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Waste and fuels from waste

Part I. Analysis of thermal decomposition

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Bretsznajder Special Chapter

Abstract Thermogravimetric studies provide the basis for qualification of materials and suitability of biomass fuels and fuels formed from waste to convert them into fuel gas generated in the generator process. The paper presents the results of the analysis of thermal decomposition (thermogravimetric research) of fuel from waste, sewage sludge and wastes from the agro-food: potato pulp and rapeseed meal. Studies have shown how some biofuels and fuel formed from waste reach the semi-coke and coke structure, which is important later, in modeling industry degassing process. The most effective seems to be using rapeseed meal in generator process, since the thermal decomposition occurs in the form of transformation in the temperature range 200–500 °C. On the basis of quantity analysis of gaseous transformation products from the above mentioned transformations, the calorific value of after process gases has been calculated. The highest calorific value is represented by a gas resulting from rapeseed meal pyrolysis $\sim 10{,}040$ kJ/Nm^3. The solid residue obtained by dry decomposition of potato pulp has the highest energy value when compared with products from other fuels.

Keywords Thermogravimetric · Waste · Pyrolysis gas · Semi-coke · Calorific value

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Introduction

The increasing demand for consumer goods effects in increasing amount of waste. Municipal and industrial waste is being created—produced by different sectors of industry and agriculture. Increasing amount of waste forces the need to manage them through implementation of recovery and recycling systems or effective disposal. Imposed levels of recovery and recycling of secondary raw materials from waste, enforce measures aimed at economic use. A large part of recycling is the recovery of energetically valuable materials. For this purpose new energetic technologies have been created. They are environment friendly and adapted to effective production of heat and electric energy. The development of these types of energy, apart from traditional boiler combustion, includes using generator processes i.e., degassing and pyrolysis. It requires implementing of new analytical methods of research, which shall enable to define energetic effectiveness of various unconventional fuels in generator processes. Much of the waste is a mixture of composite, not suitable for processing recycled material. However, if they have an energetic potential (due to containing chemical energy), then thermal processes stand in the foreground of their utilization. Energetic waste is material of natural-biological origin (plant and animal biomass), but also synthetic (e.g., plastics, rubber). However, the energy use of fuels other than conventional (e.g., coal) is associated with certain nuisances and problems. These include increased emissions of gaseous components, high temperature corrosion, and difficulties in carrying out the combustion process. Behavior of combustible materials in the process conditions in which they are subject to combustion, gasification or pyrolysis, depends on the elemental composition and the form of chemical compounds these elements make up. Elemental composition also affects (of course, beyond the process parameters) the nature of the products after process. Qualitative and quantitative composition of waste gases depends largely on the type, the relation among the elements of which the combustible particles are built, and structure of these molecules. Information on phase transformations and decomposition products is provided by thermal analysis. It is a great tool to give an energeticist relevant data, so that he can qualify fuel to proper thermal conversion process (combustion or gasification). From the thermogravimetric curve we can deduct about the composition and thermal stability of the fuel samples, the decomposition and products of this process. The results obtained with thermal analysis provide the basis to organize thermal destruction process in order to obtain certain products in established concentrations.

Many publications are devoted to the thermal analysis of various combustible substances, including waste. In work [1], the use of thermal analysis in combustion processes of various lignite types have been analyzed. In work [2], the method DSC and TG/DTG in analyzing kinetics of combustion process of silopi asphaltites have been presented. The research (especially concerning combustion kinetics) are of significant importance in the process modeling analysis, in furnace boiler. In different fuel configurations it is often quite visible the lack of experience concerning the method of using a certain fuel. In that case, such research is indispensable. Estimation of changes in activation energy plays an important role in the identification of processes such as combustion or gasification with catalytic converters. In the processes of dry organic substance decomposition, kinetics, and estimation of changes in activation energy relate to the different heating rate and the use of catalysts such as calcium. It is about the interaction of gaseous products formed in order to reduce the share of condensing vapors and tars to, e.g., increase the share of hydrogen or methane. These studies, however, go beyond the scope of this study. One of the types of waste prone to thermal destruction are worn tires, which main component is rubber. Many authors have investigated the thermal degradation of rubbers [3, 4]; thermogravimetry is commonly used to determine devolatilization characteristics and kinetic parameters of various materials; however, the elaborations are normally based on extremely simplified assumptions: TG and DTG were commonly used and DTG curve measurements have been often proposed as an identification method for rubber mixtures due to their characteristic DTG peak temperatures (for heating rates of 10 K/min, the maximum degradation rates reported are located in the temperature range of 650 K for NR (natural rubber), 720 K for SBR (styrene–butadiene rubber) and 740 K for BR (butadiene rubber) [5]. Kinetic parameters of thermal degradation process of composites were calculated from thermogravimetric analysis (TG) data [6]. Article [7] discusses the effect of crosslinking diene elastomers (BR, SBR, NBR), with the use of an organic peroxide or sulfur, on their flammability and fire hazard. On the basis of results the authors have come to conclusion that smaller flammability of SBR and NBR (butadiene–acrylonitrile rubber) vulcanizates than that of BR vulcanizates results from the formation of a carbonized isolating boundary layer in butadiene–styrene copolymer and a cyclizated isolating layer in butadiene–acrylonitrile copolymer.

Work [8] relates to experimental tests and results obtained for the study of tire waste pyrolysis, conducted by means of TG of the material and the simultaneous determination, through Fourier transform infrared (FTIR) and mass spectrometry (MS) of the decomposition products. Thermal techniques are used for the studies of polymers properties, rubber and composites and to determine the kinetic parameters of their stability and decompositions processes [9–12]. Regarding the problem of rubber waste management, the influence of isocyanate structure on properties of the rubber waste-polyurethane composites has been studied.

Devolatilization characteristics of wooden/agricultural residues, slaughter/poultry residues and a high volatile bituminous coal were investigated by TG. Experiments were carried out at the final temperature of 900 °C and at three heating rates, between 10 and 100 °C/min. Volatile products have been analyzed by FTIR gas analysis, where major pyrolysis species, as well as nitrogen compounds were quantified [13].

