THERMAL ANALYSIS IN STUDIES OF TECHNOLOGICAL WASTE MATERIALS TO BE SUBJECTED TO THERMAL TREATMENT

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Abstract

Attempt was made to evaluate the usefulness of thermoanalytical methods, combined with X-ray phase analysis and chemical analyses, for the study of thermal decomposition of waste materials to be subjected to thermal treatment.

The object of the studies were petrochemical waste materials intended to be decomposed in a rotary furnace. Results are given of the studies of five selected waste materials.

Introduction

Thermal disposal of industrial wastes has become a verified and generally approved technological process. The main advantage of this method of disposal is the considerable reduction of their mass and volume and the possibility of utilisation of the thermal energy released.

The implantation of the process of thermal disposal requires a certain knowledge of the combustion processes and information on the waste materials to be disposed of the information on the decomposition at increased temperatures can be obtained by differential thermal analysis (DTA) and thermogravimetric analysis (TG) of the given materials. A series of preliminary studies should provide information on safety and efficiency of the combustion process [1–3].

Experimental

The composition and some physicochemical properties of the selected waste materials have been presented in Table 1. Waste 1 – precipitate from the torch bucket, waste 2 – solid deposit from cleaning of fuel oil tanks, waste 3 – spent catalyst, waste 4 – precipitate from sedimentation centrifuges, waste 5 – polymeric waste material.

In the first part of the studies the waste samples were subjected to chemical and thermal analyses. The TG, DTG and DTA curves of thermal decomposition were re-

corded by means of a derivatograph (MOM, Budapest) at a heating rate of 10 K min^{-1} up to final the temperature of 1000°C in air or nitrogen atmosphere. The studies enabled to determine the steps of thermal decomposition of the wastes. Examples of thermoanalytical curves are shown in Figs 1–7.

Table 1 Results of analyses of solid waste materials to be subjected to thermal treatment

Determination		Waste 1	Waste 2	Waste 3	Waste 4	Waste 5
Dry mass on heating at 105°C	mass%	95.4	78.2	71.0	37.5	41.8
Ashes on ignition at 600°C	mass%	7.0	19.5	2.7	–	26.0
Ashes on ignition at 800°C	mass%	5.1	19.4	2.3	17.6	–
Carbon	mass%	64.6	31.6	39.8	8.2	17.7
Hydrogen	mass%	4.4	4.7	5.7	1.1	2.8
Sulfur	mass%	7.4	0.83	9.16	0.1	8.4
Chlorides (Cl^-)	mass%	0.1	<0.001	<0.001	0.003	0.023
Carbonates (CO_3^{2-})	mass%	0.3	0.6	–	11.7	–
Silica (SiO_2)	mass%	1.8	6.2	–	7.2	–
Density at 20°C	g cm^{-3}	0.4810	1.1865	2.04	1.105	1.15
pH of aqueous extract		6.0	6.5	0.591	7.7	13.0
Calorific value	kJ kg^{-1}	–	13.823	2.0	–	–
Percent contents of metals in the ashes (600°C)	mass%					
Zn		0.335	0.008	0.117	0.0037	0.0107
Mn		0.096	0.073	0.219	0.0033	0.0486
Ni		0.078	0.022	0.061	0.0016	0.0024
Cd		<0.001	<0.001	<0.001	<0.001	<0.001
Pb		0.019	0.0035	0.017	0.0007	<0.001
Na		7.01	0.756	28.4	0.0158	19.3
K		0.50	0.1141	0.810	0.0036	0.0242
Co		0.0085	0.0011	<0.001	0.0001	0.0005
Li		<0.001	0.0012	<0.001	–	<0.001
V		0.207	0.148	0.042	0.006	0.0012

On the other hand the samples of the waste materials were calcined under isothermal conditions. A weighed sample of the material was placed in a resistance furnace preheated to the temperature of measurement and was then heated for a definite time in a stream of air or nitrogen. The loss in mass was determined gravimetrically, and the ashes were subjected to X-ray diffraction analysis. The diffraction patterns were recorded in a HZG-4C diffractometer using CuK$_\alpha$ radiation.

