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The pyrolytic-plasma method and the device for the utilization of hazardous waste containing organic compounds

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HIGHLIGHTS

- A first stage of the process of waste utilization consisted in pyrolysis of waste.
- Then the pyrolytic gas was oxidized with a use of non-equilibrium plasma.
- The device for the process implementation was built and characterized.
- Correctness of the device operation was proven with a use of the decomposition of PE.
- Usefulness of the method was proven in the process of utilization of EW.

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ABSTRACT

This paper is focused on the new method of waste processing. The waste, including hazardous waste, contain organic compounds. The method consists in two main processes: the pyrolysis of waste and the oxidation of the pyrolytic gas with a use of non-equilibrium plasma. The practical implementation of the method requires the design, construction and testing of the new device in large laboratory scale. The experiments were carried out for the two kinds of waste: polyethylene as a model waste and the electronic waste as a real waste. The process of polyethylene decomposition showed that the operation of the device is correct because 99.74% of carbon moles contained in the PE samples was detected in the gas after the process. Thus, the PE samples practically were pyrolyzed completely to hydrocarbons, which were completely oxidized in the plasma reactor. It turned out that the device is useful for decomposition of the electronic waste. The conditions in the plasma reactor during the oxidation process of the pyrolysis products did not promote the formation of PCDD/Fs despite the presence of the oxidizing conditions. An important parameter determining the efficiency of the oxidation of the pyrolysis products is gas temperature in the plasma reactor.

1. Introduction

Waste is an integral part of our civilization. In today's society, the human population tends to produce a large amount of waste on yearly basis, including household and industrial waste. These waste products are likely to take up our entire living space and completely pollute the environment, in the nearby future. Additionally, this would be a terrible mismanagement, because waste can be processed into energy and furthermore it can be treated as a source of obtaining and/or recovering valuable raw materials [1–8]. This is perhaps increasingly important nowadays, as we are more aware of the depletion of natural sources of raw materials, especially the hydrocarbon fuels.

According to the European Parliament and Council Directive 2008/98/EC of 19 November 2008 [9] waste is defined as "any substance or object which the holder discards or intends or is required to discard". Directive 2008/98/EC determines the order of priority for legislation and policy concerning waste prevention and waste management. The most important aim of waste management is to prevent it's formation. However, when the waste has already been unavoidably produced, we should firstly consider re-using it. If this is not possible, the waste should be recycled and then prepared for other methods of resource recovery, for example energy pro-

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duction. At the very end of the waste management hierarchy is the disposal.

The problem that requires a solution, is finding an appropriate way of waste processing. Table 1 shows the percentage share of used methods of waste treatment in most of the European countries and in Turkey according to data for 2012 [10]. In Poland, 25.3% of waste was deposited into landfills on the ground and below it, contrasting with the Netherlands and Belgium where only 3.3% and 7.6%, of waste was disposed into landfill sites respectively. In Bulgaria and Romania, more than 90% of the waste was stored in this way. Processing of waste by recovery (other than the energy recovery and excluding storage in the excavations) was the highest in Belgium (73.2%) and the lowest in Iceland (1.0%). In Iceland, up to 67,4% of produced waste was incinerated, also with the energy recovery. In Poland, only 2.2% of generated waste was incinerated, 21.8% was stored in excavations and 50.4% was recovered in a different way (other than storing in the excavations and the energy recovery). The definition of the term "recovery" is given in Directive 2008/98/EC [9]. The recovery means "any operation the principal result of which is waste serving a useful purpose by replacing other materials which would otherwise have been used to fulfil a particular function, or waste being prepared to fulfil that function, in the plant or in the wider economy". The quoted statistics show a significant area for improvement in Poland in regards to waste recovery and disposal.

The extremely diverse characteristics of waste, including hazardous waste and a wide range of possible applications, mean that a universal method of waste processing does not exist. Hence the aim of the following work was to design, construct and test a modular large laboratory scale device in order to study the processing of waste; including hazardous waste containing organic components. This new idea of waste processing consisted of a combination of two processes: 1—the pyrolysis of waste and 2—the oxidation of the pyrolytic gas with a use of non-equilibrium plasma. Therefore, the experimental research focused on the results obtained from both of the processes.