To understand better the pyrolysis process of sewage sludge, many studies have been performed on the basis of TG alone or combined with differential scanning calorimetry (DSC) [14–16] and bench-scale fluidized bed reactors [17]. The coupling of TG and spectrometer techniques, such as Fourier transform infrared (FTIR) spectroscopy and mass spectrometry (MS), have been used in the pyrolysis of coal and biomass [18–20], and a few applications of this technique were found to deal with the pyrolysis of sewage sludge [21–23]. Pyrolysis characteristics: the pyrolysis of sludge in TG mainly occurred at temperatures lower than 550 °C. The maximum devolatilization rate and the temperature corresponding to it were increased with the increase of heating rate. Two sludge samples demonstrated different pyrolysis characteristics—one contained two stages while another only one stage—most likely due to their different natures and sources from waste water treatment processes [23].

In work [24] TG is applied to examine pyrolysis of single waste components and their blends in order to determine the composition of an unknown waste mixture. The superposition property is assumed, i.e. thermal degradation curve of the mixture is obtained as the sum of the curves corresponding to its constituents. The results show that if blended, the individual components are more clearly recognised from the differential mass loss curves. This allows better identification of the composition. Inaccuracy in determining the composition increases, if interactions occur between components, which is the case for PVC—newspaper blend. This article presents a method of estimating the energetic suitability of pyrolysis products of fuels such as: fuel from industrial waste PAS'r, sewage sludge, biomass waste from the production of rapeseed oil (extracted rapeseed meal), waste from the production of starch (potato rapeseed). Therefore, the aim of the study was to demonstrate the applicability of research for identification of phase transformations with the use of TG/MS technique, to estimate the energetic suitability of pyrolysis products of fuels mentioned below. As a first step we identify the process of coke formation by the speed of mass loss (TG curves) and the temperature range of main transformations in thermal decomposition process in anaerobic process environment (DTG curves). We then register the changes in concentration of gaseous dry decomposition products of these fuels, depending on the temperature. We also take into account the non-condensable gas concentration, which significantly affect the energy performance of their combustion—mainly in gas turbines. The energy distribution of dry products for different fuels is compared by estimating the calorific value of coke residue and gas obtained in the process. At the same time we point a possible use of certain fuels to generate reburning gases, which burnt in power boilers may cause reduction in NOx emission.

Experimental

Materials

The research was conducted on fuel formed from waste PAS'r, sewage sludge, waste of potato starch production and extracted rapeseed meal. All these materials come from Poland.

The research was based on the waste fuel PAS'r, sewage sludge, waste from the production of potato starch and extracted rapeseed meal. All materials came from Polish territory.

Fuel formed PAS'r (solid fuel alternative—minced) is produced by fragmentation to the appropriate granularity of such waste as: paper, cardboard, foil, cloth, textiles, plastic packaging, tape, cables, cleaning, clothes confiscated by customs. This waste may be contaminated with oil, grease, lubricants, paints, etc. Also used:, plastics, oil filters, outdated food, plastic packaging contaminated with pesticides and detergents, rubber wastes (in small amounts, up to 5 %), bulky waste (sofas, chairs, etc.). According to the producer, PAS'r is characterized by variable—depending on customer requirements—fuel properties, physical and chemical. This affects a wide range of changes, among others calorific value (from 10 to 15 or even 20 MJ/kg of workable mass). The company SITA from Chorzow, part of SITA SUEZ Group, produces fuel PAS'r in the Finnish installation BMH.

Sewage sludge came from a sewage treatment plant in Bialystok. It was dehydrated.

Potato pulp—the waste from the manufacture of starch and potato flour were in the form of cake—with hard grain sizes less than 15 × 20 mm. This waste—considered as a potential fuel—is basically sewage sludge obtained after the dehydration of organic wastewater, obtained in the technological process of processing potatoes. The research material came from the Food Industry Enterprises PEPEES SA in Lomza.

Extracted rapeseed meal is the final waste arising during the production of oil from crushed rapeseed and conditioned using organic solvents, then disposed in the heating process. This waste contains only 1–3 % fat, and protein from 33–37 % (often claimed 36.5 %). In connection to the expected increase in crop acreage and yield of rape, extracted rapeseed meal can also be a good component for the production of formed fuels from waste, or be used as a combustible substance for autonomous incineration process. This research material came from a fat plant in Warsaw. Samples of test materials were collected in accordance with generally accepted procedures for solid sampling. For the preparation of representative laboratory samples, obtained materials were ground and homogenized by grinding in a Scandinavian laboratory mill IKA Labortechnik.

Research on fuel properties and thermogravimetric research

The fuel properties of the waste and fuel formed from waste were marked: moisture, combustible and noncombustible parts, heat of combustion and calorific value (according to Polish Standards-PN-ISO 1171:2002, PN-ISO 1928:2002). Elemental composition of the flammable substance—carbon (C), hydrogen (H), nitrogen (N), sulfur (S) has been determined with the use of elemental analyzer CHNS, model 2400, series II by Perkin Elmer. Chlorine (Cl) has been determined according to PN-ISO 587/2000.

Samples for thermogravimetric research were dried at 105 °C to remove moisture. The amount of moisture contained in the test samples was hygroscopic moisture, which materials absorbed in preparation for the study. Thermogravimetric measurements of dry distribution were conducted in an atmosphere of neutral gas (argon), using a thermobalance Netzch STA 409, PG/2/G Luxx coupled with mass spectrometer Balzers QMS's 200th. The combination of thermogravimetry with mass spectrometry made it possible to identify the gaseous products of transformation. Samples of test materials weighing 14 mg were placed successively in the crucible with a capacity of 50 µl/min. Then they were heated to temperatures ranging from RT (reference temperature—room temperature) to 1000 °C. The rate of linear temperature rise in the atmosphere of argon (Ar), was 10 °C/min. The measuring flow rate of argon was 50 ml/min. At the same time we analyzed the changes in concentrations of selected exhaust gases using a mass spectrometer coupled with thermobalance.

