Study of Pyrolysis of Components and Mixture of Medical Waste

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The thermogravimetric study of the pyrolysis of typical components of medical waste was carried out in order to obtain detailed information on the process characteristics. Additionally, the pyrolysis of the medical waste mixture was conducted in the fixed-bed laboratory retorting system. It was shown that the main mass loss of medical waste mixture occurs in temperature ranges from 250 to 380 °C and from 400 to 500 °C. The first range is characterized by the yield of pyrolytic water and gas that contains hydrogen chloride and the bulk of HCl is released at temperatures up to 350 °C. In the second range, the bulk of the volatiles that consist mainly of pyrolytic oil are released. According to the results of the conducted study, the most environmentally safe, economical and best suitable method for solving the problem of utilization of medical waste was proposed. The method is based on two-stage pyrolysis of medical waste and includes the removal of chlorine-containing components before the main process of thermal decomposition of organic matter, which virtually eliminates the possibility of PCDD/Fs formation in the further process. The economic effect is achieved through the use of thermal potential of recyclable medical waste as an energy carrier for pyrolysis implementation.

1. Introduction

Medical waste generated during the operation of health-care agencies includes chemical, toxic and other substances and microorganisms and thus has a negative impact on humans and the environment (Rahim et al., 2015). This waste is a complex mixture of various materials such as polymers, textiles, food debris, biomaterials, rubber, metal, glass, ceramics, paper, etc., which differ greatly in their physical and mechanical properties (Windfeld and Brooks, 2015).

The most common method of medical waste disposal is incineration (Xie et al., 2009). However, the incineration of medical waste leads to the formation of large quantities of products of incomplete combustion, which include toxic and persistent organic pollutants. The presence of organochlorine compounds in the composition of medical waste promotes the formation of a large quantity of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) that pertain to extremely toxic substances (Wu et al., 2011).

Pyrolysis-base processes can be considered as an alternative to direct incineration of medical waste (Czajczyńska et al., 2017). The absence of oxygen in the pyrolysis zone of chlorine-containing wastes leads to a sharp decrease in the formation of dioxins (10 – 1,000 times) in comparison with combustion processes (Conesa et al., 2009). This fact indicates a significant advantage of pyrolysis over incineration in terms of ensuring the environmental safety of the disposal of chlorine-containing medical waste.

Most of the studies on the thermal decomposition of medical waste explore the pyrolysis of individual components or their simple mixtures (Yan et al., 2009). Additionally, some investigations focus their attention only on the concentration of the chlorine-containing compounds in the pyrolysis products, and special attention is not paid to the influence of other components of these products (López et al., 2011). In this study, a TG-DTG

analysis of individual components of the medical waste combined with data for the waste mixture obtained in a fixed-bed laboratory retort system was carried out in order to establish the best conditions for removing the chlorine-containing components from pyrolysis products, which ensure a minimum level of PCDD/Fs emissions to the environment.

2. Experimental

2.1 Materials

Direct work with medical waste is not possible due to their high epidemiological and toxicological hazards, as well as restrictions from the legislation of the Russian Federation, which prohibits contact with waste before their full disposal. In this regard, the analysis of available literature data was made to determine the morphological composition of medical waste (Kuzmin, 2007). According to the results of the analysis and taking into account the products available on the market of medical products, the average morphological composition of medical wastes was selected for the research. Table 1 represents the mass content of the tested model components of the medical waste as well as their proximate (includes the moisture, ash, fixed carbon and volatile matter) and ultimate analysis. All components of medical waste can be divided into three groups of compounds: carbohydrate containing materials (disposable tissues, cotton wool, bandages, and food waste), polyolefins (medical waste packages, biomaterial containers, and SMS-20 coverlets), and various polymers that contain nitrogen, chlorine, and sulfur atoms.

Table 1: Analysis of the tested model materials.

