

STUDIES OF THERMAL TRANSFORMATIONS OF PETROCHEMICAL WASTES FOR OBTAINING MINERAL-CARBON SORBENTS

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Abstract

In the present work an attempt was made to obtain mineral-carbon sorbents by thermal decomposition of solid waste materials containing, besides to mineral components, solid petroleum derivatives. The amount and the homogeneity of distribution of coal product formed in decomposition of organic matter on the surface of the mineral matrix, as well as the porous structure of the sorbents obtained depend largely on the conditions of calcination of the wastes used. The aim of this work was to find optimum conditions of the process. The sorptive properties of the obtained material were checked in the process of reduction of pollutants contained in industrial wastes.

Keywords: mineral-carbon sorbents, petrochemical wastes, thermal decompositions, waste water treatment

Introduction

Thermal decomposition of inorganic hydroxides and salts has been widely applied in manufacture of oxide sorbents. The method is also used for obtaining active carbons by pyrolysis of coal derivatives. The obtained carbonization products are practically inactive. The subsequent step is therefore an activation aiming at the removal of pitchy products and leading to a considerable increase of porosity [1–4].

Experimental

The object of the studies was an industrial waste material further referred to as a filtration residue obtained in preliminary process of waste water treatment on the so-called sedimentation centrifuges. The chemical composition and some physico-chemical properties of the filtration residue are given in Table 1. The material contains considerable amounts of water and hydrocarbons, but also inorganic compounds, mainly calcium and barium carbonates. It is therefore a potentially valuable raw material for obtaining, by thermal decomposition, mineral-carbon sorbents.

Table 1 Characteristics of filtration residues

Determination		Unit	Value
Dry matter at 105°C		mass%	37.5
Ashes after ignition at 800°C		mass%	17.6
Carbon		mass%	8.23
Hydrogen		mass%	1.07
Sulfur		mass%	0.10
Nitrogen		mass%	0.39
Chlorides		mass%	0.003
Carbonates		mass%	11.7
Silica		mass%	7.2
Density at 20°C		g cm ⁻³	1.105
pH of water extract (1:10)		pH unit	7.7
Calorific value		kJ kg ⁻¹	2138
Contents of:	Na	mg kg ⁻¹	223.8
	Mn	mg kg ⁻¹	130.63
	Fe	g kg ⁻¹	10.64
	Ni		74.29
	Zn	mg kg ⁻¹	151.33
	Ba	mg kg ⁻¹	108.6
	K	mg kg ⁻¹	726.51
	Mg	g kg ⁻¹	1.42
	Ca	g kg ⁻¹	72.74

The studies of the thermal decomposition were carried out both under non-isothermal and isothermal conditions.

The non-isothermal studies were carried out for samples of raw waste material and for products of its calcination at various temperatures. Thermogravimetric curves (TG, DTG and DTA) were recorded by means of OD-102 Analyzer (MOM Budapest) on heating up to 1000°C with a rate of 10°C min⁻¹ in air atmosphere.

In the isothermal studies a weighed sample of the raw material was placed in a high-temperature tubular reactor pre-heated to a temperature of measurement and was kept at that temperature for 20 min in a stream of air or nitrogen. The loss of mass was determined gravimetrically, and the degree of decomposition was evaluated from the DTA data.

The phase composition of the carbonization products obtained under isothermic conditions was studied by X-ray phase analysis. The diffraction patterns were recorded by means of an HZG4C Analyzer using the CuK_α radiation.

Attempts were made to increase the sorptive properties of the calcination products by activation. The process of activation was carried out in two ways: by roasting

the samples for 5 or 10 min at 700°C in an atmosphere of steam, or by soaking with 10% aq. H₂SO₄ followed by 15 min calcination at 600°C.

The degree of surface development in the obtained sorbents was determined by measurement of specific surface by the method low-temperature adsorption of nitrogen (S_{BET}).