Table 2 Results of studies of technological waste materials to be subjected to thermal treatment

Waste	Conditions of ignition in furnace			Loss in mass/%	
	$T/°C$	t/min	atmosphere	static conditions	dynamic conditions
1	600	20	air	68.5	42.0
	800	10	air	88.7	
	800	20	air	95.1	52.7
	800	20	N_2	55.8	
	900	20	air	95.3	58.1
2	500	20	air	80.3	72.3
	600	20	air	81.3	75.5
	900	20	air	86.0	81.9
3	500	20	air	91.1	85.1
	600	20	air	95.2	89.4
	800	15	air	92.4	
	800	10	air	97.1	
	800	20	air	97.1	96.8
	800	20	N_2	85.5	78.0
4	500	20	air	81.5	82.4
	500	20	N_2	82.0	
	600	15+5	N_2+air	83.0	
	700	20	air	83.7	83.5
	800	20	air	86.4	89.4
5	600	20	air	31.7	33.0
	800	20	air	33.7	34.0

Table 2 presents a comparison of the results obtained in the studies of waste materials under dynamic (thermogravimetric analysis) and static (isothermal combustion in electric furnace) conditions. Here is a short discussion of the results:

Waste 1 (Fig. 1). The thermal decomposition of the material proceeds essentially in two stages. The first stage proceeding within 30–260°C is featured by a small loss in mass amounting to 5.4% (TG curve). The loss in mass is accompanied by an endothermic effect on the DTA curve with a minimum at 150°C. The loss is due to evolution of water vapor or volatile organic compounds. The size of the loss observed in that temperature region is confirmed by analytical results shown in Table 1 (dry mass content at 105°C=95.4%, mass loss=4.6%). In the second stage of the reaction proceeding at 260–600°C the loss in mass amounted to 36.6% (TG curve). An analysis of the DTG curve suggests a superposition of two effects with extremums at 360 and 440°C. The shape of the DTA curve in that temperature region shows, that the first part of the second stage of reaction corresponds to a combustion of the sample (exothermic effect on the DTA curve), and in the second part the combustion is ac-
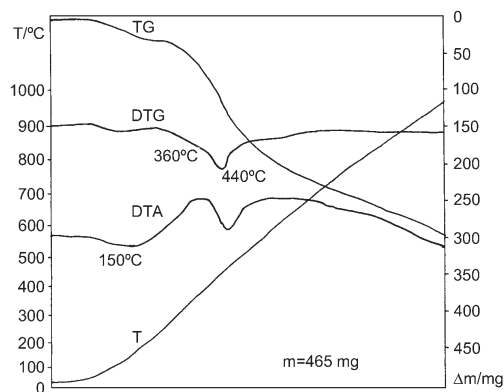
Fig. 1 Thermal analysis of waste 1 (air atmosphere)

companied by pyrolysis of the sample (an endothermic effect on the DTA curve superposed on a broad exothermic effect). Above 600°C the practically linear loss in mass of the sample is connected with combustion of the residues of combustible material present. In this region the course of the process is controlled by the access of oxidizing agent (atmospheric oxygen) and time, and it is independent of the temperature. This conclusion is also confirmed by the results of studies on thermal treatment of the waste material – ignition of the sample at a specified temperature and time in a resistance furnace.

Waste 2 (Fig. 2). The thermal decomposition of the sample proceeds essentially in three stages. In the first stage at 20–170°C the sample loses 51.1% of its mass (the TG curve). The DTG curve exhibits a thermal effect with an extremum at 120°C, accompanied by a noticeable endothermic effect on the DTA curve (with a peak at 130°C). The nature of the peaks on the DTG and DTA curves suggests the evolution of water or of a narrow fraction of low-boiling hydrocarbons. In the second stage of
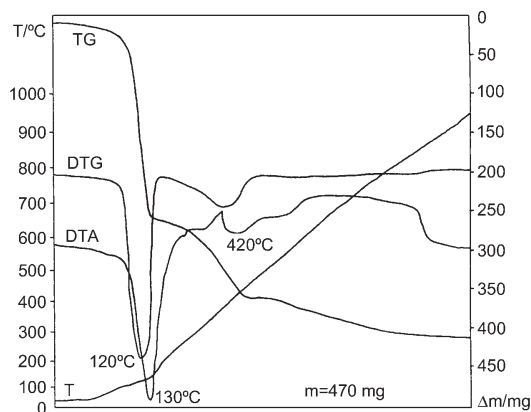

Fig. 2 Thermal analysis of waste 2 (air atmosphere)

decomposition, proceeding at 170–500°C, the loss in mass is 21.2%. The DTA curve exhibits an endothermic effect with an extremum at 420°C, superposed on a broad exothermic effect in the temperature range of 330 to 850°C. The exothermic effect is due to combustion process, and the endothermic one is connected with thermal decomposition (pyrolysis) of the material. This process if further continued in the temperature range 500–600°C. The loss of mass in this region is about 3.2% (the TG and DTA curves in Fig. 2). At temperatures exceeding 600°C only a small loss in mass due to combustion of residual organic matter is observed.

