## Article

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# Municipal Solid Waste Thermal Analysis – Pyrolysis Kinetics and Decomposition Reactions

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**Abstract:** In this study, 12 organic waste materials were subjected to TG/DTG thermogravimetric analysis and DSC calorimetric analysis. These analyses provided basic information about thermochemical transformations and degradation rates during organic waste pyrolysis. Waste materials were chosen to cover the most abundant waste that can be found in the municipal solid waste stream. Based on TG results, kinetic parameters according to Coats–Redfern method were determined. The pyrolysis activation energy was the highest for cotton 134.5 kJ·(mol·K)<sup>-1</sup> and the lowest for leather 25.2 kJ·(mol·K)<sup>-1</sup>. The DSC analysis showed number of transformations occurred during pyrolysis for each material. For each transformation, normalized energy required for transformation, or released during transformation were determined and then summarized to present energy balance. The study found that only for three waste materials: PET (-220.1 J·g<sup>-1</sup>), leather (-66.9 J·g<sup>-1</sup>), and chicken meat (-130.3 J·g<sup>-1</sup>) energy balance was negative, while the highest positive balance value was found for potato peelings (367.8 J·g<sup>-1</sup>). The obtained results may be applied for the modelling of energy and mass balance of municipal solid waste pyrolysis.

**Keywords:** TGA, DTG, DSC, thermogravimetric analysis, differential scanning calorimetry, municipal solid waste, organic waste, proximate analysis, process kinetics, Coats–Redfern method

#### 1. Introduction

Management of municipal solid waste (MSW) relates to efficiency and optimization of the process as well as sustainable use of products. Effective waste management methods focus not only on minimizing the volume of waste or eliminating sanitary hazards. An important element in the choice of waste treatment technology is the cost-effectiveness of the process [1]. In the case of thermal waste conversion, the volume of waste is significantly reduced or incinerated completely, while high process temperatures ensure the hygienization of waste [2]. Thermal processes including low-temperature pyrolysis are associated with the supply of energy to the process and its recovery in the form of heat or products such as gas, oil, or biochar. The selection of substrates for the process of lowtemperature pyrolysis is connected with thermal characteristics of waste, combustion heat, or basic technical analysis determining the content of ash, volatile matter, and fixed carbon [3]. Organic waste accounts for about 77% share of the MSW stream generated globally including food waste and green waste 44%, plastics 12%, and paper 17%. EU legislation aims to reduce the MSW stream going to landfill below 10% by 2035 [4]. Alternatively, waste going to landfills can be managed in another waste management sector, including thermal waste conversion processes to fuels that are easy to transport and store. The implementation of local pyrolysis plants contributes significantly to the reduction of greenhouse gas emissions [5]. Low-temperature pyrolysis, which is carried out at temperatures up to 500°C, initiates mainly the formation of solid products in the form of biochar. The product of low-temperature pyrolysis can be used not only as a fuel but also as a soil additive for the improvement of crop productivity, and carbon neutrality [6,7].

According to the International Confederation for Thermal Analysis and Calorimetry (ICTAC), thermal analysis is a set of research methods that provide information about the relationship between a test sample and its temperature under controlled heating or cooling conditions [8,9]. Thermal methods are used to study chemical reactions and phase transformations that take place in the material due to temperature changes. It is possible to determine the kinetic or thermodynamic parameters of the process [10]. The thermal parameters (glass transition, melting, decomposition, poly-morphic transformation, the heat of fusion, crystallization, polymorphic transformation, and specific heat) provide information about the properties of the materials studied, but also about how they were produced [10].

TGA thermal analysis is used to determine changes in physical and chemical properties at an increasing temperature as a function of time, taking into account the mass loss of the sample [11]. The physical transformations observed during the TGA study are second-order phase transformations, desorption, or evaporation. In the case of chemical transformations, changes related to oxidation degradation, decomposition, loss of volatile organic compounds (VOC) are observed [12].

Differential Scanning Calorimetry (DSC) works on the principle of measuring heat intensity, more precisely the difference in flux between the test and reference samples during thermal transformations [11]. The DSC method is used, among other things, for characterization of materials, stability studies, phase diagram evaluation, kinetics studies, or determination of heat capacity. DSC is dependent on measurement parameters such as heating rate, temperature, and sample size [13]. The measurement curve defines peaks that are assigned to exothermic and endothermic reactions. The above information leads to the possibility of studying the energy balance of materials during waste thermal treatment [14].

The combined methods of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) mainly report the changes in heat intensity due to ongoing chemical reactions combining this with the mass changes. Parameters related to phase transformations and thermal stability, latent heat enthalpy are critical in standardizing material properties in the long term [15].

This study aimed to analyze thermal characteristics of selected components of six groups of MSW: paper (fiscal receipts, cotton wool), cardboard (grey cardboard, egg cartons), textiles (cotton, natural leather), plastics (polyethylene terephthalate (PET), polyurethane (PU)), hygienic waste (pampers, leno), biodegradable waste (meat, potato peelings) [16–19]. The analyses resulted in the organic matter decomposition reaction rate constant, activation energy, and identification of thermal balance of phase transformations during thermal degradation of individual wastes. The analyses provided information on the energy intensity of the low-temperature pyrolysis of components of MSW.

#### 2. Materials and Methods

#### 2.1. Sample collection and preparation

Organic waste can be divided into six basic groups as follow: paper, cardboard, textiles, plastics, hygiene waste, biodegradable waste. For each, group two waste materials were selected to be studied. Chosen materials are presented in Table 1. The materials were dried in a laboratory dryer (WAMED, KBC-65W, Warsaw, Poland), and then they were ground using the knife mill (Testchem, LMN-100, Pszów, Poland) to a size lower than 0.425 mm to ensure homogeneity.

Waste groups	<b>Research materials</b>				
Papar	Receipt				
raper	Cotton wool				
Cardboard	Cardboard				
Caruboaru	Egg carton				
Towtilog	Cotton				
Textiles	Leather				
Diactics	Polyethylene (PET)				
Flastics	Polyurethane (PU)				
Uniona masta	Diapers				
Hygiene waste	Leno				
Piedeara dable avecto	Chicken meat				
biodegradable waste	Potato peel				

Table 1. Research materials from six basic groups of waste.

