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Thermal Decomposition of Copper Ore Concentrate and Polyethylene Composites

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Abstract. Thermal analyses (TGA and DTA) of the composite, comprised of 10% polyethylene (PE) scrap and 90% copper ore concentrate, enabled determination of the temperature range and decomposition degree of the organic matters in argon atmosphere. Products of pyrolysis were qualitatively and quantitatively determined. The results were compared to those obtained for products of pyrolysis of the composite in air. Products of pyrolysis were identified by means of the gas chromatography (GC) method alone or supported with results of mass spectrometry analyses (GC-MS).

1. Introduction

Methods for thermal recycling of plastics gain importance due to their universality and tolerance for fluctuation of purity and homogeneity of scrap, [1-6]. It resulted in the growing interest in pyrolysis of the materials. Both processing and pyrolysis of plastics may be accompanied by emission of volatile and toxic substances. Quantitative and qualitative composition of the products of pyrolysis of organic or inorganic materials are of paramount importance for the environment. To provide suitable air flow through the bed in a copper concentrate-smelting furnace, the charge material should be briquetted with use of inorganic or organic binders. Inorganic binders are mostly burnt lime, dolomite, magnesium oxide, various cement grades or water glass. As organic binders, coal-tar pitch, asphalt, waste sulphite liquor and briquette-grade viscose are used.

Apart from the above, copper ore concentrate may be bound with waste plastic scrap. Such easily available binding agent has a lot of advantages, it gives mechanically strong briquettes and it is vulnerable to thermal decomposition in a relatively low temperature range. In this context, problem of composition of the products of pyrolysis of the copper concentrate briquettes bound with 10% of plastic scrap seems to be very important.

The literature [7, 8] data refer to pyrolysis of pure plastics, only. That is why the study was aimed at qualitative and quantitative determination of products of decomposition of standard waste polyethylene scrap (PE) and of the composite material comprising copper concentrate and polyethylene scrap.

2. Experimental

2.1 Materials

As demonstrated in earlier experiments the authors Więckowska and Szyszka [9], the composite made of 90% w/w of copper concentrate and 10% w/w waste polyethylene scrap is characterized with mechanical strength and thermal resistance high enough to qualify it as the charge material for a shaft furnace. Now, authors examined composition of products of pyrolytic decomposition of the composite at the temperatures encountered in the furnace, in upper layers of the bed.

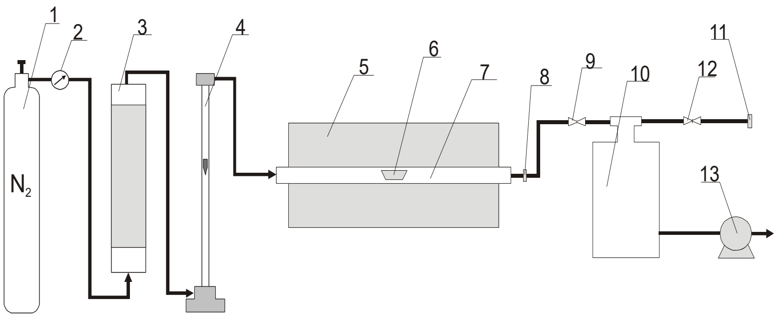
2.2 Methods

2.2.1 Differential Thermal Analysis and Thermogravimetry

Thermal analysis was carried out by means of the Perkin-Elmer DTA7 and TGA7A type analysers in the temperature range from 50 °C to 1000 °C. The sample was heated in argon at the speed of 10°C/min. The thermogravimetric analysis was carried out at the speed of 40 °C/min. The reference substance was alumina [9, 10].

2.2.2 Pyrolysis of Waste Polyethylene Scrap

Arrangement of apparatuses used for pyrolysis of waste polyethylene scrap can be seen in Figure 1. Mass of the polyethylene scrap sample was approximately 0.1 g. Pyrolysis was carried out for 20 minutes at the temperature of 500°C in a stream of nitrogen gas equal to 25 dm^3/h. Loss of weight of the sample and amounts of volatile and high-boiling decomposition products were determined. Volatile substances were collected in the flask (10) and the high-boiling decomposition products - in the filter (8) made of glass unwoven fabric. Because of considerable part of the high-boiling substances condensed on the walls of the pipe, they were washed out with methanol and collected with those extracted from the filter. After evaporation of methanol, amount of the substances was determined.



