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### THERMAL ANALYSIS OF SOLID FUELS IN AN INERT ATMOSPHERE

#### ANALIZA TERMICZNA PALIW STAŁYCH W ATMOSFERZE GAZU OBOJĘTNEGO

The paper takes the analysis of thermal studies of different types of fuels. It allowed diversification of fuels depending on their composition and origin. Consideration of coal, biomass and waste (coal mule, sewage sludge) as fuel is nowadays an important aspect of energy in our country. It should be emphasized that Poland power engineering is based up to 95% on coal – the primary fuel. Mining industry, forced to deliver power engineering more and better fuel, must however, use a deeper cleaning of coal. This results in a continuous increase waste in the form of mule flotation. The best method of disposing these mule is combustion and co-combustion with other fuels. On the other hand, commonly increasing awareness state of the environment and the need to reduce CO<sub>2</sub> emissions energy industry have committed to implement alternative solutions in order to gain power, through, i.a.: development technologies use of biomass, which is one of the most promising renewable energy sources in Poland.

The paper presents the results of research TG-DTA fuels made in an inert atmosphere.

**Keywords:** thermal analysis, coal, biomass, coal-mule, sewage sludge

W pracy przedstawiono analizę badań termogravimetrycznych różnego rodzaju paliw. Pozwoliła ona na ich zróżnicowanie w zależności od składu i pochodzenia. Rozpatrywanie, nie tylko węgla, ale również biomasy i odpadów (mułów węglowych, osadów ściekowych) jako paliw jest obecnie ważnym aspektem energetycznym w naszym kraju. Należy podkreślić, że polska energetyka oparta jest w ok. 95% na węglu. Przemysł wydobywczy zmuszony do dostarczania energetyce coraz lepszego węgla stosuje jego głębsze oczyszczanie. Powoduje to ciągły wzrost ilości odpadów w postaci mułów poflotacyjnych. Najlepszą metodą ich unieszkodliwiania jest spalanie oraz współspalanie z innymi paliwami. Z drugiej strony, z uwagi na aspekty środowiskowe i konieczność redukcji emisji CO<sub>2</sub>, przemysł energetyczny zobowiązany jest

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do wdrażania rozwiązań alternatywnych, poprzez m.in. rozwój technologii wykorzystania biomasy, która jest jednym z najbardziej obiecujących odnawialnych źródeł energii w Polsce. W artykule przedstawiono wyniki badań TG-DTA paliw, w tym odpadów, przeprowadzonych w atmosferze obojętnej.

**Słowa kluczowe:** analiza termiczna, węgiel, biomasa, muly węglowe, osady ściekowe

## Introduction

Analyzing the thermal decomposition of the fuel necessary to examine its origin, composition and structure. However, from the viewpoint of energy, regardless of the type of fuel (coal, mule coal, biomass, sewage sludge) in each of them can distinguish basic components: moisture, organic matter and mineral substance.

For example, coal has three types of moisture: transient, hygroscopic and crystallization. Transient moisture can be removed from the coal after it is dried at room temperature. The remainder after such “exertions” moisture in the fuel is called hygroscopic (coal reaches then equilibrium with atmospheric moisture). It is feature characteristic of the coal related to the degree of coalification thereof. This relationship results from changes in the porous structure of the coal connected to the processes carbonising. Hygroscopic moisture may be removed from the fuel by drying at 105÷110°C or distillation. Moisture crystallization whereas is very difficult to remove because it is related to various silicates contained in the fuel.

The mineral material is derived from plant material, from which formed the coal seams and mineral deposits mixed with particles of plant. It is a mixture of different chemical compounds (Ca, Si, Fe, Al, Mg, Na, K, Cu, P, F, Cl) and distributed elements (B, V, Ge, Ga, U). The organic material whereas mainly formed: carbon, hydrogen, oxygen, sulfur and nitrogen and trace amounts of phosphorus and other compounds.

The ash is noncombustible part of the fuel, consisting of mineral substances being a part of the coal. Together with moisture forms a fuel ballast, lowering its quality. With increasing ash content reduces so the calorific value of the fuel.

In the process of heating the organic material and mineral fuel decomposes. Then separated moisture, numerous gases and vapors organic substances, leading to the formation of a char, consisting of organic residues and changed as a result of heating minerals substances fuel (Tomeczek, 1992).

It should be noted, however, that each of the issue in the context of this work fuels stands out the specificity of behavior under conditions high temperature. Thermal analysis of fuel has so far been raised in a number of works, including (Folgueras et al., 2005; Hycaj et al., 2006; Hani et al., 2012; Lester et al., 2007; Xiao et al., 2010). From the point of view of thermographic studies missing, however, in the literature comparing fuels such varied structure and behavior.

Below, made a brief characterization of coal fuels, biomass and sewage sludge, from the point of view of their thermal decomposition.

## Coal and coal mule

Coal (Grabowska, 1963; Salcewicz & Kijewska, 1967; Roga, 1956; Kobel-Najzarek & Wasilweski, 1980) is a mixture of colloidal systems where isolated part of thermally resistant – “kernel”, composed of aromatic segment atoms carbon equally spaced at different angles relative to each other and partially interconnected hydrocarbon chains and of part thermally

unstable composed of hydrocarbon chains. Part of the thermally unstable includes compounds formed during thermal destruction of coal, distilling during anaerobic process devolatilization, called volatile parts. Percentage of volatile content depends on the degree of coalification and determines the ability of decomposing coal under the influence of the temperature.

In accordance with (Tomeczek, 1991) heating coal may therefore cause the decomposition of original carbonaceous material on volatile products, part of which after cooling to room temperature can be condensed, and the solid. The pyrolysis products at room temperature are, therefore three basic elements: gas, liquid (hydrocarbons + water), and char. Figure 1 shows the temperature regions of the release of volatile products from coal.

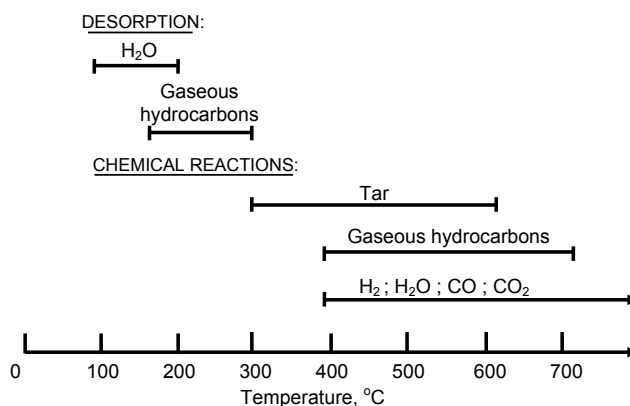


Fig. 1. Temperature regions of the release of volatile products from coal (Tomeczek, 1991)

In tables 1 and 2 presented a typical distribution of the products of low-and high-temperature pyrolysis during heating.