## 2.2. Proximate analysis

The materials were subjected to proximate analysis. The moisture content (MC) was determined using the laboratory dryer (WAMED, KBC-65W, Warsaw, Poland). The volatile matter (VM) was determined using thermogravimetry equipment consist of the laboratory balance (RADWAG, PS 750.3Y, Warsaw, Poland) coupled with the tubular furnace (Czylok, RST 40x200/100, Jastrzębie-Zdrój, Poland) by the TGA method [20]. The ash content (AC) was determined using a muffle furnace (Snol 8.1/1100, Utena, Lithuania) according to the procedure given by Syguła et al [21]. Then the fixed carbon (FC) was calculated according to J.G. Speight [22]. Additionally, volatile solids (VS) were determined using a muffle furnace (Snol 8.1/1100, Utena, Lithuania) according to Randazzo et al [23]. The VS is also known as organic matter content or loss on ignition. Next, a high heating value was determined using a calorimeter (IKA® Werke GmbH, C200, Staufen, Germany) according to Świechowski et al. [24,25].

#### 2.3. Thermogravimetric analysis (TGA)

Thermogravimetric analyses were carried out using thermogravimetry equipment consist of the laboratory balance (RADWAG, PS 750.3Y, Warsaw, Poland) coupled with the tubular furnace (Czylok, RST 40x200/100, Jastrzębie-Zdrój, Poland). The materials were dried before analysis. For each analysis, a 1.5 g sample was used. First, the sample was placed into a steel crucible. Next, the crucible was placed into the furnace and the furnace had been filled with CO<sub>2</sub> gas. CO<sub>2</sub> was delivered to the center of the furnace at 10 dm<sup>3</sup>·h<sup>-1</sup> to facilitate an inert atmosphere. After that, a sample was heated from room temperature (~20 °C) to 850 °C at 5 °C·min<sup>-1</sup> heating rate. For each sample, three replications were done.

The mass and temperature were recorded with a 1 s interval with resolutions of 0.001 g and 1 °C, respectively. The raw TGA data were smoothed using the Loess method (smoothing parameter: Span=0.05) [26]. Then, smoothed data was used for the calculation of derivative thermogravimetry (DTG).

# 2.4. Differential scanning calorimetry (DSC)

Differential scanning calorimetry was performed using a differential scanning calorimeter (Mettler Toledo, DSC 822e, Warsaw, Poland). Medium pressure crucibles (120  $\mu$ l) with a capacity of 5 mg were used for the analysis. The materials were heated from room temperature to 500 °C, at 5°C · min<sup>-1</sup>. As an inert gas, nitrogen was used at a 3.6 dm<sup>3</sup>·h<sup>-1</sup> flow rate. The analysis provided information on the type of transformations occurring during the decomposition of the materials (endothermic and exothermic). Each transformation

was characterized by: (i) the beginning transformation temperature, (ii) the peak transformation temperature, (iii) the ending transformation temperature, and energy needed or released for/from transformation.

#### 2.5. Kinetics analysis

The TG results were subjected to kinetic analysis of organic waste decomposition. In this study, the Coats-Redfern (CR) method was used to evaluate kinetic triplet. The CR is a model-free, integral method [27]. The kinetic triplet for the CR method is energy activation (*Ea*), pre-exponential factor (*A*), and order of reaction (*n*). In this study *n*, *Ea*, and *A* were determined at a heating rate of 5 °C·min<sup>-1</sup> with assumptions that  $n \neq 1$ . In the CR method, mentioned parameters are determined from kinetic plot wherein the kinetic plot for  $n \neq 1$  is  $ln = \frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}$  versus  $\frac{1}{T}$ , where:  $\alpha$  - conversion (-), *T* - absolute temperature (K), *n* - order of reaction (-) [28]. The plot provides a slope that is equal to  $-\frac{Ea}{R}$ , and intercept that is equal to  $ln = \frac{AR}{\beta E_a}$  where,  $E_a$  – activation energy (kJ·mol<sup>-1</sup>·K<sup>-1</sup>), *R* – universal gas constant (kJ·kmol<sup>-1</sup>·K<sup>-1</sup>), *A* - pre-exponential factor (min<sup>-1</sup>), and  $\beta$  - heating rate (°C·min<sup>-1</sup>) [29]. The full methodology of the CR method can be found in cited references [27-29].

## 3. Results and discussion

## 3.1. Proximate analysis

The results of proximate analysis for all materials are presented in Table 2. The data indicate that the MC for almost all materials is less than 10%, which is important for pyrolysis because a waste with low MC is considered to be a good substrate for the process [30]. The lowest MC was found for plastics; the MC was 0.36%, and 1,79 for PET and PU, respectively. The highest MC was found for biodegradable waste, the potato peel, and the chicken meat have had over 50% of moisture. The content of VS was found in all samples relatively high (82.51% - 99.81%). The VM content ranged from 69.9% for potato peel to 96.7% for cotton. Moreover, the AC remains low with values varied from 0.10% for PET to 14.53% for the receipt. High VM content indicates that tested materials are easy to ignite [31] and low ash content, indicates that there will be no problem with residual disposal when materials are used as fuel. The highest FC content was found in leather (23.0%), and the lowest in diapers (0.4%) [30]. FC is the carbon remaining after devolatilization and the higher FC content, the higher the biochar yield [32], thus leather may be a good substrate for pyrolysis. The highest higher heating value (HHV) was found for PET (42.68 MJ·kg<sup>-1</sup>), while the lowest value was found for the receipt (15.01 MJ·kg<sup>-1</sup>). The inverse proportionality was noticed between AC and HHV; lower AC implements higher HHV [33].

