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Thermogravimetric and Kinetic Study of Pyrolysis of Chlorine-Containing Medical Waste

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Abstract. In this paper, the thermal decomposition (pyrolysis) of components of medical waste that consist of polyvinyl chloride (medical oilcloth and tubes of blood transfusion systems) is investigated. Thermogravimetric analyzes were performed in the TG-DTG mode on the synchronous thermal analysis device NETZSCH STA 449 F3 Jupiter. Based on the data obtained, the calculation of the kinetic parameters of the process of thermal decomposition of the investigated samples of medical waste was performed. For tubes of blood transfusion systems, experiments were conducted to absorb gases entering from the reaction volume in order to determine the temperature range of hydrogen chloride emission.

1. Introduction

The problem of medical and biological waste utilization, which arises in the process of activity of medical, preventive and veterinary institutions, medical research institutes, and at the production of medicines, has complex character from epidemiological, ecological, hygienic, and social point of view. Over the past decade, the amount of medical waste generated in Russia has increased more than 4.3 times and amounted to 7.2 million tons in 2013 (about 1.5% of the total volume of waste production and consumption) [1]. At the same time, the total amount of medical waste belonging to dangerous (class B) and extremely dangerous in epidemiological terms (class B) in 2013 was 18.3 thousand tons, which is more than 52% higher than in 2008. Annual growth rates for this period were 11.5%, and in previous years - not more than 3.3% [2].

Existing methods of medical waste utilization can be divided into decontamination technologies (chemical and thermochemical disinfection, autoclaving, microwave exposure) and destruction (burning, pyrolysis). According to the current sanitary requirements (SanPiN 2.1.7.2790-10) [3] regardless of the method of disposal of medical waste, two basic requirements must be met: firstly, their inability to reuse and, secondly, their reliable disinfection. Compliance with the above mentioned requirements can only be fully assured by destruction technologies.

The transition to high-tech methods of diagnosis and treatment as well as an increase in the number of surgical and invasive manipulations with the use of disposable instruments and disposables, not only caused the growth of medical waste generation, but also led to a change in their composition. The main morphological groups, gradually displacing the rest, are polymeric and composite materials, rubber and textile products. In particular, the content of polymer has increased over the past 10 years averaged three times (from 5 to 15%), and in some cases their real share in the waste coming to the decontamination is 30% or more [4].



An important feature of medical waste is the presence of organochlorine compounds, in particular polyvinyl chloride (PVC), that lead during combustion to the formation of a number of incomplete combustion products in addition to traditional pollutants such as fly ash, SO₂, NO, NO₂, HCl. These products include extremely toxic organic pollutants such as polychlorinated dibenzo-*p*-dioxins (PCDD), dibenzofurans (PCDF), and polycyclic aromatic hydrocarbons (PAHs) [5]. These toxic substances even in relatively small concentrations affect almost all living organisms from bacteria to humans. Possessing high chemical resistance, they do not decompose in the environment for dozens of years, accumulate in the upper layer of the soil and enter the human body with food, water, and air. In connection with this, the strictest standards have been established for them [6]. The formation of dioxins occurs both at the stage of thermal decomposition of organic matter in the presence of oxygen and chlorine, and at cooling of combustion products (at 250 - 450 °C) in the ash particles (act as catalysts for the reactions of the PCDD/Fs chlorination) in the presence of oxygen and hydrogen chloride [7, 8]. A comparative analysis of the formation of dioxins in the combustion and pyrolysis of various materials shows that their concentration in pyrolysis products is 10 or more times lower than in combustion products under identical process conditions [9]. This fact shows significant advantage of pyrolysis over combustion in terms of ecological safety of neutralizing chlorine-containing medical waste.

In this paper, the problem of thermal decomposition (pyrolysis) of medical oilcloth and tubes of blood transfusion systems (medical waste components) consisting of polyvinyl chloride is considered. Thermogravimetric studies were carried out to obtain kinetic parameters and to reveal the temperature range of hydrogen chloride emission during pyrolysis of the materials under study.

