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Comparative Analysis of PCDD/Fs Formation during Pyrolysis and Incineration of Medical Waste

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Abstract. Medical waste is a special kind of hazardous materials, which disposal leads to considerable pollution of the environment. The widespread method of medical waste disposal is thermal treatment (pyrolysis or incineration), which gives appropriate transformation of waste into a safe form (ash) and energy. On the other hand, the thermal treatment of medical waste that contain chlorine leads to the formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), most toxic representatives of organic pollutants. This paper analyses various mechanisms of the PCDD/Fs formation during thermal treatment of chlorine-containing medical waste. The features of these mechanisms are considered. It is shown that in pyrolytic conditions the PCDD/Fs yield is much lower than under direct incineration. Optimal temperature conditions are determined, under which the formation of these compounds is minimal.

1. Introduction

Medical waste management is currently one of the most important environmental problems in connection with population growth and the increased demand for medical services [1]. The main methods of medical waste disposal are incineration, steam sterilization, and chemical or microwave disinfection [2]. Among them the priority method is the medical waste incineration [3]. The advantages of this method are a significant reduction in the volume of waste, destruction of causative organisms, and transformation of waste into ash with subsequent ash landfilling. Nevertheless, the incineration of medical waste is associated with heightened emission of pollutants, which might limit the use of this technology. Medical waste contains a much higher content of plastics than typical municipal solid waste, and as a result the incineration of medical waste leads to the formation of a large quantity of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), extremely persistent and highly toxic substances [4]. This requires expensive systems for cleaning of the medical waste incineration flue gases from PCDD/Fs [5].

PCDD/Fs are most toxic representatives of volatile organic compounds in the industrial flue gases. These chemicals are generated practically in all processes connected with the combustion of organics in the presence of various chlorine compounds (industrial and domestic coal combustion, medical and municipal waste incineration, sinter plants, cement industry, ferrous and non-ferrous metallurgy, motor transport, etc.) [6]. The US EPA guidelines set the PCDD/Fs dose limit for humans of 0.001 pg/kg of body weight in day for the most toxic 2,3,7,8-TCDD for a lifetime additional cancer risk of 10^{-6}. The lethal dose for 50% of the population is only 0.6 μg/kg of body weight [7].

Pyrolysis can be considered as an alternative to direct incineration of medical waste [8]. The essence of the process is the thermochemical decomposition of organic material at high temperatures in the absence of oxygen. Compared to incineration, pyrolysis has a lower process temperature, minor carryover of particulates, and lower emissions of air pollutants, which leads to a reduced impact on the environment. The main purpose of this work is to evaluate the efficiency of the PCDD/Fs formation at the pyrolysis of medical waste in comparison with their direct incineration and to determine the optimal process conditions that lead to minimization of the PCDD/Fs yield.

2. Mechanisms of PCDD/Fs formation

As experimental data show, PCDD/Fs are formed both in the process of organics combustion and during the motion of combustion products through heat exchangers and purification devices [9]. The mechanisms of the PCDD/Fs formation were studied both on model substances and in application to operating facilities for waste incineration. It should be noted that process of the PCDD/Fs formation under all conditions is only an insignificant side reaction in the overall combustion process. Therefore, the interpretation of experimental data on the PCDD/Fs formation is a more complicated procedure than study of the main process.

The PCDD/Fs formation occurs through heterogeneous and homogeneous pathways. The heterogeneous formation takes place mainly in the low-temperature region behind the combustion chamber as a result of heterogeneous catalytic reactions on the surface of fly ash particles. Two mechanisms of the heterogeneous pathway are proposed. The first mechanism is associated with the process of burning out the structural elements of the carbon matrix in ash particles with simultaneous chlorination of the formed dioxin structures (mechanism *de novo*). The second mechanism describes the surface-mediated formation of PCDD/Fs from small organic molecules-precursors that are adsorbed on the surface of the ash particles and then react with each other (mechanism *precursors*).