Results and discussion

The results of the fuel properties are presented in Tables 1 and 2.

Fuel formed from waste was characterized by the highest calorific value (more than 19,000 kJ/kg$_{\mathrm{dry\ wt}}$)) and the highest content of combustible elements—carbon and hydrogen. The sewage sludge had the highest ash content and the lowest carbon and hydrogen content, which was reflected in the lowest calorific value. Noteworthy is rapeseed, which in combustible material (in comparison to other fuels) contains the most nitrogen. This fact will be crucial in the implementation of thermal destruction of the fuel. Depending on the type of transformation, air and reduction conditions and the temperature of the process, may constitute an autonomous regulator of nitrogen oxide emissions.From the thermogravimetric curve we can deduct-the composition and thermal stability of the fuel sample, its decomposition and products. The results of thermogravimetric measurements for samples of tested materials are presented in the form of thermograms (Figs. 1, 2, 3, 4) showing the TG curves (weight loss as a function of temperature) and DTG = dTG/dt (rate of mass loss as a function of temperature). On DTG curves indicated temperatures, at which the rate of change is the greatest, (peaks on DTG curve) and rates of maximum change values were indicated.

Table 1 Fuel properties related to dry mass

Sample type	Fuel properties			
	Humidity/%	Combustible parts/%$_{\mathrm{dry\ wt}}$	Ash/%$_{\mathrm{dry\ wt}}$	Calorific value (kJ/kg$_{\mathrm{dry\ wt}}$)
Fuel from waste PAS'r	5.7	82.8	17.2	19,315
Sewage sludge	7.2	69.9	30.1	11,969
Potato pulp	9.5	93.1	6.9	13,108
Rapeseed meal	8.8	92.9	7.1	16,836

Table 2 Elemental composition of flammable substance (mass of dry ashless fuel)

Sample type	Elemental composition of flammable substance/%$_{\mathrm{dry\ wt}}$					
	C	H	N	S	Cl	O
Fuel from waste PAS'r	63.9	7.6	3.6	1.3	0.5	23.1
Sewage sludge	33.0	4.4	4.9	1.7	0.1	55.9
Potato pulp	43.3	6.6	1.2	1.0	0.001	47.8
Rapeseed meal	49.3	7.0	6.8	1.4	0.01	42.4

During heating of test materials to temperatures close to 150 °C, there was a small mass loss due to evaporation of moisture, which shows the first peak in the DTG curve. The rate of mass loss in the form of moisture was 0.5 %/min for potato pulp flour waste and sewage sludge. Temperature range in which the major thermic change took place—intense degassing—was from about 200 to about 500 °C, but with a maximum between 310 and 325 °C (second peak on DTG curve). Rate of mass loss during the reaction was several times higher than in the case of the moisture and lived up to 2.3 %/min for sewage sludge, 4.29 %/min for rapeseed meal and 7.24 %/min for potato pulp starch waste.

The process of dry decomposition of fuel formed from waste–PAS'r is characterized on the thermogram by five peaks on the DTG curve, from which the first three illustrate the changes in the temperature range 180 to 500 °C, and their maxima occur at temperatures: I—334 °C, II—402 °C, III—449 °C. Rate of mass loss in these reactions are at 3.8–4.8 %/min., but by far the largest amount of gas product is released during the first response phase. Another weight loss rate of 0.33 and 0.82 %/min is observed at temperatures of 500–580 °C (maximum at 556 °C) and 600–720 °C (maximum at 668 °C).

Main peak characterizing the transformation of sewage sludge, reaching a maximum at a temperature of 311.3 °C, has a shape that indicates that there are several overlapping groups of reaction (probably three). Degassing of sewage sludge (in addition to the major peaks and moisture changes) is characterized by two peaks, which maxima were recorded at temperatures of 667.2 and 990.3 °C, the weight losses are small, like the moisture losses. During the pyrolysis of potato pulp starch waste we can observe on the thermogram—in the temperature range from 600 to 700 °C—an additional, third group of transformations for which the maximum peak on DTG curve occurs at a

Fig. 1 Curves TG and DTG for formed fuel PAS'r

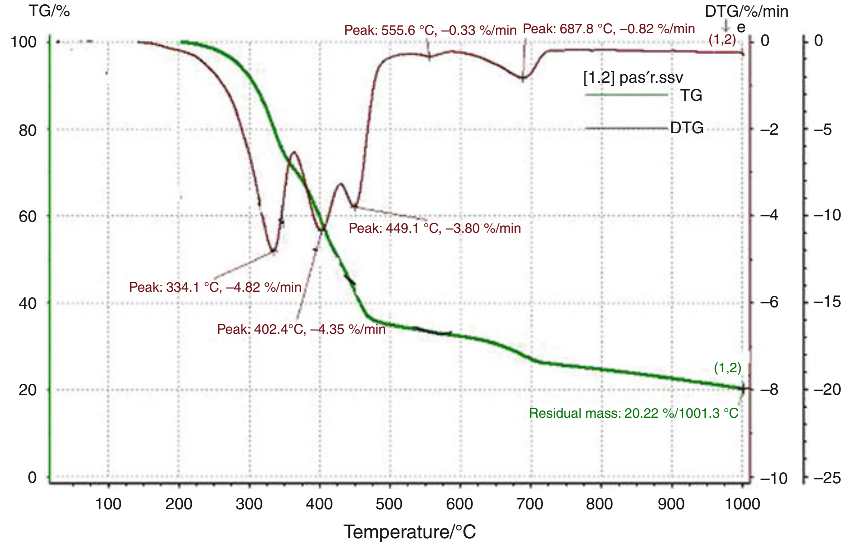
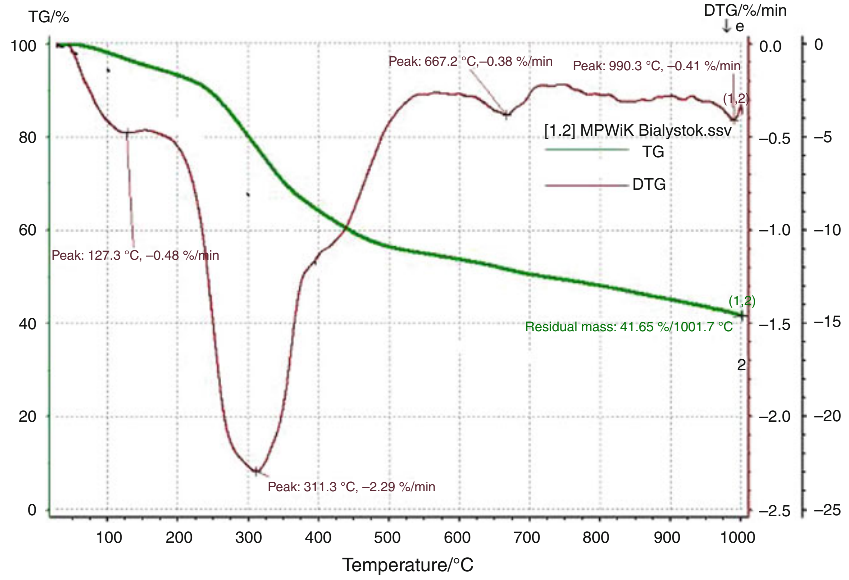


