Full Length Research Paper

Ethyl acetate removal by strong ionization dielectric barrier discharge and investigation on the decomposition pathway

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ABSTRACT

In this research, a dielectric layer made of a thin layer of α-Al_2O_3 combined with a high-frequency high-voltage power source to construct a narrow discharge gap (0.6 mm) plasma generator to degrade ethyl acetate (EA) from polluted air, as one of the typical Volatile Organic Compounds (VOCs). The electrical discharge characteristics, Specific Input Energy (SIE), energy yield (EY) and initial concentration were studied. Finally, the intermediate products generated in the EA decomposition process were analyzed and determined by GC-MS and the possible decomposition pathway was discussed. The results showed that strong ionization Dielectric Barrier Discharge (DBD) reactor has good discharge characteristics and high removal efficiency on EA. Removal efficiency of 450 ppm EA at 12 L/min could reach 90% when SIE was more than 100 J/L. Furthermore, the EY was highest (48.7 g/kWh) when SIE was 102 J/L. The removal efficiency decreased with the increase of initial concentration and gas residence time and the optimum applied voltage for each concentration is distinct and in the range of 2.6-3.4 kV. Several intermediate products including ethanol, formic acid and acetic acid were detected and the possible reaction pathway of EA degradation in strong ionization Dielectric Barrier Discharge reactor was discussed finally.

Keywords: Strong ionization discharge, Plasma, Ethyl Acetate, Removal Efficiency, Decomposition pathways

INTRODUCTION

Ethyl Acetate (EA) is an organic solvent widely used in manufacturing, pharmaceutical, and food industry, mainly as a solvent for paints, lacquers, and food flavors. Exposure to EA at high concentration is reportedly associated with a myriad of health problems including eye, nose, throat and respiratory irritation symptoms. At low concentrations EA may cause nausea, dizziness, irritation (Zare et al., 2012; Wen et al., 2005). Removal of EA from polluted air stream is thus an important issue demanding the attention of scientists and engineers.

Removal technologies include physical methods (activated carbon adsorption, condensation and absorption), chemical methods (thermal oxidation, catalytic oxidation and chemical scrubbers) and biochemical methods (activated sludge, biofilters, bioscrubbers) (Wu et al., 2016; Ragazzi et al., 2014). However, each of these traditional technologies has been reported to show some drawbacks. For example, adsorption of activated carbon and absorption of liquid result in unexpected byproducts which may cause secondary pollution; condensation is only applied for high concentrations of VOCs; thermal and catalytic oxidation have high energy consumption which means they are not economically feasible and biological methods need a large area and is efficient only for treatment of low concentration of air pollutant.

As an emerging technology for VOC degradation, non-thermal plasma (NTP) technology has a very wide application prospect. Compared with traditional technologies, NTP can remove various VOCs with low concentration at ambient temperature and atmospheric pressure simultaneously, with the advantages of high removal efficiency, strong adaptability and relatively low power consumption, thus becomes a potential and promising method for VOCs treatment (Guo et al., 2015; Li et al., 2014). It has therefore attracted the attention of researchers in the last few decades. Karakum and Deshusses (2016) investigated the removal efficiency of several common VOCs using DBD reactor under the same experimental conditions (gas residence time

0016 s, initial concentration 95-100 ppm). The following removal efficiencies were obtained: methyl ethyl ketone (50%), benzene (58%), toluene (74%), 3-pentanone (76%), methyl tert-butyl ether (80%), ethylbenzene (81%), and n-hexane (90%). The VOC removal efficiencies observed are positively correlated with the number of hydrogen atoms present in the pollutant compound structure. Ma et al., (2016) used pulsed–modulated AC power DBD reactor to degrade benzene. The study showed that pulsed-modulated DBD plasma are more effective in the use of free radicals, thereby increasing the energy yield and CO_2 selectivity during VOCs degradation. Wang et al., (2016) decomposed dimethyl amine (DMA) and N,N-dimethylformamide (DMF) with a link tooth wheel-cylinder plasma reactor. The research showed DMA is much easier to be degraded than DMF by NTP, and when DMA and DMF are mixed, DMA can significantly increase the conversion of DMF and the possible degradation mechanism of DMA and DMF was proposed.

However, current studies mainly investigated optimization of the performance of NTP reactors VOC removal by NTP combined with catalytic or photo catalytic technology, while decomposition byproducts and degradation pathway still remains nascent for most VOCs. The aim of this paper is to use the strong ionization DBD to investigate the mechanism and reactor discharge conditions required for the decomposition of Ethyl Acetate (EA). The role of important parameters such as initial concentration and input energy density were studied and the possible decomposition pathway was also studied.

