



Simultaneous removal of ethyl acetate, benzene and toluene with gliding arc gas discharge*

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Abstract: The simultaneous removal of ethyl acetate, benzene and toluene with relatively low or high initial concentration is studied using a laboratory scale gliding arc gas discharge (GA) reactor. Good decomposition efficiencies are obtained which proves that the GA is effective for the treatment of volatile organic compounds (VOCs) with either low or high concentration. A theoretical decomposition mechanism is proposed based on detection of the species in the plasma region and analysis of the decomposition by-products. This preliminary investigation reveals that the GA has potential to be applied to the treatment of exhaust air during color printing and coating works, by either direct removal or combination with activated carbon adsorption/desorption process.

Key words: Plasma, Gliding arc gas discharge (GA), Volatile organic compounds (VOCs), Simultaneous removal, Printing and coating process

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INTRODUCTION

Volatile organic compounds (VOCs) are particularly burdensome for the natural environment problems such as global warming, photochemical smog formation, stratospheric ozone depletion and tropospheric ozone increase (Fiella *et al.*, 2007; Leach *et al.*, 1999; Sakai *et al.*, 2004). In China, printing and coating industry is one of the principal stationary sources of VOCs emissions from solvents. Removal of these toxic species becomes an important task for relevant enterprises in achieving environmentally accepted pollutants levels and meeting new standard (SEPA, 1997). However, the applications of most commonly used processes in the removal of VOCs are limited due to their own disadvantages: external fuel consumption is high in the thermal incineration process; rapid catalyst deactivation is a

common problem in the catalytic incineration; activated carbon is expensive, thus making regeneration economically desirable in the activated carbon adsorption process. The combination of activated carbon adsorption and further destructive process, such as thermal incineration and catalyst incineration, has been successfully applied to industry. More advanced destructive technologies are still required for the destructive regeneration of the spent activated carbon adsorbent.

As an alternative, atmospheric non-thermal plasma has been conducted to VOCs destruction since the last 10 years by using electron-beam irradiation (Kim *et al.*, 2005; Nichipor *et al.*, 2000) and various electrical discharge systems (Schutze *et al.*, 1998; Spanel *et al.*, 2007; Subrahmanyam *et al.*, 2007; Yamamoto, 1997), which has shown a great technical and economical potential as compared with traditional methods. The most potentially attractive benefit of non-thermal plasma assisted chemical processes is that, the input energy can be used to simulate the chemical reactions but not heat the bulk gases. In

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other words, the non-thermal plasma region provides a reactive atmosphere to make the chemical reactions occur out of equilibrium with energetic costs lower than the thermodynamic ones.

Gliding arc gas discharge (GA) is an auto-oscillating phenomenon developing between at least two electrodes that are immersed in a laminar or turbulent gas flow, which provides significantly non-equilibrium plasma region at elevated power level (Fridman *et al.*, 1999; Richard *et al.*, 1996). Since the early 1990's, the above feature was utilized to develop a GA device (Czernichowski, 1994; Lesueur *et al.*, 1988) as an innovative approach to addressing energy conservation (Sreethawong *et al.*, 2007) and environmental protection (Indarto *et al.*, 2007; Marouf-Khelifa *et al.*, 2006). Previous work of our group has demonstrated the feasibility of GA in the emission control and treatment of VOCs with different chemical structures (Bo *et al.*, 2007; Yan *et al.*, 2007).

In this paper, the simultaneous decomposition of ethyl acetate ($C_4H_8O_2$), benzene (C_6H_6) and toluene (C_7H_8), which are among the key pollutants included in exhaust air during color printing and coating works, was studied using a laboratory scale GA reactor. Both dilute and concentrated simulative flues were treated, because the VOCs concentration is usually low under industrial condition, but the desorption gas after activated carbon adsorption/desorption process is a much more concentrated VOCs/air flow. The possible decomposition mechanism was also discussed based on detection of the species in the plasma region and analysis of the decomposition by-products.

