APPLICATION OF THERMAL ANALYSIS IN SOLID INDUSTRIAL WASTES TREATMENT

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The choice of an appropriate and safe disposal alternative should be based on the wide range of physicochemical examination thermal analysis in conjunction with other data enables identification of wastes, allows determination of weight losses at any stage of thermal decomposition and characterization of the combustible properties of wastes.

In this paper the physicochemical composition of some industrial wastes, which create serious hazards to the natural environment is presented.

The following waste materials were investigated:

— tar wastes from several departments of the coking plant

— paint-shop wastes from a metallurgical factory.

Thermoanalytic measurements were carried out in the dynamic atmosphere of air. Enthalpic values were calculated from the peak areas of the DTA curves.

Thermoanalytic data were compared with calorimetric results obtained from an oxygen bomb.

The disposal methods for above-mentioned wastes are proposed.

Keywords: environment, solid industrial wastes

Introduction

In the modern society of our century in order to enhance productivity it is necessary to improve the quality of both new and waste materials as well as to determine and optimize their properties.

The Cokery Enterprise produces blast-furnace coke, coke-oven gas as well as tar products of various kinds. The technological processes are accompanied by formation of wastes having unfavourable effects on the ecosystem because of emission of gases, formation of waste waters and pollution of surface and ground waters with leakages out of solid wastes [1].

Metallurgical factories are next to chemical industry in polluting the environment. Paint-shop wastes displaying a high toxity, volatily and flammability are classified as specifically hazardous to the natural environment [2].

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Environmental safe disposal methods for industrial wastes should be based on the wide range of physicochemical examination. Thermal analysis is one of the most versatile techniques, almost universally applicable the characterization of materials.

Experimental

The investigations of industrial wastes comprised:

– physicochemical analysis carried out according to Polish standards.

– differential thermal analysis, DTA — carried out through the use of Paulik-Erdey OD-102 derivatograph (MOM, Hungary). All the experiments were conducted under identical conditions: samples were heated up to 1273 K in platinum crucibles in an air atmosphere at a heating rate of 10 deg·min^{-1}, sensitivity: TG 200, the reference material being α–Al_2O_3. The standards recommended by the Standardization Committee of ICTA [3] were applied for calibration of the apparatus. Enthalpic values of reactions (ΔH_{DTA}) were calculated by the Simpson method of numerical integration of DTA curves.

– The heats of combustion (ΔH_{comb}) were determined in a KL–5 bomb calorimeter (Precyzja, Poland).

Results and discussion

Tar wastes from the coking plant

There are two main kinds of these wastes. One of them comes from the department of coal derivatives recovery (waste *A*). It consists of sewages from decanters and dividers of various reservoirs of dehydration and non-dehydrated tar. The additional factors are as well tar leakages and its distillates separated from sludges.

Another waste tar comes from the production of ammonium sulphate (waste *B*). Its main components are: free sulfuric acid, ammonium sulphate, pyridine bases and organic substances of characteristics of resins.

The physicochemical composition of wastes is presented in Table 1. The illustration of thermal decomposition is shown in Fig. 1. A coal stock and raw tar samples were presented as references. Thermal decomposition of tar waste from the decanter begins with an endothermic reaction up to the temperature of 523 K with a weight loss of 24.8%. This reaction is related with physisorbed water and volatile organics, its quantity depends on morphological and textural parameters of particles. A multi-stage exothermic process occurs up to the temperature of 1273 K to yield a total weight loss of 67.8%. The course of exothermic reactions is similar to a raw tar. In the investigated waste tar there is a lack of significant exothermic reaction caused by combustion of volatiles and fix carbon, characteristic for decomposition processes of polish black coal [4, 5].