MATERIALS AND METHODS

The schematic diagram of the experimental setup is shown in Figure 1. The main experimental apparatus includes EA generator, strong ionization dielectric barrier discharge reactor.

EA Generator

The EA generator consists of an air pump, bubbling bottle, water bath and buffer tank. The dilution air flowing into the EA bubbler and the power of the entire gas pipeline is provided by the air pump. EA was evaporated by bubbling pure air. The flow rate of EA and dilution air was controlled by rotor flow meter. The bubbler was placed in a thermostatic water bath and kept at a stable temperature of 25°C ± 1°C. By controlled flow and temperature, the actual EA gas in industries was simulated. The buffer tank slows down the flow rate, allowing the air and EA gas to be fully mixed before entering the strong ionization discharge reactor.

The Reactor System

The reactor is mainly constructed of a device producing active radicals by strong ionization discharge and high voltage high frequency power supply. The plasma reactor used in this experiment is a narrow discharge gap, thin dielectric layer plate dielectric barrier strong ionization discharge reactor. The reactor is a rectangular cube, with bulk dimension of 227 mm × 145 mm × 22 mm, heat sink housing, and an electric fan to prevent the reactor from overheating.

The schematic diagram of the strong ionization discharge reactor is shown in Figure 2. The discharge electrode is made of sintered silver metal and sprayed on its outer surface with a thin (330 μm) dielectric layer (100 mm × 190 mm) composed of a dense insulating α-Al_2O_3 powder. The plasma generator uses a double discharge channel, a narrow discharge gap (0.6 mm) structure, 0-4.0 kV voltage, 4.5-6.5 kHz frequency, 350 Td electric field strength, average electron energy of 10 eV, and $10^{15}/m^3$ average electron density (Li et al. 2016; Bai et al. 2016). The plasma power supply used in this experiment is CTP-2000K/P NTP experimental power supply. CTP-2000 K/P NTP experimental power supply can work normally and stably for a long time
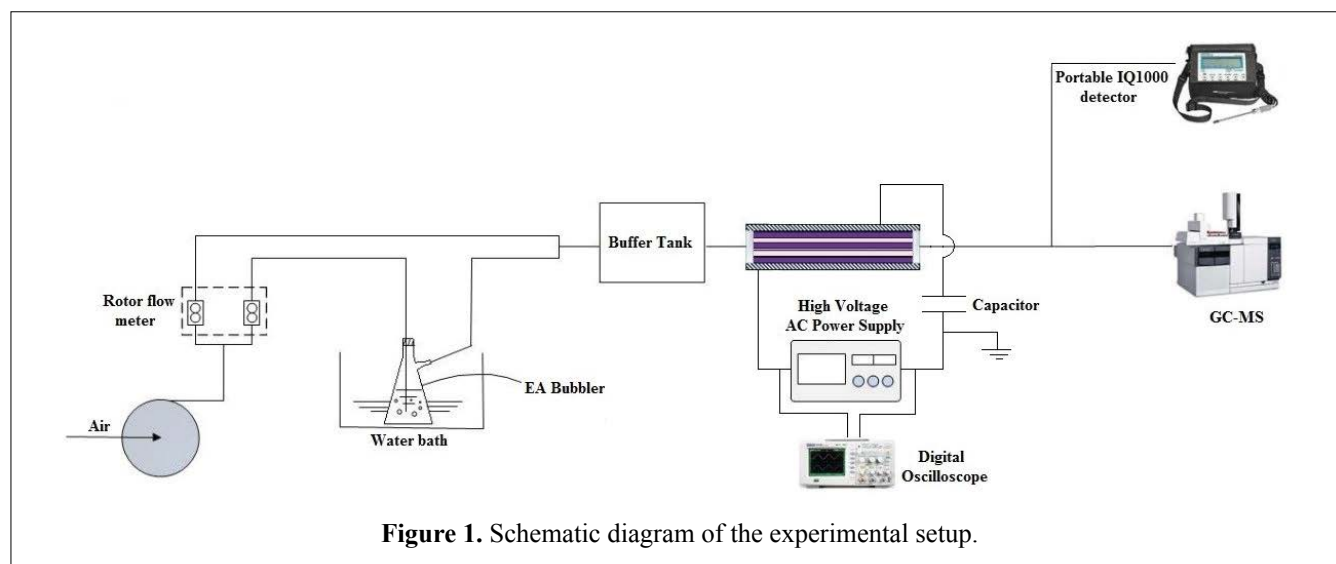
Figure 1. Schematic diagram of the experimental setup.

