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## **THERMAL DECOMPOSITION INTEGRATED WITH PLASMA OXIDATION USED FOR THE DESTRUCTION OF SELECTED SOLID AND LIQUID WASTES**

### **Keywords**

Destruction, plasma oxidation, catalytic decomposition, hazardous wastes.

### **Abstract**

A new laboratory system for hazardous waste destruction was tested at a laboratory scale. The experimental device consists of 7 units: an electrical furnace, a plasma reactor, a catalytic reactor, a water cooler, a neutraliser, a carbon adsorber and a fan. The experimental system could be built using different units depending on the waste composition with the aim to adopt the system to various kinds of wastes. The first step of the waste degradation was the thermal decomposition in argon flow. The second one was the oxidation of hydrocarbons formed in the first step using non-equilibrium plasma in the presence of oxygen. Finally, the gases leaving the plasma reactor were purified. Two types of wastes (solid and liquid) were degraded. The reduction of the mass of the waste samples was higher than 99%. The carbon dioxide was the main component of the gases that flowed out of the plasma reactor. The carbon oxide and hydrogen were present in these gases too. The condition of the oxidation of the hydrocarbons in the plasma reactor ought to be improved in the future study in order to attain a momentary concentration of CO in the gas

stream leaving the experimental system (behind the fan) compatible with obligatory standards.

## Introduction

The presence of various chemicals in wastes makes them toxic, poisonous, corrosive, flammable and explosive. Those properties cause that wastes are dangerous and can pose a substantial hazard to human health and the environment. Therefore, wastes have to be managed properly. Disposal of hazardous wastes becomes a very important factor in environmental protection. Thermal technologies are the most effective for destroying organic compounds included in wastes, and they also limit the volume of wastes and the mobility of inorganic substances. Thermal treatment can also reduce the waste toxicity and prepare a waste stream for further treatment, or it can be a final process resulting in inert solids, water and recovered materials.

There are two known categories of thermal technologies: those in which wastes are combusted in the presence of oxygen, i.e., incineration technologies; and those in which wastes are heated in the presence of little or no oxygen i.e., gasification and pyrolysis respectively [1]. Many incinerators, due to insufficient combustion temperature and insufficient excess of air, generate extremely toxic products like dioxins (PCDDs-polychlorinated dibenzo-p-dioxins) and furans (PCDFs-polychlorinated dibenzo-p-furans). It is known that to produce PCDDs/Fs, carbon, oxygen and chlorine have to be available [2] but other factors like temperature, the presence of particles and catalytic elements, the oxygen level, the carbon source, etc. also play important roles [3]. Dioxins/furans cause air pollution, but they also remain in the bottom ash and can be found in landfills.

The advantage of pyrolysis over traditional incineration is caused by relatively low temperatures (400÷ 700°C) which enables the process to reduce the costs of device exploitation and to recover some materials included in the wastes such as metals and black carbon. Pyrolysis also converts the wastes into the potentially useful gaseous products with caloric value and limits the amount of formed dusts (lack of flame), which minimises the adverse effects of hazardous materials adsorbed into them. Even though pyrolysis is recommended as a clean process, hazardous pollutants can be created in a way similar to incineration due to the oxygen presence in majority of wastes. As a result, some oxidation will occur, and products of incomplete combustion could be formed, e.g. dioxins and furans [4].

In order to safely utilise the hazardous wastes, pyrolysis should be integrated with the other technique in which pyrolysis gases, (appearing as a result of thermal treatment of wastes under inert atmosphere) could be burned and converted into a mixture of CO<sub>2</sub>, H<sub>2</sub>O and other inorganic compounds

depending on the waste composition, e.g. HCl. Plasma oxidation seems to be an adequate process for this purpose. Plasma is a physical state in which groups of ions, radicals, and electrons dissociated from electrically neutral gases are randomly spaced, and it can easily activate even chemically stable substances. Many works concerning the clean-up gas system from technological processes indicate the high efficiency of the plasma methods [5]. The plasma treatment of gases is frequently applied to remove toxic organic compounds from the air, e.g. toluene, xylene, heptane, cyclohexane and freon [6]. Plasma is also used for natural environmental protection in processing metallurgical, medical and municipal solid wastes [7]. The abundant ultraviolet radiation in plasma can dehydrogenate organic chlorine/bromine [8]. The catalyst can also destroy chlorinated organic compounds in a small concentration (especially PCDDs/Fs) with simultaneous oxidation components [9].

