DISPOSAL OF PLASTIC SCRAPS ARISING FROM FOOD AND PHARMACEUTICAL INDUSTRY. COMPARISON BETWEEN DIRECT COMBUSTION AND PYROLYSIS PROCESSES

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The disposal of three of more diffused plastics (PE, PP, and PET), that are used in the food and in the pharmaceutical industry, was studied by comparing the direct combustion of the polymer and its pyrolysis, with a successive combustion of the gas phase produced during the process.

The samples were characterized by heat of combustion determination (calorimeter bomb) TG-MS/TG-GC-MS, DSC.

Among processes advantages, direct combustion presents a plant simplicity, while pyrolysis presents the availability to use the produced hydrocarbon gas phase as energy vector in devices which can be not necessarily near to the treatment plant.

Keywords: plastics disposal, combustion, pyrolysis, TG-MS/TG-GC-MS characterization

1. Introduction

Disposal laws prevent, for the food and the pharmaceutical industries, the recycling of plastic scraps. For this reason, other disposal methods are required.

Currently there are no concrete data on the amount of plastic waste resulted from both pharmaceutical and food industries.

Most plastic waste derived from this type of industries are plastic packaging waste. In Romania, each year are put on the market 350,000 tones of plastic packaging. Only 14,28 % are recycled. By 2013, Romanians will have to recycle 22,5% of all plastic waste placed on the market, according to GD no. 621/2005. In Italy are recovered 348 million tones of packaging waste of the total generated, 34% representing plastic packaging waste.

Among the valorisation of the polymer energy content, direct combustion and pyrolysis were compared under different points of view.

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Direct combustion presents a plant simplicity, but requires the use of the produced heat near to the disposal plant. Moreover, the combustion of the solid waste, may presents emission problems, due to the particulate formation.

Pyrolysis and gasification were pursued as viable option for the disposal of plastic waste. In past, some Authors have found these processes economically unattractive, because the operating costs and the ones for the separation of the products mixture [1].

Pyrolysis, in fact, presents a molecular weight distribution of the products that results quite broad and, in consequence, gives a low quality combustible. However, other researchers retain pyrolysis one of the best method to recover materials and energy from plastic, using only the 10 % of the energy content of the waste polimer to promote the pyrolysis process [2, 3].

At present, the instability of the fuel prices, gives renewed interest to pyrolysis of plastic waste, especially when the process gives a mixture of hydrocarbons at moderate temperatures and oil feedstock for petrochemicals industry [4]. Moreover, toxic products are concentrated in the solid residue, avoiding emission of particular pollutants. These reasons give to pyrolysis process an environmental friendly character. Finally, catalytic pyrolysis was studied for the decrease of the temperature of the process, and for an upgrading of the selectivity in the products, giving a narrow molecular weight distribution of the pyrolysis products [1, 4-6].

2. Results and Discussions

2.1 Materials and Methods

Plastics samples were trade polymers used and furnished by the Bormioli Rocco S.p.A.

The samples were characterized by high heating value determination, by a calorimeter bomb, TG-MS/TG-GC-MS, for the determination of the gaseous species evolved during the pyrolysis process, DSC, for the determination of the heat required by the pyrolysis reactions.

In the pyrolysis tests carried out, a LabSys Setaram thermobalance was used. This TG/DTA thermobalance operates in the 20–1000°C range, under 100 $cm^3 \cdot min^{-1}$ He flow, with a heating rate of 10 °C·min^{-1}. Samples were analysed by using a 0.1 cm^3 alumina crucible and α-Al_2O_3 as reference.

A VG-QMD-1000 Carlo Erba Instruments quadrupole mass spectrometer was used as detector of the evolved gas species. Electron impact mass spectra (70eV) were continuously registered and stored with frequency of 1 scan·s^{-1} ranging from 2 to 500 amu.

In TG-GC-MS measurements, gas chromatographic (GC) analyses were carried out on an HRGC Carlo Erba Instruments chromatograph, equipped with a

GR8 Bimatic thermostatted micro-valve for gas sampling, and the VG-QMD-1000 Carlo Erba Instruments quadrupole mass spectrometer as detector [7].

Chromatographic elution's were performed by using OV1 Mega (25 m, 0.32 mm) and poraPLOT Q Chrompack (25m, 0.32 mm) capillary columns with a temperature program of 30°C for 5 min, followed by 10°C·min^{-1} heating rate up to 200°C, held for 15 min. Helium was used as carrier gas with 15 kPa inlet pressure.

