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ESCUELA TÉCNICA SUPERIOR DE INGENIERÍA DE BILBAO
BILBOKO INGENIERITZA GOI ESKOLA TEKNIKOA

Ph.D. THESIS

CHEMICAL RECYCLING OF MUNICIPAL PACKAGING WASTE BY PYROLYSIS

A dissertation submitted to the University of the Basque Country

for the degree of Ph.D. in Environmental Engineering by:

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Bilbao, 2011

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ISBN: 978-84-694-9477-6

A mis padres

En primer lugar me gustaría expresar mi agradecimiento a la directora de la tesis, la Dra. Isabel de Marco, por su dedicación, predisposición y aportaciones, y especialmente por depositar su confianza en mí desde el principio y haberme permitido una formación predoctoral inmejorable. Asimismo, no me puedo olvidar del colectivo de becarios del departamento, por contribuir a generar un ambiente de trabajo saludable durante estos años y con quienes tantos buenos momentos he compartido. Junto con ellos, mi agradecimiento a los miembros del grupo de investigación SuPrEn, especialmente a Marifeli Laresgoiti, por su inagotable paciencia y sus innumerables consejos técnicos en el laboratorio. Por último, debo agradecer al programa de formación de investigadores del Gobierno Vasco (BFI07.249) y al Ministerio de Educación y Ciencia (CTQ 2007-67070/PPQ) la ayuda económica para llevar a cabo la realización de esta tesis doctoral.

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ABSTRACT

The present doctoral thesis centers on studying pyrolysis as a chemical recycling technique for rejected packaging waste fractions coming from separation and sorting plants. The pyrolysis experiments have been carried out in a lab-scale installation equipped with a 3.5 L semi-batch reactor and a condensation and collection system for the liquids and gases generated.

In the present thesis, an experimental study on the conventional pyrolysis process applied to the aforementioned waste fractions has been conducted, as well as the study of non-conventional or advanced pyrolysis processes such as catalytic and stepwise pyrolysis. The study of the operating parameters has been carried out using a mixed plastics simulated sample, the composition of which is similar to that found in real fractions, and subsequently the optimized process has been applied to real packaging waste. An exhaustive characterization of the solids, liquids and gases obtained in the process has been made after each experiment and their potential uses have been established. Finally, an empirical model that will predict the pyrolysis yields (% organic liquid, % aqueous liquid, % gases, % char, % inorganic solid) as a function of the composition of the initial sample has been developed.

As a result of the experimental work done, the requirements have been established for an industrial packaging waste pyrolysis plant that aims to be sufficiently versatile as to generate useful products regardless of the nature of the raw material.

RESUMEN

La presente tesis doctoral se centra en el estudio del proceso de pirólisis como técnica de reciclado químico de fracciones rechazo de plantas de separación y clasificación de residuos municipales de envases y embalajes. Los ensayos de pirólisis se han llevado a cabo en una planta piloto provista de un reactor semi-batch de 3,5 L de capacidad y un sistema de condensación y recolección de los productos líquidos y gaseosos generados.

En la presente tesis se ha realizado un estudio experimental del proceso de pirólisis convencional aplicado a los residuos de envases mencionados, así como un estudio de procesos de pirólisis no convencionales o avanzados, como son la pirólisis catalítica y la pirólisis por etapas. El análisis de los parámetros de operación se ha llevado a cabo utilizando como muestra una mezcla de plásticos simulada, de composición semejante a las fracciones reales, y posteriormente se ha aplicado el proceso optimizado a residuos reales de envases y embalajes. En todos los ensayos se han caracterizado exhaustivamente los productos sólidos, líquidos y gaseosos obtenidos, determinando su composición y propiedades, y estableciendo sus potenciales utilidades. Finalmente, se ha establecido un modelo empírico que permite predecir los rendimientos de pirólisis (% líquido orgánico, % líquido acuoso, % gases, % char, % sólidos inorgánicos) en función de la composición de la muestra inicial.

En base al trabajo experimental realizado se han establecido los requisitos que debería cumplir una planta industrial de pirólisis de residuos de envases a fin de ser suficientemente versátil para generar productos aprovechables cualquiera que sea la naturaleza de la materia prima.

LABURPENA

Pirolisia hiriko ontzi-hondakinen erreusen birziklapenerako aukera gisa aztertu da tesi lan honetan. Pirolisi saiakuntzak 3,5 litro bolumeneko “semi-batch” erreaktoreaz eta likido eta gas produktuen kondentsazio eta bilketen sistemaz osatutako laborategiko instalazio batean egin dira.

Lan honetan, pirolisi konbentzionalaz gain, pirolisi prozesu aurreratuak ere aztertu dira, besteak beste, pirolisi katalitikoa edota etapaz etapa egindako pirolisia. Lan parametroak simulatutako lagin bat erabiliz aztertu eta optimizatu dira eta, ondoren, lortutako parametroak lagin errealen saiakuntzetan erabili dira. Saiakuntza guztietan, lortu diren produktu gaseoso, likido eta solidoak sakonki karakterizatu dira eta ondoren izan litzaketen erabilerak aztertu dira. Azkenik, pirolisi errendimenduak (likido organikoak %, likido urtsuak %, gasak %, “char” %, solido inorganikoak %) erabilitako laginaren konposizioaren arabera zenbatesteko tresna bat garatu da (modelo enpirikoa).

Egindako lan esperimentalean oinarrituta, ontzi-hondakinen erreusa tratatzeko instalazio industrial batek bete beharreko baldintzak ezarri dira, instalazioa, lehengaiak edonolako ezaugarriak dituztelarik, produktu baliagarri bihurtzeko gai izan dadin.

CHAPTER 1

SCOPE AND OBJECTIVES

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The main objective of this doctoral thesis is, on the one hand, to study the viability of the pyrolysis process as an alternative means of treating packaging waste fractions from municipal separation and sorting plants, and, on the other hand, to optimize the process with the aim of establishing the basis for potentially implementing it on an industrial scale. The work done here has a special environmental and social interest because it attempts to offer a technical and environmentally feasible solution to a problem originating in the immense generation of packaging waste found every day. Achieving said main objective requires the realization of the following partial aims and steps:

1. Commissioning of the pyrolysis installation working with real waste: Adjusting the temperature controller parameters of the reactor (PID type), optimization of the liquid condensing system and preliminary testing of the catalytic pyrolysis systems (homogenous/heterogeneous catalysis, liquid phase/vapor phase contact).

2. Characterization of the rejected fraction coming from the packaging waste sorting and separation plants: Sampling at different times, studying the temporal evolution of the fraction, component identification and proximate and elemental analysis; establishment of a simulated sample representative of what is found in real samples.

3. Thermal or conventional pyrolysis: Study the influence of temperature and time on the quantity and characteristics of the solids, liquids and gases obtained from pyrolysis of the simulated sample of invariable composition.

4. Catalytic pyrolysis: Study the influence of the type of catalyst and temperature on the quantity and characteristics of the solids, liquids and gases obtained from catalytic pyrolysis of the simulated sample of invariable composition. Study the utilization of used and regenerated catalysts. Compare with the thermal process.

5. Study alternative means of reducing the chlorine content of pyrolysis products: stepwise pyrolysis and pyrolysis with adsorbents. Optimizing both processes working with the simulated sample of invariable composition.

6. Study of the behavior of individual components and simple mixtures in pyrolysis, as well as conducting a mathematical treatment of the data, in order to design an empirical model to predict the pyrolysis yields (% organic liquid, % aqueous liquid, % gases, % char, % inorganic solid) of municipal packaging waste streams as a function of the composition of the sample.

7. Application of the optimized pyrolysis process to real samples. Characterization of the solid, liquid and gaseous fractions that result from pyrolysis and determination of possible uses or market options of these products.

CHAPTER 2

BACKGROUND AND CURRENT STATUS OF THE ISSUE

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Packaging of consumer products has increased exponentially in recent decades. Despite a general growing awareness around the production of waste and the specific policies adopted by the European Union (EU) especially in recent years, all countries in the EU-27 have registered an increase in packaging goods present in the market per capita during the period 1997-2007 (European Environment Agency, 2010).

The advantages of packaging products in terms of protection, preservation, logistics (manipulation, transportation, storage) and marketing have given rise to a continuous and growing generation of a type of municipal solid waste (MSW) known and classified in current legislation as packaging waste. Packaging waste has three chief characteristics: almost instantaneous generation (very short useful life), decentralized production and multiple and variable composition, with the presence of numerous and diverse components, each of which require a different recycling method. For this reason it is necessary to improve and design new treatment processes for these complex waste products; the goal being to increase recycling rates and to advance toward the concept of zero waste.

2.1. GENERATION AND MANAGEMENT OF PACKAGING WASTE

In Table 2.1 are the figures for the generation and recycling rate of municipal packaging waste produced in the EU-27 for the year 2006.

Table 2.1. Generation and recycling of packaging waste by material in the EU-27 (in tons) (table created from data collected by Eurostat, 2006)

Material	Generated[1]	Recycled	% Recycled
Paper/Carton	32 052 221	24 020 593	68.0
Metal	4 915 997	3 235 876	56.1
Glass	16 654 545	10 064 085	54.9
Wood	12 852 376	4 905 859	30.4
Plastic	15 081 980	4 015 322	**26.0**
Other	229 631	-	-
Total	**81 786 749**	**46 241 736**	**47.1**

[1] Tons of waste registered and declared by waste management systems.

As is made evident by the table, the main materials used for packaging are paper/cardboard, metal, plastic, wood and glass. These materials have very diverse properties and for this reason it is critical that they be separated and each treated differently. Currently, every member state of the European Union has selective collection of glass containers and practically all members have developed a system to collect paper and cardboard packaging waste. Collecting plastic material depends heavily on management systems implemented in each country and on the specific products they are targeting. The fact that plastics form a very diverse family of distinct mixed materials, make it the material with the lowest recycling rate in Europe (26%) as can be seen in Table 2.1.

The selective collection system used in Spain for packaging material is based on the utilization of colored containers for the separation of the most important families of waste products. The best known and most ubiquitous are the blue container for paper/cardboard, the green container for glass and the yellow container for plastics, Tetra-brik and metal. Currently, wood does not have its own collection container and is picked up at bulk trash collection points.

Spain has an integrated management system (IMS) in place to control the generation and treatment of packaging waste, as well as to comply with the reclamation and recycling objectives under EU regulations. The IMS is managed by Ecoembalajes España (Ecoembes) for paper/cardboard, plastic, metal and wood packaging and by Ecovidrio for glass packaging. Data on the generation and recycling of these waste materials in Spain in 2009 can be seen in Table 2.2.

Table 2.2. Generation and recycling of packaging waste by material in Spain (in tons)

(table made from data taken from Ecoembes' annual report 2009 and from www.ecovidrio.es, 2009)

Material	Generated[1]	Recycled	% Recycled
Paper/Cardboard	801 980	675 661	84.2
Metal	342 257	244 185	71.3
Glass	1 252 637	751 582	60.0
Wood	10 993	5 380	48.9
Plastic	732 626	306 941	**41.9**
Other	6 304	-	-
Total	**1 894 161**	**1 232 168**	**65.1**

[1] Tons of waste registered and declared by waste management systems.

Table 2.2 shows that recycling rates in Spain are higher than the European average, reaching an overall recycling rate of 65.1%. In terms of individual recycling of the various materials, it can be seen that the tendency follows what the rest of Europe is doing. Plastic again has a lower recycling rate (41.9%) falling way short of the recycling rates of paper/cardboard (84.2%) and metal (71.3%). It is remarkable that the percentage of plastic waste being recycled is less than that of wood (48.9%), which does not have its own container. This fact highlights the difficulty faced when recycling certain fractions of plastic waste.

The fundamental reasons that underlie the low recycling rates of plastic waste are that the low cost of the plastics used in packaging do not drive the recycling process and that waste fractions include diverse families of mixed plastics of varying sizes and compositions, which need to be separated before being treated in order for effective recycling. For this reason, packaging waste deposited in the yellow containers (for plastic, metal and food/drink cartons) is separated at the sorting plants.

Today, there are 94 sorting plants for packaging waste distributed throughout Spain. In these plants, separation and sorting of the distinct material is done through a combined process of manual inspection and automatic selection; the separated materials are then sent to recycling companies. The level of technology used at these plants varies depending on the composition of the material they need to process. Currently 40 plants have equipment to automatically select fractions of PET, HDPE, film (LDPE), mixed plastic, aluminum, ferrous packages and food/drink cartons (Ecoembes 2009).

In the province of Bizkaia (Spain), the plant Bizkaiko Zabor Birziklategia (BZB), situated in the town of Amorebieta, has been in charge since 1999 of the separation and sorting of packaging waste generated in this territory. This plant separates the following fractions: (1) HDPE, (2) film (LDPE), (3) PET, (4) food/drink cartons, (5) aluminum, (6) ferrous packages and (7) mixed plastic, under which other plastics (PP, PS, PVC, etc.) which are not any of the aforementioned fractions and plastics of the aforementioned ones which are not sent to recycling companies due to noncompliance of the technical specifications of recovered material (dictated by Ecoembes) are included. Furthermore, the plant also separates material that does not belong in the yellow container, such as paper/cardboard or glass. Lastly, in the separation process a rejected fraction is generated that contains material from all of the previously mentioned fractions that was not separated out, generally due to their shape or small size.

In the BZB plant, the process begins by tearing open the plastic bags and sending the packaging waste through two trommels (mesh sizes: 200 mm and 80 mm) and then through two ballistic separators. The first steps select by size, separating the fine and small material thanks to the trommels' rotating drums. The ballistic separators sort out the material by shape (flat or rounded). After passing through these two pieces of equipment, plastic film is separated pneumatically and metallic material is separated mechanically with magnetic equipment for ferric metals and a Foucault separator for the non-ferric metals (namely aluminum).

Once the metallic material is separated out, the process to separate the plastic fractions of interest by means of an “autosorter” begins. Near infrared optical readers identify the distinct materials brought up by a conveyor belt and separate the material out pneumatically. After the automatic separation, a manual separation step is taken to optimize the quality of the fractions. Every obtained fraction of interest is compacted in a press forming high-density bales that are then sent to their corresponding recycler. The rejected fraction is then sent for incineration. In Figure 2.1 a schematic flow chart is laid out of the BZB packaging waste separation and sorting plant.

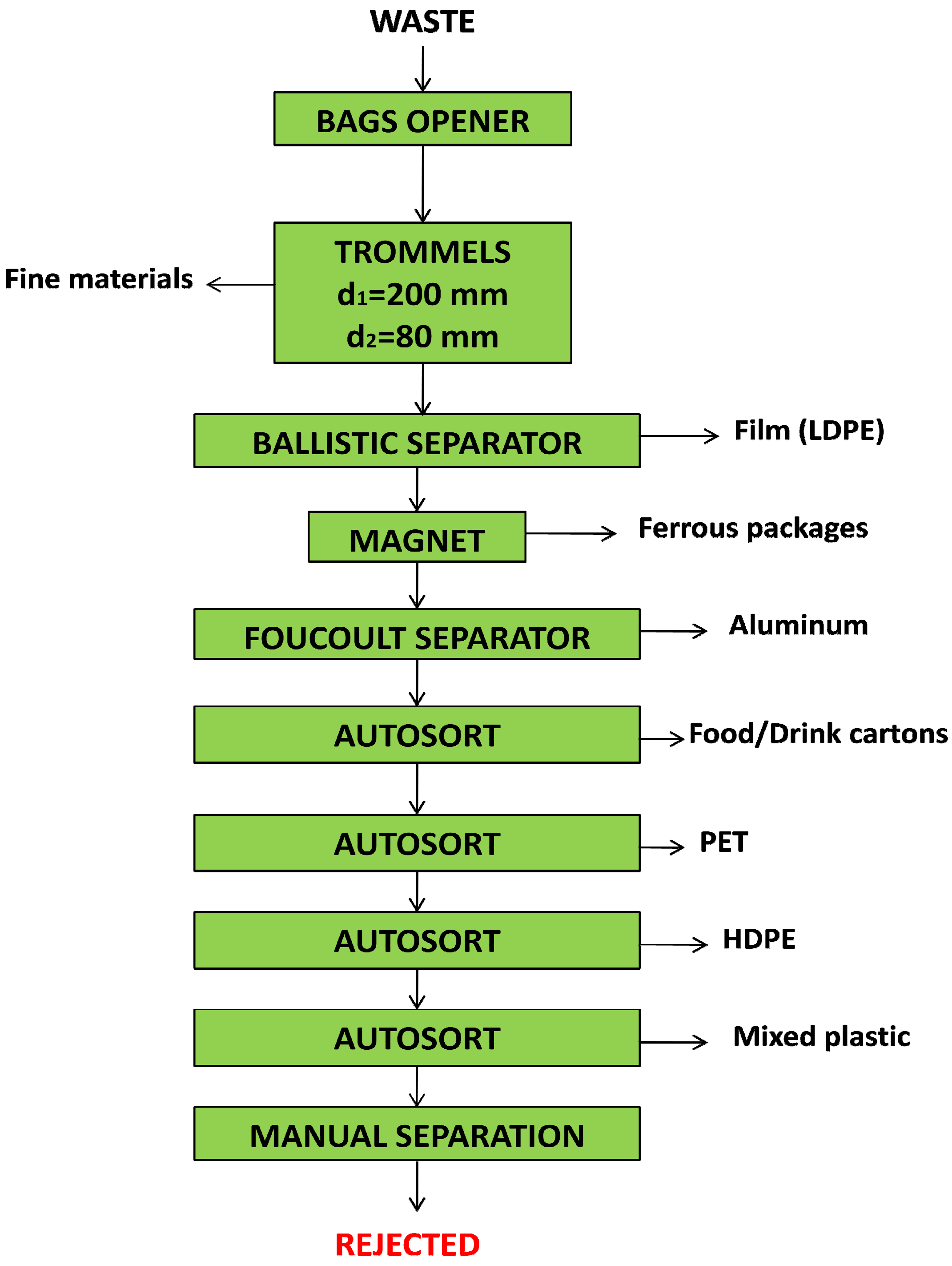


Figure 2.1. Schematic flow chart of the BZB packaging waste separation plant

The production data for fractions of interest of the Amorebieta plant for the year 2009 are displayed in Table 2.3 and Figure 2.2.

Table 2.3. Fractions of interest production at BZB in 2009

(table created from data from www.ecoembes.com)

Material	**Annual recovery (kg)**
Food/drink cartons	1 479 120
Ferrous packages	2 244 380
Aluminum	90 400
Paper/Cardboard	17 780
HDPE	949 220
LDPE	3 450 716
Mixed plastic	1 803 570
PET	1 431 780
Total	**11 466 966**

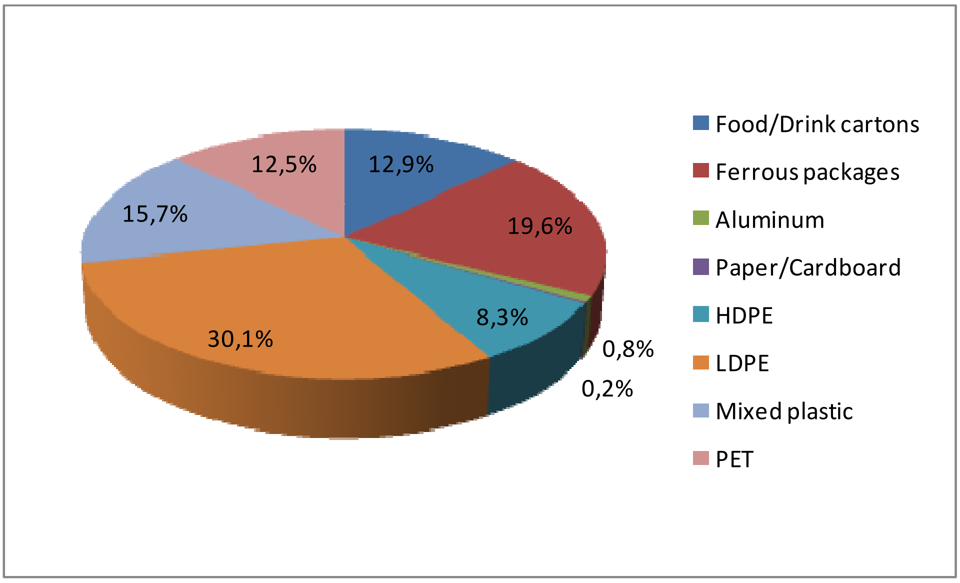


Figure 2.2. Pie chart of fractions of interest production at BZB in 2009 (www.ecoembes.es)

From the table and the figure, it can be seen that LDPE is the most recovered material, followed by steel and the mixed plastic fraction. At the extreme low end are aluminum and paper/cardboard, the latter can be explained in part by the fact that it does not belong in the yellow containers.

These diagrams do not show the amount of the rejected fraction generated, this information is found in Table 2.4 where the production data from the five packaging separation plants in the Basque Country in 2009 is found. Moreover, included as well is the average yield recovered in 2009 at the plants in the Basque Country and throughout Spain.

Table 2.4. Output and rejected fraction data from separation plants in 2009 (table created from data from www.ecoembes.com)

Plant	**Input (kg)**	**Output (kg)**	**Yield (wt.%)**	**Reject (wt.%)**
Amorebieta	15 581 659	11 466 966	73.6	26.4
Jundiz	4 237 870	2 380 270	56.2	43.8
Legazpi[1]	1 927 920	1 455 130	75.5	24.5
Legazpi[2]	1 984 615	1 489 390	75.0	25.0
Urnieta	6 365 870	4 557 060	71.6	28.4
Basque Country average	30 097 934	21 348 816	**70.4**	**29.6**
National average	-	-	**55.4**	**44.6**

[1] Community of Sasieta; [2] Waste consortium of Gipuzkoa

In Table 2.4 it can be seen that, just as has been commented before, the yield from each plant depends on the quality of the technology in place and thus the amount of reject produced varies as a function of the separation plant itself. According to the data on Table 2.4, the average production of rejected fraction for the whole of the country was nearly 45 wt.% of the entering material in 2009 whereas the average for the Basque Country was around 30 wt.%. In both cases the average is very high and paints a clear picture as to the annual tonnage of waste from light packaging that currently has no recycling alternative other than to be sent for incineration or landfill. To be more specific, in the province of Bizkaia, this amount surpassed 2800 tons in the year 2009 (Garbiker, 2009).