Material	*MC, %	**VS, %	**VM, %	**FC, %	**AC, %	HHV, MJ·kg <sup>-1</sup>
Chicken	53.3	95.71	86.50	9.50	3.93	25.18
Potato Peel	51.2	86.69	69.90	18.70	11.93	17.63
Cotton	4.56	99.65	96.70	2.90	0.33	22.37
Leather	9.88	94.60	73.40	23.00	3.50	22.84
Receipt	5.66	82.51	76.10	9.40	14.53	15.01
Cotton Woll	5.22	99.41	95.00	4.50	0.56	16.27
Polyethylene (PET)	0.36	99.81	89.30	10.60	0.10	42.68
Polyurethane (PU)	1.79	91.54	86.10	8.30	5.57	15.83
Diapers	3.34	86.73	89.40	0.40	10.63	28.37
Gauze	3.84	99.08	95.30	4.00	0.60	19.43
Cardboard	5.76	85.24	71.30	17.80	10.93	15.70
Egg Carton	5.60	82.98	77.30	10.00	12.60	16.58

Table 2. Proximate analysis results of research materials.

*as received basis	
**dry basis	

## 3.2. Kinetics analysis

Based on the Coats-Redfern method kinetic parameters such as activation energy, reexponential, and the order of a reaction were determined. The parameters for all samples along with the linear regression coefficient are summarized in Table 3. The average activation energy values ranged from 25.2 kJ·(mol·K)<sup>-1</sup> for leather to 134.5 kJ·(mol·K)<sup>-1</sup> for cotton with a standard deviation of 1.5 kJ·(mol·K)<sup>-1</sup> and 18.7 kJ·(mol·K)<sup>-1</sup>, respectively. Materials with lower energy activation make better feedstock for the thermochemical process, as high energy activation causes slowing down the chemical reaction [34]. The pre-exponential factor is directly related to the number of times the volatiles will collide causing a reaction [35]. The pre-exponential factor values ranged from 2.0 min<sup>-1</sup> for leather to 2.3 min<sup>-1</sup> for cotton. This shows the dependence that the higher the pre-exponential factor, the higher the activation energy. The determination coefficient (R<sup>2</sup>) for all samples, except for cotton wool and PET, was above 0.90, which indicates that the reaction order was correctly determined for all tested materials [27].

Mataila	Charles Charles	n	Ea	Α	<b>R</b> <sup>2</sup>
Materials	Statistics	-	kJ·(mol·K)-1	min <sup>-1</sup>	-
Descipt	Mean	3.52	126.6	$1.4 \cdot 10^{9}$	0.96
Receipt	SD	0.20	8,7	$1.5 \cdot 10^9$	
Catton wool	Mean	2.31	68,7	8.0·10 <sup>3</sup>	0.89
Cotton wooi	SD	0.10	0.5	$8.0 \cdot 10^{2}$	
Candhaand	Mean	1.46	32.7	10.0	0.93
Cardboard	SD	0.19	4.6	8.0	
Egg corton	Mean	2.24	63.9	$1.9 \cdot 10^4$	0.96
Egg carton	SD	0.37	14.1	$3.2 \cdot 10^4$	
Catton	Mean	3.67	134.5	2.3·10 <sup>11</sup>	0.96
Cotton	SD	0.44	18.7	3.9·10 <sup>11</sup>	
Loothor	Mean	1.25	25.2	2.0	0.96
Leather	SD	0.09	1.5	1.0	
Polyethylene	Mean	2.31	117.0	$4.8 \cdot 10^{6}$	0.87
(PET)	SD	0.01	1.0	7.2·10 <sup>5</sup>	
Polyurethane	Mean	1.60	51.5	5.3·10 <sup>3</sup>	0.95
(PU)	SD	0.63	24.3	9.0·10 <sup>3</sup>	
Diamore	Mean	1.41	62.1	6.5·10 <sup>3</sup>	0.91
Diapers	SD	0.52	29.8	6.0·10 <sup>3</sup>	
Lana	Mean	1.60	55.9	6.3·10 <sup>2</sup>	0.94
Leno	SD	0.16	9.0	8.0·10 <sup>2</sup>	
Chickon most	Mean	2.38	76.4	$1.5 \cdot 10^4$	0.97
	SD	0.07	2.8	$7.3 \cdot 10^{3}$	
	Mean	2.48	71.7	$7.9 \cdot 10^4$	0.97
Potato peel	SD	0.42	10.7	$8.7 \cdot 10^4$	

**Table 3.** Kinetics analysis of research materials with  $\beta$ =5 K·min<sup>-1</sup>.

3.3.1. Paper

<sup>3.3.</sup> TG/DTG and DSC analysis

A decrease in mass as a function of temperature for the receipts (Fig. 1a) and the cotton wool sample was observed (Fig. 1b). The lag phase of the cotton lasted 36 minutes and the receipts lasted 50 minutes to temperatures of 194 and 258°C, respectively. The most dynamic weight decreases for cotton wool occurred between 77 and 101 minutes from 396 to 513°C respectively) while for receipts between 68 and 95 minutes from 350 to 480°C.

A decrease in mass for these materials was related to the decomposition of organic compounds such as hemicellulose, cellulose, and lignin. Thermal degradation of these compounds occurs in the ranges of  $220 \div 320^{\circ}$ C,  $320 \div 400^{\circ}$ C,  $320 \div 900^{\circ}$ C, respectively [36,37].



Figure 1. Characteristics of the TG/DTG of paper waste; (a) receipt (b) cotton wool

The three transformations in both receipt (Fig. 2a) and cotton wool (Fig. 2b) have been identified during DSC tests. The first and the second are exothermic and the third is endothermic. These transformations are also characterized by similar start and end temperatures. The balance of these transformations is higher for the cotton wool sample. Both samples are composed mainly of cellulose. The receipts will additionally include the compounds present in the carcasses. The first of the transformations, in both samples, occurred at about 200°C. It explains the onset of hemicellulose depolymerization, and in the case of receipts, it may also be related to bisphenol A, which is present in some receipts. The boiling point of this compound is 220°C. The temperatures of the other two transformations indicate that they have associated with the decomposition of biopolymers: hemicellulose in 220 ÷ 320°C, cellulose in 320 ÷ 400°C, and lignin in 320 ÷ 900°C.

