

INFLUENCE OF TEMPERATURE ON THE PRODUCTS OBTAINED IN PYROLYSIS OF WASTE PACKING AND PACKAGING PLASTICS

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Abstract: The objective of this work is the study of pyrolysis as a feedstock recycling process, for valorising the rejected streams that come from industrial plants, where packing and packaging wastes are classified and separated for their subsequent mechanical recycling. A representative sample of these rejected streams has been pyrolysed under nitrogen in a 3,5 dm³ autoclave at 460, 500 and 600° C for 30 minutes to analyze the influence of temperature in the products obtained. Waste packing pyrolysis liquids are a complex mixture of organic compounds containing valuable chemicals as styrene, ethyl-benzene, toluene, etc. Pyrolysis gases are mainly composed of hydrocarbons together with some CO and CO₂, and have very high gross calorific values (GCV). Almost no solids are obtained in pyrolysis of waste packing plastics.

Temperature plays a significant role in the pyrolysis process. At 460° C total conversion of the waste plastics is achieved. Raising temperature gives rise to higher gas yields and lower liquid yields. The characteristics of pyrolysis products, especially the liquid fraction, vary significantly with temperature. At 460° C wax-like products are obtained, at 500° C high viscosity liquids and at 600° C more fluid and aromatic liquids are obtained.

Keywords: pyrolysis; thermolysis; feedstock recycling; plastic wastes.

1. Introduction

Nowadays plastic consumption is more than ever increasing. Annual consumption of plastics in Occidental Europe is about 60 million tons, of which about 40 % are used in packing and packaging applications, that in a very short period are converted to wastes, yielding about 15 million tons of such wastes per year [1]. At present, in Europe, about 50% of the annually generated plastic wastes are valorized, 60 % by incineration with energy recovery and about 40 % by recycling. Most of the recycled plastics are mechanically recycled, while less than 1% is chemically recycled.

The EU legislation (Directive 2004/12/CE) obliges to valorise (energy recovery + recycling) 60 % of the packing and packaging wastes, with at least 55-85 % of recycling. For this to be possible, on the one hand municipal (yellow) containers for such wastes have been set out in different UE countries, and on the other hand industrial separation and classification plants, which receive the yellow containers contents as raw materials, are being operated on an industrial scale. In such plants the wastes are separated in different fractions (steel, tetra-brick, aluminium cans, different plastics, etc.) and then sent to recycling companies. However, a significant amount of the income materials cannot be properly classified or separated and are rejected. Such rejects are composed of many different materials (PE, PP, PS, PVC, PET, ABS, aluminium, film, etc.), which are very much intermingled; consequently it is not technical or economically viable an ulterior separation, and therefore they can only be incinerated or land-filled. In this paper a mixture of plastics with the same components and proportions as a real rejected stream was prepared and pyrolysed at different temperatures, in order to on the one hand evaluate the potential of pyrolysis as a feedstock recycling technique for plastic packaging wastes and on the other hand determine the influence of this parameter in the characteristics of the products obtained.

In the pyrolysis process (heating without oxygen), the organic components of the material are decomposed generating liquid and gaseous products, which can be useful as fuels and/or sources of chemicals. If there were inorganic components in the waste (metals, fillers...) they would remain practically unaltered after pyrolysis, and they might be recycled or reused. The rejects from plastic packages coming from separation plants have rather low inorganic contents, so if it was not worth recycling pyrolysis solids they would be a minimum waste to be land-filled. Pyrolysis is especially appropriate for products or streams of wastes which are a mixture of different plastics for which mechanical recycling is not feasible; such is the case of the fraction that has been studied in this work.

2. Experiment

2.1 Characteristics of the sample pyrolysed

The typical composition of the rejects of a waste packing separation and classification plant was determined characterizing real samples rejected from an industrial plant located in Amorebieta, in the north of Spain. Homogeneous samples with such typical composition were prepared for the pyrolysis experiments, using pellets (≈ 3 mm size) of the following materials: polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET) and polyvinyl chloride (PVC). Additionally a finely ground sample (< 1 mm) was prepared for characterization purposes. The determined composition, which is presented in tab. 1, is quite similar to those proposed by other authors as representative of municipal plastic waste compositions [2,3].