2.2. LEGISLATIVE ASPECTS

Packaging waste is regulated by Spanish Law 11/1997 on Packaging and Packaging Waste which incorporates Directive 94/62/EC of the European Parliament and Council regarding packaging and packaging waste. This directive sought to coordinate the laws governing the management of packaging and packaging waste across all of the member states of the European Union. The end goal was to prevent or reduce the impact on the environment and avoid commercial obstacles between the distinct member states. In addition, it defined the concepts of reuse, recovery and recycling and it established compulsory benchmarks in terms of recovery and recycling rates.

This directive was modified by Directive 2004/12/EC that, together with the introduction of certain criteria related to the concept of packaging itself, established new and more demanding objectives aimed at both reducing environmental impact of packaging waste and making the internal market more consistent with regards to the recycling of these materials. This directive was partially transposed into Spanish law by Royal Decree 252/2006, and despite clearly defining the objectives, it left certain aspects up for interpretation as to what was considered recovery, energy recovery and disposal.

Currently, the recently approved Directive 2008/98/EC on waste from the European Parliament and Council is in the draft phase of incorporation into national law in Spain. This directive simplifies and modernizes the current legislation thanks to the integration of other directives (including that on packaging and packaging waste) and the incorporation of new definitions. For example, in this directive a new concept is clearly defined: "Recovery". This concept includes recycling and energy recovery, but is subject to climate factors in accordance with an efficiency formula that must be reviewed within two years. This way, the concept will be distinguished from that of "disposal” if certain energy efficiency thresholds are surpassed in the waste incineration plants.

The directive also broadly defines recycling, including both mechanical and chemical recycling. Furthermore, it strengthens the waste prevention policy by establishing goals to develop prevention programs, and it promotes reuse and recycling through the establishment of selective collection objectives.

The new directive also clearly defines, in Article 4, a hierarchy that will serve as a priority order in both legislation and policy of waste prevention and management. This hierarchy must be observed except in cases with good reason, justified by life-cycle thinking of the overall impacts of the generation and management of such waste. Said hierarchical order is as follows: prevention, reuse, recycling, other types of recovery (for example energy recovery) and disposal. Lastly, the new directive revises and updates the recycling and recovery objectives for various types of waste, including plastic waste, of which 50 wt.% will have to be recycled by the end of the year 2020. In Table 2.5 the evolution of the laws governing packaging waste and recycling objectives is presented.

Table 2.5. European and Spanish regulations on packaging waste and recycling objectives

European Directive	Transposed Spanish Law	Plastics recycling objective	Compliance deadline
94/62/EC	Law 11/1997	Undefined	-
2004/12/EC	Royal Decree 252/2006	22.5 wt.%	2008
2008/98/EC	Draft June 2010	50.0 wt.%	2020

Table 2.5 highlights how the European Union is becoming increasingly demanding in terms of the levels of recycling of plastic waste, which began with an undefined level in Directive 94/62/EC to proposing that half the weight of all plastic waste be recycled under Directive 2008/98/EC. If we compare this recycling objective with the current state of plastic waste recycling in Spain (41.9 wt.%, Table 2.2) and Europe (26 wt.%, Table 2.1) it becomes clear that there is still an appreciable gap to overcome in order to achieve the goal proposed by the directive, and work to close the gap must begin in the next few years.

Given this situation, studying how to chemically recycle the reject fractions from light packaging separation plants seems inevitable. The reasons are twofold: to comply with the hierarchical order as stipulated by the Directive and to increase the percentage of plastic waste being recycled.

2.3. ALTERNATIVE MEANS OF RECYCLING PLASTIC WASTE

This section will introduce alternative means of treating plastic waste: mechanical recycling and the chemical recycling processes. After analyzing each method, selection of the technique chosen for the experiments carried out in the present doctoral thesis will be justified.

2.3.1. Mechanical Recycling

Mechanical recycling basically consists of melting and remolding plastic waste to reuse the material in new applications. Besides these basic operations, mechanical recycling usually is complemented with separation, milling and cleaning processes. Necessary separation before recycling is a key process parameter because if complex separation steps have to be taken, the technique becomes economically unsustainable. For this reason, in facilities that mechanically recycle plastic waste, strict quality parameters are in place for waste to be admitted (like maximum levels of impurities), a factor that limits the use of this method in the treatment of mixed plastic streams.

Mechanically recycled plastic is habitually used for applications that are less demanding than those of virgin plastic because of degradation of its esthetic (grayish color) and mechanical properties with respect to virgin products. Furthermore, the application of post-consumer recycled plastics is not permitted in the food sector. However, mechanical recycling is the method applied at the industrial level currently for PE, PET and the mixed plastic fraction coming from industrial packaging waste separation plants.

2.3.2. Chemical Recycling

Chemical recycling is cataloged as a series of processes in which polymers are broken down by heat and/or chemical agents producing a large variety of products depending on the process employed. These products can be (1) monomers, which are the raw materials used in the synthesis of plastics, (2) hydrocarbon mixtures analogous to petroleum, from which many chemical products and/or alternative fuels can be obtained, or (3) gases that can be used as energy source or for chemical synthesis. In Figure 2.3 the chemical recycling processes are outlined.

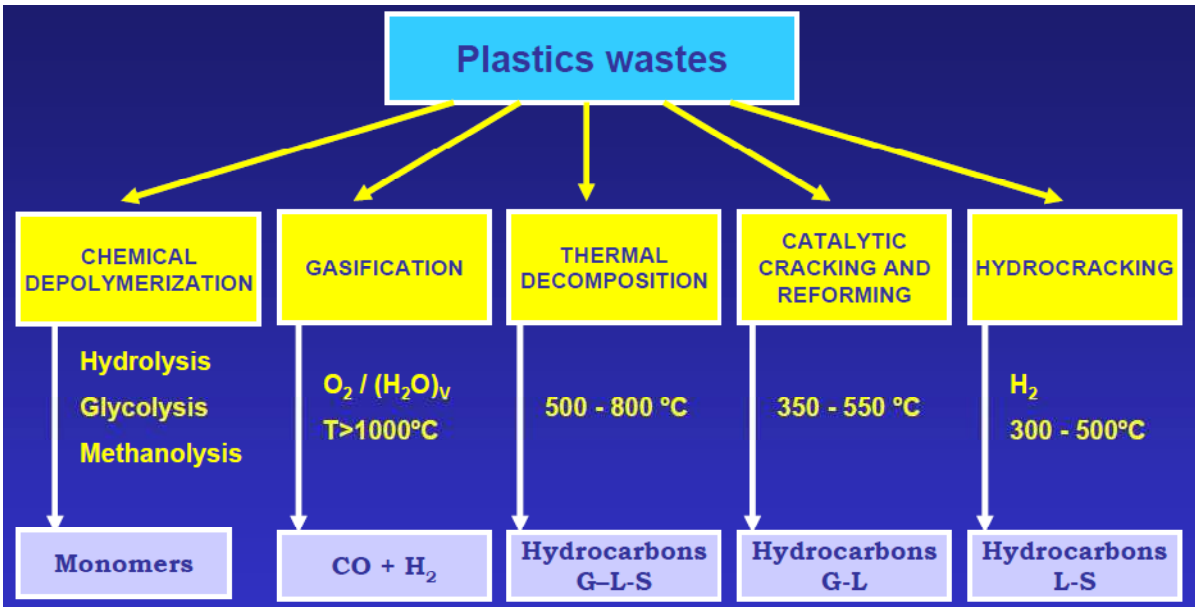


Figure 2.3. Chemical recycling processes of plastics (Serrano, 2008)

These processes include:

- Chemical depolymerization, which breaks down polymers by means of chemical substances in order to obtain starting monomers for plastics or other chemical products of a certain added value.
- Gasification, where polymers are broken down at high temperatures (≈ 1000 ºC) in the presence of oxygen and/or water vapor to obtain syngas ($CO + H_2$), which can be used as an energy source, metallurgical reducer or for synthesis of chemical products.
- Hydrogenation, which consists of breaking down the polymer at moderate temperatures (300-500 ºC) in the presence of hydrogen to obtain chiefly liquid hydrocarbons.
- Pyrolysis or thermal cracking, a process that breaks down polymers with only the use of moderate temperatures (400-700 ºC), yielding solid, liquid and gaseous products.
- Catalytic pyrolysis or catalytic cracking, a process similar to thermal pyrolysis but in the presence of catalysts, which increases the quality of the products obtained and/or allows the process to be carried out at lower temperatures.

Except for the process of chemical depolymerization, for whose application it is critical the exhaustive separation of the income material, the rest of the techniques are thermal processes capable of treating complex samples of plastics and yielding products that possess similar characteristics to products derived from non-renewable sources (petroleum, natural gas).

In the analysis of alternative treatment methods for the rejected fraction coming from packaging waste separation and sorting plants, chemical depolymerization was omitted right away due to the high levels of purity of the polymers needed to apply this technique, a condition that would not be met by this rejected fraction. Among the thermal treatment methods, hydrogenation was omitted due to the requisite of using hydrogen in the process, an expensive chemical for which specific security protocols had to be designed. Gasification was excluded because of the extremely high temperatures needed to completely destroy the polymer structure in order to obtain CO and H_2 (higher energy consumption), and because a further synthesis process is required in order to obtain valuable chemicals from syngas.

For these reasons, thermal and catalytic pyrolysis processes were elected so as to look at low-cost technologies at moderate temperatures that, furthermore, directly generate a wide variety of products (solid, liquid and gaseous fractions) with a broad range of potential applications.

2.4. PYROLYSIS OF PLASTIC WASTE. STATE OF THE ART

This section will be describing the fundamental theory of catalytic and thermal pyrolysis, in addition to explaining what each technique offers to the treatment of plastic waste.

2.4.1. Pyrolysis or Thermal Cracking

Pyrolysis is the heating of the material in an inert atmosphere, a process that decomposes the organic part of the material and generates liquids and gases that can be used as fuels and/or a source of raw materials. The inorganic components (fillers, metals, glass, etc.) remain practically unaltered in the solid fraction and free of the binding organic material, which makes it possible for them to be reused. This technique is especially good for complex polymer waste that contains a number of highly mixed materials because a prior separation step is not needed.

The reaction mechanisms of thermal cracking of polymers depend on the type of polymer being treated. For thermoplastic materials (the family of materials containing packaging plastics) these mechanisms are normally divided into three categories (Van Krevelen and Te Nijenhuis, 2009):

1. “End-chain scission”, a process by which the breaking of the polymer structure happens as a result of the successive loss of a small molecule, located at the end of the polymer chain, and a long fragment of the chain. In cases in which the small molecule is the starting monomer, the thermal decomposition is a depolymerization. This is the typical thermal decomposition mechanism of polymethylmethacrylate, from which an almost complete monomer conversion from thermal decomposition can be obtained (Buekens and Huang, 1998).

2. “Random-chain scission”, a process in which the polymer chain breaks randomly, generating a large number of differently sized primary products that later can also undergo other random scissions. The majority of polyolefins are decomposed by this mechanism, for example PE and PP.

3. “Chain-stripping”, a process which consists in the abstraction of the functional substituents present on the chain, generating an unsaturated polymer structure that later can be further degraded by means of any of the previously described mechanisms. This is the case in the decomposition of PVC, which generates HCl in the abstraction phase of the –Cl group.

In practice, these mechanisms happen simultaneously in the thermal decomposition of a single polymer. So for example, some studies conclude that even though the decomposition of PE and PP happens mostly by means of random-chain scission, these polymers also decompose by end-chain scission (Aguado and Serrano, 1999; Murata et al., 2002). Likewise, the decomposition of PS has been described also as mixture of these two mechanisms (Buekens and Huang, 1998; Ahmad et al., 2010), dominated in this case by end-chain scission, whereas in the two-step thermal degradation process of PVC chain stripping is responsible for the primary degradation and random-chain scission for the secondary (Bockhorn et al., 1999a; Kim, 2001).

The reactions produced when these mechanisms take place are free radical reactions and follow the habitual steps of initiation, propagation and termination (Lee, 2006). In the first step the C-C bonds are broken giving rise to primary free radicals. In the propagation step, inter and intramolecular hydrogen transfer reactions are produced, as well as new breaks of C-C bonds. All of this gives rise to the formation of secondary, more stable free radicals and to olefinic species. These secondary free radicals can undergo new beta scissions (C-C breaks) generating new olefinic groups and new free radicals. This step can be more or less prolonged as a function of the operational conditions, especially that of temperature. In the termination phase, bimolecular reactions are mainly produced, either by disproportionation or union of radicals.

In thermal cracking processes of plastics, aside from these reactions, other reactions like isomerization, cyclization, aromatization, species recombination, etc., can be produced; and when working with mixed plastics, many of these reactions happen simultaneously in a way that interactions among the resulting primary products from the decomposition of each component is, in practice, inevitable (Williams and Williams, 1999a; Murata et al., 2009). This complex reaction scheme is what makes predicting the generated species of pyrolysis of complex mixtures so difficult.

There is a considerable volume of published information on the thermal pyrolysis of various plastic materials which endorses the validity of this process as an alternative recycling method. The behavior of these plastic materials in pyrolysis has been studied in different experimental installations, such as thermobalances (e.g. Bockhorn et al., 1999b; Saha et al., 2008)**,** micro pyrolysis coupled with GC-MS (e.g. Blazsó et al., 2002; Serrano et al., 2005), fixed bed reactors (e.g. Demirbas, 2004; Marcilla et al., 2009), fluidized bed reactors (e.g. Williams and Williams, 1999b; Kaminsky and Núñez Zorriqueta, 2007), spouted bed reactors (e.g. Aguado R. et al., 2003, 2005), vacuum pyrolysis installations (e.g. Miranda et al., 1999; Karaduman et al., 2001) and pressure pyrolysis autoclaves (e.g. Pinto et al., 1999; Onwudili, 2009). In each one of these studies the operational variables of the process have been thoroughly analyzed; however, it is very difficult to compare the results obtained with different reactor geometries due to the fact that the characteristics of the products obtained do not only depend on the raw material used or the operational conditions but also on the characteristics of the system used, the size and shape of the reactor, the heat transfer efficiency, the sample size, the residence time, etc.

Furthermore, the majority of the studies on pyrolysis of plastics has been conducted with samples of virgin plastic (e.g. Kiran et al., 2000; Angyal et al., 2007) and with individual plastics in order to explore the decomposition kinetics (e.g. Faravelli et al., 2001; Broadbelt and Levine, 2009) or the products distribution (e.g. Wiiliams and Williams, 1999b; Yoshioka et al., 2004). However, pyrolysis of plastics coming from real waste streams has scarcely been studied. In Europe only a few works of Kaminsky et al. (1997, 1999) have been published and in Asia a few more studies have been carried out (Bhaskar et al., 2003; Lee 2007) due to the high development and implementation of these processes in Asia, especially in Japan.

2.4.2. Catalytic Pyrolysis or Catalytic Cracking

Catalytic cracking of plastic waste has been studied over the past few years as a way to improve thermal cracking. Using catalysts affords the following advantages (Aguado J. et al., 2006):

- Reduction of time and temperature of the reaction, with the consequent decrease in energy consumption.
- Better selectivity to desired compounds depending on the characteristics of the catalyst.
- Avoiding the formation of undesired compounds, for example, inhibiting the formation of halogenated compounds from samples containing PVC.

Contrary to thermal cracking, the mechanism by which the plastic is decomposed in the presence of catalysts depends on the type of catalyst used. Up to now, the more studied catalysts have been solid acid catalysts (especially zeolites) because their acidity enormously favors cracking reactions. White (2006) explained the catalytic degradation mechanism of PE in the presence of these type of catalysts (MCM-41, HZSM-5). According to White, this mechanism begins with the protolysis of PE at Brönsted acid sites ($H^+ S^-$), forming a carbenium ion on the surface of the catalyst:

$$C_nH_{2n+2} + H^+S^- \rightarrow C_mH_{2m+2} + C_{n-m}H^+_{2(n-m)+1}S^- \qquad (1)$$

In the propagation stage, the polymer fragments undergo disproportionation reactions with the carbenium ions formed; these ions can also undergo beta scissions giving rise to olefins and even smaller secondary carbenium ions:

$$C_nH^+_{2n+1}S^- \rightarrow C_xH_{2x} + C_{n-x}H^+_{2(n-x)+1}S^- \qquad (2)$$

When these superficial carbenium ions are small enough, they are desorbed from the surface of the catalyst, giving way to the end of the process:

$$C_nH^+_{2n+1}S^- \rightarrow C_nH_{2n} + H^+S^- \qquad (3)$$

Formation of aromatics and coke in the catalyst also occurs by means of reactions involving carbenium ions. According to the study of White (2006), the formation of aromatics from straight chain paraffin polymers is attributed to cyclization and dehydrogenation reactions of olefinic ions that result from the thermal cracking of carbenium ions. In addition, the formation of coke is owed to the formation of doubly charged ions (positively charged) in a way that they stay tightly adhered to the basic surface of the catalyst (S^-). The ions do not take part in more reactions nor do they allow the sites they occupy to host any more reactions. Aguado J. et al. (2006) concluded that apart from these reactions, isomerization and oligomerization reactions can take place simultaneously with cracking in the presence of acid catalysts.

All of these reactions occur to a greater or lesser extent depending on the characteristics of the catalysts used. Furthermore in most cases, as has been explained earlier, reactions of thermal cracking take place simultaneously to a greater or lesser extent chiefly as a function of temperature. For this reason, in this situation it is also a difficult task to deduce the mechanisms produced in catalytic cracking of mixed plastics.

The catalytic pyrolysis processes of plastics can be divided into two categories according to the placement of the catalyst (Buekens and Huang, 1998; Sakata et al., 1999; Lee, 2006). One category is for the processes that are said have "liquid phase contact”, in which the catalyst is mixed directly with the sample in a way that during the process it is in direct contact with the melted plastic. The other category is for the processes that have "vapor phase contact" in which the catalyst is placed in a second reactor in such a way that the process is strictly thermal cracking followed by the catalytic treatment of the products formed.

The majority of the information published to date on catalytic pyrolysis is related to processes in which the catalyst is in liquid phase contact being that, firstly, in this arrangement the catalyst acts on the decomposition process itself (in the case of vapor phase contact the catalytic action comes after decomposition). Secondly, there are certain advantages the liquid phase contact disposition offers over the other, for example, only one reactor is needed and energy is saved by reducing the residence time and the temperature needed when the catalyst-polymer contact is direct (Aguado J. et al.

2006) Additionally, selecting a good liquid phase contact catalyst can increase the conversion into desired products, thus obviating later treatment.

Opposing these advantages, the main drawback to using catalysts in liquid phase contact is the poor contact between catalyst (solid particles) and the melted polymer (highly viscous semisolid), thus it is necessary to use high catalyst to polymer ratios (1/10-2/10) for the catalysis to take effect. This problem can be minimized by using homogenous catalytic systems, or rather, using catalysts that are soluble in the melted polymer, so that the contact improves notably and the quantity of catalyst used can be reduced.

Examples of these catalysts are some Lewis acids like $AlCl_3$, metallic tetrachloroaluminates of generic formula $M(AlCl_4)_n$ and the most recent organic ionic liquids (Aguado J. et al., 2006). Kaminsky and Nuñez Zorriqueta (2007) used $AlCl_3$, $TiCl_4$ and mixtures of both in pyrolysis of PP and attained a significant reduction in the process temperature and high selectivity to desired products (light gases and oils) with small amounts of catalyst. Nevertheless, this type of catalyst has not supplanted the traditional heterogeneous system (solid-melted polymer) because the substances utilized are habitually composed of chlorine, which upon melting and mixing with the raw material can be carried over with the reaction products, giving rise to problems of corrosion and contamination of the products (Aguado and Serrano, 1999).

For heterogeneous catalysis processes (solid catalyst), many catalysts or substances deemed as good candidates have been studied. The most studied have been mesostructured catalysts (Serrano et al., 2000; Aguado J. et al., 2007), metal oxides (Zhou et al., 2008; Siddiqui and Redhwi, 2009) and above all, solid acids, catalysts used traditionally in petrochemical processes for the cracking of heavy feedstocks. Among them, one must highlight the use of pure zeolites (e.g. Vasile et al., 2001; Serrano et al., 2005; Hernández et al., 2007) and zeolite-based catalysts like fluid cracking catalysts (FCC) (Miskolczi et al., 2004a; Olazar et al., 2009).

Zeolites are crystalline microporous aluminosilicates. Currently there are more than 100 known types of zeolite (Aguado et al. 2006) and they can be classified according to the pore size, their internal structure and aluminum content. Changing these variables drastically affects the catalytic properties of each zeolite. The possibility of reacting with larger or smaller molecules (what is called shape selectivity) depends on the size of the pore and the internal structure, furthermore, the aluminum content directly determines the acidic properties of the zeolite. It is normal to find Lewis and Brönsted acid sites in their structure, which gives zeolites their great potential for cracking, an important property when working with macromolecules (plastics). These favorable characteristics are what have allowed them to slowly displace the rest of the heterogeneous catalysts.

Yet, zeolites are expensive and can influence the economy of a process whose end goal is the recycling of waste. To this end, over the last few years the possibility of using substances at low or no cost as catalysts has been studied. These could be byproducts of industrial processes or catalysts that are used up by other processes in such a way that they can be incorporated at zero cost to the treatment of waste. Within this field, a broad study of used FCCs has been conducted (e.g. Corma and Cardona, 2000; Lee et al., 2002) and to a much lesser extent Red Mud has been studied (Yanik et al., 2001, 2006).

Red Mud is a byproduct of alumina production by means of the Bayer process. In this process, bauxite is digested with sodium hydroxide at high pressure and temperature, in order to obtain the dissolution of the aluminum oxide. The non-dissolved solid, once separated from the basic solution and dried, is known as Red Mud. This solid is composed of a mixture of substances that were present in the original mineral (Fe_2O_3, Al_2O_3, SiO_2, TiO_2, Na_2O, CaO, MgO, K, Cr, V, Ni, Cu, Mn, Zn, etc.) and its composition can vary widely as a function of the minerals used and of the process parameters (Wang et al., 2008; Batra and Sushil, 2008). Generally, the component found in the highest concentration is Fe_2O_3, being that this is what gives Red Mud its typical reddish color and its hydrogenating catalytic properties. Thus, Red Mud has been used as a hydrogenation catalyst, for example, in the liquefaction of coal and biomass (Eamsiri et al., 1992; Legarreta et al., 1997) or in the hydrogenation of anthracene. Nevertheless, its Al_2O_3 content also gives it a certain acidic nature; this possible dual behavior and zero cost make Red Mud an interesting catalyst for the study of the cracking of plastic waste.

2.4.3. Industrial Application of Chemical Recycling

Figure 2.4 shows the percentages of chemical and mechanical recycling of all plastic waste in the European Union. It is necessary to make clear that these data refer to the totality of plastic waste (municipal and industrial) while the data in Table 2.1 (previously presented) referred only to municipal plastic waste used in packaging applications.

