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Thermodynamic Aspects of Dioxin Precursors Neutralization by Plasma Methods

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Abstract. The problem of increasing the efficiency of thermal methods for waste disposal due to the plasma methods introduction at the stage of toxic gaseous afterburning is considered. Dioxins, synthetic organic substances from the class of chlorocarbons, are by far the most toxic substances produced by humans. The main source of their formation is incineration plants, pulp and paper, electrical industry, etc. In addition, the formation of dioxins can lead to the interaction under certain conditions of some organic compounds – precursors of dioxins. Taking into account these circumstances, we consider the reactions that characterize the processes of high-temperature neutralization of dioxin precursors – chlorobenzene, phenol, biphenyl, and trichloroethylene. On the basis of thermodynamic analysis, a high probability of their spontaneous oxidation and decomposition at temperatures above 500 K is shown. The decomposition efficiency increases with increasing temperature, thereby confirming the possibility of these products neutralization under plasma heating conditions. The scheme of the plasma afterburning technology and the results of the heating temperatures calculation for toxic gases in the mixing chamber of the plasma torch are shown. The results indicate that plasma heating provides the temperature range necessary for the effective decomposition of dioxin precursors.

INTRODUCTION

The problem of using thermal methods in waste disposal technologies, as a rule, is associated with the need to use expensive methods for cleaning waste gases containing high-hazard substances – dioxins and their precursors, nitrogen oxides, etc. It is possible to increase the efficiency of such methods by introducing plasma methods of waste disposal at the afterburning stage of toxic gaseous emissions [1,2]. It is obvious that the applicability of plasma incineration should be justified both by the nomenclature of toxic waste and by the efficiency of the technology.

METHOD

Dioxins, synthetic organic substances from the class of chlorocarbons, are by far the most toxic substances produced by humans. The main source of their formation is incineration plants, pulp and paper, electrical industry, etc. The process of decomposition of dioxins into safe compounds is a big problem due to the fact that in the combustion chambers during cooling, the reverse process is possible – the synthesis of dioxins from the formed substances. In addition, the formation of dioxins can lead to the interaction under certain conditions of some organic compounds – precursors of dioxins. In particular, such conditions include temperatures of 150^0C and above, ash particles in flue gases, an alkaline environment, etc. [3,4].

Precursors include substances that precede the formation of a particular compound. Possible precursors of dioxins can be benzene (C_6H_6), chlorobenzene (C_6H_5Cl), phenol (C_6H_5OH), diphenyl ($C_{12}H_{10}$), trichloroethylene (C_2HCl_3) and some other substances [5] that can not only retain their properties under various conditions, but also form dioxins (Table 1). In this regard, the question of their thermodynamic stability at high temperatures becomes relevant.

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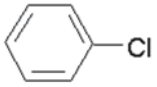
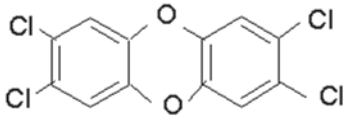
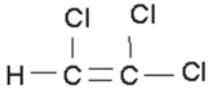
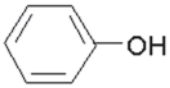
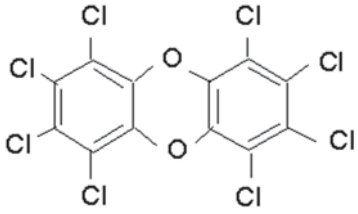
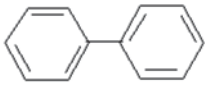
TABLE 1. Formation of dioxins from some precursors.

Precursors		Possible dioxins	
Title	**Structural formula**	**Title**	**Structural formula**
Chlorobenzene		Tetrachlorodibenzo-p-dioxin	
Trichloroethylene			
Phenol		Octachlorodibenzo-p-dioxin	
Diphenyl			

The decomposition of dioxin precursors when heated in an oxygen-containing environment is usually accompanied by the release of carbon dioxide and water. During the oxidation of halogen-derived aromatic compounds and aliphatic hydrocarbons, chlorine is also released. The main condition for the thermal oxidation of dioxin precursors is a multiple excess of oxygen. Otherwise, when there is a lack of oxygen and low temperatures in the reaction sphere, the opposite process begins – the formation of dioxins [5].