The differential scanning calorimeter on plastic was made by using a DSC 92 SETARAM instrument. For experimental procedure, about 20 mg of sample were used. This instrument operates in a range that goes from environmental temperature (25˚C) until 600˚C. The chosen speed of heating was 10 ˚C/min, in a nitrogen atmosphere.

The Mahler calorimeter used for the determination of the calorific value of substances is a Calorimat CBM Cecchinato. The calorimetry bomb, after the sample charge, is saturated with 21-25 bar of pure oxygen.

2.2 Pyrolysis of plastics

Polyethylene thermal decomposition, in inert atmosphere, takes place in a single step in the 400-510°C interval, with a maximum rate at 475°C. Thermogravimetric analysis reveals a mass loss of 95.2% which corresponds a gas phase evolution of more species.

In fact, the evolution of more hydrocarbons is observed; alkanes and alkenes up to C_{12}, which presence % is summarized in Table 1. Alkenes represent the 70% of the gas phase evolved; in particular 1-alkenes are the main species observed. Their formation takes place through a mechanism that implies firstly the polymer chains break, with the formation of two primary radicals. By hydrogen transfer rearrangement reactions, these radicals become secondary radicals, and a successive β C-C scission produces another primary radical, with the elimination of a 1-alkene [8, 9]. Evolved 1-alkenes can be undergone to rearrangements by isomerization reactions, that can be promoted by the high temperature of the pyrolysis process. Isomerization and successive radical chains break, and hydrogen transfer reactions, bear to the evolution of the observed dialkenes and alkanes.

Polypropylene pyrolytic decomposition takes place in a single step in the 350-500°C interval, with a maximum rate at 460°C. Thermogravimetric analysis reveals a mass loss of 97.0% which corresponds, also in this case, a gas phase evolution of more species, summarized in Table 1.

Experimental data agree with the ones of other Authors [6, 8].

PET pyrolytic decomposition takes place in a single step in the 430-480°C interval, with a maximum rate at 460°C. Thermogravimetric analysis reveals a

mass loss of 90.0% which corresponds, the main evolution of CO_2, CO, Benzene and Toluene, Methane and Ethylene.

Finally, the pyrolysis carried out on a blend of plastics (33%PE, 33%PP, and 33%PET) presents features that reflect the above analyses and the composition of the polymers blend, as reported in Table 1.

Table 1

Chemical composition of the gas phase evolved at 490 and 455°C, during thepyrolysis process of PE, PP, PET, and the blend of the three polymers, respectively.

Chemical compound	PE	PP	PET	BLEND
	Percentage [%]			
CO	---	---	33.1	11.0
CO_2	---	---	39.0	13.0
C_1, C_2	2.5	10.8	6.4	6.6
C_3	12.2	43.8	---	18.7
C_4	14.8	8.9	---	7.9
C_5	11.6	20.8	---	10.8
C_6	17.6	9.9	---	9.2
$> C_6$	41.3	5.8	---	15.7
Benzene	---	---	17.1	5.7
Toluene	---	---	4.0	1.3
Styrene	---	---	0.4	0.1

For the blend of polymers, on the basis of the gaseous products evolved during the pyrolysis process, and their heat of combustion, an HHV of 2480 kJ/mol was estimated for the produced gas phase. Considering an average molecular weight of 70 (C_5) for the evolved gas species, the HHV, reported in kcal/kg results 8464 kcal/kg.

DSC analysis for PE sample reveals a enthalpy of 70.7 J/g for the melting of the polymer (in the 78.5 – 148.5 °C interval), and 487.9 J/g for the pyrolysis reaction, this last in the 395-525°C interval.

PP sample presents a similar behaviour, with melting and pyrolysis enthalpy values slightly lower. Finally, for PET sample the DSC analysis reveals a enthalpy of 35.8 J/g for the melting of the polymer (215-295°C interval), and 192.1 J/g for the thermal decomposition reaction, that occurs in the 379-504°C range.

Obtained results were applied for the scaling of a pilot plant for the pyrolysis of 1000 t/year (about 120 kg/h) of non recyclable plastics.

