Paper

Study on Atmospheric Pressure Plasma Reactor for Biphenyl Decomposition

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Among several techniques of decomposition of dioxins offered by the present technology, possibility of application of atmospheric pressure arc was investigated. The treated substance was biphenyl due to a high risk involved while using pure dioxins during the experiment. The performance of hollow plasma reactor was investigated. In the experiment, discharge gaps' dimensions were from 5 to 20 mm, the source current ranged from 50 A to 150 A. Biphenyl was partly decomposed in a short time due to the high arc plasma temperature. Except the gaseous products, solid naphthalene and amorphous carbon were formed.

Keywords: biphenyl, dioxins, hollow cathode, plasma arc discharge

1. Introduction

Dioxins are one of the most dangerous, environmentally stable and hardly treatable groups of the by-products, not produced commercially but formed during various technological processes (incineration of garbage containing chlorinated compounds, petroleum industry, exhaust gases from automobiles powered with leaded gasoline, production of plastics, of 2,4,5-trichlorophenol, pesticides and herbicides (silvex), paper, paints, cement and kiln, metallurgy) and during the fires of forests. Dioxins were intensively generated from the beginning of the 20th century but the problem of their toxicity appeared during last 10–15 years (1) (2). It was confirmed that above compounds might cause cancer, birth defects, chloracne, and the disorders of brain, liver, immune system, and hormonal system (3). The maximal safe dose based on multi-site carcinogenic effect of dioxin according to EPA is 6.4×10^{-15} g and the reference dose (excluding cancer) is 1×10^{-12} g/kg/day. Drinking water level, considered as a safe for ten days exposure is 1×10^{-7} mg/dm^3.

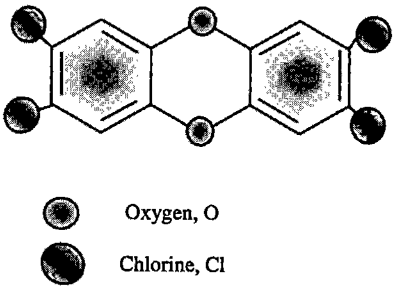

Fig. 1. The structure of TCDD

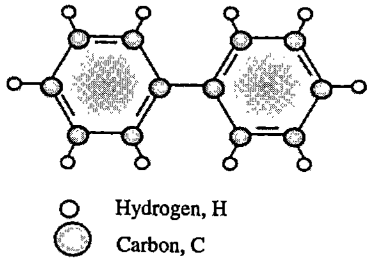

Fig. 2. The structure of biphenyl

Dioxin was primarily used as a name of the odorless, tasteless crystalline powder of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), formerly present in formulas of some pesticides and in 1987 classified as a possibly carcinogenic to humans by IARC (International Agency for Research on Cancer) and 10 years later as a carcinogen (4). Chemical structure of TCDD molecule is shown in Fig. 1. However, presently, the term "dioxin" is used to name the wide range of compounds (about 209 dioxins and dioxin like congeners if we include polychlorinated biphenyls, and over 1,000 including polycyclic aromatic hydrocarbons) with similar chemical structure. They are stable, lipofile, nonflammable, not readily biodegradable and tend bioaccumulate in food chains. Many dioxin isomers might be produced during the combustion process. In spite of this, above 870°C dioxins are destroyed.

The 98% of human exposure to TCDD is due to consuming contaminated food. The other ways are the absorption through skin, breathing contaminated air, and drinking polluted water (almost negligible).

For above reasons, working on the reduction of emission of dioxins and on the new de-pollution techniques become one of the important challenges for researchers all around the world (5)~(11). TCDD might be removed from air by direct photolysis. Many attempts to decrease amount of dioxins including the bioremediation of polluted soil (very low mobility of TCDD in soil),

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catalytic extraction and dechlorination, oxidation and AOP (Advanced Oxidation Processes) as same as the high temperature incineration have been done.

The treatment of large organic molecules using the plasma techniques was proposed to improve the purification of exhaust gases, which contained the dangerous compounds. Pulsed corona discharge, gliding arc, pulsed arc, electrohydraulic discharge, barrier discharges, superposed discharges and variety of possibilities related to the thermal plasma applications might be examples of the multiplicity of investigated methods(12)~(15).

The pollution control by application of the hollow cathode plasma arc is presented in this paper. The hollow cathode enabled to treat biphenyl directly because of arc plasma generated around the cathode. The dosing of biphenyl powder throughout the cathode, which was hollowed, allowed to introduce the pollutant straightly and precisely into the plasma zone. The present results, taken at atmospheric pressure are shown.