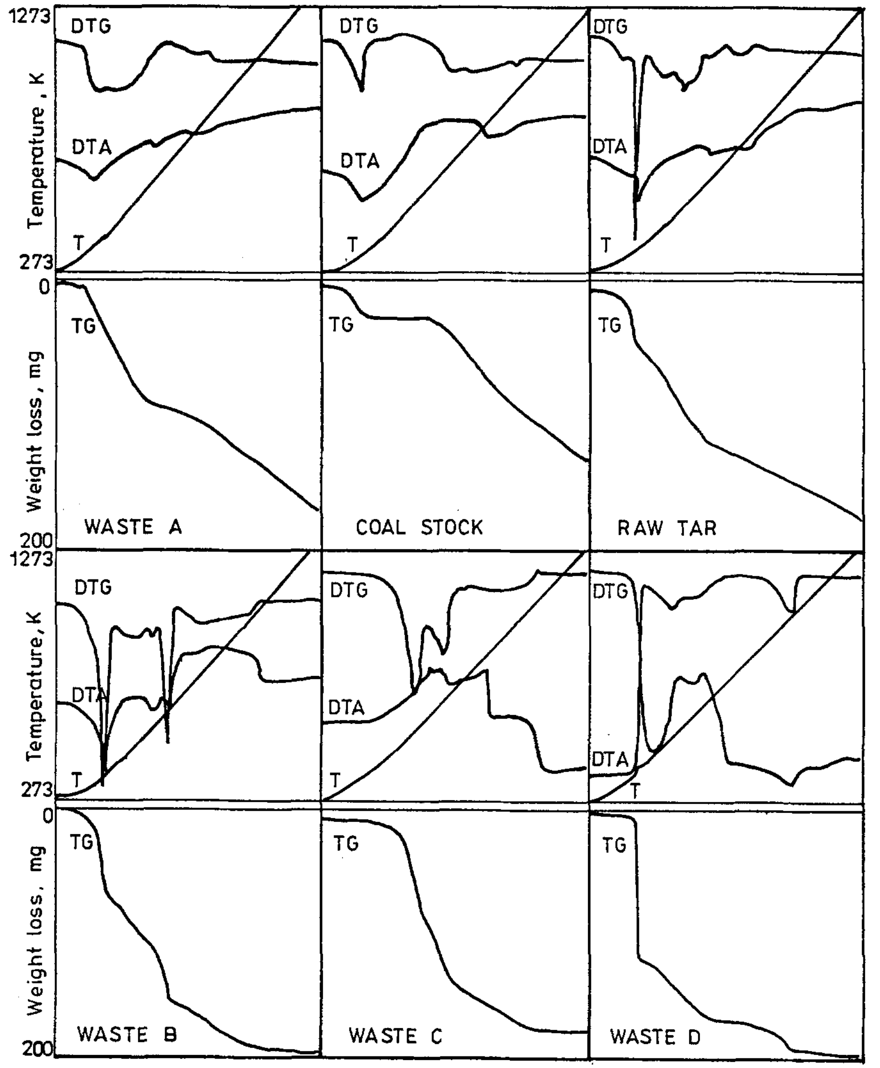

Fig. 1 Thermoanalytical curves of industrial wastes

The plots of thermal decomposition of waste tar *B* are characteristic for decomposition of $(NH_4)_2SO_4$ [5] with initial evaporation of film-water and volatile

Table 1 Physicochemical composition of wastes

Waste	Weight loss at 378 K / %	Water content – xylene meth. / %	Weight loss at 823 K / %	SiO_2 +part. insolub. in strong acids / % dry solids	$\Delta H_{comb.}$ / kJ/g	ΔH_{DTA} / kJ/g	$\frac{\Delta H_{comb.}}{\Delta H_{DTA}}$	Ether extract / %	Nitrogen NH_4 / %	Nitrogen organic / %	Sulphur / %	Naphtalene / %
A. Tar waste from the decanter	13.39	4.85	88.13	3.19	33.40	1.48	22.6	8.91	n.d.	0.70	0.76	10.0
B. Tar waste from the production of $(NH_4)_2SO_4$	39.29	35.88	98.58	0.43	12.59	1.44	8.7	8.86	5.43	0.25	12.32	11.24
								Metals / % dry solids				
								Ca	Fe	Pb	Cr	Zn
C. 'Wet' paint-shop waste from the bottom of paint cabin	75.49	n.d.	48.35	6.67	26.66	5.98	4.5	0.59	4.04	0.70	1.87	3.40
D. 'Dry' paint-shop waste from the bottom of paint cabin	3.66	n.d.	58.98	9.30	11.25	6.14	1.8	5.65	1.04	8.52	0.66	0.40

products of tar. The decomposition continues to run at a varying rate up to 1073 K to yield a total weight loss of 98.6%.

The calculated effects of the decomposition reactions are much lower than those measured in the oxygen bomb. The higher $\Delta H_{comb}/\Delta H_{DTA}$ values are characteristic for typical organic wastes (waste *A*). For waste *B*, where the main component is ammonium sulphate there is a less difference between both values.

