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SIMULTANEOUS THERMOGRAVIMETRIC AND MASS SPECTROMETRIC ANALYSIS OF THE PYROLYSIS OF MUNICIPAL SOLID WASTES AND POLYETHYLENE TEREPHTHALATE

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A thermogravimetric (TG) and mass spectrometric (MS) study was carried out of the process of devolatilization of the organic fraction of municipal solid wastes (OFMSW) and polyethylene terephthalate (PET). This involved an analysis of the heating profiles in an inert atmosphere for each of these residues separately and for a mixture made up of half of each by mass. The fit between the experimental and calculated values was checked by means of the least squares method. No interaction at all was observed between the two types of waste when the fit between the experimental and theoretical figures was checked, in the light of the low values obtained from the objective function showing fit. The study of mass spectrometry shows major emissions of energy-producing gases although fewer pollutants are emitted.

Keywords: *mass spectrometry, municipal solid waste, PET, pyrolysis, thermogravimetry*

Introduction

In view of the real growth which is taking place in the generation of municipal solid waste, management of such substances requires both modification of social habits to decrease their production and the use of one or another of the methods available to allow their reuse or elimination to the greatest extent possible. The technological development in some methods, permit the generation of energy (pyrolysis followed by the use of the gas obtained to act as an energy source) while others (recycling and composting) contribute indirectly to energy savings or to the conservation of resources.

Pyrolysis treatment for municipal solid waste has been found to provide alternative resources in the form of energy and chemical raw materials. An appropriate method of pyrolysis may provide a solution for the problems of waste disposal.

Plastic wastes, whose volume is steadily increasing, have the disadvantage of not being biodegradable. In particular, polyethylene terephthalate (PET) is the material of choice for manufacturing containers for the mass drinks market. Hence, PET is a plastic commonly present in municipal solid waste.

Approximately 15 million tonnes of post-consumer plastic are generated in Europe as a whole. Only 7% of this is recycled to produce low grade plastic products, while the rest is disposed of in landfills or incinerated. Among the various polymers involved, around 7.6% by mass of these residues is made up of PET [1].

The use of wastes to recover energy by pyrolysis, thermal analysis and mass spectrometry are considered very useful analytic tools, as demonstrated by numerous studies listed in the bibliography [2–4].

A combination of MS and TG in one system offers several advantages in determining gas emissions from thermal processes. These include real-time analysis and qualitative and quantitative analysis [5, 6].

The objective of the present work was to carry out a thermogravimetric study of the process of pyrolysis of the organic fraction of municipal solid waste (OFMSW) and of polyethylene terephthalate (PET) plastics, and of a mixture made up of 50% each of these two types of waste, determining possible interactions related to the temperature range at which components the mixture degrades as well as the amount of residual char obtained at the end of the experiments. The study also covered characterization of the gaseous fraction through mass spectrometry.

Experimental

Materials

The raw material whose thermal decomposition was studied consisted of:

- organic fraction of municipal solid wastes (OFMSW)

The source-sorted organic fraction of municipal solid waste was dried at 110şC for 12 h prior to the experiments and then was shredded to produce particles 2 mm in diameter.

- polyethylene terephthalate (PET)

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The PET was collected from beverage bottles. The material was carefully cut and milled to the appropriate size (pieces below 2 mm) to carry out the pyrolysis in a TG.

The raw materials were analysed, taken a representative sample, to determine the main properties affecting emissions (Table 1). Moisture was determined in a Selecta THREOVEN with forced ventilation. Volatile matter and ash were analysed with a Thermolyne 48000 muffle furnace with automatic temperature control. Spanish standards UNE 32002, 32019 and 32004 were followed for the determination of moisture, volatile matter and ash, respectively. An elemental analysis was also performed so as to determine the amounts of the main chemical elements present in the sample: carbon, hydrogen, nitrogen, sulphur, chlorine and oxygen, the last by subtraction. For the first three elements, a LECO CHN-600 apparatus following ASTM standard D-5373 was used. Total sulphur was determined with a LECO SC-132 according to ASTM standard D-4239. The Eschka method was used to determine chlorine content according to ASTM D-2361. Calorific value was determined with a LECO AC-300 using the adiabatic method in accordance with the UNE 32006 standard.