No.	Model materials	Content wt.%	Proximate analysis, wt.%[a]				Ultimate analysis, wt.%[a]						LHV, MJ/kg
			M	ASH	FC	VM	C	H	N	O	S	Cl	
	Carbohydrate containing materials												
1	Disposable tissues	24.0	0.30	0.82	19.99	78.89	47.23	6.43	-	45.23	-	-	17.70
2	Cotton wool	6.5	0.23	0.36	20.09	79.32	45.34	6.84	-	47.23	-	-	17.27
3	Bandage	6.5	0.18	0.20	20.13	79.49	44.68	6.65	-	48.29	-	-	16.74
4	Food waste	11.0	1.26	2.59	24.65	71.50	42.39	6.27	-	47.49	-	-	15.65
	Polyolefins												
5	Waste package	5.5	-	3.20	30.66	66.14	80.83	15.97	-	-	-	-	43.83
6	Biomaterial container	5.5	-	-	0.18	99.82	84.54	15.46	-	-	-	-	44.56
7	SMS-20 coverlet	30.0	0.18	-	20.33	79.49	86.39	13.43	-	-	-	-	43.10
	N, Cl, and S containing polymers												
8	Nitrile gloves	5.5	-	1.50	11.05	87.45	77.32	8.27	12.90	-	-	-	34.72
9	PVC coated oilcloth	2.2	-	22.24	15.04	62.72	32.78	4.11	-	-	-	40.88	15.34
10	Rubber tourniquet	3.3	-	31.26	0.89	67.85	54.19	8.06	-	-	6.49	-	27.37

[a]As-received basis.

2.2 Analytical methods

Thermal analysis of medical waste samples was carried out on the device NETZSCH STA 449 F3 Jupiter in TG-DTG mode to a final temperature of 900 °C with a heating rate of 10 °C/min. The reaction volume of the device before analysis was vacuumed and then filled with molecular nitrogen to provide an inert environment. The reaction volume during the experiment was also blown with nitrogen at a flow rate of 50 mL/min. Measurements were carried out in corundum (Al2O3) crucibles with a volume of 0.3 mL. Changes in mass during heating were recorded. The results of the thermogravimetric analysis (TG) and the differential thermogravimetric analysis (DTG) presented in this study were corrected using the baseline obtained by measuring the empty crucible.

The composition of the pyrolysis gas was carried out on the chromatograph LXM-2000M with a thermal conductivity detector of the DTP type, which has a high sensitivity to organic compounds. The chromatograph has the software "Zet-lab" that allows the signal processing.

2.3 Experimental procedure

The study of the pyrolysis of the medical waste mixture was conducted in the fixed-bed laboratory retorting system. Experiments on the retorting system were carried out as follows. The pre-crushed mixture of medical waste was loaded into the retort, after which it was sealed and installed in an electric furnace. The condensation system (double-neck flask and gasholder) was attached to the retort and the retort was heated at a rate of 10 °C to a given final temperature. Liquid pyrolysis products were discharged and condensed in the cooled double-

neck flask, and the pyrolysis gas was collected in the gasholder. After completing the experiment and cooling the electric furnace, the volume of the collected pyrolysis gas was recorded, and the system was disassembled. The masses of the obtained products were determined, namely, semi-coke (solid residue of the pyrolysis process), total liquid products and pyrolysis gas (by difference). An extraction method was used to separate the oil and pyrogenic water. After determining the weight values of all pyrolysis products, the material balance of experiments was made up.

3. Results and discussion

3.1 TG and DTG analysis

The results of the TG-DTG analysis of various model components of medical waste are presented in Figure 1. The measured data were obtained at a heating rate of 10 °C in nitrogen atmosphere. Each curve on TG and DTG diagrams is normalized to the initial mass of the test sample. Data of the DTG analysis are expressed in terms of the volatiles yield rate.
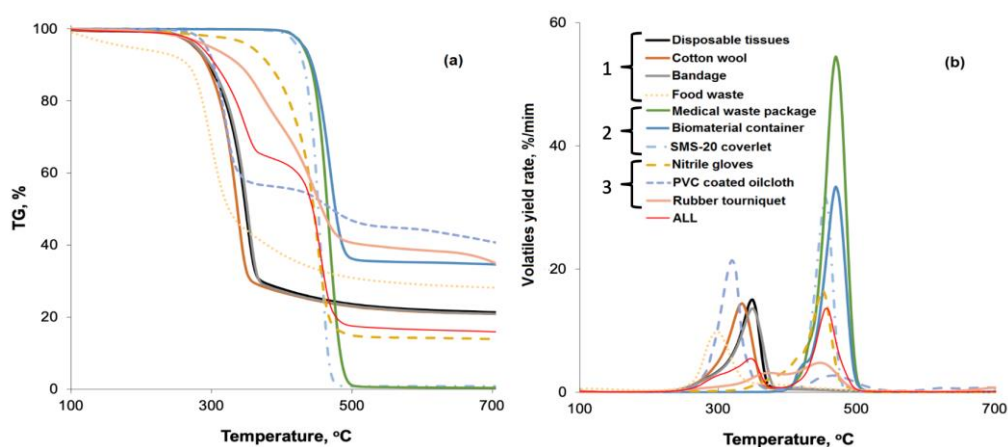