The energy balance determines the amount of energy transformations occurring during the thermal conversion process of tested materials (Tab. 4). Reactions are divided into exothermic and endothermic reactions. Three transformations occurred in the thermal analysis of the receipt. The first transformation was exothermic (5.3 J·g<sup>-1</sup>), the second transformation exothermic (344.6 J·g<sup>-1</sup>) and the last transformation endothermic (-135.9 J·g<sup>-1</sup>). The energy balance of thermal transformation of the receipts was positive (214.0 J·g<sup>-1</sup>). In the case of cotton wool, the first transformation was exothermic (21.0 J·g<sup>-1</sup>), the second transformation exothermic (399.0 J·g<sup>-1</sup>) and the last transformation endothermic (-123.3 J·g<sup>-1</sup>). The energy balance of the thermal conversion of this material was exothermic (296.4 J·g<sup>-1</sup>).



Figure 2. Characteristics of the DSC of paper waste; (a) receipt (b) cotton wool

DSC character-	Type of			Tra	nsformati	ion			_
istics	material	1	2	3	4	5	6	7	_
The tempera-									
ture of transfor-		196.8	276 7	421 5	_	_	_	_	
mation begin-		170.0	270.7	421.0					
ning, °C									
The tempera-	Receipt								
ture of transfor-	Receipt	212.7	314.1	426.1	-	-	-	-	
mation peak, °C									
The tempera-									
ture of transfor-		221.7	336.0	429.6	-	-	-	-	
mation end, °C									
Energy balance, J.	g-1	5.3	344.6	-135.9	-	-	-	-	214.0
The tempera-									
ture of transfor-		204.4	291 7	434 7	_	_	_	_	
mation begin-		201.1	271.7	101.7					
ning, °C									
The tempera-	Cotton								
ture of transfor-	wool	238.9	311.8	436.1	-	-	-	-	
mation peak, °C									
The tempera-									
ture of transfor-		251.3	324.8	444.1	-	-	-	-	
mation end, °C									
Energy balance, J.	5-1	21.0	398.7	-123.3	-	-	-	-	296.4

 Table 4. Normalized transformation energy for successive transformations of tested paper waste and energy balance of the process

3.3.2. Cardboard

In the case of cardboard (Fig. 3a), the first mass decrease occurred around 28 minutes at 150°C, and the second, which was much faster, occurred at 73 minutes at 375°C. The first one lasted about 18 minutes and the second 28 minutes. The mass decreases ended at 239 and 510°C, respectively. For the egg cardboard (Fig. 3b), the weight decrease occurred at about 64 minutes at 330°C and lasted for 32 minutes. The decrease in weight for cardboard and egg cartons will mainly be related to the decomposition of the pulp, which consists of biopolymers such as cellulose, hemicellulose and lignin, and ashes. The decrease in mass begins between 200 and 300°C and is associated with the aforementioned biopolymers [38].



Figure 3. Characteristics of the TG/DTG of cardboard waste; (a) cardboard (b) egg cardboard

DSC characteristics of cardboard (Fig. 4a) show four transformations - the first, second and third are exothermic, while the fourth is endothermic. Cardboard is a cellulosic material, so both its thermal decomposition and phase transformations should be like those of leno, cotton, and paper waste. Unprocessed cardboard contains approximately 32% hemicellulose, 6% lignin, 48% cellulose, and 14% inorganic matter. The same will be the case with the egg cardboard sample (Fig. 4b) [36]. The similarity of these materials is that the first transformations are exothermic while the last ones are endothermic. It is associated with the breakdown of hemicellulose, cellulose, and lignin. They will be therefore distributed between 220 and 900°C.

Four transformations occurred in the thermal analysis of cardboard. The first three transformations were exothermic leading to releasing of heat 12.1 J·g<sup>-1</sup>, 357.0 J·g<sup>-1</sup>, 10.4 J·g<sup>-1</sup>, respectively (Tab. 5). The last transformation was endothermic -188.8 J·g<sup>-1</sup>. The energy balance of the thermal transformation of the cardboard was positive (190.8 J·g<sup>-1</sup>).

There were three thermal transformations during the thermal analysis of egg cardboard. The first transformation was exothermic (67.0 J·g<sup>-1</sup>), the second transformation was also exothermic (159.5 J·g<sup>-1</sup>), however, the last transformation was endothermic (-132.4 J·g<sup>-1</sup>). The energy balance of thermal egg cardboard conversion was exothermic (94.0 J·g<sup>-1</sup>).



Figure 4. Characteristics of the DSC of cardboard waste; (a) cardboard (b) egg cardboard

DSC character-	Type of			Tran	sformation				_
istics	material	1	2	3	4	5	6	7	_
The tempera-									
ture of transfor-		174.6	271.6	339 1	433 5	_	_	_	
mation begin-		174.0	271.0	007.1	100.0				
ning, °C									
The tempera-	Cardboard	196.2	307.6	355.7	436.5	-	-	-	
ture of transfor-	Curaboura								
mation peak, °C									
The tempera-									
ture of transfor-		209.6	323.3	367.2	447.2	-	-	-	
mation end, °C									
Energy balance, J	g-1	12.1	357.0	10.4	- 188.8	-	-	-	190.8
The tempera-									
ture of transfor-		219.7	293.3	460.2	-	_	_	-	
mation begin-			_,,,,,	1001					
ning, °C									
The tempera-	Egg carton								
ture of transfor-	288 сагон	252.7	318.4	461.6	-	-	-	-	
mation peak, °C									
The tempera-									
ture of transfor-		289.5	338.8	464.7	-	-	-	-	
mation end, °C									
Energy balance, J.	g <sup>-1</sup>	67.0	159.5	- 132.4	-	-	-	-	94.0

**Table 5.** Normalized transformation energy for successive transformations of tested cardboard waste and energy balance of the process

The TG/DTG curves for natural leather and cotton textile are shown in figures 5a and 5b. For cotton textile, the first stage of the process, i. e. the lag phase, took longer at about 53 minutes than for natural leather at 23 minutes. The weight drop of the leather sample clearly shows two distinct weight drops, the first between 23 and 53 minutes at 130 to 274°C, and the second between 70 and 116 minutes for 360-585°C, respectively. The last weight drop for natural leather occurred at 167 minutes and for cotton at 170 minutes of measurement [39].



