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STUDIES ON ENERGY RECOVERY OF TEXTILE WASTE

BY

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Abstract. In this work, the thermal and energy properties of four types of textile wastes were evaluated: cotton, wool, polyester and acrylic. For this purpose, thermogravimetric analysis in nitrogen atmosphere with three heating rates in the temperature range 25-600ºC was used. The processing of the thermogravimetric curves allowed the determination of the temperatures at which 5% ($T_{5\%}$) and 30% ($T_{30\%}$) of the sample mass was lost, with which the statistical heat resistance index (T_{HRI}) of the textile waste was evaluated. Using the recorded thermogravimetric curves, the activation energy for the main stage of thermal decomposition was calculated by applying the ASTM E-698 standard method. The enthalpy of combustion of the textile waste was also determined using the Berthlot-Mahler-Krocker calorimeter.

Keywords: textile waste, thermogravimetric characteristics, kinetic parameters, combustion enthalpy.

1. Introduction

The current energy crisis, exacerbated by the war in Ukraine, has increased researchers' concerns about finding alternative fuels. In the chemical

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industry, cement plants are some of the biggest energy consumers. The use of waste as an alternative fuel in this industry leads to lower specific energy consumption, conservation of non-renewable resources and a reduction in the amount of waste released into the environment. A considerable amount of textile waste is dumped in landfills, and about two thirds of it is man-made fibres that can take up to 200 years to decompose (Ozsin and Pütün, 2022). The European Environment Agency expects clothing consumption to increase by 63%, from 62 million tonnes in 2019 to 102 million tonnes in 2030 (Stefan *et al*., 2022). This growth will also generate a sharp increase in textile waste that could be recovered. Around 92 million tonnes of textile waste are produced annually worldwide (Tang, 2023). It is expected that in 2050 from the US alone, approximately 19 million tonnes of textile waste will be generated in landfills (Baloyi *et al.,* 2024). Recent studies have shown that adding textile waste to municipal waste improves its heat capacity from 5000 kJ/kg to 9000 kJ/kg (Lu *et al*., 2017).

Kramens *et al*. have tested the possibility of using textile waste (cotton and polyester) to produce pellets mixed with biomass for use in small-scale energy production plants. They assumed that the amount of separately collected textiles in Estonia would increase to 90,000 tonnes per year from 2025 (Kramens *et al*., 2023). For pellets containing 20% textile waste (cotton fibres) and 80% pine wood chips they reported a calorific value of 19.7 MJ/kg, and for pellets containing 10% textile waste (polyester) and 90% pine wood chips, a calorific value of 20.39 MJ/kg (Kramens *et al*., 2023). The energy properties of cotton and polyester fibre blends were evaluated by Chen and Zhao using microscale combustion calorimetry (MCC). They found that the blend has a higher total heat release capacity (THR) than the sum of the individual cotton and polyester samples as single fibres, showing interactions between the two components that increase the flammability of the blend (Chen and Zhao, 2016). An extensive literature review has recently been conducted by Lee et al. examining the possible contribution of pyrolysis in the textile waste recycling process (Lee *et al*., 2023). The authors pointed out that pyrolytic oil obtained from textile waste has a heat capacity ranging from 11.5 to 20 MJ/kg, but not yet comparable to that of diesel fuel which is about 42 MJ/kg. In contrast, the solid residue obtained after pyrolysis of textile waste has a heat capacity ranging from 16 to 30 MJ/kg, values comparable to the heat capacities of coal which range from 16 to 26 MJ/kg (Lee *et al*., 2023).