Figure 1: Thermogravimetric (a) and volatile yield rate (b) curves of medical waste components.

Analysis of the data presented in Figure 1 shows that the thermal destruction of the first group of medical waste model components consisted mainly of cellulose (disposable tissues, cotton wool, bandages, and food waste) occurs in three main stages. At the first stage, the raw materials are dried in the temperature range from 50 to 105 °C. The mass change at this stage is almost negligible, which corresponds to data of the proximate analysis of the feedstock. Further heating of the raw material is accompanied by the destruction of organic compounds and the volatiles release. The process occurs in the temperature range of 300 - 400 ° C, and the maximum mass loss is observed at a temperature near of 350 ° C. This range corresponds to the stage of active pyrolysis, which is accompanied by a weight loss of about 70 %. The cleavage of C-O bonds in the original cellulose molecule leads to the formation of CO_2, CO, and H_2O (Yang et al., 2007). At the third stage, the process of passive pyrolysis occurs in the temperature range from 400 to 900 °C.

Thermal decomposition of the second group of medical waste components (polyolefins) occurs in two stages. The volatile release process at the first stage takes place in the temperature range of 430 - 490 °C. This range corresponds to the active pyrolysis with a high yield of liquid oil (up to 90 wt.%). The liquid oil components can be grouped into different organic compound classes, namely, naphthenes (cycloalkanes), n-alkanes, n-alkenes, and aromatics (Onwudili et al., 2009).

Such polymers as butadiene-nitrile rubber, polyvinyl chloride, and rubber, which are included in the third group of medical waste components, have different thermal degradation mechanisms. Thermal decomposition of nitrile gloves occurs in two stages. The process of active gas evolution progresses in the temperature range of 414 - 475 °C, and the maximum mass loss occurs at a temperature of 450 °C. The formation of such products as hydrocyanic acid, acrylonitrile, vinyl acetonitrile, and ammonia is possible. After 500 °C, mainly carbon is concentrated in the solid residue, and the content of hydrogen and nitrogen is minimal.

The thermal decomposition of PVC coated oilcloth can be described by three-stage mechanism. The first stage represents the PVC dehydrochlorination at 280 – 340 °C with the formation of conjugated double bonds in polyene chains of the forming intermediate product (Lu et al., 2019). This process is accompanied by the emission of HCl and small amounts of the aromatics (43.6 % of sample mass loss). The second stage describes

the cracking of the intermediate product in the temperature range 420 – 520 °C and the formation of char with the emission of volatiles (11.6 % of sample mass loss). The volatiles consist of alkyl and condensed aromatics as well as small amount of HCl and chlorinated compounds (Yu et al., 2016). At the third stage (7.5 % of sample mass loss), a pronounced peak is absent.

Thermal decomposition of the rubber tourniquet occurs in three stages: 310 - 492 °C (58.94 %), 640 - 735 °C (7.22%), and 740 - 920 °C (1.74 %). The first stage with a peak at 447 °C is associated mainly with the separation of sulfur and the decomposition of the organic part of the original molecule. It can be assumed that the second stage describes the decomposition of mineral additives with the maximum intensity at 699 °C and mass loss of 7.22 %. At the third stage, the process of passive pyrolysis occurs, accompanied by a weight loss of 1.74 % and associated with the rupture of C-C bonds.