Our main task in the study is to develop a new technology of hazardous waste destruction that is safe for the environment. In order to realise the intention, we have designed and built an experimental system to utilise the wastes at a laboratory scale [10] on the basis of our previous researches, concerning the decomposition of plastic wastes [11]. We predict that many wastes such as derivatives of petroleum, paints, electronic scrap (containing chlorinated/brominated materials) and plastics could be degraded in our device.

The aim of this research is to test a new laboratory system for hazardous waste destruction. The system is mainly based on the processes of thermal waste decomposition in an electric furnace and the oxidation of gases, lowering the furnace in a non-equilibrium plasma reactor working on the basis of gliding discharge. The influence of chemical and physical properties of the waste on the course of the process is examined too. Two types of wastes are selected for experiments: a) a liquid waste - used up oil from the vacuum pump and b) a solid chemical waste - contaminated mannite  $C_6H_8(OH)_6$ , which is applied in medicine, pharmaceutical industry and in synthetic resin production as a pure material.

## 1. Experimental procedure

The laboratory experimental system (LES) had a modular construction (Fig.1) and consisted of the following units: an electrical furnace (unit 1), a plasma chamber (unit 2), a catalytic reactor (unit 3), a water cooler (unit 4), a neutraliser (unit 5), a carbon adsorber (unit 6) and a ventilator (unit 7). The wastes were thermally decomposed in the presence of flowing argon in the unit 1. Then gases released from the electrical furnace (off-gases) were oxidised (burned) in non-thermal plasma, generated by gliding discharge (so called GlidArc-unit 2). Then the gases were introduced into the catalytic reactor (unit 3), which additionally can destroy the halogenated compounds (especially

PCDDs/Fs). After being released from the catalyst, gases were cooled (unit 4) and then purified by a neutralizer/adsorber module (unit 5+6).

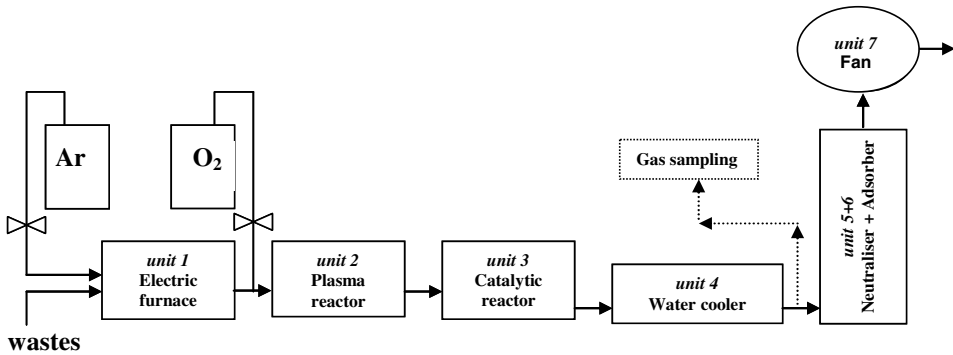


Fig. 1. The scheme of modular LES for hazardous wastes destruction

Gliding arc discharge at atmospheric pressure offers high-energy efficiency and selectivity for chemical reactions [12, 13]. The plasma reactor with cylindrical geometry used in the LES consisted of three stainless steel knife-shaped electrodes and one ignition electrode. The gliding arc discharge is fed by a 3-phase and high voltage power system. AC voltage applied during our experiment was  $\sim 1.7$  kV with the discharge current of  $\sim 1$  A. The electrodes were positioned in the fast gas flow that, in our experiment, was a mixture of off-gases, argon (carrying gas) and oxygen (working gas). The total flow rate of argon and oxygen was  $0.99 \text{ Nm}^3/\text{h}$ . The oxygen concentration in the initial mixture was 20%. The temperature in the zone of gliding discharge and the energy of the formed high-speed electrons was high enough [14] to break strong covalent bonds of hazardous organic compounds, e.g. chlorinated [15] and fluorinated [16] hydrocarbons.