Acrylic textile wastes were evaluated for thermal behaviour by Nahil and Williams in a nitrogen atmosphere at a heating rate of 5ºC/min by thermogravimetric analysis. The authors identified a significant amount of carbonaceous residue at the end of the test, namely 44%. Also, in the temperature range 270-500ºC they found two steps that were associated with the decomposition of polyacrylonitrile and polyvinyl acetate present in this type of textile waste (Nahil and Williams, 2010). White and coloured cotton waste was evaluated by thermogravimetric analysis by Liu *et al*. They found that thermal decomposition of coloured cotton waste starts at 354ºC compared to white cotton waste which decomposes in one step starting at 379ºC (Liu *et al*., 2023). Baccouch *et al*. evaluated the thermal behaviour in nitrogen atmosphere for cotton and polyester textile waste and blends thereof. For cotton waste they found a main stage starting at 315ºC corresponding to α-cellulose decomposition, and for polyester waste and cotton/polyester blends they identified two decomposition stages one starting at 350ºC and the other at 450ºC, although other studies in the literature indicate only one degradation stage for polyester waste (Baccouch *et al*., 2022). A kinetic study of the thermal decomposition process in nitrogen and in air for cotton waste was carried out by Brillard et al. The kinetic parameters were determined by applying a differential isoconversional kinetic model based on thermogravimetric curves recorded at the following heating rates 5, 10, 20, 30, 40 and 50ºC/min. The apparent activation energy calculated for cotton waste was 200.1 kJ/mol and the preexponential factor $2.82 \cdot 10^{17}$ s^{-1} (Brillard *et al*., 2017).

In this study the thermal and energy properties of four types of textile waste were evaluated: cotton, wool, polyester and acrylic, applying thermogravimetric analysis and determination of the enthalpy of combustion using the Berthlot-Mahler-Krocker calorimeter. The main thermogravimetric characteristics and kinetic parameters were evaluated for each waste type. The enthalpy of combustion was also determined.

2. Materials and methods

Four types of textile waste were subjected to thermal and energy analysis: cotton (BM), wool (L), polyester (PL) and acrylic (AC). A Mettler Toledo 851^e was used for this purpose. Thermogravimetric (TG) and derived thermogravimetric (DTG) curves were recorded in the temperature range 25-600ºC, with three heating rates 10, 15 and 20ºC/min. The tests were performed in nitrogen atmosphere and the mass of the samples ranged from 2.4 to 4.6 mg. With the $STAR^e$ SW 9.10 software for the analysis cell, mathematical processing of the TG and DTG curves was carried out to obtain the main thermogravimetric characteristics, as well as their kinetic processing.

The thermogravimetric curves provide information on the thermal stability of the analysed textile waste. The main thermogravimetric characteristics evaluated are: T_{onset} - temperature at which degradation starts; T_{peak} - temperature at which the degradation rate is maximum; T_{endset} - temperature at which the degradation process ends; percentage mass loss (W) and amount of residue.

The kinetic parameters of the textile waste subjected to thermogravimetric analysis were determined with the Kissinger integral method - ASTM E-698.

Under conditions of maximum degradation rate, the standard ASTM E-698 method can be applied, which uses the following relationship proposed by Kissinger to determine the activation energy:

$$ln\frac{a}{T_{peak}^2} = \ln\frac{\mathrm{AR}}{\mathrm{E_a}} - \frac{\mathrm{E_a}}{\mathrm{R}}\cdot\frac{1}{T_{peak}} \quad (1)$$

where a is the heating rate, R is the universal gas constant, E_a - the activation energy and A - the pre-exponential factor.

Determination of the enthalpy of combustion was carried out using the Berthlot-Mahler-Krocker calorimeter.

The sample mass under analysis was weighed on the analytical balance and the temperature variation due to the combustion reaction of textile waste was determined. The combustion enthalpy was calculated with relation 2:

$$\Delta H^0{}_{C,298} = \frac{-\mathrm{C}\cdot\Delta\mathrm{T} - \mathrm{m_{Fe}}\cdot\Delta\mathrm{H^0}_{\mathrm{C,298}}(\mathrm{Fe})}{\mathrm{m_p}} \quad (2)$$

where C = 1.04· 104 J/K is the heat capacity for the calorimeter, m_{Fe} is the mass of iron burned in grams, $\Delta H^0_{C,298}$(Fe)= -6.658· 103 J/g is the standard enthalpy of combustion for iron and mp is the amount of waste burned in the calorimetric pump. From the plot of temperature as a function of time (Fig. 1) during the course of the experiment, ΔT was determined.