1 - nitrogen gas cylinder; 2 - pressure gauge; 3 - filter for nitrogen; 4 – rotameter; 5 - tubular furnace with controlled temperature; 6 - ceramic combustion boat with the sample; 7 - china tube; 8 - filter made of glass unwoven fabric; 9 - needle valve; 10 - hermetic flask; 11 - silicone membrane for sampling; 12 - ground valve; 13 - vacuum pump

Figure 1. Arrangement of the apparatuses used for examination of pyrolysis of plastics

Carbon dioxide was determined with the gas chromatograph of the N-505 type equipped with a thermal conductivity cell (katharometer). Analysis was carried out with a steel column 4 mm dia. and 1m long, filled with silica gel 50 –100 mesh at temperature of 25 °C. The bridge of the gas detector was supplied with current of 268 mA. The carrying gas was hydrogen, passing with the flow rate of 40 ml/min.

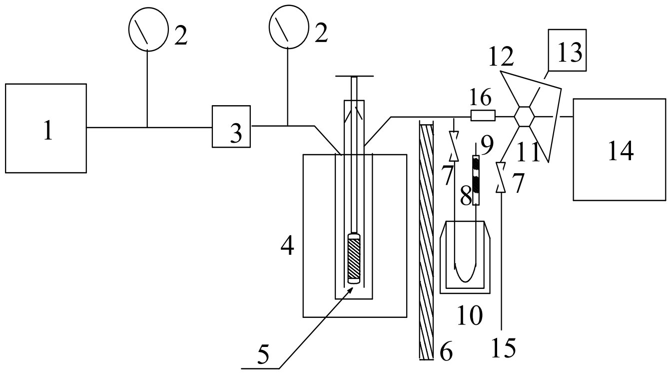
Analyses of the volatile products of pyrolysis of PE were carried out with a gas chromatograph, equipped with flame ionizing detector (GC-FID). It was a German apparatus of the GCHF.18.3 type, equipped with a steel column 2m x 3mm filled with 7% SE30 + 0.21% Carbowax 20 M on Chromosorb W, 60-80 mesh. The high-boiling substances were identified with the gas chromatographic method supported by mass spectrometry (GC-MS). The Hewlett Packard 5890 type apparatus was used. Particular compounds were separated in the capillary column filled with

Crosslinked 5% PH ME Silicone, 25 m long and 0.30 mm dia. The analyses were carried out at the following temperature program: 45 °C (2 min) $\xrightarrow{15\,°C/min}$ 310 °C (10 min) for the mass range from 10 to 400 m/z.

Particular compounds were identified by comparison of their retention time with those for reference samples. The GC-MS analyses were based on the spectral database WILEY 138. Quantities of particular substances were determined by comparison with respective calibration curves.

2.2.3 Thermal Decomposition of the Composite

Composite of 10% PE and 90% copper ore concentrate was prepared as described in Więckowska and Szyszka [11]. For arrangement of the system used for pyrolysis of the composite and for sampling of the gas products see Figure 2.



1 - air cylinder; 2 - pressure gauges; 3 - flow controller; 4 - high-temperature oven with a flow through reactor and a mechanism enabling maintaining of the sample out of the high-temperature zone; 5 – sample; 6 - heat shield; 7 – valves; 8 - sampler with two layers of active carbon; 9 - outlet of gases to the atmosphere; 10 - cold trap (Dewar's flask with cooling medium); 11 - six-way valve; 12 – loop; 13 - cylinder with hydrogen (carrier gas); 14 - gas chromatograph; 15 - ventilating hood; 16 - dust filter

Figure 2. Principle scheme of the system used for pyrolysis of the composite and for sampling of gas products

Pyrolysis of the PE 10% composite (approx. 2.5 g) was carried out within the temperature ranges of 420 - 500, 510 - 600 and 610 –750 °C in air stream of 7 cm^3/min. Degradation products were collected in the cold trap (10) and in the adsorption-type sampler (8).

