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Decomposing Biphenyl with a Hollow Cathode Plasma

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Abstract

A hollow cathode plasma instrument has been designed to decompose hazardous chemicals. Biphenyl was selected as the test chemical, because it has a polynuclear molecular structure as same as the toxic DIOXINs. In addition, it is non-toxic and cheaper. Amorphous-carbon, the most possible decomposed product from biphenyl, was detected in the experimental residue. To decompose wastes more efficiently, the evaporating time of waste corpuscles must be taken into account. The temperature of the plasma was measured with a spectrometer. For Ar plasma of 50~150A in current and 0.02~0.1MPa in pressure, its temperature at the middle point between the electrodes decreases with pressure from 16,000 to 8,000K according to Line Pair Method. It a little increases with the current at 0.1MPa, and then little changes at 0.05MPa and Lower.

1. INTRODUCTION

With the improvement of our life, hazardous chemicals are being caused days and nights. Some ones have been found very toxic, such as polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and part of polychlorinated biphenyls (PCBs). The toxic PCDDs, PCDFs and PCBs are normally called DIOXINs. They are stable, colorless and no smell. Many researches have proved that these chemicals can cause terrible diseases, such as cancer or endocrinopathy. DIOXINs are very stable to acids through alkalis. Nevertheless, DIOXINs can be easily decomposed under temperature higher than 1,000K [1],[2].

As the fourth state of matter, plasma has the characters of high temperature. The temperature of the plasma is usually higher than 5,000K. It is a temperature that is enough to decompose even to ionize any matters. Therefore, we try to use plasma to decompose the toxic chemicals.

This paper will introduce our research about destroying biphenyl by a hollow cathode plasma instrument. Biphenyl was selected as the test chemical because it has a polynuclear molecular structure as DIOXINs. See Fig.1. It is non-toxic and cheaper. The former is much convenient in experiments.

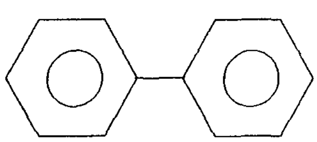


Fig.1 Biphenyl

2. PHYSICAL AND CHEMICAL PROPERTIES OF BIPHENYL

Biphenyl is colorless to pale yellow solid, with a very characteristic odor. The molecular formula of biphenyl is $C_{12}H_{10}$ and the molecular weight is 154.

Table 1 Physical and chemical properties of biphenyl and T_4CDD[3]

	biphenyl	2,3,7,8-T_4CDD
Melting Point	68.6 ~ 87°C	305 ~ 306°C
Boiling Point	246 ~ 255.9°C	421.2 ~ 444.5°C
Water Solubility	7 g/m³	0.0193mg/m³
Heat of Fusion	4.18kcal/mol	9.30kcal/mol
Entropy of Fusion	12.2 cal/mol•K	16.49 cal/mol•K
Vapor Pressure	5.61 Pa at 25°C	2.0×10^{-7} Pa at 25°C
Density	0.866g/cm³	1.827g/cm³
TEQ	non-toxic	1

Biphenyl is non-toxic, though it has a polynuclear molecule structure, such as DIOXINs. The reason is that biphenyl contains no chlorine. DIOXINs have a common character of containing chlorine. And, normally, the more the chlorine atoms contained in a molecular of a chemical, the more toxic the chemical is. The most toxic DIOXIN is 2,3,7,8-T_4CDD. It contains 4 chlorine atoms at the 2,3,7,8 positions.

The physical and chemical properties of biphenyl and 2,3,7,8-T_4CDD are shown in Table 1 in comparison.

3. EXPERIMENTAL METHOD

Figure 2 shows a hollow cathode plasma

instrument. It can completely treat the biphenyl directly because the arc plasma can generate around the cathode. The biphenyl powder of ca.0.2mm in diameter was fed every several mg into the chamber by using a small injector through inside of the hollow cathode with a flowing Ar gas of about 3l/min. The high temperature generated by the plasma torch decomposed the biphenyl between the electrodes. And the residue chemicals were caught with a glass fiber filter at the exit of the chamber.

