
CONTRIBUTION OF POLYOLEFINS, POLYSTYRENE AND CELLULOSIC MATERIALS TO THE QUALITY OF PACKAGING WASTE PYROLYSIS PRODUCTS

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Abstract

Three of the main components of municipal packaging wastes (polyolefins, polystyrene and paper/cardboard), as well as a real sample coming from a municipal packaging waste sorting plant, have been pyrolyzed, at 500 °C in a fixed bed reactor. Polyolefins yield mainly alkenes, polystyrene generates mainly aromatics (> 60% styrene) and paper/cardboard gives rise to a lot of water (> 75%), oxygenated compounds, char and CO₂. The real sample liquids contain an aqueous and an organic phase, this later much more similar to PS liquids than to polyolefins liquids. There are beneficial interactions among the components which promote aromatics generation and prevent char and long-chain alkenes formation.

Keywords: pyrolysis, packaging wastes, polyolefins, polystyrene, cellulosic wastes

Introduction

One of nowadays most important waste is packaging waste. In the European Union about 18 million tonnes of this waste are generated each year. All over the world different initiatives for valorising packaging waste are being launched. In Europe the 2004/12/EC Packing and Packaging Directive obliges to recycle at least 55 % of packaging waste. In many European countries packaging wastes are selectively collected in at least three types of municipal containers: one for glass, one for paper and cardboard and one for plastic and metallic packaging. Since the later contains a mixture of materials, in order to recycle them it is previously necessary to separate them in sorting plants where the waste is separated in different fractions (steel, aluminum, tetrabrick®, different plastics), which are then sent to recycling companies. In such plants there is a fraction left which is not worthwhile further separating, and it is frequently incinerated or landfilled. Such rejected fraction is mainly composed of plastics, but also contains some tetrabrick®, aluminum and steel, which has not been possible to recover, and some mistaken materials (paper, glass, non-packaging plastics), which should have not been placed in the metallic and plastic packaging municipal container. In order to increase recycling rates and fulfill the requirements of the 2004/12/EC Directive, recycling of such rejected fraction becomes a necessity, and since mechanical separation and recycling is not technically or economically viable, feedstock recycling is a very appropriate technique for such waste rejected stream. In this work pyrolysis of the main components of such stream, individually, as well as of a whole real sample from a Spanish sorting plant has been investigated

Experimental procedure

Characteristics of the samples pyrolyzed

The amount and composition of rejected fractions coming from packaging waste sorting plants, vary significantly depending on the characteristics and efficiency of the sorting facility and also depending on the inhabitants

habits and on the time of the year. Along three years the authors have collected up to seven samples of rejected stream coming from a sorting industrial plant where the packaging wastes of the province of Biscay (north of Spain) are sorted. Table 1 shows the main types of materials that composed such samples and their concentration range. A detailed description of such samples has been presented elsewhere [1]

Table 1.- Main type of materials in rejected streams from a packaging waste sorting plant

Material	Concentration range
Plastics (PE, PP, PS, PET, other polymers)	33 - 97
Cellulosic materials (paper, tetrabrick®, wood, clothes, etc.)	≈0 - 44
Inorganics (glass, ceramics, metals, batteries, etc.)	≈0 - 45
Others (multimaterial packages, medical waste, printed circuit boards, etc)	≈0 - 5

It can be seen that there is a wide variation in the proportion of each type of material. Rejected streams from sorting plants should be mainly composed of plastics, however due to inefficiency or malfunction of the sorting plant, and also due to the fact that mistaken materials (toys, paper, clothes, etc) are frequently placed in the municipal plastic and metallic packaging container, a significant and unpredictable proportion of non-plastic materials can be present in such streams, as it occurs in the case studied in this work. Plastics and cellulosic material are the components which can be transformed into liquids and gases in pyrolysis processes. Table 2 shows the concentration range (in an inorganics-free basis) of the main types of polymers contained in the above mentioned samples. It can be seen that the most abundant components are polyolefins, polystyrene, and cellulosic materials. Therefore the quality of pyrolysis products will be mainly determined by these components. In this work a polyolefin (PE/PP=50/50) sample, a PS

Table 2.- Types of polymers in real rejected streams from a packaging waste sorting plant (inorganics-free basis)

Material	Range composition of several samples	Specific composition of the sample pyrolyzed
Polyolefins (PE + PP)	27 - 75	27,5
Polystyrene (PS)	6 - 25	10,7
Polyethylene terephthalate (PET)	2 - 9	8,1
Polyvinyl chloride (PVC)	≈0 - 4	1,6
Other plastics	≈0 - 10	4,0
Cellulosic materials	≈0 - 60	48,1

sample, a paper/cardboard sample and a real rejected sample from a packaging sorting plant (composition presented in table 2), have been pyrolyzed. Solid, liquid and gaseous products were thoroughly characterized.