Considering the toxicity of dioxins, they were replaced by less harmful biphenyl, (diphenyl, diphenol, phenylbenzene, $C_6H_5C_6H_5$, molar mass 154.21 g/mole), which also has polynuclear structure. Though, after the longer exposition, $C_6H_5C_6H_5$ is considered hazardous and affects human body in many ways (irritating skin, eyes, respiratory tract, affecting liver and nervous system). The airborne exposure limit for biphenyl is 0.2 ppm. This aromatic hydrocarbon is a pleasant smell, white or slightly yellow crystalline solid, which in our case was powdered (average diameter of single crystal was 0.2 mm). Biphenyl is soluble in alcohols and ethers, almost insoluble in water. It reacts very slowly with ozone and slowly with OH radicals.

Flash point of diphenyl is 113°C, autoignition temperature ranges 540°C, melting point is about 69–71°C, boiling point is about 254–255°C. Density of biphenyl is 1.041 g/dm^3 (16). The chemical structure of described congener is presented in Fig. 2.

2. Experimental Set-up

The experiment was performed in a glass chamber,

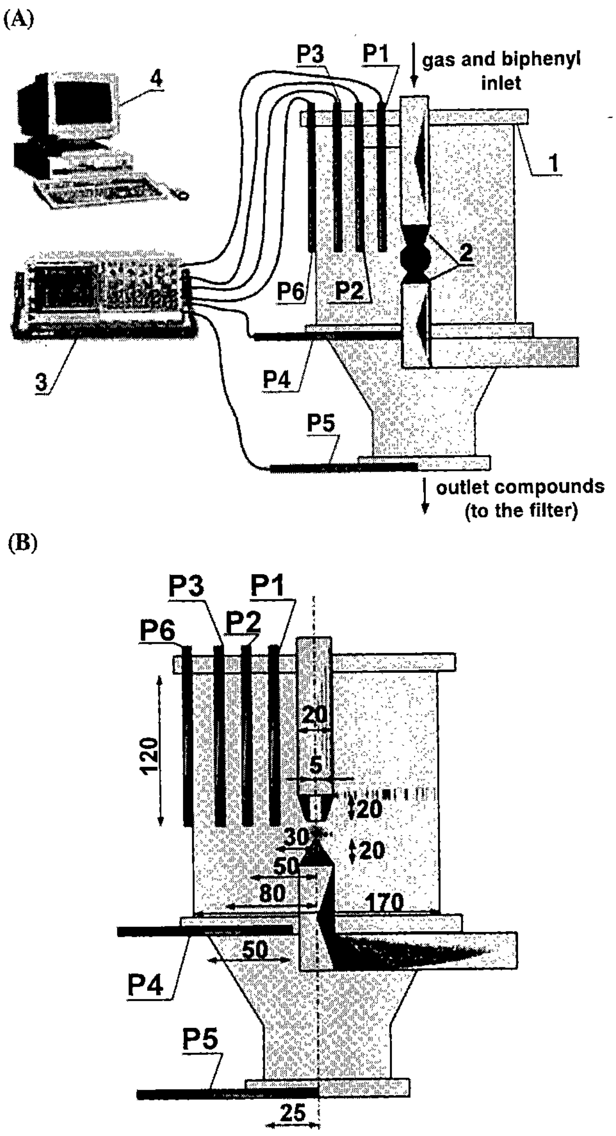

Fig. 4. Set up for the measurement of temperature inside the chamber: (A) General view (reaction chamber, 2-electrodes, 3-oscilloscope with 701880 temperature module, P1-P6-thermocuples), (B) Dimensions of the apparatus

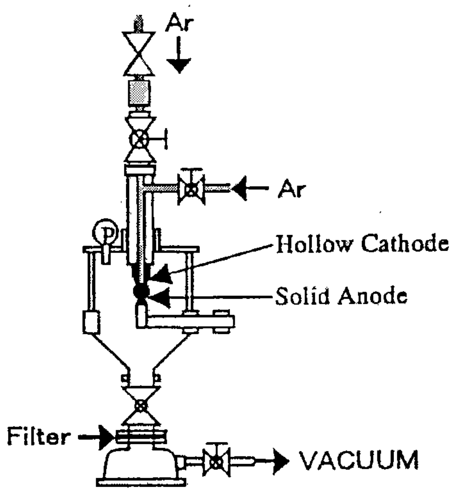

Fig. 3. Experimental apparatus

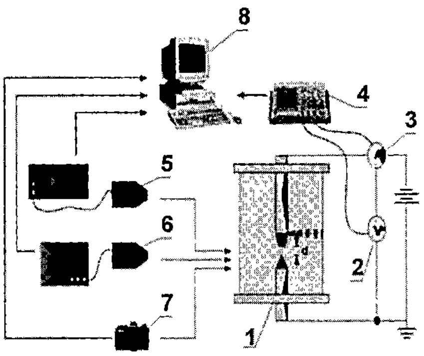

Fig. 5. Set up for the measurement and recording system (1-reaction chamber, 2-voltage probe, 3-current probe, 4-oscilloscope with 701853 high-resolution isolation module, 5-spectrograph, 6-ICCD camera, 7-digital camera, 8-computer)

where the hollow cathode and solid anode were placed. The electrodes were water-cooled. Scheme of the experimental apparatus is shown in Fig. 3. The chamber was filled with the argon gas up to 0.1 MPa.