The main part of the catalytic reactor is the catalyst, made of cordierite covered with the following oxides:  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$  and  $\text{WO}_3$ . The catalyst was applied for the destruction of gaseous chlorinated organic pollutants from waste incinerators [17-19]. The catalytic reduction of dioxins/furans concentration was performed in the temperature range of  $150\text{--}400^\circ\text{C}$  [18]. Polyaromatic hydrocarbons (PAHs) may be destroyed on  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$  catalyst [18]. Also the reduction of nitric oxides (in the presence of ammonium) known as the SCR (Selective Catalytic Reduction) process is possible to perform on this catalyst [20, 21].

A water cooler is used to avoid recombination reactions of gaseous molecules that inhibit the formation of dioxins and furans ('*de-novo*' reaction) and to remove the moisture from gases for protection of a carbon adsorber.

Both, a neutralizer ( $\text{NaOH}/\text{Al}_2\text{O}_3$ ) and activated carbon used as the adsorber were employed to purify gas from acid components and from fine particles and other toxic vapour-phase residue, respectively.

The fan was employed to facilitate the gas flow through the apparatus and to prevent the leakage of gases from the system to the environment.

The experimental system can be built using different units, depending on the waste composition with the aim to adopt the system to various kinds of wastes. For example, a catalytic reactor should be used only when halogen compounds in significant concentration occur in the composition of waste. In our research, the simplified laboratory system without the catalytic reactor was applied.

The sample of waste was placed in the electric furnace before the experiment. Then the furnace was hermetically closed. In our experiment, the masses of wastes were 11.2 g and 14.8 g of used oil and contaminated mannite, respectively. After argon flow, switching on the temperature program of furnace was plugged in and the gliding discharge was initiated. Then oxygen was introduced into the plasma reactor. During the waste destruction process gases were sampled after the water cooler (Fig. 1). The process was ended when the concentration of  $\text{CO}$  and  $\text{CO}_2$  in gas samples was significantly lowered. The concentration of  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{H}_2$  in the gas was measured using gas chromatograph-Agilent Technologies 6890N with thermal conductivity detector (TCD). The analysis was carried out using an external standard method and a column 1.5 m long and a 3 mm internal diameter, filled with Carboxen 1000. The carrier gas was argon (19.0 ml/min).

The samples of wastes were characterised by thermogravimetric (TG) and differential scanning calorimetric (DSC) analyses using DuPont Instruments TGA-951 and DSC-910, respectively. TG and DSC measurements were carried out at  $10\text{ }^\circ\text{C}\times\text{min}^{-1}$  heating rate under argon atmosphere with the flow rate of  $50\text{ cm}^3\text{min}^{-1}$ .

Elementary analysis of both wastes was performed using Perkin Elmer Elemental Analyzer 240 and Heraeus Elemental Analyzer vario EL III.

## 2. Results and discussion

The results of the elementary analysis of the wastes are presented in Table 1. The used up oil contains about two times more weight % of carbon than contaminated mannite. A slight content of chlorine is observed in both samples. The mannite molecule contains six atoms of oxygen ( $\text{C}_6\text{H}_8(\text{OH})_6$ ). Wherefore, a summary content of individual elements in mannite is much lower than 100%.

Table 1. Elementary composition of wastes

Waste	Composition; weight %					
	C	H	N	F	Cl	S
Oil (a)	84.85	12.17	-	-	0.25	0.21
Mannite (b)	39.20	7.12	-	-	0.25	-

The thermogravimetric, derivative thermogravimetric and differential scanning calorimetric analyses of a and b samples (Figs. 2 and 3) gave information on the thermal stability of examined wastes.

The mass of used oil sample began to decrease at the temperature of 100°C. It was a result of sample evaporation. Also, the thermal decomposition of oil proceeded along with the increase of temperature. The oil was decomposed most intensively at the temperature range of 180÷300°C. The maximum of the DSC curve was observed at the temperature of 230°C. Both processes, the evaporation and the thermal decomposition, occurred in the wide range of temperature (100÷350°C). Probably it was a result of a multicomponent composition of used oil.