Discussion of results

Thermoanalytical curves obtained for the filtration residue are shown in Fig. 1. Thermal decomposition of the sample proceeds essentially in two stages. In the first step proceeding within 20–280°C the sample loses 77.6% of its mass. The loss is associated with a large endothermic effect on DTA curve (with a peak at 160°C), which passes slowly into a small exothermic effect near the end of this temperature region. The processes occurring in this stage are: sample dehydration, elimination of low-boiling hydrocarbons and, at higher temperatures, also partial oxidation of organic substances present. In the second stages, at temperature range 700–800°C, a small (about 6%) loss in mass is accompanied by an endothermic effect on DTA curve, with a peak at 790°C, due to decomposition of carbonates.

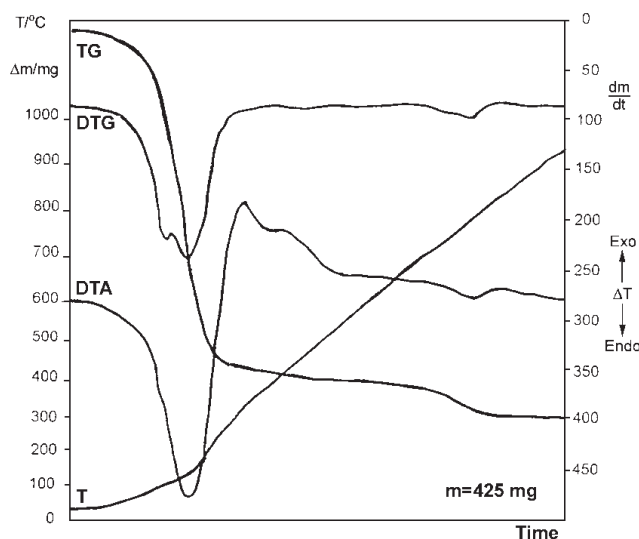


Fig. 1 Thermogravimetric curves of filtration residue

Thermogravimetric curves recorded for selected products of calcination of the samples at various temperatures in air atmosphere are shown in Figs 2–5, and those observed in nitrogen atmosphere are given in Figs 6 and 7.

Calcination of filtration residue at 700°C for 20 min in air atmosphere results in full decomposition of the organic matter contained. The results of X-ray diffraction

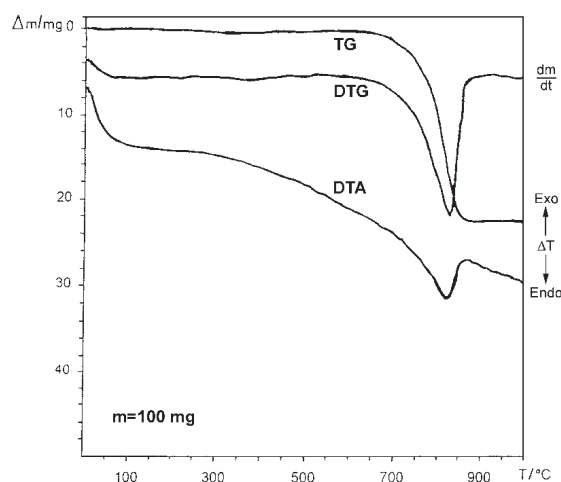


Fig. 2 Thermogravimetric curves of a product of carbonization at 700°C for 20 min in air

studies (Fig.9) show that the solid residue contains SiO_2 and CaCO_3 . Thermogravimetric curves of the sample comprise only a thermal effect due to decomposition of carbonates (Fig. 2).

Table 2 Specific surface, density and grain size of carbonization products obtained from filtration residues under different conditions

Calcination temperature/°C	Time/min	Gas atmosphere	Specific surface $S_{\text{BET}}/\text{m}^2 \text{g}^{-1}$	Density/ g cm^{-3}	Mean grain size/Å
350	20	air	57.5	1.47	708.8
450	20	air	43.9	1.75	782.5
500	20	air	31.9	1.01	943.8
600	20	air	33.4	2.00	896.8
350	20	N_2	25.5	1.71	1377.8
450	20	N_2	51.4	1.86	627.0
500	20	N_2	44.9	1.94	690.7
600	20	N_2	38.2	2.00	784.4
350	15+5	air+ N_2	43.5	1.72	803.1
450	15+5	air+ N_2	43.7	1.92	712.8
500	15+5	air+ N_2	43.4	1.83	754.6
600	15+5	air+ N_2	35.9	1.94	860.4

