Naphthalene decomposition by atmospheric gliding arc gas discharge

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Abstract: Physical characteristics of dc gliding arc atmospheric discharge, i.e. arc voltage, current, lifetime and non-equilibrium portion, are investigated under different external resistors. Effects of carrier gas and external resistor on naphthalene destruction efficiency and energy efficiency are also examined. The results show the highest naphthalene decomposition efficiency is obtained when the carrier gas is oxygen and the external resistor is 50 kΩ.

Keywords: gliding arc, plasma, polycyclic aromatic hydrocarbons, decomposition

1 Introduction
Naphthalene is one kind of Polycyclic Aromatic Hydrocarbons (PAHs) and major component of the char produced during the incomplete combustion fossil fuels and the biomass pyrolysis process [1]. It is known that the naphthalene emission has been strictly limited by all countries because of its carcinogenic property. Recently, researchers have been developing several types of efficient technologies to abatement of naphthalene and other PAHs, such as non-thermal plasma, electron beam plasma, catalytic oxidation and so on [2-4]. Presently, we have studied the naphthalene decomposition by gliding arc discharge, which has been utilized for removal of some other gas pollutants and considered as an efficient tool by many scientists.

2 Experimental setup and analysis method
The experimental setup (Fig. 1) consists of naphthalene-containing gas generation system, gliding arc plasma generation system, off-gas absorption system and electrical measurement system. Powdered naphthalene is placed in the glass bottle and is heated to 40°C with water bath. The naphthalene vapor is carried by N₂ gas flow and sprayed into gliding arc plasma reactor. The gliding arc plasma generation system consists of a dc power supply (0 – 6150V, 900W), a resistance (50 – 93kΩ) and a gliding arc reactor. In order to analyze the reaction products, the gas flow passes through the absorption bottle containing hexane. The off-gas is analyzed qualitatively by FTIR spectrometer. We conduct each experiment for 3 minutes. Reaction products in the absorption solution are analyzed by the gas chromatography with mass spectrometry detection (GC/MS). The arc voltage and current intensity are measured synchronously by an oscilloscope.

3 Results and discussion
3.1 Gliding arc gas discharge physical properties
The gliding arc gas discharge is an auto-oscillating phenomenon developed between at least two electrodes. When the high voltage power supply provides high enough voltage between electrodes, the gas flow between the electrodes gap is broken down and the arc is formed. The arc is then pushed downstream by the gas flow and glides along the electrode surface until it quenches. After the decay of discharge, there is a new breakdown at the narrowest gap between electrodes and the cycle repeats. According to the circuit arrangement of dc gliding arc plasma generation, Fridman et al have divided a gliding arc cycle into a quasi-equilibrium phase and a non-equilibrium phase by using the critical electrical parameter values[5, 6]. Mutaf-Yardimci et al have studied the effect of the gas flow rate and the external resistance on the arc voltage and current, which indicates the physical properties of gliding arc gas discharge are related to those two factors[7]. Therefore, it is necessary to examine the effect of gas flow rate and external resistance on the gliding arc characteristics such as average arc voltage, current, lifetime and non-equilibrium portion before the analysis of naphthalene degradation process.

The effect of external resistance is investigated keeping the other parameters constant. The average arc voltage, current, lifetime and non-equilibrium portion are presented in Fig. 2, when the N₂ gas flow rate is fixed at 5 l min⁻¹ and the external resistances are 50 kΩ, 70 kΩ and 93 kΩ, respectively. It should be noted that the
non-equilibrium ratios in the gliding arc plasma are calculated based on the gliding arc theory: gliding arc will transmit to non-equilibrium when its current is below the critical value.

\[ \eta_e = \frac{(X_{in} - X_{out})}{P_{GA}} \times 100\% \]  

(2)

Where \( X_{in} \) is the initial naphthalene concentration, \( X_{out} \) is the final naphthalene concentration, \( f_{gas} \) is the carrier gas flow rate and \( P_{GA} \) is the power of gliding arc plasma.

The results at all the operation conditions are presented in Fig. 3. The naphthalene destruction efficiencies are varied from 54% to 92% at different working conditions. When oxygen is used as carrier gas, the efficiency can be achieved up to 92% at the external resistance of 50 kΩ. It is obvious that the variation trends caused by external resistance are independent to the carrier gas type. The decomposition efficiencies decrease with the rising of external resistance, which is ascribed to the dramatic influence of the arc current. Reduction of the gliding arc length, as well as the yield of active species induced by decreasing of arc current inhibits the naphthalene destruction process assisted by gliding arc plasma. As one can observe in Fig. 3, the efficiency of treatment is evidently greater when the gliding arc plasma is working in the oxygen than when the carrier gas is either nitrogen or air. Because of the electron attachment property of oxygen and the consumption of electron by reaction in air, the gliding arc currents in oxygen and air are lower than in nitrogen. This sparser energetic electron density has negative effect on the destruction process. On the other aspect, ozone and O radical can be produced in the oxygen gliding arc plasma, which enhance the naphthalene decomposition. The high degradation efficiencies with carrier gas of oxygen and nitrogen indicate that the treatment process is dominated by impact of high energy electron and oxidation of free radicals. When gliding arc plasma work in the air, the reaction between oxygen and nitrogen consume a part of electrons, radicals and energy, which leads to the low efficiency with the carrier gas of air.
Energy efficiencies in the nitrogen plasma displayed in Fig. 4 illustrate the increasing trend of energy efficiency with the rising of external resistance value. The highest destruction energy efficiency is 2.38 g/kWh. The above discussions about physical characteristics of gliding arc plasma indicate that the non-equilibrium degree in gliding arc plasma is strengthened when the external resistance increases. Therefore, the variation of naphthalene destruction energy efficiency to the external resistance and gliding arc physical properties reveal that the cheapest case of naphthalene decomposition corresponds to the gliding arc of highest non-equilibrium degree.