TABLE 1

Products low-temperature carbonization of coal (400÷750°C) (Pitt & Millward, 1979)

Gaseous phase, volume fractions %		Light liquid hydrocarbons, volume fractions %		Tar, volume fractions %		Coke
H <sub>2</sub>	10	paraffin	46	benzene, toluene, xylene,	1,5	containing 8-20% of the volatiles
CH <sub>4</sub> +higher hydrocarbons	65	olefins	16	phenol	1,5	
CO	5	cyclo-paraffins	8	cresol	4,5	
CO <sub>2</sub>	9	cyclo-olefins	9	xilenols	7,0	
other	11	redolences	16	other phenols	16,0	
		other	5	basic tar	2,0	
				paraffin oil	3,5	
				other redolences	38,0	
				pitch	26,0	
The yield of 1 ton of coal 100 m <sup>3</sup> *		0,011-0,016 m <sup>3</sup>		0,077-0,086 m <sup>3</sup>		0,75 t

\* normal conditions

TABLE 2

Products high-temperature carbonization of coal (900÷1100°C) (Pitt &amp; Millward, 1979)

Gaseous phase, volume fractions %		Light liquid hydrocarbons, volume fractions %		Tar, volume fractions %		Coke
H <sub>2</sub>	50	benzene	72	benzene, toluene, xylene,	20,6	containing 1-2% of the volatiles
CH <sub>4</sub> + higher hydrocarbons	34	toluene	13	phenols and cresols	1,5	
CO	8	xylene	4	xlenols	0,5	
CO <sub>2</sub>	3	alicyclic compounds	5	other phenols	1,0	
other	5	aliphatic compounds	6	naphthalene	8,9	
				anthracene	1,0	
				other redolences	24,6	
				basic tar	1,8	
				pitch	60,0	
The yield of 1 ton of coal 100 m <sup>3</sup> *		0,014 m <sup>3</sup>		0,027-0,032 m <sup>3</sup>		0,75 t

\* normal conditions

Occurrence of individual reactions or areas secretion of individual products depends not only on the type of fuel, but also on the thermal conditions (temperature, pressure, gas composition) in its environment (Table 3).

Stands out series of processes using the phenomenon of pyrolysis:

1. Carbonation – pyrolysis of coal directed mainly for the production of tar. It is conducted at temperatures up to 750°C (low-temperature carbonization).
2. Coking – pyrolysis directed mainly to produce coke. Is conducted at a temperature above 900°C (high-temperature carbonization).
3. Hydrolysis – pyrolysis in the presence of hydrogen for obtaining of light aromatics.
4. Fast pyrolysis – pyrolysis occurring at higher heating speeds, above 1 K/s, oriented to maximize the yield of gas and tar.
5. Pyrolysis plasma – pyrolysis occurring in high-temperature plasma, focused on the production of acetylene.

TABLE 3

Conditions for thermal devolatilization (Tomeczek, 1991)

Desirable product volatile	Type of heating	Temperature of devolatilization	Time residence of the solid phase	Residence time of volatiles at temperature of devolatilization
tar	fast	500°C	long	short
liquid hydrocarbons	fast	750°C	long	long
gas	fast	1000°C	long	—
CH <sub>4</sub>	fast	600°C	long	—
H <sub>2</sub>	fast	1000-1100°C	long	—
C <sub>2</sub> H <sub>2</sub> + unsatd	instant	1200°C	long	middle
CO	—	750°C	long	—

Kröger i Brückner (1961) illustrate the mechanism of pyrolysis in the form of scheme (Fig. 2):

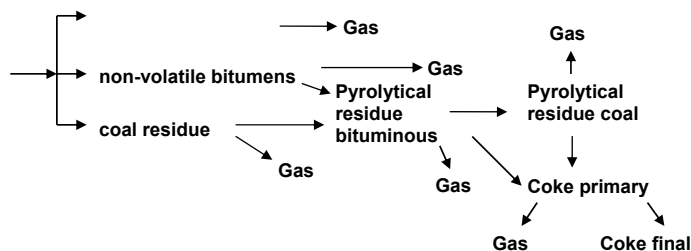


Fig. 2. Mechanism of coal pyrolysis (Kröger & Brücker, 1961)

In the literature, however the most cited is a very simple mechanism of the pyrolysis developed by van Krevelen (Van Krevelen & Schuyer, 1959) (Fig. 3).

Coal at a temperature above 300°C passes through depolymerization of the unstable intermediate state, called metaplast. This state is partly responsible for the behavior of the plastic coal. Metaplast disintegrates in second reaction on semi-coke and primary volatile products (tar and gas primary). Thus formed semi-coke is then divided into gas and coke.

- I. Coking coal (P) → metaplast (M)
- II. Metaplast (M) → semi-coke (R) + primary gas (G<sub>1</sub>)
- III. Semi-coke (R) → coke (S) + secondary gas (G<sub>2</sub>)

Fig. 3. Mechanism of coal pyrolysis (Van Krevelen & Schuyer, 1959)

Reaction I is a reaction depolymerization, in which is formed unstable product an intermediate – metaplast – responsible for the behavior of coal in a plastic state.

Reaction II corresponds to “karking” process, during which are eliminated the non-aromatics group. This reaction is accompanied by re-condensation units metaplast and formation semi-coke. At the end of this process, coal mass solidifies again. Gas evolution causes ballooning coal.

Reaction III is the reaction of the secondary devolatilization, during which the individual elements forming semi-coke combined as a result of discharge of methane and – particularly at higher temperatures – a hydrogen, giving such a large sipes, which are in the coke.

The most interesting aspects illustrates the range of 400-500°, ie gas evolution due to the decomposition, which accompanied by a momentary liquefaction or plasticizing of the mass coal. Softening phenomenon occurs however, only in coals a limited range of degree of coalification (from approximately 85 to 92%*C*). Although coals of lower degree of coalification give off also during heating a large amount of gas, but not soften. It explains why the final product is composed of with powdery of coke. Anthracite during heating give off a small amount of gaseous products, and the residue after heating only can be distinguished from the starting material.

The results of differential thermal analysis discussed in the paper (Van Krevelen & Schuyer, 1959) coal show, that under heating take place in the coal mass most of all three the following consecutive endothermic reactions. Initial hump, which was developed as a result of water removal, lies near the temperature of 150°, except coals spanning a range meta-anthracite, in which this the range coalification not been noted at this temperature the thermal effect. The second hump is associated with the chemical degradation coal and occurs in the range temperature 350-550°, which this the scope is – as already stated above – the range of devolatilization primary. The

hump occurs within a temperature range 600–700° is a measure of the secondary devolatilization, and also highly endothermic. Curves for anthracite may be presumed that at temperature about 400 takes exothermic reaction.

In the papers (Grabowska, 1963; Salcewicz & Kijewska, 1967; Roga, 1956; Kobel-Najzarek & Wasilweski, 1980) in detail discuss the distribution of coal in conditions high temperature. During the evaporation of moisture attributable to on range the temperature from 80°C to 150°C may be some relaxation of the structure of substances. Coal takes heat for to activating molecules, for loosening forces of Van der Waals, and preparation carbonaceous substance to a chemical reaction. It was found, that to a temperature about 350°C in the coal, no place none greater macroscopically visible changes.