Products collected in the sampler (active carbon, sampling and control layers) and those washed out from walls of the tube, were extracted with CS_2 (carbon disulphide produced by Sigma-Aldrich, spectrometric grade). Chromatographic analyses were carried out with the GC-MS HP 5890 II type apparatus, equipped with quadruple detector and a capillary column HP 5MS, 30 m, 0.25 ID, 0.25 df. Helium gas was used as the carrier. The analyses were carried out at the following temperature program: 40 °C (8 min.) $\xrightarrow{4\,°C/min}$ 80 °C , next $\xrightarrow{8\,°C/min}$ 250 °C . Temperature of 250 ºC was maintained to the end of the analysis. Due to technical limitations, the substances, which have retention times below 600 s, are not analysed by the mass spectrometer and not shown in the GC-MS chromatogram.

3. Results and discussion

3.1 Thermal Analysis of the Composite

The PE 10% composite, formed at 180 °C, gives three endothermic peaks (Figure 3). The TGA curve (Figure 4) proves that loss of weight of the sample begins at temperature approximating to 164 ºC, which is due to loss of water. Organic binder decomposes itself at temperature range from 415 – 500 ºC, showing maxima at 472 ºC and at 477 ºC. Overall loss of mass amounts to 27%. Decomposition of inorganic substances occurs above temperature of 772 °C (Figure 4).

3.2 Analysis of Products of the Pyrolysis of Polyethylene Waste Scrap

Thermal decomposition of polyethylene scrap at temperature of 500 ºC in nitrogen atmosphere resulted in generation of 73 volatile and non-volatile compounds. The temperature was selected because of the thermal analysis showed that it assures complete decomposition of polyethylene when the maximum amounts of products are formed. Amounts of particular products collected were re-calculated to determine the yield from 1 g PE [12, 13]. Percentage shares of particular components of the PE decomposition products are specified in Table 1.

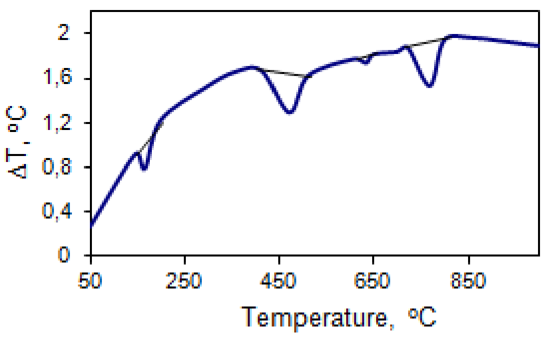


Figure 3. Differential thermal analysis of the PE-10 % composite sample

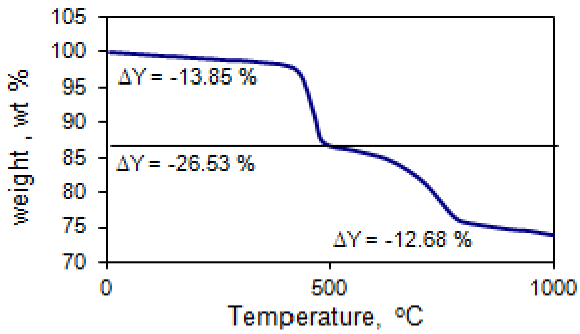


Figure 4. Gravimetric thermal analysis of the PE-10 % composite sample

Table 1. Percentage shares of particular components of the PE decomposition products at temperature of 500 °C