EXPERIMENTAL INVESTIGATION

Experimental setup

The schematic diagram of the experimental

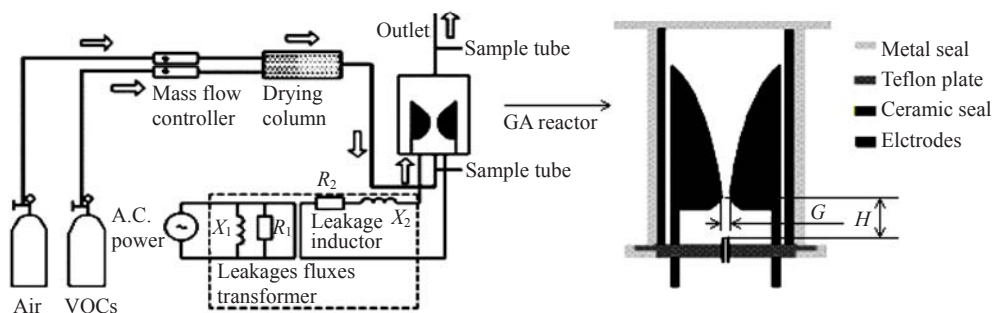


Fig.1 Schematic of experimental setup

setup is shown in Fig.1. It mainly consists of a gas feed system, a GA reactor with its power supply, and an analysis system. The simulative VOCs flue results from the mixing of a VOCs flow with a carrier gas flow. The concentration of VOCs is controlled by means of mass flow meters. The gas enters the GA reactor after passing through a drying column packed with a silica-gel desiccant to eliminate the influence of atmosphere water vapor. GA reactor mainly consists of two knife-shaped electrodes fixed on a Teflon bed plate, a nozzle with inner diameter 1.5 mm, a ceramic seal and a metal seal. Two electrodes are connected to a 50 Hz high voltage transformer (220 V/10 kV) with leakage fluxes. The effect of leakage fluxes determines a reactance that produces a constant RMS (Root Mean Square) value of current in the secondary coil. Two gas sample tubes are fixed in the front and back of the GA reactor for the analysis of the gas composition before and after discharge, respectively. In this work, the electrode gap G was set as 3 mm, and the vertical distance between electrode throat and nozzle outlet H was 15 mm.

GA plasma phenomenon

Fig.2 shows the high speed camera photographs of the evolution of GA phenomenon. The images of arc column motion were captured by a high-speed, rugged HG-100K digital camera (CMOS sensor, 1504×1128 pixels) and the sample frame rate is set as 2000 frames/s. The pictures were recorded and then analyzed by a MotionCentral Program.

GA phenomenon started at the shortest gap between the electrodes by an initial breakdown of the gas to be processed (Fig.2a). Then during few milliseconds the arc was pushed by the flow along the electrodes (Fig.2b) until the rupture of the ionized column. This event was followed by a new

breakdown at the electrode throat and the cycle repeated as long as the voltage delivered by the transformer was high enough. It was hard to geometrically define well the arc motion, and the cycle period of arc motion (from initial breakdown to rupture) was observed irregular (in the range of 9~11 ms in the present work) even though all experiment parameters were kept constant, which could be mainly attributed to the strong turbulence of the gas flow.

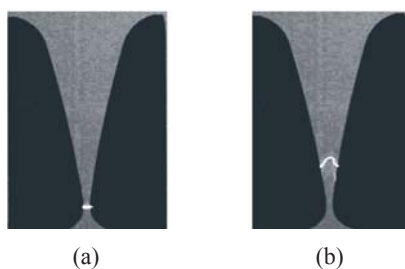


Fig.2 High speed camera photographs of GA evolution
(a) Initial breakdown; (b) Gliding arc

Analytical methods

The detection of species is achieved using an emission spectrometer equipped with a 1200 groves/mm grating motor. The blaze wavelength is 350 nm and the maximum resolution is 0.1 nm.

Decomposition experiments are conducted at atmospheric pressure and room temperature. Under each set of conditions, 20 min is allowed for stabilization before quantitative analysis. The discharge by-products were quantified by means of a NICOLET NEXUS 670 Fourier Transform Infrared (FTIR) spectroscopy equipped with a DTGs KBr detector. The spectral resolution is 4 cm^{-1} and every measurement is repeated four times. The temperature of sample cell is maintained at $180\text{ }^{\circ}\text{C}$.

We define the VOCs decomposition efficiency η , by-product selectivity S , and the carbon balance B_C as:

$$\eta (\%) = (X_0 - X) / X_0 \times 100\%,$$

$$S_{\text{CO}_2} (\%) = V_{\text{CO}_2} / [6 \times (X_{\text{C}_6\text{H}_6} - X_{\text{C}_6\text{H}_6}) + 7 \times (X_{\text{C}_7\text{H}_8} - X_{\text{C}_7\text{H}_8}) + 4 \times (X_{\text{C}_4\text{H}_8\text{O}_2} - X_{\text{C}_4\text{H}_8\text{O}_2})] \times 100\%,$$

$$S_{\text{CO}} (\%) = V_{\text{CO}} / [6 \times (X_{\text{C}_6\text{H}_6} - X_{\text{C}_6\text{H}_6}) + 7 \times (X_{\text{C}_7\text{H}_8} - X_{\text{C}_7\text{H}_8}) + 4 \times (X_{\text{C}_4\text{H}_8\text{O}_2} - X_{\text{C}_4\text{H}_8\text{O}_2})] \times 100\%,$$

$$B_C (\%) = S_{\text{CO}_2} + S_{\text{CO}},$$

where X_0 is the VOCs initial concentration, X is the

VOCs final concentration, V is the by-product concentration.