The DSC curve of contaminated mannite has two maximums. The first maximum occurred at the temperature of about 160°C. It could be supposed that the sample was melted at this temperature, because a pure D-mannite melts at the temperature of 166°C. The second maximum was present at the temperature of 340°C. Simultaneously, the mass loss of the sample is the highest then. The mass loss was started at the temperature of about 230°C and was finished at the temperature of about 350°C. The mass of the sample decreased as a result of the thermal decomposition process proceeded under atmospheric pressure. Pure mannite evaporates without decomposition only under low pressure (in the order of a few hundred Pa).

On the basis of TG measurements, it could be concluded that the process of evaporation and thermal decomposition of the used oil sample in the electric furnace will occur at the temperature range of 100÷400°C, while the thermal decomposition of contaminated mannite will perform at the temperature range of 230÷350°C. As a result of these processes, hydrocarbons should be present in the mixture of gases flowing out of the furnace. It could be expected that the concentration of hydrocarbons would be meaningful with maximum values at the temperature that corresponds to the biggest mass loss of the sample.

The process of the hydrocarbon's oxidation will occur in the presence of oxygen at the plasma reactor located behind the furnace. The CO and CO<sub>2</sub> will be formed in the process. The time of detention of gases in the plasma reactor is very short (in the order of ms). Thus, the concentration of CO and CO<sub>2</sub> in the gases flowing out of the plasma reactor should be changed in a way similar to the hydrocarbon's concentration in gases flowing out of the furnace during the

waste decomposition process. Certainly, it concerns the direction of concentration changes but not the absolute value of concentration.

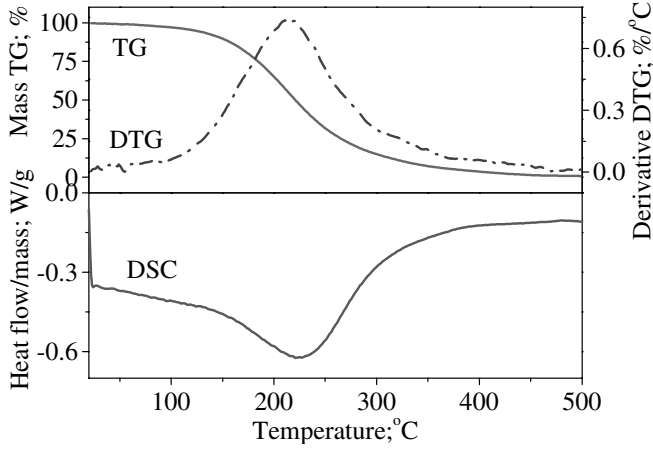


Fig. 2. TG, DTG and DSC curves of used up oil. The DSC peak at  $\sim 230^{\circ}\text{C}$  (endothermic transition), connected with mass loss (TG and DTG) indicates the maximum of evaporation and thermal degradation of the sample

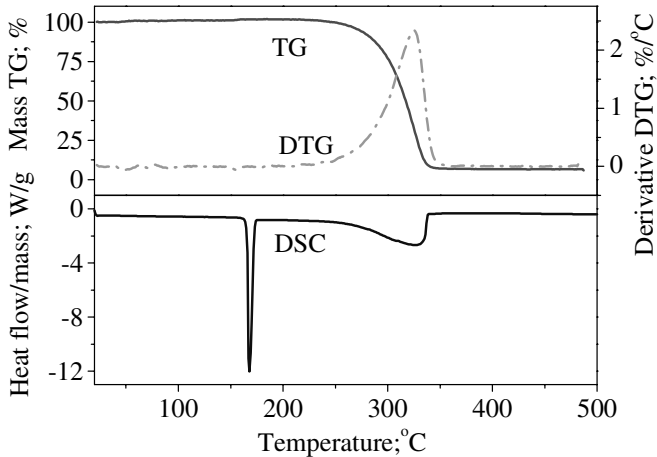


Fig. 3. TG, DTG and DSC curves of contaminated mannite. The DSC peak at  $\sim 160^{\circ}\text{C}$  (endothermic transition) which does not connect with mass loss on TG plot indicates the melting point. The DSC peak appeared at  $\sim 340^{\circ}\text{C}$  with mass loss observed on TG indicates the maximum of sample thermal decomposition

The concentration of carbon oxide and carbon dioxide during the process of waste decomposition is presented in the Figs. 4 and 5. The hydrogen and oxygen concentrations in gases discharging from the plasma reactor are also shown. The hydrogen could be formed both in the furnace during the decomposition of wastes and in the plasma reactor as a result of incomplete oxidation of hydrocarbons. Also, the temperature in the electric furnace was demonstrated in these figures.