No.	**SPECIFICATION**	Formula	Molecular weight	Concentration [mg/m³]	Yield [mg/1g PE]
1.	Carbon oxide	CO	28	465.3	53.0
2.	Carbon dioxide	CO_2	44	368.7	42.0
7.	Aliphatic hydrocarbons C_1-C_4	C_nH_{2n+2}	16-58	3279.2	373.5
8.	Pentane	C_5H_{12}	72	670.8	76.4
9.	Hexane	C_6H_{14}	86	467.1	53.2
11.	Heptane	C_7H_{16}	100	285.3	32.5
34.	1-Pentadecylene	$C_{15}H_{30}$	210	134.3	15.3
37.	1-Hexadecylene	$C_{16}H_{32}$	224	129.1	14.7
40.	1-Heptadecylene	$C_{17}H_{34}$	238	128.9	14.8
43.	1-Octadecylene	$C_{18}H_{36}$	252	132.6	15.1
46.	1-Nonadecylene	$C_{19}H_{38}$	266	108.0	12.3

At temperature of 500°C, the PE decomposition products consist of volatile and non-volatile substances. The first group consisted of carbon oxide, carbon dioxide, aliphatic hydrocarbons C1-C4, pentane, hexane and heptane (Figure 5). The second group comprised of 1-tetradecylene, 1-pentadecylene, 1-hexadecylene, 1-heptadecylene, 1-octadecylene, 1-nonadecylene, 1-ejcosane and 1-tricosane.

The volatile and non-volatile decomposition products, except of carbon oxide, are not dangerous for the environment and are non-toxic.

3.3 Products of Pyrolysis of the 10% PE Composite

Pyrolysis of the 10% PE composite in air was examined in an experimental system (Figure 2) at three temperature ranges i.e. at 420-500 ºC, 510-600 ºC and 610-700 ºC. Decomposition products specific for particular temperature ranges are presented in Figs. 7 - 12 and in respective Tables 2 - 7.

The examinations carried out within the whole temperature range from 420ºC to 750 ºC proved that products of pyrolysis largely depend upon temperature of the process.

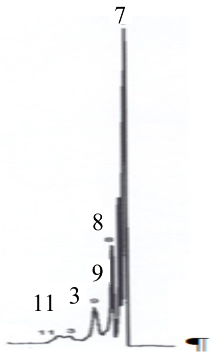


Figure 5. Chromatogram of volatile products of pyrolysis obtained with the GCHF.18.3 type apparatus. The identified compounds are numbered as in the Table 1.

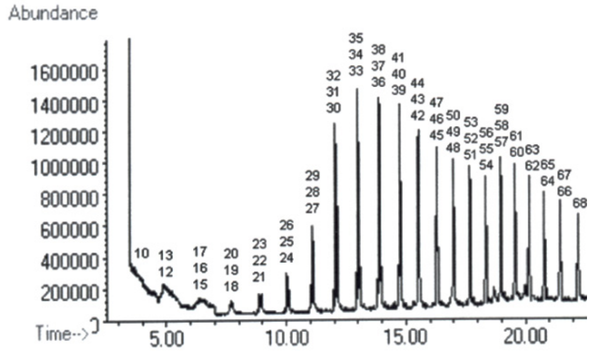


Figure 6. Chromatogram of high-boiling products of pyrolysis obtained with the Hewlett Packard GC-MS 5890 type apparatus. The identified compounds are numbered as in the Table 1.

Table 2. Products of pyrolysis of the 10% PE composite at temperatures of 420 – 500 ºC (substances collected in the cold trap)

No.	Specification	Percentage %
1.	4-methylheptane	13.80
2.	2-metyl-2-heptene-4-ketone	11.49
3.	2-ethyl hexylester of acetic acid	58.97

Table 3. Products of pyrolysis of the 10% PE composite at temperature of 420 – 500 ºC (substances adsorbed on activated carbon)

No.	Specification	Percentage %
1.	1-cyclopentylethanone	12.88
2.	4-methylheptane	30.22
3.	4,4-dimethyl-2-pentene	12.13
4.	1,2,3-trimethylcyclopentane	44.76

Table 4. Products of pyrolysis of the 10% PE composite at temperature of 510 – 600 ºC (substances collected in the cold trap)

No.	Specification	Percentage, %
1.	1,2,3-trimethylcyclopentane	56.68
2.	3-ethyl hexane	10.07

Table 5. Products of pyrolysis of the 10% PE composite at temperature of 510 – 600 ºC (substances adsorbed on activated carbon)