As follows from the previous discussion, the thermal decomposition of PVC in an inert environment proceeds predominantly with the formation of hydrogen chloride from bound chlorine. For the quantitative determination of hydrogen chloride, separate experiments were performed with alternating dynamic and isothermal regimes. On the way of the volatile components yield from the device, two sequentially connected absorbers with distilled water were placed to absorb hydrogen chloride. HCl concentrations were determined in five temperature ranges. The results of the analysis are shown in Table 2. As can be seen from the table, the bulk of hydrogen chloride (about 88.5 %) is released at temperatures up to 350 °C, which is in good agreement with the results of other studies (Lu et al., 2019). Hydrogen chloride is not shown in Table 2, because the vapor-gas mixture released during pyrolysis enters the condensation system before being collected in a gas meter for chromatographic analysis, and hydrogen chloride passes from gaseous to liquid phase under interaction with condensing water vapor.

Table 2: Temperature ranges of hydrogen chloride yield.

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

3.2 Mixture pyrolysis in fixed-bed retorting system

The effect of process temperature on the distribution of pyrolysis products of the medical waste mixture in the fixed-bed reactor is shown in Figure 2. The behavior of the pyrolytic char (solid residue) is described by a monotonic decrease of its concentration up to 12 wt.% (daf) at temperature near 650 °C. It should be noted that the pyrolysis temperature was controlled using a thermocouple placed on the wall of the retort. Separate experiments have shown that the temperature gradient between the wall and the center of the retort for the studied materials does not exceed 20 °C at a heating rate of 10 – 20 °C/min.

As measurements show, the pyrolysis oil concentration initially increases with temperature growth, reaches a maximum of 50 wt.% (daf) at $T = 600$ °C, and then begins to decrease. The decrease can be explained by the secondary reactions of the oil decomposition at high temperatures into lighter hydrocarbons and non-condensable gas after this product emission into the free space of the reactor. The concentration of the pyrogenic water depends slightly on the pyrolysis temperature and is equal approximately to 15 wt.% (daf). The pyrogenic water is formed from the thermal decomposition of cellulose that is presented in the medical waste mixture. The concentration of non-condensable gases in the pyrolysis products is characterized by a monotonic growth with increasing temperature. The main components of the non-condensable gases at low temperatures are CO_2, CO, and CH_4. Their concentrations received by methods of gas chromatography at $T = 400$ °C are shown in Table 3.

Table 3: The non-condensable gas composition measured at 400 °C.

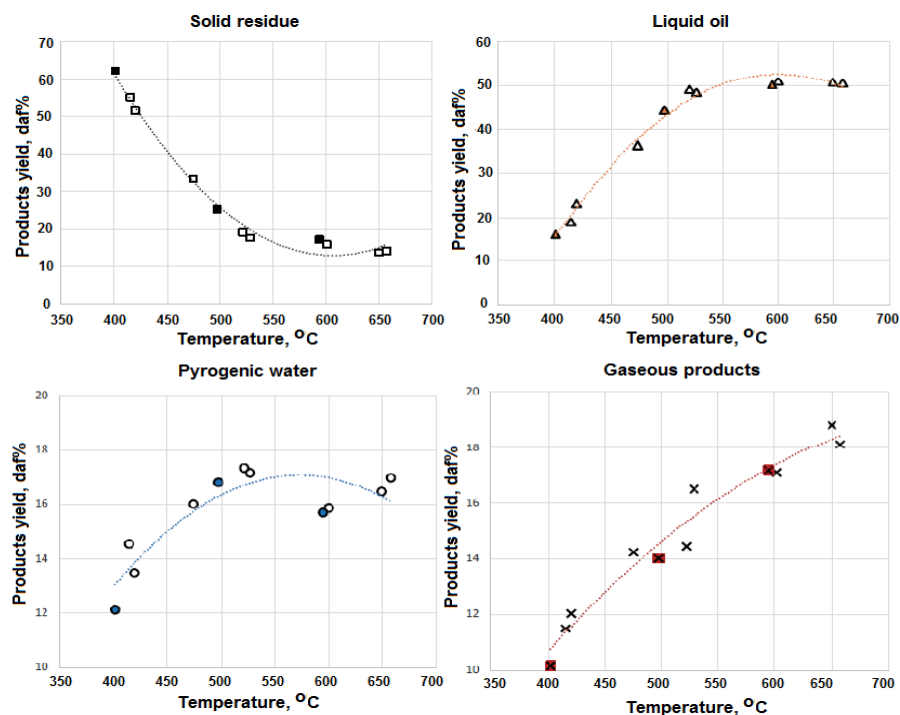| Component	H_2	CO_2	CO	CH_4	C_2H_6	Others
Concentration, wt.%	0.20	65.59	24.20	8.05	1.58	0.38