Figure 2. Schematic diagram of strong ionization discharge.
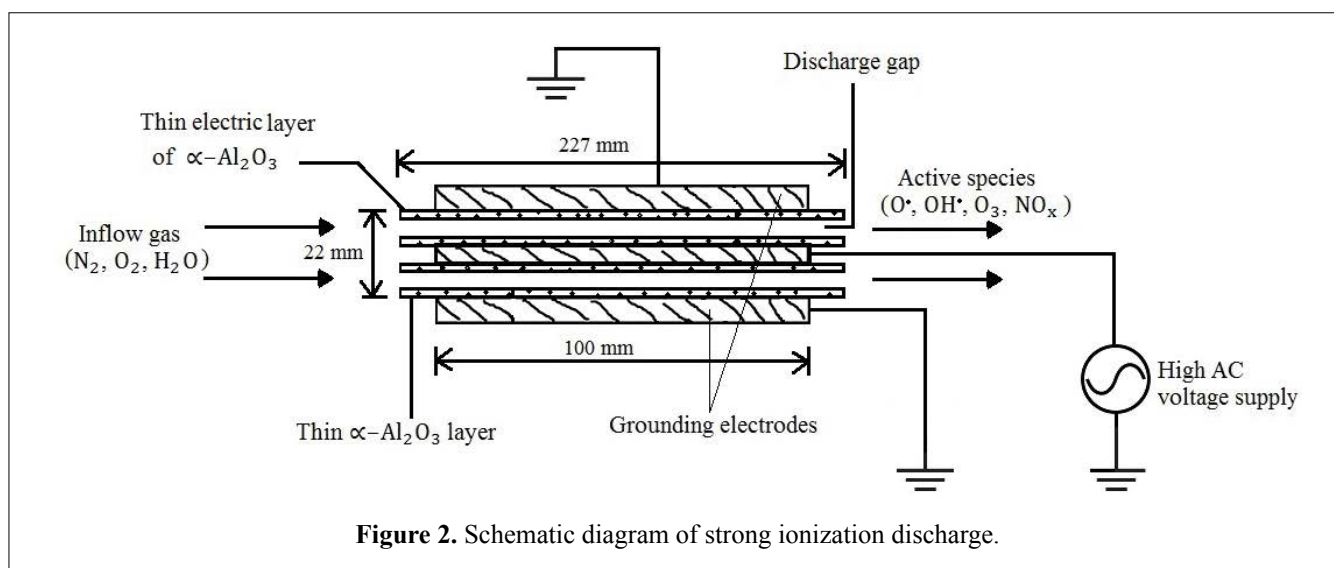
at any pressure, and can adapt to the dielectric barrier, bare electrode and other discharge mode, having a wide range of applications.

Analysis Methods

The EA concentrations at the inlet and outlet of strong ionization DBD reactor were initially detected by a VOC online detector (MODEL IQ1000, IST Corporation, USA) and then verified and accurately measured by the gas chromatograph (GC-2010, Shimadzu Corporation, Japan) equipped with a flame ionization detector (FID) based on peak areas. The intermediates and final products during EA removal were determined by GC-MS (Agilent 6890-59758, Shimadzu Corporation, Japan). The effective voltage was monitored by voltmeter and the peak voltage, current and frequency of the reactor were measured by a digital storage oscilloscope (Jet 354A, LeCroy Wave, USA). The applied input voltage was detected by a high voltage probe (Tektronix P6015A), while the voltage across the external capacitor (4.7 μF) was measured by a voltage probe (Tektronix TCP2020).

The definition of EA removal efficiency (η) is as follows:

$$\eta(\%) = \frac{C_{in} - C_{out}}{C_{out}} \times 100\%$$

(1)

where the C_{in} and C_{out} are the EA inlet and outlet concentrations in ppm.

The average discharge power (P) is calculated by:

$$P = f \int_0^t V(t)I(t)dt$$

(2)

where V(t) and I(t) are the pulsed discharge voltage (V) and current (A), respectively. These two parameters were monitored by a digital oscilloscope (Jet 354A, LeCroy Wave, USA).

The specific input energy (SIE) is an important parameter commonly used to investigate VOC decomposition and is calculated using the equation:

$$SIE = \frac{P}{Q} \times 60$$

(3)

where P is the average discharge power (W) and Q is the gas flow rate (L/min)

The energy yield (EY) can be expressed as follows:

$$EY = \frac{C_{in} - C_{out}}{SIE} \times \frac{3.6 \times M}{24} \left(\frac{g}{kWh}\right)$$

(4)

where M is the molecular weight of EA, the value 24 is the molar volume of gas (L/mol) under the ambient condition (around 25°C); 3.6 are the unit conversion coefficient (Ma et al., 2016).