Fig. 2 Curves TG and DTG for sewage sludge



temperature of 671 °C, and the mass loss rate is 0.54 %/min. Loss of mass in this reaction group, however, was small. Temperature range relevant to the degassing process in the case of rapeseed meal is between 175 °C (the beginning) and 550 °C (the end).

Summary data on the rate of mass loss as a function of temperature are shown in Table 3.

Qualitative and quantitative analysis of gaseous products of transformation

Measurements using the mass spectrometer were carried out on-line with thermogravimetric measurements. Gaseous decomposition products were identified. Figures 5, 6, 7, and 8 show the changes in concentration of the basic gas products in dry decomposition process, where *m*/*z*: 2–H_2, 16–CH_4, 17–NH_3, 18–H_2O, 28–CO, 44–CO_2. Water evaporating in the initial stage of heating at temperatures up to 150° C is the moisture in the fuel sample tested, the water appearing in the process of thermal destruction is the reaction water.

Table 4 shows the comparison of quantity (as percentage mass rate $\%_{\mathrm{mass}}$) of fundamental transformation gaseous products, of researched and discussed materials. Apart from gaseous products, a solid product was also taken into account (as a carbonizate).

Figures 9, 10, 11, and 12 show the changes in other product concentration, but the concentration is small.

Table 5 summarizes the results of quantitative analysis of only gaseous decomposition products in combustible materials. These are the molar rates of these compounds, expressed in (%). In addition to the coupled elements of

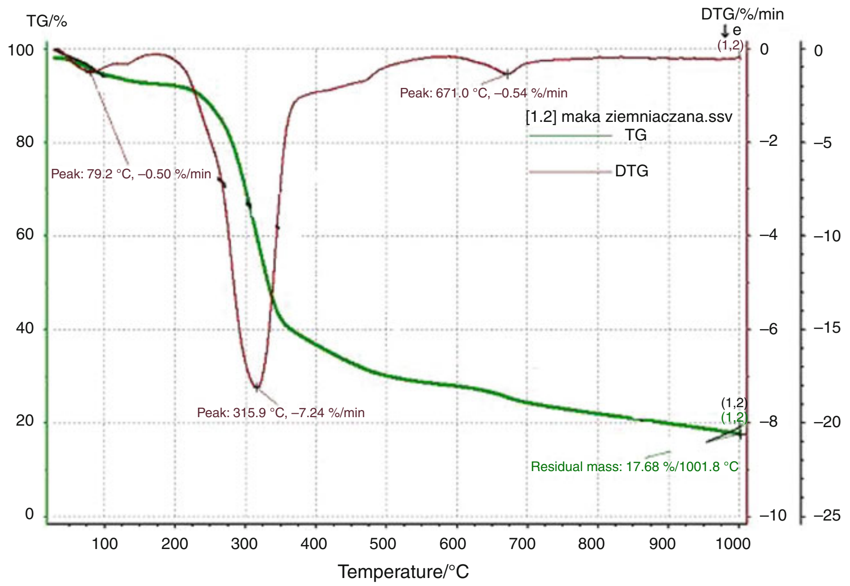


Fig. 3 Curves TG and DTG for potato pulp

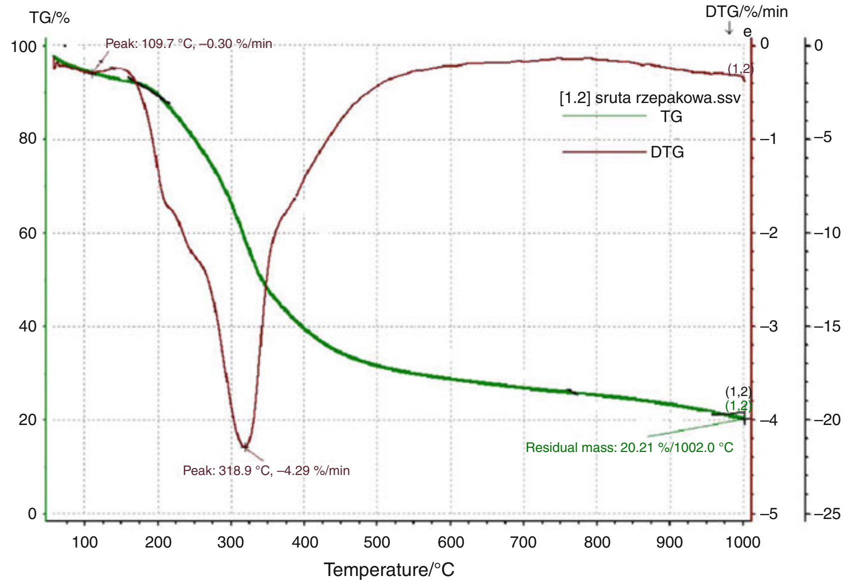


Fig. 4 Curves TG and DTG for rapeseed meal

carbon and hydrogen (H_2, CH_4, H_2O, CO, CO_2, C_2H_6, C_2H_4, C_2H_2), the combination of nitrogen in the form of NH_3 and HCN are also given. These compounds are of importance in the organization of thermal destruction processes of the fuel, because they participate in the autonomous reduction of nitrogen oxides emissions.