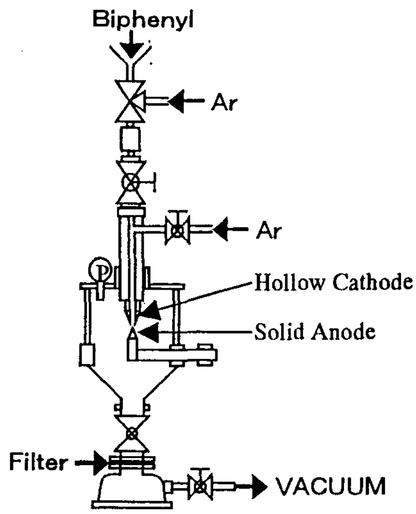


Fig.2 Principle of the Test Instrument

The test circuit is shown in Fig. 3. The test currents were 50A, 100A, 150A. The voltage between the electrodes was measured to be about 14-21V, according to the pressure of the working gas.

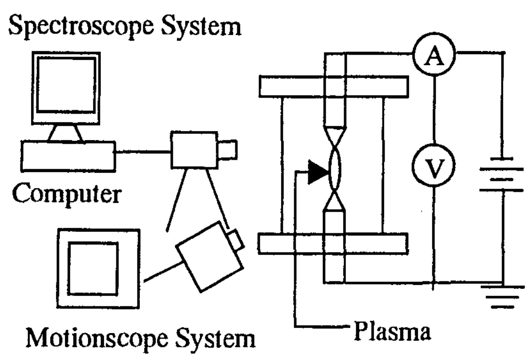


Fig.3 Test Circuit

A spectrometer was used to measure the temperature of the plasma. Meanwhile, a motion scope took down the dynamic phenomena of the plasma.

Figure 4 shows one of the spectral lines of Ar plasma at 100A and 0.1MPa. Figure 5 shows two pictures of the plasma taken by the motionscope, indicating a falling bright particle.

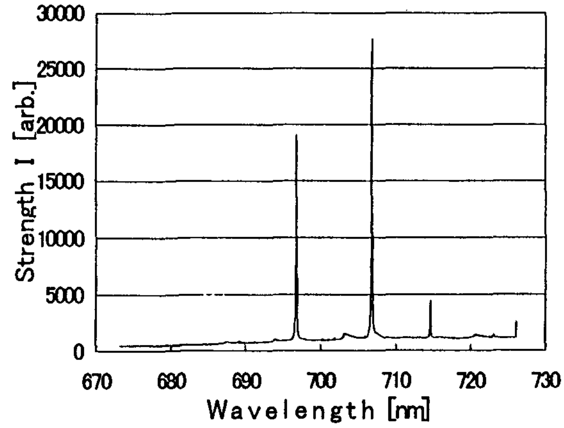


Fig.4 Spectral Lines of Ar Plasma at 100A and 0.1MPa

4. Ar PLASMA GENERATED BY THE HOLLOW INSTRUMENT

4.1 The temperature of Ar plasma

The temperature of the plasma was a main parameter for decomposing biphenyl. It was measured at the middle point between electrodes with a spectrometer, and then calculated according to Line Pair Method under a condition of LTE as follows:

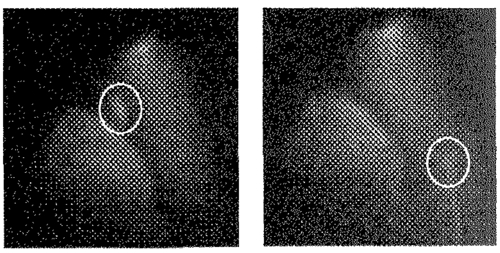
$$\log(I_{nm}\,\lambda_{nm} / A_{nm}\,g_n) = -\,5039.6\,E_n / T + \log C \quad (1)$$

where the subscript n, m represents the upper and lower energy levels, respectively. I is the measured intensity of the line radiation. λ (nm) is the wave length of the light. A (s^{-1}) is the Einstein transition probability, g_n is a constant for the upper energy level, and E_n (eV) is the energy of the upper energy level. With a spectral line, an En ~ log f (I) plot comes. The gradient of the plot reveals the temperature.