RESULTS AND DISCUSSION

Decomposition performance

1. Dilute VOCs decomposition

In this section, the initial concentration of ethyl acetate, benzene and toluene was set at the value of 1000×10^{-6} , 300×10^{-6} and 360×10^{-6} , respectively, which was close to the typical concentration of above target VOCs in the emission from industrial printing and coating process. The total flow rate was maintained at a fixed value: 12.7 Sl/min (where 'Sl' stands for 'standard liter').

Fig.3 shows the FTIR results of mixture gas before and after treatment by the GA discharge with air as the carrier gas. Experimental results showed that typical absorption spectra of three target VOCs decreased dramatically after discharge, and the decomposition efficiency of ethyl acetate, benzene and toluene was 91.4%, 82.6% and 83.9%, respectively, that the major discharge by-products were identified as H_2O , NO_2 , CO_2 and CO , and the concentration of NO_2 , CO_2 and CO in effluent was 5726.2×10^{-6} , 1339.3×10^{-6} and 1183.5×10^{-6} , respectively, that the value of B_C was close to 100%, which indicated that CO_2 and CO were the main carbonaceous by-products and no obvious hydrocarbon was detected in effluent, and that the selectivity of CO_2 (78.91%) was obviously higher than that of CO (18.46%), which indicated that CO was further transformed to CO_2 in air background.

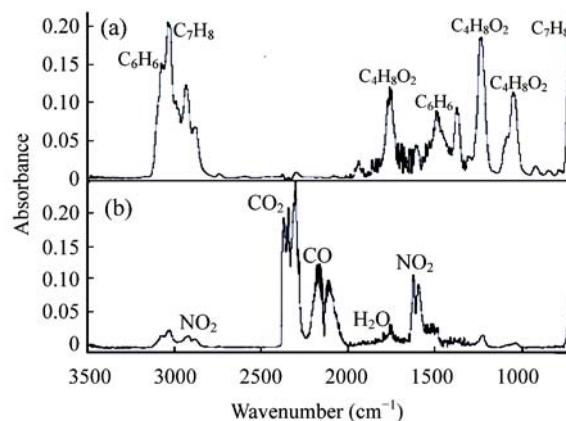


Fig.3 VOCs FTIR absorption spectra before (a) and after (b) treatment by GA discharge

2. Concentrated VOCs decomposition

The concentration of ethyl acetate, benzene and toluene was set as 10000×10^{-6} , 3000×10^{-6} and 3600×10^{-6} , respectively, assuming the value of absorption/desorption coefficient is 10. High concentration VOCs in a flue was introduced into the GA reactor for two runs treatment. Each run was completed with the same condition except that in Run 1# the flue was untreated, while in Run 2# the inlet gas was the effluent emitted from Run 1#. The total flow rate was 12.7 Sl/min.

Table 1 shows the decomposition efficiencies of target VOCs in high initial concentration condition after two runs treatment. It was found that the final decomposition efficiency of ethyl acetate, benzene and toluene could achieve 85.2%, 88.3% and 85.3%, respectively. The decomposition efficiencies of target VOCs in Run 2# were higher than those in Run 1#, which could be mostly attributed to the decrease of the inlet VOCs concentrations.

Table 1 VOCs decomposition efficiencies in high initial concentration condition

Target VOCs	$X_0 (\times 10^{-6})$	η (%)		
		Run 1#	Run 2#	Final
$C_4H_8O_2$	9500	50.4	70.2	85.2
C_6H_6	3000	57.5	72.5	88.3
C_7H_8	4000	52.3	69.2	85.3

Decomposition mechanism

1. Spectroscopic analysis of plasma region

The species formed in air discharge plasma region were detected with spectroscopic emission, and the result has been presented in Fig.4. The flow rate was set as 20 Sl/min, and the experiment was carried out in the absence of VOCs: the inlet reactant gas was air only.