The electric characteristics measurements and photographs of the discharge were done at first in pure argon

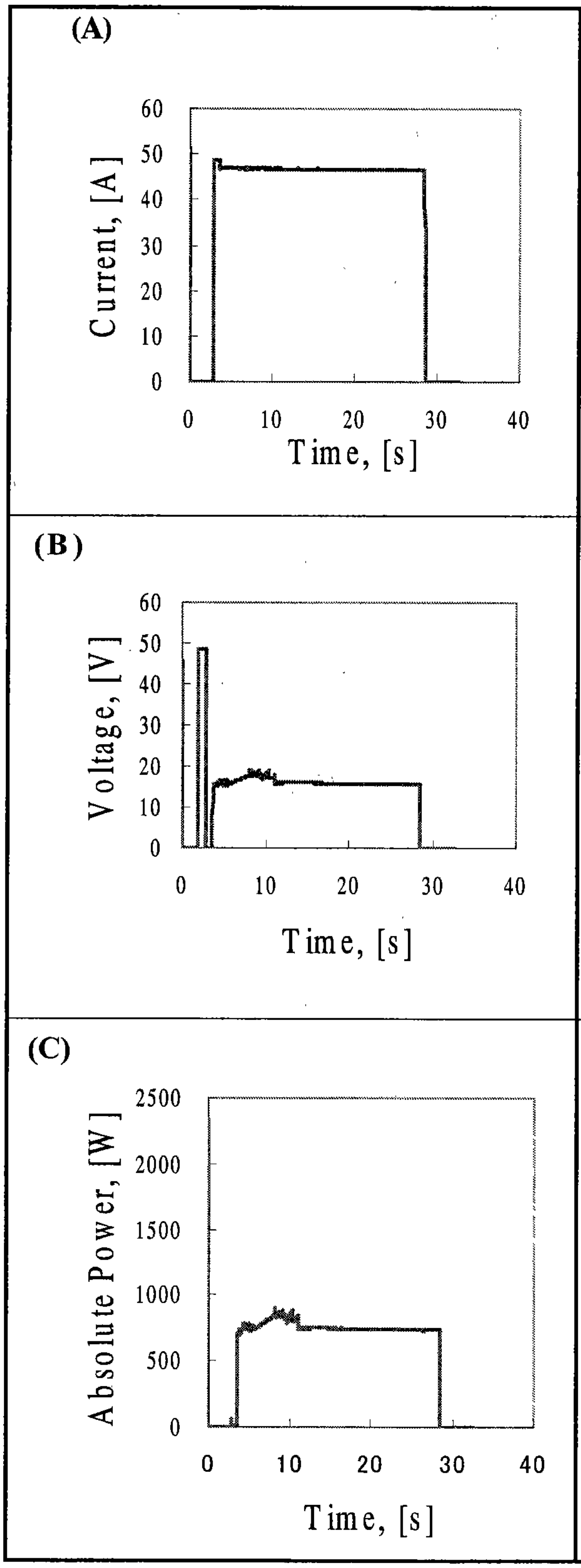

Fig. 6. The electrical parameters of the apparatus: (A) current, (B) voltage and (C) absolute power. Pure argon, discharge gap 5 mm, source current 50 A