Table 1 Chemical analysis (%) of dried the organic fraction of municipal solid waste (OFMSW) and polyethylene terephthalate (PET)

	OFMSW	PET
Moisture	10.80	0.20
Volatile Matter[a]	76.93	91.80
Ash[a]	7.69	<0.20
Carbon[b]	52.26	62.70
Hydrogen[b]	6.49	4.35
Nitrogen[b]	2.72	<0.10
Sulphur[b]	0.26	<0.02
Chlorine[b]	1.33	<0.02
Oxygen[b,c]	38.27	>32.81
H.H.V./MJ kg^{-1}	19.96	23.04
L.H.V./MJ kg^{-1}	18.61	22.17

[a]results expressed as a percentage of dry matter,
[b]results expressed as a percentage of dry matter free of ashes, [c]calculated by difference

Methods

Thermogravimetric analysis

Thermogravimetric analysis was carried out using a TA Instruments SDT2960, which is able to provide a continuous measurement of simple mass as a function of time or of temperature and also give a DTG signal (rate of mass loss) when used with the appropriate software. Thermogravimetric runs were performed for each of two residues studied; OFMSW and PET. The initial sample mass was 5 mg, this being distributed uniformly over the base of the sample holder so as to facilitate the transfer of heat and of material. The atmosphere used was helium with a flow rate of 100 mL min^{-1}. Prior to the start of heating, a flow of helium was passed through the oven for 10 min in order to remove any remaining air. Once this purge period was completed, heating from room temperature up to a final temperature of 800şC commenced, at a heating rate of 50°C min^{-1}. The experiments were repeated three times in order to evaluate their reproducibility [7].

The experiments on mixtures were performed in exactly the same way using the same procedure as single components. The experiments on mixtures were performed with a sample mass of 10 mg [2]. In these experiments the OFMSW was placed at the bottom of the sample cup and PET at the top. This ensures the best possible mixing, because the plastic melts before or at the same temperature range at which the organic residues start to decompose and will have the possibility to interact [8].

Interactions between mixes of wastes. Calculation of objective functions

The aim of the objective functions is to determine the degree of fit between the theoretical values, calculated on the assumption that there is no interaction at all between the components in the mixture, and those obtained experimentally using a thermobalance. The least squares method was used to minimize differences between the measured and the calculated values. The objective function (FO) defined in the following way [2]:

$$\mathrm{FO}=\sum_{\mathrm{N}}[y_{\mathrm{exp}}-Y_{\mathrm{calc}}]^2$$

y_{exp} is the measured value of a TG or DTG mixture curve, Y_{calc} is the calculated value, N is the number of data points taken into account

There is no predefined value for the objective function that would represent a good fit. These values depend on the number of points considered for each graph that it is intended should be fitted. Hence, an equal number of points will always be used, so that the values are comparable among themselves. In accordance with the equation corresponding to the objective function, the best fits would give the smallest values, since essentially they are the sum of the differences between the experimental and the calculated values.

If the superposition principle is assumed, the thermal degradation curve for a mixture is calculated as the sum of the contributions of the corresponding individual components [9]. The weighed sum method has the formula:

$$Y_{\mathrm{calc}} = \sum_{\mathrm{i}=1}^{\mathrm{n}} x_{\mathrm{i}}\, y_{\mathrm{i}}$$

x_{i}, the mass fractions of each component i in the mixture, y_{i}, the measured value of a TG or DTG curve of constituent i, n is the number of components taken into account.

The weighed sum method was applied both to the TG and to the DTG curves, with data measured between 200 and 700°C with a step size of 1°C being utilized [9].