Figure 2: Temperature dependence of the yield of various pyrolysis products in fixed-bed reactor.

3.3 Medical waste treatment method

An essential feature of high-temperature method for the disposal of chlorine-containing medical waste should be the absence of conditions for the formation of PCDD/Fs that are highly toxic and persistent organic pollutants. These conditions include the presence of an appropriate temperature range, chlorine-containing compounds or chlorinated precursors such as chlorinated benzenes and phenols, carbonaceous matrix, molecular oxygen, etc. (Altarawneh et al., 2009). The concentration of chlorine-containing compounds is a key parameter of the process, since in their absence PCDD/Fs are not formed.

In the low temperature range, the PCDD/Fs formation occurs mainly via heterogeneous mechanisms. The *de novo* mechanism is associated with the process of burning out the structural elements of the carbon matrix in the solid residue and 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 (Gao et al., 2017). The PCDD/Fs formation from chlorophenols in the surface-mediated *precursor's* mechanism occurs in the temperature range from 200 to 500 °C (Lomnicki and Dellinger, 2003). The *homogeneous* gas-phase mechanism describes the PCDD/Fs formation from chlorophenols, and in pyrolytic conditions works in the high temperature range from 600 to 800 °C (Altarawneh et al., 2009).

According to the results of the conducted study, the most environmentally safe, economical and best suitable method for solving the problem of utilization of medical waste is their two-stage pyrolysis. The appropriate waste treatment facility should consist of a two-section pyrolysis chamber that is warmed outside by the heat from the combustion of the pyrolysis products. In the first section of the chamber with the temperature of about 350 °C, the chlorine-containing components (in the main HCl) are emitted into the gas phase. The gaseous products escaped from the first section are washed with cold aqueous alkaline solution to remove HCl. The products not condensed during washing are flared in the burner at 1000 - 1350 °C together with the main part of the pyrolysis products that are released in the second section of the chamber at a temperature near 600 °C. The solid residue of pyrolysis (pyrolytic char) is removed from the second section and subjected to steam gasification in a separate device at a temperature of 800 – 900 °C until carbon is completely depleted. The flue gases formed during the combustion of pyrolysis products are cooled in the heat exchanger, cleaned in the gas cleaning system and emitted to the atmosphere.

Thus, the task of guarantee the ecological safety of the environment in the proposed method of the medical waste treatment is achieved by removing chlorine-containing components before the main process of thermal decomposition of organic matter, which virtually eliminates the possibility of PCDD/Fs formation in the further

process. The concentrated gas-vapor mixture released during pyrolysis is burned at a temperature of 1000 - 1350 °C, which ensures complete combustion of all organic components, including harmful ones, and thus guarantees their flame neutralization. The economic effect is achieved through the use of thermal potential of recyclable medical waste as an energy carrier.

4. Conclusions

Experimental study conducted in this work has shown that the pyrolysis of medical waste is characterized by two ranges of intensive emission of volatile products. In the first range (250 – 380 °C), pyrolytic water and gas, consisting mainly of a mixture of CO_2, CO, and CH_4, are released. The main mass of HCl (more than 90 %) is also escaped at this range. The second range (400 – 500 °C) is characterized by an intense release of liquid products (pyrolytic oil). The maximum oil yield is near 50 wt.% (daf) at the temperature of about 600 °C. These data allow offering the two-stage mechanism for the disposal of medical waste, in which HCl is removed from the system at the first stage, and liquid products obtained in the second stage are used as an energy carrier for the pyrolysis process. This solution leads to minimization of the PCDD/Fs formation at the disposal of medical waste.

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