The *de novo* process takes place in a narrow temperature range from 250 to 350 °C with an oxygen concentration in the gas flow of the order of several percents [10]. Various mineral compounds based on Cu, Fe, Al, and Si, which are present in the ash particles, act as catalysts for the reactions of the PCDD/Fs chlorination. The oxygen concentration in the gas flow is an important parameter of the *de novo* process. As experimental data show, PCDD/Fs are not formed at low and high concentrations of O_2. This proves that the *de novo* process is the minor stage of heterogeneous oxidation of various condensed carbon structures in the ash particles. The *de novo* mechanism is prevailing in a cooling section of the waste incinerator, where the flue gases are cooled up to 200 °C [9]. Kinetic modeling of this mechanism is based on a global reaction describing the carbon gasification and the PCDD/Fs formation [11].

The *precursor's* mechanism describes the surface-mediated formation of PCDD/Fs from various aromatic hydrocarbons (mainly chlorophenols) that are present in the gas phase [12]. These precursors are generated at the initial stage of the combustion process as a result of thermal destruction of the organic mass of the solid waste and the yield of hydrocarbon compounds into the gas phase. Aromatic hydrocarbons are also formed in the process of soot formation from acetylene that is one of the intermediate products of combustion of all hydrocarbon fuels. The presence of various chlorine compounds in the gas phase leads to chlorination of both molecules-precursors and reaction products. A multistep kinetic model of the *precursor's* mechanism was developed on the base of experimental data for surface-mediated conversion of chlorophenols to the PCDD/Fs [13]. The efficiency of the *precursor's* mechanism is approximately equal to the efficiency of the *de novo* mechanism.

The *homogeneous* pathway of the PCDD/Fs formation describes the gas-phase reactions of structurally related precursors such as chlorophenols, chlorobenzenes, and other aromatic compounds [14]. It was thoroughly studied both experimentally [14, 15] and theoretically [16] and includes the following chemical stages: the production of phenoxy radical from phenol molecule, self-condensation of molecules and radicals, cyclization of the formed structures with production of PCDD/Fs molecules, and reactions of chlorination. The homorogeneous pathway of the PCDD/Fs formation gives about 30% of the total amount of PCDD/Fs yield under most process conditions [9].

3. Results and discussion

The comparative analysis of the process of PCDD/Fs formation during the thermal processing of medical waste in oxidative and pyrolytic conditions is important from the point of view of using pyrolysis as an alternative technology with respect to direct incineration of waste. Since the available kinetic models of the process are based on experimental data, it makes sense to limit the consideration of the problem only by analyzing the measured concentrations of PCDD/Fs in real installations in their dependence on the main process parameters (temperature, oxygen concentration, catalyst type, etc.).

The *de novo* PCDD/Fs synthesis is implemented by the afterburning of the residual carbon in the ash particles in the presence of inorganic chlorine compounds and a metal catalyst. Figure 1 shows the temperature dependence of the PCDD/Fs concentrations obtained in conditions of the *de novo* synthesis by different authors at various experimental installations [17-21]. The oxygen concentration in the experiments is equal approximately to 10 vol.%, and the average carbon content in the ash is equal to 20 mg/g of the ash. Since the absolute values of the PCDD/Fs concentrations strongly depend on the specific experimental conditions, the mentioned data are normalized to the maximum values. The least-square approximation (solid line) describes well the scatter of experimental points. It can be seen that the process of the PCDD/Fs formation occurs in the temperature range from 250 to 400 °C with a concentration maximum at $T = 300$ °C fixed in all experiments.
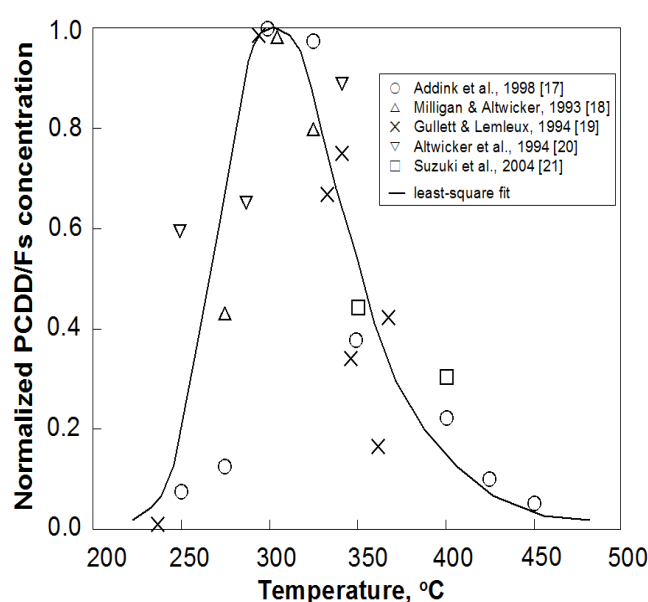