Calorific value of processed gases and carbonizate

From the point of energetic utilization of process gases, their caloric content is important. Knowing the quantitative composition of combustible gases (in the form of % mol rates), the calorific value LHVg was calculated in (kJ/kmol) using the formula (1):

$$\begin{aligned}\mathrm{LHVg} = {} & 282984 \cdot \mathrm{CO} + 241818 \cdot \mathrm{H_2} + 802320 \cdot \mathrm{CH_4} \\ & + 1256460 \cdot \mathrm{C_2H_2} + +1323870 \cdot \mathrm{C_2H_4} \\ & + 1428780 \cdot \mathrm{C_2H_6}\ (\mathrm{kJ/kmol}). \qquad (1)\end{aligned}$$

Values obtained according to (1) were calculated to obtain LHVg values given in (kJ/Nm^3). Calorific value LHVg* of pyrolytic gases were calculated also with the use of formula (2) given in [25–27]:

$$\begin{aligned}\mathrm{LHVg}^* = {} & 126.36 \cdot \mathrm{CO} + 107.98 \cdot \mathrm{H_2} + 358.18 \cdot \mathrm{CH_4} + \\ & + 590.36 \cdot \mathrm{C_2H_4} + 637.72 \cdot \mathrm{C_2H_6}\ \left(\mathrm{kJ/Nm^3}\right), \qquad (2)\end{aligned}$$

where (as present authors [25–27]) CO, H_2, CH_4, C_2H_4 and C_2H_6 were the molar percentages of components of the

Table 3 The data rate of mass loss as a function of temperature

Sample type	Peaks on DTG curve			Global mass loss/%	Residue/%
	Reaction group	Temp./°C	Speed of mass loss/%/min		
Fuel PAS'r	I	334.1	−4.82	79.78	20.22
	II	402.4	−4.35		
	III	449.1	−3.80		
	IV	555.6	−0.33		
	V	687.8	−0.82		
Sewage sludge	I	127.3	−0.48	58.35	41.65
	II	311.3	−2.29		
	III	667.2	−0.38		
	IV	990.3	−0.41		
Potato pulp	I	79.2	−0.50	82.32	17.68
	II	315.9	−7.24		
	III	671.0	−0.54		
Rapeseed meal	I	109.7	−0.30	79.79	20.21
	II	318.9	−4.29		

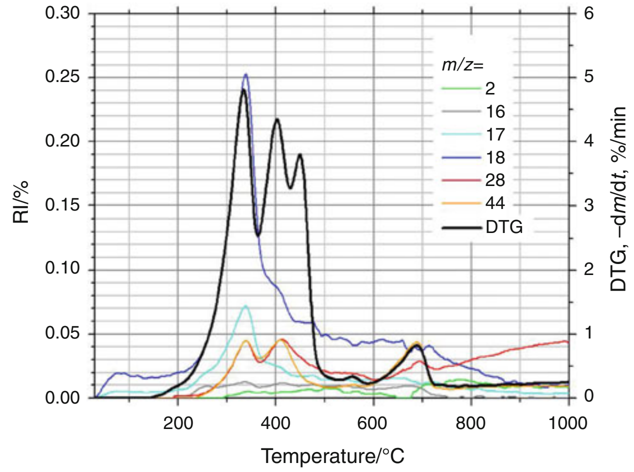


Fig. 5 Fuel PAS'r. Changes in concentrations of fundamental transformation gaseous products

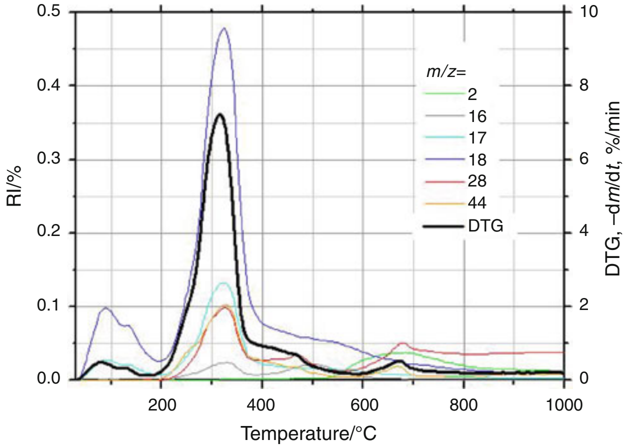


Fig. 7 Potato pulp. Changes in concentration of fundamental transformation gaseous products

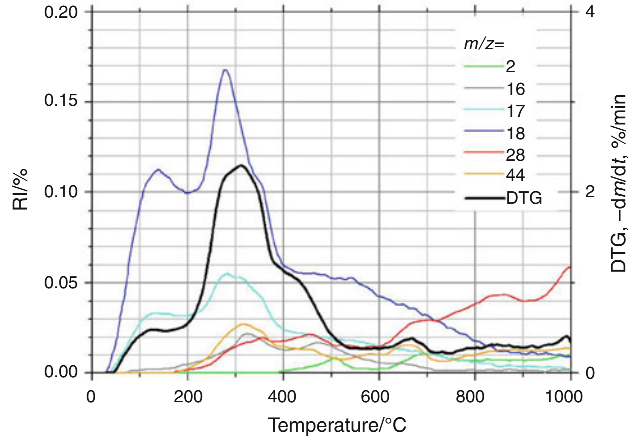


Fig. 6 Sewage sludge. Changes in concentrations of fundamental transformation gaseous products