RESULT AND DISCUSSION

Electrical Discharge Characteristics

The increasing electric field accelerates electrons, resulting in more micro-discharges and active species in the plasma. Moreover, the electrode emits more secondary electrons and can excite the collision of EA molecules with electrons. The typical voltage and current waveforms of the strong ionization DBD displayed on the oscilloscope is shown in Figure 3. The amplitude of the applied voltage is 3.5 kV, with the corresponding current waveform showing several short peaks which indicates micro discharge activity in the DBD plasma. Each pulse correlates with a series of micro discharges.
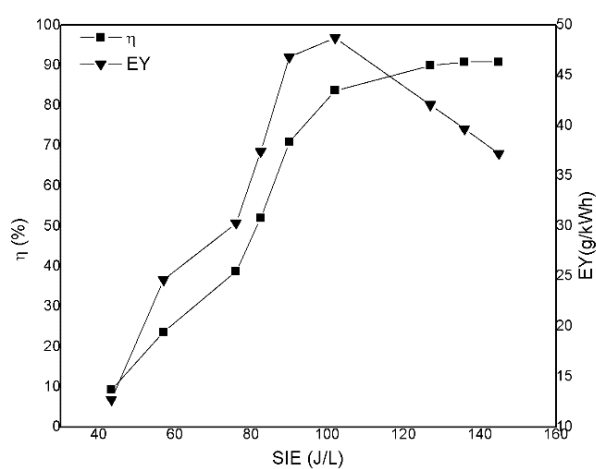
Effect of SIE on EA removal and Energy yield

The effect of SIE values on the EA removal efficiency and energy yield was investigated by changing SIE value from 40 to 160 J/L with constant frequency (5.71 kHz), a constant flow rate (12 L/min) and constant inlet concentration (450 ppm). The removal efficiency of EA rises with increase of SIE.

The rise is very fast in the range of 40-100 J/L, as the SIE
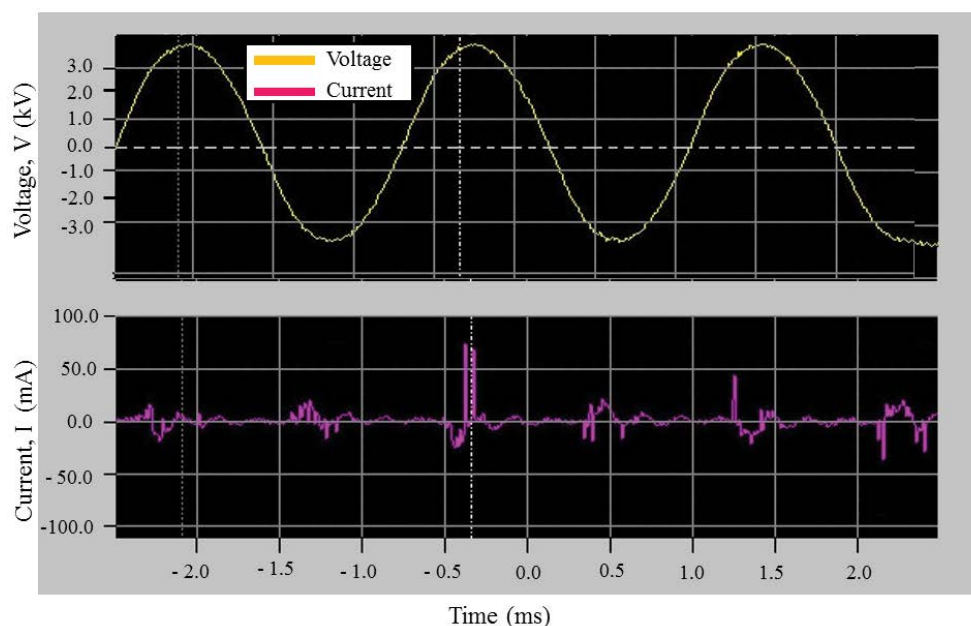
Figure 3. Typical voltage and current waveforms of strong ionisation Dielectric Barrier Discharge in air, displayed on the oscilloscope.