2. Experimental

Thermal analysis of PVC samples was carried out using the NETZSCH STA 449 F3 Jupiter in TG-DTG mode, to a final temperature of 900 °C with a heating rate of 20 °C/min. Before the analysis, the reaction volume of this apparatus was pumped down and then filled with nitrogen (N₂) to provide an inert atmosphere. During the experiment, the reaction volume was also blown off with nitrogen at a flow rate of 50 ml/min. The measurements were made in corundum (Al₂O₃) crucibles with a volume of 0.3 ml. During the heating, changes in mass were recorded. The results of the thermogravimetric analysis (TG) and differential thermogravimetric analysis (DTG) presented in this study were corrected using the baseline obtained by measuring the empty crucible.

Previous studies have shown that thermal decomposition of PVC without access to air proceeds usually with the formation of hydrogen chloride from bound chlorine [10]. For the temperature of hydrogen chloride extraction from PVC, separate experiments were carried out with alternating dynamic and isothermal segments (used to change absorbers) in five temperature ranges: 40 - 250, 250 - 300, 300 - 350, 350 - 400, 400 - 920 °C. The gases released during the pyrolysis of PVC from the reaction volume of the synchronous thermal analysis device were entering the system of absorbers filled with distilled water. As a result of the dissolution of hydrogen chloride in water, hydrochloric acid (HCl) forms. After the experiment based on titration method, the concentration of trapped hydrogen chloride was determined.

We used the following PVC samples: an adhesive medical liner with PVC coating from CJSC Vitalfarm (PVC-1) and PVC tubes from a blood transfusion device (PC 23-07) manufactured by Sintez OJSC (PVC-2).

3. Results and discussion

Thermal decomposition of PVC with heating up to 800 °C and above usually takes place in two stages. This is indicated by the appearance of two distinct maxima at 270 °C (yield of HCl) and 450 °C (emission of hydrogen, methane and other hydrocarbons) under conditions of continuous heating [11, 12]. PVC (the chemical formula [-CH₂-CHCl-]_n) consists of 56.5% of Cl, 38.7% of C and 4.8% of H. During the PVC thermal decomposition, non-volatile carbon is concentrated in a solid residue in an amount of ~ 20%. It is worth noting that in the production of PVC products, plasticate is used with

predetermined physical and mechanical properties. For these purposes, special additives (plasticizers) are included into the composition of the PVC product, the content of which in the initial composition can reach 50%.

3.1. TG-DTG analysis of samples

The results of the thermogravimetric analysis of PVC-1 and PVC-2 samples are shown in Fig. 1a and Fig. 1b, respectively. As it can be seen from Fig. 1a, the mass loss of the first sample occurs in three stages: 280 - 340 °C (43.56%), 420 - 520 °C (11.63%), and 585 - 795 °C (7.54%). It can be assumed that the first stage with a peak at 320 °C is associated, mainly, with the separation of hydrogen chloride from the PVC molecule. At the second stage with the greatest intensity at 465 °C, the decomposition of the organic part of the PVC molecule occurs. At the third stage, a pronounced peak is absent, and the process of thermal decomposition occurs because of the organic plasticizer presence in the PVC composition. In addition to the organic plasticizer, mineral additives were probably used in the production of PVC-1, as evidenced by a relatively high residual mass of 37.27%. The thermal decomposition of the second sample occurs, as it shown in Fig. 1b, in two stages: 280 - 360 °C (71.50%), 450 - 500 °C (17.33%). As in the case of the PVC-1 sample, the first stage is associated with the release of hydrogen chloride, and the second stage is associated with the decomposition of the organic part of the PVC molecule. In the temperature range 500 - 900 °C, the heating was accompanied by a gradual loss of mass by 2.35%. Unlike the first sample, in which mineral additives were supposed to be present, the residual mass in the second sample is 8.82%, which indicates the use of predominantly organic plasticizers that reduced the yield of non-volatile carbon.