In the first stage devolatilization, falling in range the temperature from 350 to 500°C followed already changes physico-chemical and reactions chemical accompanying plasticized. Depending on the type of coals, the maximum plasticity fall in the range of temperatures from 360°C (type of coal 32÷34) to 400°C (type of coal 35÷36). The higher is the heating rate, this the phenomenon of plasticity occurs intensively, because under these conditions the rate of melting is greater than the rate of decomposition of bitumens. At the same time with the phenomenon of melting is carried distillation and decomposition of pyro-genetic same components of coal, form gases and vapors, which puffing semiliquid the plastic mass of coal. The pressure generated in the coal during plasticity called is expansion. In the case of young coals liquid mass of plastic does not resist of resistance emitting the gases. For coals standing on a higher degree of coalification liquid products decomposition put considerable resistance emitting a gases, as a result of what liquid mass swells. Puffing phenomenon occurs, and the heated coal rapidly expands. Coals which are on the highest spot of metamorphic transformations (the highest degree of coalification) also does not undergo the process of puffing, in view of low content volatile. From the point of view of chemical, during this period occurs in coal intense detachment side chains and radicals, and solidifying carbonaceous substance loses weight more the hydrogen and oxygen than carbon. Disconnected radicals and chains combine with each other and distilled off in the form of great-tar. Grabowska (Grabowska, 1963) concluded, that the total amount of formed products volatile in time the thermal destruction the coal (on the type of 32 to 37 including) to a final temperature plastic state, about 500°C, is independent of the heating rate of coal. Above the temperature 500°C increasing the heating rate increases the degree of devolatilization of the lower types of coals, of the type 35 is almost meaningless, whereas for a type of 37-less. Increase the temperature from 500 to 700°C lead to secretion of products volatile of the solidified semi-char. They are initially products ended of chemical reactions. At the same time begins the process of polymerization and condensation the carbonaceous substance. In substances volatile there is increasing of amount products of these reactions is water, carbon monoxide and carbon dioxide, methane. In the period of second devolatilization separates significantly less of part volatile than in the first. Also observed a significant decrease in content the hydrogen and increase content of carbon. In this range temperature there are two parts contraction of the semi-char: 500÷600°C – contraction is minimal, and the devolatilization is still quite intense and 600÷700°C – contraction is large, and the devolatilization is inhibited. Also occurs during this period very significant increase actual density and strength of porous substance semi-chars, increases also proper strength carbonaceous substance. It is proposed that the increase of actual density is caused by mainly internal compaction connected with aromatization structure. Both of these factors are responsible for the increase in strength porous structure semi-chars, which undergoes at this time stiffening, but has main affected increasing of the density actual, while the partial – devolatilization.

In the third period, above 700°C, weighing the evolution of the volatile components is negligible, they contain mostly hydrogen and methane. At this stage, contraction is initially very large, but from 800°C decreases, reducing the strength of the porous structure, whereas intensively increases proper endurance substance semi-chars and the indicator of coalification.

As a result of the ongoing still contraction occurs increase of the density actual, both of these parameters grow less intensively than in the second period. The effect of these transformation is persuasible also inhibition increase of the strength porous of char, most likely through formation in the walls of a large number of micropores.

A significant part in the balance of production and utilization of coal are fine-grained fractions of coal originating from extraction processes, enrichment and use of hard coal and brown coal. These include coal mules, flotation waste, dust coke and coke breeze from the gasification process. Mule coal constitute of minor fractions of coal of calorific value even below 10 MJ / kg, characterized by the ash content within the limits of 35-60% and moisture in the range of 25-30% (Hycnar et al., 2005). It showed a similar kinetics of thermal process to coal (Kijo-Kleczkowska, 2013). In the past, mules coal were used in small amounts. Most of them were regarded as waste and stored in settling tanks. They are currently use in blends energy, both from current production processing plants, as well as with settlers (Lorenz & Ozga-Blaschke, 2005).

## Biomass

When comparing energy properties of biomass and coal, identical quality elementary composition of these two fuels can be noticed. Diversity is present however, in terms of quantity. An advantage of biomass is definitely lower sulphur and ash content as compared to fossil fuels. However, its unfavorable feature should be emphasised, namely high and variable moisture content, reducing the calorific value of the fuel.

Biomass reaction and its decomposition under the effect of high temperatures can be discussed on the example of wood (Kordylewski, 2005). Owing to high moisture content and volatile parts it has individual special nature of heating, drying, degassing and combustion. Moisture removal from wood requires delivery of roughly 1.6 kJ of energy per a kilogram of water (Tillman et al., 1981). Thermal decomposition of wood already starts at the temperature of approximately 220°C, while its particular components decompose in the following temperatures (Tillman et al., 1981):

- hemicellulose: 220÷320°C,
- cellulose: 320÷370°C,
- lignin: 320÷500°C.

Qualitative difference between thermal decomposition of hemicellulose (cellulose and hemicellulose) and lignin was noticed – the first one undergoes “deeper” thermal decomposition, producing more volatile products, while lignin gives more coke residues. Atmosphere and temperature have a large impact on the composition of wood thermal decomposition products. Free oxygen supply and high temperature (flame combustion) are favourable for faster generation of volatile parts, while in conditions of oxygen shortage and in low temperature (oxygen) more carbonisation product is present. Such a nature of changes is related to the change of tar, which at a high temperature undergoes secondary decomposition to volatile substances and in low – undergoes carbonisation (Tillman et al., 1981). The largest number of volatile parts is generated from wood heated at the temperature of 250÷450°C (Prosiński, 1984) and the most important

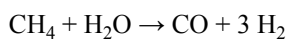
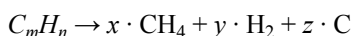
gaseous components include: CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, H<sub>2</sub>. More important liquid components of thermal decomposition of wood are: water, methanol, acetic acid, acetic aldehyde and tar. The coke residue after wood (carbonisation product) being degassed is popularly known as charcoal.

## Sewage sludge

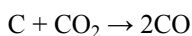
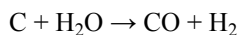
Sewage sludge is characterised by great amount of volatile parts, comparable to brown coal. However, it has definitely lower content of solid flammable part as compared to coal and biomass and demonstrate high reactivity of fuel. Production, properties and methods of sewage sludge disposal have been widely discussed, e.g. in papers (Bień & Wystalska, 2008; Kijo-Kleczkowska et al., 2013; Środa et al., 2013; Kijo-Kleczkowska et al., 2012; Środa et al., 2012a, 2012b).

For instance, in (Bień & Wystalska, 2008), on the basis of the available literature, the process of sewage sludge pyrolysis was discussed in detail, which is predominantly conducted in range of temperatures 250÷1000°C (Żygadło, 2001; Piecuch et al., 2002). Depending on the temperature applied, we distinguish low- and high-temperature pyrolysis. During waste treatment at the temperature within 450÷500°C reference is made to low-temperature pyrolysis, while at the temperature within 700÷800°C high-temperature pyrolysis occurs (Rosik-Dulewska, 2002).

The main reactions occurring in the gaseous form during pyrolysis are (Wandrasz, 2000):



while in the solid phase:



$m, n, x, y, z$  — partition coefficients.

As a result of the pyrolysis process, solid, liquid and gaseous products are obtained. Mutual proportions of particular phases and their composition depend on the temperature and pressure of the process, type of waste and its physical-chemical properties. The liquid phase has the greatest share and almost independent from temperature (about 60%). As the temperature grows, also the gaseous phase share grows and solid decreases (Rosik-Dulewska, 2002).

The gaseous phase obtained in the process of pyrolysis contains mainly steam, hydrogen, methane, ethane and their homologues, higher aliphatic hydrocarbons, carbon monoxide and dioxide and other gaseous compounds, such as: H<sub>2</sub>S, NH<sub>3</sub>, HCl, HF, HCN. The solid phase is the so-called peastone coke, inert substances and dusts with substantial heavy metals content. The liquid phase are water and oil condensates, consisting of a mixture of oils and tars, water and organic components (acids and alcohols) (Rosik-Dulewska, 2002; Piecuch et al., 2002).