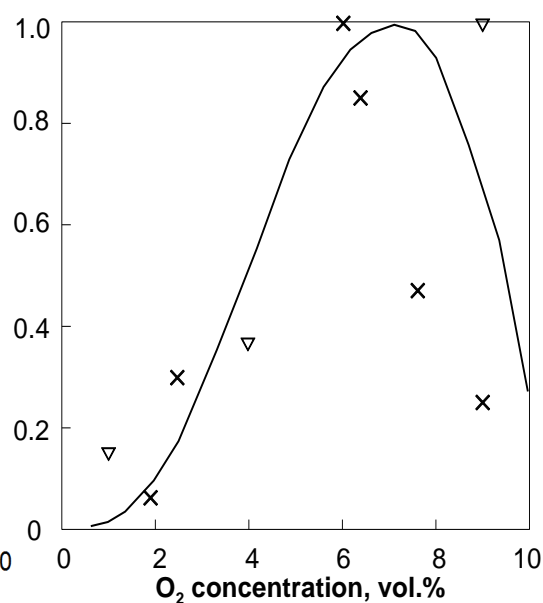**Figure 1.** Temperature dependence of PCDD/Fs concentration in *de novo* process.

Figure 2. O$_2$ dependence of PCDD/Fs concentration in *de novo* process.

The absolute PCDD/Fs concentrations in examined experiments vary within wide limits from 0.03 µg/g of the fly ash [21] to 7.7 µg/g of the fly ash [19]. To evaluate the PCDD/Fs toxicity, the concentrations of the PCDD/Fs congeners must be multiplied by toxicity equivalence factors TEF that relate the toxicity of the individual PCDD/F congeners to the toxicity of 2,3,7,8-TCDD [22]. This procedure determines the toxicity equivalence (TEQ) concentrations of PCDD/Fs. The average PCDD/F concentration in modern large-scale waste incinerators before air pollutant control devices is around of 100 ng/Nm^3 of the flue gases or 4 ng-TEQ/Nm^3 [23]. The EU standard for the PCDD/Fs concentration in the waste incineration flue gases before its emission into the atmosphere is equal to 0.1 ng-TEQ/Nm^3 [24]. Corresponding PCDD/Fs content in the fly ash has limit of 1.0 ng-TEQ/g of the fly ash.

The dependence of the PCDD/Fs concentration on the oxygen content in the carrier gas stream at the temperature $T = 300$ °C, at which the concentration reaches the maximum, is shown in Figure 2. It can be seen that the maximum PCDD/Fs yield in accordance with the *de novo* mechanism is observed in the range of oxygen concentrations from 4 to 10 vol.%. The maximum PCDD/Fs concentration is observed at the oxygen content of the order of 6 vol.%. At higher and lower oxygen concentrations, the yield of dioxins and dibenzofurans decreases sharply. Therefore, in pyrolytic conditions, when the oxygen concentration in the surrounding gaseous medium is less than 1 vol.%, PCDD/Fs practically do not form in accordance with the *de novo* mechanism.
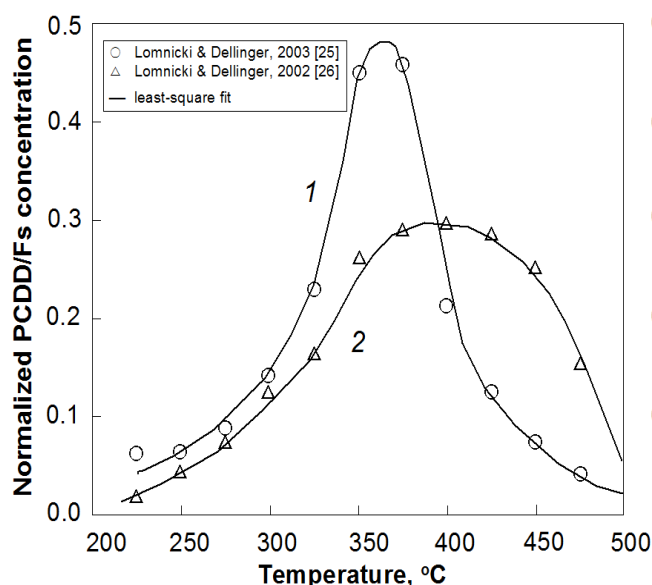