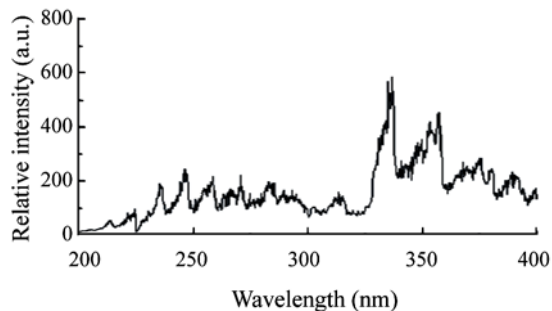
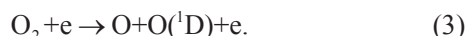


Fig.4 Spectroscopic emission in air discharge plasma region

NO radicals were identified clearly in the discharge: the 200~300 nm scans were dominated by the NO ($B^2\Pi-X^2\Pi$) β band and NO ($A^2\Sigma^+-X^2\Pi$) γ band. After the generation of high energetic electrons, which has been recognized as the initial step for all further reactions in the plasma region (Futamura *et al.*, 1997; Mok and Nam, 2002), N_2 and O_2 from carrier gas were dissociated by electron impact:



The $O(^1D)$ in Eq.(3) is one of the excitation states of O atom. Then, NO radicals were formed with the recombination of N and O radicals:



N_2^+ ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$) 1st negative system was detected after 330 nm (as shown in Fig.4), which indicated the existence of the ionization of N_2 :



Above limited analysis on the chemical property of the plasma region indicated that, energetic electrons, radicals (N, O and NO) and ions (N_2^+) were involved in the VOCs decomposition process.

2. Decomposition by-products analysis

As mentioned before, inorganic oxides (H_2O , NO_2 , CO_2 and CO) were the main discharge by-products under air atmosphere (as shown in Fig.3). The presence of oxygen induces the oxidation of nitrogen and VOCs to NO_2 , CO_2 , CO and H_2O . To get insight into the decomposition mechanism, the discharge experiments under nitrogen atmosphere were carried out. In this case, the possibility of the oxidation of VOCs molecules caused by O radicals form background was eliminated, and we try to find other pathways included in the decomposition process.

Fig.5 shows the FTIR results of the discharge by-products of benzene, toluene and ethyl acetate with nitrogen as carrier gas. Benzene, toluene and ethyl acetate were treated separately with the initial concentration of 180×10^{-6} , 150×10^{-6} and 700×10^{-6} , respectively. The flow rate was set as 12.7 Sl/min.

Experimental results showed that under nitrogen condition, acetylene (C_2H_2) ($3373.9\sim 3165.2\text{ cm}^{-1}$) and hexane (C_6H_{14}) ($2995.7\sim 2843.5\text{ cm}^{-1}$) were the main by-products of benzene while also obvious C_2H_2 was detected after discharge of toluene and ethyl acetate, and that small amounts of CO and CO_2 were found as the decomposition by-products of ethyl acetate in nitrogen atmosphere.

The formations of the gaseous by-products shown in Fig.5 such as C_2H_2 , C_6H_{14} , CO and CO_2 could be mainly attributed to the recombination of the radicals formed in the following two channels.

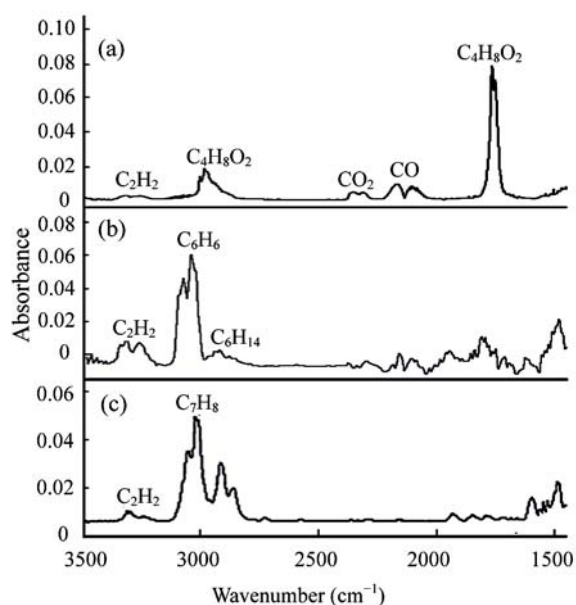


Fig.5 FTIR absorption spectra of benzene and toluene after discharge in nitrogen atmosphere

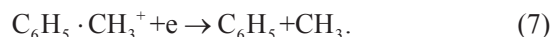
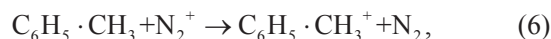
(a) After discharge ethyl acetate; (b) After discharge benzene; (c) After discharge toluene

Channel 1: VOCs dissociations by electron impact.