With regard to TG/DTG measurements of sewage sludge, it is worth paying attention to the paper (Hycaj et al., 2006). Samples of three types of sewage sludge were heated in neutral atmosphere with constant velocity 10°C/min. The measurements made it possible to distinguish three basic fuel degassing stages. It has been stated that initially the sludge loses its moisture, and then there is a two-step degassing process of volatile parts, with various speed of their separa-



tion. The first stage of heating, from ambient temperature to ca. 110°C is related to separation of analytical moisture, included in the studied sewage sludge samples. In the range of temperatures 130-210°C all the studied types of sludge demonstrated further sample mass loss that can be interpreted as loss of water chemically related to fuel (Biaggini et al., 2002). Some people emphasise that drying fuels can be slightly delayed due to high heat of water vaporisation (Yu et al., 2002). Then, it is possible to observe sludge organic matter decomposition. In the scope of temperatures 200-330°C thermal decomposition of lignin and hemicellulose components begins. In the scope of degassing temperatures 330-400°C cellulose decomposes (Collura et al., 2005). In the next stage the organic matter is decomposed, being the product of active sludge operation (Fogueras et al., 2005). The most intensive degassing is observed within the temperatures 210 and 410°C. In this temperature range, cellulose undergoes decomposition, which originates from waste paper and plant matter contained in sewage. According to (Honda et al., 2002; Li et al., 2001) cellulose may constitute twenty to thirty some per cent of sewage sludge dry mass. Therefore, it may be concluded that the main component of the studied sludge are substances created in initial sludge. In this scope of temperatures curves have a very similar course. The maximum peak finishes before the sample reaches the temperature of 400°C. The next temperatures range (410-550°C) corresponds to volatile parts decomposition arising during active sludge operation on sewage (Collura et al., 2005). This stage indicates the greatest share in the sample of components arisen during active sludge operation. It should also be emphasised that the sewage sludge contains clay minerals, whose main component is kaolinite, whose decomposition to the so-called metakaolinite takes place in the range of temperatures 450-700°C and involves dehydroxylation and water separation (Saikia et al., 2002). The next stage of sludge decomposition takes place in the scope of temperatures between 670 and 750°C, with maximum at 710°C. This peak is certainly the responsibility of calcium carbonate decomposition contained in the sewage sludge, added to the sludge as part of hygienisation (Biaggini et al., 2002; Collura et al., 2005). On this basis we can speak about the quantity of lime added to sediment in different treatment plants. Samples of fuels subject to higher temperatures demonstrated further mass loss. At this stage such significant peaks were not observed, however, high processes temperature indicates that there is further decomposition of mineral substances of the studied sewage sludge.

## 1. Experimental studies

**Thermogravimetry TG** is an instrumental analytical method based on recording mass changes in the studied fuel sample at simultaneous growth in temperature according to the controlled programme, which is presented graphically by means of a thermogram.

**DTG curve** presents changes in the speed of substance decomposition at temperature growth.

**Differential thermal analysis DTA** is an instrumental analytical method based on recording temperature differences ( $\Delta T$ ) between the studied substance ( $T_s$ ) and the reference substance (TR) in relation to time or temperature as two samples located in identical conditions in the environment heated in a controlled manner (Szumera, 2012, 2013).

Thermal analysis was conducted on 8 kinds of fuels: energy willow, sewage sludge from three treatment plants (A, B, C), brown coal, hard coal, coal sludge and anthracite. Fuels (in the analytical state) were ground in a laboratory mill and then sifted through a sieve below 100  $\mu\text{m}$ .

## 1.1. Characteristics of fuels used in researches

Table 4 shows the analysis of selected chemical properties of sewage sludge used in the study. Table 5 presents the elementary and technical analysis of sewage sludge in reference to coal and biomass. It should be noted the content of volatile matter and carbon in fuels and their calorific value significantly affect the combustion process.

TABLE 4

Analysis of selected chemical properties of sewage sludge used in the study

Rate	Unit	Result research granules A	Result research granules B	Result research granules C	Permissible content heavy metals in municipal sewage sludge, according to Regulation Minister of the Environment of 13 July 2010 (for use in agriculture and land reclamation for agricultural purposes)	
Reaction	unit pH	7,4	7,0	7,8		
Water content	%	4,60	7,00	14,7		
Loss on ignition	%	55,6	64,2	56,4		
Ammonium	% <sub>d.w.f.</sub> *	0,17	0,27	0,38		
Kjeldahl nitrogen	% <sub>d.w.f.</sub> *	3,9	5,1	4,1		
Phosphorus	% <sub>d.w.f.</sub> *	3,0	3,2	3,3		
Calcium	% <sub>d.w.f.</sub> *	4,7	3,1	4,9		
Magnesium	% <sub>d.w.f.</sub> *	0,53	0,67	0,73		
Cadmium	mg/kg <sub>d.w.f.</sub> *	5,9	2,3	< 1		to 20
Chromium org.	mg/kg <sub>d.w.f.</sub> *	340	160	80		to 500
Copper	mg/kg <sub>d.w.f.</sub> *	360	470	210		to 1000
Nickel	mg/kg <sub>d.w.f.</sub> *	190	97	19		to 300
Lead	mg/kg <sub>d.w.f.</sub> *	160	62	12	to 750	
Mercury	mg/kg <sub>d.w.f.</sub> *	0,61	0,50	0,48	to 16	
Zinc	mg/kg <sub>d.w.f.</sub> *	2400	950	1000	to 2500	

\*<sub>d.w.f.</sub> – dry waste residue

TABLE 5

Technical and elementary analysis of fuels used in studies

Fuel type	Technical analysis				Elementary analysis				
	Humidity content	Content of volatile elements	Ash content	Heat of combustion	Content of coal element	Content of hydrogen element	Content of nitrogen element	Content of oxygen element	Content of total sulphur
	$W^a$	$V^a$	$A^a$	$Q_i^a$	$C_i^a$	$H_i^a$	$N^a$	$O_d^a$	$S_i^a$
	%	%	%	kJ/kg	%	%	%	%	%
1	2	3	4	5	6	7	8	9	10
Biomass (energetic willow)	8,27	70,53	4,55	15825	40,90	6,07	2,73	37,30	0,18
Sewage sludge A	4,94	51,44	36,44	12574	30,77	3,92	4,26	18,23	1,44
Sewage sludge B	5,31	52,59	32,46	13801	32,43	4,30	5,47	18,42	1,61

1	2	3	4	5	6	7	8	9	10
<b>Sewage sludge C</b>	6,74	46,40	38,16	11104	27,50	3,72	4,24	18,73	0,91
<b>Brown coal</b>	14,46	37,11	18,42	16165	43,16	3,08	0,55	19,81	0,52
<b>Hard coal</b>	2,66	30,90	2,36	31198	79,33	4,33	1,27	9,75	0,30
<b>Coal mule</b>	4,51	20,45	39,43	15024	40,12	2,82	0,54	12,11	0,72
<b>Anthracite</b>	1,50	3,00	2,50	39350	93,00	1,70	0,06	1,01	0,23

## 1.2. Test stand and measurement methods

The research was conducted by means of STA 449 F3 Jupiter device by NETZSCH, being the property of the Department Thermophysical Research Laboratory of the Faculty of Material Engineering and Ceramics of the AGH University of Science and Technology, enabling simultaneous thermal analysis with the use of two research techniques: Thermogravimetry and Differential Thermal Analysis (TG-DTA) in relation to one sample (Fig. 3, Tab. 6).