Pyrolysis experiments

The pyrolysis experiments were carried out with 100 g of sample, at 500 °C, for 30 minutes once reached reaction temperature, in nitrogen atmosphere, and using an unstirred stainless steel 3.5 dm³ reactor, which was heated at 20 °C min⁻¹. Pyrolysis liquids and solids were weighed after the experiment to determine their yield in weight %, while gas yield was calculated by difference.

Results and Discussion

The solid, liquid and gas yields obtained in the pyrolysis experiments are presented in table 3.

Table 3.- Pyrolysis yields (weight % inorganic free basis)

Material	Solid	Liquid		Gas (by diff)
		Organic	Aqueous	
Polyolefins	0	55,2	0	44,8
Polystyrene	0,7	97,5	0	1,8
Cellulosic	34,1	5,0	29,8	31,1
Real sample	13,4 (19,0) ^a	41,4 (32,5) ^a	14,6 (16,6) ^a	30,7 (31,8) ^a

^a Theoretical mathematical yield calculated according to the sample composition and to the pyrolysis yield of the individual components

It can be seen that the behavior of the 3 materials pyrolyzed is completely different. On the first place it must be mentioned that the cellulosic material yields important proportions of aqueous phase and of solid (char), while polyolefins do not produce neither aqueous phase nor char, and polystyrene does not yield aqueous phase but generates a very low proportion of char. Secondly it can be seen that polyolefins give rise to comparable proportions of gases and liquids, while polystyrene is converted almost completely to liquids. As far as the real sample is concerned, table 3 includes (in brackets) the pyrolysis yields calculated according to the proportions of the components in the sample and the pyrolysis yields of the individual components; in such calculation the effect of PET, PVC and "other plastics" has been neglected, it has been considered as if the sample were only composed of polyolefins (31,9 %),

polystyrene (12,4 %) and cellulosic materials (55,7 %). Comparing real and theoretical yields it can be seen that there are some kind of beneficial interactions when the materials are pyrolyzed together, since less char and more organic liquids, than the theoretical value are obtained. An explanation to this fact may be that hydrogen rich free radicals coming from the polymers somewhat inhibit the recombination of the hydrogen depleted free radicals coming from cellulosic materials that tend to form char. Nevertheless it must be born in mind that the other components which have not been considered, may also have an influence, and also that metals present in the real sample may also have some kind of catalytic effect.

A summary of the characteristics of the pyrolysis liquids is presented in table 4. GC/MS and elemental analyses showed that there are clear differences among the quality of such liquids. Those derived from polyolefins are mainly composed of alkenes and cycloalkanes and have a significant proportion of >C13 compounds, which gives them a wax-like consistency. Those derived from PS are low viscosity liquids, mainly composed of aromatics and with an styrene content > 60%. Liquids from cellulosic wastes are mainly composed of water (up to 78 %), this is corroborated by its low carbon content and extremely high H/C ratio, mixed with some organic oxygenated compounds (phenols, ketones, carboxylic acids, etc.). Concerning the real sample, the results reported in table 4 correspond to the organic phase. They are more similar to PS liquids than to PE/PP ones, so the interactions among the different waste components prevents the formation of long-chain-alkenes and promotes aromatics formation (toluene+styrene+ethyl-benzene was > 55%). The aqueous phase of the real sample liquids was equivalent to that of the cellulosic liquids: it was mainly composed of oxygenated compounds. Concerning pyrolysis gases, they are mainly composed of hydrocarbons in the case of PE/PP and PS, while the cellulosic derived gases have a very high CO_x content (> 70 vol %) and the real sample gases contain comparable proportions of hydrocarbons and of CO_x.

Table 4.- Characteristics of pyrolysis liquids

Material	PE+PP	PS	Cellulosic	Real ^a
C (wt%)	81,7	91,9	7,1	89,1
H(wt%)	12,5	7,8	10,5	9,3
H/C atomic	1,8	1,0	17,8	1,2
HHV (MJ kg ⁻¹)	45,3	41,4	2,7	41,4
Aromatics	19,2	96,5	8,0	96,6
Non Aromatics	71,6	0	90,2	3,4
No identified	9,2	3,5	2,8	0
C5-C9	45,3	85,1	n.d.	75,1
C10-C13	26,7	1,2	n.d.	17,7
> C13	18,8	10,2	n.d.	7,2

^a Characteristics of the organic phase n.d. not determined

References

[1] A. Lopez-Urionabarrenechea et al. *Applied Energy* 98, (2012) 524-53.