

# Study on the Thermal Decomposition of Plastic Residues

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The use of plastics in the last decades significantly increased, thus plastic recycling processes are needed. Generally, mixtures of plastic materials are disposed together, hence the recovery of the polymeric material is difficult and expensive. Plastic residues could be valorized by thermal degradation processes aimed at recovering energy and/or valuable compounds for chemical industry. The main technologies used for this purpose are gasification and pyrolysis. The latter is a thermal degradation process that occurs in the absence of oxygen at moderate temperature (300-700°C), that could be used to recover the thermal power of biomasses. The reaction products are bio-oil, biogas and biochar. The aim of this work was to employ pyrolysis to energetically exploit different pure plastic materials, namely polyethylene terephthalate (PET), polyamide (Nylon-6), polyvinyl chloride (PVC) and polyurethane (PU), as well as a complex one such as end of life tyres (ELT). The reaction was performed at 400 °C for 90 min. The pyrolysis system was composed by a tubular quartz reactor heated with a tubular vertical oven. An integrated condenser was used to separate the liquid reaction products, while the incondensable gases were collected in a latex balloon. The reaction products were quantified gravimetrically and, in order to evaluate the functional groups, characterized by FTIR analysis. The reaction gases were also analyzed by GC-MS to determine the composition of this fraction. Results obtained from the different plastics were significantly different in terms of distribution and composition. In particular, PET produced a biogas consisting mainly of acetaldehyde and hydrocarbons, while the liquid fraction was composed of benzoic and terephthalic acids. Nylon-6 degraded producing a large amount of reaction gas (65 g/100g) composed of ammonia and light hydrocarbons, while the reaction liquid was mainly caprolactam. Around 53 g/100g of PVC reaction products were gaseous, mainly hydrochloric acid, followed by toluene and benzene at high concentrations. The degradation of PU produced a reaction gas, mainly composed by formic and acetic aldehydes. ELT pyrolysis was responsible for the production of high amounts of solid residue, while reaction gas and liquid seemed to be mainly constituted by hydrocarbons. In general, the study of pure plastic pyrolysis could help to better understand the thermal decomposition of complex plastic residues such as ELT.

## 1. Introduction

In the last decades the plastic consumption is continuously increasing, because it plays a fundamental role in many products in various sectors such as packaging, healthcare, construction, etc. On the market there are several plastic materials, with different properties and applications depending on their use (Williams et al., 1997). Polyethylene terephthalate (PET), which is the standard plastic with the highest consumption, is used especially in the packing sector (Grause et al., 2011). Nylon-6 is generally used for products that need high resistance, like wheels, connections and bearing (Ahn et al., 1997). Polyvinylchloride (PVC) is a polymer with high chemical resistance that can be mixed with several additives, allowing the production of plastic material with several chemical and physical properties (Xu et al., 2002). Polyurethane (PU) is widely used because it can be expanded as foam and can be utilized as filler in different sectors (Saha et al., 2008). ELT are mainly composed by hydrocarbons and they are considered as non-hazardous wastes (Antoniou and Zabaniotou, 2015).

The huge plastic demand led to growing accumulation of plastic wastes, which take very long to degrade naturally. Therefore, the continuous disposal of plastics in landfill is a false solution (Pinto et al., 1999). One of

the possible means to mitigate this problem is to increase plastic recycling. Generally, mixtures of plastic materials are disposed together, and the recovery of the polymeric material is difficult and expensive (Arena et al., 2003). A promising alternative is the recovery of the energetic potential of the polymeric material through thermal degradation processes (López et al., 2010).

Pyrolysis is a thermochemical process carried out in absence of oxygen, whose resulting products are a liquid fuel, a gas and a char with composition and proportions depending on process conditions and feedstock characteristics (Bhaskar et al., 2003). Pyrolysis of plastic residues enables the thermal degradation of long chain polymeric molecules into smaller ones; moreover it is considered a green technology when the pyrolysis by-products have a calorific value that can be reused to compensate the overall energy demand of the process (Sharrudin et al., 2016).

The aim of this work was to investigate the pyrolysis of different pure plastic materials such as PET, Nylon-6, PVC and PU as well as of a complex one like end of life tires.