Figure 4. Effect of SIE (Specific Input Energy) on ethyl acetate removal efficiency and energy yield.(initial concentration, 450ppm; frequency, 5.71 kHz gas flow rate, 12 L/min).

value increases to more than 100 J/L, the rate of increase in removal efficiency becomes slow, while removal efficiency tends to be a stable value 91%, as shown in Figure 4.
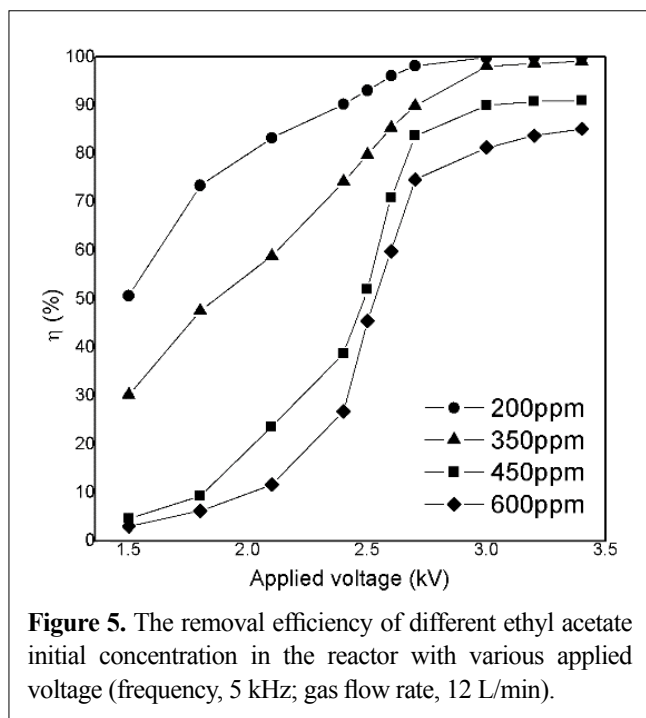
This is because when the frequency is constant, the energy density is mainly related to the applied voltage. As the applied voltage increases, the energy density also increases, thus, increasing the electric field strength between the electrodes, resulting in more oxidative active particles and free activity. Even though a further increase in the energy density proportionally increases the active particles and

radicals in the electric field, the concentration of ethyl acetate in the reactor remains constant, so the upward trend of the removal efficiency of the pollutants gradually becomes gentle.

Figure 4 on the other hand, shows the impact of SIE on removal efficiency and EY. The EY first rapidly increased from 12.8 to 48.7 g/kWh at SIE of 10-100 J/L and then rapidly dropped to 37.24 g/kWh at SIE of 100-145 J/L. This shows that more energy was probably used for unnecessary heating, generating photons, or formation of discharge byproducts. In this experiment, when the EA concentration is 450 ppm, SIE is in the range of 100-110 J/L, and EY is highest.

Effect of Initial Concentration on EA Removal

The initial concentration is a significant parameter for EA removal. As shown in Figure 5, different concentrations (200 to 600 ppm) of EA were investigated in the strong ionization DBD reactor. For all the concentrations investigated, the removal efficiency of EA increased until its increasing trend tended to be gentle or increased to some stable value with the increase of applied voltage. In this case, increasing the voltage will only result in higher energy consumption. It can be seen from Figure 5 that lower EA concentration (200 ppm) was easily removed when the electrical voltage was more than 2.4 kV, with the removal efficiency exceeding 90%. However, when the concentration increased to 600 ppm, the removal efficiency was only 24.8%. A similar phenomenon was noticed at the concentration of 350 ppm and 400 ppm and the EA removal efficiency was clearly increased at 2.6 kV.

Figure 5. The removal efficiency of different ethyl acetate initial concentration in the reactor with various applied voltage (frequency, 5 kHz; gas flow rate, 12 L/min).

This is because the number of high-energy electrons and active particles in the reactor is substantially constant when the voltage is constant. At the same flow rate, an increase in the concentration of ethyl acetate in the gas means that the probability of high-energy and active particles colliding with the average inelastic collision of each ethyl acetate molecule is reduced, resulting in a decrease in the proportion of oxidized and decomposed ethyl acetate molecules as a whole. The degradation efficiency is lowered. It can be seen from the figure that the optimum applied voltages of different concentrations are slightly different, and the optimum applied voltage ranges from 2.6 to 3.4 kV.

Analysis of Byproducts and the Possible Degradation Pathway of EA

When the input energy was sufficient, most of its EA molecules are oxidatively decomposed into CO_2 and H_2O. In order to further qualitatively analyze the intermediate products produced in the degradation reaction, the experiment used dichloromethane as the absorbent to collect the intermediate products produced in the reactor when the input energy was relatively low, and then analyzed and detected these byproducts by GC-MS.