DISCUSSION

The high-temperature oxidation processes of the dioxin precursors listed above can be represented by the following reaction equations:

$$2C_6H_5Cl + 14{,}5O_2 = 12CO_2 + 5H_2O + Cl_2 \quad (1)$$

$$C_6H_5OH + 7O_2 = 6CO_2 + 3H_2O \quad (2)$$

$$C_{12}H_{10} + 14{,}5O_2 = 12CO_2 + 5H_2O \quad (3)$$

$$2C_2HCl_3 + 4{,}5O_2 = 4CO_2 + H_2O + 3Cl_2 \quad (4)$$

The possibility of spontaneous transformation of substances was evaluated by the change in the Gibbs free energy of the reaction at a given temperature T:

$$\Delta G = \Delta H^0_{298} - T\Delta S^0_{298}, \quad (5)$$

where ΔH^0_{298} is the change in the standard enthalpy of the reaction, ΔS^0_{298} is the change in the standard entropy of the reaction. The calculated values of the Gibbs energy for reactions (1) - (4) are given in the Table 2. The temperature dependences are shown in Fig. 1.

TABLE 2. Thermodynamic parameters for dioxin precursor oxidation reactions.

Reaction	ΔH^0_{298}, *(kJ)*	ΔS^0_{298}, *(kJ/K)*	ΔG, *(kJ)*				
			T=500 K	T=1000 K	T=2000 K	T=3000 K	T=4000 K
1	-6045.24	2.88	-7485.24	-8925.24	-11805.24	-14685.24	-17565.24
2	-2921.61	0.27	-3056.61	-3240.61	-3461.61	-3731.61	-4001.61
3	-6132.12	3.30	-7782.12	-9432.12	-12732.12	-16032.12	-19332.12
4	-1821.24	0.14	-1891.24	-2031.24	-2101.24	-2241.24	-2381.24

As follows from the Table 2, the oxidation processes of precursor substances are characterized by an exothermic effect. The probability of spontaneous oxidation already at 500 K is quite high and increases with increasing temperature. Especially low values of the Gibbs energy at high temperatures are characterized by the oxidation reactions of chlorobenzene (1) and biphenyl (3). Consequently, the complete decomposition of these compounds is possible at lower temperatures. From Fig. 1 it can be seen that the changes in the Gibbs energy of high-temperature decomposition of phenol and trichloroethylene are close and change almost equally with increasing temperature. However, their complete decomposition will require higher temperatures than, for example, with chlorobenzene.

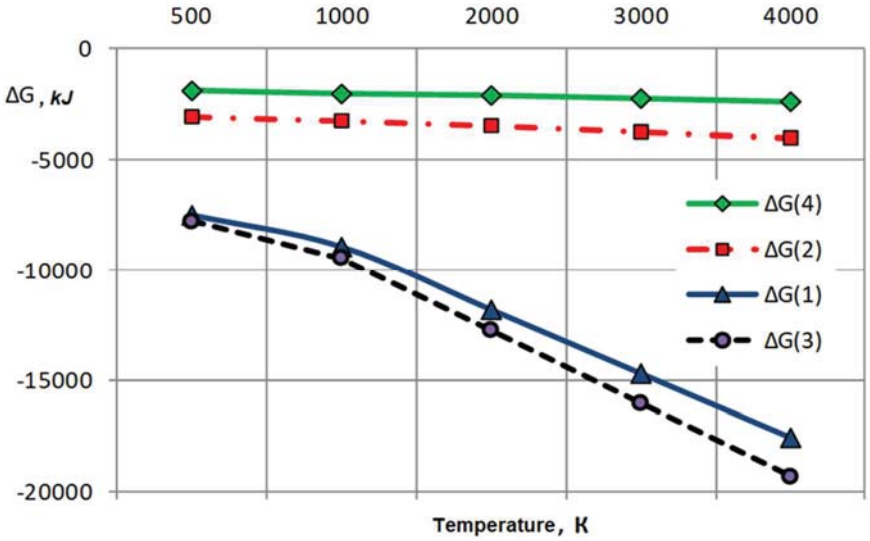


FIGURE 1. Temperature dependence of the change in the Gibbs energy of reactions (1) - (4)

Chlorine released during the oxidation of precursors in reactions (1) and (4) is a dangerous component in the system of reaction products due to the ease of its interaction with many organic substances with the subsequent formation of dioxins. Obviously, it is necessary to use technologies for its capture by chemical or physico-chemical methods, or high-speed quenching (cooling) for products of high-temperature decomposition of dioxin precursors.

As a technology for the neutralization of dioxins and their precursors, the system of plasma afterburning of gaseous toxic waste proposed by the authors can be used [6,7]. Figure 2 shows a scheme of such an afterburner. This device consists of a plasma torch with a mixing chamber (MC) of plasma-forming and toxic gases. In the MC, the incoming volume of the recycled gas is heated using plasma jets of various configurations. Supply of toxic gases – through 4 pipes with a diameter of 4 mm, located perpendicular to the MC axis at a distance of 11 mm from the nozzle. According to the results of the research carried out by the authors, the optimal design and technological features of the afterburner are determined. The gas-dynamic parameters of the air-plasma flow in the MC with a plasma arc length of at least 170 mm and a temperature on the axis of the MC of at least 7000 K were determined using mathematical modeling methods in the SolidWorks software. This device provides heating of the neutralized gas mixture in the range of 2-10 ms at

average temperatures of 2000-4000 K. The temperature distribution along the calculated trajectories in the MC is shown in Fig. 3. It is obvious that plasma heating provides the temperature range necessary for the effective decomposition of dioxin precursors.