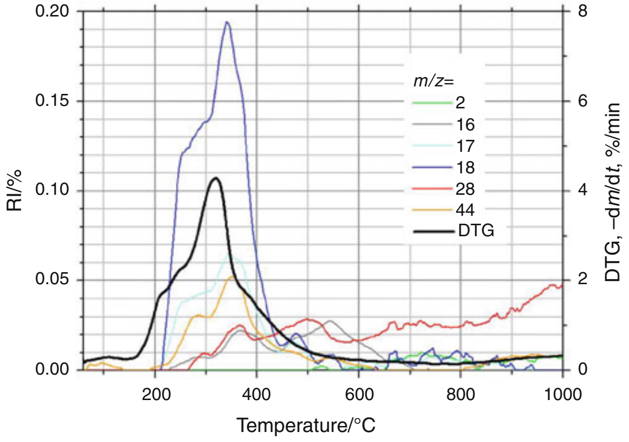


Fig. 8 Rapeseed meal. Changes in concentrations of fundamental transformation gaseous products

Table 4 Rate of transformation products in (%$_{mass}$), created in the temperature range RT (reference temperature–room temperature)/1,000 °C

Sample type	Gas products/%$_{mass}$						Solid residue
	H_2	CH_4	Vapor H_2O	CO	CO_2	Other	
Fuel PAS'r	0.2	0.6	13.5	8.2	11.3	46.0	20.2
Sewage sludge	0.1	1.0	17.6	8.2	9.2	22.2	41.7
Potato pulp	0.4	0.7	23.4	11.6	14.8	31.4	17.7
Rapeseed meal	0.2	1.3	9.9	8.1	10.0	50.3	20.2

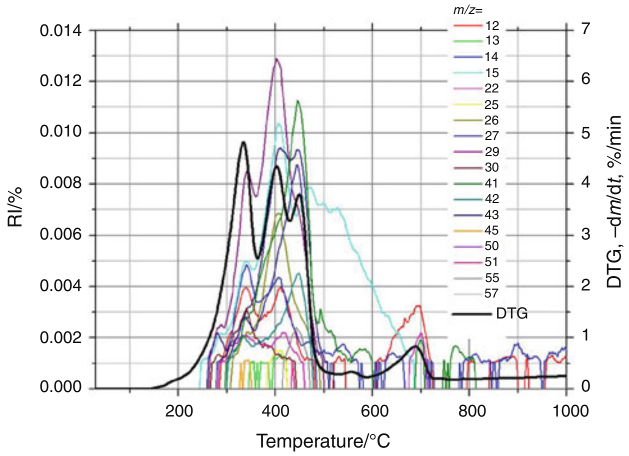


Fig. 9 Fuel PAS'r. Changes in concentrations of other transformation gaseous products

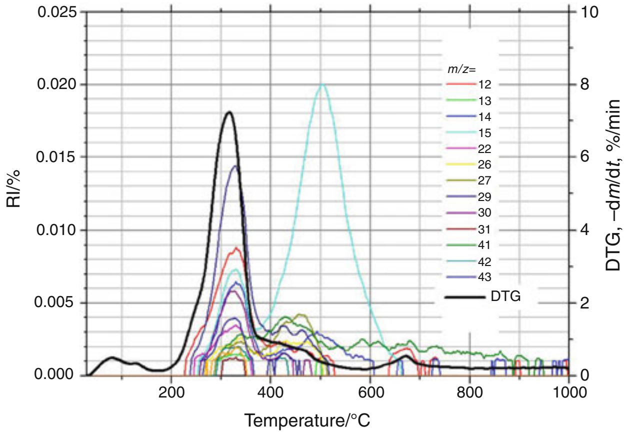


Fig. 11 Potato pulp. Changes in concentrations of other transformation gaseous products

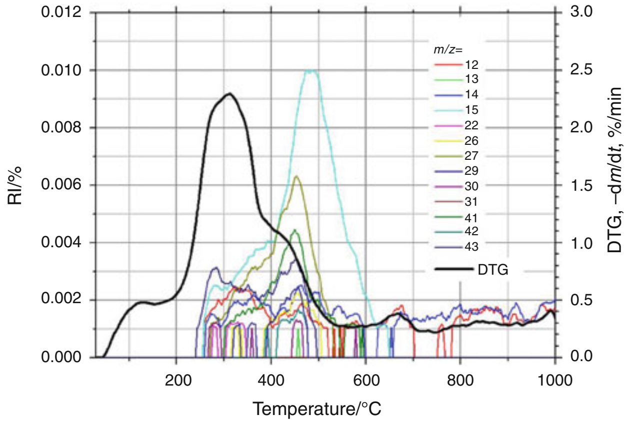


Fig. 10 Sewage sludge. Changes in concentrations of other transformation gaseous products

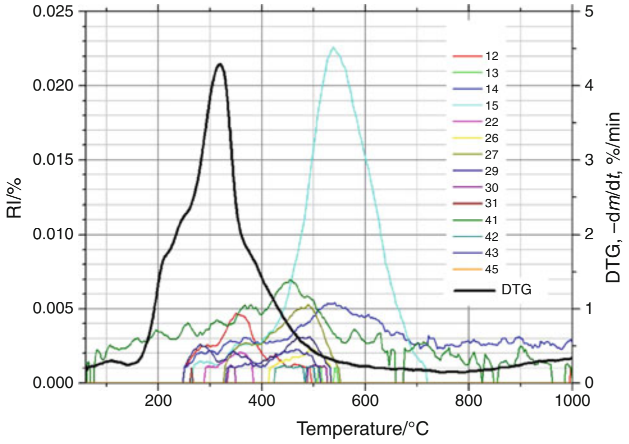


Fig. 12 Rapeseed meal. Changes in concentrations of other transformation gaseous products

product gas. The formula (2) does not include hydrocarbon C_2H_2. Calculated LHVg according to formula (1) and LHVg* according to formula (2) are presented in Table 6.

Solid residue in the form of trial phases of carbonizate, is a product of stored energy, which can be used. Taking [28] coke ash-free calorific value as 32,600 kJ/kg and taking into account ash content of the fuel (Table 1) and the amount of solid post pyrolysis residues (Table 4) its calorific value was calculated.