## 2. Materials and methods

### 2.1 Polymeric materials

The pyrolysis reaction was performed on different pure plastic residues such as polyethylene terephthalate (PET), polyamide (Nylon-6), polyvinyl chloride (PVC) and polyurethane (PU), as well as a complex one like end of life tyres (ELT).

### 2.2 Experimental design

Thermal pyrolysis was performed in a tubular quartz reactor connected to a condenser able to separate liquid from gaseous products, connected at the top to a reflux condenser (Figure 1). Briefly, about 10 g of sample were charged into the reactor, and then the system was purged with nitrogen. The reactor was put into an oven (Carbolite, MTF 10/25/130, Pocklington, UK), and the reaction temperature set at 673 K for 90 min. The incondensable gases, called reaction gas (RG), were collected into latex balloons located on the top of the reflux condenser and after the condenser. The condensable gases, called bio-oil (RL), were condensed and collected in a flask. After pyrolysis, the solid residue (SR) was collected and washed with ethanol to recover the heavy bio-oil fraction.

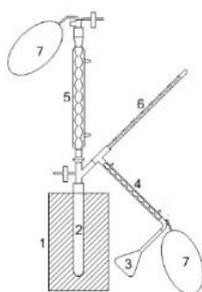


Figure 1: Pyrolysis reaction system. 1) Oven with temperature control, 2) quartz reactor, 3) flask (bio-oil collector), 4) condenser, 5) reflux condenser, 6) thermometer, 7) latex balloon (reaction gas collector).

### 2.3 FTIR analysis

The polymeric materials (PET, Nylon 6, PVC, PU and ELT) and the reaction products of thermal pyrolysis (RG, RL, RS) were analyzed by Fourier Transform Infrared Spectroscopy (FTIR) using a Nicolet 380 Spectrometer (Thermo Scientific, Madison, WA, USA). All the spectra were elaborated by the Omnic Lite Software (Thermo Electron Corporation, Madison, WA, USA). To analyze the solid residues, samples were mixed with KBr (1:50 w/w) and pressed, while liquid samples were deposited on a KBr pressed disk. RG were forced to pass through an IR glass cell with KBr windows and analyzed by the same spectrometer.

### 2.4 GC and GC-MS analyses

All RG samples were analyzed using a gas chromatograph, model 4890 (Agilent Technologies, Santa Clara, CA, USA), with FID detector. The instrument was equipped with a Varian capillary column, model Molsieve 5A/Porabond Q Tandem (Agilent). Helium (purity > 99.9%) was used as a carrier gas at a flow rate of 1.6 mL min<sup>-1</sup>. The column temperature was initially set at 343 K, increased up to 503 K at 10 K min<sup>-1</sup>. Using a 500 µL

gas chromatography syringe, 400  $\mu\text{L}$  of sample were injected with a split ratio of 1:10. RL samples were diluted with  $\text{CHCl}_3$  up to a ratio of 1:10 (v/v) and analyzed by a gas chromatography-mass spectrometer (GC-MS), model Focus-ISQ (Thermo Scientific, Milan, Italy) (Romero et al., 2018).

### 3. Results and discussion

#### 3.1 Reaction yields

Thermal pyrolysis was performed at 673 K for 90 min, and the reaction products were classified as reaction gas (RG), reaction liquid (RL) and solid residue (SR). Table 1 lists the reaction yields of these fractions obtained from each of the selected plastic residues, namely polyethylene terephthalate (PET), polyamide (Nylon-6), polyvinyl chloride (PVC) and polyurethane (PU). It is possible to observe that the polymer residue that led to the highest RG yield was Nylon-6 (65.69 g/100g), followed by PVC (53.01 g/100g), while the lowest yield of RG was produced by PFU (13 g/100g), while a mixture of them showed a much lower conversion (SR = 82 g/100g).