Figure 5. Characteristics of the TG/DTG of textile waste; (a) cotton textile (b) leather

The DSC characteristics of the cotton textile are shown in figure 6a. Five transformations are visible, one exothermic and four endothermic. The first transformation started at about 251°C. At this temperature, hemicellulose, and cellulose, which are the main components of cotton, are broken down. Also, further transformations that originate at about 310 to 415°C, respectively, will be associated with transformations of these biopolymers [40].

Comparing the DTG curves of lenos (fig. 9b) and cotton (fig. 5a), only one exothermic transformation occurred for these materials. The transformations of the lenos sample compared to the cotton sample started at lower temperatures and ended at higher temperatures. The two materials tested differ in the number of agents added - in the case of lenos it was just hydrogen peroxide, whereas in the case of cotton it could be several different compounds associated with fabric dyeing. According to the characteristics of textile dyeing technology in the EU, in addition to dyes, these can be agents such as sodium hydroxide, sodium carbonate, sodium chloride, or sodium sulfate. They melt at 318-323°C, 854°C, 801°C and 884°C respectively [41]. This shows that sodium hydroxide may have affected the exothermic peak that occurred between 310 - 319°C. Like the leno between 380 - 600°C. there will be a main pyrolysis process that will produce L-glucose and various combustible lenos. In addition, there are several dyes of various origins that can affect the thermal decomposition process and phase transformations of the cotton sample. Such dyes may include canthaxanthin - melting point 217°C, vitamin B2 - melting point 290°C, sodium chlorate - melting point 247°C, boiling point 300°C, para-aminophenol - melting point 186°C, boiling point 284°C.

Figure 6b shows the DSC characteristics for natural leather, used in the textile industry are composed of water, proteins, fats, and mineral salts. Since protein denaturation occurs at temperatures below 100°C, the peaks in Figure 6b cannot be assumed to be associated with protein transformation. It is more likely that they are related to fat breakdown and protein denaturation products. In addition, agents added to the hides during processing and dyes will react during the transformation. The first three transformations are exothermic and the next two are endothermic.

Five transformations occurred in the thermal analysis of cotton textile. The first transformation was exothermic (412.4 J·g<sup>-1</sup>), the second transformation endothermic (-37.4 J·g<sup>-1</sup>), the third transformation endothermic (-48.4 J·g<sup>-1</sup>), the fourth transformation endothermic (-17.2 J·g<sup>-1</sup>) and the last transformation was also endothermic (-34.2 J·g<sup>-1</sup>). The energy balance of thermal transformation of the cotton textile was exothermic (275.2 J·g<sup>-1</sup>) (Tab. 6).

Five thermal transformations occurred during the process of thermal leather analysis. The first transformation was exothermic (25.2 J·g<sup>-1</sup>), the second transformation exothermic (54.4 J·g<sup>-1</sup>), the third transformation exothermic (4.9 J·g<sup>-1</sup>), the fourth transformation endothermic (-128.9 J·g<sup>-1</sup>) and the last transformation endothermic (-22.4 J·g<sup>-1</sup>). The energy balance of thermal material conversion was negative (-66.8 J·g<sup>-1</sup>) (Tab. 6).



Figure 6. Characteristics of the DSC of textile waste; (a) cotton textile (b) leather

 Table 6. Normalized transformation energy for successive transformations of tested textile waste

 and energy balance of the process

DSC character-	Type of			Transf	ormation			
istics	material	1	2	3	4	5	6	7
The tempera- ture of transfor- mation begin- ning, °C	Cotton textile	250.8	310.1	334.8	408.3	414.5	-	-

The tempera-								_
ture of transfor-	286.9	312.6	338.4	408.5	415.6	-	-	
mation peak, °C								
The tempera-								
ture of transfor-	305.1	319.5	345.0	411.5	418.2	-	-	
mation end, °C								
Energy balance, J·g <sup>-1</sup>	412.4	- 37.4	-48.4	- 17.2	- 34.2	-	-	275.2
The tempera-								
ture of transfor-	1/8 8	213.1	300 5	159 3	480.3			
mation begin-	140.0	210.1	500.5	437.3	400.5	-	-	
ning, °C								
The tempera-								
ture of transfor-	187.0	248.9	308.9	460.6	485.9	-	-	
mation peak, °C								
The tempera-								
ture of transfor-	200.1	262.7	330.8	466.1	489.8	-	-	
mation end, °C								
Energy balance, J·g <sup>-1</sup>	25.2	54.4	4.9	- 128.9	- 22.4	-	-	- 66.8

## 3.3.4. Plastics

Figures 7a and 7b show the TG/DTG curves of PU and PET. Polyurethane began to decompose much faster than PET (Fig. 7a). The first noticeable mass decrease occurred at about 58 minutes of the process at a temperature of about 295°C. For the PET sample, the first noticeable decrease in mass occurred around 95 minutes at 480°C. The time at which the greatest decrease in material weight occurred was 24 min and 57 min for PET and PU, respectively. The thermal decomposition time of the PET sample started at a much higher temperature and was more than twice lower than that of the PU sample. The end of weight loss occurred at 119 minutes for PET and 114 minutes for PU at 595 and 572°C, respectively. The first slight weight loss may be due to the phase change of compounds that are added to the plastics during their production, or the phase change associated with the transition from the solid to the plastic phase. PU sample weight was observed from about 120°C, but up to 300°C the decreases were small (Fig. 7b). These decreases can be combined with the transformations of isocyanates, which have a boiling point of about 208°C. The most dynamic mass decrease was observed in the temperature range from 320 to 600°C. The decrease in weight of this material will be mainly related to the decomposition of polyols, the second of the two main components of polyurethane [42].