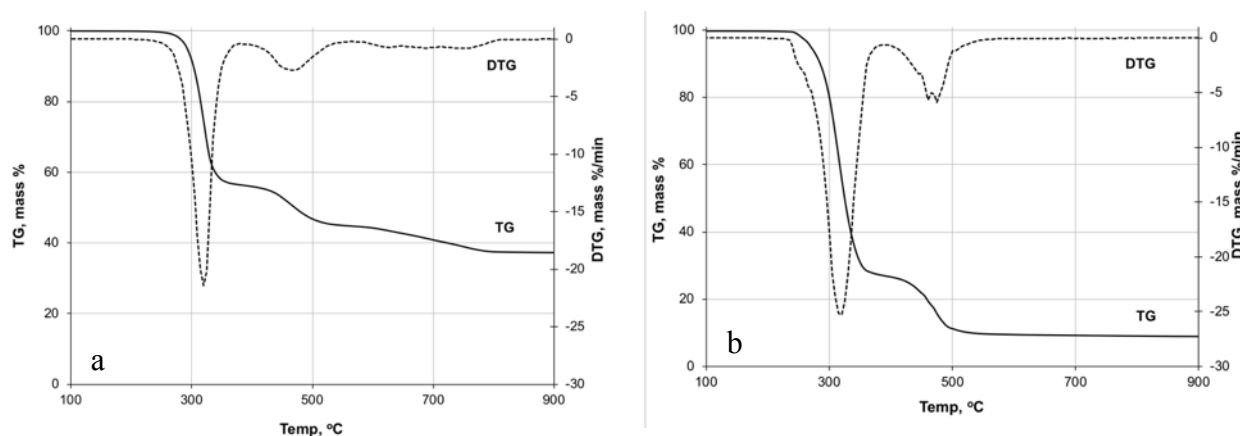


Figure 1. TG and DTG curves for PVC-1 (a) and PVC-2 (b) samples during pyrolysis.

3.2. Determination of the kinetic parameters of the process

An important task of this work was to determine the kinetic parameters of the thermal decomposition of the components of medical waste for further calculation studies. The rate constant of the reaction depends on the temperature and can be described by the Arrhenius equation $k = A \times \exp(-E/RT)$, where A is the pre-exponential factor, min^{-1} ; E is the activation energy, J/mol ; $R = 8.31 \text{ J/(mol}\cdot\text{K)}$ is the universal gas constant; and T is the reaction temperature, K . Figure 2 shows the experimental dependences of the reaction rate constants on temperature obtained in this study.

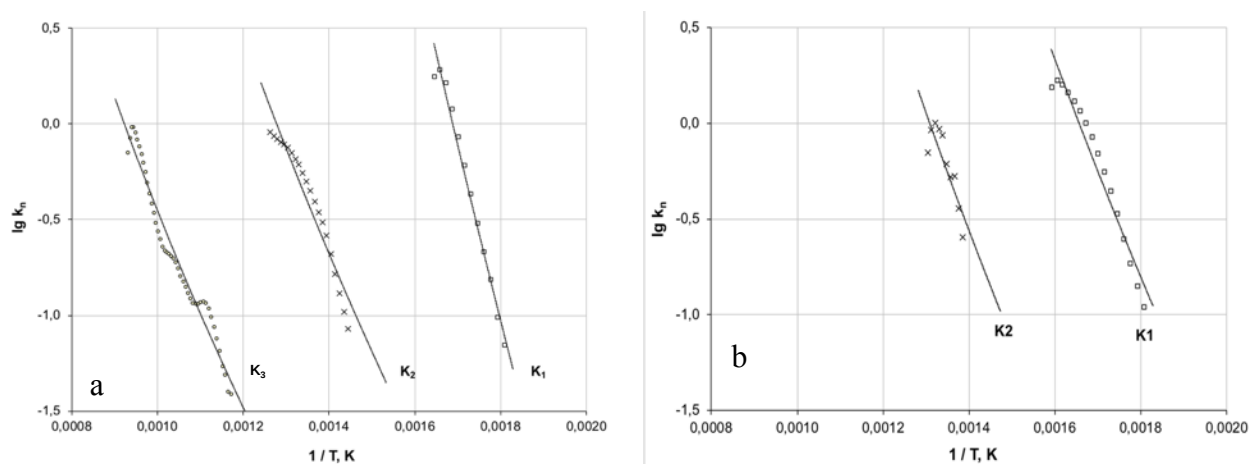


Figure 2. Dependence of the reaction rate constant on time for samples of PVC-1 (a) and PVC-2 (b).