Table 1: Yields (%) of reaction gas (RG), reaction liquids (RL) and solid residue (SR)

	RG (g/100g)	RL (g/100g)	SR (g/100g)
PET	28.02	23.00	48.80
PVC	53.01	6.71	40.28
PU	25.11	19.00	55.89
Nylon-6	65.69	13.73	20.59
ELT	12.89	3.91	82.20

#### 3.2 Reaction gas characterization

Figure 2 shows the FTIR spectra of the reaction gases from thermal pyrolysis of the selected plastic materials. All the spectra displayed the typical band of the asymmetric stretching of carbon dioxide at  $2342\text{ cm}^{-1}$ , its roto-vibrational deformation (O-C-O) at  $669\text{ cm}^{-1}$  and its overtones at  $3726$  and  $3627\text{ cm}^{-1}$ . The roto-vibrational band of CO stretching mode was visible at  $2143\text{ cm}^{-1}$ . Moreover, all the spectra presented the bands of methane stretching deformation at  $3016$  and  $1304\text{ cm}^{-1}$ , and the characteristic one of ethylene at  $949\text{ cm}^{-1}$ .

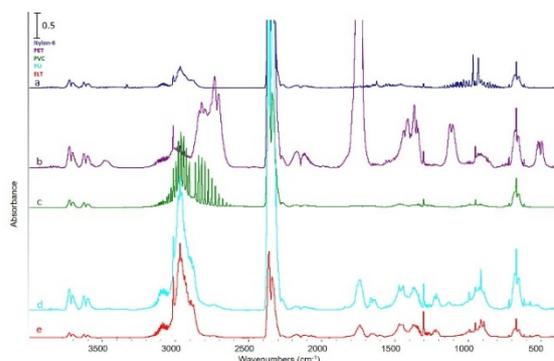


Figure 2: FTIR spectra of reaction gases from thermal pyrolysis of a) Nylon-6, b) PET, c) PVC, d) PU and e) ELT.

Analyzing the PET spectrum, it was possible to observe the characteristic bands of acetaldehyde at  $3483\text{ cm}^{-1}$ , the C-H stretching of aldehydes at  $2821$  and  $2730\text{ cm}^{-1}$ , the C=O stretching at  $1759\text{ cm}^{-1}$  and the  $-\text{CH}_2$  deformation at  $1411\text{ cm}^{-1}$  likely due to the presence of monomeric ethylene glycol in the reaction gas. The presence of hydrochloric acid can be clearly inferred from the PVC spectrum by the roto-vibrational bands in the region between  $3061$ - $2675\text{ cm}^{-1}$ , the bands of  $-\text{CH}_2$  scissoring at  $1425\text{ cm}^{-1}$  and that of H-C-H wagging mode at  $946\text{ cm}^{-1}$ . The PU spectrum exhibited the stretching band of C=O at  $1743\text{ cm}^{-1}$  and those of  $-\text{CH}_3$  deformation at  $1473$  and  $1377\text{ cm}^{-1}$  that confirmed the presence of acetone. There were also the  $-\text{CH}$  weak aromatic bands at  $3150$  and  $3016\text{ cm}^{-1}$  and those of C=C stretching at  $1663\text{ cm}^{-1}$ ,  $-\text{CH}_2$  deformation of alkanes at  $1473\text{ cm}^{-1}$  and N=O stretching at  $1232$  and  $1216\text{ cm}^{-1}$ . The Nylon-6 spectrum revealed the presence of ammonia due to the C-N and amide bonds broken, with the symmetric and asymmetric characteristic bands of

C-N between 3487 and 3143  $\text{cm}^{-1}$ , the asymmetric H-N-H deformation at 1625  $\text{cm}^{-1}$  and the symmetric N-H deformation at 950  $\text{cm}^{-1}$ . The end of life tyres (ELT) spectrum presented the -CH stretching at 3016  $\text{cm}^{-1}$ , the -CH bending at 1303  $\text{cm}^{-1}$ , the C=C stretching at 1650  $\text{cm}^{-1}$  and the -CH<sub>2</sub> deformation at 1470  $\text{cm}^{-1}$ , thereby confirming the presence of alkenes in the reaction gas.

Table 2 lists the percentage composition of main compounds identified in the reaction gases by GC. The results confirmed those of FTIR, in that, the major components for all the plastic residues, except PVC, were carbon dioxide and monoxide, acetaldehyde and butene, while, as expected, the main RG component from PVC pyrolysis was hydrogen chloride. The RGs were then classified in five different classes: hydrocarbons, acids, oxygenates, nitrogenates and chlorinates.