Calculation relations LHVg applied according to formula (1) and LHVg* according to formula (2), give similar values. The formula (2) does not include hydrocarbon C_2H_2 Analyzing the values in Table 6, it is worth to notice the high calorific value of gas product resulting from

Table 5 Molar percentages of gaseous transformation products, created in the temperature range RT (reference temperature–room temperature)/1,000 °C

Sample type	Gas products/$\%_{mol}$										
	H_2	CH_4	Vapor H_2O	CO	CO_2	C_2H_6	C_2H_4	C_2H_2	NH_3	HCN	Other
Fuel PAS'r	4.3	4.1	39.4	18.9	11.5	2.0	0.9	0.5	12.2	1.0	5.2
Sewage sludge	3.1	5.2	45.7	16.6	8.3	1.4	0.9	0.2	15.7	0.7	2.2
Potato pulp	6.5	3.3	44.2	17.3	9.8	1.9	0.6	0.3	12.4	0.3	3.4
Rapeseed meal	2.7	7.5	32.4	20.7	10.2	4.3	2.7	0.2	13.3	0.8	5.2

Table 6 The calculated values of fuel gases and carbonizate

Sample type	Fuel PAS'r	Sewage sludge	Potato pulp	Rapeseed meal
LHVg acc. to (1)/(kJ/Nm^3)	6407.1	5830.3	5802.9	10040.6
LHVg* acc. to (2)/(kJ/Nm^3)	6127.8	5719.0	5635.8	9929.7
LHV of carbonizate/(kJ/kg)	4,900	9,100	19,900	11,500

decomposition of dry rapeseed meal ~10040 kJ/Nm^3. This value exceeds the calorific value of post pyrolisis gas obtained from pyrolysis of other combustible materials studied, which values range from 5,800–6,400 kJ/Nm^3. The solid after process residue (carbonizate), obtained by dry decomposition of potato pulp, has a high calorific value compared to carbonizates of other fuels. Comparing LHV of carbonizate and taking into account the ash content of individual fuels (Table 1), clearly visible is the effect of the amount of ash on the heating value (LHV) of carbonizate. The reason for the relatively lower calorific values of post pyrolysis gases LHVg obtained in the experiment (confirmed by formula (2) according to [25]) is: (i) the slow process of degradation of dry fuels tested—10 °C/min, (ii) higher ash content in fuels. Higher heating values of pyrolysis gas 10,000–15,000 kJ/Nm^3 are obtained in the process of fast pyrolysis [25, 29] and materials with low ash content.

For example, in [25], where we analyzed the biomass fuel from tobacco waste - the heating speed of biomass samples was 20 °C/min, and ash content 1.5 %, obtained calorific value of gas amounted to 11,990 kJ/m^3. Process temperature has a significant effect on gas composition, and thus on its calorific value. When it comes to literature data on the calorific value of gaseous fuels produced from sewage sludge, in the work [30] it is shown that the LHV takes different values from 6,600 to 8,600 kJ/Nm^3 (depending on the type of sludge and operating conditions). Yet, the LHV of pyrolysis gases of fuels formed from furniture waste (with similar properties as SRF1) obtained in a pilot industrial scale ranged from 5,600 to 11,000 kJ/m^3 [31]. Our previous studies of calorific value of non-condensing gas produced in the industrial technology of wood pyrolysis (birch, hornbeam), showed a value of about 6,000 kJ/Nm^3.

Conclusions

Thermogravimetric studies provide the basis of qualifications of materials and suitability of biomass fuels and fuels formed from waste, converting them into fuel gas generated in the generator process. Studied degradation rate of fuel and temperature range in which they occur are different with the constant speed of heating each sample.

In terms of calorific value of gas obtained, the use of extracted rapeseed meal in the process of pyrolysis turned out to be the most efficient. Its thermal decomposition, of a single transformation, was observed in the temperature range 200–500 °C (with a maximum occurring at about 320 °C). Higher energy efficiency of gas products is justified by higher molar shares of such hydrocarbons as CH_4, C_2H_6, C_2H_4 and CO. It is believed, that these hydrocarbons were formed from the degradation of difficult volatile fat substances, absent in the other test materials. The presence of C_nH_m, NH_3 and HCN in the process gases suggests that the extracted rapeseed meal can be a good natural reburning fuel. Such fuels are used in power boilers to reduce NOx emission. Results of our own research conducted in technical conditions, gave grounds to the conclusion, that prolonged process of thermal destruction of extracted rape meal favors increasing the participation of CO in the after pyrolysis gases, which also affects the growth of their calorific value in relation to gases derived from other fuels.

In the case of biomass materials 500 °C is the temperature limit, beyond which there is solely pyrolysis coke, which is the most advantageous from the viewpoint of the gasification process, as practically from this moment the fuel contains the greatest amount of carbon.

The main thermal decomposition of fuel formed from waste mainly occurs in the same range as the biomass waste (200–500 °C).

Above the temperature of 500 °C there is semi-coke, which degasses into a coke until the temperature reaches 725 °C. Multiple phase transitions (and multiple materiality of fuel) suggests, that further research work should consider partial energy and material balances characteristic for each peak. On this basis, it will be possible to identify the usefulness of those fuels for degassing, gasification or combustion processes. It may occur that the technology of gasification (halfcombustion) for multicomponent fuels from waste is beneficial.

Calorific values of afterpyrolysis gases LHVg obtained in the research indicate differences in relation to the results presented in the literature [25, 29–31]. The differences in these values are caused by different speeds of heating the samples (fast pyrolysis, slow pyrolysis) and a higher ash content in research materials. On the other hand, calculation relations LHVg applied according to formula (1) and LHVg* according to quoted in [25–27] formula (2), give similar values (Table 6; the formula (2) does not include hydrocarbon C_2H_2).