The plastic material is subject to a thermal treatment, in an inert atmosphere, at 600˚C. The results obtained reveal a mass loss of 90% which corresponds the gas phase evolution described in the characterization of the

process. The 10% mass of carbonic residue (char) will be subject to another thermal treatment in order to recover its energy content.
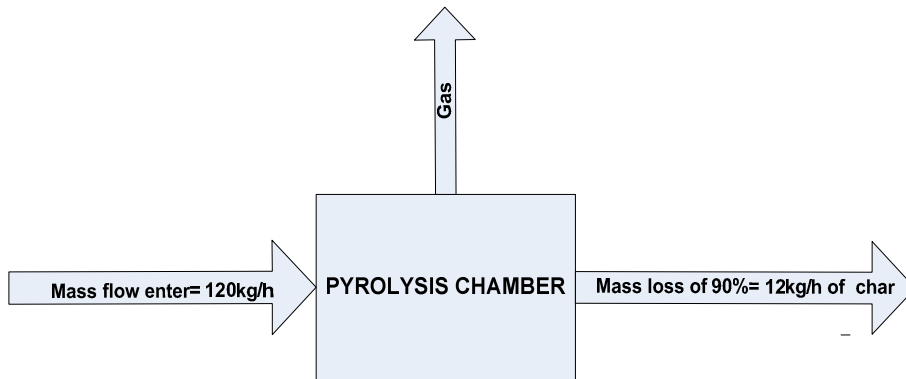

Fig. 2. Mass balance of the pyrolysis chamber

Considering a specific heat for the polymers of 0,25 kcal/°C kg, 17400 kcal/h are required for the heating of the plastics to the pyrolysis temperature.

Among pyrolysis reaction, the higher endothermic value of the thermal decomposition (case of polyethylene) was take in consideration for the energy balance, thus, about 14000 kcal/h are required by the pyrolysis of the plastics.

The total energy required by the process results 31400 kcal/h. Moreover, considering a 50 % energy efficiency of the system, about 63000 kcal/h are required for the pyrolytic decomposition of the plastics.This energy may be produced by the combustion of the pyrolysis residue (char HHV is estimated around 7000 kcal/kg), or by the combustion of a little amount (<10%) of the gas phase produced by the pyrolysis process.

2.3 Direct combustion of plastics

For the direct combustion of the plastic scraps, the value of the produced heat by their combustion was determined by a series of calorimetric test (Mahler calorimeter bomb). The experimental runs during the calorimetry of the sample PP ,PE, PET with time are shown in figure 3, 4 and 5.

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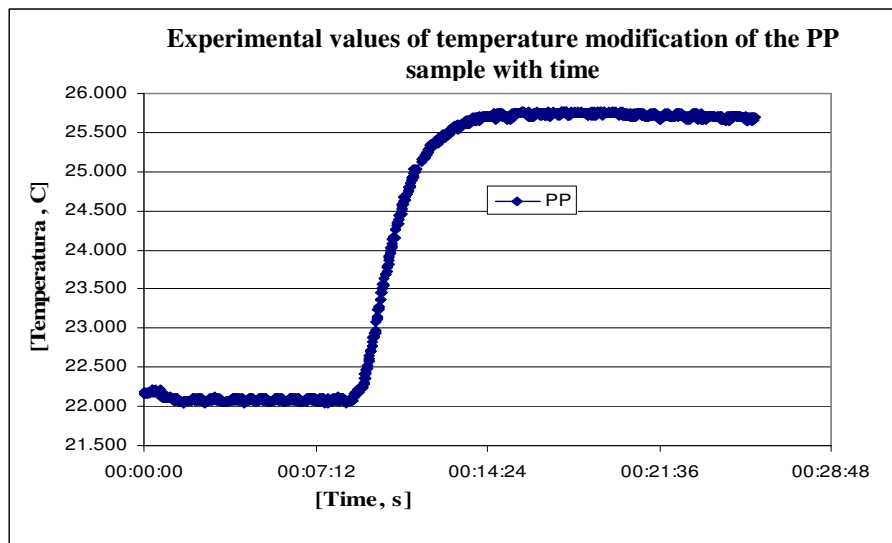M.Ragazzi, Elena Cristina Rada

