldehyde converts to CO_2 or CO more easily than benzene hydrocarbons. Benzene had the highest R_{CO_2} while its R_{total} was lowest among the three benzene hydrocarbons. The order of R_{HC} was p-xylene>toluene>benzene. These results proved that the oxidation degree of benzene was highest in benzene hydrocarbons [16-18]. The order of R_{CO} was p-xylene>toluene>benzene>formaldehyde in dry air, however, it was opposite in humid air.

In addition, yellow solid deposits were also found on the electrodes and reactor wall when benzene

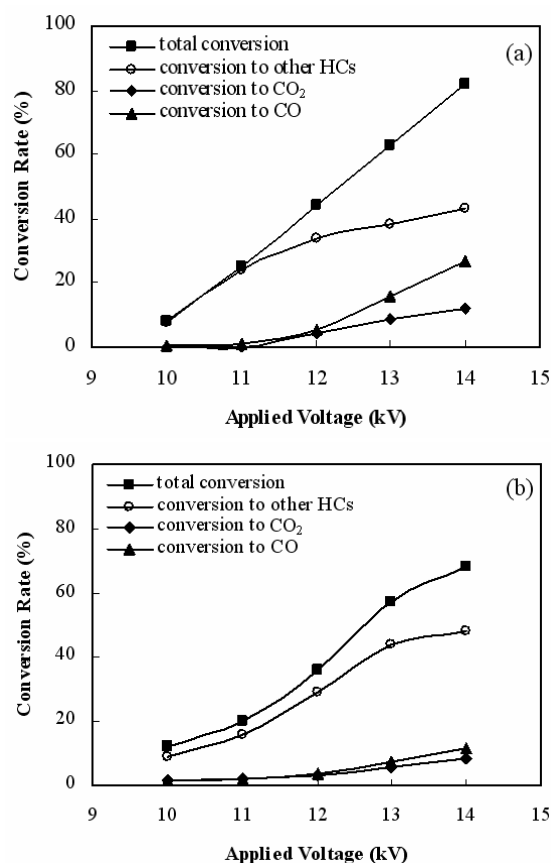


Fig. 5. P-xylene decomposition as a function of applied voltage at room temperature. (a) 165 ppm C_8H_{10} + dry air (b) 165 ppm C_8H_{10} + air with 2.5% H_2O

hydrocarbons were decomposed in the reactor. The sticky deposits are soluble in organic solvents such as acetone and ethanol, and almost insoluble in water [19]. The components of these solid deposits are complex and have not been analyzed in this study.

TABLE I.
THE DECOMPOSITION RATES OF FOUR VOCx AT THE VOLTAGE OF 14KV.

R_{total} (%)		Formaldehyde	Benzene	Toluene	p-xylene
R_{total}	a	97	36	65	82
	b	74	31	57	68
R_{CO_2}	a	86.5	19.1	16.2	12
	b	57.2	15.9	10.5	8.3
R_{CO}	a	10.3	11.5	17.4	26.7
	b	16.7	13.6	12.4	11.4
R_{HC}	a	0.2	5.4	31.4	43.2
	b	0.1	1.5	34.1	48.3

B. Formation of Other Byproducts

The ozone and NO_x formations were also investigated for VOCs decomposition by non-thermal plasma, as shown in Fig.6 and Fig.7.

Fig.6 shows that ozone formation decreased in the presence of VOCs, compared with pure dry air. Two factors are likely to lead to this result, that is, [O] atom needed for ozone generation preferably reacts with VOC molecules; and [O] atom formation is suppressed because more energy is consumed in the formation of other active species.

Fig.7 shows that NO_x concentration was very low, about 10 ppm in the pure dry air and it had a slight increase when the VOCs were added into the air.

C. Energy Efficiency of the reactor

The specific energy density and the energy efficiency are the important parameters to evaluate the plasma reactor. These two parameters for the four VOC were studied, as shown in Fig.8 and Fig.9.

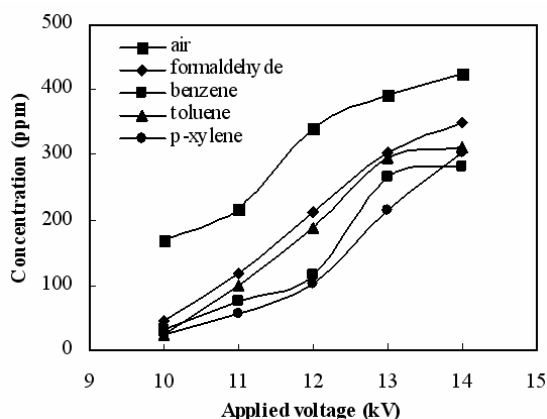


Fig. 6. Ozone formation as a function of applied voltage at room temperature. 41 ppm HCHO or 175 ppm C₆H₆ or 171 ppm C₇H₈ or 165 ppm C₈H₁₀ + dry air