The bond energy of C-C in $C_4H_8O_2$ and C_7H_8 is 4.33 and 4.23 eV, respectively; the bond energy of C-H in $C_4H_8O_2$, C_6H_6 and C_7H_8 is 4.16, 4.90 and 3.84 eV, respectively; the C-O bond energy in $C_4H_8O_2$ is 3.97 eV. Hence, the mean energy of the free electrons in gliding arc plasma region ($\sim 5\text{ eV}$) is high enough to break the C-C, C-H and C-O bonds in target VOCs molecules. The electron impacts on VOCs molecule can lead to the creation of radicals. Fig.6 presents the electron impacts dissociation of ethyl acetate molecule and the possible radicals formed (1~7 in Fig.6 (b)).

Channel 2: reactions between ions and VOCs.

VOCs molecules get the charge from the ion in the charge transfer process, and then recombine with a free electron, resulting in the formation of radicals. For example:



3. Theoretical decomposition process

On the basis of above experimental results and analysis, the schematic of the VOCs removal process under air condition can be depicted as Fig.7. The production of reactive radicals and ions may be initiated by background gas dissociation and ionization induced by electrons. The electron impact dissociation on the VOCs molecules and the charge transfer between VOCs molecules and ions are two important channels of the formation of radicals. The

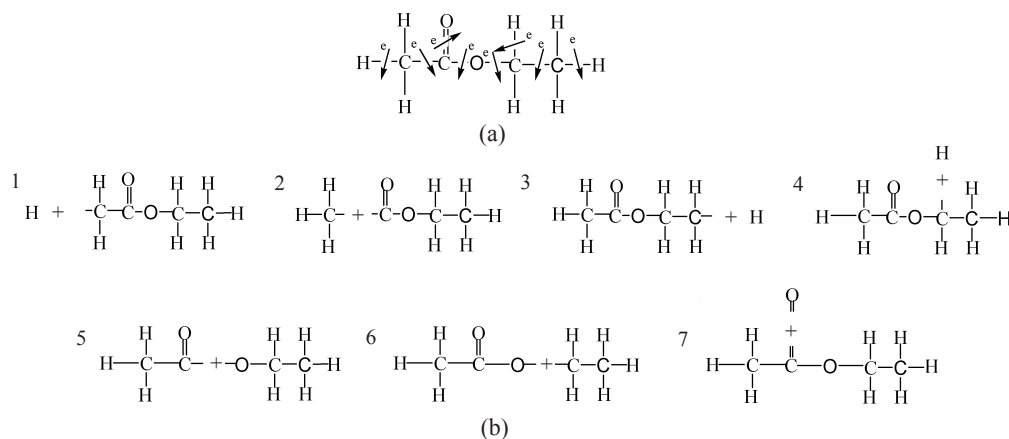


Fig.6 Schematic of (a) ethyl acetate dissociations by electron impact and (b) possible by-products

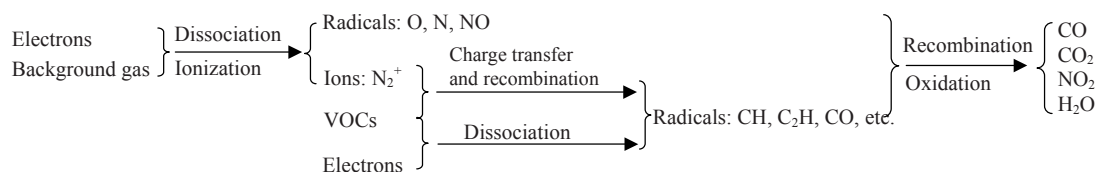


Fig.7 Schematic of VOCs removal process with air as background gas

recombination of radicals and the oxidation process (in the condition of the presence of oxygen) cause the formation of final products, i.e., H₂O, CO₂, CO and NO₂.

CONCLUSION

The simultaneous removal of ethyl acetate, benzene and toluene using a laboratory scale GA reactor has been carried out. Following conclusions were obtained:

(1) Three target VOCs with either relatively high or low concentrations were reduced considerably with GA reactor. This technique provides an innovative option for the treatment of exhaust air during color printing and coating works, by either directly removal or combination with activated carbon absorption/desorption process.

(2) Reactive radicals (N, O and NO) and ions (N₂⁺) are the main species detected in the plasma region.

(3) The GA plasma induced VOCs decomposition process can be summarized as following reactions: the electron impact dissociation on both VOCs and background gas, the charge transfer between VOCs molecules and ions, the radical recombination, and the oxidation (in the condition of the presence of oxygen).

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