2. Experimental

2.1. Modular large scale laboratory device for waste utilization (MLDWU)

In the design of the device for the waste disposal and/or utilization it is assumed that: 1—the waste will contain organic components which can be processed by the pyrolysis process, 2—pyrolysis will be carried out in an inert gas atmosphere in order to reduce the probability of formation of polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), 3—hydrocarbons which will form a component of the gases after the thermal decomposition of waste will be oxidized with the use of pure oxygen instead of oxygen from the air in order to avoid the formation of NO_x, 4—gases after the oxidation will be cooled and cleaned of dust, acidic and other harmful components including the PCDD and PCDF, and 5—the device will be constructed on a large laboratory scale.

MLDWU consisted of five modules: 1—a module of a pyrolytic reactor; 2—a module of a plasma reactor; 3—a module of a heat exchanger; 4—a module of a catalytic reactor, and 5—a module a neutralizer/adsorber (Fig. 1).

The module of the pyrolytic reactor consisted of the pyrolytic reactor and the feeder of solid waste. The pyrolytic reactor consisted of: 1—pyrolysis chamber in the form of a cylinder made of heat-resistant steel; it was closed by flap, 2—an electric heater, 3—argon feeding system and 4—system for protection against breakdown. The pyrolysis of waste was carried out in the inert gas (argon) atmosphere (Ar_I). The working gas, the heated argon was introduced into the pyrolytic chamber from the bottom and flowed upwards through the chamber. The feeder worked in the flow of argon (Ar_{II}). The process of pyrolysis was carried out in isothermal conditions. In the pyrolytic reactor the pressure (p) and the temperature of pyrolysis were measured. The pyrolytic gas containing argon and hydrocarbons. During the pyrolysis of a single waste sample, the momentary total concentration of hydrocarbons in the pyrolytic gas (C_Σ) should reach a maximum. At the time corresponding to the maximum of hydrocarbon concentration in the pyrolytic chamber, the maximum momentary pressure (p) should be reached (Fig. 1).

Subsequently, the pyrolytic gas were oxidized with the use of oxygen in the module of plasma reactor. The module of plasma reactor consisted of: 1—the plasma reactor, operating on the principle of gliding discharge, 2—the electric power supply essential for generating the discharge, and 3—the measuring systems enabling the measure of: the flow of oxygen and reactor cooling water, temperature of the gas in the reactor and the power supplied to the reactor. The plasma reactor was built with a steel tube closed on one side with disk, in which three knife-shaped electrodes, an ignition electrode and a set of special nozzles introducing gases into the reactor were located. The total gas flow through the plasma reactor amounted to between 3.00–10.0 Nm^3/h. These gases consisted of oxygen and the mixture of pyrolytic gas and argon. The gases leaving the module of the pyrolytic reactor and the oxygen were introduced into the plasma reactor separately and were mixed just before the discharge zone. The temperature of the gas in the plasma reactor was measured in the axis of the reactor outside the discharge zone at distance of about 50 mm from the gas outlet from the plasma reactor. The plasma reactor was supplied with high-voltage sinusoidal alternating current with 50 Hz of frequency. The plasma generated in gliding discharge was a non-equilibrium plasma that is characterized by high temperature of the inert gas (up to 2500 K depending on the discharge power) and the presence of high energy electrons (1 eV) [11]. In such conditions, chemical reactions are initiated not only by collisions of molecules of gas or vapour with electrons, but also by high temperature. The components of the pyrolytic gas introduced into gliding discharge with oxygen were decomposed and oxidized. The power (P) supplied to the plasma reactor depends on the qualitative and quantitative composition of the pyrolytic gas. It reaches a minimum at the time corresponding to the maximum of momentary temperature measured at the end of the plasma reactor (t) (Fig. 1)

The plasma reactor is a universal device. It can be used not only for the full oxidation of hydrocarbons, but also in the same reactor, a so called "syngas" (a mixture of carbon monoxide and hydrogen) or short-chain aliphatic hydrocarbons and/or carbon black can be obtained [12–19]. The combustion of these compounds can recover energy. This is one of the ways of the waste utilization. As a result, the waste utilization can be carried out in various ways in the same device by changing only the conditions of process. It can also be expected that different conditions (from the conventional combustion reaction) in the plasma reactor will not promote the formation of polynuclear/polycyclic aromatic compounds and their derivatives [20–24]. Consequently, a low concentration of PCDDs and PCDFs in the exhaust gases emitted from the utilization process of waste containing chlorine is expected [25,26].

In the module of heat exchanger, the gases after the oxidation reaction were cooled. The module of heat exchanger consisted of: 1—a shell-and-tube heat exchanger cooled by water 2—a vessel for the condensed water vapour and 3—connecting pipe to sampling the post-reaction gas. The measurement of the volume of post-reaction gas and its temperature was performed after the heat exchanger.