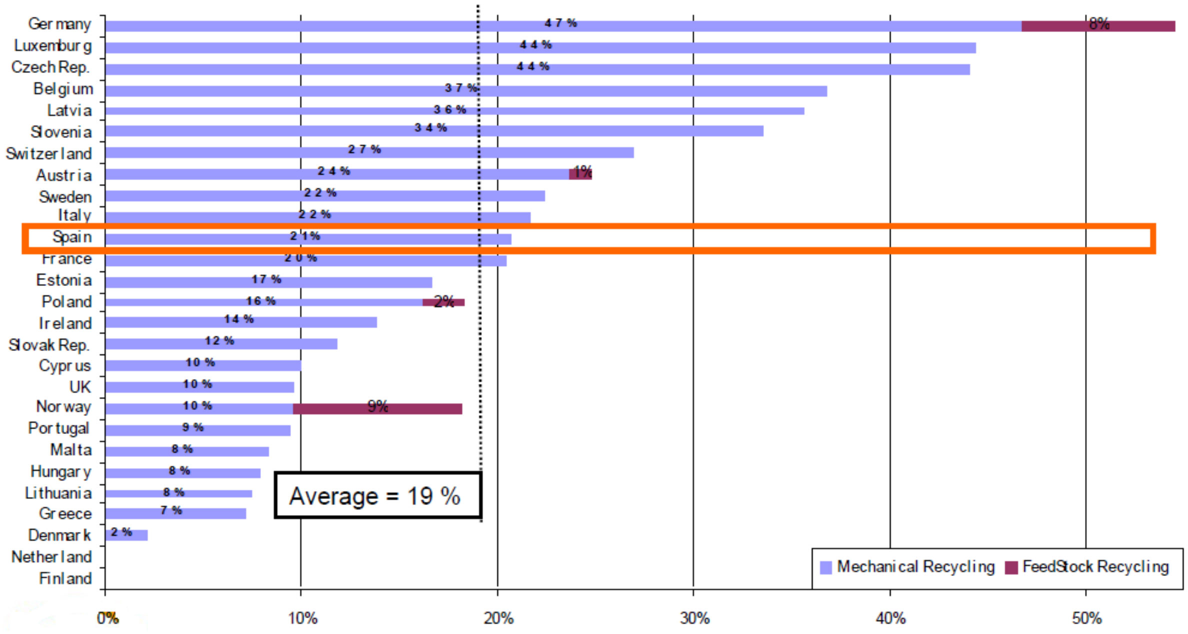


Figure 2.4 Percentages of chemical and mechanical recycling of plastic packaging waste in the EU (Vossen, 2008)

Figure 2.4 highlights that currently the vast majority of plastic waste is being recycled mechanically. Leading the way in chemical recycling of plastic waste is Norway (9%) and Germany (8%), and it is worth mentioning that only four countries in the European Union (Norway, Germany, Poland and Austria) employ this treatment at an industrial scale. Furthermore, these chemical recycling rates do not reflect in any way processes that are exclusively designed for the chemical recycling of this waste. That is to say, these numbers are not from plastic waste treatment plants, rather these are industrial facilities that take the waste as a substitute for other materials. Within this context, various studies have been conducted in recent years, but currently plastic waste in Europe is being used exclusively in steel production processes. In such processes, plastic waste is introduced into blast furnaces and, upon being exposed to very high temperatures (≈2200 ºC), is gasified forming a CO-rich syngas that is used as reducer agent in the conversion of

Fe_2O_3 to elemental Fe. An example of this process can be seen at the blast furnaces of VoestAlpine in Linz, Austria (Plastics Europe, 2009).

The world leader in industrial scale chemical recycling of plastic waste is Japan, where, as highlighted in Figure 2.5, there are 17 chemical recycling plants in which different treatment technologies are applied.

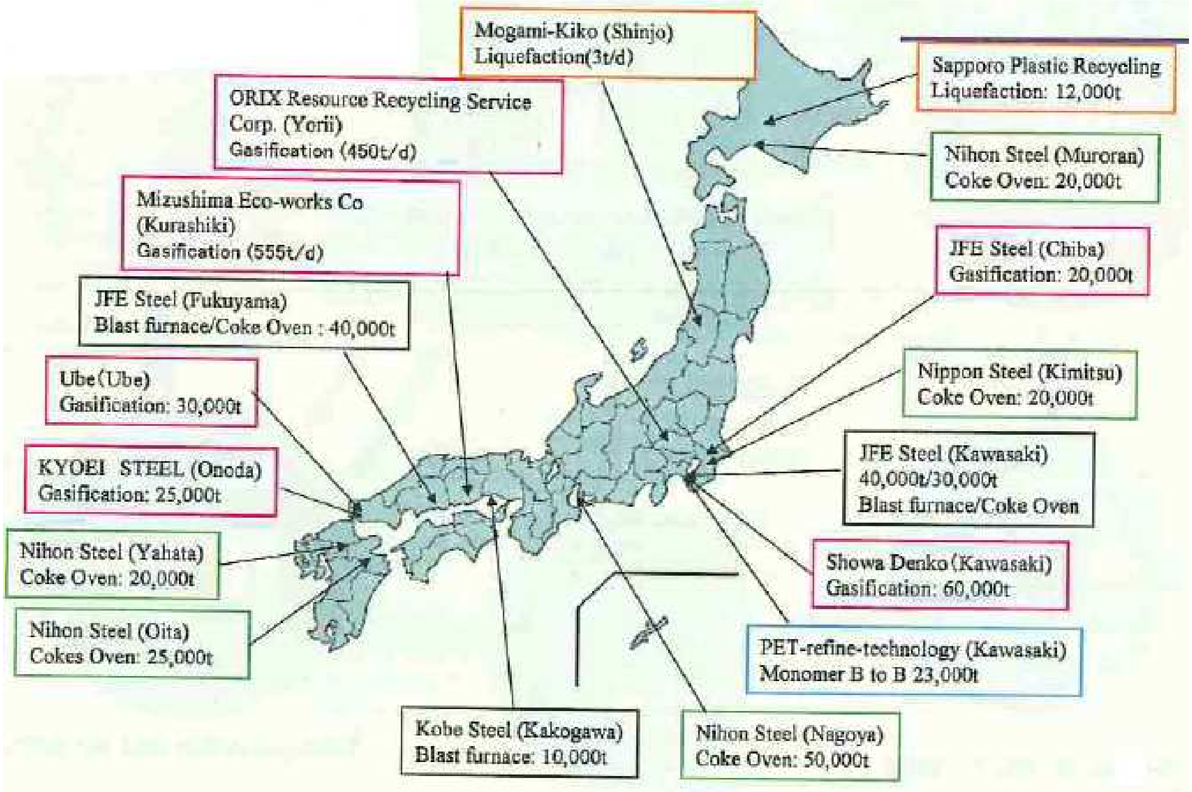


Figure 2.5. Chemical recycling processes of plastic waste implemented in Japan (Ida, 2009)

Eight of these plants are applications of blast furnaces or coke ovens and the nine remaining are actual chemical recycling plants, six being highlighted as gasification plants spread across the country. It can also be seen that there is a PET chemical depolymerization plant in Kawasaki and two plants that apply a process called liquefaction. As is illustrated in Figure 2.6, which corresponds to the flow sheet of the liquefaction plant in the city of Sapporo, this process basically consists of a pyrolysis section coupled with various processes to purify the products obtained. These products are principally liquid in nature hence the name liquefaction. The liquid products obtained in this plant are used for energy production in diesel engines.

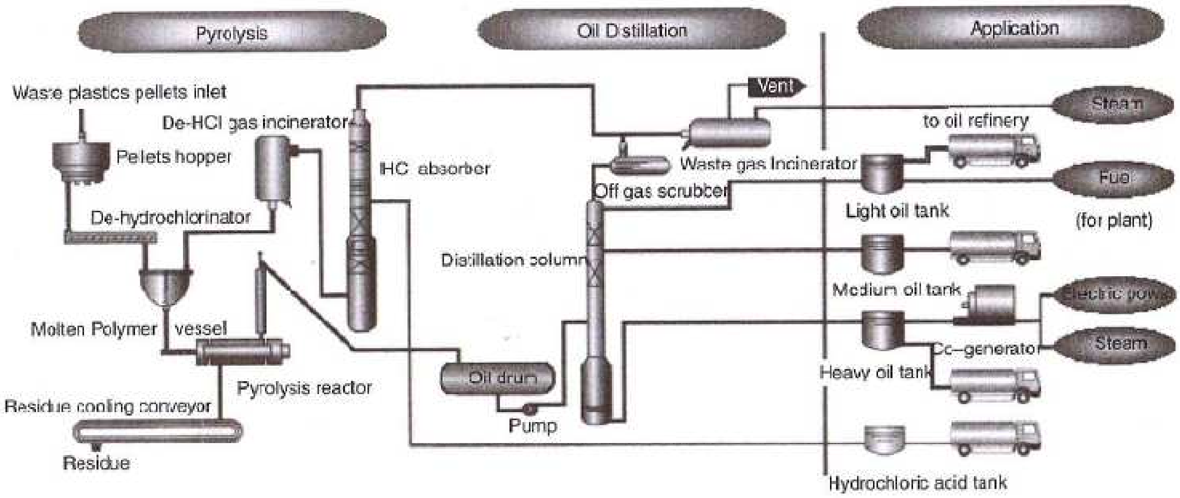


Figure 2.6 Flow sheet of the liquefaction plant in Sapporo (Japan) (Ida, 2009)

In Europe, pyrolysis got a large boost in the 1990s and various pilot plants for the pyrolysis treatment of MSW were built, especially in Germany and France (Malkow, 2004). Implementation of pyrolysis in applications of plastic waste is in the research and development phase. A few industrial scale plants have been built, like that in the Canton of Zug in Switzerland or the plant in Portloaise (Ireland) managed by Cynar PLC. Also, different technologies exist and are prepared to be commercialized; some are patented by companies like BASF and BP (Al-Salem et al., 2009). However, the majority of these processes have not yet reached sufficient levels of commercial profitability, and some of the aforementioned plants find themselves closed due to lack of financing, and are awaiting reformation, additional research and improvements. In Spain, the use of pyrolysis to recycle plastic waste is also starting to develop. Up to date, there is a constructed plant designed by Idom in Cerceda (A Coruña), which is still in the testing phase analyzing what type of waste it will be able to handle (Sagarduy, 2008).

Currently, more research and studies are necessary before the implementation of a process of this type. Some economic studies indicate that key issues concern the correct location of the plant so as to minimize transport costs of the waste on the one hand, and of the products on the other hand, and so be able to take advantage of the industrial facilities with cracking units like petrochemical plants, for example, when the time comes to purify the products obtained. In addition, having enough supply of waste as to overcome scaling issues is understood as another essential factor (Westehout, 1998).

Among the interesting aspects to research, it's worth highlighting: (1) the study of the versatility of the process to treat spatially and temporally variable heterogeneous mixtures of plastics that also contain other non-plastic materials (aluminum, iron, paper, glass, etc.), (2) the analysis of the different methods to dechlorinate the products since the initial sample may contain PVC, (3) the study of possible cost reductions to the process through the utilization of low-cost but effective catalysts, which will improve the properties of the products obtained and (4) a global prediction of pyrolysis yields depending on the sample composition in order to avoid preliminary semi-industrial trials. The present doctoral thesis aims to answer all of these questions.

CHAPTER 3

EXPERIMENTAL PROCEDURE

EXPERIMENTAL PROCEDURE

3.1. PYROLYZED SAMPLES

The pyrolysis experiments were carried out using two types of samples: real waste samples coming from an industrial packaging separation plant and a simulated sample prepared in the lab. The characteristics of both types of samples are described below.

3.1.1. Real Samples

The real waste samples used in this study are the rejected fractions of Bizkaiko Zabor Birziklategia (BZB), an industrial packaging waste separation and classification plant located in the province of Bizkaia (Spain), which is described in section 2.1. To carry out the pyrolysis experiments, six 30-kilogram samples were taken directly from the plant between 2007 and 2010.

The components of these rejected fractions were identified by a visual inspection based on previous experience and knowledge, as well as by simple identification techniques (flame color, smoke, density). The quantification of each material in the samples was made by taking a representative sample by cone quartering procedure and weighing the quantity of each material in this representative sample. Then, the proportions calculated for the representative samples were extrapolated to the entire samples.

After that, the last sample was separated and other three samples were taken from it adequately selecting some materials of interest: a commodity plastics-rich sample (described here as real sample 7), a cellulose-based materials-rich sample (described here as real sample 8) and the very same sample 6 but without the majority of its inorganic materials (described here as real sample 9). The detailed composition of these 9 real samples is presented in Table 3.1.

Table 3.1. Detailed composition of the real samples pyrolysed (wt.%)

MATERIAL	REAL SAMPLE 1	REAL SAMPLE 2	REAL SAMPLE 3	REAL SAMPLE 4	REAL SAMPLE 5	REAL SAMPLE 6	REAL SAMPLE 7	REAL SAMPLE 8	REAL SAMPLE 9
COMMODITY PLASTICS									
PE	39.50	13.44	5.26	13.35	9.59	5.69	17.24	-	8.42
PE film	-	50.55	9.40	1.52	1.84	0.68	2.06	-	1.01
PP	34.17	9.63	8.19	15.61	6.07	8.29	25.11	-	12.27
PP film	-	4.92	2.07	1.23	0.95	1.26	3.82	-	1.86
PS/HIPS	9.33	4.07	8.78	5.95	9.92	10.80	32.72	-	15.98
EPS (Expanded PS)	6.93	2.53	1.01	2.15	1.52	0.71	2.15	-	1.05
PET	2.94	2.88	7.33	2.30	1.33	2.91	8.81	-	4.31
PVC	4.16	4.28	1.42	0.56	0.67	2.67	8.09	-	3.95
SUBTOTAL	**97.03**	**92.30**	**43.46**	**42.67**	**31.89**	**33.01**	**100.0**	-	**48.85**
OTHER THERMOPLASTICS & THERMOSETS									
SAN	-	-	-	-	0.92	0.47	-	-	0.70
POM	-	-	-	0.03	0.74	0.25	-	-	0.37
PC	-	0.11	0.04	0.59	0.35	0.85	-	-	1.26
PMMA	-	-	0.48	0.39	0.24	0.43	-	-	0.64
Foam (PUR)	-	-	0.07	0.16	0.32	0.04	-	-	0.06
PA	-	-	0.36	0.18	0.22	-	-	-	-
ABS	2.24	-	2.30	1.70	0.20	0.38	-	-	0.56
Thermoset resin	-	-	-	0.13	0.05	0.28	-	-	0.41
Elastomer	-	-	0.08	1.72	0.48	0.13	-	-	0.19
Latex	-	-	0.37	0.69	-	-	-	-	-
SUBTOTAL	**2.24**	**0.11**	**3.70**	**5.59**	**3.52**	**2.83**	-	-	**4.19**

CELLULOSE-BASED MATERIALS									
Paper / Cardboard	0.35	2.80	33.25	2.98	8.26	20.82	-	77.48	30.81
Wood / Cork	-	0.07	0.28	2.36	0.68	1.42	-	5.28	2.10
Tetra-brik	-	1.50	7.82	-	-	1.89	-	7.03	2.80
Gardening waste	-	0.01	0.24	0.40	0.35	2.56	-	9.53	3.79
Clothes	-	-	2.15	0.06	0.22	0.18	-	0.68	0.27
SUBTOTAL	**0.35**	**4.38**	**43.74**	**5.80**	**9.51**	**26.87**	**-**	**100.0**	**39.77**
INORGANICS									
Glass	-	0.01	0.60	34.01	39.48	19.81	-	-	-
Arid / Ceramic	-	-	1.04	5.51	6.15	5.96	-	-	-
Aluminium film	0.19	0.64	1.53	1.78	3.29	4.18	-	-	-
Magnetic metal	-	0.20	1.25	0.90	1.82	0.04	-	-	-
No magnetic metal	-	0.42	1.12	0.96	0.25	2.44	-	-	-
Battery	-	-	-	2.08	-	-	-	-	-
SUBTOTAL	**0.19**	**1.27**	**5.54**	**45.24**	**50.99**	**32.43**	**-**	**-**	**-**
COMPLEX MATERIALS (ORGANIC + INORGANIC)									
ABS + Aluminium	-	-	-	-	1.26	-	-	-	-
PP film+ Aluminium film	0.17	-	-	-	0.78	0.16	-	-	0.24
PVC + Aluminium (blister)	-	-	0.21	-	0.41	0.24	-	-	0.35
PE + Aluminium	-	1.23	-	-	-	0.66	-	-	0.98
Printed circuit board	-	-	0.02	-	-	0.32	-	-	0.47
Complex packaging	0.02	0.64	2.95	-	0.23	3.48	-	-	5.15
Medical waste	-	0.07	0.38	0.70	1.41	-	-	-	-
SUBTOTAL	**0.19**	**1.94**	**3.56**	**0.70**	**4.09**	**4.86**	**-**	**-**	**7.19**
TOTAL	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**

Once the components were identified and quantified, the sample was ground down in a rotor blade mill with interchangeable screens of varying mesh sizes to produce the desired particle size. The mesh size of the screen used was 8 mm, which therefore produced a sample of particles sized 8 mm and smaller, particles that are small enough so as to obtain homogenous and representative samples for the pyrolysis runs. In Figure 3.1 two photographs of a real sample are shown, one is how it looks coming out of the BZB plant (a) and the other is how it looks after milling (b).

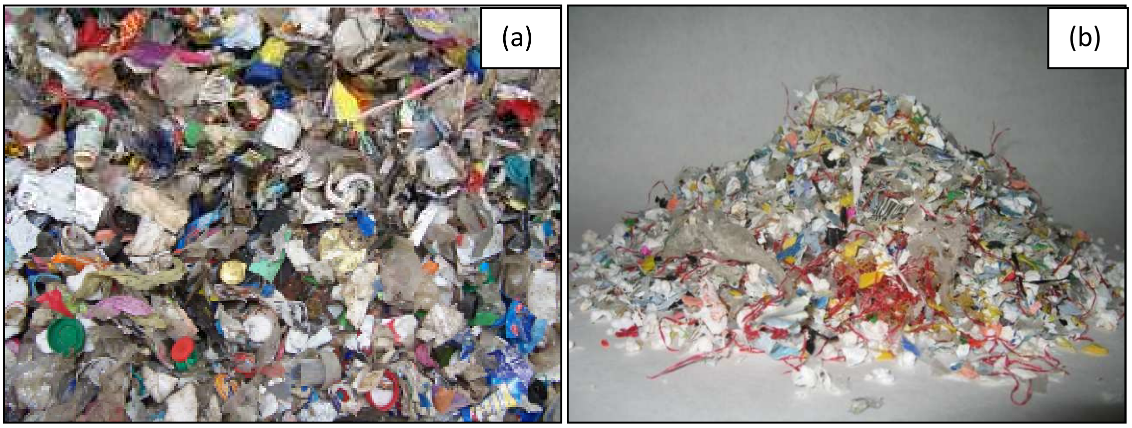


Figure 3.1. Photos of a real sample as it leaves the BZB plant (a) and after being milled as it is introduced into the reactor (b)

3.1.2. Simulated Sample

Additionally, for the purposes of having consistency and invariability, a sample similar to the real ones was prepared (hereinafter "simulated sample") from pure plastics. The materials used were the five main plastic components found in the real samples (PE, PP, PS, PET and PVC). More specifically: virgin PE (PE-017/PE-071), used for household applications, provided by Repsol Química S.A., virgin PP (PP-040), used for general applications, provided by Repsol Química S.A., virgin PS (HIPS-DL471) provided by Dow Chemical, waste PET, washed and milled, coming from recycled bottles and provided by Remaplast S.A., a Spanish company devoted to municipal plastics recycling, and waste PVC, from a variety of bottles, provided by Gaiker, a Spanish Technology Center dedicated to research and innovation in recycling and recovery of plastics among other research areas.

These materials were mixed according to the average proportions of the plastics contained in the six real samples while keeping in mind data taken from literature citing the average composition of municipal plastic waste in Europe (Miskolczi et al. 2004b, Kaminsky and Nuñez Zorriqueta 2007, Carvalho et al., 2009). The composition of this simulated sample is presented in Table 3.2.

Table 3.2. Composition of the simulated sample (wt.%)

PE	**PP**	**PS**	**PET**	**PVC**
40	35	18	4	3

The object of using the simulated sample was to have a homogenous sample that is invariable and has a perfectly known composition. This allows for the study of the influence of the operational variables in the pyrolysis process and how to optimize the process while avoiding interference from compositional variations that may occur in the real samples.

In the case of the simulated sample, prior milling was not necessary before running the pyrolysis tests because the virgin plastics utilized came in pellet form of a sufficiently small size for the runs (≈ 3 mm).

3.2. CATALYSTS

In the work done for the present doctoral thesis, three catalysts were used: a commercial ZSM-5 type zeolite, Red Mud and commercial $AlCl_3$. The zeolite was provided by the American company Zeolist International (Ref. CBV 5524G) and the $AlCl_3$ (98%) by Sigma-Aldrich (Ref. 20,691-1). The Red Mud was obtained from the German aluminum company Vaw Lünen; the composition of which is shown in Table 3.3.

Table 3.3. Composition of Red Mud (wt.%) (dried basis)

Fe_2O_3	Al_2O_3	TiO_2	SiO_2	CaO	Na_2O	Others[1]
36.5	23.8	13.5	8.5	5.3	1.8	10.6

[1] By difference

The three catalysts were utilized in the state in which they arrived, without performing any preparation or activation operation. The characterization results of the catalysts are presented in the “Results and Discussion” section of this doctoral thesis.

3.3. PYROLYSIS EXPERIMENTS

3.3.1. Pyrolysis Plant

The pyrolysis experiments were carried out in a lab-scale installation consisting of a reaction area (reactor and furnace) and a condensation and collection area for the liquid and gaseous products generated. In Figures 3.2 and 3.3 a flow sheet and photograph of the installation used can be seen.