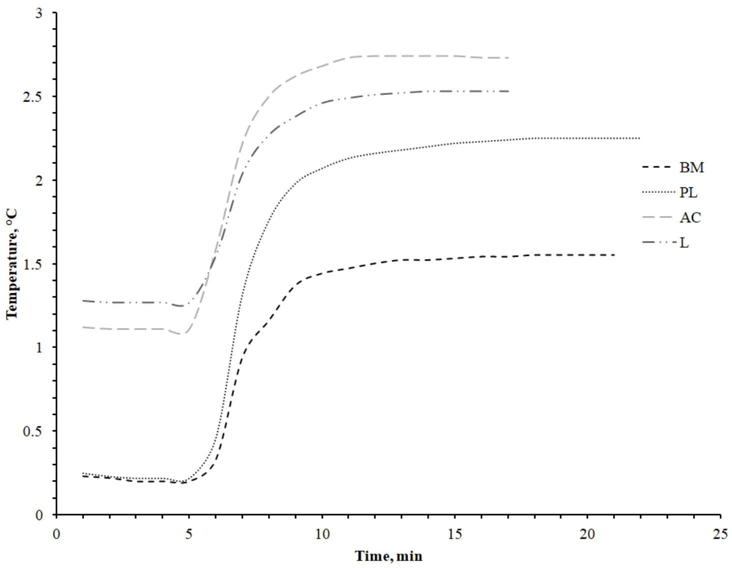

Fig. 1 − Temperature variation as a function of time.

3. Result and Discussions

Figure 2 shows the TG curves for the four textile wastes recorded at 10ºC/min and Figure 3 shows the DTG curves recorded at the same heating rate. It can be seen that the BM and L samples have a moisture removal step up to about 100ºC and then thermal decomposition in the inert atmosphere occurs in one step. The decomposition of textile waste AC and PL also occurs in one step.

From the TG and DTG curves recorded at different heating rates, the main thermogravimetric characteristics were extracted as shown in Table 1.

In the case of BM waste in the first step moisture removal takes place which is found to be about 3%. Thermal decomposition then takes place in a single step in the temperature range 330-400ºC, with the temperature at which the degradation rate is maximum at about 369ºC. Cotton waste consists mainly of cellulose. The thermogravimetric characteristics identified in this study are similar to what has been reported by other researchers in the literature (Ruiz *et al.*, 2023). Liu *et al*. obtained T_{peak} = 378.92ºC for red cotton textile waste and T_{peak} = 384.90 ºC for white textile waste (Liu *et al*., 2023).

For wool waste up to 110ºC, desorption of physically bound water and dehydration of wool fibre occurs. The second process, similar to those reported in other studies in the literature, occurs in the temperature range 240-450ºC and consists of disulfide bond breaking which may be accompanied by sulphur dioxide release (Cheng *et al*., 2016). At a temperature of 600ºC there is a residue of about 30%.

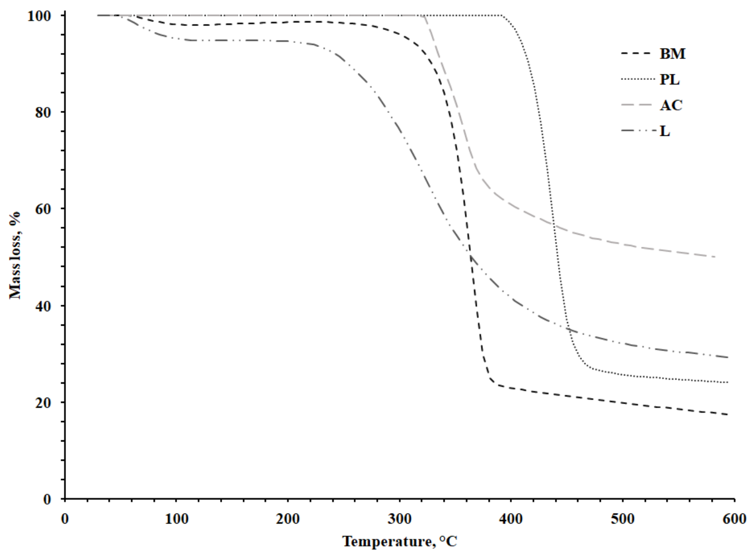

Fig 2 – TG curves at heating rate of 10ºC/min.