Fig.3. Experimental values of temperature modification of the PP sample with time
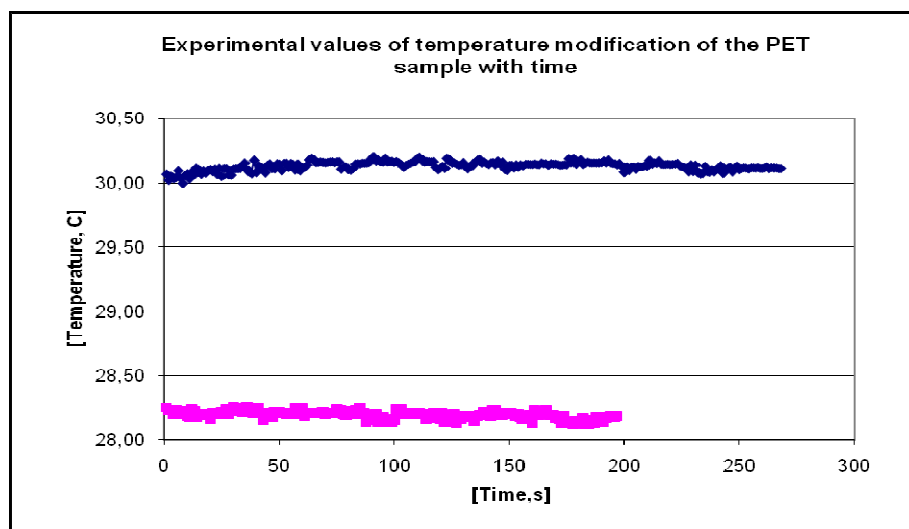

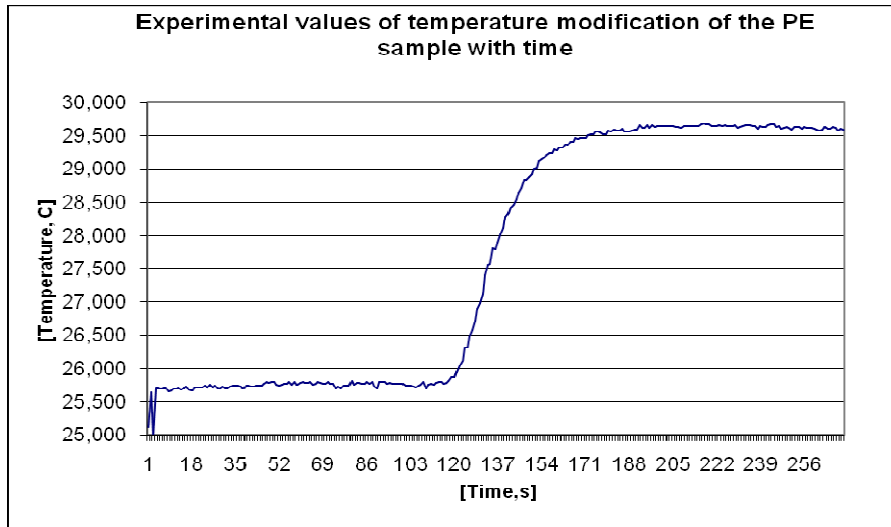Fig. 4. Experimental values of temperature modification of the PET sample with time

Fig. 5. Experimental values of temperature modification of the PET sample with time

The measured value, reported in Table 2, were compared with the ones determined by the use of more models.

Table 2

HHV of the plastic sample from experimental data

Type of plastic sample	HHV [kJ/kg]
Polypropylene (PP)	43,50
Polyethylene (PE)	44,70
Polyethylene terephthalate (PET)	21,01
Blend of PP , PE,PET	36,03

These values were compared with the ones determined by using the Dulong's formula [10] Based on this formula, the HHV is determinated by equation 1:

$$HHV= 8080C+34,460H-4,308O+2250S \ [kcal/kg] \qquad (1)$$

where C, H, O and S are the mass fraction of the elemental composition of the polymer.High Heating Values, reported as kJ/kg, result for PE and PP samples 29,014 kJ/kg, while for PET sample the model gives a HHV value of 21,143 kJ/kg, very close to the one measured by using the calorimeter bomb.

Finally, for the blend of polymers, High Heating Value of 26,127 was calculated.

3. Conclusions

Considering the same disadvantage due to the transport of the plastic scraps to the treatment place, direct combustion presents a plant simplicity, beside the consequence due to the combustion of a solid, such as particulate emission, and the use of the produced heat near to the disposal plant.

Pyrolysis presents the availability to use the produced hydrocarbon gas phase as energy vector in devices which can be not necessarily near to the treatment plant. Disadvantage are the relative plant complexity and the production of the pyrolysis solid residue (about 3-5% for PE and PP, 10% for PET), graphitized carbon that can be however burned in the same plant, or in another furnace.

R E F E R E N C E S

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