Mass spectrometry analysis

Gases emitted during the thermal conversion process were monitored with a Balzers ThermoStar GSD 300 mass spectrometry apparatus. Analysis was carried out with the mass spectrometer directly linked to the gas off-take of the thermal analysis equipment. The connection between the thermobalance and the mass spectrometer was by means of a capillary kept at a temperature of 200°C. In this way, the data obtained from the mass spectrometer corresponded to the emissions released by the samples undergoing devolatilization in the thermobalance. Several authors, for instance Hatton [10], have studied the optimal linkage between TA and MS. Such a linkage allows the relative concentrations of gas emitted to be determined under near-equilibrium conditions, although it lengthens the response time for the MS signals. For this reason, thermal and spectrometric analyses in this study were not in precise synchrony [5].

The evolution profiles for m/z ratios of 2, 15, 18, 26, 28, 39, 42, 43, 44, 55, 64 and 91 were monitored. Table 2 shows the assignments of each of these signals to different compounds. These assignments are in accordance with published details in the literature and take into account the ions of the compounds expected from pyrolysis [4]. These gas emissions are of importance from two points of view, their energy value and the environmental damage they may cause [11].

Table 2 Assignments for each signal from the mass spectrometer

m/z	Ion	Mainly due to
2	H^+	hydrogen
15	CH_3^+	methane
18	H_2O^+	water
26	CN^+, $C_2H_2^+$	HCN, ethylene, aromatics
28	CO^+	carbon monoxide
39	$C_3H_3^+$	propylene, aromatics
42	CH_2CO^+, $C_3H_6^+$	aldehyde, propane
43	CH_3CO^+, $C_3H_7^+$	carboxylic acid, propane
44	CO_2^+	carbon dioxide
55	$C_4H_7^+$	butane
64	SO_2^+	sulphur dioxide
91	$C_7H_7^+$	aromatics

As N_2 has the same molecular mass as CO, helium was used instead of nitrogen for the inert atmosphere, making CO determination possible by mass spectrometry. No appreciable differences were detected in TG profiles [12].

Results and discussion

Characterization of materials

The results of the element and proximate analyses for the two types of waste are shown in Table 1. The following may be noted.

OFMSW ash yield is low (7.7%), but PET shows much lower ash yield values (<0.20%). PET samples yield a larger amount of volatiles (92%), although OFMSW also has a high volatile yield (77%).

The higher heating values of dry OFMSW samples are low, not quite reaching 20 MJ kg^{-1}, while PET has a heating value of around 23 MJ kg^{-1}.

With respect to the analysis of elements, it may be stated that OFMSW has higher hydrogen, nitrogen, sulphur, chlorine and oxygen content than PET, while PET shows a higher carbon content than does OFMSW.

Thermogravimetric analysis

Figure 1 shows the TG and DTG curves for pyrolysis of the organic fraction of municipal solid waste and polyethylene terephthalate, which relate to pyrolysis at a heating rate of 50°C min^{-1}. On the basis of the mass loss curve for the process of pyrolysis of OFMSW it may be observed that there is a tendency for a percentage of residues of around 25% to remain by 800°C. Devolatilization should be practically complete by then under the conditions in which the procedure is

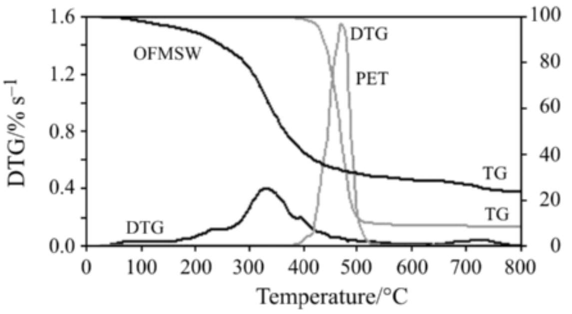

Fig. 1 Non-isothermal TG and DTG curves for OFMSW and PET obtained under helium at 50°C min^{-1}

performed. There is an initial loss of mass, between 90 and 200°C, corresponds to the driving out of moisture from the sample. It is between 200 and 400°C that devolatilization chiefly takes place. After 400°C mass is lost more slowly up to 800°C, the end temperature of the process, due to an organic material more stable and difficult to degrade. As may be observed, the range of temperatures over which devolatilization of the residues of an organic nature occurs is quite large, running from 200°C up to 550°C for OFMSW, probably as a consequence of the heterogeneity of the organic matter present in such wastes. It is observed a last stage of decomposition between 650–800°C probably due to carbonate decomposition reaction [13].