The meaningful concentration of CO and CO<sub>2</sub> during the used oil decomposition appeared between the 35<sup>th</sup> and 125<sup>th</sup> minute of the process duration. It corresponds to the temperature range in the electric furnace of 300÷400 °C. The oxygen concentration achieved the minimum in those intervals of time and temperature. It correlated with the maximum of CO and CO<sub>2</sub> concentration. It could be concluded that the most intensive process of used oil degradation proceeded in the furnace at the temperature range of 300÷400°C. That interval of temperature was shifted to the temperature higher of about 100°C than the temperature noticed in TG analysis.

The meaningful concentration of CO, CO<sub>2</sub> and H<sub>2</sub> during the mannite decomposition process was observed in the interval of time between the 60<sup>th</sup> and 90<sup>th</sup> minute. In this range of time, the temperature of the furnace increased from 330 to 360°C. The maximum of CO, CO<sub>2</sub> and H<sub>2</sub> concentration and the minimum of oxygen concentration corresponded to the furnace temperature of about 350°C. The results were in good agreement with parameters specified from TG measurement for contaminated mannite.

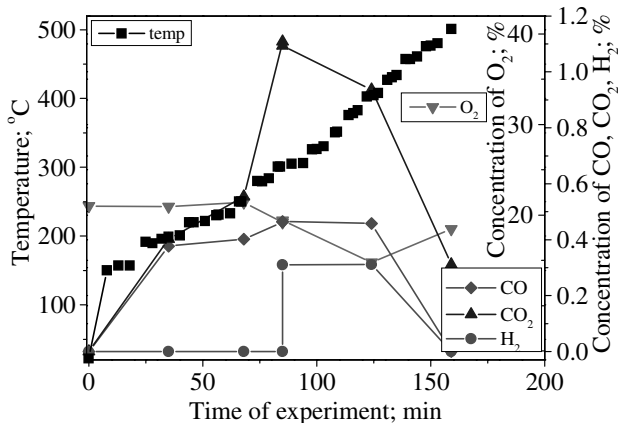


Fig. 4. The temperature in electric furnace, the concentration of CO, CO<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub> measured after water-cooler during the process of used oil decomposition (mass of the oil sample: 11.2 g)



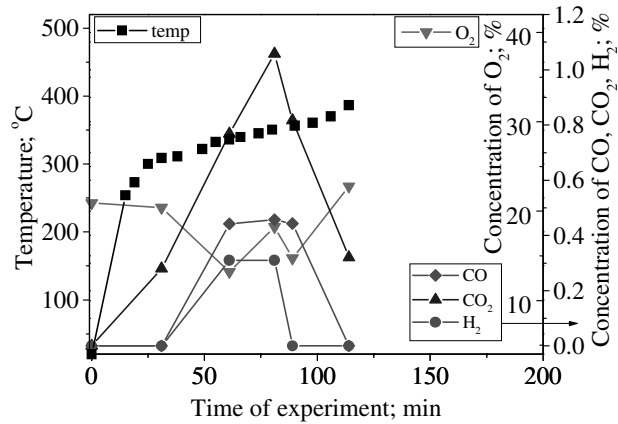


Fig. 5. The temperature in electric furnace, the concentration of CO, CO<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub> measured after water-cooler during the process of contaminated mannite decomposition (the mass of the mannite sample: 14.8 g)

It can be assumed that the results of the thermogravimetric analysis can facilitate the choice of the temperature program of the electric furnace for the process of waste decomposition before the experiment. It was particularly true when the waste was characterised almost by a unary composition and a definite type of the process of waste mass thermal reduction in the furnace. The contaminated mannite was the example of such a waste.