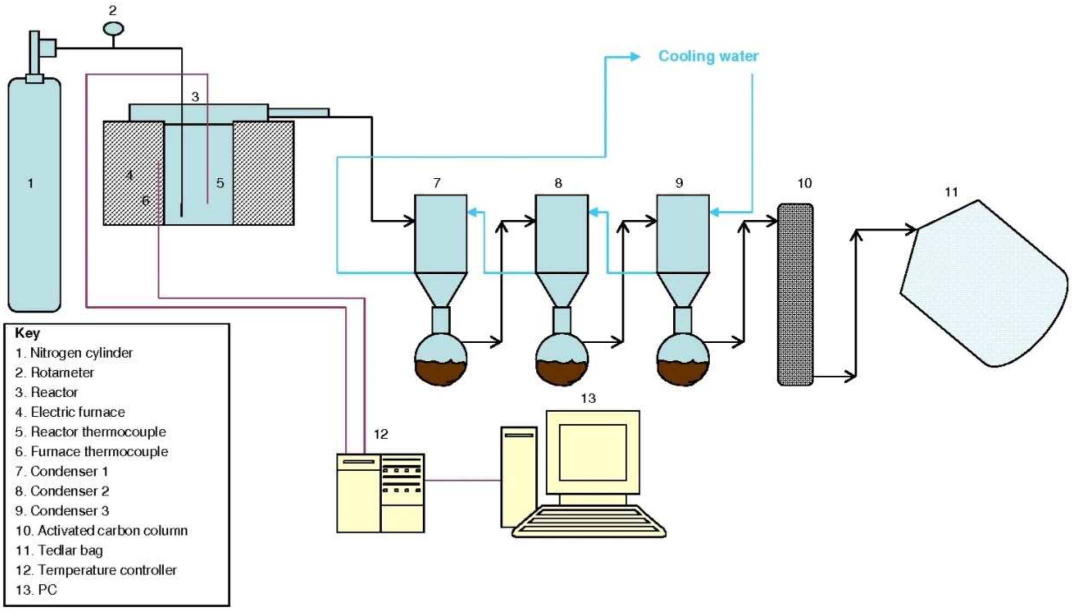


Figure 3.2. Flow sheet of the installation used for the pyrolysis experiments

The reactor used is a fixed bed, SS-304 stainless steel, 3.5 Liter capacity reactor (3). The heating takes place in electric furnace of Watlow fiber (4); the furnace is made of SS-304 and has a high-temperature resistant heating element and ceramic fiber insulation. The furnace is possessed of 2,600 W of power at 120 V and its maximum operating temperature is 1093 ºC. The technical specifications of both the reactor and the furnace are outlined in Tables 3.4 and 3.5 respectively.

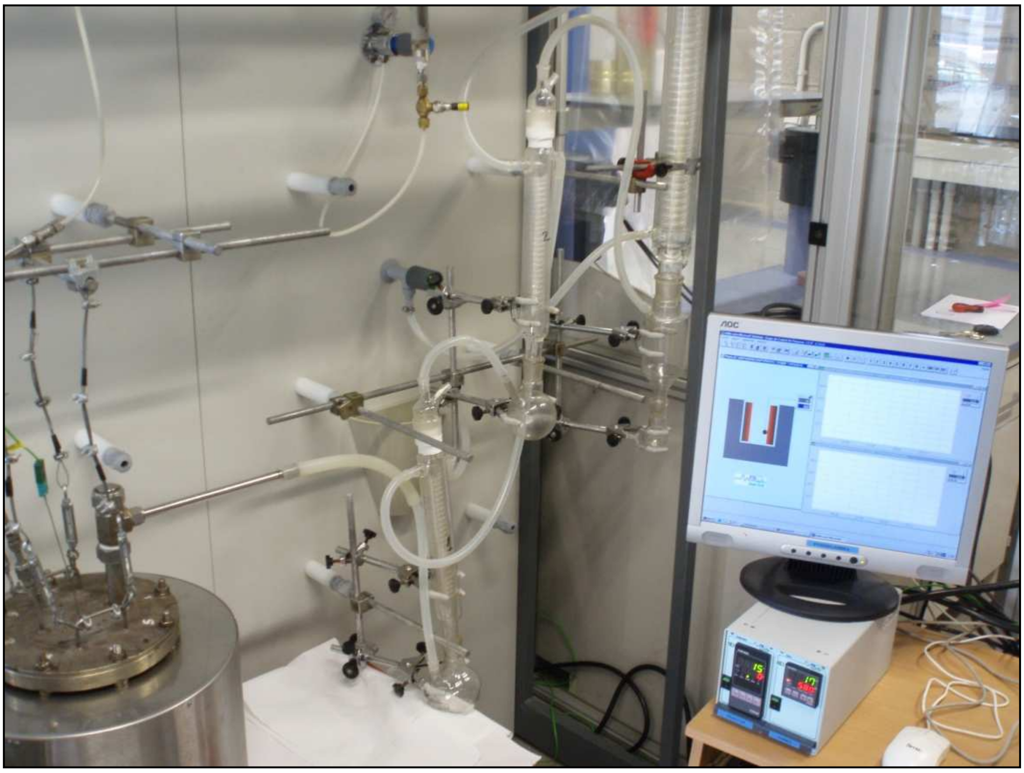


Figure 3.3. Photograph of the pilot plant used for the pyrolysis experiments

Table 3.4. Pyrolysis reactor specifications

CONSTRUCTION MATERIAL SS-304		
MAXIMUM OPERATING CONDITIONS:		Temperature: 1000 ºC
		Pressure: 5 bar (0.5 MPa)
SHAPE: Cylindrical		
INTERNAL DIMENSIONS:		Diameter: 150 mm
		Height: 329.9 mm
		Volume: 3500 cm^3
THICKNESS: 6.90 mm		
CLOSURE: 8 Screw closure flange		
ACCESSORIES:	Inlet tube	Ext. diam. 1/4” (6.35 mm)
		Length: 343 mm
	Outflow tube:	Ext. diam. 1” (25.4 mm)
		Length: 163 mm
	Perforated grill:	Perforations 10 mm in diameter
	Thermocouple casing:	Total length: 193 mm
		Ext. diameter: 1/4” (6.35 mm)
		Thickness: = 0.035” (0.88 mm)

Table 3.5. Pyrolysis furnace specifications

CONSTRUCTION MATERIAL: SS-304
HEIGHT: 135 mm
WIDTH: 150 mm
DEPTH: 255 mm
VOLTAGE: 120 V ; POWER: 2.6 kW
MAXIMUM TEMPERATURE: 1093 °C
OPERATIONAL AMBIENT TEMPERATURE RANGE: 5-40 ºC
STORAGE TEMPERATURE RANGE: -20-70 ºC
OPERATIONAL HUMIDITY RANGE: 5-80%

The sample temperature is measured with a K type thermocouple (5) placed inside a casing which is in contact with the sample. The analog temperature signal is read by a proportional–integral–derivative controller (PID) made by TOHO (12). As a function of the set-point temperature, the controller generates a 4-20 mA control signal to regulate the power supplied to the furnace. Furthermore, there is a thermocouple in the interior wall of the heater (6) that measures the temperature in this area and provides an output signal read by a second PID controller (12) (TIA loop), which cuts the power supply to the heater if the temperature surpasses the preset limit.

This control system is also digitally connected to the computer (13) in way that it can be managed either from the electronic control unit or from the computer. The automatization software allows for the creation of procedures, so the processes can evolve over preset periods of time or can be based on previously programmed events, such as temperature reached. On top of that, the software allows collecting data from the process variables, in this case the reaction temperature. Figure 3.4 illustrates an example of the process temperature registration of a pyrolysis run carried out at 500 ºC.

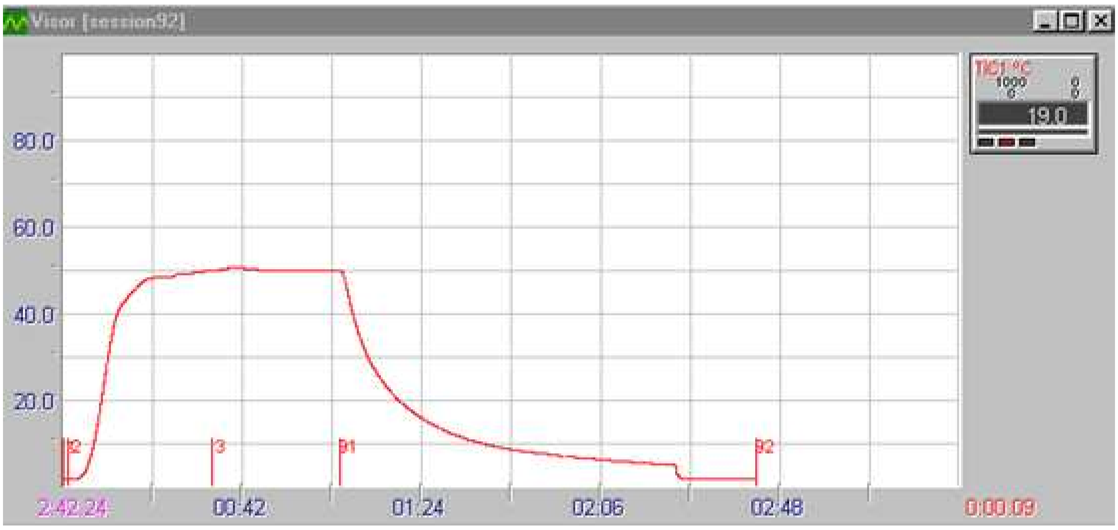


Figure 3.4. Temperature recording (pyrolysis run at 500 ºC)

The pyrolysis plant also has a condensation system for the liquid products derived from pyrolysis, commonly denominated as “oils”. The condensation system consists of a series of three water-cooled gas/liquid separators (7, 8, 9). The uncondensed products pass through an activated carbon column (Panreac granular 1 with granules measuring 1.25-3.15 mm) for purification (10) and are collected in their totality in Tedlar plastic bags (11). The pilot plant is also possessed of a Fischer & Porter rotameter (2) that has a needle valve that regulates the nitrogen flow pumped into the reactor. The nitrogen used (1) is supplied by Air Liquide and has a purity grade higher than 99.999% (nitrogen number 1). Gas is pumped into the reactor from the bottom and through a perforated plaque; this allows the nitrogen to circulate from bottom to top, assuring that all vapors generated are displaced.

3.3.2. Experimental Procedure

3.3.2.1. Thermal and Catalytic Pyrolysis Experiments

In a typical run, 100 g of a sample is placed inside the reactor and then the reactor is closed. In the experiments with real samples, the particle size of the samples was 8 mm and when experimenting with the simulated samples, the pellets were around 3 mm in size. Given that the pyrolysis yields are measured by difference in weight, it is critical to precisely weigh the sample, as well as the reactor and all of the components of the condensation system all before loading the reactor and setting up all the equipment.

Once the plant is set up, the nitrogen feed is opened and its flow is regulated to 1 dm^3 min^{-1}. The flow of nitrogen is started a few minutes before the run to ensure an inert atmosphere within the reactor and is maintained throughout the experiment to guarantee that the reaction vapors are carried away and collected as they are generated. Next, the thermocouple is placed in the measuring casing, the flow of cooling water is turned on and the computer is used to program the control sessions. Lastly, the system is heated at a rate of 20 ºC min^{-1} until the desired temperature is reached; this temperature is maintained for the duration of the isothermal period decided for each test. All the process is automatically controlled by the computer.

Once the run has finished, the quantity of pyrolysis liquids and solids (material remaining in the reactor) generated is determined by measuring the difference in weight (before and after reaction) of the material in the condensation system and the reactor respectively. When pyrolysis liquids are composed by an organic phase and an aqueous phase, both phases are separated and weighed in order to calculate their corresponding yields. The pyrolysis yields are calculated based on the quantity of the sample introduced initially into the reactor. The gas yield is normally determined by difference except in the experiments that were run for the express purpose of analytically measuring the gas yield for said experiment. In such experiments, total gas quantification is made as follows: (1) mass quantification (mg mL^{-1}) of each gaseous component is determined by GC-FID/TCD; (2) total pyrolysis gas volume is measured and (3) the quantities of the gaseous compounds are extrapolated to the total volume. In these experiments mass balance closure (% liquids, % gas, % solids) was about 90 wt.%.

In the catalytic pyrolysis experiments the catalyst is first mixed with the sample in a sample to catalyst ratio of 10:1 and then the run proceeds as normal. In these cases, the catalyst remains in the reactor after the run along with the pyrolysis solids. For the solid yield calculation the quantity of catalyst introduced is subtracted from the total amount of solids obtained.

3.3.2.2. Dechlorination Experiments

Two types of dechlorination experiments were conducted: pyrolysis adding a solid adsorbent in the reactor and stepwise pyrolysis. Both methods aim to keep the chlorine from PVC from mixing with the pyrolysis products which would create chlorinated hydrocarbons. In the first case, chlorine is kept in the reactor by physical and chemical adsorption whereas in the second case, there is a low temperature (≈300 ºC) preliminary stage for the chlorine to be liberated from the polymer structure of PVC and separated from the rest of the products before the decomposition of the rest of the plastics.

The pyrolysis with adsorbents experiments are carried out in the same manner as the catalytic pyrolysis runs, that is, the adsorbent is mixed with the sample in the reactor and then the run is carried out as normal. The adsorptive material used was precipitated calcium carbonate with purity higher than 98.5% supplied by Panreac. Based on bibliographic data (Beckmann et al., 2001; Jiang et al., 2008), 4.65 g of calcium carbonate was mixed with the sample, which corresponds to a 3:1 stoichiometric ratio of Ca:Cl.

In the stepwise pyrolysis experiments, before the activated carbon column, a bubbler is installed containing 200 mL of 0.25 M sodium hydroxide solution prepared from a 50 wt% sodium hydroxide solution supplied by J.T. Baker. The purpose of the bubbler is to trap the released HCl and prevent it from travelling to the gas bags. The amount of chlorine retained is calculated after analyzing the solution by liquid ionic chromatography.

3.4. CHARACTERIZATION AND ANALYSIS TECHNIQUES

3.4.1. Characterization of Initial Samples

In order to characterize the real and simulated samples, a small fraction of each was ground down to a particle size under 1 mm. This was done to conduct the characterization analyses as they require a small particle size to ensure accuracy. This fine milling was performed in cryogenic conditions to keep the material from fusing in the mill and degrading. First, the material was ground down in a rotor blade mill to a particle size of 5 mm, then, after cryogenically freezing the sample with liquid nitrogen, the material was milled down to the desired size of less than 1 mm for the characterization analyses.

3.4.1.1. Elemental Analysis (C, H, N, S, Cl)

The real and simulated samples were characterized by means of elemental analysis of carbon (C), hydrogen (H), nitrogen (N), sulfur (S) and chlorine (Cl). Determining the percentages of C, H and N was done with a LECO CHN-600 automatic analyzer, which complies with the ASTM D5373 standard for elemental analysis of fuels. The elemental analysis with this analyzer is based on the complete and instantaneous oxidation of the sample through combustion with pure oxygen at 950 ºC. Among others, the main products formed are CO_2, H_2O and NO_x, which are swept away via a carrier gas (oxygen for CO_2 and H_2O, helium for the NO_x) and selectively separated in specific columns. The CO_2 and H_2O are measured by specific infrared detectors that use as a reference value that of pure oxygen. NO_x are reduced before measurement, which is done like elemental nitrogen, through a thermal conductivity detector that uses as a reference value that of helium. In a normal analysis, 0.1 g of sample is placed in tin capsules that are then placed directly into the combustion furnace.

For the sulfur measurement, a LECO SC-132 automatic analyzer was used; this analyzer complies with the ASTM D1552, D4239 and D5106 standards for elemental analysis of fuels. In this case, the samples were placed in ceramic crucibles and burned in pure oxygen at 1350 ºC; the sulfur content is measured by the amount of SO_2 counted in an infrared detector. The initial quantity of sample was 0.1 g.

The percentage of chlorine in the samples was determined by using method 5050 of the United State Environmental Protection Agency (EPA) for the determination of total chloride in solid waste, virgin and used oils, fuels and related material. The method consists of oxidizing the sample in a calorimeter (in this case the calorimeter used was the one described in section 3.4.1.3) and collecting the gases generated by the combustion, including hydrogen chloride, in a basic solution that is placed with the sample inside the calorimetric bomb. The chlorine from the sample, which has transformed into HCl during combustion, remains in the form of chloride dissolved in the basic solution. This solution is later analyzed to determine the amount of chlorides in the solution. Once the concentration of chlorides in the basic solution is determined, it is necessary to extrapolate this value to the weight of the sample that was placed inside the calorimetric bomb. In this way, the percentage of chlorine in the original sample can be determined.

The weight of the initial waste samples for the determination of chlorine was 0.5 g. The basic solution used was 0.25 M NaOH, prepared from a 50 wt.% liquid NaOH solution from the J.T. Baker Company. To determine the amount of chlorides in this solution, a DIONEX ICS-3000 ionic chromatograph was used. The details of the method employed can be seen in Table 3.6.

Table 3.6. Method used in the DIONEX ICS-3000 ionic chromatograph

Column	Dionex IonPac AS19
Guard column	Dionex IonPac AG19
Eluent	NaOH (17.5 mM)
Flow rate	1.0 mL min^{-1}
Oven temperature	30 ºC
Cell temperature	35 ºC
Injection volume	25 µL
Suppressor	Dionex ASRS-ULTRA II 4-mm
Suppressor intensity	44 mA
Data collection rate	5 Hz s^{-1}

The eluent for the ionic chromatograph was also prepared from the J.T. Baker NaOH solution. In order to quantify the chloride in the basic solutions obtained, the ionic chromatograph was calibrated using a commercial salt of sodium chloride from Fluka with a ≥99.5% purity grade. Furthermore, the efficiency of the method itself (percentage of chlorine recovered after all of the described analytical steps) was highly scrutinized and quantified by applying the method to an oil sample whose chlorine content was known. More specifically, the IKA AOD 1.11 control standard oil that has a chlorine content of 0.98 ± 0.05 wt.% was used.

3.4.1.2. Thermogravimetric Analysis (TGA)

Distinct parameters of the initial samples were studied by thermogravimetric analysis: thermal characterization (of the individual components and of the mixed samples), proximate analysis, the examination of the dechlorination efficiency, and the determination of the minimum temperature required for complete pyrolysis. To complete this, two thermobalances were used: a METTLER TOLEDO TGA/SDTA851^e and a LECO TGA-500. The main difference between the two lies in that the latter allows for macro sample analysis (up to 2 grams samples) and it is used when it is critical to ensure the representivity of the sample or when macro samples are needed for subsequent analyses after TGA. The thermobalances employed and the parameters studied are described at length in the following sections.

3.4.1.2.1. Thermal Characterization

Thermal characterization of the principal components present in the samples (PE, PP, PS, PET, PVC, paper) and real samples alike was carried out with the METTLER TOLEDO TGA/SDTA851^e thermobalance. With this thermobalance, the sample is placed in a crucible that rests on a balance inside the furnace, where different atmospheres can be used. A thermocouple permits the continuous recording of the weight loss of the material as a function of temperature and atmosphere (inert or reactive).

For each thermal characterization run, approximately 7.5 mg of sample was used and heated at 20 ºC min^{-1} from room temperature until 600 ºC. To ensure an inert atmosphere during decomposition, 50 ml min^{-1} of N_2 was pumped into the furnace. The temperatures at which the sample underwent the maximum rate of decomposition were determined from the derivative thermogravimetric curve (DTG).

3.4.1.2.2. Proximate Analysis

Proximate analysis is the group of tests from which the percentages of moisture, volatile material and ash of a sample are determined. Proximate analyses of the real and simulated samples were executed using the LECO TGA-500 thermobalance, which determines these properties in accordance with ASTM D3173-85, ASTM D3175-82 and ASTM D3174-82 standards respectively. The proximate analysis method is programmed into the thermobalance so it sequentially and automatically determines the three properties of the sample (moisture, volatiles, ash). The conditions of the determination of each property (programming method) according to the corresponding standards are detailed in Table 3.7.

Table 3.7. Programming method for the determination of moisture, volatiles and ash

ASTM Standard	Property	T (ºC)	Time (min)	Atmosphere
D3173-85	Moisture	106	Until constant weight	N_2
D3175-82	Volatiles	950	7	N_2
D3174-82	Ash	750	Until constant weight	O_2

Operational setup of the LECO TGA-500 thermobalance is the same as the METTLER TOLEDO TGA/SDTA851^e, but as mentioned before it allows for the analysis of macro samples and this is recommendable for the characterization of mixed plastic waste samples. For this analysis, 1 g of sample was used for each run.

3.4.1.2.3. Study of Dechlorination Efficiency

The goal of this study, which was carried out only on the simulated sample, was to determine the temperature and time conditions at which the dechlorination of the sample was most efficient. To do so, the amount of chlorine was measured in the sample before and after each thermogravimetric analysis, during which the sample was subjected to a determined dechlorination time and temperature. With the goal of having enough sample in order to analyze the residual chlorine that remained after the dechlorination phase, the LECO TGA-500 thermobalance was again used.

In this case, 1 g of sample in pellet form was heated at 20 ºC min^{-1} until reached the established dechlorination temperatures, which varied between 275 and 300 ºC. Once the corresponding temperature was reached, the temperature was maintained at that level during predefined dechlorination times, which varied between 30 and 120 minutes. To ensure an inert atmosphere during all dechlorination runs, 50 ml min^{-1} of N_2 was pumped into the furnace.

3.4.1.2.4. Determination of Minimum Temperature for Complete Pyrolysis

Lastly, the LECO TGA-500 thermobalance was used in order to establish the minimum temperature necessary for complete pyrolysis. That is to say, to establish the temperature at which the sample is completely decomposed. For these analyses, the same amount and type of sample, particle size, heating velocity and N_2 flow were used as in the earlier case (study of dechlorination efficiency). Distinct temperatures and time periods were used to study each case.

3.4.1.3. Higher Heating Value (HHV)

The HHV of the real and simulate samples were determined using the LECO AC-300 automatic calorimeter, which combusts the samples in a calorimetric bomb complying with the ASTM D3286 standard. This technique is based on the combustion of the sample with pure oxygen in a high-pressure container (calorimetric bomb) situated inside a water bath. The heat released from the combustion is measured as the change in temperature of the water that surrounds the bomb and this change is proportional to the heating value. The samples are placed inside a crucible in the bomb, where the ashes will remain after combustion. The sample size for these tests was 0.5 g.

3.4.2. Characterization of Pyrolysis Liquids

Upon finishing each run, the pyrolysis liquids are collected and analyzed as quickly as possible as to avoid further degradation. The pyrolysis liquids are a complex mixture of aliphatic, cyclic and aromatic hydrocarbons with a number of carbon atoms ranging from C5 to more than C30. Furthermore, depending on the composition of the initial sample, the pyrolysis liquids can have two phases, an organic phase and an aqueous phase. Generally, a comprehensive characterization was carried out on the organic phase of pyrolysis liquids, while the aqueous phase was only quantified and identified by gas chromatography-mass spectrometry (GC-MS). The techniques and methods employed in the characterization of the pyrolysis liquids are described in the following sections.