The analysis of thermogravimetric curves obtained for the products of calcination at 350, 450 and 500°C in air atmosphere (Figs 3–5) shows that thermal dissociation of carbonates at temperatures 700–900°C is accompanied by oxidation of highly condensed substances resulting from carbonization processes. The fact is evidenced

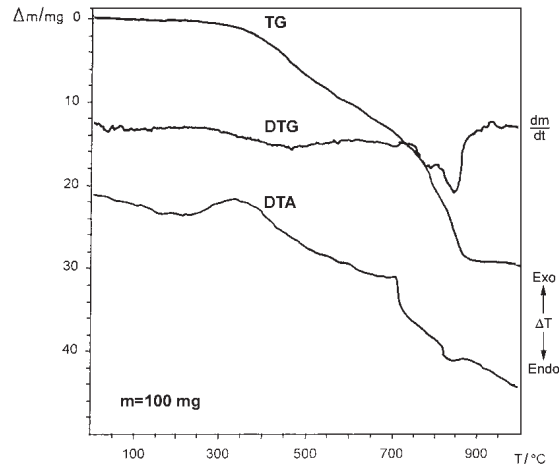


Fig. 3 Thermogravimetric curves of a product of carbonization at 350°C for 20 min in air

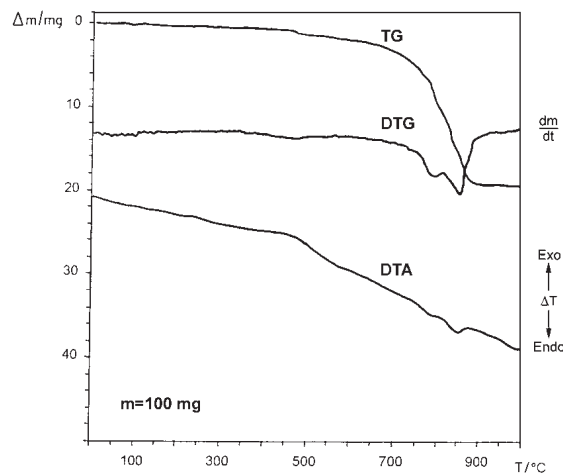


Fig. 4 Thermogravimetric curves of a product of carbonization at 450°C for 20 min in air

both by a two-stage loss in sample mass (DTG curve) and a faint endothermic effect due to decomposition of carbonates compensated by exothermic effect of combustion. Besides, thermogravimetric curves of carbonization products obtained at 350, 450 and 500°C show, in temperature range 350–450°C, a decrease of mass loss and intensity of associated exothermic effect with increasing carbonization temperature. This is probably due to formation of more strongly condensed carbon structures at increasing carbonization temperatures. This phenomenon is reflected in the size of specific surface which falls down with increasing carbonization temperature of the cake samples (Table 2).

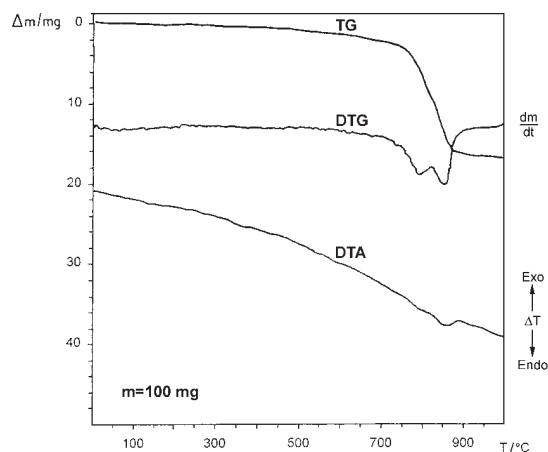


Fig. 5 Thermogravimetric curves of a product of carbonization at 500°C for 20 min in air