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References

1. Kök MV. An investigation into the combustion curves of lignites. J Therm Anal Calorim. 2001;64:1319–23.
2. Kök MV. Non-isothermal DSC and TG/DTG analysis of the combustion of silopi asphaltites. J Therm Anal Calorim. 2007; 88(3):663–8.
3. Aylón E, Callèn MS, López JM, Mastral AM, Murillo R, Navarro MV, Stelmach S. Assessment of tire devolatilization kinetics. J Anal Appl Pyrol. 2005;74:259.
4. Gonzàlez JF, Encinar JM, Canito JL, Rodrìguez JJ. Pyrolysis of automobile tyre waste. Influence of operating variables and kinetic study. J Anal Appl Pyrol. 2001;58-59:667.
5. Williams PT, Besler S. Pyrolysis-thermogravimetric analysis of tyres and tyre components. Fuel. 1995;74:1277–83.
6. Sułkowski WW, Danch A, Moczyński M, Radoń A, Sułkowska A, Borek J. Thermogravimetric study of rubber waste-polyurethane composites. J Therm Anal Calorim. 2004;78:905–21.
7. Rybiński P, Janowska G, Kucharska-Jastrząbek A, Pająk A, Wójcik I, Wesołek D, Bujnowicz K. Flammability of vulcanizates of diene rubbers. J Therm Anal Calorim. 2010;. doi: 10.1007/s10973-011-1728-x.
8. Galvagno S, Casu S, Martino M, Di Palma E, Portofino S. Thermal and kinetic study of tyre waste pyrolysis via TG–FTIR–MS analysis. J Therm Anal Calorim. 2007;88(2):507–14.
9. Dispenza C, Spadaro G. Cure kinetics of a tetrafunctional rubber modified epoxy-amine system. J Therm Anal Calorim. 2000;61: 579–87.
10. Molto J, Font R, Conesa J. Kinetic model of the decomposition of a PET fibre cloth in an inert and air environment. J Anal Appl Pyrolysis. 2007;79:289–96.
11. Burlett DI. Thermal techniques to study complex elastomer/filler systems. J Therm Anal Calorim. 2004;75:531–44.
12. Benavides R, Castillo BM, Castaneda AO, Lopez GM, Arias G. Different thermo-oxidative degradation routes in poly(vinyl chloride). Polym Degrad Stab. 2001;73:417–23.
13. Di Nola G, de Jong W, Spliethoff H. TG–FTIR characterisation of coal and biomass single fuels and blends under slow heating rate conditions: partitioning of the fuel-bound nitrogen. Fuel Process Technol. 2010;91:103–15.
14. Stolarek P, Ledakowicz S. Thermal processing of sewage sludge by drying, pyrolysis, gasification and combustion. Water Sci Technol. 2001;44(10):333–9.
15. Font R, Fullana A, Conesa JA, Lavador F. Analysis of the pyrolysis and combustion of different sewage sludges by TG. J Anal Appl Pyrolysis. 2001;58:927–41.
16. Gomez-Rico MF, Font R, Fullana A, Martin-Gullon I. Thermogravimetric study of different sewage sludges and their relationship with the nitrogen content. J Anal Appl Pyrolysis. 2005; 74:421–8.
17. Shen L, Zhang DK. An experimental study of oil recovery from sewage sludge by low-temperature pyrolysis in a fluidised-bed. Fuel. 2003;82(4):465–72.
18. Yang H, Yan R, Chen H, Lee HD, Liang DT, Zheng C. In-depth investigation of biomass pyrolysis based on three major components:hemicellulose, cellulose and lignin. Energy Fuels. 2006; 20(1):388–93.
19. Arenillas A, Pevida C, Rubiera F, Garcia R, Pis JJ. Characterisation of model compounds and a synthetic coal by TG/MS/FTIR to represent the pyrolysis behaviour of coal. J Anal Appl Pyrolysis. 2004;71(2):747–63.
20. Fang MX, Shen DK, Li YX, Yu CJ, Luo ZY, Cen KF. Kinetic study on pyrolysis and combustion of wood under different oxygen concentrations by using TG–FTIR analysis. J Anal Appl Pyrolysis. 2006;77(1):22–7.
21. Otero M, Diez C, Calvo LF, Garcia AI, Moran A. Analysis of the co-combustion of sewage sludge and coal by TG–MS. Biomass Bioenergy. 2002;22(4):319–29.
22. Karayildirim T, Yanik J, Yuksel M, Bockhorn H. Characterisation of products from pyrolysis of waste sludges. Fuel. 2006;85: 1498–508.
23. Shao J, Yan R, Chen H, Wang B, Lee DH, Liang DT. Pyrolysis characteristics and kinetics of sewage sludge by thermogravimetry Fourier transform infrared analysis. Energy Fuels. 2008;22: 38–45.
24. Heikkinen J, Spliethoff H. Waste mixture composition by thermogravimetric analysis. J Therm Anal Calorim. 2003;72:1031–9.
25. Yang Y, Tan L, Jin S, Lin Y, Yang H. Catalytic pyrolysis of tobacco rob: kinetic study and fuel gas produced. Bioresour Technol. 2011;102:11027–33.
26. Cheng G, Zhang L, He P, Yan F, Bo Xiao B, Tao Xu T, Jiang Ch, Zhang Y, Guo D. Pyrolysis of ramie residue: kinetic study and fuel gas produced in a cyclone furnace. Bioresour Technol. 2011;102:3451–6.
27. Cheng G, Zhang L, He P, Yan F, Xiao B, Xu T, Jiang Ch, Zhang Y, Guo D. Pyrolysis of ramie residue: kinetic study and fuel gas produced in a cyclone furnace. Bioresour Technol. 2011;102: 3451–6.
28. Hwang IH, Matsuto T, Tanaka N, Sasaki Y, Tanaami K. Characterization of char derived from various types of solid waste from the standpoint of fuel recovery and pretreatment before landfilling. Waste Manag (Oxford). 2007;27:1155–66.
29. Kantarelis E, Zabaniotou A. Valorization of cotton stalks by fast pyrolysis and fixed bed air gasification for syngas production as precursor of second generation biofuels and sustainable agriculture. Bioresour Technol. 2009;100:942–7.
30. Karayildirim T, Yanik J, Yuksel M, Bockhorn H. Characterisation of products from pyrolysis of waste sludges. Fuel. 2006;85: 1498–508.
31. Avenell ChS, Sainz-Diaz CI, Griffitchs AJ. Solid waste pyrolysis in pilot-scale batch pyrolyser. Fuel. 1996;75:1167–74.