No.	Specification	Percentage, %
1.	4-methyl-1-heptene	8.33
2.	Toluene	28.97
3.	1-octene	6.43
4.	Octane	4.66
5.	5-ethyl-2,4-dimethyl-2-heptene	5.05
6.	3-methylheptylacetate	25.39

At temperatures from 420 ºC to 500 ºC, the 10% PE composite generated 15 decomposition products, mainly 2-ethylhexyl ester of acetic acid, 4-methylheptane and 1,2,3-trimethylcyclopentane (see Figure 7, Figure 8 as well as Table 2 and Table 3).

In the temperature range of 510-600 ºC, generation of 36 organic compounds occurred, probably decomposition products of the binder residue and of copper concentrate itself. The products were composed mainly of 3-ethylhexane, 1,2,3-trimethylcyclopentane, toluene and 3- methylheptyl acetate (Figure 9, Figure 10, Table 4 and Table 5). The most of the gaseous decomposition products were generated in the temperature range of 610-750 ºC. Among 51 organic compounds, 3-methyl-3-butene-2-on, 2-ethylhexyl ester of acetic acid, 3-ethylhexane, 1,3-dimethylcyclopentane and nonane prevailed (Figure 11, Figure 12 and Table 6 and Table 7). It is noteworthy that at any temperature of pyrolysis, hazardous dioxins were not formed.

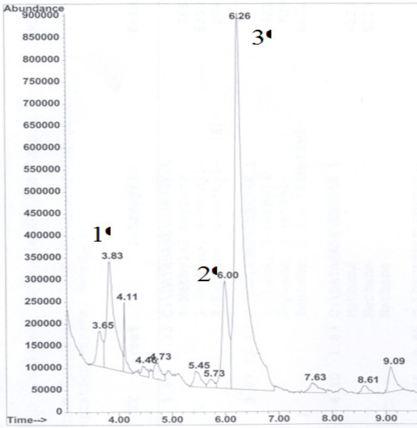


Figure 7. Chromatogram GC-MS of the products of pyrolysis of the 10% PE composite at temperature of 420– 500ºC (substances collected in the cold trap). Numbers in Table 2.

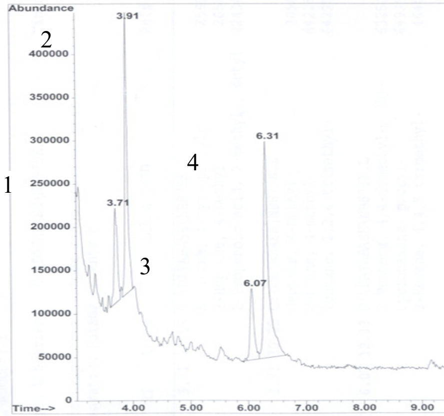


Figure 8. Chromatogram GC-MS of the products of pyrolysis of the 10% PE composite at temperature of 420 – 500 ºC (substances adsorbed on activated carbon). Numbers in Table 3.

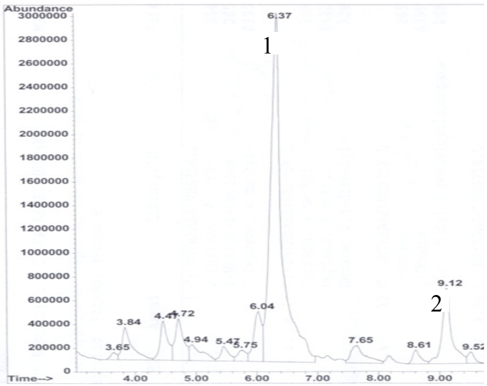


Figure 9. Chromatogram GC-MS of the products of pyrolysis of the 10% PE composite at temperature of 510 – 600 ºC (substances collected in the cold trap). Numbers in Table 4.