PET presents rather high thermal stability, since emission of volatiles starts at temperatures above 300°C [1]. Furthermore, it produces them over a limited temperature range (400 to 550°C) in which the solid decomposes quickly and where around 90% of the process is completed. This may be due to a greater homogeneity of its organic material content. After this main loss of mass, the solid continues decomposing smoothly until 800°C, whereupon no appreciable decomposition reaction is present. As it is known that the melting point of PET lies between 250 and 350°C, it is possible to state that the loss of volatile materials takes place from an already melted state of this substance. The volatile content of this plastic is very high, since no more than around 9% of residue remains after a process of pyrolysis at a final temperature of 800°C, with devolatilization in the thermobalance being almost complete. The ‘orderly’ structure of this organic material, which is also more abundant, leading to bigger losses of mass, explains why devolatilization takes place over a narrower range of temperatures, at which, essentially, depolymerization of the melted polymer occurs.

Interactions between OFMSW and PET

The incorporation of a plastic into a mixture with organic waste leads to a devolatilization profile with two mass loss intervals attributable to the two components. Each of the wastes in the mixture behaved as an independent system, retaining its own temperature interval for devolatilization and temperature level at which the rate of loss of mass was at its greatest.

The mass loss (TG) and rate of mass loss (DTG) profiles recorded experimentally in the thermobalance and those calculated on the assumption that there were no interactions between the components making up the mix coincided almost perfectly.

Graphs for the mixtures retain the DTG profiles of each of the wastes composing them, that is to say, the wastes behave like independent systems. Two peaks are observed, one corresponding to the devolatilization of the organic waste fraction and the other to the devolatilization of PET (Fig. 2). These occur in the same temperature ranges at which these processes take place in heat treatment of each of the types of waste on an individual basis.

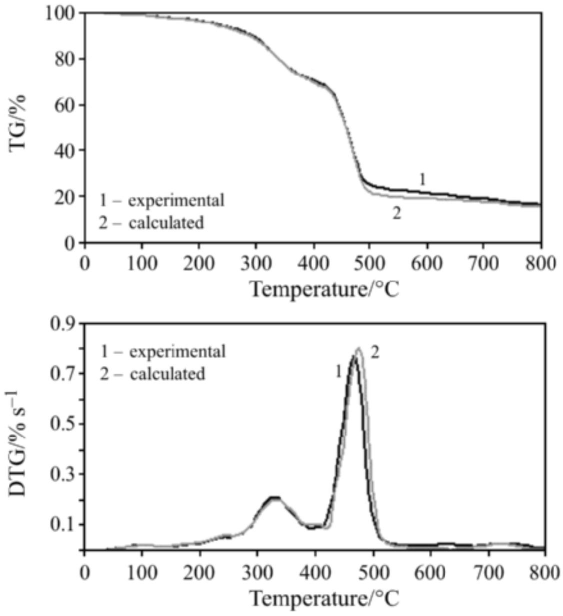

Fig. 2 TG and DTG experimental and calculated profiles of the pyrolysis process of the mixture of OFMSW and PET

The value for the objective function based on the method of least squares, which attempts to minimize the sum of the differences between the experimental and calculated plots, is 0.27 for the process of pyrolysis. In the light of the fact that the aim of the least squares method is to keep differences between observed and expected results as small as possible, this result indicates a good fit between the two plots, theoretical and experimental. It may be concluded that there is no interaction between the wastes during the progression of devolatilization.

Mass spectrometry analysis

In the light of results reported in the literature [4], the following mass to charge ratios were chosen for study: 2, 15, 18, 26, 28, 39, 42, 43, 44, 55, 64 and 91. Figures 3 and 4 show the results for each mass to charge (*m*/*z*) relationship and waste type studied.

Data were normalized so that each compound (ion) detected in MS had its own response factor and so that the intensities of the same compound for different samples could be compared [14]. In the case of intensities with different *m*/*z* signals, however, only the shape and the characteristic temperatures of the peak can be compared [5].