3.4.2.1. Phase Separation

The cases in which the pyrolysis liquids contained two phases, the separation of the two was achieved by funnel decanting for simple separations and by using a centrifuge for the mixtures that did not separate well by decanting. In these instances, an Alresa brand centrifuge, model Digecen with digital regulation and display, was used. Centrifugation took place for 30 minutes at 2000 rpm.

3.4.2.2. Chromatography (GC-MS)

The composition of the organic and aqueous phases of pyrolysis liquids was determined using gas chromatography coupled with a mass detector (GS-MS), an AGILENT 6890 and an AGILENT 5973 respectively. Analysis quality (purity of 99.9%) tetrahydrofuran (THF) was used as a solvent and was supplied by Panreac. The samples were dissolved before analysis in a 1/100 ratio for organic phases and 1/10 to analyze the aqueous phases. Choosing the solvent was diligently studied due to the complex nature of pyrolysis liquids, which, as said before, are mixtures of compounds with carbon numbers that range from C5 to more than C30. The selected solvent must guarantee the complete dissolution of the mixture and in turn not “hide” significant quantities of compounds that appear during the retention time window, a period of time when the detector is programmed to be off because it is the time when the solvent is eluted. THF, toluene and hexadecane were studied, with THF emerging as the solvent that satisfied to the largest degree the described criteria. THF (C_4H_8O), besides being a good solvent of organic compounds, is a relatively small molecule that, with the method utilized, quickly elutes the column in a way that it does not interfere greatly with the chromatogram. The method used was the same for both the organic and aqueous phases except for the mass range, which is lower when the aqueous phase is analyzed. In Table 3.8 the conditions of the method utilized in the GC-MS analysis are detailed.

Table 3.8. Method utilized in the GC-MS analysis

Column	HP5MS
Carrier gas	He
Carrier gas flow per column	1.0 mL/min
Initial temperature/time	40 ºC / 10 min
Heating rate	8 ºC/min
Final temperature/time	280 ºC / 10 min
Injector temperature	280 ºC
Injection volume	1.0 µL (_plit 100:1)
Detector temperature (Quad/Source)	150 ºC / 230 ºC
Acquisition Mode	Scan
Mass Range (organic phase)	50-550 a.m.u.
Mass Range (aqueous phase)	10-300 a.m.u.

3.4.2.3. Elemental Analysis (C, H, N, Cl)

The elemental analysis of the pyrolysis liquids was done using equipment and methods described in section 3.4.1.1. The amount of sample used was again 0.1 g for the LECO CHN-600 analyzer and 0.5 g for the chlorine content analysis method. The operating procedures were exactly the same as those described in the aforementioned section.

3.4.2.4. Thermogravimetric Analysis (TGA)

The 1:100 solutions in THF used to determine the composition of the pyrolysis liquids by way of GC-MS were also subjected to thermogravimetric analysis. The object being in this case to determine what percentage of the solution volatilizes at 280 ºC that, as can be seen in Table 3.6, is the injection temperature of the chromatograph. With this analysis it can be known if the composition obtained by GC-MS is representative of the whole sample. For these thermogravimetric analyses the LECO TGA-500 thermobalance was used as described in section 3.4.1.2.2. The sample weight used was 1.0 g.

3.4.2.5. Higher Heating Value (HHV)

The higher heating value of the pyrolysis liquids was determined by utilizing the LECO AC-300 automatic calorimeter described in section 3.4.1.3. The operating procedures to determine the HHV of a liquid sample with this equipment are identical to those described in the previously mentioned section. The sample size used was 0.5 g.

3.4.3. Characterization of Pyrolysis Gases

Pyrolysis gases are principally composed of hydrocarbons, H_2, CO and CO_2. Characterization of pyrolysis gases consisted of the determination of their composition and higher heating value (HHV). The composition was determined using chromatography, while the HHV was calculated theoretically.

3.4.3.1. Chromatography (GC-TCD/FID)

Chromatography of the pyrolysis gases was carried out with a KONIK KNK-3000-HRGC gas chromatograph (GC) equipped with two independent detectors: a flame ionization detector (FID) and a thermal conductivity detector (TCD). The compounds analyzed were H_2, CO, CO_2, H_2S, alkanes up to C6 and alkenes up to C6. For the simultaneous separation and determination of this complex mixture of gas compounds, the chromatograph has two columns interconnected with themselves and with the detectors through a system of valves. This creates a multidimensional chromatography system in a single furnace. In Table 3.9 the columns used and the conditions maintained in the analysis method of the pyrolysis gases are detailed.

In the molecular sieve column, H_2, CO, N_2 and O_2 are separated out, while the rest of the compounds are separated in the Chromosorb column. Once all of the components are separated, H_2, CO, CO_2, H_2S, N_2 and O_2 are detected in the TCD, while the hydrocarbons are detected in the FID. The gases were analyzed with He as a carrier gas except in the case of the H_2, which was analyzed using Ar due to the higher sensitivity achieved in the TCD to identify this compound in the presence of Ar.

Table 3.9. Method utilized in the GC-TCD-FID analysis

Columns	Molecular sieve 13X Chromosorb 102
Carrier gas	He / Ar
Carrier gas flow per column	48 mL/min
Initial temperature/time	40 ºC / 10 min
Heating rate	6 ºC/min
Final temperature/time	200 ºC / 10 min
Injector temperature	110 ºC
TCD detector temperature	110 ºC
FID detector temperature	200 ºC

To quantify these compounds, four standard samples were prepared by the Air Liquide Company according to the specifications indicated in Tables 3.10, 3.11, 3.12 and 3.13.

Table 3.10. Concentrations of the standard sample of H_2 and N_2

Component	Concentration
H_2	10 vol.%
N_2	10 vol.%
Ar	rest

Table 3.11. Concentrations of the standard sample of H_2S, CO and CO_2

Component	Concentration
H_2S	1 vol.%
CO	3 vol.%
CO_2	4 vol.%
N_2	rest

Table 3.12. Concentrations of the alkane standard sample

Component	Concentration
CH_4	1 vol.%
C_2H_6	3 vol.%
C_3H_8	4 vol.%
C_4H_{10}	1000 ppm
C_5H_{12}	1000 ppm
C_6H_{14}	1000 ppm
N_2	rest

Table 3.13. Concentrations of the alkene standard sample

Component	Concentration
C_2H_4	1 vol.%
C_3H_6	1 vol.%
C_4H_8	1 vol.%
C_5H_{10}	1 vol.%
C_6H_{12}	1 vol.%
N_2	rest

3.4.3.2. Calculation of Higher Heating Value (HHV)

The HHV of pyrolysis gases is a theoretical calculation based on composition determined by chromatography and the higher heating values of the individual components that make up the pyrolysis gas at 20 ºC and 1 bar (standard laboratory conditions). The heats of the combustion used for this calculation are listed on Table 3.14.

Table 3.14. HHV of the individual components of the pyrolysis gas (Aspen Plus 7.1, 2009)

Component	HHV (MJ kg^{-1})
Hydrogen	141.8
Carbon monoxide	10.1
Hydrogen sulfide	16.5
Methane	55.5
Ethane	51.9
Propane	50.3
n-Butane	49.5
n-Pentane	48.6
n-Hexane	48.3
Ethene	50.3
Propene	48.9
1-Butene	48.4
1-Pentene	47.8
1-Hexene	47.6

3.4.4. Characterization of Pyrolysis Solids

Pyrolysis solids are comprised of an organic, carbonaceous product called char, and the inorganic material from the initial sample which remains unaltered after the pyrolysis process. After each run, the pyrolysis solids were collected and characterized according to the following techniques and methods.

3.4.4.1. Elemental Analysis (C, H, N, Cl)

The elemental analysis of the pyrolysis solids was done using equipment and methods described in section 3.4.1.1. The procedure to conduct an elemental analysis on the pyrolysis solids is exactly the same as the procedure described in the previously mentioned section. The amount of sample used was 0.1 g for the LECO CHN-600 analyzer and 0.5 g for the chlorine content analysis method.

3.4.4.2. Proximate Analysis

The proximate analysis of the pyrolysis solids was conducted using the LECO TGA-500 thermobalance described in section 3.4.1.2.2. In this same section an explanation of the method for the analysis can be found. The sample size used was 1 g.

3.4.4.3. Higher Heating Value (HHV)

The higher heating value of the pyrolysis solids was analytically determined using the LECO AC-300 automatic calorimeter described in section 3.4.1.3. The operational procedure is identical to that described in the mentioned section. A 1 g sample size was used.

3.4.5. Characterization of Catalysts

3.4.5.1. Textural Analysis: Nitrogen Adsorption-Desorption Isotherms

The textural properties of the catalysts were calculated from the adsorption-desorption isotherms of N_2 at 77 K in a Quantachrome automatic analyzer, AUTOSORB-1. Gas adsorption is the technique most used when evaluating the specific surface of a solid and characterizing its porous texture. The most common procedure is based on the determination of the nitrogen adsorption-desorption isotherm at its boiling point (77 K).

The determination of said isotherm consists of the representation of the volume of nitrogen adsorbed per gram of material as a function of equilibrium pressure. Pressure is normally expressed as relative pressure (P/P_0), where P_0 is the saturation pressure of N_2 at 77 K.

Prior to analysis, the samples were degassed at 573 K for 12 hours in a vacuum to eliminate the majority of the gaseous or liquid contaminants retained in the pores of the external surface. For the characterization of the zeolites, approximately 0.02 g of sample was used whereas in the characterization of the Red Mud, 0.2 g of sample was used. The surface areas were calculated using the BET equation and the external surface areas were calculated by using the t-plot method. The total pore volume was measured at $P/P_0 = 0.99$.

3.4.5.2. Acidity. Temperature-Programmed Desorption (TPD) of Ammonia

Temperature programmed desorption of ammonia is a widely used technique to characterize the acid sites of catalysts. This technique involves saturating a catalyst in ammonia in such a way so the ammonia stays adsorbed in the catalyst's acid sites. Later the catalyst is heated, and during the heating process the temperature at which the ammonia desorbs is measured. The amount of ammonia desorbed at a given temperature range is taken as a measure of the acid site concentration, whereas the temperature range at which most of the ammonia is desorbed indicates the acid strength distribution (Hidalgo et al., 1984; Resini et al., 2003).

Acidity of the catalysts was measured on a Micromeritics AutoChem 2910 instrument. Prior to adsorption experiments, the samples (86-300 mg) were first pretreated in a quartz U-tube in a nitrogen stream at 500 °C. Then, they were cooled down to 100 °C in a N_2 flow of 20 $cm^3\ min^{-1}$ before the ammonia adsorption started. The adsorption step was performed by admitting small pulses of ammonia in Ar at 100 °C until saturation. Subsequently, the samples were exposed to a flow of argon (50 $cm^3\ min^{-1}$) for 2 hours at 100 °C in order to remove reversibly and physically bound ammonia from the surface. Finally, the desorption was carried out from 100 to 500 °C at a heating rate of 10 °C min^{-1} in an Ar stream of 50 $cm^3\ min^{-1}$. This temperature was maintained for 15 minutes until the adsorbate was completely desorbed.

3.4.5.3. Scanning Electron Microscopy (SEM)

Electron microscopy is a technique that allows for the retrieval of localized information of the studied sample. This is contrary to what is obtained by using the majority of the catalyst characterization techniques, which is information averaged over the entire sample used. In scanning electron microscopy, the electron beam is swept over the entire surface so a detector can capture the low-energy secondary electrons emitted by each point on the surface. These electrons, being low in energy, are readsorbed by the adjacent atoms and consequently only the secondary electrons generated near the surface are able to escape the sample. In this way, the characteristics of the secondary electrons (those that make it to the detector) represent the characteristics of the surface of the sample.

The SEM images presented in this thesis were obtained using a LEO 1525 microscope belonging to the Institute for Technical and Macromolecular Chemistry (TMC) of the University of Hamburg, where the doctoral candidate studied for three months to enrich his training in the field of pyrolysis.

3.4.5.4. Catalyst Regeneration

In cracking reactions of hydrocarbons, coke deposition is the fundamental cause of catalyst deactivation. These are carbonaceous deposits that strongly adsorb to the surface of the catalyst, blocking part of their active sites. The grade to which coke forms is also related to the acidity of the acid sites. One option to regenerate these catalysts is the calcination or oxidation of the coke at high temperatures (approximately 500-600 ºC).

The regeneration of the used catalysts was carried out with the LECO TGA-500 thermobalance described in section 3.4.1.2.2. The regeneration process has two steps. In the first step the catalyst is heated under nitrogen flow up to 550 ºC and maintained at that temperature for 30 minutes and in the second step the coke is eliminated by combustion under oxygen flow at the same temperature until weight loss is no longer detected.

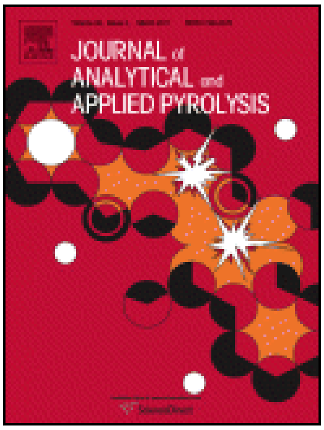
CHAPTER 4

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

The results and discussion of this Ph.D. thesis are presented as a compilation of research articles which have already been published or are at present under revision. Those papers already published are attached in the publishing format of the corresponding journal, while those not yet published are presented in a free format but with the very same contents as those sent to the journal.

4.1. PYROLYSIS PLANT COMMISSIONING: PID CONFIGURATION, CONDENSATION SYSTEM AND CATALYST CONTACT MODE EVALUATION



Article: *Pyrolysis of the rejects of a waste packaging separation and classification plant*

Authors: *Isabel de Marco, Blanca María Caballero, Alexander López, María Felisa Laresgoiti, Amelia Torres, María Jesús Chomón.*

Journal: *Journal of Analytical and Applied Pyrolysis 85, 384-391.*

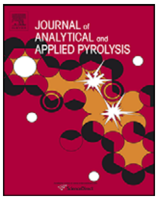
Year of publication: *2009*

J. Anal. Appl. Pyrolysis 85 (2009) 384–391

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap



Pyrolysis of the rejects of a waste packaging separation and classification plant

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ARTICLE INFO

Article history:
Received 30 June 2008
Accepted 18 September 2008
Available online 27 September 2008

Keywords:
Pyrolysis
Recycling
Plastics wastes
HZSM-5
Red mud
$AlCl_3$

ABSTRACT

Plastic wastes coming from a waste packaging separation and classification plant have been pyrolysed in a semibatch nonstirred autoclave, swept by a continuous flow of N_2. The plastic waste contains 39.5% PE, 34.2% PP, 16.2% PS and EPS, and some other minor materials. Temperatures in the range 400–600 °C have been explored, and it has been found that over 460 °C total thermal decomposition of the waste plastics takes place. Three catalysts have been tested: HZSM-5, red mud and $AlCl_3$. Solid yields about 5–7%, liquid yields in the range 40–70% and gas yields in the range 12–24% were obtained. The liquid products were a mixture of C_5–C_{20} compounds with a very high proportion of aromatics (>70%). Such liquids contain significant amounts of valuable chemicals such as styrene (20–40%), toluene (9–15%) and ethylbenzene (7–16%) and have rather high GCV (40–43 MJ kg^{-1}). Thermal pyrolysis oils were a wax-like product which solidified at room temperature, whereas the oils obtained with any of the catalysts were less viscous and maintained in liquid state at room temperature. HZSM-5 favoured gas production and, increased the aromaticity and decreased the carbon number of the oils. $AlCl_3$ did not modify pyrolysis yields but gave rise to lighter liquids. Red mud produced higher liquid yields and the liquids were less viscous, but it was not observed a clear effect on the carbon number of the oils.

1. Introduction

Plastic consumption has drastically increased in the last decades. Annual consumption per person in Occidental Europe is about 100 kg; this means that about 50 million tons of plastics are annually consumed. Such consumption gives rise to about 23 million tons of plastic wastes, most of which (18.3 Mt) come from packing and packaging. The EU Packing and Packaging Waste Directive (2004/12/CE) sets as objective for 2008 a total valorisation rate (energy recover + recycling) of 60% with at least 55–85% recycling. In Spain 60% total valorisation has been achieved, but not the minimum 55% recycling. Plastics are the packaging materials with a lower recycling rate (just 29% in Spain), and it is getting more and more difficult to increase such rate, since the streams left are increasingly complex and intermingled.

The general objective of this paper is to study experimentally the suitability of the pyrolysis process as an alternative for the valorisation of real streams of plastics coming from packing and packaging wastes, concretely the rejects from a waste packaging separation and classification industrial plant in which the wastes of the packing and packaging municipal container are separated in different fractions (steel, tetra-brick, aluminium, cans, different plastics) and then sent to recycling companies. The rejected fraction, about 30% is composed of many different materials (PE, PP, PS, PVC, PET, ABS, aluminium, film, etc.), which are very much intermingled, and for which it is not technical or economically viable an ulterior separation, and therefore they can only be incinerated or land-filled.

In pyrolysis processes (heating without oxygen), the organic components of the material are decomposed generating liquids (oils) and gaseous products, which can be useful as fuels and/or sources of chemicals. The inorganic ingredients (fillers, metals, etc.) remain practically unaltered and free of the binding organic matter and therefore they could be reused in certain applications (additive or fillers for other plastics) or as a last resort it would be a minimum waste to be land-filled. Pyrolysis is especially appropriate for products or streams which contain different plastics and other ingredients both organic and inorganic, as is the fraction that has been studied in this work, since it enables to treat all the ingredients together.

It has been reported, that the oils obtained in pyrolysis of polyolefins and polyolefin containing plastic mixtures are frequently wax like semisolid products. In order to obtain more light and valuable products catalysts may be used. The advantages of catalytic pyrolysis compared to thermal pyrolysis have been reported by several authors (e.g. [1,2]): lowering of the reaction

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doi:10.1016/j.jaap.2008.09.002

temperatures, faster cracking reactions which lead to shorter residence times, selectivity towards valuable products, etc.

Two types of catalysts have been studied in polymer pyrolysis: homogeneous catalysts, such as $AlCl_3$, $TiCl_4$ [3], red mud [4], etc. and heterogeneous catalysts either conventional acid solids like silica alumina zeolites, FCC catalysts, etc. (e.g. [5–10]), or more novel ones such as aluminium pillared clays [11–12] or nanocrystalline zeolites (HZMS-5) [13–15].

Heterogeneous catalysts are claimed to be easier to separate and recover from the reaction medium; however they may present a limited activity due to the difficult access of the bulky plastic molecules to the internal acid sites. Nanocrystalline zeolites-like HZMS-5 may overcame this problem since its nanometer crystal size provides a high external surface area accessible to the high molecular weight polymer molecules.

Homogeneous catalysts are used mixed with the polymer and therefore it is quite difficult to recover them. Consequently the use of cheap products as red mud is of the most interest. Red mud has been used as hydrogenation catalyst for coal and biomass liquefaction [16–19] and for anthracene hydrogenation [20], as hydrodechlorination catalyst [21–23] and as gas clean-up catalyst for the destruction of certain emissions as for instance in catalytic combustion of methane [24,25], etc. A very interesting review of catalytic applications of red mud has been published by Sushil and Batra [26]. There are no published reports of plastic pyrolysis with red mud except for a study carried out by Yanik et al. [4] about the effect of red mud in degradation of PVC containing polymer mixtures.

In this paper a study of the effect of three different types of the above-mentioned catalysts, HZMS-5, red mud and $AlCl_3$, on pyrolysis of a polyolefin rich waste sample is presented. The sample is the rejected fraction from a waste packaging separation and classification industrial plant.

2. Experimental

2.1. Characteristics and origin of the sample pyrolysed

The sample that was used for the experiments was provided by BZB, a waste packaging separation and classification plant in Bizkaia (Spain). In this plant the wastes of the packing and packaging municipal container are separated in different fractions (steel, tetra-brick, aluminium, cans, and different plastics) and the separated fractions are sent to recycling companies. There is a rejected fraction which amounts up to ≅27% which is composed of many different materials (PE, PP, PS, PVC, PET, ABS, aluminium, film, etc.), which are very much intermingled and for which it is not technical or economically feasible an ulterior separation; consequently such rejected fraction can only be incinerated or land-filled.

The materials composition of such sample was determined by manual separation of the different components and visual identification based on the knowledge and experience of the operators, and in doubtful cases, by infrared spectroscopy or simple identification tests such as flame colour, fumes characteristics, etc. The material contents of the sample are presented in Table 1. It can be seen that more than 90% of the sample is composed of plastics and that polyethylene and polypropylene are the predominant ones, followed by polystyrene.

After the identification and quantification of the components, the whole sample (≅10 kg) was ground to a particle size under 8 mm. Homogeneous and representative 100 g samples were separated for the experiments by successively dividing the original sample and subsamples into fourths. One of such 100 g samples was cryogenically ground to a particle size <1 mm and was then characterized. The elemental composition and gross calorific value of the sample is presented in Table 2. It can be seen that the sample contains a rather low amount of inorganic material (2.9%), a certain amount of Cl which probably comes from the PVC contained in the sample, a very high GCV and a H/C atomic ratio of 1.72 which is coherent with the material contents of the sample (mainly olefinic and some aromatics).

Table 1
Components of the sample pyrolysed (wt.%).

Material	Weight %
Polyethilene (PE)	39.5
Polypropylene (PP)	34.2
Polystyrene (PS)	9.3
Expanded polystyrene (EPS)	6.9
Polyvinyl chloride (PVC)	4.2
Polyethylene terephthalate (PET)	2.9
ABS	2.2
(PP + Al) film	0.2
Al film	0.2
Paper	0.4

2.2. Pyrolysis experiments

The pyrolysis experiments were carried out in nitrogen atmosphere in a stainless steel unstirred autoclave. In a typical run, 100 g of sample are placed into the reactor, which is sealed. Then nitrogen is passed through at a rate of 1 $dm^3\,min^{-1}$ and the system is heated at a rate of 15 °C min^{-1} to the desired temperature, and maintained there for 30 min. It has been proved by the authors that in the mentioned installation after 30 min no more pyrolysis products evolve from the autoclave [27–29]. The temperature used in the experiments was mainly 500 °C, except in a few experiment devoted to analyse the influence of this parameter. All through the run the vapours leaving the reactor flow to a series of gas–liquid separators where the liquids are condensed and collected. The uncondensed products are collected as a whole in Tedlar plastic bags, to be tested by gas chromatography with FID and TCD detectors.