The largest fraction of hydrocarbons in RG was obtained from pyrolysis of ELT (65.51 g/100g), of which they represented the most abundant class, followed by that of PU (63.2 g/100g), PVC (24.3 g/100g), PET (20.8 g/100g) and Nylon-6 (8.6 g/100g), while the highest fraction of oxygenates came from PET (79.2 g/100g), followed by ELT (34.5 g/100g), PU (31.5 g/100g) and Nylon-6 (20.9 g/100g). The fraction of nitrogenates in Nylon-6 RG was mainly composed by ammonia (70.4 g/100g), while that of chlorinates in PVC RG by hydrogen chloride (73.2 g/100g). RG could be used to produce energy, provided that nitrogenates and chlorinates are removed before use in order to make it cleaner and richer in hydrocarbons (Angelidaki et al., 2018).

*Table 2: Main compounds identified by GC analysis in the reaction gases from thermal pyrolysis of different plastic materials.*

	PET (g/100g)	PVC (g/100g)	PU (g/100g)	Nylon-6 (g/100g)	ELT (g/100g)
Ammonia	-	-	0.95	0.78	3.93
Methane	2.06	-	1.90	1.72	8.27
Carbon monoxide	19.12	-	3.65	4.60	6.65
Carbon dioxide	15.25	-	29.06	59.32	9.71
Ethylene	4.51	-	2.85	2.58	5.30
Ethane	0.36	-	6.20	2.09	11.41
Formic aldehyde	0.38	-	18.21	2.72	-
Methanol	0.16	-	-	1.57	-
Acetal aldehyde	52.62	-	21.40	19.30	15.38
Propane	0.99	-	1.61	-	9.91
Butene	-	-	5.69	0.93	22.32
Acetone	-	-	8.46	1.35	3.80
Hydrogen chloride	-	75.89	-	-	-
Furan	2.88	-	-	-	-
Ethyl acetate	-	-	-	0.50	-
Butane	-	-	-	-	1.29
Pentane	-	-	-	-	1.24
Benzene	0.91	22.59	-	-	0.81
Styrene	0.19	1.52	-	-	-
Toluene	0.29	-	-	-	0.42
Cyclopentane	-	-	-	0.54	-
Butanol	-	-	-	2.01	-
Ethylbenzene	0.27	-	-	-	-

### 3.3 Reaction liquid characterization

Chapter 2 Figure 3 illustrates the FTIR spectra of reaction liquids from thermal pyrolysis of the selected plastic materials. The PET spectrum displayed the characteristic band of -OH stretching between 3100 and 2548  $\text{cm}^{-1}$  and those of C=O, O-C-O and aromatic C=C stretching at 1962, 1288 and 1600  $\text{cm}^{-1}$ , respectively. Similarity of these bands with the characteristic ones of benzoic acid confirms the results obtained by Grause et al. (2011). The PVC spectrum presented aliphatic -CH stretching between 2952 and 2961  $\text{cm}^{-1}$ , C=O stretching at 1698  $\text{cm}^{-1}$ , C-C stretching between 1200-800  $\text{cm}^{-1}$ , aromatic C=C bond between 1589 and 1460  $\text{cm}^{-1}$ , C-Cl deformation at 724  $\text{cm}^{-1}$  and Si-O stretching at 1116  $\text{cm}^{-1}$ . These bands can be assigned to the presence of ketones, aromatic compounds and unreacted PVC, except that of Si-O band probably due to the use of silicon as polymer filler (Karayildirim et al., 2006). The PU spectrum presented the typical bands of the aliphatic -CH stretching between 2968 and 2929  $\text{cm}^{-1}$ , the -NH stretching at 3363  $\text{cm}^{-1}$ , the -OH stretching at 3363  $\text{cm}^{-1}$ , the

C=O stretching at  $1711\text{ cm}^{-1}$ , the  $-\text{CH}_2$  bending at  $1467\text{ cm}^{-1}$  and the Si-O bond stretching between  $1094$  and  $920\text{ cm}^{-1}$  likely because of the use of silicon surfactant (Lim et al., 2008). The spectrum of Nylon-6 exhibited the  $-\text{NH}$  stretching at  $3293\text{ cm}^{-1}$ , the aliphatic  $-\text{CH}$  stretching between  $2928$  and  $2856\text{ cm}^{-1}$  and the deformation of  $-\text{NH}$  bond and the C=O stretching at  $1663\text{ cm}^{-1}$ , which can be ascribed to its complete depolymerization to caprolactone (Czernik et al., 1998). The ELT spectrum presented at wavenumbers  $> 3000\text{ cm}^{-1}$  the aromatic  $-\text{CH}$  stretching and  $< 3000\text{ cm}^{-1}$  the aliphatic  $-\text{CH}$  stretching, at  $1454\text{ cm}^{-1}$  the  $-\text{CH}_2$  bending, at  $1600\text{ cm}^{-1}$  the aromatic C=C bending and its overtones and at  $1029\text{ cm}^{-1}$  the Si-O bond stretching. These bands in the ELT spectrum were likely due to the formation of toluene or its derivatives, while the Si-O band to silicon used as a polymer filler.