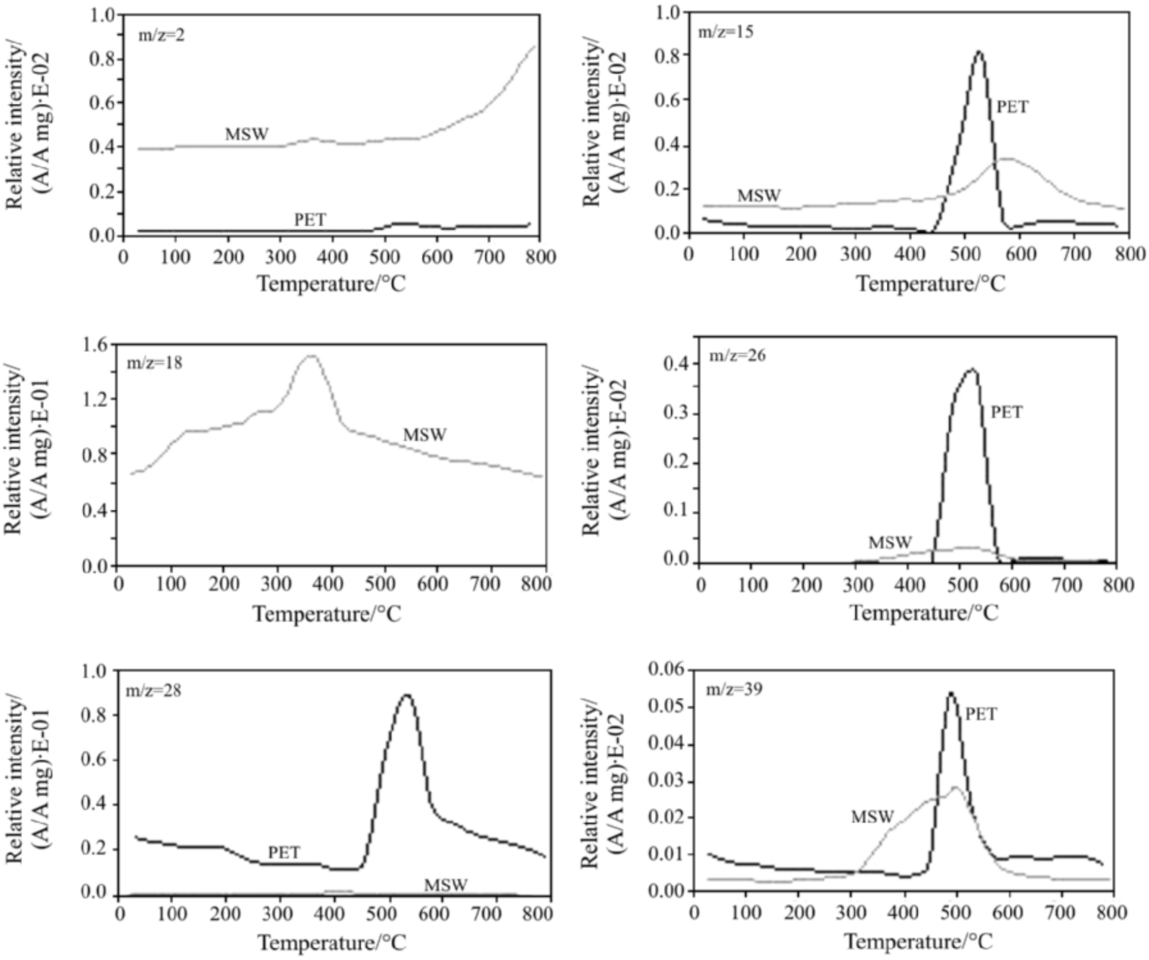

Fig. 3 Evolution profiles of the OFMSW and PET pyrolysis products at 50°C min^{-1} *m*/*z*=2, 15, 18, 26, 28 and 39

In general, for each type of waste a single peak is to be seen in the various emission profiles studied. For the municipal solid waste this peak had shoulders, leading to the conclusion that the process of decomposition takes place over more than one stage. This is not the case for the break-down of PET.