Figure 3. Surface-mediated PCDD/Fs formation from chlorophenols in oxidative (*1*) and pyrolytic (*2*) conditions.
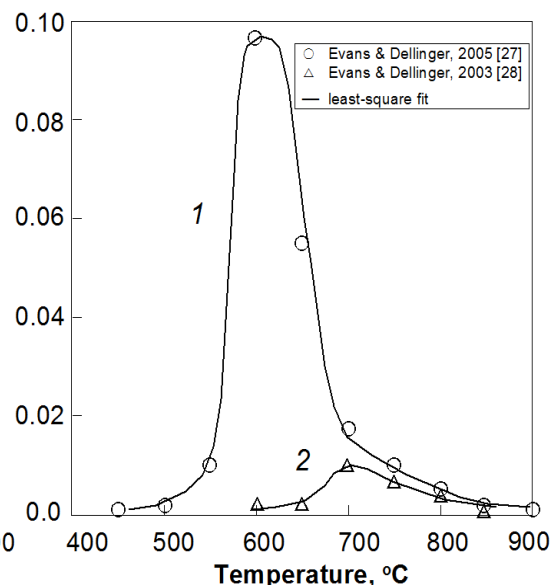
Figure 4. Gas-phase PCDD/Fs formation from chlorophenols in oxidative (*1*) and pyrolytic (*2*) conditions.

The surface-mediated *precursor's* mechanism describes the PCDD/Fs formation from chlorophenols and other aromatic compounds in the condensation reactions catalyzed by transition metals presented in the fly ash particles [25]. The most active metals involved in this process are cooper and iron ions. Figure 3 presents the temperature dependence of the PCDD/Fs concentrations obtained in conditions of oxidation and pyrolysis of 2-monochlorophenol (2-MCP) on the surface of dispersed cooper oxide particles $CuO(5\%)SiO_2$ [25, 26]. For convenience of comparison, the PCDD/Fs concentrations were normalized to the initial 2-MCP concentration. As can be seen from the data presented, the PCDD/Fs formation occurs in the temperature range from 200 to 500 °C, which indicates that the process is surface catalytic. In the pyrolytic conditions, the PCDD/Fs yield is somewhat lower, and the maximum of the PCDD/Fs concentration shifts to a region of higher temperatures by about 50 °C.

The *homogeneous* gas-phase mechanism describes the PCDD/Fs formation from chlorophenols, polychlorinated benzenes, and hydroquinones [9]. Figure 4 shows the PCDD/Fs concentrations at the oxidation and pyrolysis of 2-MCP as a function of the process temperature [28, 29]. Noticeable PCDD/Fs concentrations are observed in the temperature range from 500 to 800 °C. This is explained by the fact that the reactions of PCDD/Fs formation are "frozen" at temperatures below 500 °C, and at temperatures above 800 °C, the mechanism of their destruction is activated. As in the case of the surface-mediated *precursor's* mechanism, the maximum of the PCDD/Fs concentration in the pyrolytic conditions is shifted by 100 °C toward higher temperatures. However in absolute terms, the

homogeneous oxidation process gives the maximum PCDD/Fs yield ten times bigger. Analysis of the data obtained in [28, 29] shows that dioxins are formed mainly in pyrolytic conditions, and dibenzofurans are formed mainly under oxidative conditions.