Studies have shown that non-thermal plasma degradation of gaseous pollutants can be divided into two paths. The first is direct oxidation, that is, the direct impact of high-energy electrons. When the energy of high-energy electrons is the same or similar to some of the bond energies of molecules, the chemical bonds are destroyed, thereby destroying the structure of the molecules. The other is indirect oxidation, that is, high-energy electrons collide with H_2O, O_2 and N_2 and then strong oxidizing active particles are generated.

Since the concentration of gas molecules such as H_2O, O_2 and N_2 in the reactor is much larger than the molecular concentration of gaseous pollutants, so the second effect is dominant (Zhou et al. 2003; Song et al. 2002).

The structure and individual chemical bond energies of ethyl acetate are shown in Figure 6. The C=O is 7.55 eV, C–H is 4.29 eV, C–C is 3.44 eV and C–O is 3.38 eV (Zheng et al., 2014). So theoretically, C–C and C–O bonds may be destroyed firstly to form the following groups CH_3, $CH_3CH_2OCO\cdot$, $CH_3COOCH_2\cdot$, CH_3COO, CH_3CH_2, CH_3CH_2O and CH_3CO. These groups may be further cleaved by higher energy electrons into smaller molecules such as CH_3, CH_3CH_2, CH_3CH_2O, CH_2O, $OHCO$, CH_3OH.

Zheng et al., 2014 studied the possible reaction pathways for the degradation of acetone by packed bed dielectric barrier discharge. It has been found that due to the large amount of highly oxidizing active particles in the discharge gap, the above groups will be rapidly oxidized, and the methyl group plays a key role in the oxidation process. Similar to the degradation process of acetone, methyl (CH_3) can be further decomposed by high-energy electrons and radicals during the degradation of ethyl acetate, resulting in the formation of CH_2 groups, and further reacting with O and OH groups to form methanol (CH_3OH), formaldehyde (CH_2OH) and formic acid ($HCOOH$). The resulting above groups such as ethyl (CH_3CH_2), acetate (CH_3COO), and acetyl (CH_3CO) may collide with O and OH radicals to cause a series of oxidation reactions to finally form ethanol (C_2H_5OH), and acetaldehyde (CH_3CHO) and acetic acid (CH_3COOH). Sawyer et al. (1994) reported that the main intermediates of platinum/alumina catalyzed oxidation of ethyl acetate are ethanol, acetaldehyde and acetic acid which is the similar substances as our research. Combined with the measured product ethanol, formic acid and acetic acid and the above analysis, a possible degradation path of ethyl acetate as shown in Figures 7 and 8 was obtained.