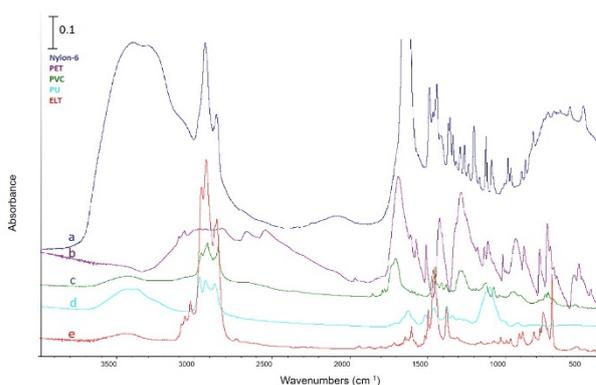


Figure 3: FTIR analysis of reaction liquids from thermal pyrolysis of a) Nylon-6, b) PET, c) PVC, d) PU and e) ELT.

### 3.4 Solid residue characterization

Except for small variations in the intensity of the peaks and the wavenumber, the spectra of Nylon-6, PU and ELT solid residues presented almost the same bands as the liquid almost the same bands as the reaction liquids (Figure 4). While, the PET spectrum presented the  $-\text{CH}$  aromatic stretching at  $3000\text{ cm}^{-1}$  and the C-O stretching between  $1300$  and  $1060\text{ cm}^{-1}$ , the last being associated to the formation of polyether from partial depolymerization of PET. In the PVC spectrum it is possible to observe the characteristic bands of water, i.e. those of the  $-\text{OH}$  asymmetric stretching at  $1934\text{ cm}^{-1}$ , the  $-\text{OH}$  scissoring at  $1634\text{ cm}^{-1}$  and the water release at  $534\text{ cm}^{-1}$ . Moreover, there were the bands of  $-\text{CH}$  stretching between  $2952$  and  $2929$  and the  $-\text{CH}$  bending at  $1451\text{ cm}^{-1}$ .

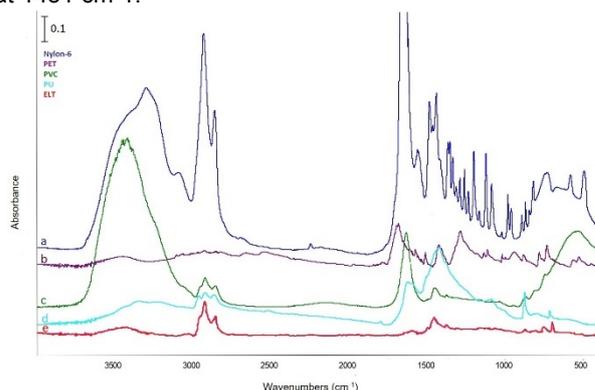


Figure 4: FTIR analysis of solid residue from thermal pyrolysis of a) Nylon-6, b) PET, c) PVC, d) PU and e) ELT.

## 4. Conclusion

The thermal pyrolysis of different polymeric residues was performed to investigate the distribution of reaction products and their characterization. All the polymeric materials widely decomposed during the pyrolysis at  $673\text{ K}$ . The reaction gases were mainly composed of combustible compounds; thus, they could be used as a biofuel to produce energy. The reaction gases released from the pyrolysis of PVC, PU and Nylon-6 that

contained also chlorine and nitrogen, should be purified to be used as fuel gases. Moreover, monomers of the different polymer residues could be recovered from reaction liquids and solid residues. Therefore, thermal pyrolysis would offer a solution to solve the problem of plastic waste accumulation into the environment, producing energy through the reaction gases and allowing for monomer recovery from reaction liquids and solid residue.

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