Fig. 3. Test stand (STA 449 F3 Jupiter of NETZSCH)

TABLE 6

The measurement parameters

Type of furnace	Pt S
Type of media	TG-DTA
Type of measurement	Sample with correction
Type of the crucible / cover	Al <sub>2</sub> O <sub>3</sub> / no
Atmosphere / rate of gas flow	Argon / 40 ml/min

Program of temperature	24-1200°C
The rate of heating	10 K/min
Weights of samples for measurement in an argon atmosphere:	mg
Biomass (energetic willow)	31,6
Sewage sludge A	37,4
Sewage sludge B	32,9
Sewage sludge C	36,2
Brown coal	33,3
Hard coal	32,7
Coal mule	36,8
Anthracite	39,3

### 1.3. Experimental studies results

Figures 4-12 illustrate the results of fuels thermal measurements TG-DTA performed in the argon atmosphere. In connection with literature review conducted in the Introduction, an analysis of fuels behaviour in given conditions was prepared (Table 7-17).

Typical stages and peaks accompanying intensity of the process were also emphasised in tables.

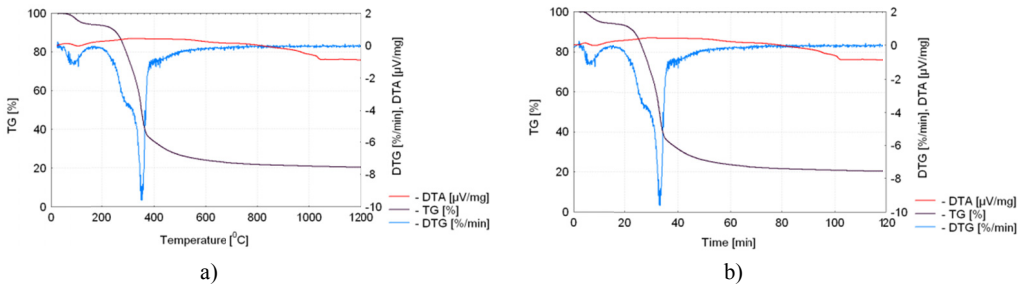


Fig. 4. Curves TGA-DTA for the pyrolysis of energetic willow: a) with respect to the process temperature; b) with respect to time of the process

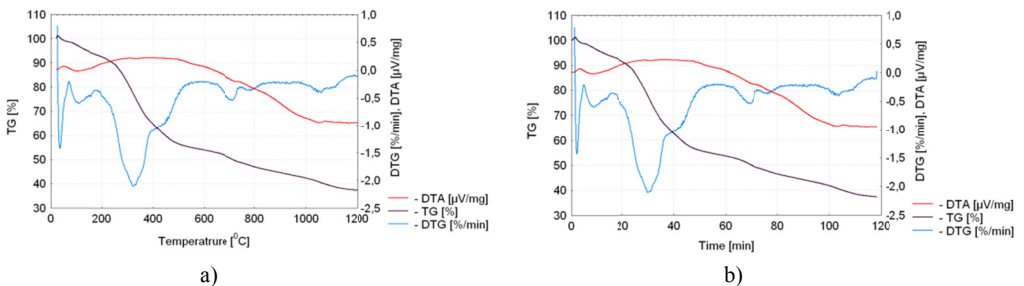


Fig. 5. Curves TGA-DTA for the pyrolysis of sewage sludge A: a) with respect to the process temperature; b) with respect to time of the process

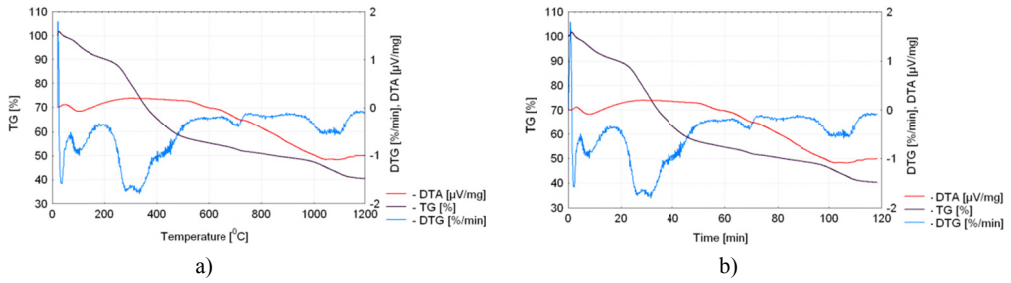


Fig. 6. Curves TGA-DTA for the pyrolysis of sewage sludge B: a) with respect to the process temperature; b) with respect to time of the process

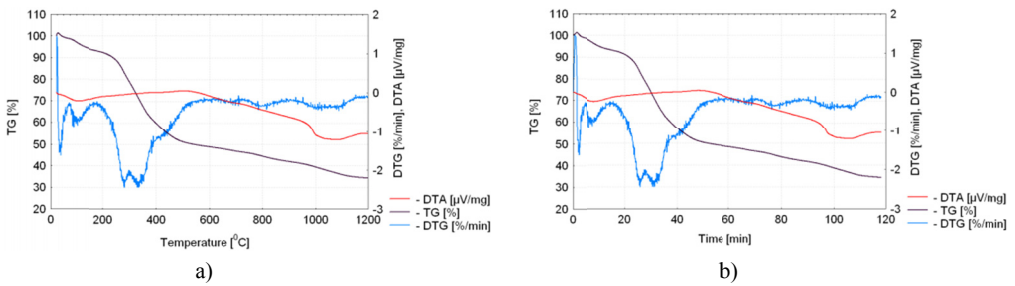


Fig. 7. Curves TGA-DTA for the pyrolysis of sewage sludge C: a) with respect to the process temperature; b) with respect to time of the process

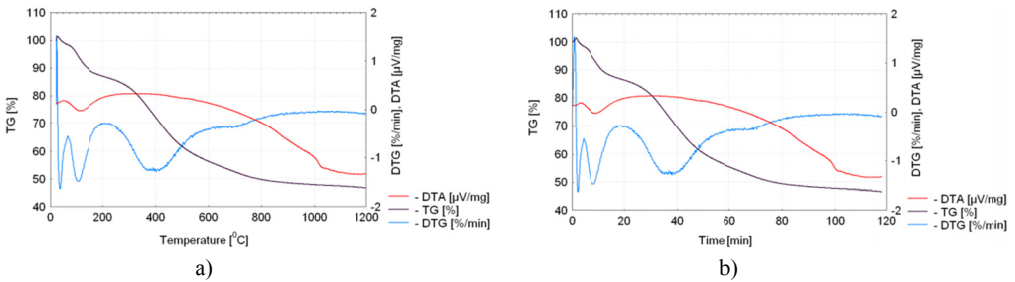


Fig. 8. Curves TGA-DTA for the pyrolysis of brown coal: a) with respect to the process temperature; b) with respect to time of the process