**Analysis of Cost and Feasibility of Strong Ionization Dielectric Barrier Discharge**

The degradation of ethyl acetate by strong ionization

Figure 6. The structure of ethyl acetate showing the dissociation energies of chemical bonds.
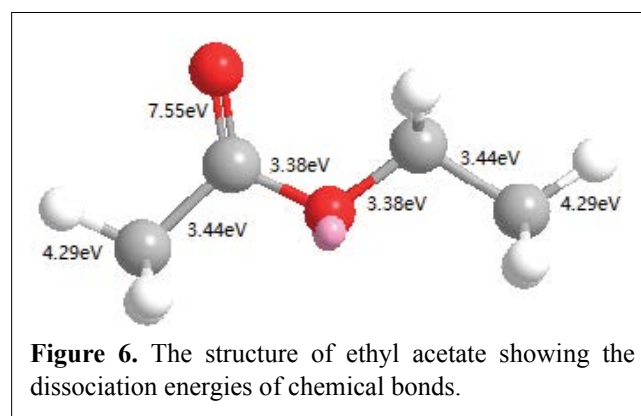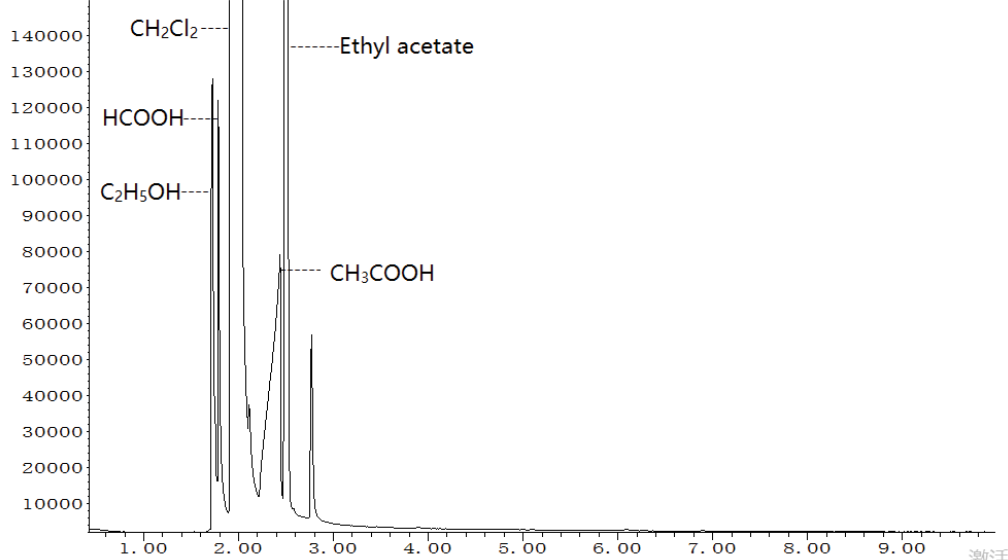
Figure 7. GC-MS of intermediate byproducts formed in during the decomposition of ethyl acetate by the strong ionization DBD reactor (SIE, 27.7 J/L; voltage, 1.5 kV; Frequency, 4.95 kHz; initial concentration, 350 ppm; gas flow rate, 10 L/min; sample collection time, 40 min; gasification chamber temperature, 230°C ion source temperature, 250°C quadrupole temperature, 150°C split ratio, 10:1; injection volume,1 μl. initial column temperature, 35°C).
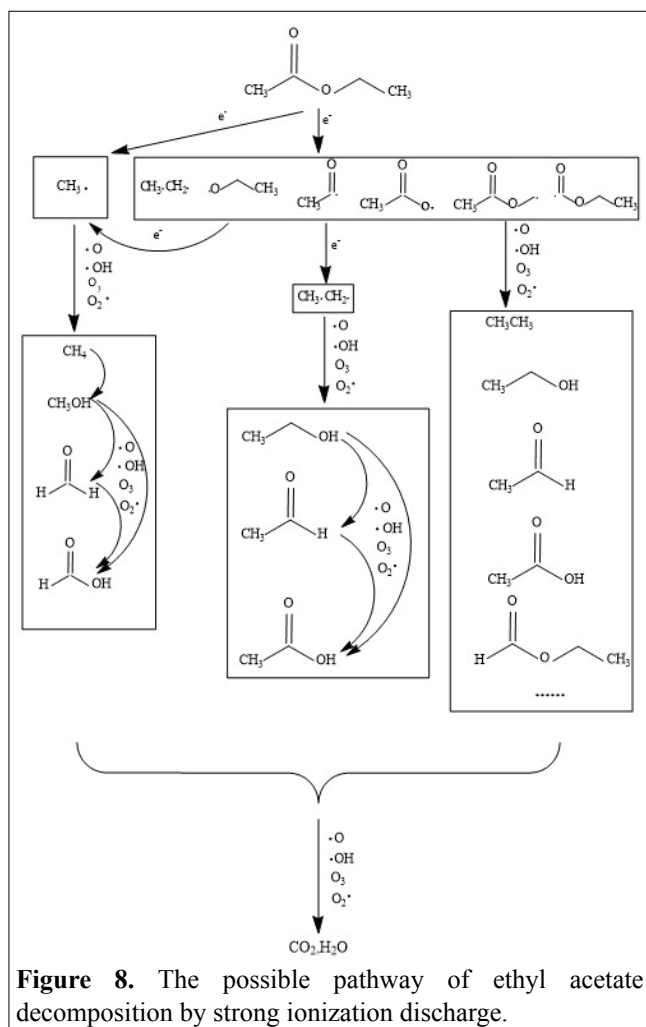
Figure 8. The possible pathway of ethyl acetate decomposition by strong ionization discharge.

discharge has both theoretical and practical significance. The study shows that removal efficiency of ethyl acetate by strong ionization discharge is appreciably high; thus a feasibility analysis from an economic perspective for industrial application of waste gas treatment and the cost of experimental equipment is discussed in this section.

As seen from the previous study, when the initial concentration was 450 ppm, frequency was 5.71 kHz, gas flow rate was 12 L/min and applied voltage was 2.8 kV, the removal efficiency was high and the energy yield was highest. Degradation of ethyl acetate by experimental apparatus under the above experimental conditions, the current and voltage of the experimental device was detected by digital oscilloscope, voltage probe and current probe and the output power was calculated by equation (2). From this calculation, the power consumption of the experimental device for one hour is 0.175 kWh, the power consumption of ethyl acetate treated with 1m3 is 0.243 kWh. There are deviations in industrial electricity costs in various provinces and cities in China. Taking Jiangsu Province as an example, the peak electricity cost is 0.844 yuan/kWh. Therefore, the operating system of this experiment requires 0.2 yuan for 1 m³ ethyl acetate. Therefore, the operation cost of degradation of ethyl acetate by strong ionization discharge is low and this technology has a good application prospect and economic value in the industry.