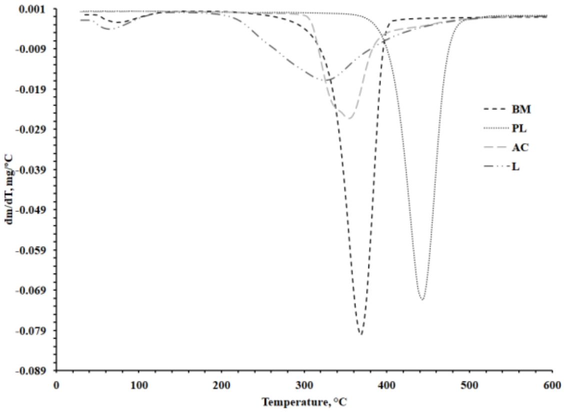

Fig. 3 − DTG curves at heating rate of 10ºC/min.

Table 1

Thermogravimetric characteristics at different heating rates

Sample	Heating speed (ºC/min)	T_{HRI} (ºC)	Step	T_{onset} (ºC)	T_{peak} (ºC)	T_{endset} (ºC)	W (%)	Amount of residue (%)
BM	10	167.1	I	52	68	98	2.38	16.44
			II	335	363	379	81.18	
	15	170.1	I	53	68	100	3.17	20.09
			II	335	369	387	76.74	
	20	171.3	I	64	77	109	3.02	15.14
			II	334	371	392	81.84	
L	10	145.4	I	51	64	99	5.55	28.93
			II	246	326	440	65.52	
	15	147.5	I	55	68	110	6.03	30.84
			II	247	329	446	63.13	
	20	150.9	I	57	75	115	6.09	31.04
			II	249	337	464	62.87	
AC	10	172.5	I	319	356	466	52.11	47.89
	15	175.7	I	328	366	485	53.68	46.32
	20	182.8	I	350	373	387	55.03	44.97
PL	10	204.9	I	402	436	461	78.14	21.86
	15	212.4	I	398	442	473	74.69	25.31
	20	215.2	I	413	448	474	80.19	19.81

Thermal decomposition of acrylic waste occurs in the temperature range 320-490ºC, a stage that can be associated with the decomposition of polyacrylonitrile. At the end of the test, an amount of carbonaceous residue of approximately 46% results, similar to what has been reported by other researchers in the literature (Nahil and Williams, 2010).

In the case of polyester waste thermal decomposition in an inert atmosphere occurs in a single step with the temperature at which the decomposition rate is maximum at about 440ºC (Baccouch *et al.*, 2022).

For all textile wastes analysed the results presented in Table 1 indicate that with increasing degradation rate the decomposition mechanism is preserved, only a shift of the main thermal characteristics towards higher temperatures occurs.

The processing of thermogravimetric curves using the STAR^e software version SW 9.10 allowed the determination of temperatures at which 5% ($T_{5\%}$) and 30% ($T_{30\%}$) of the sample mass was lost, neglecting moisture loss, with which the statistical heat resistance index was evaluated (Bai *et al.*, 2023; Zhao *et al.*, 2022).

$$T_{HRI} = 0.49\cdot[T_{5\%} + 0.6\cdot(T_{30\%} - T_{5\%})] \tag{3}$$

The obtained results are shown in Table 1 and according to them the series of thermal stability increase of analyzed textile waste is: L < BM < AC < PL.