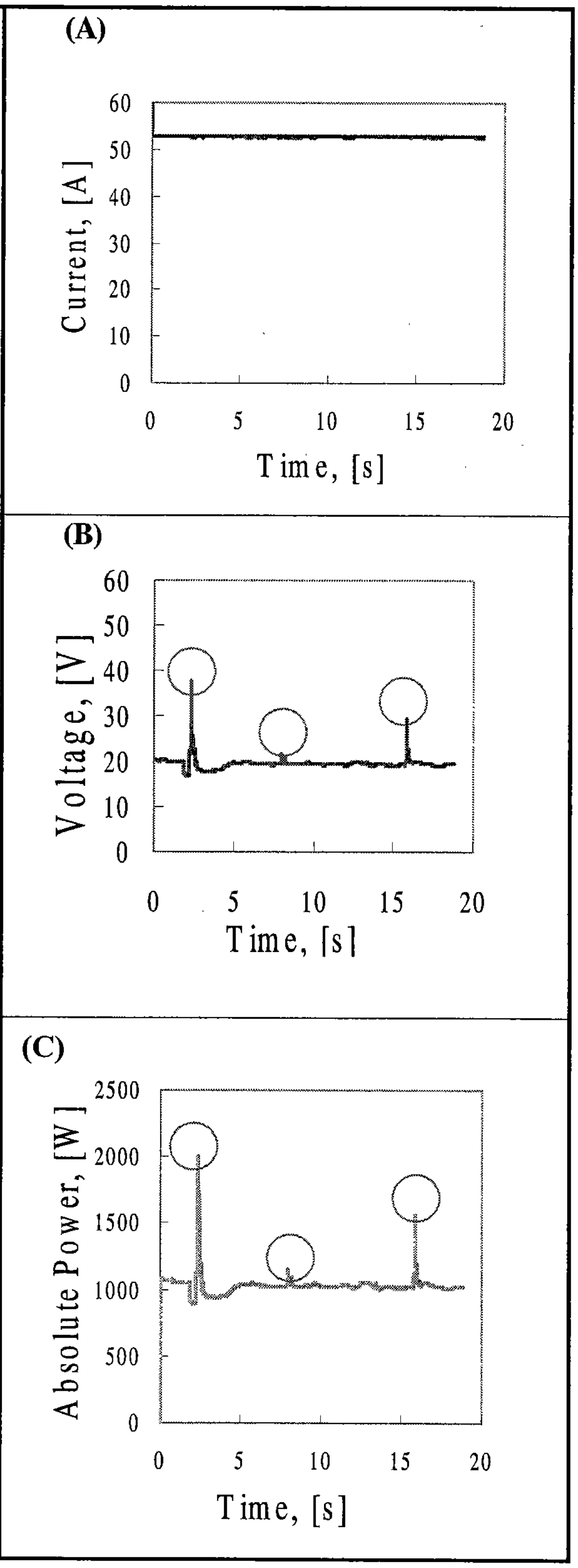

Fig. 7. The electrical parameters of the apparatus: (A) current, (B) voltage and (C) absolute power. Argon with dosed biphenyl powder, discharge gap 5 mm, source current 50 A

(at 3 dm^3/min flow rate) and then, without the gas flow.

In the next step, 0.2 g of biphenyl (slightly more than 0.001 mol) was slowly introduced into the chamber with argon as the carrying gas. Argon flow rate was the same as in the first part of the experiment. Biphenyl is insoluble in water but due to the humidity, adhesion to the walls of the apparatus took place, what was the reason of lessening of the amount of biphenyl in the discharge zone.

Electric power supply was DC Daihen inverter. Voltage between electrodes ranged up to 30 V. Measured temperature of plasma (17) was about 12,000 K. In that case the temperature was measured in the middle point between electrodes using the spectrograph and then calculated according to the Line Pair Method. The vector of flow in the temperature gradient of gas flow in the chamber was also discussed elsewhere (18). Plasma current ranged up to 150 A.

The velocity of the gas in the discharge region was about 30 m/s and according the calculations, the passing time for the single particle ranged 17 ms.

The arrangement of the probes for measuring the temperature of the gas in the chamber is shown in Fig. 4. The thermocouples R type probe (Platinum Rhodium/Platinum (Pt-Rh/Pt)) with the maximum working temperature of 900°C (P1, P2) and K type probe (Chromel/Alumel (Ni-Cr/Ni-Al)) of 750°C (P3-P6) were used.

During the experiment, the motion of the particles in the chamber and the discharge was observed using ICCD motionscope Redlake Imaging (type FL 800-453-1223, Model 100-0016), the spectra were taken by spectrograph Atago Bussan Triax-320 and the waveforms were recorded using DL708E Yokogawa oscilloscope with 701853 high resolution isolation module. The measurement and data recording system is presented in Fig. 5.

The solid products were collected on a fiber filter, which was placed at the lowest part of the chamber and partly analyzed using thermogravimetry (TG), differential thermal analysis (DTA), gas chromatography (GC) and mass spectrometry (MS).

3. Results and Discussion

3.1 Electrical Parameters of the Reactor and the Discharge Observations

The effects of the decomposition process and the observation of the discharge were performed at current of 50 A, 100 A, 120 A and 150 A. The discharge gap sizes were 5 mm, 8 mm, 10 mm, 12 mm and 15 mm.

The electrical characteristics with absolute electric power of the apparatus during pure argon flow and during the addition of diphenyl are presented in Fig. 6 and Fig. 7, respectively. The time delay observed in the Fig. 6 is resulted by starting the measurement before the discharge ignition.

The discharge photos (taken by the digital camera Olympus Camedia C-820L in pure argon) showing the dependence of discharge area on the size of discharge gap and on applied current are shown in Fig. 8.