PART I PYROLYSIS

Tab. 1 Composition of the sample pyrolyzed (weight %)

Material	PE	PP	PS	PET	PVC
Composition	40	35	18	4	3

The moisture and ash contents of the samples were determined by thermogravimetric analysis, and the elemental composition with automatic CHN and S determinators, and by analysing the gases generated in the combustion of the sample for Cl determination. The gross calorific value (GCV) was determined with an automatic calorimetric bomb. The results are presented in Tab. 2.

Tab. 2 Elemental composition and GCV of the samples pyrolysed (weight % in wet basis)

Parameter	Moisture	Ash	C	H	N	Cl	Others	H/C	GCV (MJ kg ⁻¹)
Value	0.1	0.0	84.7	12.5	<0.1	1.1	1.5	1.8	43.9

2.2 Pyrolysis experiments

The pyrolysis experiments were carried out at 460, 500 and 600° C in nitrogen atmosphere, using an unstirred stainless steel 3,5 dm³ autoclave. In a typical run 100 g of the sample are placed into the reactor, which is then sealed. Nitrogen is passed through at a rate of 1 dm³ min⁻¹ and the system is heated at a rate of 20 °C min⁻¹ up to the selected temperature, and is maintained there for 30 minutes. It has been proved by the authors that in the mentioned installation after 30 minutes no more pyrolysis products evolve from the autoclave [4]. All through the run the vapours leaving the reactor flow to a series of water cooled gas-liquid separators where the liquids are condensed and collected. The uncondensed products are passed through an activated carbon column and collected as a whole in Tedlar plastic bags, to be afterwards tested by gas chromatography. Solid and liquid pyrolysis yields are determined in each experiment by weighing the amount of each obtained, and calculating the corresponding percentage, while the gas yield is determined by difference.

3. Results and Discussion

The mean value of the liquid, gas and solid yields (weight %), obtained in three pyrolysis runs carried out at each temperature, which did not differ more than 3 points in the percentage, are presented in Tab. 3 .

Tab. 3 Pyrolysis yields (weight %)

FRACTION	460° C	500° C	600° C
Liquids	72.0	65.2	42.9
Gas	26.9	34.0	56.2
Solids	1.1	0.8	0.9

It can be seen in Tab. 3 that while the solid yield has a constant value in all the experiments, the gas and liquid yields are strongly influenced by temperature, and the higher the temperature, the higher the gas yield and the lower the liquid yield obtained. This has also been reported by many other authors, e.g. [2,5], and it is attributed to the stronger cracking of C-C bonds that is produced at higher temperatures, which gives rise to lighter hydrocarbons with shorter carbon chains. In all cases, a small quantity of solid product ($\approx 1\%$ wt) was obtained in spite of the absence of inorganic matter in the original sample (see Table II); this is attributed to char formation, due to secondary repolymerisation reactions among the polymer derived products. The authors [4,6] and also other research groups [7,8] have obtained a certain amount of char in the pyrolysis of many polymeric materials. A study carried out by Van Krevelen [9] about the thermal decomposition of polymers, concludes that char is formed in the decomposition of certain polymers, and that the char forming tendency depends on the chemical structure of the polymer; such tendency increases when the polymer contains groups capable of reacting with hydrogen atoms of the polymeric structure, such as $-\text{Cl}$, $=\text{O}$, etc., which is the case of PVC and PET, both of them contained in the raw sample.