For the obtained values of the rate constants, the kinetic parameters of the reactions were determined. The results of the calculation are presented in Table 1.

Table 1. Kinetic parameters of samples thermal decomposition.

Sample	Reaction No.	$\Delta T, ^\circ C$	$\Delta m, \%$	A, min^{-1}	$E, \text{kJ/mol}$
PVC-1	1	280 - 340	43.56	1.85×10^{14}	163.0
	2	420 - 520	11.63	1.19×10^7	107.5
	3	585 - 795	7.54	3.69×10^5	113.5
PVC-2	1	280 - 360	71.50	8.07×10^{10}	125.5
	2	450 - 500	17.3	2.28×10^{14}	206.6

A comparison of the calculated and experimental thermal decomposition data for PVC-1 and PVC-2 samples is shown in Figure 3.

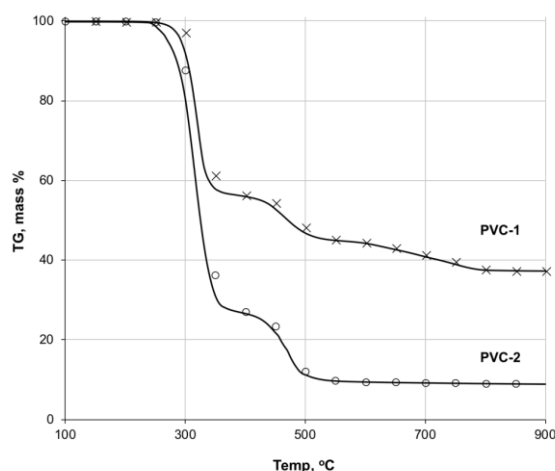


Figure 3. Comparison of calculated and experimental TG curves for PVC-1 (a) and PVC-2 (b) samples.

3.3. Determination of the temperature range of hydrogen chloride

One way to reduce the formation of PCDD and PCDF at the utilization of medical waste is their preliminary dechlorination. Therefore, an important task of the work was to identify the temperature range, at which the main amount of hydrogen chloride was released. The results of the analysis are presented in Table 2.

Table 2. Temperature range of hydrogen chloride yield.

Temperature, °C	40 - 250	250 - 300	300 - 350	350 - 400	400 - 920
HCl yield, %	9.88	37.04	41.51	8.56	3.01

As it can be seen from Table 2, the bulk of hydrogen chloride (~ 88.5%) is released at temperatures up to 350 °C, which complies well with the literature data [13, 14].

4. Conclusions

Based on the results of the TG-DTG analysis of samples of medical waste components containing polyvinyl chloride (PVC), the kinetic parameters of the thermal decomposition process were calculated. For the first sample (adhesive medical liner), the following kinetic parameters for three stages of the process were obtained: activation energy E is equal to 163.0, 107.5, and 113.5 kJ/mol; the pre-exponential factor A is equal to 1.85×10^{14} , 1.19×10^7 , and $3.69 \times 10^5 \text{ min}^{-1}$, correspondingly. For the second sample these values for two stages of the process are amounted as: activation energy E is equal to 125.5 and 206.6 kJ/mol; the pre-exponential factor A is equal to 8.07×10^{10} and $2.28 \times 10^{14} \text{ min}^{-1}$. The capture of hydrogen chloride at its yield from the reaction volume showed that its main part (~ 88.5%) is released at a temperature of up to 350 °C.

5. References

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