Solid and liquid pyrolysis yields were determined in each experiment by weighing the amount of each obtained, and calculating the corresponding percentage, while the gas yields were determined by difference. Each result presented in this paper is the mean value of the data obtained in at least two equivalent experiments which did not differ more than two points in the pyrolysis yields.

2.3. Catalysts

Three catalysts have been tested in the pyrolysis of the plastics wastes. A commercial zeolite HZMS-5, a Lewis acid, $AlCl_3$ and red mud, which is a byproduct of Bayer process for alumina production from bauxite. The composition of the red mud used in the experiments is presented in Table 3; it has a particle size of 5–100 μm. It has been reported [26] that the specific BET surface area of red mud generally lays in the range of 20–30 $m^2\,g^{-1}$.

Table 2
Elemental composition (wt.%) and gross calorific value (GCV) (MJ kg^{-1}) of the sample pyrolysed.

C	H	N	S	Cl	Inorganics	Others[a]	H/C atomic ratio	GCV
82.8	11.9	0.2	0.3	1.5	2.9	0.4	1.72	41.49

[a] Determined by difference.

Table 3
Composition of the red mud used in the experiments (wt.%) (dried basis).

Al_2O_3	TiO_2	SiO_2	CaO	Fe_2O_3	Na_2O	Others[a]
23.8	13.5	8.5	5.3	36.5	1.8	10.6

[a] Determined by difference.

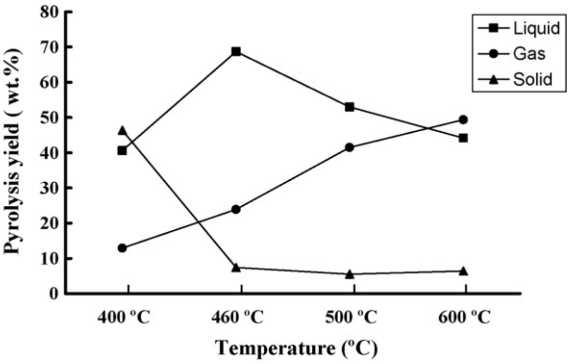

Fig. 1. Pyrolysis yields at different temperatures (wt.%).

All the catalysts were used in liquid phase contact mixed with the plastic waste in a proportion of 10 wt.%. The zeolite was also used in vapour phase contact, making the pyrolysis vapours pass through a catalytic bed placed in a chimney coupled to the head cover of the liner in which the sample was introduced in the autoclave.

3. Results and discussion

A first set of experiments was carried out in order to analyse the influence of temperature in the pyrolysis of the plastic waste sample. The pyrolysis yields obtained are presented in Fig. 1. It can be seen that at 400 °C pyrolysis was incomplete since 46.4% of solids remain in the autoclave, while at temperatures ≥460 °C solid yields are rather low (≅5–7%) and there is no further decrease of such yield with temperature. The solid obtained at any of these temperatures was a powdery black product. It is a mixture of the inorganics of the original sample (≅3% according to Table 2) and carbonaceous material (char) formed during the pyrolysis process, due to secondary repolymerisation reactions among the polymer-derived products. The authors [27,30–33] and other research groups (e.g. [34–38]) have also obtained a certain amount of char in the pyrolysis of many polymeric materials.

On the other hand, Fig. 1 shows that, as might have been expected, there is a decrease in liquid yield and an increase in gas yield with temperature. Another worth mentioning effect of temperature is the decrease of the liquids viscosity; the liquid obtained at 460 and 500 °C were wax-like products which solidified at ambient temperature, while the 600 °C liquids were much less viscous and maintained in liquid state at room temperature. Both the increase in gas yield and the decrease in the viscosity of the liquids are obviously due to the higher thermal cracking that is produced at higher temperatures.

In this first set of experiments several problems raised. (1) There was a rather poor temperature control during the 30 min reaction; about 40 °C around the set point. (2) The air-cooled gas–liquid separators were not effective enough to condense all the liquid products; consequently some liquids were condensed in the gas collecting bags. (3) The semisolid consistency of the liquid products caused operating problems such as the obstruction of tubes and the difficulty in collecting the whole liquid samples. In order to solve these problems two sets of experiments were carried out. The first one included some modifications of the pyrolysis installation in order to improve liquid condensation and temperature regulation, and the second one involved the use of different catalysts with the aim to achieve the production of less viscous products.

Table 4 includes the pyrolysis yields obtained with different layouts of the pyrolysis installation. It can be seen that the use of water-cooled instead of air-cooled condensers brings about a significant increase of the liquid yield (≅8 points); however it was observed that liquid products were still condensed in the gas collecting bag. For this reason an activated carbon column was placed before the gas collecting bag, which retained all the uncondensed liquid products, giving as a result a completely clean gas in the plastic bags. The amount of liquids retained in the activated carbon column was about 7% with respect to the amount of pyrolysed sample. On the other hand, different PID control parameters were tested. Table 4 shows the results obtained with the initial PID parameters (P: 35, I: 240 and D: 20), with which the temperature varied about 40 °C around the set point, and the optimum last PID parameters (P: 40, I: 400 and D: 100), with which the temperature remained absolutely invariable, except for a momentary 10 °C over-temperature the first time the set point was reached. On view of this result it was decided to use the later PID parameters in the subsequent experiments.

It is worth mentioning that using these later PID parameters lower liquid yields and higher gas yields were obtained. This may be attributed to the decrease in heating rate (from 25 to 15 °C min^{-1}) caused by the change of the PID parameters. The explanation to this fact may be that lower heating rates cause longer residence times, favouring secondary reactions which break down higher molecular mass species into gaseous products. On

Table 4
Influence of different configurations and layouts of the installation on the pyrolysis yields (wt.%).

Condensating system	Air-cooled condensers	Water-cooled condensers	Water-cooled condensers + activated carbon	Water-cooled condensers + activated carbon
Temperature control (PID parameters)	P = 35 I = 240 D = 20	P = 35 I = 240 D = 20	P = 35 I = 240 D = 20	P = 40 I = 400 D = 100
	Heating rate			
	≅25 °C min^{-1}	≅25 °C min^{-1}	≅25 °C min^{-1}	≅15 °C min^{-1}
% Liquids	51.0	59.6	58.0	42.5
% Retained by activated carbon	–	–	7.0	10.5
% Gas (by difference)	42.0	34.4	29.0	41.5
% Solids	7.0	6.0	6.5	5.5

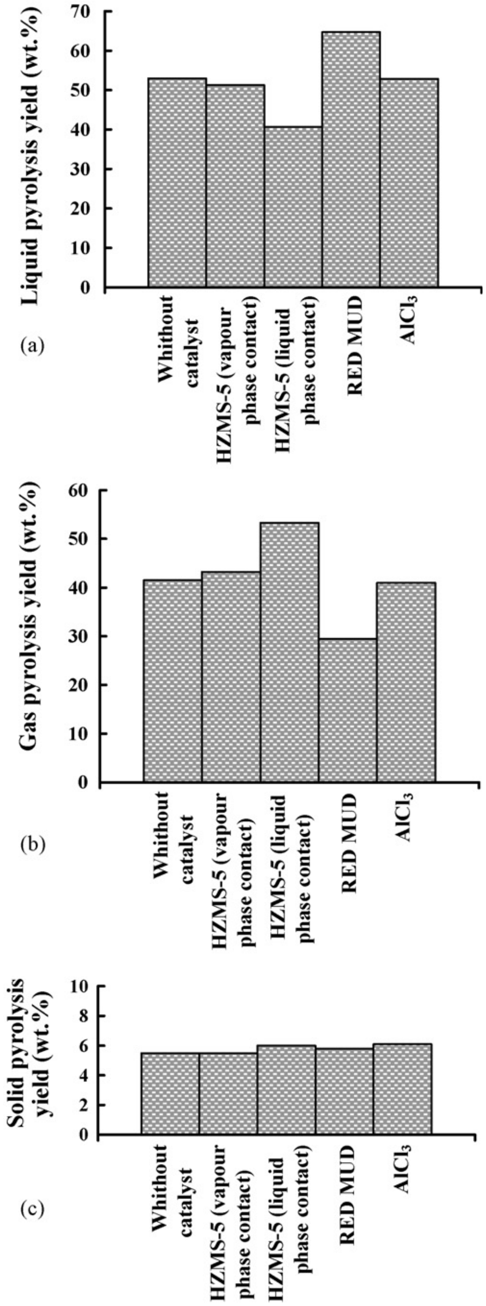

Fig. 2. Pyrolysis yields obtained with different catalysts (wt.%): (a) liquid yields, (b) gas yields, (c) solid yields.

this matter there is not a total agreement in the literature. While some authors claim that high heating rates enhance bond breaking and favour the production of small molecules [39,40] others state that high heating rates and short residence times with rapid quenching of the products are regarded as favouring the formation of liquid products [41–46].

A series of experiments were conducted to analyse the influence of catalysts on pyrolysis products. These experiments were carried out at 500 °C with the water-cooled condensers, the activated carbon column and the later PID parameters. The pyrolysis yields obtained are presented in Fig. 2. The liquid yield includes the condensed liquids plus the products retained in the activated carbon column.

Fig. 2 shows that when HZMS-5 is used in vapour phase contact the pyrolysis yields are very similar to those obtained without catalyst. Additionally the liquid products obtained were almost as viscous as those of thermal pyrolysis and also solidified at room temperature. So it seems that there is hardly any catalyst effect, which may be attributed to the fact that preferential paths are formed in the catalytic bed, through which the pyrolysis vapours pass through with almost no contact with the catalyst. On the contrary when HZMS-5 catalyst is used in liquid phase contact there is a significant catalytic effect, which causes a decrease in liquid yield with a consequent increase in gas yield; additionally the liquid products obtained were less viscous than those of the thermal pyrolysis and maintained in liquid state at room temperature. Therefore the catalyst promotes cracking of the macromolecules generating more gases and lower molecular weight, and consequently less viscous, liquids. Several authors have studied the effect of HZMS-5 in polymers pyrolysis (e.g. [13,47,48]) and all of them agree that this catalyst increases the gas yield on detriment of liquid yield.

Concerning red mud Fig. 2 shows that it has also a significant catalytic effect, though in this case contrary to HZMS-5, it increases liquid yield and decreases gas yield. Additionally the liquids were also less viscous than those obtained in thermal pyrolysis and did not solidify at room temperature. This was a very interesting result since red mud is a cheap by-product of the alumina industry and therefore is a low cost catalyst. Yanik et al. [4] have also studied the effect of red mud in the degradation of PVC containing polymer systems. Such authors did not find a significant effect of red mud on the pyrolysis yields of PE, PP and PS, nor in the carbon number distribution of the liquid products, but they did find a very significant effect in dechlorination of PVC containing mixtures; they recovered more than 90% of feed chlorine as HCl.

As far as $AlCl_3$ is concerned, Fig. 2 shows that the results are quite similar to those obtained without catalysts; however the viscosity of the liquid products was very much lower than that of thermal pyrolysis liquids and such liquids did not solidify at room temperature. Therefore there must have been some kind of catalytic effect.

The elemental composition and gross calorific value of the pyrolysis liquids obtained with the different catalysts are presented in Table 5. It can be seen that there are no significant differences among the results obtained either with the catalysts or without catalyst. It is worth mentioning that the liquids obtained at every temperature have rather high GCV, comparable to those specified for heating fuels. It has to be mentioned that a significant proportion of the chlorine of the raw sample is present in the liquids, which limits the immediate use of these liquids as fuels. Unfortunately the amount of chlorine in the oils of catalytic pyrolysis is higher than in thermal pyrolysis oils; this observation is coincident with what has been reported by Yanik et al. [4] about the catalytic effect of red mud on the degradation of PVC containing polymer mixtures.

The GC/MS analyses of the pyrolysis liquids are presented in Table 6. For the shake of reduction only those compounds with a percentage quantified area greater than 1% have been included. When the match quality of the identification result provided by the MS search engine, was lower than 90%, the result was not considered valid and no name is specified in Table 6. It can be seen that the plastic waste pyrolysis liquids are composed of a mixture of organic compounds of 6–16 carbons with very high proportion of aromatics. Styrene is the most abundant product with percentage areas ranging from 21% with $AlCl_3$ catalyst to 37% in thermal pyrolysis. The next compounds in abundance are toluene (9–14%) and ethylbenzene (8–16%). Somewhat similar results were obtained by Kaminsky and Kim [49] who pyrolysed municipal plastic wastes quite similar to the one used in this work. Although the plastic waste is mainly composed of polyolefins (PE and PP), the pyrolysis oils have more than 70% area of

Table 5
Elemental composition (wt.%) and gross calorific value (GCV) (MJ kg^{-1}) of the pyrolysis liquids.

	Without catalyst	HZSM-5		RED MUD	$AlCl_3$
		Vapour phase contact	Liquid phase contact		
C	85.5	86.6	84.8	83.3	87.6
H	11.4	10.2	11.0	11.4	12.3
N	0.2	0.2	0.2	0.2	0.2
Cl	0.8	n.d.[b]	1.9	1.1	n.d.[b]
Others[a]	2.9	3.0	4.0	5.1	–
H/C atomic ratio	1.60	1.40	1.56	1.66	1.68
GCV	41.06	44.20	40.64	42.84	43.00

[a] Determined by difference.
[b] Not determined.

aromatics, which may be attributed to ciclation of olefin structures followed by dehydrogenation reactions that take place during the pyrolysis process. There are many references in the literature which report that aromatics are produced in the pyrolysis of polyolefins (e.g. [1,3,49–51]) but not in such a high proportion as in this study. On the contrary when pyrolysing municipal plastic wastes Kaminsky and Kim [49] did obtain oils with an aromatic content similar or even higher than that obtained in this work (70%). The reason for this high proportion of aromatics may be the specific composition of the sample pyrolysed. Both in Kaminsky study and in this work, plastic wastes contained a significant proportion of PS and also some polyester (PET), which are both aromatic polymers. Cracking of these polymers obviously generates aromatic products but it seems that they also promote an increase in aromatics coming from other polymers. Angial et al. [51] found that the concentration of polystyrene affected both the quantity and quality of degradation products increasing the concentration of aromatics in the naphtha-like fraction. Williams and Williams [52] and Madorsky [53] also obtained styrene and other aromatic hydrocarbons including toluene, ethylbenzene, naphthalene, etc. On the contrary Williams

Table 6
GC/MS analyses of the pyrolysis liquids (compounds with more than 1% area).

t_R (min)	Molecular formula	Tentative assignment	Whithout catalyst	HZSM-5		Red mud	$AlCl_3$
				Vapour phase contact	Liquid phase contact		
5.06	C_6H_{12}	Methylpentene or cyclohexane	1.2	<1%	1.1	<1%	
12.84	C_7H_8	Toluene	10.9	14.4	9.1	11.1	12.5
15.84							2.0
16.10	C_9H_{18}	Dimethylheptene	4.9	1.6	3.8	3.5	<1%
16,89	C_8H_{10}	Ethylbenzene	9.4	9.4	7.7	8.5	16.2
17.17	C_8H_{10}	Xylene	1.9	7.6	1.8	2.4	5.4
17.92	C_8H_8	Styrene	37.4	26.4	33.6	33.3	21.0
17.99	C_8H_{10}	Xylene		1.4	<1%	<1%	1.9
18.80		–	1.4	2.0	2.1		
18.99	C_9H_{12}	Isopropylbenzene	<1%	<1%	<1%	<1%	3.3
20.11	C_9H_{12}	Ethylmethylbenzene		3.2			1.9
20.63	C_9H_{10}	Methylethenylbenzene	4.4	5.0	4.1	5.1	1.1
20.75	$C_{10}H_{20}$	Decene	1.7		1.7	1.6	<1%
20.95	C_9H_{12}	Trimethylbenzene		1.9			2.5
20.96	–	–			<1%	1.0	
21.77	C_9H_{10}	Propenylbenzene	<1%	1.3	<1%	<1%	<1%
22.08	C_9H_{10}	Indane					1.1
22.31	C_9H_8	Indene	<1%	2.1	<1%	1.0	<1%
22.48	$C_{10}H_{14}$	Diethylbenzene		1.1			
23.14	$C_{11}H_{22}$	Undecene	1.2		1.2	1.1	<1%
23.28	$C_{10}H_{12}$	Methylindane					1.6
24.00	C_9H_{10}	Methylstyrene	<1%				1.3
24.70	$C_{10}H_{10}$	Methylindene		1.8	<1%	1.1	1.0
25.22	$C_{12}H_{24}$	Dodecene	1.1		1.2	1.1	<1%
25.48	$C_{10}H_8$	Naphtalene	<1%	1.8	1.3	2.0	2.2
27.11	$C_{13}H_{26}$	Tridecene	1.2		1.3	1.4	<1%
27.43	–	–	1.1		1.0	1.1	
27.62	$C_{11}H_{10}$	Methylnaphtalene		2.4	1.1	2.0	1.7
27.73	–	–	<1%	<1%	<1%	1.1	
27.95	$C_{11}H_{10}$	Methylnaphtalene	<1%	<1%	<1%	1.0	1.0
28.86	$C_{14}H_{28}$	Tetradecene	1.3		1.2	1.1	
29.07	$C_{12}H_{10}$	Phenylbenzene	<1%	<1%	<1%	1.0	<1%
30.50	$C_{15}H_{30}$	Pentadecene	1.1	<1%	1.1	1.1	<1%
32.04	$C_{16}H_{32}$	Hexadecene	<1%	<1%	<1%	<1%	<1%
33.37	$C_{15}H_{16}$	Phenylpropylbenzene	<1%	<1%	1.0	1.4	<1%
33.50	$C_{17}H_{34}$	Heptadecene	<1%		<1%	<1%	<1%
34.25	–	–			<1%	1.0	
34.88	$C_{18}H_{36}$	Octadecene	<1%		<1%	<1%	<1%
36.20	$C_{19}H_{38}$	Nonadecene	<1%		<1%	1.0	<1%
37.88	$C_{16}H_{12}$	Phenylnaphthalene	1.2	1.5	1.4	1.7	1.1
Total			77.7	82.9	73.7	83.5	77.1

[54] as well as Pinto et al. [55] did not detect styrene in their pyrolysis products, due to the fact that these authors carried out their experiments under N_2 pressure and it has been reported that under elevated pressures styrene and PS derivatives shift to ethylbenzene and cumene [56,57].

The possibility of obtaining valuable aromatic hydrocarbons, such as styrene, toluene, ethylbenzene, etc. from the waste plastic sample used, confers pyrolysis a potential attractive as source of chemical feedstock.

In order to better analyse the effect of catalysts on the characteristics of pyrolysis liquids, all the compounds identified by GC/MS, including those with % area <1%, have been grouped in three categories according to their number of carbons: C_5–C_9, C_{10}–C_{13} and $>C_{13}$; additionally total aromatics have been quantified. The results are presented in Fig. 3, which shows that there is an increase in the proportion of aromatics with all the catalysts tested, except with HZMS-5, when it is used in vapour phase contact; this confirms, as has been mentioned before, that with the layout used in this work for the catalyst HZMS-5 with vapour phase contact no catalytic activity is produced.

There are multiples references in the literature which also report that the use of cracking catalysts such as FCC catalysts or zeolites promotes the generation of aromatics [1,15,48,50,58,59].

Concerning the number of carbons of the oils products, Fig. 3 shows that in all cases only 13% or less are heavy oils ($>C_{13}$) and more than 70% are products in the range of gasolines (C_5–C_9). It has been reported that with HZMS-5 [8,15,48,51] high molecular weight compounds are significantly reduced. In this work, this effect can be observed with HZMS-5 in liquid phase contact and with $AlCl_3$, which both yield less heavy oils ($>C_{13}$) than in thermal pyrolysis. However such effect is not very much pronounced, which is attributed to the fact that the temperature used (500 °C) is rather high and therefore significant thermal cracking is produced simultaneously with catalytic cracking.

Concerning $AlCl_3$ Kaminsky and Nuñez [3] have reported that in pyrolysis of polypropylene small amounts of this catalyst produce at 400 °C similar products to those obtained in 500 °C thermal pyrolysis. On the contrary Ishaq et al. [60] have reported that there was no beneficial influence of $AlCl_3$ on plastics pyrolysis. In this work the results presented up to now show a perceptible effect of this catalyst in pyrolysis products. However it was observed that some corrosion of the installations was produced due to the formation of HCl. Additionally it was found that some of the catalyst evolve (possible sublimation) from the autoclave, since the amount of catalyst in the solid pyrolysis products was much lower than the amount of catalyst initially used; there are material safety data sheets of $AlCl_3$ which report that it may sublime at temperatures around 200 °C. Therefore the authors have rejected $AlCl_3$ as pyrolysis catalyst for future investigations.

Fig. 3 shows that with red mud and with HZMS-5 in vapour phase contact there is no reduction in high molecular weight products content. Similarly in the study about the catalytic effect of red mud in PVC containing polymer mixtures. Yanik et al. [4] reported no catalytic effect of red mud on cracking. However it must be remembered that in this work some kind of catalytic activity takes place with red mud, since the oils obtained with such catalyst were liquid at room temperature, contrary to the waxy products obtained in thermal pyrolysis. Additionally the already presented Fig. 2 showed that liquid yields with red mud were higher than in thermal pyrolysis. Therefore these observations put forward the interest of investigating more thoroughly the catalytic effect of red mud in plastics pyrolysis.