Tab. 4 GC-MS analysis (area %) and GCV of the liquids

	460° C	500° C	600° C
Aromatics	71.7	73.9	99.3
Non aromatics	22.3	22.4	0.4
Non identified	6.0	3.7	0.3
C5-C9	78.1	79.6	70.6
C10-C13	7.4	9.4	23.8
>C13	8.5	7.3	5.3
Main components	Styrene: 45.5 Toluene: 9.9 Ethylbenzene: 7.1	Styrene: 48.4 Toluene: 8.1 Ethylbenzene: 5.0	Styrene: 32.4 Toluene: 17.5 Ethylbenzene: 8.1
GCV (MJ kg ⁻¹)	43.5	43.3	40.8

Tab. 4 shows the main characteristics of the liquids obtained in the experiments. The liquid derived from the 460° C experiment was a wax-like product, which is due to the presence of long non aromatic chains. The characteristics of the 500° C experiment liquid are quite similar to those of the 460° C run, however it was not a wax but a high viscosity liquid at room temperature, which may be due to its slightly higher aromatics and C5-C9 contents. On the other hand, the liquid derived from the 600° C experiment was a dark coloured fluid product which resembled petroleum fractions and which contained large quantities of aromatics, more than 99 area%. Several authors have reported that the formation of aromatics in thermal processes at low temperatures (460-500° C) the aromatics are probably derived from the aliphatic hydrocarbons formed in the primary decomposition, via Diels-Alder

reaction and followed by a dehydrogenation step [10,11]. Since Diels-Alder reactions are exothermic and reversible, they will be produced to a lesser extent at higher temperatures. Therefore, such mechanism does not justify the increase in aromatics with temperature observed in this study, since if Diels-Alder reactions are reversed, polyenes formation will be favoured and less aromatics will be produced. Alternatively, it has been proposed [11] that at higher temperature highly stable aromatics are directly produced by means of the so called pyrosynthesis reactions.

In all cases, styrene is the main component of the organic liquids, reaching almost 50 weight% in the 500°C experiment. Other aromatic products obtained in significant proportions are toluene and ethyl-benzene. Therefore valuable chemicals can be recovered from pyrolysis organic liquids. On the other hand, Table IV shows that pyrolysis oils have very high GCVs, similar to those of conventional liquid fuels, so they may be considered as an appropriate alternative to fossil fuels.

Concerning gases, Tab. 5 shows that they are composed of hydrocarbons from C1 to C6, hydrogen and some carbon dioxide and monoxide. The gases from the 600° C experiment have the highest H₂ and short chain hydrocarbons (C1-C2) contents, which is due to the stronger cracking of C-C bonds produced at higher temperatures. In any case, the GCV of every of the pyrolysis gases is higher than the GCV of natural gas (44 MJ kg⁻¹) and for this reason they can be used as energetic source for the process, and the surplus may be valorized.

Tab. 5 GC-TCD/FID analysis (weight %) and GVC of the gases

Experiment	H ₂	CO+CO ₂	C1	C2	C3	C4	C5+C6	GCV (MJ kg ⁻¹)
460° C	0.4	3.6	7.9	21.3	29.8	18.1	18.8	48.6
500° C	0.4	3.6	8.3	22.2	29.1	17.6	18.7	48.6
600° C	0.7	2.7	13.0	29.6	28.2	16.3	7.5	49.8

4. Conclusion

Feedstock recycling by pyrolysis of packing and packaging plastic wastes is a promising technique for valorising this kind of wastes, since conversions to liquid + gas higher than 95% can be obtained. The temperature of the process plays a very important role in the distribution and quality of the pyrolysis products. On the one hand, low temperatures leads to the generation of a high proportion of wax-like paraffinic/olefinic liquids. On the other hand, high temperatures give rise to very aromatic liquids and to more H₂ and short chain hydrocarbons in the gases. In every case, some char is formed as a result of secondary repolymerisation reactions among the polymer derived products.

Concerning the applications of pyrolysis products, liquids may be used as high GCV alternative fuels or as a source of valuable chemicals, such as styrene, toluene or ethyl-benzene. The gaseous fraction can be used to supply the energetic demand of the

process and the surplus may be used for additional power generation. Finally, the remaining solid may find applications such as solid fuel, pigment, activated carbon, low quality carbon black, etc.

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