In the spectral lines of a pure Ar plasma shown in Fig. 4, the vertical coordination is the intensity, I_{nm}, while the horizontal axis is the wave length λ(nm) of the light.

To erase the influence of the continuous spectrum, the area method was used to deal with the data. If the area intensity value of the spectral line is substituted into Eq.(1), the temperature as a function of pressure of the working gas comes downward with the pressure form 16,000 to 8,000K as shown in Fig.6. The temperature of the pure Ar plasma becomes 13,000~16,000K roughly even from 0.02MPa to 0.05MPa, in 50A through 150A. But, it a little bit increases with the current, when the atmosphere is 0.1 MPa. It may be mainly caused by the electron temperature higher than ion temperature at lower pressure. The electron temperature decreases with increment of the pressure and approaches to the ion and gas temperature at near 0.1MPa.

In our case, the temperature of the plasma was higher than 8,000K, no matter what the test current and Ar gas pressure were.



(a)0ms (b)2ms

Fig.5 Dynamic Pictures of an Element passing through the Plasma

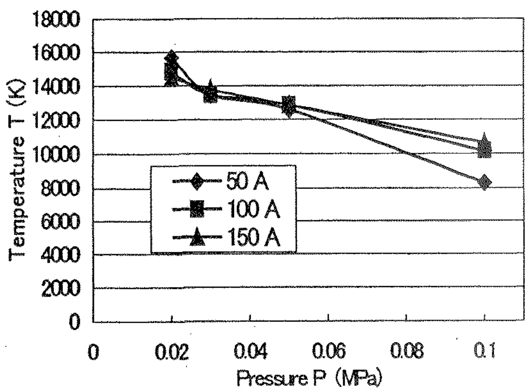


Fig.6 The plasma temperature vs. pressure

4.2 The terminal voltage of the plasma

The average voltage between the electrodes was measured as shown in Table 2.

Table 2 Voltage between the electrodes (V)

	0.02MPa	0.03MPa	0.05MPa	0.1MPa
50A	21.3	20.0	16.7	16.0
100A	17.0	15.4	14.6	14.1
150A	14.6	14.5	14.4	15.1

The first ionizing energy of Ar is 15.0eV. The average terminal voltage of the plasma is in the range of 14.1V to 21.3V. The voltage would be mainly the cathode potential drop and the anode potential drop. Therefore, the 5mm gap may be too short to get a normal plasma.

4.3 Conditions needed for decomposing biphenyl

It should be noticed that the time for decomposing the biphenyl particles should be a sum of the evaporating time t_v of corpuscles and the time for decomposing molecules of biphenyl.

Researches [4,5] about heat transfer to corpuscles from thermal plasma have proved that the time t_v needed for evaporating corpuscles of some materials can be expressed in Eq.(2):

$$t_v = r_{w0}^2/K \qquad (2)$$

where r_{w0} (m)is the radius of the corpuscles when the corpuscles is put in the plasma, and K (m^2/s) is an evaporating constant changed by materials of the corpuscle, the working gas of the plasma and the temperature of the plasma.

According to [4], the value of K for water and some materials in Ar plasma is in the magnitude of 10^{-7}~10^{-8} m^2/s. Therefore, the time for a r_{w0} = 0.1mm corpuscle made of the above materials, will be about 0.1s to 1s. It is quite a long time for such a procession.

Owing to the similar polynuclear molecular structure of biphenyl and DIOXINs, the decomposing time of biphenyl is supposed to be in the same magnitude as that of DIOXINs.