Peaks, visible in Fig. 7 and indicated by the circles,

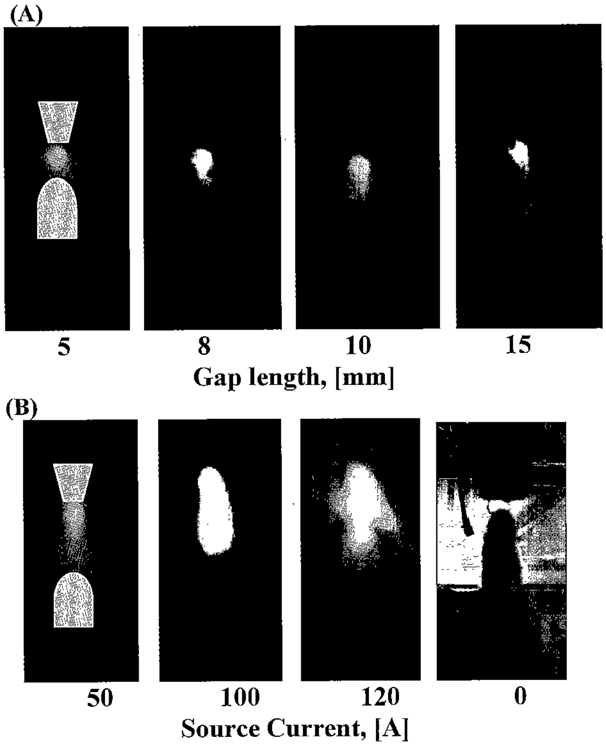

Fig. 8. Photos of the arc discharge in pure argon in the dependence on the discharge gap at 50 A (A), and on the applied current at 10 mm gap length (B)

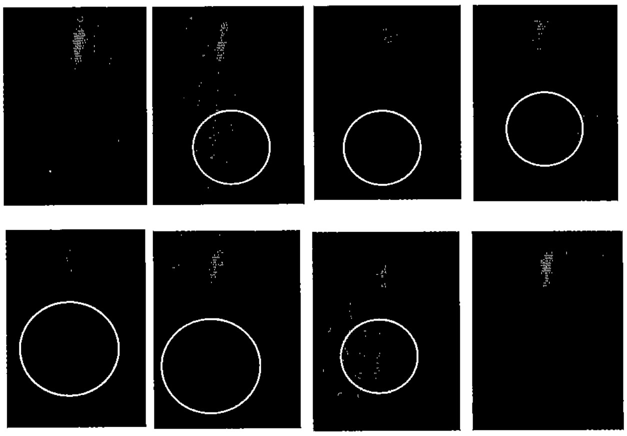

Fig. 9. Movement of the biphenyl particle inside the plasma in a 10 mm gap

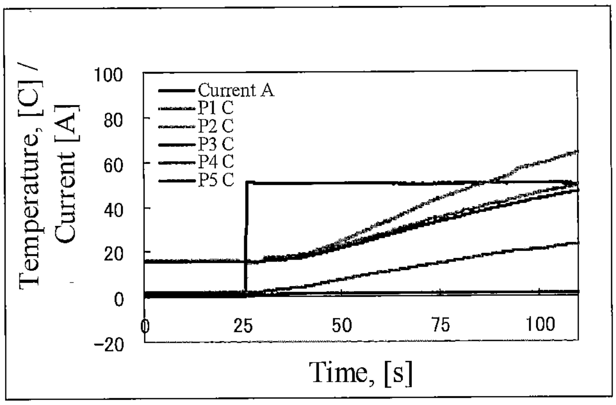

Fig. 10. Development of the gas temperature with time in the chamber. Substrate gas: pure argon, source current 50 A, gap size 5 mm

correspond to the procedure of passing of a group of particles lumped together (with increased volume) through the discharge area. The increasing of voltage between electrodes and absolute power took place during this process. Some kind of the surface discharge on the mentioned particle could occur besides the melting, sublimating and thermal decomposition of this aromatic hydrocarbon. The movement of the particle of biphenyl in the plasma core was taken by the ICCD camera with 1,000 shots/sec speed. Consecutive pictures of its path are presented in Fig. 9.

3.2 Measurement of Temperature in the Chamber

The development of the argon gas temperature in the glass chamber was measured using thermocouples at constant gas flow of 3 $\mathrm{dm}^3/\mathrm{min}$ and at atmospheric pressure.

The pressure was controlled and stabilized during the experiment. The cooling water temperature was 2°C and the ambient temperature was 4°C.