CONCLUSION

This study has investigated the mechanism, reactor discharge conditions, and the possible decomposition Pathways in the

decomposition of EA using the strong ionization dielectric barrier discharge reactor at atmospheric pressure. Firstly, the strong ionization DBD reactor used in this experiment has a good discharge characteristic with appreciably good removal efficiency on EA. At 450 ppm of EA and 12 L/min flow rate, removal efficiency could reach 90% when SIE was more than 100 J/L. Meanwhile, the EY was highest (48.7 g/kWh) when SIE was 102 J/L. Secondly, initial concentration was an important factor affecting removal efficiency. The removal efficiency decreased with the increase of initial concentration. Finally, the GC-MS spectrum showed ethanol, formic acid and acetic acid as possible intermediates, allowing for the discussion of possible pathway of EA decomposition.

ACKNOWLEDGMENT

REFERNCES

Bai M, Zheng Q, Tian Y, Zhang Z, Chen C, Cheng C, Meng X (2016). Inactivation of invasive marine species in the process of conveying ballast water using, OH based on a strong ionization discharge. Water. Res. 96: 217-224.

Guo Y, Liao X, Fu M, Huang H, Ye D (2015). Toluene decomposition performance and NOx by product formation during a DBD-catalyst process. J. Environ. Sci. 28(2): 187-194.

Karatum O, Deshusses M (2016). A comparative study of dilute VOCs treatment in a non-thermal plasma reactor. Chem. Eng. Sci. 294: 308-315.

Li Y, Fan Z, Shi J, Liu Z, Zhou J, Shangguan W (2014). Removal of Volatile Organic Compounds (VOCs) at Room Temperature Using Dielectric Barrier Discharge and Plasma-Catalysis. Plasma Chemistry and Plasma Processing. 34(4): 801-810.

Li Y, Yi R, Yi C, Zhou B, Wang H (2016) Research on the degradation mechanism of pyridine in drinking water by dielectric barrier discharge. J. Environ. Sci. 53(3): 238-247.

Ma T, Jiang H, Liu J, Zhong F (2016) Decomposition of Benzene Using a Pulse-Modulated DBD Plasma. Plasma Chemistry and Plasma Processing, 36(6): 1533-1543.

Ragazzi M, Tosi P, Rada EC, Torretta V, Schiavon M (2014). Effluents from MBT plants: Plasma techniques for the treatment of VOCs. Waste. Manag. 34(11): 2400-2406.

Sawyer JE, Abraham MA (1994). Reaction Pathways during the Oxidation of Ethyl Acetate on a Platinum/Alumina Catalyst. Ind. Eng. Chem. Res. 33(9): 2084-2089.

Song YH, Kim SJ, Choi KI, (2002). Effects of adsorption and temperature on a nonthermal plasma process for removing VOCs. J. Electrostat. 55(2): 189-201.

Wen JP, Yu C, Xiaoqiang J, Dongyan C (2005). Simultaneous removal of ethyl acetate and ethanol in air streams using a gas–liquid–solid three-phase flow airlift loop bioreactor. Chem. Eng. Sci. 106(2): 171-175.

Wang W, Fan X, Zhu T, Wang H (2016). Removal of gas phase dimethylamine and N,N dimethylformamide using non-thermal plasma. J. Environ. Sci. 299: 184-191.

Wu CH, Lin CW (2016). Electricity generation and kinetic aspects of a biotrickling filter-microbial fuel cell for the biofiltration of ethyl acetate vapor from waste gas. J. Taiwan. Inst. Chem. E.

Zare H, Najafpour G, Rahimnejad M, Tardast A, Gilani S (2012). Biofiltration of ethyl acetate by Pseudomonas putida immobilized on walnut shell. Bioresour. Technol. 123(2): 419-423.

Zheng C, Zhu X, Gao X, Liu L (2014). Experimental study of acetone removal by packed-bed dielectric barrier discharge reactor. Journal of Industrial & Engineering Chemistry. 20(5): 2761-2768.

Zhou YX, Yan P, Cheng ZX, Nifuku M (2003). Application of non-thermal plasmas on toxic removal of dioxin-contained fly ash. Powder. Technol.135-136: 345-353.