Waste 3 (Fig. 3). The thermal decomposition proceeds in two stages. In the first stage, in the temperature range 10–230°C the material loses 31% of its mass. The TG curve exhibits, in this region, a characteristic 'step', associated with thermal effects on the DTG curve (at 140°C) and on the DTA curve (endothermic effect with a peak
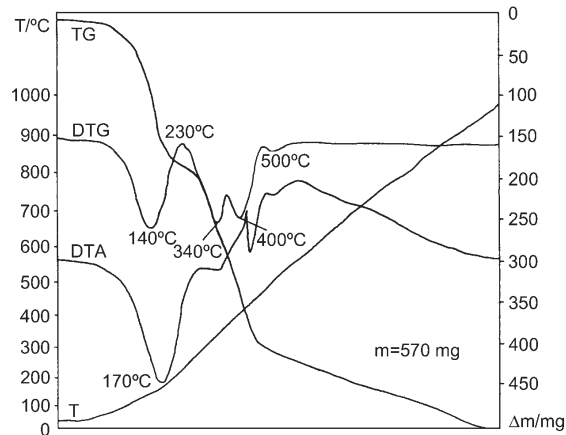

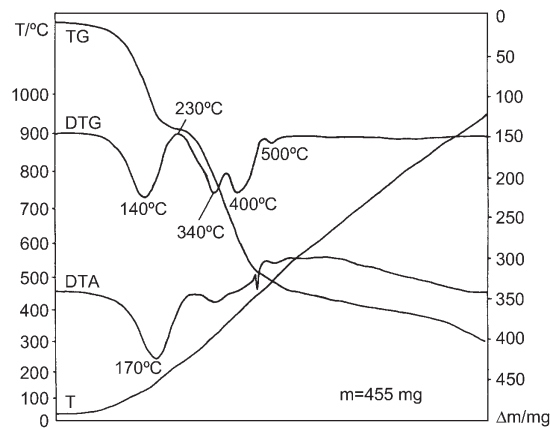**Fig. 3** Thermal analysis of waste 3 (air atmosphere)

Fig. 4 Thermal analysis of waste 3 (nitrogen atmosphere)

at 170°C). Such a course of the process suggests that this stage is featured by dehydration of the sample or elimination of a volatile organic compound. The loss of mass in this temperature range is confirmed by analytical results included in Table 1 (the dry mass content at 105°C is 71%, thus the loss is 29%). In the second stage (230–600°C) the material loses further 58.4% of its mass. The rate of the mass decrease varies in temperature, as it may be seen by 3 effects on the DTG curve, with extremums at 340, 400 and 500°C. The shape of the DTA curve exhibits a complicated nature of the processes. The broad exothermic effect associated with violent combustion process is superposed with rather sharp endothermic effects due to pyrolytic processes. The thermal treatment of the waste material ends practically at 600°C. For the sake of comparison a thermoanalytical curve of the waste material was also taken in nitrogen atmosphere (Fig. 4). The main decomposition stages were identical with those found in air atmosphere, but the exothermic effects on the DTA curve were weaker, which may be accounted for lesser participation of combustion processes.
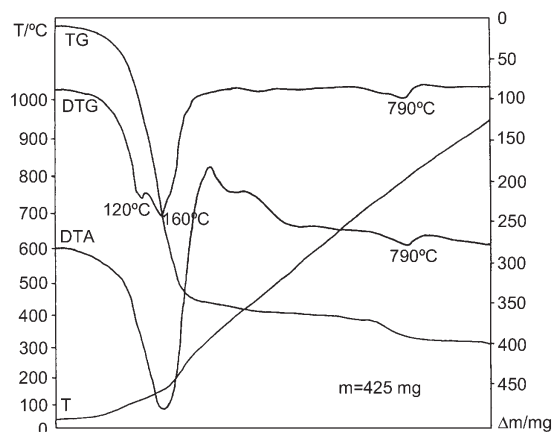

Fig. 5 Thermal analysis of waste 4 (air atmosphere)

Waste 4 (Fig. 5). The thermal decomposition proceeds in two stages. In the first stage, at temperatures within 10–280°C, the material loses 77.6%. The loss is associated with a large endothermic effect on the DTA curve (a peak at 160°C), which in the upper temperature region passes into a small exothermic effect. This stage proceeds with a consumption of external energy, but it may be realized in the low-temperature section of a rotary furnace (sample dehydration, evaporation of low molecular mass organic compounds). The second stage of decomposition, proceeding within 700–800°C with an endothermic effect on the DTA curve at 790°C, and an extremum on the DTG curve at that temperature, is associated with a mass loss about 6% on the TG curve. This stage may also comprise the decomposition of inorganic carbonates. From the ecological viewpoint the carbonates might be left in the ashes and the technological process might be effected at lower temperatures.