The development of gas temperature in the chamber with time registered by thermocouples at source current 50 A and gap size 5 mm is presented in Fig. 10. Figure 11

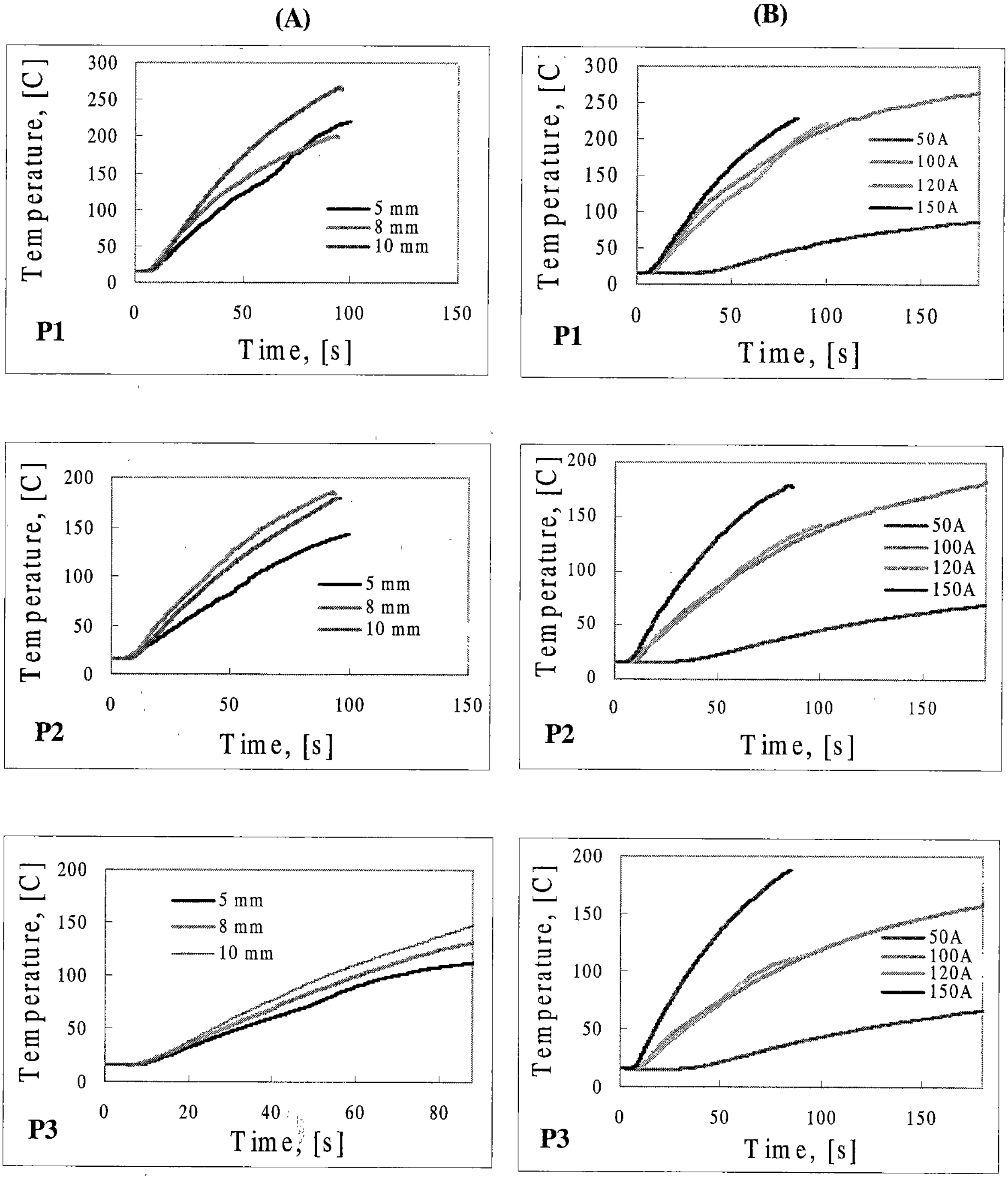

Fig. 11. Gas temperature in the chamber measured by the thermocouples on the position P1, P2 and P3 versus time for various gap spaces at 120 A (A) and various source currents at 5 mm of gap space (B). Substrate gas: pure argon

shows the gas temperature in the chamber versus time for various gap spaces at 120 A (A) and various applied currents at 5 mm of gap space (B) for 3 different points in the chamber (determined by the positions of thermocouples: P1, P2, and P3).

The temperature increased with the extending of time of experiment (Fig. 10) as it was expected and with the extending of the gap space (Fig. 11(A)), and with source current (Fig. 11(B)). Temperature of plasma ranges about 12,000 K but gas temperature in the chamber is much lower and might be not sufficient to decompose the particles reflected from the lower cathode into the chamber filled with gas during the short time experiment. The data were taken in a real time because of thermocouple several seconds response time and the temperature loss on the thermocouple was not taken unto consideration. However, it might play the crucial role for the proper data acquisition in case of 100 and 120 A, when only the slight difference in the registered data took place. It is probable, that the temperature inside the apparatus would achieve the required level (870°C close to the electrodes, at least) with time and could be satisfactory for the treatment purposes. Above assumption however, could not be confirmed experimentally in regard to cooling conditions of the electrodes and possibility of their damage after carrying out the experiment for long time. With increasing the temperature to the required value the gas cooling and the different type cooling systems for electrodes have to be installed.