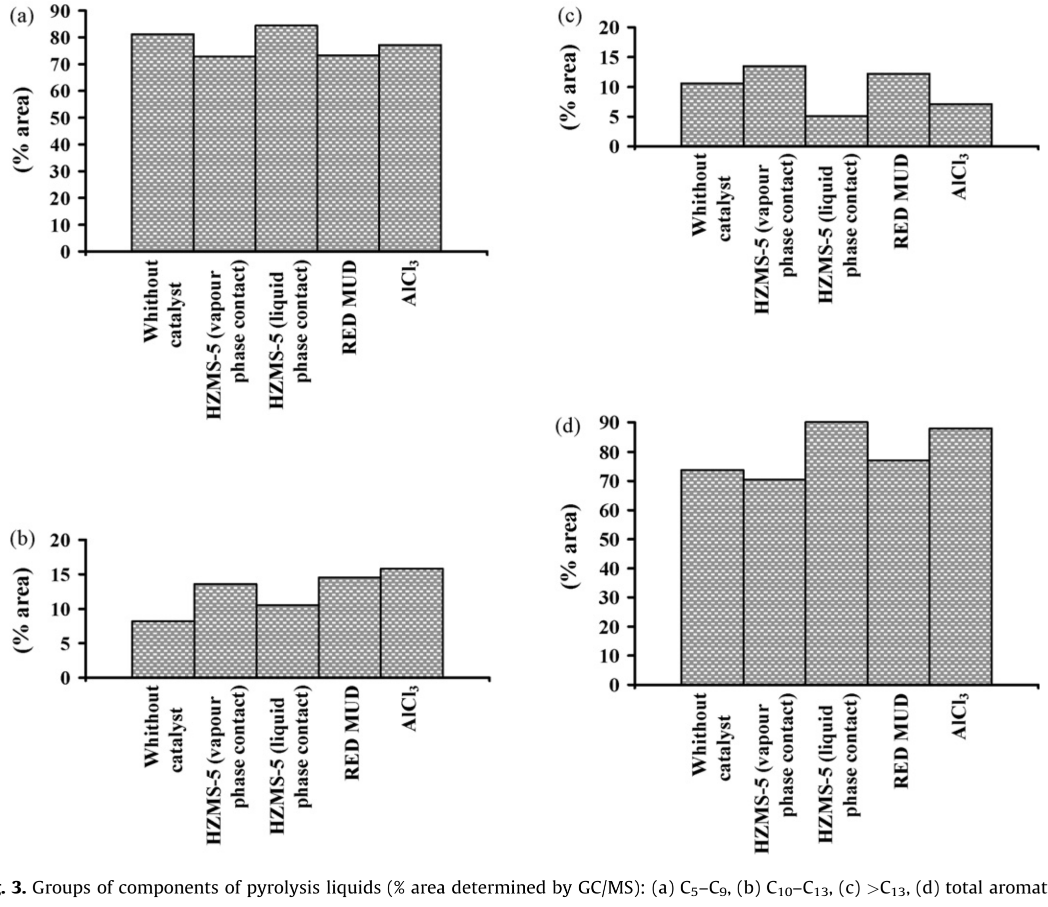

Fig. 3. Groups of components of pyrolysis liquids (% area determined by GC/MS): (a) C_5–C_9, (b) C_{10}–C_{13}, (c) $>C_{13}$, (d) total aromatics.

Table 7
Volumetric composition (vol.%) and gross calorific value (GCV) (MJ m^{-3} N) of the pyrolysis gases.

	Whithout catalyst	HZSM-5		Red mud	$AlCl_3$
		Vapour phase contact	Liquid phase contact		
Methane	27.5	7.7	15.7	16.4	26.4
Ethane	15.2	10.9	8.1	10.6	12.6
Ethene	26.7	20.6	15.8	20.7	15.1
Propane	1.6	2.9	3.0	1.5	4.6
Propene	22.2	28.7	30.2	22.9	17.1
Butane	–	2.4	19.4	0.4	1.6
Butene	1.0	11.9	0.9	14.0	2.4
Pentane	–	3.8	2.3	1.7	2.5
Pentene	–	2.6	1.0	0.4	1.5
CO	2.5	–	–	0.8	–
CO_2	3.3	–	0.4	3.8	0.9
H_2	–	5.9	3.2	6.8	15.3
GCV	61.86	85.7	84.19	71.55	62.52

Table 8
Elemental composition (wt.%) of the pyrolysis solids.

	Whithout catalyst	HZSM-5		Red mud	$AlCl_3$
		Vapour phase contact	Liquid phase contact		
C	48.0	40.5	42.8	64.9	n.d.[b]
H	1.9	1.2	2.4	2.8	n.d.[b]
N	0.9	0.7	1.3	1.4	n.d.[b]
Inorganics	48.3	50.8	45.9	27.9	n.d.[b]
Others[a]	0.9	6.8	42.8	3.0	n.d.[b]

[a] Determined by difference.

[b] Not determined.

The composition of pyrolysis gases is presented in Table 7. It can be seen that in all cases they are composed of hydrocarbons together with small quantities of CO, CO_2 and H_2 in some cases. Concerning the effect of catalysts on gas composition Table 7 shows that as a general rule less light gases ($C_1 + C_2$) and more heavy gases ($C_3 + C_4 + C_5$) are obtained in catalytic pyrolysis than in thermal pyrolysis. Their GCV is very high, even higher than that of natural gas (31 MJ m^{-3} N). Therefore these gases could widely provide the energy requirements of the process plant, and the surplus could make the process more profitable.

The composition of pyrolysis solids is presented in Table 8. The results are given on a catalyst free basis. It can be seen that carbon amounts up to 50–60% of the solids. Such carbon corresponds to the carbonaceous product (char) previously mentioned, that is formed during pyrolysis. Most of the remaining solids are the inorganic matter contained in the original sample. The pyrolysis solids are at first sight a useless product of the pyrolysis process, which most probably would have to be landfilled. Anyhow it would be a minoritary by-product of the pyrolysis process, since the volume of the original plastic waste is reduced by more than 90%.

4. Conclusions

The main conclusions that can be drawn from this study are presented below. Plastic wastes rejected from waste packaging separation and classification plants can be valorised by means of pyrolysis, yielding great valuable liquids (styrene, ethylbenzene, toluene, etc.), gases with a very high GCV and a very low proportion of solids.

Temperatures over 460 °C are enough to produce complete decomposition of the plastic wastes in thermal pyrolysis.

The oils obtained in thermal pyrolysis are wax like products which solidify at room temperature, whilst the oils obtained in catalytic pyrolysis are fluid and maintain in liquid state at room temperature.

The pyrolysis yields and the characteristics of the products obtained are influenced by not so obvious factors as heating rate, PID regulation control parameters and layout of the installation (number and type of condensers). The use of activated carbon is rather convenient to withdraw condensable liquids from the gas stream.

In agreement with other authors HZMS-5 is a convenient catalyst since it produces more valuable liquids (more aromatic and of lower molecular weight).

$AlCl_3$ also generates lighter liquid products but it was discarded as catalyst for future studies since it causes corrosion problems due to HCl generation, and because it may sublime during the pyrolysis process evolving from the autoclave with the liquids and gases.

Red mud produces more liquids which in addition are less waxy and more aromatic than those of thermal pyrolysis, but no effect of red mud on the oils carbon number was observed. It is worthwhile a more thorough investigation of the effect of red mud on pyrolysis of plastic wastes.

Acknowledgements

The authors thank the Spanish Ministry of Education and Science (MEC) (CTQ 2007-67070) and the Basque Government (ETORTEK 2007 IE07-207) for financial assistance for this work.

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4.2. SIMULATED SAMPLE RUNS

4.2.1. Thermal pyrolysis

Article: *Influence of time and temperature on pyrolysis of plastic wastes in a semi-batch reactor*

Authors: *Alexander López, Isabel de Marco, Blanca María Caballero, María Felisa Laresgoiti, Aitziber Adrados.*

Journal: *Chemical Engineering Journal.*

State: *Under review.*

Abstract

The objective of this work is the study of the influence of temperature and time in the products obtained in the pyrolysis of plastic wastes. The thermal behavior of a mixture which resembles municipal plastic wastes has been studied both in a thermogravimetric analyzer and in a 3.5 dm^3 semi-batch reactor in order to establish the most appropriate time-temperature combination for plastic waste pyrolysis. It has been proved by the authors that temperature has a strong effect in the characteristics of pyrolysis liquids and to a lesser extent in gas and solid properties. At the lowest temperature, a great proportion of a high viscosity liquid product with high content of long hydrocarbon chains is obtained, while at high temperatures a lower proportion of liquids with a high content of aromatics is produced. On the other hand, the effect of time is not as strong as that of temperature except when total pyrolysis is not achieved. 500 ºC and 30 minutes have been found to be the most appropriate parameters for the pyrolysis of such plastic wastes in the semi-batch reactor.

Keywords: pyrolysis, thermolysis, feedstock recycling, thermal decomposition, plastic wastes, semi-batch reactor.

1. Introduction

The production of plastic goods has drastically increased in the last few decades. At present, 60 million tons of such products are produced in Occidental Europe and about 40% of them are estimated to be consumed in packing and packaging services, a short life application which leads to the generation of almost 15 million tons of plastic wastes per year [1]. Nowadays, in Europe, only about 24% of the annually generated plastic wastes coming from household packaging applications are recycled, most of them by means of mechanical processes, while the chemical recycling rate of these wastes is less than 1% and restricted to blast or clinker furnace applications. New processes are needed to increase the chemical recycling percentage, and pyrolysis may be an attractive alternative since it provides an opportunity to obtain valuable liquid and gas fuels from plastic wastes.

In the pyrolysis process (heating in an oxygen free atmosphere), the organic components of the material are decomposed generating liquid and gaseous products, which can be useful as fuels and/or sources of chemicals. The inorganic materials (fillers, metals) remain practically unaltered and free of the binding organic matter; therefore, metals could be separated and the remaining solid may be reused (additive, filler, pigment) or as a last resort, it would be a minimum waste to be landfilled. Pyrolysis is an especially appropriate recycling technique for waste streams containing different plastics and other materials, for which mechanical recycling is not feasible.

The pyrolysis of virgin and waste plastics has been intensively studied in the last years. Several reactor geometries and experimental configurations have been proved, from micro-pyrolyzers and thermogravimetric analyzers (TGA) used for analytical pyrolysis studies [2-4] to medium and large scale plants, mainly fluidized bed units, focused on industrial implementation [5-6]. Despite the fact that batch and semi-batch reactors can suffer from temperature gradients due to the low thermal conductivity and high viscosity of plastic wastes, they have also been used to a great extent in lab-scale applications, since they are usually easier to design and operate. Besides, they enable to work with large samples and with great particle sizes, which are closer conditions to those of potential industrial applications.

The influence of operating parameters cannot be easily extrapolated from one installation to another, since such influence usually depends on the specific characteristics of the process. Up to now, temperature has been one of the most studied operating variables, since it is the parameter which most affects thermal cracking of plastics, and as a consequence it has a strong effect on pyrolysis products and on secondary reactions [7-9]. Such reactions are very much influenced by residence time, however, there are few reported studies in the literature about the influence of time on pyrolysis products and the few reported studies have been carried out mainly in fluidised bed units [10-11] or in batch reactors (closed autoclaves) [12-13]. In this paper, an experimental study of the influence of time and temperature on pyrolysis of a complex plastic mixture has been carried out in order to establish the optimum time-temperature combination that enables to obtain the best quality products.

On the other hand, most of the above mentioned studies have been carried out with individual plastics or with simple mixtures of very few plastics which do not resemble complex real plastic wastes. There are almost no pyrolysis studies which include PVC and PET in the plastic samples, since these two plastics may cause several operating problems such as corrosion or pipeline obstructions. In this paper, the results obtained in pyrolysis of a complex plastic mixture which includes both PVC and PET in similar proportions to real plastic wastes is presented. A more thorough characterization of pyrolysis products than that usually found in the literature is included, which is essential information to establish the potential applications of pyrolysis products.

2. Materials and methods

2.1. Materials

The plastic mixture which was used for the experiments was composed of the following materials: (1) virgin PE (PE-017/PE-071) provided by Repsol Química S.A. and used for household applications, (2) virgin PP (PP-040) provided by Repsol Química S.A. and used for general applications, (3) virgin PS (HIPS-DL471) provided by Dow Chemical, (4) waste PET, washed and milled, coming from recycled bottles and provided by Remaplast S.A., a Spanish company devoted to municipal plastics recycling, and (5) waste PVC coming from a variety of bottles and provided by Gaiker, a Spanish Technology Centre dedicated to research and innovation in recycling and recovery of plastics among other research areas.

The proportions of the plastics in the mixture were 40 wt.% PE, 35 wt.% PP, 18 wt.% PS, 4 wt.% PET and 3% PVC. This composition was established characterizing real samples rejected from an industrial plant located in Amorebieta, in the north of Spain [14, 15]. All the plastic materials were used in pellet size (≈ 3 mm) for the pyrolysis experiments; additionally finely ground samples (≤ 1 mm) were prepared for characterization purposes and some TGA analyses.

The characterization results of the plastic mixture and the individual plastic components are presented in Table 1. As it can be seen, the plastic mixture is mainly composed of carbon and hydrogen (84.7 and 12.5 wt.% respectively) as a consequence of the high PE, PP and PS content of the sample (93 wt.%), materials which are composed just by carbon and hydrogen; this fact also explains its high higher heating value (HHV). It must be mentioned that the sample also contains 1.1 wt.% of chlorine, due to the presence of a 32.4 wt.% chlorine containing PVC in the mixture.

Table 1. Moisture, ash and elemental composition (wt.%) and HHV (MJ kg^{-1}) of the plastic mixture pyrolysed and the individual components used in the mixture

	Plastic mixture	**PE**	**PP**	**PS**	**PET**	**PVC**
Moisture	0.1	0.1	0.0	0.2	0.4	0.2
Ash	0.0	0.0	0.0	0.0	0.0	0.0
C	84.7	85.5	85.7	91.9	63.2	44.4
H	12.5	14.3	14.3	7.9	4.4	5.7
N	<0.1	n.d.[b]	n.d.[b]	0.1	n.d.[b]	0.2
Cl	1.1	n.d.[b]	n.d.[b]	n.d.[b]	n.d.[b]	36.3
Others[a]	1.5	0.1	0.0	0.0	32.4	13.2
H/C Ratio	1.8	2.0	2.0	1.0	0.8	1.5
HHV	43.9	45.9	45.8	41.4	22.6	26.0

[a] By difference

[b] Not detected

2.2. Experimental

The thermal behavior of the individual plastics was studied using a Mettler Toledo TGA/SDTA851 analyzer. The analyses were conducted with 7.5 mg samples, which were heated under nitrogen flow (50 mL min^{-1}) to 600 ºC at a rate of 20 ºC min^{-1}. The temperatures of the maximum degradation rates were determined from the derivative thermogravimetric (DTG) plot. Additionally, thermogravimetric analyses of the mixed sample were carried out with a LECO TGA-500 analyzer. In this case, a total sample mass of 0.5 g was heated at a rate of 20 ºC min^{-1} to the desired temperature and maintained there for 30 minutes; nitrogen was passed through at a rate of 4.5 dm^3 min^{-1} during the analysis.

The pyrolysis experiments were carried out using an unstirred stainless steel 3.5 dm^3 reactor. In a typical run, 100 g of the sample were placed into the reactor and nitrogen was passed through at a rate of 1 dm^3 min^{-1}; the system was heated at a rate of 20 ºC min^{-1}. In the experiments devoted to the study of temperature, the sample was heated to 460 (the minimum total pyrolysis temperature), 500 or 600 ºC and maintained there for 30 minutes. This time was chosen as standard for the study of the influence of temperature based on previous studies carried out by the authors with other polymeric wastes [16-18]. The influence of time in pyrolysis was explored using 0, 15, 30 and 120 min reaction times and the best temperature selected in the previous series of experiments. Reaction times below 30 min were studied in order to determine if with shorter times total decomposition of the sample could also be achieved as with 30 min, but obviously with the corresponding energy saving. On the other hand, 120 min was chosen as a large enough time to confirm that (1) further reactions do not take place over 30 min, (2) solid yields could be not reduced to zero and (3) the products characteristics were not modified with longer reaction times.

During each run the vapors leaving the reactor flowed to a series of running water cooled gas-liquid separators where the condensed liquids were collected. The uncondensed products were passed through an activated carbon column and collected as a whole in Tedlar plastic bags, to be afterwards tested by gas chromatography. The experimental set-up is presented in Figure 1. The amount of solids (products in the reactor after pyrolysis) and liquids obtained were weighed, and the pyrolysis yields were calculated as weight percentage with respect to the amount of raw material pyrolysed. Gas yields were as a general rule calculated by difference. Some experiments were specifically devoted to directly quantify the amount of gases by gas chromatography; in such experiments a closure of the mass balance of about 90 wt.% was obtained.

The results of the pyrolysis yields which are presented in "Results and Discussion" section of this paper are the mean value of at least three different pyrolysis runs carried out in the same conditions and which did not differ more than three points in the percentage. After each pyrolysis run, the whole solids, liquids and gaseous products were collected and characterized.

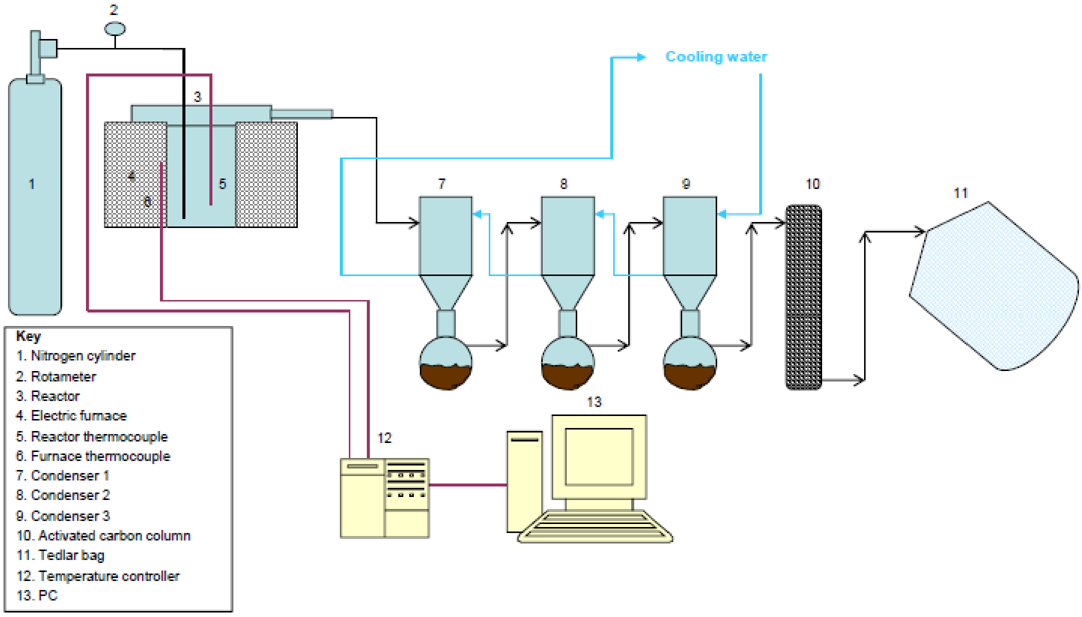

Figure 1. Flow sheet of the experimental set-up used

2.3. Analytical techniques

Both the raw materials and the solid and liquid pyrolysis products obtained were thoroughly characterized using the following analytical techniques. The moisture and ash contents of the samples were determined by thermogravimetric analysis according to D3173-85 and D3174-82 ASTM standards respectively, and the elemental composition with an automatic CHN analyzer. Chlorine was determined following the method 5050 of the Environmental Protection Agency (EPA) of the United States. The higher heating value (HHV) was determined with an automatic calorimetric bomb.

Additionally, pyrolysis liquids were also analyzed by gas chromatography coupled with mass spectrometry detector (GC-MS). When the match quality of the identification result provided by the MS search engine was lower than 85%, the result was not considered valid and these compounds are classified as “No identified” in the corresponding tables in this paper. The compounds names correspond to the tentative assignments provided by the MS search engine and have been contrasted, as far as possible, with bibliographic data and occasionally with calibration standards.

Pyrolysis gases were analyzed by means of a gas chromatograph coupled with thermal conductivity and flame ionization detectors (GC-TCD/FID). Due to the difficulty in distinguishing among isomers from C3 to C6, such discrimination has not been made. The HHV of the gases was calculated according to their composition and to the HHV of the individual components.

3. Results and Discussion

3.1. Influence of temperature

3.1.1. Thermogravimetric analyses

Figure 2 shows the DTG plot of the individual plastics used in the sample, in which the temperatures of maximum degradation rates can be seen.

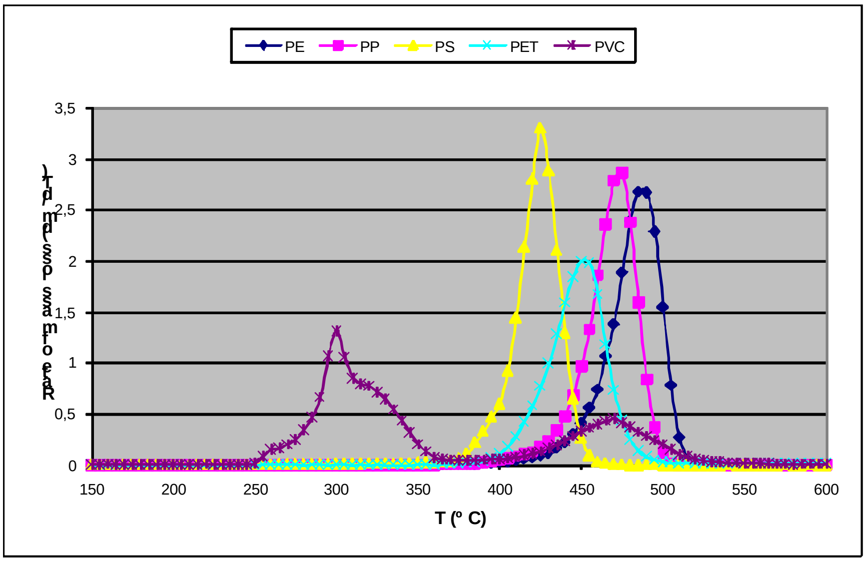

Figure 2. DTG plot of the individual plastics used in the mixture

As expected, PE, PP, PS and PET suffered one-step degradation while in the PVC plot two temperatures of maximum degradation rate can be observed, as a consequence of its two-step decomposition mechanism (HCl release and decomposition of the remaining polyene). On the other hand, the results obtained in the thermogravimetric analyses carried out with the mixed sample are shown in Table 2.

Table 2. Thermogravimetric analyses of the mixed sample

Temperature (ºC)	**400**	**425**	**450**	**460**	**500**
Weight loss (wt.%)	88.2	99.4	99.7	99.9	100.0

As it can be seen, complete decomposition of the sample was only achieved at 500 ºC although from 425 ºC pyrolysis can be considered almost complete. On the contrary, pyrolysis ratio at 400 ºC was just 88.2 wt.%, which means that a significant amount of sample remained unpyrolyzed. For the lab scale pyrolysis plant, 460 ºC was selected as the minimum temperature to be tested in order to guarantee complete conversion, taking into account the poor heat transmission of semi-batch reactors.

3.1.2. Pyrolysis yields

The liquid, gas and solid yields (weight %), obtained at the different temperatures are presented in Table 3.

Table 3. Effect of temperature on pyrolysis yields (wt.%)

TEMPERATURE (ºC)	**Liquids**	**Gases**	**Solids**
460	72.0	26.9	1.1
500	65.2	34.0	0.8
600	42.9	56.2	0.9

It can be seen that while the solid yield has almost a constant value in all the experiments, 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. 7, 19-20], 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.