A calculation result [6] of 99.99% thermal decomposing time for 2,3,7,8-T_4CDD under different temperature can be a help for us to get a rough image about decomposing biphenyl, as shown in Fig.7. If the line in the figure can be extended to 2,000°C, then the time for 99.99% 2,3,7,8-T_4CDD thermal decomposition will be within microseconds. It is much shorter than the time for evaporating the particles.

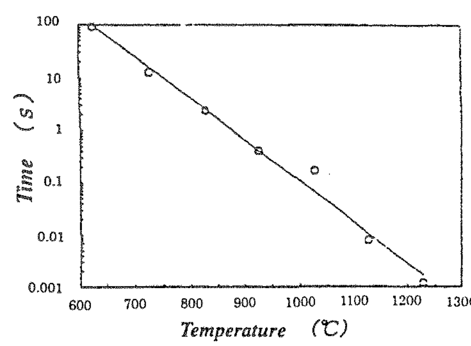


Fig.7 Necessary time for 99.99% 2,3,7,8-T_4CDD thermal decomposition

In our case, the gap between the electrodes was 5mm. The force on the particles was mainly considered as gravity. Then the time for biphenyl corpuscles to pass through the high temperature region in the plasma was estimated to be about 3ms. But for evaporating the biphenyl particles, it needs much longer time.

5. The contents of the residue

The residue was collected with a filter during the experiment. The color of the filter became black after experiment. The filter was analyzed by Laser-Raman-Spectrometry. Amorphous-carbon, the most possible decomposing product from biphenyl, was detected as shown in Fig.8.

The amorphous-carbon proved that the polynuclear structure can be destroyed by the hollow cathode plasma. Therefore, the method can be applied to decompose DIOXINs.

However, the residue also contained a lot of biphenyl. It is impossible to evaporate the particles within the high temperature region, because the time to evaporate the particle is much longer than the time for the particle to pass through the region. The time for evaporating biphenyl particles must be taken into account, or the biphenyl should be already almost gasificated before entering into the region.

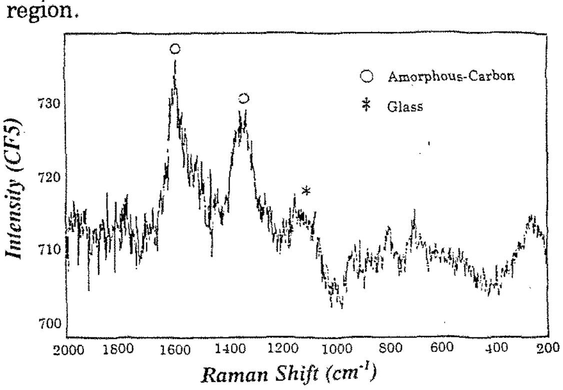


Fig.8 Laser-Raman Spectrometry

6. Further work

6.1 Promoting the experimental method

To increase the decomposition efficiency, waste should be gasified before putting into the plasma. In addition, the electrode gap should be increased to prolong the time for the corpuscles of the waste to pass the high temperature region, and get a more efficient temperature measurement.

6.2 Method to decompose DIOXINs

The aim of this research is to decompose DIOXINs. Therefore, finding the efficient parameter's cooperation such as current, pressure, rate of the gas flow and length of the electrode gap etc. should be emphasized.

6.3 Method for deducing the temperature of the plasma

For efficient decomposing of wastes, convenient, fast temperature analyzing method is expected.

7. Conclusions

(1) The amorphous-carbon proved that the polynuclear structure can be destroyed by the hollow cathode plasma. Therefore, this method can be applied to decompose DIOXINs.

(2) The temperature of the hollow cathode plasma of 50~150A and 0.02~0.1 MPa is measured to be higher than 8,000K at the middle point between electrodes according to Line Pair Method. It decreases with pressure from 16,000 to 8,000K and a little bit increases with current from 8,000 to 11,000K at 0.1MPa and little changes at lower pressure.

(3) To increase the decomposing efficiency, biphenyl should be evaporated before input in the plasma chamber. And the electrodes gap should be increased to prolong the time of biphenyl corpuscles passing through high temperature region.

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