3.3 Decomposition of the Biphenyl Biphenyl was partly decomposed by high temperature arc plasma during the experiment.

The visible product of the reaction was basically the dark, amorphous carbon, which was collected on the filter and walls of the chamber.

Spectra were taken during the arc discharge observation in the apparatus using spectrograph with the resolution of 0.05 nm/point (26.4 A/mm). Some peaks, corresponding to the amorphous carbon and CH could be resolved as shown in Fig. 12.

Small amount of biphenyl particles was observed on the filter. It was caused by a shorter than sublimating time period of stay of large radius particle in the area of plasma or it's extruding from this area through the bouncing from the lower electrode.

The filter weight after processing of biphenyl was only slightly increased (from 0.22 g to 0.3 g in average), what proves, that there are several gaseous products of the reaction (for instance: methane, ethane, etc.), which should be analyzed in the next stage of the experiment.

The filter was further analyzed using the thermogravimetry (by TG8120) combined with the differential thermal analysis technique and then, gas chromatography with mass spectrometry to determine the composition of formed gas. Those methods allow to deter-

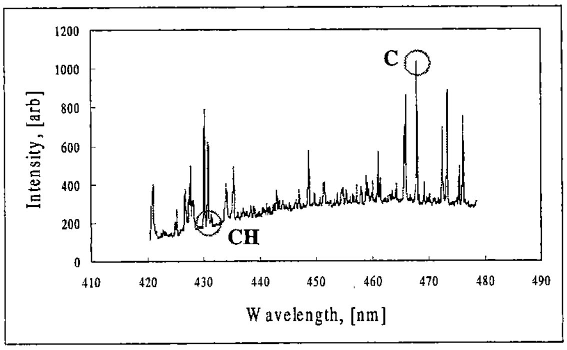

Fig. 12. Spectrum taken during the biphenyl decomposition, source current 50 A, gap size 10 mm

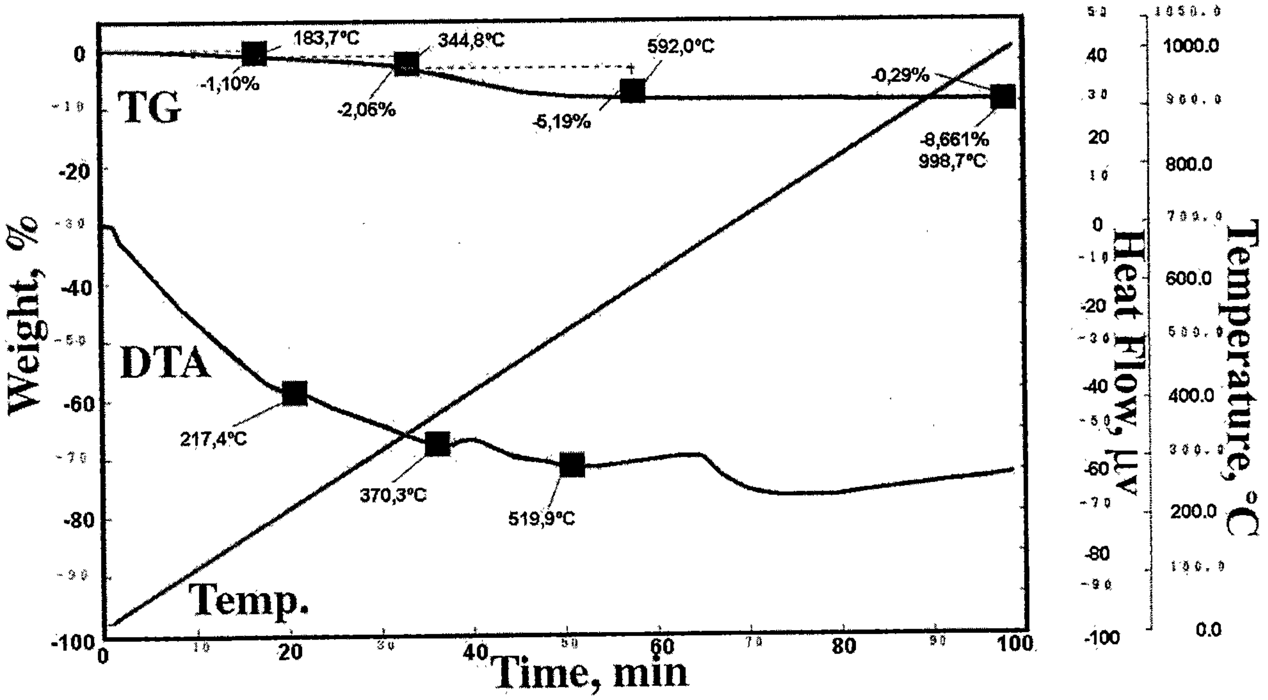

Fig. 13. TG/DTA chart for the filter analysis performed in controlled atmosphere (air flow 200 ml/min)