3.3 Analysis of the by-products in the naphthalene decomposition process

The products mixtures have been absorbed and then analyzed quantitatively and qualitatively by GC/MS. Chromatographic separations are carried out on a 60-m DB-5 silica-fused capillary column with internal diameter 0.25mm and a stationary phase film thickness of 0.25 μm. The temperature program for GC oven is: initial temperature 70°C, hold for 5 min; 70 - 270°C at 8°C/min; 270°C hold for 30 min. Carrier gas: Helium, 1ml/m; hydrogen, 3.5ml/m. Injector and detector temperature are set to 250°C and 280°C, respectively. Mass spectrometer working condition: electron impact ionization 70eV, ion source temperature 250°C. The mass range is selected from 50 – 300 m/z. Some of gas phase by-products, insoluble in hexane solvent, are quantified by Fourier Transform Infrared (FTIR) spectroscopy.

All the identified stable by-products at different experiment conditions are listed in the table 1. Comparing with the undecomposed naphthalene, all the by-product concentrations are very low. When the carrier gas is nitrogen, we detect more by-products than when the carrier gas is either oxygen or air. By-products in nitrogen discharge are classified in four groups: (i) two-ringed compounds with N-containing substituent; (ii) two ringed compounds without substituent; (iii) one-ringed compounds; (iv) hydrogen cyanide. Based on the qualitative analysis of the destructed mixture, some possible decomposition pathways are proposed. The first step of naphthalene destruction in nitrogen plasma is dehydrogenation and ring cleavage by energetic electron. Subsequently, some two-ringed compounds with and without N-containing substituent are formed, such as 1-Naphthalenamine, 1, 2-dihydronaphthalene, and 2-cyanonaphthalene. These decomposed products are more easily destructed in plasma area by electrons and radicals and the subordinated products are formed, such as 2,5-dimethyl-benzonitril. Carbonization phenomenon is found during the experiment with the carrier gas of nitrogen, which can be confirmed by the detection of hydrogen cyanide in the gas. Therefore, it is possible to state that the electron impact has play a dominant role on the naphthalene degradation process by nitrogen gliding arc discharge.

<table>
<thead>
<tr>
<th>Carrier gas</th>
<th>By-products</th>
<th>GC/MS</th>
<th>FTIR</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2</td>
<td><img src="image" alt="By-products" /></td>
<td>☑</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO2, CO, H2O, hydrocarbon</td>
<td></td>
<td>☑</td>
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<tr>
<td>Air</td>
<td><img src="image" alt="By-products" /></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>NO2, CO2, CO, H2O</td>
<td></td>
<td>☑</td>
</tr>
<tr>
<td>N2</td>
<td><img src="image" alt="By-products" /></td>
<td>☑</td>
<td></td>
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<td></td>
<td>HCN</td>
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</table>

When the naphthalene destruction process is performed in the oxygen gliding arc plasma, the by-products are distinct from those in the nitrogen discharge. Because of the ozone and O radical generation, the ozone and O radical oxidation can be imagined however oxygen has electron attachment property. Since the combination of strong oxidation and high energy electron impact, much fewer by-products in hexane solvent such as one-ringed and two-ringed compounds are detected. Contrarily, we detect more types of gas phase products when the carrier gas is oxygen. The degradation pathway could not be proposed for a few identified by-products. However, the highest destruction efficiency and the properties of oxygen plasma may suggest that the ozone, O radical...
oxidation associated with electron impact plays a crucial role in the destruction process. A few kinds of by-products, 1-nitronaphthalene and 2-nitroethenyl-benzene, in the hexane solvent are detected when the carrier gas is dry air. The presence of these two by-products indicates the reactions between the nitric oxides and unstable intermediates. Except CO2 and H2O, NO2, an unfavorable product, as the highest concentration gas phase products is identified by FTIR spectrometer, which suggests that some part of energy in plasma is utilized for dissociation of nitrogen and oxygen and some portion of radicals do not react with naphthalene but product nitric oxides. The lower destruction efficiency with carrier gas of dry air may be attributed to the energy, energetic electron and radical consumption by reaction between nitrogen and oxygen.

4 Conclusion
The investigations of dc gliding arc plasma physical properties and its application on naphthalene destruction under different carrier gases and external resistances have been carried out. The results show that the gliding arc voltage, non-equilibrium portion increase with the increasing of external resistor value, and arc current, arc lifetime exhibit the reverse variation trend. It is also found that the highest destruction efficiency can be achieved up to 92% when the carrier gas is oxygen and the external resistor value is 50 kΩ. The naphthalene decomposition efficiency decreases with the increasing of external resistance, independent of the carrier gas. The highest destruction energy efficiency under nitrogen carrier gas is 2.38 g/kWh at the external resistance of 93 kΩ. Analysis of the by-products and destruction efficiencies under different carrier gases indicates reactions between naphthalene and radicals, especially O radicals, are the predominant channels to the naphthalene destruction process.

References