Figure 7. Characteristics of the TG/DTG of plastic waste; (a) PET (b) PU

For PU, seven transformations were recorded during DSC analysis (Fig. 8b). Polyurethane materials lose their thermal strength between 150 and 200°C, decomposing into products of different compositions and toxicity [43]. The first transformation occurred between 63.93 and 160.99°C. Due to the large range of temperatures, it is not possible to identify which compounds have been transformed - it could be mannitol or erythritol, which have melting points of 168 and 120°C, respectively. Another one of the transformations from 190.98 to 215. 96°C can be associated with the boiling of ethyl glycol - 198°C, melting of perseitol - about 185°C, boiling of xylitol - 216°C or isocyanate - 208°C. The third transformation started at 218.70°C and ended at 239°C - this is associated with the boiling of polycarbonate, which has a melting point of 230°C, or the melting of inositol (222 -227°C). Another transformation that can be related to the phase transformations of polyols starts at 288. 94 and ends at 324.69°C. In this temperature range, glycerol - 209°C, inositol - 291°C, perseitol - 296°C, and erythritol - about 330°C boils. The transformations described so far are not responsible for the significant mass loss that occurred between 300 and 550°C (Fig. 8). The last transformation  $(373.56 - 460.17^{\circ}C)$ , which is the most exothermal, is related to the critical point of glycol, whose critical point temperature is 446°C.

The DSC curve of PET material shows that the first transformation occurred between 240.24 and 260.73°C (Fig. 8b). At the same temperature, however, there was no change in mass during DTG/TG analysis. In the case of PET, the first decrease in mass occurred at around 300°C and the second at around 400°C, but they were small at the 0.01 g level. A noticeable decrease in mass did not occur until about 480°C and continued until about 600°C.

Two transformations occurred in the thermal analysis of PET. The first transformation was endothermic (-36.0 J·g<sup>-1</sup>) and the second transformation was endothermic (-184.1 J·g<sup>-1</sup>). The energy balance of thermal transformation of the PET was negative (-220.2 J·g<sup>-1</sup>) (Tab. 7).

Seven thermal transformations occurred in the process of thermal PU analysis. The first transformation was exothermic (9.2 J·g<sup>-1</sup>), the second transformation exothermic (15.4 J·g<sup>-1</sup>), the third transformation exothermic (6.8 J·g<sup>-1</sup>), the fourth transformation exothermic (4.3 J·g<sup>-1</sup>), the fifth transformation exothermic (3.5 J·g<sup>-1</sup>), the sixth transformation



exothermic (2.0 J·g<sup>-1</sup>) and the last transformation exothermic (133.9 J·g<sup>-1</sup>). The energy balance of the thermal conversion of the material was exothermic (175.0 J·g<sup>-1</sup>).

Figure 9. Characteristics of the DSC of plastic waste; (a) PET (b) PU

 Table 7. Normalized transformation energy for successive transformations of tested plastic waste and energy balance of the process

DSC character-	Type of	Transformation								
istics	material	1	2	3	4	5	6	7	-	
The tempera-										
ture of transfor-		240.2	455 1							
mation begin-		240.2	455.1	-	-	-	-	-		
ning, °C										
The tempera-	PFT									
ture of transfor-	1 1 1	253.9	454.4	-	-	-	-	-		
mation peak, °C										
The tempera-										
ture of transfor-		260.7	459.7	-	-	-	-	-		
mation end, °C										
Energy balance, J·g	r-1	-36.0	-184.1	-	-	-	-	-	- 220.2	
The tempera-										
ture of transfor-		63.9	191 0	218 7	241.8	262 5	288.9	373.6		
mation begin-		00.7	171.0	210.7	211.0	202.0	200.9	070.0		
ning, °C										
The tempera-	PU									
ture of transfor-	10	115.6	207.4	225.7	247.0	271.4	305.0	419.7		
mation peak, °C										
The tempera-										
ture of transfor-		161.0	216.0	239.1	259.3	282.2	324.7	460.2		
mation end, °C									_	

Energy balance, J·g <sup>-1</sup>	9.2	15.4	6.8	4.3	3.5	2.0	133.9	175.0

#### 3.3.5. Hygiene waste

The TG/DTG curves of hygiene waste are shown in Figure 9a diapers and 9b leno. The first noticeable mass decrease for both materials was observed around 70 minutes at 355°C for pampers and 345°C for leno. The most dynamic mass decrease lasted 51 and 48 minutes and ended at 620°C and 571°C, respectively. In the case of diapers (Fig. 9a), their weight loss will be related to the distribution of superabsorbent (superabsorbent polymers) and cellulose. They account for 33% and 24% of the weight of disposable diapers, respectively [44]. In the case of leno (Fig. 9b), the decrease in mass will be mainly due to the decomposition of cotton, i. e. cellulose, from which the dressing leno is made. The most dynamic weight loss began at 300°C.



Figure 9. Characteristics of the TG/DTG of hygiene waste; (a) diapers (b) leno

The DSC curve produced for the diapers is shown in Figure 10a. Six transformations four endothermal and two exothermal were observed during the study. The first two transformations occur in the temperature ranges 124.34 - 131.35°C and 156.12 - 172.11°C. These transformations can be related to the melting point of PEHD plastic, 125°C, which represents about 2.2% of the diaper weight, and the melting of polypropylene-PP, 5.8% of the disposable diaper, which occurs between 160 and 170°C [39]. The next two exothermal transformations are related to the decomposition of cellulose pulp, which constitutes about 24%, and the decomposition of superabsorbents, which constitute about 33% of the pampers weight. Cellulose pulp, like biopolymers, decomposes between 220 and 400°C (hemicellulose and cellulose). This form of cellulose, due to prior processing, can begin to decompose at lower temperatures than the cellulose contained in cardboard or plants. The third transformation will result from the decomposition of hemicellulose, while the fourth from the decomposition of cellulose. The latter two, like the first two, are endothermic. They occur at higher temperatures than the others - between the end of the fourth transformation and the beginning of the fifth, there is a difference of about 115°C. These transformations may result from the decomposition of lignin, but may also be associated with the decomposition of substances formed during earlier transformations [36].