The temperature ranges at which the emission profiles lie run from 300°C up to 600°C for hydrocarbons (*m*/*z*=26, 39, 42, 43, 55), with a maximum at around 500°C. Decomposition of PET does not start until a temperature of 450°C is reached, as may be observed in all of the profiles studied. Emission of methane (*m*/*z*=15) begins at some point between 300 and 450°C as a function of the waste involved and increases up to 550°C, whereupon it tends to decrease. Methane (CH_4) is a gas of importance for its energy value, because of its high calorific value, 12.99 MJ Nm^{-3} [6]. The higher the volatile matter content, the greater the likelihood of groups producing CH_4 during pyrolysis processes [5]. Hence, the intensity of the emissions relating to PET is striking. A similar pattern is shown by the profile for hydrogen (*m*/*z*=2). Hydrogen peaks were detected in the final stages of thermal decomposition, this being due to the fact that, as the temperature rises, a fragmentation of hydrocarbons takes place, showing up as an increase in hydrogen and methane. The hydrogen derived from this is only part of the hydrogen present in the sample, there being more in MSW than in PET. Oxygen (O_2) content plays a major part in the release of hydrogen, due to the formation of water (H_2O). Hydrogen is also a gas of considerable value from the point of view of energy, thanks to its high calorific value, 41.22 MJ Nm^{-3} [6].

During thermal decomposition two stages may be observed in the evolution of water (*m*/*z*=18). Up to 200°C a peak is observed, corresponding to the evaporation of the water contained in the sample. Development of H_2O above 300°C is due to the breaking down of groups that contain oxygen, principally hydroxide (OH) groups, giving rise to the formation of pyrolysis water over a wide range of temperatures.

The maximum emission of carbon monoxide (CO) is observed at higher temperatures depending on the oxygen content of the waste. Carbon monoxide is significant for energy production because of its high calorific value, 12.87 MJ Nm^{-3} [6]. This mass to charge ratio, *m*/*z*=28, does not just relate to CO, but