The assessment of the thermal stability of materials should also include the kinetic study of decomposition processes. Therefore, the following kinetic parameters were evaluated: apparent activation energy (Ea), reaction order (n) and pre-exponential factor (lnA) for the main decomposition step, applying the ASTM E-698 standard method, under maximum degradation rate conditions. The values of the calculated kinetic parameters under maximum degradation rate conditions are given in Table 2.

Table 2

Kinetic characteristics obtained by method E-698

Sample	ln A	Ea (KJ/mol)	n
BM	32.49	197.04	1
L	10.51	77.59	1
AC	18.49	123.08	1
PL	31.46	214.25	1

(A - pre-exponential factor; Ea - apparent activation energy; n - reaction order)

The lowest value for activation energy was found for wool-type waste, for which the lowest thermal stability was previously established. For cotton waste the activation energy value is close to the value reported by other researchers in the literature (Brillard *et al.*, 2017). The highest value for activation energy was obtained for polyester type waste which also showed the highest statistical heat resistance index.

The combustion enthalpy for textile waste was calculated with equation (2). The results obtained are presented comparatively in Table 3. The best value for the enthalpy of combustion was obtained for acrylic waste, which according to the results presented above also showed the highest amount of carbon residue (about 46%) which in the calorimetric pump contributed to energy generation. Ujam and Eboh obtained a combustion enthalpy of -20551.01 J/g for textile waste mixtures using the calorimetric pump (Ujam and Eboh, 2012). Boumanchar et al. reported combustion enthalpy values for cotton fibre waste of -17500 J/g and for textile blends -26400 J/g (Boumanchar *et al.*, 2019).

Table 3
Energy characteristics

Sample	Sample mass (g)	Burnt wire mass (g)	$\Delta H^0_{c,298}$(J/g)
BM	0.7973	0.0275	-17379.8
L	0.5981	0.0095	-21803.6
AC	0.5996	0.0050	-28043.2
PL	0.8986	0.0184	-23358.0

Given the results obtained, we can consider that textile waste can be exploited as an energy source.

4. Conclusions

The thermal behaviour of four types of textile waste in a nitrogen atmosphere with three heating rates in the temperature range 25-600ºC was evaluated. The processing of thermogravimetric curves allowed the determination of temperatures at which 5% ($T_{5\%}$) and 30% ($T_{30\%}$) of the sample mass was lost, with which the statistical heat resistance index (T_{HRI}) of the textile waste was evaluated. According to the results obtained the series of the increase in thermal stability of the textile waste analyzed is: L < BM < AC < PL. ASTM E-698 standard method was applied under maximum degradation rate conditions for the evaluation of kinetic parameters. The highest value for activation energy was obtained for polyester waste, showing the best thermal stability. The combustion enthalpy determined for the textile waste ranges from -17.39 MJ/kg to -28.04 MJ/k, so we can state that the textile waste can be exploited as an energy source.

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STUDII PRIVIND VALORIFICAREA ENERGETICĂ A DEȘEURILOR TEXTILE

(Rezumat)

În această lucrare s-au evaluat proprietățile termice și energetice pentru patru tipuri de deșeuri textile: bumbac, lână, poliester și acrilice. În acest scop s-a utilizat analiza termogravimetrică în atmosferă de azot, cu trei viteze de încălzire în intervalul de temperatură 25-600ºC. Prelucrarea curbelor termogravimetrice a permis determinarea temperaturilor la care s-a pierdut 5% ($T_{5\%}$) și 30% ($T_{30\%}$) masă de probă cu ajutorul cărora s-a evaluat indicele statistic de rezistență la căldură (T_{HRI}) a deșeurilor textile. S-a calculat utilizând curbele termogravimetrice înregistrate, energia de activare pentru etapa principală de descompunere termică, aplicând metoda standardizată ASTM E-698. De asemenea, s-a determinat entalpia de combustie a deșeurilor textile cu ajutorul calorimetrului Berthlot-Mahler-Krocker.