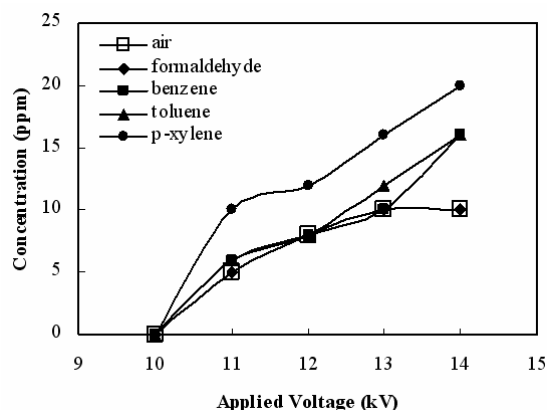


Fig. 7. NO_x formation as a function of applied voltage at room temperature. 41 ppm HCHO or 175 ppm C₆H₆ or 171 ppm C₇H₈ or 165 ppm C₈H₁₀ + dry air

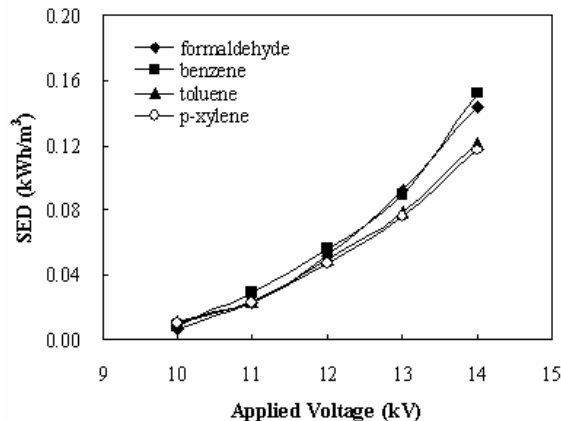


Fig.8. SED for four VOCs as a function of applied voltage

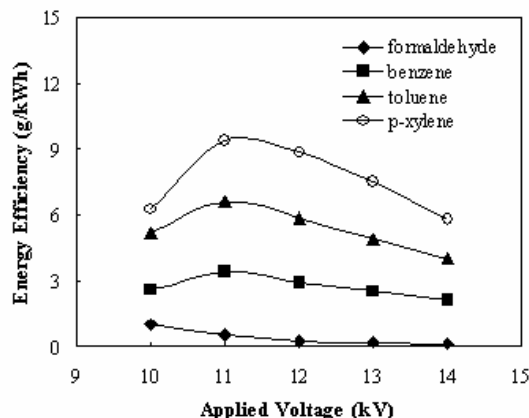


Fig. 9. the energy efficiency for four VOCs as a function of applied voltage

As seen from Fig.8, the specific energy density increased with the increasing voltage, and the range of the value is from 6.7×10^{-3} to $0.15 \text{ kW}\cdot\text{h}/\text{m}^3$.

From Fig.9, We can see that the energy efficiency for formaldehyde decreased with the increasing voltage. While for benzene, toluene and p-xylene, the energy efficiency increased firstly and then decreased. The highest values for formaldehyde, benzene, toluene and p-xylene are $1.05 \text{ g}/\text{kW}\cdot\text{h}$, $3.4 \text{ g}/\text{kW}\cdot\text{h}$, $6.6 \text{ g}/\text{kW}\cdot\text{h}$ and $9.4 \text{ g}/\text{kW}\cdot\text{h}$, respectively.

IV. CONCLUSION

The low concentration VOCs decompositions by positive DC streamer discharge were comparatively investigated in the same reaction condition. The following conclusions can be drawn.

(1) The rates of formaldehyde, benzene, toluene and p-xylene decomposition by positive streamer discharge are up to 97%, 36%, 65% and 82%, respectively.

(2) The decomposition products of these VOCs are mainly CO₂, CO and other hydrocarbons. Besides, about 400 ppm O₃ and 10 ppm NO_x were formed for the gas

ionization.

(3) The order of the R_{CO_2} is formaldehyde>benzene>toluene>p-xylene whether in the dry air or humid air. The order of the R_{CO} is p-xylene>toluene>benzene>formaldehyde in the dry air while it is opposite in the air with 2.5% water. And the order of R_{HC} is p-xylene>toluene>benzene>formaldehyde in both cases. The chemical structures have an important effect on products distributions.

(4) The specific energy density (SED) increased with the increasing voltage, the range is from 6.7×10^{-3} to $0.15 \text{ kW}\cdot\text{h}/\text{m}^3$. The energy efficiency for formaldehyde, benzene, toluene and p-xylene are $1.05 \text{ g}/\text{kW}\cdot\text{h}$, $3.4 \text{ g}/\text{kW}\cdot\text{h}$, $6.6 \text{ g}/\text{kW}\cdot\text{h}$ and $9.4 \text{ g}/\text{kW}\cdot\text{h}$, respectively.

ACKNOWLEDGEMENT

This research was supported by National Natural Science Foundation of China, project number 20677004.

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