Figure 10b shows the DSC analysis of the dressing leno. According to the manufacturer's description, it is made of 100% cotton and is bleached with hydrogen peroxide. The thermal decomposition of this material will be related mainly to the decomposition of the cellulose fibres of which cotton is composed and to the reactions that hydrogen peroxide will undergo. The first endothermic transformation originates at 110°C and is related to the breakdown of cotton fibers, which occurs between 110 and 150°C. This transformation can also be associated with the boiling of hydrogen peroxide, whose boiling point is set at 150°C. During these transformations, primarily physical changes occur in the cotton fibers. The subsequent transformations can be related to the decomposition of the main component of the leno, namely cellulose and hemicellulose, whose decomposition occurs from 220 to 400°C. The largest and most dynamic mass loss occurred between 380 and 600°C. The main pyrolysis process also occurs at these temperatures. In this temperature range, L-glucose and various combustible gases are formed. Above 430°C - the sixth and seventh transformations - dehydration and carbonization processes occur, competing with the production of L-glucose. A decarboxylation process also takes place, resulting in the release of carbon dioxide. With increasing temperature, the carbon content increases. Pyrolysis of cotton products produces compounds such as water, carbon monoxide, carbon dioxide, alcohols, aldehydes, ketones, esters, ethers, and benzene. However, these compounds are only formed by the pyrolysis of non-combustible cotton.

Six transformations occurred in the process of thermal analysis of the diapers. The first transformation was endothermic (-10.4 J·g<sup>-1</sup>), the second transformation endothermic (-26.8 J·g<sup>-1</sup>), the third transformation exothermic (10.8 J·g<sup>-1</sup>), the fourth transformation exothermic (105.1 J·g<sup>-1</sup>), the fifth transformation endothermic (-58.9 J·g<sup>-1</sup>) the last transformation endothermic (-9.3 J·g<sup>-1</sup>). The energy balance of the thermal transformation of the paragon was exothermic (10.5 J·g<sup>-1</sup>) (Tab. 8).

Seven thermal transformations occurred in the thermal leno analysis process. The first transformation was endothermic (-0.92 J·g<sup>-1</sup>), the second transformation endothermic (-16.9 J·g<sup>-1</sup>), the third transformation endothermic (-1.0 J·g<sup>-1</sup>), the fourth transformation exothermic (164.6 J·g<sup>-1</sup>), the fifth transformation exothermic (-72.7 J·g<sup>-1</sup>), the sixth transformation endothermic (-31.1 J·g<sup>-1</sup>) and the last transformation endothermic (-40.3 J·g<sup>-1</sup>). The energy balance of the thermal conversion of the material was exothermic (1.4 J·g<sup>-1</sup>) (Tab. 8).



Figure 10. Characteristics of the DSC of hygiene waste; (a) diapers (b) leno

DSC character-	Type of			Tra	insformation	tion			
istics	material	1	2	3	4	5	6	7	
The tempera-									
ture of transfor-		174 4	156 1	193.2	2874	433.6	475 5	_	
mation begin-		121.1	100.1	170.2	207.1	100.0	170.0		
ning, °C									
The tempera-	Diapers								
ture of transfor-	1	127.4	163.2	205.8	305.3	457.9	478.1	-	
mation peak, °C									
The tempera-		101.1	4 = 0.4	045 (	010.0	170.4	101.0		
ture of transfor-		131.4	172.1	217.6	318.2	473.1	481.8	-	
mation end, °C		10.4	•	10.0	4054	-0.0	0.0		
Energy balance, J•g	-1	- 10.4	- 26.8	10.8	105.1	- 58.9	- 9.3	-	10.5
The tempera-									
ture of transfor-		110.1	244.4	255.2	283.2	417.48	445.9	465.1	
mation begin-									
ning, °C									
The tempera-	Leno								
ture of transfor-	20110	120.3	249.3	256.9	298.1	425.59	449.6	474.9	
mation peak, °C									
The tempera-									
ture of transfor-		127.9	254.6	258.3	308.0	434.95	455.3	481.7	
mation end, °C									
Energy balance, J·g	-1	- 0.92	- 16.9	- 1.0	164.6	- 72.7	- 31.1	- 40.6	1.4

 Table 8. Normalized transformation energy for successive transformations of tested hygiene waste and energy balance of the process

#### 3.3.6. Biodegradable waste

The TG/DTG curves for poultry meat in Figure 11a and for potato peelings Figure 11b. The most dynamic weight loss for poultry meat was observed between 72 and 107 minutes at temperatures of 370 - 540°C. For potato peelings, the most dynamic decrease occurred between 65 and 85 minutes, between 333 - 430°C, respectively. The weight loss in the case of potato peels (Fig. 11a) will be related to the thermal decomposition of starch, while in the case of chicken it will be related to the decomposition of proteins (Fig. 11a).

The first decrease in weight of the potato peel sample was recorded at about 220°C. Between 220 and 350°C, the mass loss was slow and about 6%. On the other hand, in the temperature range 350 - 450°C, there was a faster mass decrease (about 45 % relative to the mass at 350°C) [45]. The most dynamic weight loss for potato peelings occurred in a shorter time than for cellulosic materials which are related to the degree of polymerization of starch, which is usually lower than the polymerization of cellulose. Further weight loss was about 20 % of the initial weight [46].

The main component of chicken meat, besides water, is protein about 24%, and fat about 2%. The decrease in weight is mainly related to the decomposition of fats because the proteins in meat are decomposed in 59,66 and 82°C (myosin, collagen, and sarcoplasmic proteins, actin), so they decomposed during the drying of the material in 105°C. The greatest weight loss of the chicken meat sample, compared to the potato peel sample, occurred at lower temperatures.