At the beginning stage of the furnace heating, the temperature increased with the rate of  $20^{\circ}\text{C min}^{-1}$  from the room temperature to  $150^{\circ}\text{C}$  and  $250^{\circ}\text{C}$  for oil and mannite, respectively. The high rate of increasing temperature cut down duration of the experiment. At the second stage of the process of oil decomposition, the temperature of furnace increased with a mean rate of  $2.5^{\circ}\text{C min}^{-1}$  from the temperature of  $150^{\circ}\text{C}$  to the end of the process. The decomposition of mannite proceeded at the temperature of furnace growing with a mean rate of  $1.0^{\circ}\text{C min}^{-1}$  from the temperature  $250^{\circ}\text{C}$  to the end of the process. The temperature programs of the furnace were well selected for both processes, because the reduction of mass of the waste samples was higher than 99%. It means that the samples were decomposed in the furnace almost completely.

Carbon dioxide was the main product of the oxidation of hydrocarbons in the plasma reactor. The hydrocarbons did not completely oxidise, because carbon oxide appeared in gases flowing out of the reactor during the most intensive decomposition of wastes. Then, the small concentration of hydrogen occurred in the gases too. Hydrogen did not oxidise to H<sub>2</sub>O. Thus, the condition of the oxidation of hydrocarbons in the plasma reactor ought to be improved in the future study in order to attain a momentary concentration of CO in the gas

stream leaving the experimental system (behind the fan) compatible with obligatory standards [22].

## Conclusions

- The modular laboratory system consisted of the electric furnace, the plasma reactor; the water cooler, the neutraliser/adsorber and the fan is a good tool for hazardous waste destruction.
- The results of TG analysis can facilitate a choice of the temperature program of the electric furnace for the process of waste decomposition before the experiment. Particularly, when the waste was characterised by almost an unary composition and a definite type of the process of waste mass thermal reduction in the furnace. The contaminated mannite was the example of such a waste.
- The condition of hydrocarbons oxidation in the plasma reactor ought to be improved in the future study in order to attain a momentary concentration of CO in the gas stream leaving the experimental system (behind the fan) compatible with obligatory standards.
- The reduction of the mass of the waste samples was higher than 99%. It means that the samples were decomposed in the furnace almost completely.

## Acknowledgements

*Scientific work financed by the Ministry of Science and Higher Education and carried out within the Multi-Year Programme “Development of innovativeness systems of manufacturing and maintenance 2004–2008”.*

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## **Termiczno-plazmowy proces destrukcji wybranych odpadów stałych i ciekłych**

### **Słowa kluczowe**

Niszczanie niebezpiecznych odpadów, odpady niebezpieczne, utlenianie plazmowe, rozkład katalityczny.

### **Streszczenie**

Skonstruowano i wykonano nowy laboratoryjny układ aparaturowy dla rozkładu odpadów niebezpiecznych. Urządzenie składało się z 7 modułów (elektryczny piec do pirolizy, reaktor plazmowy, reaktor katalityczny, chłodnica, neutralizator, adsorber, wentylator), które mogą być zmieniane i dopasowywane w zależności od rodzaju odpadów. Na pierwszym etapie procesu, odpady ulegają rozkładowi termicznemu w piecu elektrycznym w obecności argonu.

Powstałe podczas rozkładu termicznego węglowodory były utleniane w reaktorze plazmowym w obecności tlenu. Następnie gazy opuszczające reaktor plazmowy były oczyszczane. Celem pracy było przetestowanie układu laboratoryjnego w procesie rozkładu dwóch odpadów ciekłego (zużyty olej do pomp próżniowych) i stałego (przeterminowany odczynnik chemiczny – mannit). Redukcja masy próbek obydwu odpadów była wyższa niż 99%. Głównym składnikiem gazów po procesie utlenienia był  $\text{CO}_2$ . W gazach wypływających z reaktora plazmowego występował również CO i  $\text{H}_2$ . Stężenie CO było na tyle znaczące, że należy w przyszłych badaniach polepszyć warunki procesu spalania dla obniżenia tego stężenia.