The analysis of the PCDD/Fs formation in various mechanisms of the process makes it possible to determine the optimum conditions of the pyrolysis of chlorine-containing medical waste, in which the PCDD/Fs yield is minimal. Firstly, the *de novo* mechanism does not work at temperatures above 500 °C. The absence of an oxygen blowing during the pyrolysis of solid waste leads to a minimum carryover of ash particles from the reaction zone. Since the *de novo* mechanism is responsible for the PCDD/Fs formation in ash particles, the subsequent combustion of gaseous products of the pyrolysis with the purpose of obtaining thermal energy followed by cooling of combustion products before their emission into the atmosphere is not accompanied by the PCDD/Fs formation in notable quantities.

Secondly, the surface-mediated *precursor's* mechanism takes place in the same temperature range as the *de novo* mechanism. On the other hand, the maximum PCDD/Fs yield in the *homogeneous* gas-phase mechanism under pyrolytic conditions is 30 times less than the corresponding yield in the surface-mediated *precursor's* mechanism. And, finally, the *homogeneous* gas-phase process of the PCDD/Fs formation in pyrolytic conditions begins at temperatures above 600 °C with an efficiency of 10 times less than in oxidizing conditions. This allows to offer the optimum temperature for the pyrolysis process in the range from 500 to 600 °C.

Table 1. PCDD/Fs concentrations (pg-TEQ/g) in products of pyrolysis and oxidation of chlorine-containing solid waste.

Process	Gas		Oil		Char	
	PCDDs	PCDFs	PCDDs	PCDFs	PCDDs	PCDFs
Pyrolysis	0.069	0.243	2.045	3.900	0.371	0.449
Oxidation	9.395	102.008	99.653	1141.195	0.509	1.022

The experimental data analyzed above are obtained using model substances. In real conditions, there may be some deviations from the regularities of the behavior of the PCDD/Fs concentrations received with the model substances. Table 1 shows the PCDD/Fs concentrations measured in products of pyrolysis and oxidation of chlorine-containing solid waste at the temperature of 600 °C [29]. As can be seen from the Table 1, PCDD/Fs at the given temperature practically do not form in the solid residue (char). The main content of PCDD/Fs is noted in liquid products (oil) of thermal processing of solid waste, which at $T = 600$ °C are in the gaseous state. Under oxidizing conditions, the PCDD/Fs concentration exceeds by more than two orders of magnitude the corresponding concentration obtained under pyrolytic conditions. It should be noted that, both in oxidizing and pyrolytic conditions, the concentration of dibenzofurans exceeds the concentration of dioxins.

The main source of chlorine in these experiments is polyvinylchloride (PVC). An increase in the chlorine content in the chemically reacting system leads to an increase in the degree of chlorination of PCDD/Fs. In the absence of PVC, polychlorinated dioxins and dibenzofurans are not formed. In this regard, various methods of waste dechlorination before pyrolysis are proposed that start at the temperatures less than 250 °C [30].

4. Conclusions

The *de novo* mechanism of the PCDD/Fs formation, which is associated with the process of burning out the structural elements of the carbon matrix in ash particles, occurs in the temperature range from 250 to 400 °C. In the pyrolytic conditions, when the O_2 concentration in the surrounding gas is less than 1 vol.%, this mechanism practically do not form PCDD/Fs. The PCDD/Fs formation from chlorophenols in the surface-mediated *precursor's* mechanism occurs in the temperature range from 200 to 500 °C. The *homogeneous* gas-phase mechanism describes the PCDD/Fs formation from

chlorophenols, and in pyrolytic conditions works in the temperature range from 600 to 800 °C. Therefore, the optimum temperature for the pyrolysis process is in the range from 500 to 600 °C.

The absence of an oxygen blowing during the pyrolysis of solid waste leads to a minimum carryover of ash particles from the reaction zone. Therefore, the cooling of the pyrolysis products down to 200 °C before their emission into the atmosphere is not accompanied by the PCDD/Fs formation in notable quantities in accordance with the *de novo* mechanism or the surface-mediated *precursor's* mechanism.

5. References

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