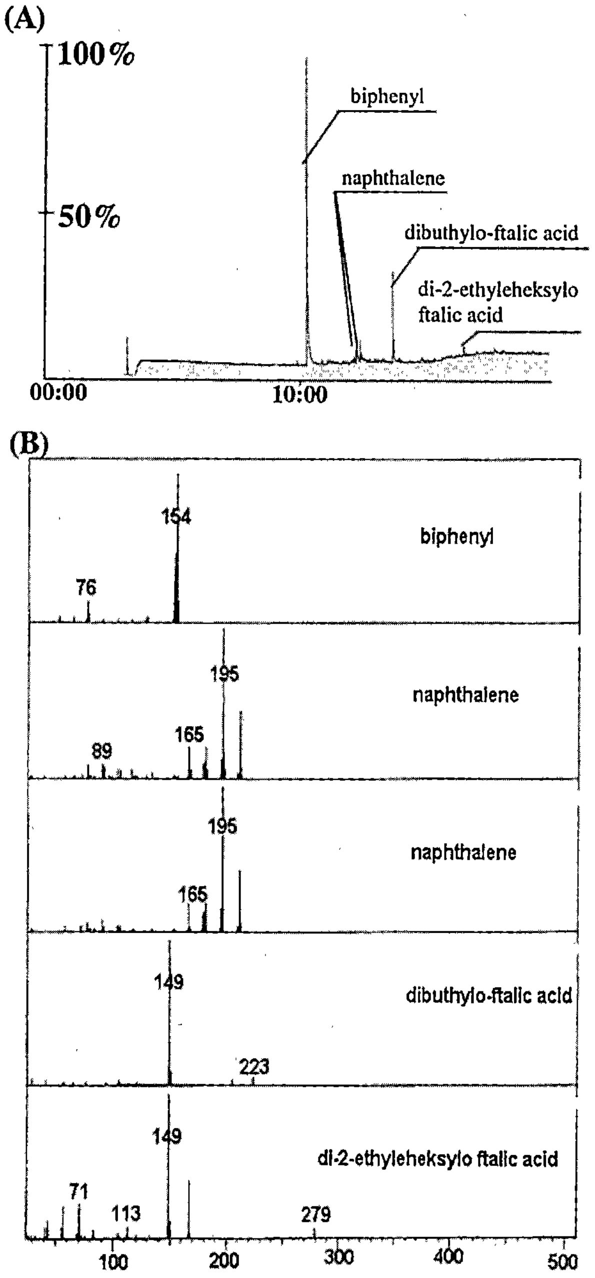

Fig. 14. GS/MS chromatogram (A) and analysis of the observed peaks (B)

mine the mass change of specimen as a function of temperature by heating of two samples (investigated one and a standard one with known thermal response) in precisely controlled rate and environment. Parameters during the analysis were as follow: maximal temperature 1,000°C, heating rate 10°C/min, sampling 0.40 sec for nitrogen and 0.70 sec for air, gas flow rates: 400 ml N_2/min and 200 ml Air/min. Pt differential thermocouple was used. TG/DTA chart for air is presented in Fig. 13. In the both of cases N_2 and air were reduced by 9%. Small peaks in DTA curve may suggest proceeding of the endothermic reactions and some combustion processes. The GS/MS chromatogram is shown in Fig. 14(A) and analysis of the observed peaks is presented in Fig. 14(B).

According to the performed analysis, the dust collected on the filter contained 860 μg of not decomposed biphenyl. Small amounts of naphthalene, dibuthylo-ftalic acid and di-2-ethyleheksylo ftalic acid were found besides biphenyl.

The decomposition process might be performed at the higher current to reduce the half-products and the remained pollutant. However, it was difficult to obtain the proper arc discharge in the wider gap space in this condition. On the other hand, wide gap size was considered as the most advantageous because of the natural increasing of reaction volume. The most stable discharge, which guaranteed the constant apparatus work was obtained at 50–100 A and at 5–10 mm gap space.

4. Conclusions

It is possible to decompose biphenyl by the arc plasma. Still, the way of dosing biphenyl to the apparatus to assure its constant work should be improved by gasifying the substrate.

It is necessary to achieve the uniform and large volume arc discharge in the apparatus. The plasma temperature is high enough to decompose biphenyl but the gas temperature in the chamber is lower than required for treatment of aggregates of particles, which pass too fast through the plasma or are thrown away of its area, thus might be not fully decomposed.

To achieve the efficient decomposition of biphenyl, the time of presence of single biphenyl particle in the discharge region should be extended. Thus, further research on the possibility of enlarging the gap size has to be done.

It is promising to carry out the experiment at the lower current to save the energy.

After necessary improvements, presented method can be also applicable for the treatment of dioxins and PCB.

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