Figure 11. Characteristics of the TG/DTG of biodegradable waste; (a) poultry meat (b) potato peel

Five endothermic transformations were observed during the DSC analysis of poultry meat (Fig. 12a). They occurred in the following temperature ranges: 171. 47 - 205. 52°C; 245,38 - 278,31°C; 281,29 - 291,74°C; 406,11 - 411,45°C; 414,83 - 425,95°C. Comparing these data with the results of DTG/TG analysis, there was no mass decrease during the first transformation - this is probably due to the difference between the actual temperature of the reactor and the temperature of the sample, or there is a chemical reaction taking place which results in a new product. The first transformation can be related to the transformation of arachidonic acid, whose boiling point is 170°C. The second may be related to

the chemical reaction of erucic acid (boiling point 265°C). As with arachidonic acid, no decrease in weight was observed during DTG/TG analysis. For the subsequent transformations, no links were found with which to associate them. Poultry meat also contains other acids with higher boiling points, i. e. palmitic acid (351°C), oleic acid (360°C) or nervonic acid (479.2°C), and cholesterol, whose boiling occurs at 360°C. The transformations occurring at this time are likely related to the decomposition of the charred sample.

Potato peelings (Fig. 12b) are characterized by three transformations: vitrification (164.19 - 181.05), exothermal transformation (230.89 - 254.11) and endothermal transformation (415.72 - 420.85). The second, exothermal, transformation occurred at temperatures of 230.89 - 254.11°C. The last transformation, of an endothermal nature, was observed between 415.72 and 420.85°C. These transformations have not been characterized in any of the above publications. Furthermore, no exothermal transformations occurred in any DSC analysis of potato starch. These transformations may be related to the previous drying of the potato sample and thus to the thermal decomposition of the unfolded proteins.

Five transformations occurred in the thermal analysis of chicken meat. The first transformation was endothermic (-26.3 J·g<sup>-1</sup>), the second transformation endothermic (-19.4 J·g<sup>-1</sup>), the third transformation endothermic (-3.1 J·g<sup>-1</sup>), the fourth transformation endothermic (-44.6 J·g<sup>-1</sup>) the last transformation endothermic (-37.0 J·g<sup>-1</sup>). The energy balance of the thermal transformation of the paragon was endothermic (-130.3 J·g<sup>-1</sup>).

Three thermal transformations occurred in the thermal analysis of potato peelings. The first transformation occurred but its value equilibrated, the second transformation exothermic ( $470.3 \text{ J} \cdot \text{g}^{-1}$ ), the third transformation endothermic ( $-102.5 \text{ J} \cdot \text{g}^{-1}$ ). The energy balance of the thermal conversion of the potato peel was exothermic ( $367.8 \text{ J} \cdot \text{g}^{-1}$ ).



Figure 12. Characteristics of the DSC of biodegradable waste; (a) chicken meat (b) potato peel

 
 Table 9. Normalized transformation energy for successive transformations of tested biodegradable waste and energy balance of the process

DSC character-	Type of	Transformation								
istics	material	1	2	3	4	5	6	7		

									_
The tempera-									_
ture of transfor-		171 5	245.4	201 2	406 1	111 0			
mation begin-		171.5	243.4	201.5	400.1	414.0	-	-	
ning, °C									
The tempera-	Chicken								
ture of transfor-	meat	198.8	259.3	290.7	406.8	419.6	-	-	
mation peak, °C									
The tempera-									
ture of transfor-		205.5	278.3	291.7	411.5	426.0	-	-	
mation end, °C									
Energy balance, J·g <sup>-1</sup>		- 26.3	- 19.4	- 3.1	- 44.6	- 37.0	-	-	- 130.3
The tempera-									
ture of transfor-		164 0*	230.9	415.7	-	-	-	-	
mation begin-		104.2							
ning, °C									
The tempera-	Potato								
ture of transfor-	peel	172.6*	243.7	416.8	-	-	-	-	
mation peak, °C									
The tempera-									
ture of transfor-		181.1*	254.1	420.9	-	-	-	-	
mation end, °C									
Energy balance, J·g <sup>-1</sup>		-	470.3	- 102.5	-	-	-	-	367.8

#### 5. Conclusions

Twelve main organic components of municipal solid waste were subjected to proximate analysis, and TG/DTG/DSC thermal analysis.

The proximate analysis showed that the most moisture waste was found in the biodegradable group (chicken residues and potato peal) with moisture content over 50%. The driest materials were found in the plastic group, namely PET, and PU. The PET also had the highest calorific value of 42 MJ·kg<sup>-1</sup>.

Among all tested waste, plastics materials showed the greatest differences in weight loss. The PET material the highest weight loss, around 91%, whereas the PU had the lowest weight loss, around 60%. In the case of the rest tested groups, the differences between materials weight losses were much less visible, and for the hygienic and biodegradable waste groups differences were small.

Kinetics analysis was performed using the Coats-Redfern method at heating rate of 5 °C·min<sup>-1</sup>. For tested materials, the activation energy varied from 25.2 kJ·(mol·K)<sup>-1</sup> up to 134.5 kJ·(mol·K)<sup>-1</sup> for leather and cotton, respectively. The mane vale was found to be 74.3 kJ·(mol·K)<sup>-1</sup>. The reaction order differs significantly for each material from 1.41 to 3.52 for diapers and receipt, respectively.

Based on DSC analysis, the balance of thermal transformations during pyrolysis was calculated, which indicates wider possibilities of understanding the transformations occurring during thermal treatment of waste. For all tested materials, the highest and positive energy balance occurred for potato peels (367.8 J·g<sup>-1</sup>) while the lowest and negative balance was determined for PET plastic (-220.1 J·g<sup>-1</sup>).

The study provided information about the physical properties of main organic waste, and its thermal behavior during low-temperature pyrolysis, and showed that each component had different properties and thermal degradation behavior. Determining properties and obtained knowledge has an essential meaning for the pyrolysis of municipal solid fractions. The study shows that when waste is processed there is a need-to-know what type of waste is processed because each of them needs different conditions to get the same conversion. Nevertheless, the study did not cover the interactions between materials and possible catalysis effects between materials. Therefore next, interactions between materials during the pyrolysis process should be tested to assure possibilities of mixed municipal waste pyrolysis optimization.

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