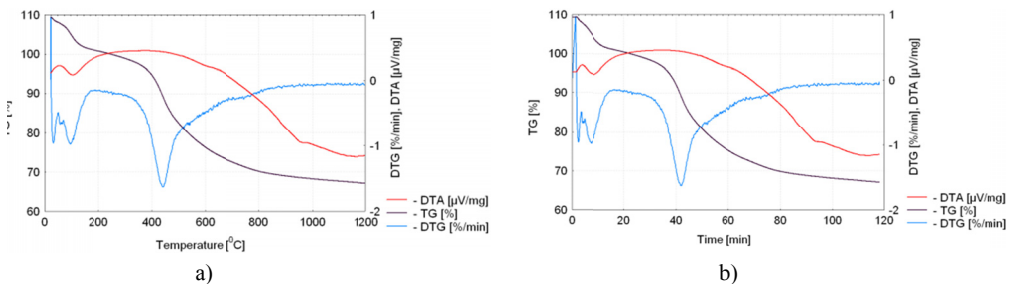


Fig. 9. Curves TGA-DTA for the pyrolysis of hard coal: a) with respect to the process temperature; b) with respect to time of the process

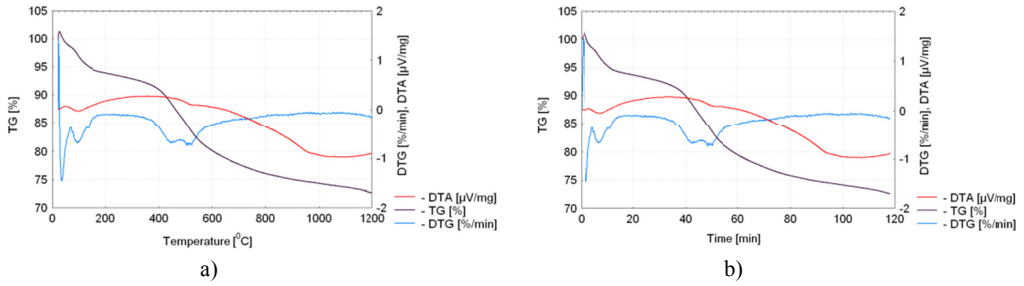


Fig. 10. Curves TGA-DTA for the pyrolysis of coal mule: a) with respect to the process temperature; b) with respect to time of the process

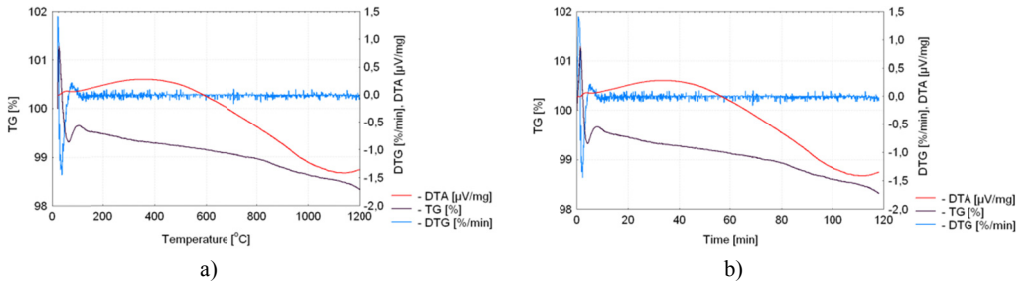


Fig. 11. Curves TGA-DTA for the pyrolysis of anthracite: a) with respect to the process temperature; b) with respect to time of the process

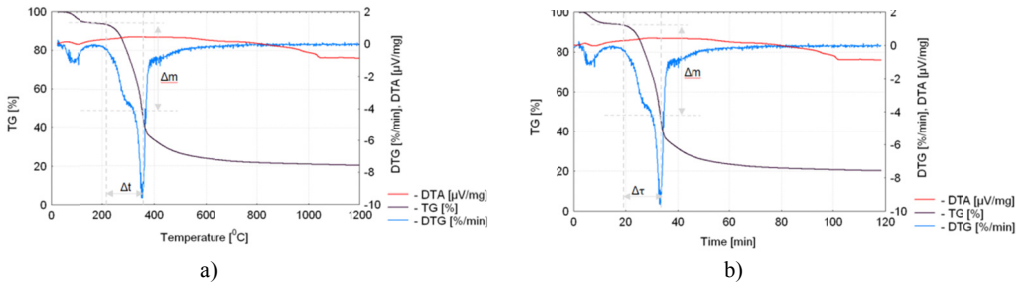


Fig. 12. Methodology of reading of the maximum rate weight loss for example of curves TG-DTA for the pyrolysis of energetic willow: a) with respect to the process temperature; b) with respect to time of the process

TABLE 7

Percentage change in mass of fuel analyzed at intervals of time at 20 min

Fuel	Time of process, min					
	0÷20	20÷40	40÷60	60÷80	80÷100	100÷118
<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>
<b>Biomass (energetic willow)</b>	$\Delta m = 6,6\%$	$\Delta m = 61,7\%$	$\Delta m = 8\%$	$\Delta m = 2\%$	$\Delta m = 0,7\%$	$\Delta m = 0,5\%$
<b>Sewage sludge A</b>	$\Delta m = 8,56\%$	$\Delta m = 28,81\%$	$\Delta m = 9,14\%$	$\Delta m = 7,12\%$	$\Delta m = 4,66\%$	$\Delta m = 4,46\%$

1	2	3	4	5	6	7
<b>Sewage sludge B</b>	$\Delta m = 10,56\%$	$\Delta m = 26,14\%$	$\Delta m = 8,7\%$	$\Delta m = 4,27\%$	$\Delta m = 4,14\%$	$\Delta m = 5,95\%$
<b>Sewage sludge C</b>	$\Delta m = 8,63\%$	$\Delta m = 34,05\%$	$\Delta m = 8,89\%$	$\Delta m = 4,65\%$	$\Delta m = 5,16\%$	$\Delta m = 4,37\%$
<b>Brown coal</b>	$\Delta m = 13,59\%$	$\Delta m = 17,07\%$	$\Delta m = 14,1\%$	$\Delta m = 6,01\%$	$\Delta m = 1,64\%$	$\Delta m = 1,07\%$
<b>Hard coal</b>	$\Delta m = 8,9\%$	$\Delta m = 8,4\%$	$\Delta m = 16,7\%$	$\Delta m = 5,4\%$	$\Delta m = 1,6\%$	$\Delta m = 1,4\%$
<b>Coal mule</b>	$\Delta m = 6,18\%$	$\Delta m = 3,7\%$	$\Delta m = 10,68\%$	$\Delta m = 3,69\%$	$\Delta m = 1,65\%$	$\Delta m = 1,57\%$
<b>Anthracite</b>	$\Delta m = 0,55\%$	$\Delta m = 0,18\%$	$\Delta m = 0,15\%$	$\Delta m = 0,2\%$	$\Delta m = 0,29\%$	$\Delta m = 0,31\%$