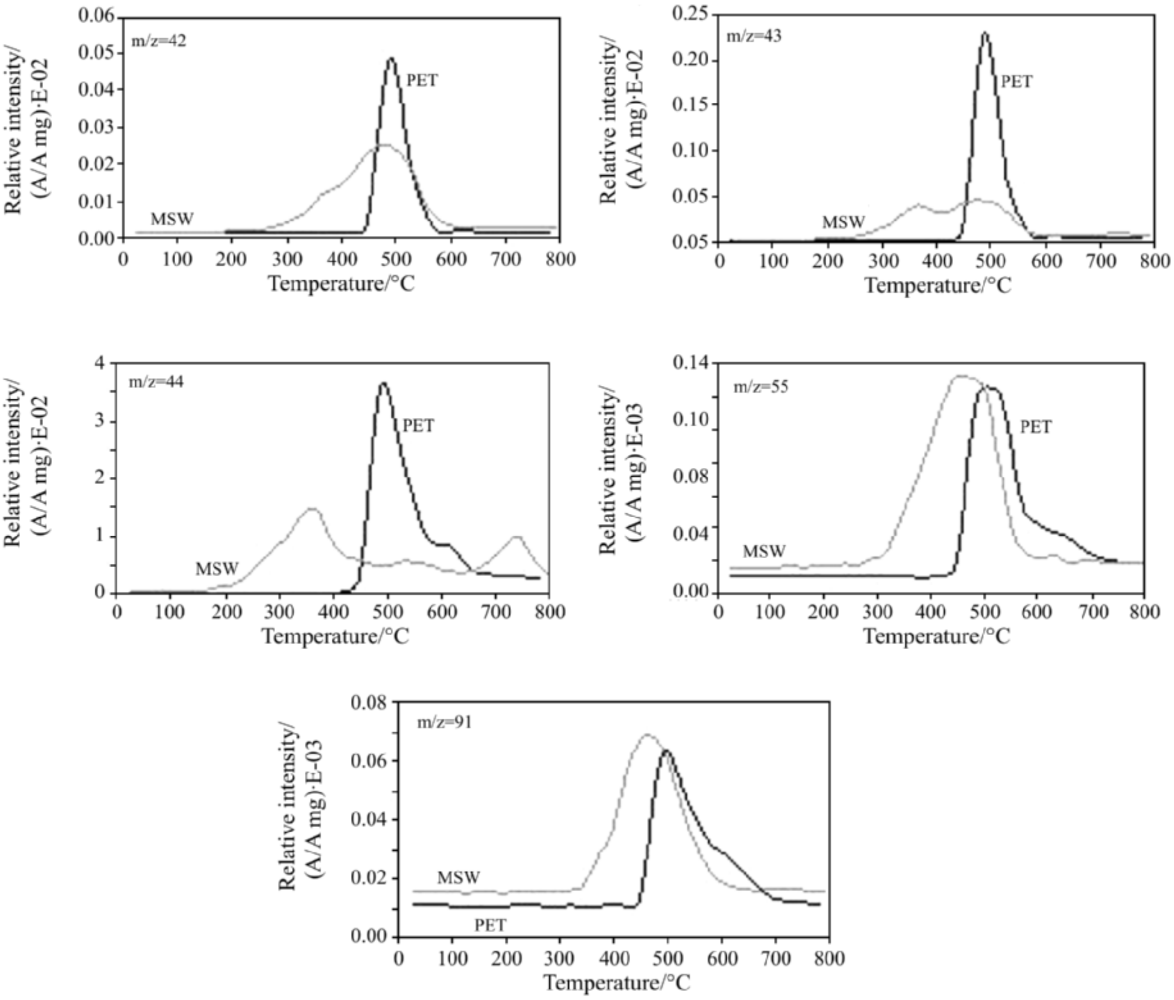

Fig. 4 Evolution profiles of the OFMSW and PET pyrolysis products at 50°C min^{-1} m/z=42, 43, 44, 55 and 91

also to volatilized nitrogen which has crossed over to a gaseous state and to ethylene.

The emission profiles for carbon dioxide (m/z=44) go up to higher temperatures as a consequence of the break-down of thermically stable structures. Moreover, CO_2 at high temperatures may be due to the decomposition of carbonates, as can be seen in the devolatilization of OFMSW at temperatures as high as between 600 and 800°C.

No emissions of sulphur dioxide (SO_2) were detected, nor of sulphur in its reduced form of hydrogen sulphur (H_2S).

Emissions of aromatic compounds were also detected at m/z=91, a signal corresponding to toluene. In this case the intensity of emission from PET was not particularly noteworthy in comparison with that from OFMSW.

Conclusions

Pyrolysis of the organic fraction of municipal solid wastes (OFMSW), PET and mixtures of OFMSW with PET were investigated by thermal analysis. The process of devolatilization occurs at different temperature ranges for the differing types of waste. This shows that the organic matter present in the wastes behaves differently in respect of devolatilization in the two cases of municipal waste and of plastic. The range of temperatures over which devolatilization of OFMSW occurs is quite large (200–500°C), probably as a consequence of the heterogeneity of the organic matter. PET presents high thermal stability, since emission of volatiles starts at temperatures above 300°C and it produces over a limited temperature range (400–500°C) this may be due to a greater homogeneity of its organic material content. Nevertheless, it is possible to state that devolatilization is practically total by 550 to 600°C in all cases.

The rate with which the loss of mass takes place (DTG), together with the percentage of carbonized product from the process, is in accordance with what was to be expected on the basis of immediate analysis of the various types of wastes. Nonetheless, the percentage of carbonized material in the organic wastes indicates that devolatilization is not total under the operating conditions used.

A mixture of OFMSW and PET gave the same results as those for the unmixed substances separately. On the basis of the thermogravimetric study of the mixtures of waste, it is possible to say that they would appear to behave as independent systems, presenting virtually no interaction, as confirmed by the fit of the graphs of calculated outcomes and of those obtained by experiment and supported by the low values for the objective function utilized.

A study of the mass spectrometry results reveals major emissions of energy-producing gases during pyrolysis, although fewer pollutants are emitted. The products of the pyrolysis process are principally hydrocarbons, hydrogen, carbon monoxide and carbon dioxide.

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