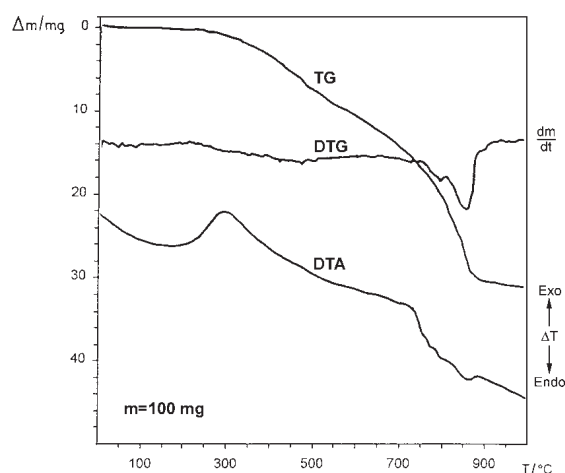


Fig. 6 Thermogravimetric curves of a product of carbonization at 350°C for 20 min in nitrogen atmosphere

As follows from the obtained results, the development of the specific surface depends not only on the contents of total carbon in the condensates formed, but also and primarily on their chemical structure. The pyrolysis of filtration residues at temperatures up to 600°C in nitrogen atmosphere gives mineral-carbon preparations of relatively low specific surface (Table 2). A lower specific surface, as compared with carbonizates obtained in air atmosphere, is due to the presence of unburned tarry residue.

In cases where filtration residues were calcined for 15 min at temperatures 350–600°C in nitrogen atmosphere with short (5 min) after-burning in air, the obtained products had similar carbon contents and specific surface irrespective the cal-

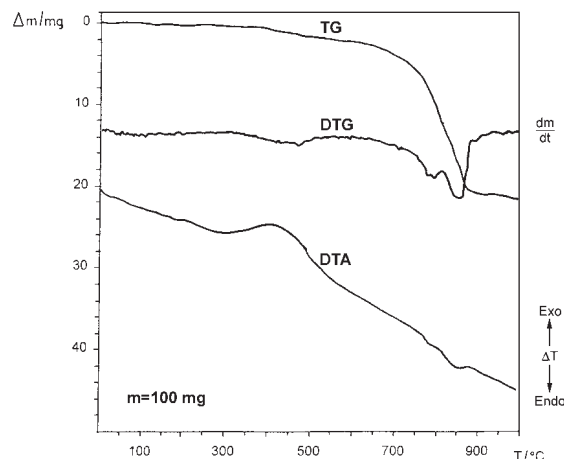


Fig. 7 Thermogravimetric curves of a product of carbonization at 600°C for 20 min in nitrogen atmosphere

ination temperature applied (example of termogravimetric curve on Fig. 8 and data in Table 2).

Attempts of activation of the carbonized products by treatment with steam or solutions of sulfuric acids gave positive effects in increasing the specific surface (Table 3). The effect, more distinct in samples treated with H_2SO_4 , was a result of partial dissolution of surface layer of the mineral matrix. Combined with additional heating for 15 min at 600°C the treatment resulted in the development of microporous structure of the preparation and doubling of its specific surface.

Table 3 Specific surface, density, and grain size of carbonization products activated under different conditions

Activation conditions	Specific surface $S_{\text{BET}}/\text{m}^2 \text{g}^{-1}$	Density/ g cm^{-3}	Mean grain size/ Å
No activation	25.5	1.71	1377.8
700°, steam, 5 min	41.7	2.07	694.1
700°, steam, 10 min	33.4	1.99	904.9
10% H_2SO_4 15 min at 600° in N_2 atm	54.9	2.11	618.4

Carbonization conditions: 350°C, nitrogen atmosphere, 20 min

The obtained mineral-carbon materials have been utilized as coagulating sorbents in treatment of waste water from refinery and petrochemical processes. Some results obtained with carbonization products of filtration residues calcined for 20 min at 350°C, activated with 10% H_2SO_4 and then roasted for 15 min at 600°C in nitrogen atmosphere are shown in Table 4.