This kind of wastes due to a high calorimetric values are most commonly disposed by adding to coal charge. They can be also combusted in incinerating plants of non-typical arrangement [6] what is poor efficiency with regard to supply management, but guarantees the whole final neutralization of wastes. Waste tar from the production of ammonium sulphate after required neutralization can be used for coal charge briquetting or as bonding material for other industry branches [6].

Paint-shop wastes

They come from the bottom of paint rooms (waste *C*) or from their walls and floors (waste *D*). Their physicochemical compositions presented in Table 1 are related to kind of painting materials, frequency and methods of the neutralization. The 'wet' wastes are periodically removed from the bottom of the cabin and after dewatering transported to a special dumping ground. The 'dry' wastes are a mixture of spend paint materials and lime, mechanically removed after lime-milk washing from floors and walls of the cabin.

There are many differences in their physicochemical compositions, to say nothing of their moisture. The higher amounts of calcium and lead in 'dry' waste is caused by kind of used pigment (PbO) and by presence of lime. In 'wet' waste are presented in relatively high concentration: iron (from pigment or scale), chromium and zinc (from pigments).

Much more higher value of heat of combustion measured after drying procedure for 'wet' waste is difficult to explain. It may be caused by a higher content of painting materials in the waste, although organic matters determined as weight losses at 823 K are for both wastes similar and amount for 'wet' and 'dry' ones 48.35 and 58.98%, respectively.

The courses of the decomposition curves presented in Fig. 1 are different. In the case of waste *C* a significant exothermic effect is found caused by reactions of oxidation in the temperature range of 423 to 895 K. The decomposition continues to run up to 1073 K to yield a total weight loss of 74.6%.

In the initial stage of the thermal decomposition of 'dry' waste occurs a slight rapid exothermic reaction at the temperature of 468 K with a corresponding high weight loss amounts to 38.6%. From there the process runs slower with a two-stage exothermic effects up to temperature of 803 K. An endothermic reaction with a minimum 1043 K is connected with decarbonization of $CaCO_3$. Total weight loss at 1058 K amounts to 62.9%.

The enthalpic values calculated from the peak areas of the DTA curves are for the both wastes similar and amount to 5.98 and 6.15 kJ/g dry solids, respectively.

The wastes of that kind are generally disposed of the special sites or, after solidification, deposited on sanitary landfills. Taking into account their hazardous character and high calorific values they may be disposed by combustion (with other flammable waste materials produced by the same plant).

Conclusion

1. Despite their non-homogeneous nature, industrial wastes undergo thermal decomposition according to known and described models and references.

2. The calculated enthalpic data should be not compared with measured calorimetric values for all types of industrial wastes. Processes that occur in an air dynamic atmosphere of thermal analysis have a less intensive course than those in an oxygen bomb. The more mineral nature the waste has the more approximate the calculated and measured values are.

3. Thermal analysis provides valuable data on the possibility of solid waste disposal by thermal methods, which are very often suggested for the most successful waste management.

References

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Zusammenfassung — Die Wahl einer geeigneten und sicheren Entsorgung sollte auf breitangelegten physikalisch-chemischen Untersuchungen basieren. Thermoanalyse in Verbindung mit anderen Angaben, die eine Identifikation von Abfallstoffen ermöglichen,

ermöglicht die Bestimmung des Masseverlustes zu einem beliebigen Zeitpunkt während der Zersetzungsreaktion sowohl die Charakterisierung der Verbrennungseigenschaften des Abfalles.
Es wird hier die physikalisch-chemische Zusammensetzung einiger Industrieabfälle beschrieben, die eine große Gefahr für die natürliche Umwelt darstellen.
Folgende Abfallmaterialien wurden untersucht:
- Teerabfälle aus einigen Bereichen einer Koksfabrik
- Lackierabfälle aus einer Metallfabrik

In dynamischer Luftatmosphäre wurden thermoanalytische Messungen durchgeführt, sowie anhand der Peakflächen der DTA-Kurven Enthalpiewerte errechnet.
Die thermoanalytisch erhaltenen Angaben wurden mit den Werten aus einer Sauerstoffbombe verglichen.
Eine Entsorgungsmethode für obengenannte Materialien wird empfohlen.