TABLE 8

Percentage change in mass of fuel analyzed at intervals of temperature at 200°C

Fuel	Temperature of process, °C					
	0÷200	200÷400	400÷600	600÷800	800÷1000	1000÷1200
<b>Biomass (energetic willow)</b>	$\Delta m = 6,3\%$	$\Delta m = 60,2\%$	$\Delta m = 9,5\%$	$\Delta m = 2\%$	$\Delta m = 1\%$	$\Delta m = 0,6\%$
<b>Sewage sludge A</b>	$\Delta m = 7,44\%$	$\Delta m = 27,61\%$	$\Delta m = 11\%$	$\Delta m = 6,95\%$	$\Delta m = 4,7\%$	$\Delta m = 5,05\%$
<b>Sewage sludge B</b>	$\Delta m = 9,66\%$	$\Delta m = 24,81\%$	$\Delta m = 10,46\%$	$\Delta m = 4,34\%$	$\Delta m = 3,58\%$	$\Delta m = 6,93\%$
<b>Sewage sludge C</b>	$\Delta m = 7,53\%$	$\Delta m = 32,62\%$	$\Delta m = 11,04\%$	$\Delta m = 4,33\%$	$\Delta m = 5,04\%$	$\Delta m = 5,2\%$
<b>Brown coal</b>	$\Delta m = 12,93\%$	$\Delta m = 14,98\%$	$\Delta m = 15,99\%$	$\Delta m = 6,5\%$	$\Delta m = 1,9\%$	$\Delta m = 1,18\%$
<b>Hard coal</b>	$\Delta m = 8,6\%$	$\Delta m = 6\%$	$\Delta m = 18,4\%$	$\Delta m = 6,4\%$	$\Delta m = 1,8\%$	$\Delta m = 2,2\%$
<b>Coal mule</b>	$\Delta m = 5,96\%$	$\Delta m = 2,94\%$	$\Delta m = 11,03\%$	$\Delta m = 4,07\%$	$\Delta m = 1,74\%$	$\Delta m = 1,73\%$
<b>Anthracite</b>	$\Delta m = 0,53\%$	$\Delta m = 0,19\%$	$\Delta m = 0,14\%$	$\Delta m = 0,18\%$	$\Delta m = 0,33\%$	$\Delta m = 0,31\%$

TABLE 9

Characteristic stages of the process and peaks during the pyrolysis of energetic willow

Measurement	Characteristic stages of the process and peaks			
	Heating, evaporation of moisture, devolatilization	Devolatilization	Devolatilization	Devolatilization
<b>Temperature [°C]</b>	24÷150	150÷200	200÷400	400÷1200
<b>Time [min]</b>	0÷15	15÷18,4	18,4÷38	38÷120
<b>TG [%]</b>	5,5	0,5	60,3	13,3
<b>DTG [%/min]</b>	P(84°C; 6 min)	—	P(351°C; 33,3 min)*	—
<b>DTA [µV/mg]</b>	P(101°C; 7,8 min) Effect endothermic	—	—	P(1045°C; 102,3 min) Effect endothermic

\* maximum rate of process; P – characteristic peak; t – temperature, °C; τ – time, min

TABLE 10

Characteristic stages of the process and peaks during the pyrolysis of sewage sludge A

Measurement	Characteristic stages of the process and peaks					
	Heating, evaporation of moisture	Evaporation of moisture, devolatilization	Devolatilization	Devolatilization	Devolatilization	Devolatilization
1	2	3	4	5	6	7
<b>Temperature [°C]</b>	24÷70	70÷180	180÷539	539÷647	647÷734	734÷1200
<b>Time [min]</b>	0÷4,6	4,6÷15,6	15,6÷51	51÷62,7	62,7÷71,2	71,2÷120
<b>TG [%]</b>	1,1	5,5	38,1	2,3	3,7	12

1	2	3	4	5	6	7
<b>DTG [%/min]</b>	P(34°C; 2 min)	P(107°C; 8,7 min)	P(319°C; 30 min)*	—	P(711°C; 69 min)	P(1059°C; 104 min)
<b>DTA [μV/mg]</b>	—	P(104°C; 7,7 min) Effect endothermic	—	—	—	P(1054°C; 103 min) Effect endothermic

\* maximum rate of process; P – characteristic peak; t – temperature, °C; τ – time, min

TABLE 11

Characteristic stages of the process and peaks during the pyrolysis of sewage sludge B

Measurement	Characteristic stages of the process and peaks								
	Heating	Evaporation of moisture, devolatilization	Devolatilization	Devolatilization	Devolatilization	Devolatilization	Devolatilization	Devolatilization	Devolatilization
<b>Temperature [°C]</b>	24÷69	69÷170	170÷213	213÷530	530÷658	658÷742	742÷981	981÷1152	1152÷1200
<b>Time [min]</b>	0÷4,5	4,5÷14,6	14,6÷19,8	19,8÷52	52÷64,3	64,3÷72	72÷96	96÷113,2	113,2÷120
<b>TG [%]</b>	1,6	6,7	1,7	33	3	2,4	4,1	6,9	0,1
<b>DTG [%/min]</b>	P(36°C; 2 min)	P(102°C; 8 min)	—	P(281°C; 26,3 min) P(333°C; 31,4 min)*	—	P(713°C; 69,2 min)	—	P(1078°C; 107 min)	—
<b>DTA [μV/mg]</b>	—	P(102°C; 7,8 min) Effect endothermic	—	—	—	—	—	P(1048°C; 102,4 min) Effect endothermic	—

\* maximum rate of process; P – characteristic peak; t – temperature, °C; τ – time, min

TABLE 12

Characteristic stages of the process and peaks during the pyrolysis of sewage sludge C

Measurement	Characteristic stages of the process and peaks			
	Heating, evaporation of moisture	Evaporation of moisture, devolatilization	Devolatilization	Devolatilization
<b>Temperature [°C]</b>	24÷69	69÷174	174÷535	535÷1200
<b>Time [min]</b>	0÷4,7	4,7÷15,8	15,8÷50,5	50,5÷120
<b>TG [%]</b>	1,2	5,2	43,4	15,7
<b>DTG [%/min]</b>	P(38°C; 2,4 min)	P(99°C; 7,7 min)	P(281°C; 26 min)* P(329°C; 30,8 min)	—
<b>DTA [μV/mg]</b>	—	P(102°C; 8,3 min) Effect endothermic	—	P(1065°C; 104 min) Effect endothermic

\* maximum rate of process; P – characteristic peak; t – temperature, °C; τ – time, min



TABLE 13

Characteristic stages of the process and peaks during the pyrolysis of brown coal

Measurement	Characteristic stages of the process and peaks				
	Heating, evaporation of moisture	Evaporation of moisture, devolatilization	Devolatilization	Devolatilization	Devolatilization
Temperature [°C]	24÷63	63÷180	180÷246	246÷578	578÷1200
Time [min]	0÷4,2	4,2÷16	16÷22,4	22,4÷56,3	56,3÷120
TG [%]	1,6	10,9	1,8	28,5	10,2
DTG [%/min]	P(36°C; 2 min)	P(102°C; 8 min)	—	P(401°C; 37,8 min)*	—
DTA [μV/mg]	—	P(113°C; 9 min) Effect endothermic	—	—	—

\* maximum rate of process; P – characteristic peak; *t* – temperature, °C; *τ* – time, min

TABLE 14

Characteristic stages of the process and peaks during the pyrolysis of hard coal

Measurement	Characteristic stages of the process and peaks				
	Heating, evaporation of moisture	Evaporation of moisture, devolatilization	Devolatilization	Devolatilization	Devolatilization
Temperature [°C]	24÷50	50÷167	167÷342	342÷691	691÷1200
Time [min]	0÷3,5	3,5÷15	15÷33	33÷66,8	66,8÷120
TG [%]	1,2	6,8	3,4	25,2	5,6
DTG [%/min]	P(32°C; 2,3 min)	P(56°C; 3,8 min)	—	P(442°C; 41,8 min)*	—
DTA [μV/mg]	—	P(105°C; 8 min) Effect endothermic	—	—	P(963°C; 93,7 min) Effect endothermic