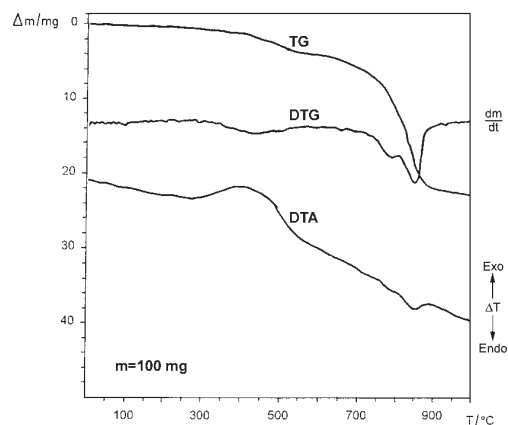


Fig. 8 Thermogravimetric curves of a product of carbonization at 500°C for 15+5 min in nitrogen+air atmosphere

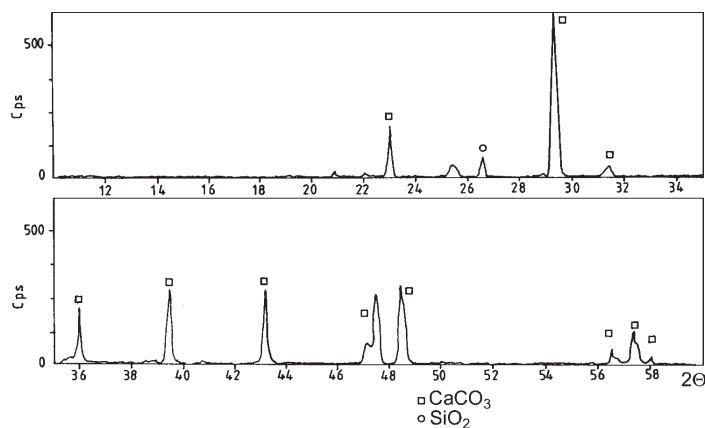


Fig. 9 X-ray diffraction pattern of carbonization product obtained from a filtration residue

Table 4 Treatment of industrial waste by carbonization product (sorbent) obtained from filtration residue

Amount of sorbent/g	Chlorides/ mg dm^{-3}	ChOD/ $\text{mgO}_2 \text{ dm}^{-3}$	Solid suspensions/ mg dm^{-3}	Ether ext./ mg dm^{-3}	pH	Turbidity/ NTU
0.25	536.9	1125.0	1000	36	5.22	9.92
0.50	546.9	1050.0	1400	77	5.34	20.6
0.75	536.9	1012.5	1510	67	5.57	20.7
1.0	536.9	987.5	1655	94	5.99	25.9
Untreated waste	532.0	2763	1770	509	7.40	26.5

An evidence of high sorptive capacity of the obtained materials is the high degree of reduction of hydrocarbon contents and turbidity of the waste waters treated.

Conclusions

Complex analysis of the results obtained in the studies performed leads to the following conclusions:

- Application of the methods of differential thermal analysis gives a possibility of determining the conditions for thermal decomposition that permit to obtain products of highly developed specific surface.
- Some waste materials of petrochemical industry are good raw materials for obtaining mineral–carbon sorbents useful in treatment of industrial waste waters.
- Use of mineral–carbon sorbents, obtained from solid industrial wastes, in treatment of waste waters, permits closed-circuit material runs of some technological processes.

References

- 1 B. Pacewska, P. Stefaniak, D. Szychowski, A. Klepańska, T. Żmijewski and P. Turowski, Seminar: Proecological management of waters and sewages in the refining and power engineering industry, Płock 1999.
- 2 E. Drąg and M. Rutkowski, Seminar: Proecological management of waters and sewages in the refining and power engineering industry, Płock 1999.
- 3 Notification patent (RP), P.330 514 (1998).
- 4 W. S. Komarow, Adsorbents and their properties, WAT, Warszawa 1983.