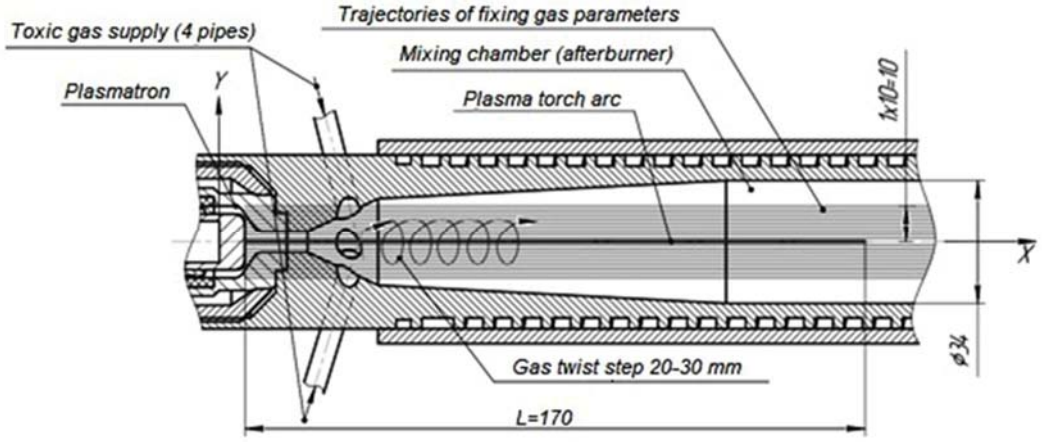


FIGURE 2. Scheme of a plasma afterburner for toxic waste

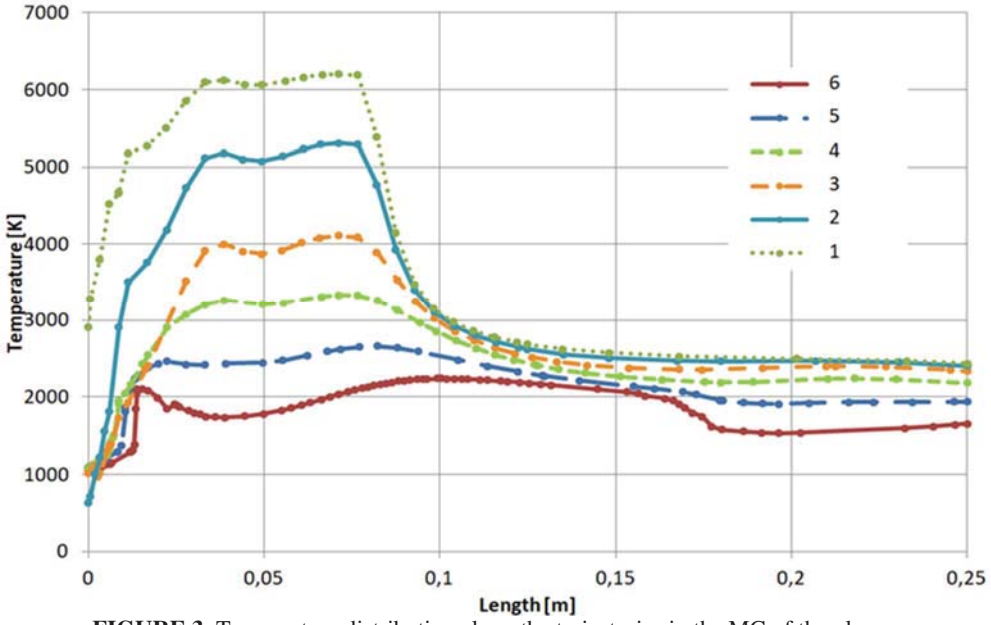


FIGURE 3. Temperature distribution along the trajectories in the MC of the plasma afterburner (1-6-trajectory numbers (as you move away from the X-axis))

CONCLUSION

Thus, it is established that the process of high-temperature oxidation of dioxin precursors proceeds spontaneously in a wide temperature range. The thermodynamic probability of precursors decomposition increases with increasing temperature. The use of plasma incineration methods ensures their heating and decomposition in the specified temperature ranges and can be used at the stage of afterburning of gaseous emissions containing products of the considered composition.

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