Waste 5 (Fig. 6). The decomposition proceeds essentially in two stages. The first stage, proceeding at the temperatures 10–180°C, is featured by sample dehydration and evaporation of low-boiling organic compounds. The loss of mass in this stage reaches 22.34% (TG curve). The loss is associated with a large endothermic effect on the DTA curve at 120°C and an extremum on the DTG curve at 110°C. In the second stage proceeding within 180–740°C the loss of sample mass amounts to 11.7% (TG curve). In that region the DTA curve has a broad exothermic effect due to combustion of the waste material. The loss of sample mass, reaching 34.04%, ends at 740°C. For the sake of comparison the thermal analysis of waste 5 was repeated using a nitrogen atmosphere (Fig. 7). Also in this case 2 stages of decomposition were observed. In the first stage, at 20–180°C, the sample lost 19.3% (TG curve). The loss was associated with an endothermic effect on the DTA curve at 115°C and an extremum on the DTG curve at 110°C. In the second stage (180– 740°C) the loss in mass was 12.8% (TG curve). A broad exothermic effect on the DTA curve observed
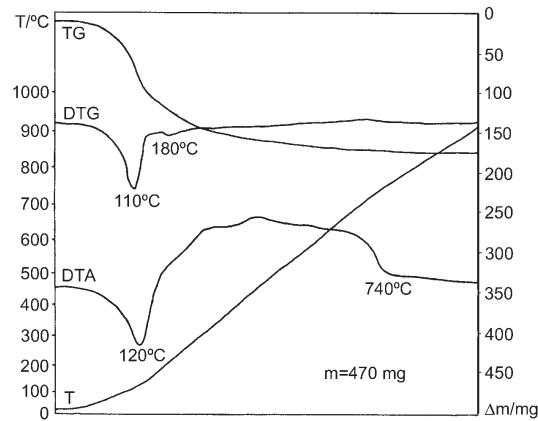

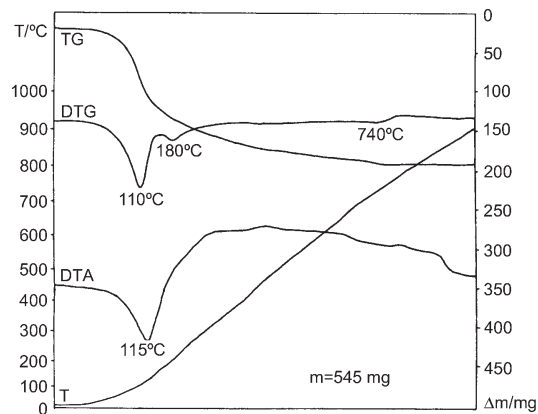**Fig. 6** Thermal analysis of waste 5 (air atmosphere)

Fig. 7 Thermal analysis of waste 5 (nitrogen atmosphere)

in this stage is connected with combustion processes. The loss of mass attains 32.1% at 740°C and further increase of temperature, up to 1000°C, only small residues are ignited, with a negligible loss in mass (TG curve). Comparison of Figs 6 and 7 shows that in these two cases the process of decomposition is similar and such are also the mass losses.

Samples of ashes obtained in burning samples 4 and 5 at different conditions in a resistance furnace were studied by X-ray phase analysis. In the ashes from waste 4 the main phases were $CaCO_3$ and SiO_2, whereas in those from sample 5 mainly Fe_2O_3 was found. The knowledge of phase composition of the ashes is valuable information in selection of the most appropriate method for their utilization.

Conclusions

The studies of physicochemical transformations occurring during ignition of solid waste materials under dynamic conditions, accompanied by the studies of calcination products obtained under static conditions, may be very useful in the study of the steps of decomposition in the temperature range up to 1000°C and, in determining the most appropriate conditions (temperature, duration and kind of atmosphere) for thermal treatment of each individual waste material.

The knowledge of physicochemical transformations of the wastes, depending on temperature, time, and composition of the gas atmosphere, enables a reasonable determination of parameters of their thermal treatment with the aim of obtaining ashes of the required properties. Such a knowledge is very important for the proper selection of methods for further utilization of the ashes.

References

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