\* maximum rate of process; P – characteristic peak; *t* – temperature, °C; *τ* – time, min

TABLE 15

Characteristic stages of the process and peaks during the pyrolysis of coal mule

Measurement	Characteristic stages of the process and peaks				
	Heating, evaporation of moisture	Evaporation of moisture, devolatilization	Devolatilization	Devolatilization	Devolatilization
Temperature [°C]	24÷68	68÷150	150÷380	380÷566	566÷1200
Time [min]	0÷4,5	4,5÷13	13÷36	36÷55	55÷120
TG [%]	1,51	3,73	2,93	10,52	8,59
DTG [%/min]	P(35°C; 2 min)	P(92°C; 7 min)	—	P(442°C; 42 min) P(503°C; 48 min)*	—
DTA [μV/mg]	—	P(92°C; 7 min) Effect endothermic	—	P(526°C; 51 min)	—

\* maximum rate of process; P – characteristic peak; *t* – temperature, °C; *τ* – time, min

Characteristic stages of the process and peaks during the pyrolysis of anthracite

Measurement	Characteristic stages of the process and peaks	
	Heating, evaporation of moisture	Devolatilization
Temperature [°C]	24÷74	74÷1200
Time [min]	0÷5,3	5,3÷120
TG [%]	0,52	1,18
DTG [%/min]	P(36°C; 2,3 min)*	—
DTA [μV/mg]	—	P(342°C; 31,7 min); P(1140°C; 112 min) Effect endothermic

\* maximum rate of process; P – characteristic peak;  $t$  – temperature, °C;  $\tau$  – time, min

TABLE 17

Maximum rate of mass loss of fuel

Fuel	Maximum change in of the fuel mass reading from the curve TG/DTG			Steps of process
Biomass (energetic willow)	$t_1 = 200^\circ\text{C}$ $\tau_1 = 18,4$ min	$t_2 = 351^\circ\text{C}$ $\tau_2 = 33,3$ min	$\Delta t = 151^\circ\text{C}$ $\Delta\tau = 14,9$ min $\Delta m = 44,3\%$	Devolatilization
Sewage sludge A	$t_1 = 180^\circ\text{C}$ $\tau_1 = 15,6$ min	$t_2 = 319^\circ\text{C}$ $\tau_2 = 30$ min	$\Delta t = 139^\circ\text{C}$ $\Delta\tau = 14,4$ min $\Delta m = 14,9\%$	Devolatilization
Sewage sludge B	$t_1 = 213^\circ\text{C}$ $\tau_1 = 19,8$ min	$t_2 = 333^\circ\text{C}$ $\tau_2 = 35$ min	$\Delta t = 120^\circ\text{C}$ $\Delta\tau = 15,2$ min $\Delta m = 15,5\%$	Devolatilization
Sewage sludge C	$t_1 = 174^\circ\text{C}$ $\tau_1 = 15,8$ min	$t_2 = 281^\circ\text{C}$ $\tau_2 = 26$ min	$\Delta t = 107^\circ\text{C}$ $\Delta\tau = 10,2$ min $\Delta m = 10,6\%$	Devolatilization
Brown coal	$t_1 = 246^\circ\text{C}$ $\tau_1 = 22,4$ min	$t_2 = 401^\circ\text{C}$ $\tau_2 = 37,8$ min	$\Delta t = 155^\circ\text{C}$ $\Delta\tau = 15,4$ min $\Delta m = 13,7\%$	Devolatilization
Hard coal	$t_1 = 342^\circ\text{C}$ $\tau_1 = 33$ min	$t_2 = 442^\circ\text{C}$ $\tau_2 = 41,8$ min	$\Delta t = 100^\circ\text{C}$ $\Delta\tau = 8,8$ min $\Delta m = 9\%$	Devolatilization
Coal mule	$t_1 = 380^\circ\text{C}$ $\tau_1 = 36$ min	$t_2 = 503^\circ\text{C}$ $\tau_2 = 48$ min	$\Delta t = 123^\circ\text{C}$ $\Delta\tau = 12$ min $\Delta m = 7,01\%$	Devolatilization
Anthracite	Negligible content moisture and the volatile components in the fuel leads to a smooth progress of the release process of pyrolysis over the entire range of time and temperature			

$t$  – temperature, °C;  $\tau$  – time, min

The analyses presented in tables 7 and 8 confirm that fuel composition plays an important role in its behaviour in high-temperature conditions. High moisture and volatile parts content in fuel intensifies the heating process and degassing in initial stages of the process and at lower temperatures (e.g. energy willow – up to 40 min. and 400°C). Higher carbonised fuels behave

differently. In their case, shift of pyrolysis stages towards higher temperatures and later process times may be observed (e.g. hard coal – up to 60 min. and 600°C).

TG-DTG curves present a number of effects related to fuel mass loss. DTG curve suggests in addition an effect related to two overlapping processes. Such behaviour of thermal curves indicates release and decomposition of particular components. In the case of all fuels in temperatures of about 100°C an endothermic effect may be observed, connected with moisture vaporisation from the fuel. The percentage change in fuel mass, with regard to the time or temperature, at a given stage of the process indicates an effect dominant in the course of decomposition of a given kind of fuel. The most intensive decomposition speed, connected with its reactivity, confirmed with maximum fuel mass loss was identified, however, after exceeding 100°C, which involves volatile parts release from the fuel (degassing). This process is more or less intensive, depending on the type of fuel (Table 9-17). The methodology of determining the greatest process speed is presented in Fig. 12. It has been stated along with fuel calorific value increase, the maximum change in its mass takes place at a later stage of the process, at higher temperature.

As has already been mentioned, particular stages of high temperature process can overlap. An example may be all the studied types of sewage sludge and coal sludge, in the case of which within the range of 200-600°C two endothermic peaks may be observed, indicating release of various kinds of fuel components, which has already been mentioned in the introduction to this paper. Therefore, it suggests the need to analyse gas composition emitted during the process, which is the subject matter of subsequent authors' works.

Minor increase/decrease in the DTA curve for all fuels is hard to be connected with specific transformations. In such conditions, endothermic effects may be sought, or exothermic relating to, among others, transformation, crystallisation, phases melting or structure polymorphic transformations. However, all these processes are not related to mass change. In the case of all fuels at the temperature of approximately 1000°C endothermic bending was observed, which is not accompanied by mass change. This suggests the effect of ash melting of the studied samples at a given time of the process.

## 2. Conclusions

The paper presents results of thermal TG/DTG and DTA analyses of various kinds of fuels (biomass, three types of sewage sludge, brown coal, hard coal, coal sludge and anthracite) conducted in neutral atmosphere. Their analysis allowed to demonstrate the impact of composition and origin of fuel on its behaviour in high-temperature conditions. Thermal analysis, due to its simplicity, proves effective in observation of changes profile in fuel mass, as well as readout of the maximum value of its reactivity, ash quantity or total time of the process. In the analysis on the basis of TG/DTG and DTA curves, characteristic process stages were highlighted as well as peaks accompanying fuel decomposition and its components release.

According to what has been stated above, it is planned to continue thermogravimetric analyses in the oxidation atmosphere, as well as measurements designed to analyse the composition of gases emitting in the course of the process. It will allow one to explain, e.g. double peaks visible in the analysed curves.

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