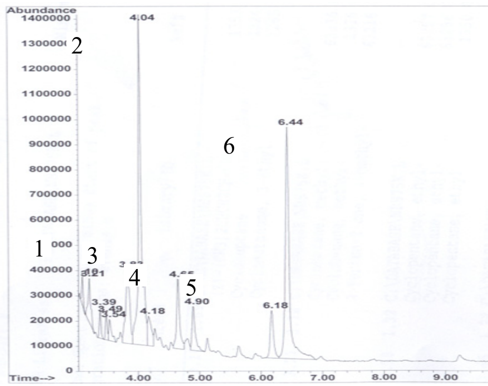


Figure 10. Chromatogram GC-MS of the products of pyrolysis of the 10% PE composite at temperature of 510 – 600 ºC (substances adsorbed on activated carbon). Numbers in Table 5.

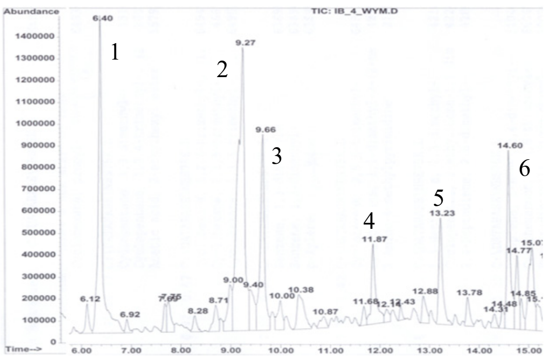


Figure 11. Chromatogram GC-MS of the products of pyrolysis of the 10% PE composite at temperature of 610 – 750 ºC (substances collected in the cold trap). Numbers in Table 6.

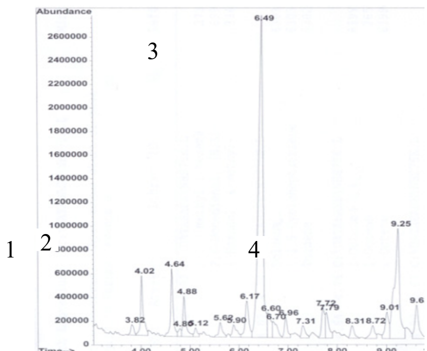


Figure 12. Chromatogram GC-MS of the products of pyrolysis of the 10% PE composite at temperature of 610 – 750 ºC (substances adsorbed on activated carbon). Numbers in Table 7.

Table 6. Products of pyrolysis of the 10% PE composite at temperature of 610 – 750 ºC substances collected in the cold trap)

No.	Specification	Percentage, %
1.	1,3-dimethylocyclopentane	14.77
2.	3-ethylhexane	21.34
3.	nonane	9.14
4.	4-methyl-2-heptanone	3.99
5.	1,2,3-trimethylbenzene	4.51
6.	3,4- dimethyl-1-oktene	6.82

Table 7. Products of pyrolysis of the 10% PE composite at temperature of 610 – 750 ºC (substances activated on activated carbon)

No	Specification	Percentage, %
1.	Toluene	4.38
2.	1-Oktene	4.76
3.	2-Ethylhexyl ester of acetic acid	39.78
4.	3-methyl-3-butene-2-on	15.56

4. Conclusions

Thermal analysis of the composite of copper ore concentrate and polyethylene, used as a binding agent, proved that organic substances of the binder decompose at temperatures below 500 ºC, whereas inorganic substances of the concentrate decompose at approx. 700 ºC. Thermal decomposition of polyethylene scrap alone at temperature of 500 ºC showed that the products are mainly alkanes C1-C7, some higher alkanes, alkenes and dienes. In total, approx. 70 volatile organic compounds were formed.

Thermal decomposition of composite material showed that a part of the organic binder decomposes well above 500 °C. Products of pyrolysis are similar to those obtained from polyethylene alone, i.e. hydrocarbons (4-methylpentane, methane, octane and 3-ethylhexane) and considerable amounts of oxygen compounds like esters, ketones and alcohols. Probably, the inorganic substances of the copper concentrate act as catalysts of oxidation of the hydrocarbons and are responsible for generation of the esters, ketones and alcohols.

Within the temperature range of 610-750 ºC the whole composite matters decompose, giving a mixture of many organic compounds. However, dioxins are not formed.

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