Table 3 shows that although the original sample did not contain inorganic matter (see Table 1), in all the experiments a small quantity (0.8-1.1 wt.%) of solid products was obtained; this is attributed to char formation, due to secondary repolymerization reactions among the polymer derived products. Char formation in pyrolysis of polymeric wastes is a well documented fact which has been reported and studied before by many research groups [e.g. 21-24].

3.1.2. Pyrolysis liquids

A summary of the results obtained in GC-MS analysis is presented in Tables 4, 5 and 6. In Table 4 total aromatics (mono and poly-aromatics), non-aromatics and unidentified compounds have been quantified, in Table 5 pyrolysis liquids compounds have been grouped according to their number of carbons (C5–C9, C10–C13 and >C13) and in Table 6 the main components of the pyrolysis liquids have been included.

Table 4. Aromatic and non-aromatic compounds found in the pyrolysis liquids (% area)

EXPERIMENT		**460 ºC**	**500º C**	**600 ºC**
AROMATICS	Mono-aromatics	68.0	69.7	70.8
	Indane derivatives	n.d.[a]	1.1	6.1
	Poly-aromatics (PAH) and derivatives	3.7	3.1	22.4
	TOTAL	**71.7**	**73.9**	**99.3**
NON-AROMATICS	Naphthenes	0.9	n.d.[a]	n.d.[a]
	Lineal olefins	14.4	15.1	0.4
	Branched olefins	7.0	7.2	n.d.[a]
	TOTAL	**22.3**	**22.3**	**0.4**
UNIDENTIFIED		**6.0**	**3.8**	**0.3**

[a]Not detected

First of all, Table 4 shows that oddly in spite of having pyrolysed a plastic mixture mainly composed of long saturated hydrocarbons (PE and PP), no paraffin are obtained in the liquid fraction. This may be explained as follows; when the long polymer chains are cracked, they generate lots of free radical fragments which need to be stabilized. These radical fragments can further (1) form a double bond generating olefins, (2) combine each other yielding cycled structures (naphthenic compounds), (3) release hydrogen being later transformed into highly unsaturated products or into aromatics. Additionally, it must also be mentioned that the values presented in Tables 4-6 are %

area and not wt.%, thus the relative amounts of aliphatic and aromatic products are not straight reflected by these values due to the response differences of different kinds of organic compounds in MS.

The pyrolysis liquids obtained at 460 and 500 ºC are mainly composed of aromatics (71.7 and 73.9% area respectively) and unsaturated hydrocarbons (22.3% area in both cases). There are many references in the literature which report that aromatics are produced in the pyrolysis of pure polyolefins [e.g. 24-26], but there are also references which indicate that aliphatic and naphthenic compounds are the predominant products [7, 9]. The fact of the matter is that the formation of aromatics strongly depends on the reactor design and the operating conditions used; when quite high temperatures and long reaction times are used, as in this study, high contents of aromatics are obtained. On the other hand, when complex plastic mixtures are pyrolysed, there are interactions among the polymers derived products which give rise to the formation of aromatics. Williams and Williams [27] as well as Pinto et al. [28] obtained higher proportions of aromatics in pyrolysis of plastic mixtures than those expected based on the aromatics contents obtained in pyrolysis of the pure components.

It can also be seen in Table 4 that the liquids obtained at 600 ºC are almost totally composed of aromatic compounds while there are almost no olefin and naphthenic compounds. The increase in aromatics with temperature has been reported before by other authors [e.g. 5, 7, 9], which states that aromatics are formed by means of secondary reactions which are produced to a major extent at high temperatures. The results in Table 4 indicate that olefin structures are precursors for aromatics formation since their proportion decreases from 22.3% area to 0.4% area as temperature is raised from 460 to 600 ºC. However, there is no agreement in the literature about the aromatics formation mechanisms; two main routes have been suggested: Diels-Alder reactions followed by dehydrogenation [29], and unimolecular cyclation reactions followed by dehydrogenation [9], which some authors call “pyrosynthesis”. When complex mixtures are pyrolysed, the combination of both mechanisms is the most probable route to form cyclic structures.

It is also worth noting that the increase in aromatics obtained at 600 ºC corresponds mainly to the formation of poly-aromatic hydrocarbons (PAH) and their derivatives, since the mono-aromatics contents are similar at all the temperatures. Therefore, it may be stated that PAH are formed by means of secondary reactions which are consequently favoured at high temperatures. It has been proposed that the direct combination of aromatic rings is the mechanism for the formation of PAH at high temperatures [30].

Table 5. C5-C9, C10-C13 and >C13 fractions of the pyrolysis liquids (% area)

EXPERIMENT		**460 ºC**	**500º C**	**600 ºC**
C5-C9	Aromatics	68.0	69.2	70.6
	Non-aromatics	10.1	10.4	n.d.[a]
	TOTAL	**78.1**	**79.6**	**70.6**
C10-C13	Aromatics	1.2	3.1	23.3
	Non-aromatics	6.3	6.3	0.4
	TOTAL	**7.4**	**9.4**	**23.8**
>C13	Aromatics	2.5	1.7	5.3
	Non-aromatics	6.0	5.6	n.d.[a]
	TOTAL	**8.5**	**7.3**	**5.3**

[a] Not detected

Table 5 shows the proportions of the C5-C9, C10-C13 and >C13 fractions of the pyrolysis liquids. C5-C9 is the main fraction in all the pyrolysis experiments; this is a rather convenient result from the point of view of potential applications of these liquids, since C5-C9 is the gasoline carbon number range. This light and highly aromatic fraction should be used blended with other non-aromatic petrochemical fractions in order to adjust the aromatic content of the final desired product. >C13 fraction, as expected, decreases as the temperature of the experiment is increased, since the formation of small molecules is favored at high temperatures. Such effect has also been reported before by other authors [31-32]. It can also be seen that in the liquids obtained in the 600 ºC experiment C10-C13 fraction reaches the highest value (23.8% area); the detailed GC-MS results indicate that this value mainly corresponds to PAH and their derivatives which, as it has been shown in Table 4, are quite abundant in the 600 ºC liquids.

The main individual components of the pyrolysis liquids are presented in Table 6. For the sake of reduction only those compounds with a percentage quantified area greater than 3% have been included.

Table 6. Main components of the pyrolysis liquids determined by GC-MS (% area)

COMPOUND	**460 ºC**	**500 ºC**	**600 ºC**
Toluene	9.9	8.1	17.5
Dimethyl-heptene	6.7	5.9	n.d.[a]
Ethyl-benzene	7.1	5.0	8.1
Xylenes	<3.0	<3.0	4.5
Styrene	45.5	48.4	32.4
α-methyl-styrene	3.6	4.2	4.4
Napththalene	<3.0	<3.0	6.5
Methyl-napththalene	n.d.[a]	n.d.[a]	5.1

[a]Not detected

Table 6 shows that in every case, styrene is the most abundant product with percentage areas ranging from 32% to almost 50% area. The next abundant products are toluene (8–17.5% area) and ethyl-benzene (5–8% area). It can be stated that there is some kind of relation among the yields of these three chemicals since the addition of the three yields is quite similar at the three temperatures (62.5, 61.5 and 58.0% area respectively). Broadly speaking, the tendency is that fluctuations in styrene yield are approximately counterbalanced by toluene and ethyl-benzene yields. Onwudili et al. [13] suggested that toluene and ethyl-benzene may be formed by the reaction of styrene itself, rather than from the direct degradation of the original sample, which is in agreement with the results obtained in this study. It is also worth noting that styrene yield significantly decreases from 500 to 600 ºC which indicates that styrene was formed at lower temperatures and then was decomposed to other chemicals, mainly toluene and ethyl-benzene. The results obtained by other authors in the pyrolysis of polystyrene [13, 33] also indicated that the decrease of styrene yield is due to secondary reactions.

The elemental composition and higher heating value (HHV) of the pyrolysis liquids obtained in each experiment are presented in Table 7.

Table 7. Elemental composition (wt.%) and HHV (MJ kg^{-1}) of the pyrolysis liquids

EXPERIMENT	C	H	Cl	Others[a]	H/C Ratio	HHV
460 ºC	87.7	11.7	0.4	0.2	1.6	43.5
500 ºC	86.5	11.3	0.5	1.5	1.6	43.3
600 ºC	89.2	9.0	1.1	0.7	1.2	40.8

[a]By difference

The carbon and hydrogen content of the liquids follow the same tendency as that observed in the GC-MS analysis; the H/C ratio decreases as the temperature is raised, due to the greater aromatization that is produced at 600 ºC. The chlorine content also increases with temperature, which may be explained as follows: at higher temperatures radical fragments are more quickly generated and may have more opportunities to interact with the HCl which evolves from PVC at very low temperatures before it leaves the reactor, yielding as a consequence more chlorinated liquids.

Concerning the “others” percentage in the liquids, it most probably corresponds mainly to oxygen derived from PET, since it is an oxygenated polymer. The detailed GC-MS analysis showed that there are some oxygenated compounds in the liquids, such as acetylcyclopentanone and methyl-butanol. However, they have not been included in Table 4 since they are present in very low proportions (<0.5 % area). Most of the oxygen derived from PET is transformed into CO and CO_2, as it will be seen in section 3.1.3.

It is worth mentioning that pyrolysis oils have very high HHV, similar to those of conventional liquid fuels, so they may be considered as an appropriate alternative to fossil fuels, since although in terms of energy efficiency the HHV of the oils is comparable to that of the original samples (see Table 1), the advantage of pyrolysis is that it transforms a solid plastic waste into more valuable and easily handled fuels. However, the chlorine contained in the liquids, which is derived from the PVC of the plastic mixture, would probably condition their application as liquid fuels. However, different alternatives may be proposed to overcome this problem, such as the use of solid adsorbents mixed with the plastic mixture or the stepwise pyrolysis. In a previous paper published by the authors [34] such alternatives were studied and it was concluded that the chlorine content of the liquids coming from PVC containing plastic mixtures can be drastically reduced by carrying out a low temperature dechlorination step prior to pyrolysis.

With a view of select the most appropriate pyrolysis temperature, it must be mentioned that although Tables 5 to 7 show that 460 ºC and 500 ºC liquids are quite similar, 460 ºC liquids were much more viscous than 500 ºC liquids, almost solid at room temperature, and this caused operating problems (pipes obstruction) during the pyrolysis run. Additionally, the high PAH content of the liquids obtained at 600 ºC makes them inappropriate for application from an environmental point of view. Therefore, 500 ºC was chosen as the most appropriate temperature for the subsequent study of the influence of time.

3.1.3. Gas composition

Table 8 shows that pyrolysis gases are composed of hydrocarbons ranging from C1 to C6, hydrogen and some carbon dioxide and monoxide.

Table 8. GC-TCD/FID analysis (wt.%) and HHV (MJ kg^{-1}) of pyrolysis gases

EXPERIMENT	**460 ºC**	**500 ºC**	**600 ºC**
H_2	0.4	0.4	0.7
CO	1.6	0.7	0.7
CO_2	2.0	2.9	2.0
Methane	7.9	8.3	13.0
Ethane	10.1	10.0	10.3
Ethene	11.2	12.2	19.3
C3	29.8	29.1	28.2
C4	18.1	17.6	16.3
C5	9.3	9.5	5.3
C6	9.5	9.2	4.2
HHV	48.6	48.6	49.8

It can be seen that in the 600 ºC experiment greater quantities of C1-C3 gases (70.8 wt.%) and consequently less C4-C6 gases (25.8 wt.%) were produced compared to the experiments carried out at 460 and 500 ºC (59.0 and 59.6 wt.% respectively of C1-C3 gases and 36.9 and 36.3 wt.% respectively of C4-C6 gases). This is quite in accordance with the stronger cracking that is produced at the highest temperature. This tendency to produce lighter hydrocarbons can be clearly observed in methane and ethylene yields, which vary from 7.9 and 11.2 wt.% respectively at 460 ºC to 13.0 and 19.3 wt.% respectively at 600 ºC. This behavior was also observed by Mastral et al. [35] in the pyrolysis of polyethylene in a fluidized bed reactor. On the other hand, it can also be seen that the gases derived from the experiment carried out at 600 ºC produced more hydrogen than those derived from the low temperature runs, which can be attributed to the hydrogen release reactions that are produced in the formation of aromatics, which is favored at high temperatures.

It is also worth noting that the HHV of all the gases is in the range of that of natural gas (48-53 MJ kg^{-1}). For this reason pyrolysis gases may be used as gaseous fuels to supply the energetic demand of the process, and the surplus may be valorized.

3.1.4. Pyrolysis solids

The composition of the pyrolysis solids is presented in Table 9.

Table 9. Moisture, elemental composition (wt.%) and HHV (MJ kg^{-1}) of the pyrolysis solids

EXPERIMENT	Moisture	C	H	Cl	Others[a]	H/C Ratio	HHV
460 ºC	0.1	92.0	3.9	0.1	4.0	0.5	38.5
500 ºC	0.2	93.7	3.5	0.3	2.3	0.4	38.2
600 ºC	0.1	91.7	2.3	0.3	5.6	0.3	36.8

[a] By difference

The pyrolysis solids hardly differ one another, and are composed by carbon, which corresponds to the carbonaceous product (char) previously mentioned which is formed during pyrolysis, some hydrogen and a slightly variable quantity of other elements. A slight decrease of the H/C ratio with temperature can be observed; it is a consequence of the stronger carbonization that is produced at higher temperatures. The pyrolysis solids are in all cases carbonaceous materials with very high HHV which can be used as an alternative to fossil solid fuels.

3.2. Influence of time

As it has been mentioned before, 500 ºC was considered the most appropriate temperature to carry out the experiments devoted to study the influence of time on plastic wastes pyrolysis. The effect of reaction time was explored in the range 0-120 min. reaction time was counted from the moment the experiment temperature was reached. The results obtained are shown below.

3.2.1. Pyrolysis yields

The evolution of the liquid, gas and solid yields (wt.%) as a function of time is presented in Figure 3.

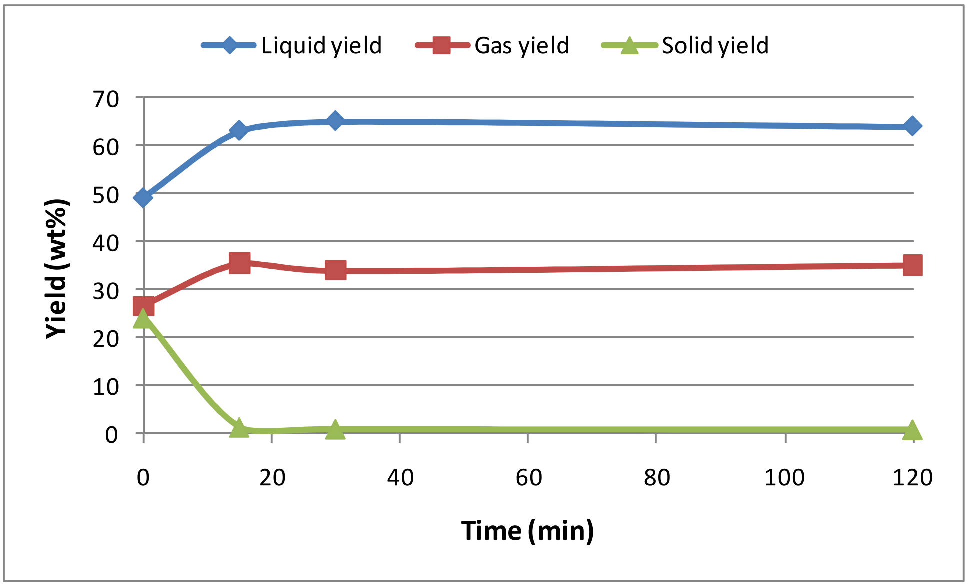

Figure 3. Pyrolysis yields (wt.%) as a function of time at 500 ºC

It can be seen that for 0 min a significant conversion to gases and liquids (75.9 wt.%) is produced, which has taken place just during the heating and cooling stages of the process, due to the high thermal inertia of the reaction system. From this time on, solid yield quickly decreases and remains practically constant over 15 min, which indicates that complete decomposition of the sample has been achieved; the solid yield is very low (≈ 1 wt.%) and corresponds to char formed during the process, and it cannot be further decomposed whatever the reaction time is. Concerning liquid yield, it increases from 0 to 30 minutes, reaching the highest value (65.2 wt.%) at 30 min; no further increase in liquid yield was observed over 30 min. Similar effect of time on liquid yields was found by Lee [36] who showed that once total pyrolysis is achieved, liquid yield remains constant regardless of the reaction time used.

3.2.2. Pyrolysis liquids

The results obtained in the GC-MS analysis of the liquids are presented in Figures 4 and 5. All the identified compounds have been grouped in: aromatics, lineal olefins and branched olefins. Additionally, these compounds have also been grouped according to their number of carbons: C5–C9, C10–C13 and >C13 compounds.

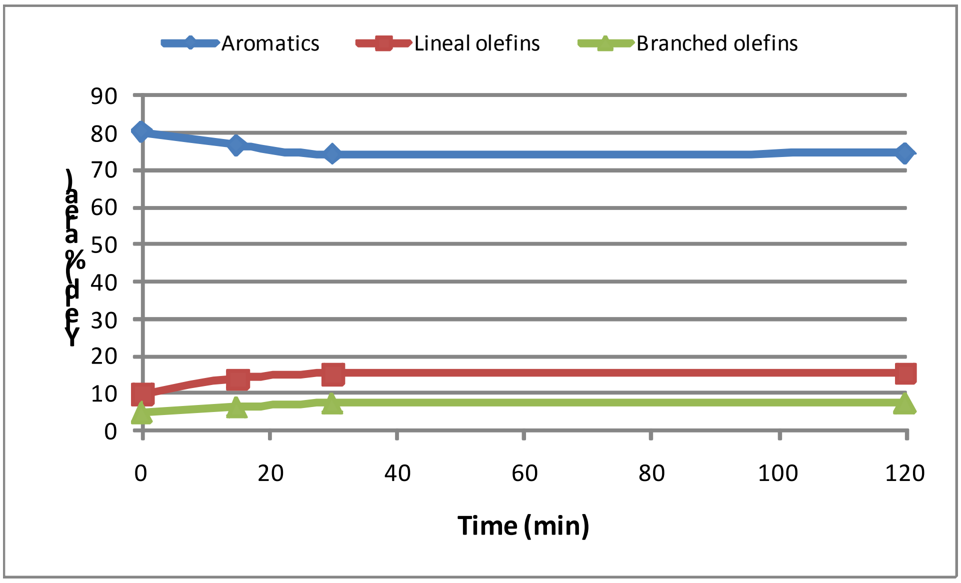

Figure 4. Aromatics, lineal olefins and branched olefins yields (% area) as a function of time at 500 ºC

Figure 4 shows that non-aromatics increase from 0 to 30 min and then remains constant. Consequently, the maximum aromatics yield was obtained in the 0 minutes experiment (80.1% area). Lee et al. [37] obtained 60% of aromatics in the initial stages of the reaction in pyrolysis of PE, PP and PS mixtures at 350 ºC. These authors suggested that such high aromatics content was due to PS decomposition, which takes place at lower temperatures than polyolefins (see Figure 2) and produces high quantities of aromatics. The results obtained in this paper cannot only be explained by such theory because at 500 ºC and 0 min as much as 75.9 wt.% of the initial sample was pyrolysed, and the proportion of PS in the sample was only 18 wt.%, so the aromatics come from some other materials than PS and they must be produced by secondary reactions that take place at the early steps of the process. According to the thermal decomposition temperature of the plastics used in the experiments (Figure 2), the plastic mixture which was left in the reactor in the 0 min run must be mainly composed of PE and some PP, and this may be reason why olefins increase from 0 to 30 min, since in this period only PE and PP are decomposed and no interactions with the other plastics are produced.

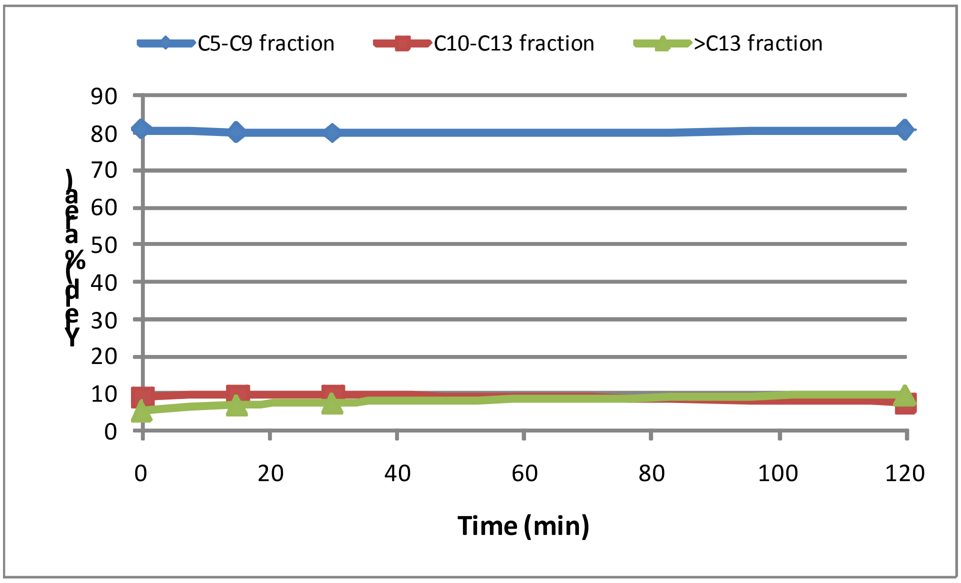

Figure 5. C5-C9, C10-C13 and >C13 fractions (% area) as a function of time at 500 ºC

Figure 5 shows that there is only a slight influence of time in the different carbon number fractions yields. While C5-C9 and C10-C13 fractions remain practically unaltered, a slight increase in the >C13 fraction can be observed. The increase in long chain compounds with time may be attributed to the fact that the plastics or their derived products which remain more time in the reactor decompose generating heavier products than those generated in the early stages of the process.

Table 10 shows the main chemicals found in the pyrolysis liquids.

Table 10. Main components of the pyrolysis liquids obtained at 0, 15, 30 and 120 min determined by GC-MS (% area)

COMPOUND	**0 min**	**15 min**	**30 min**	**120 min**
Toluene	11.3	10.7	8.1	8.8
Dimethyl-heptene	4.1	4.1	5.9	5.7
Ethyl-benzene	7.6	7.5	5.0	5.7
Styrene	42.2	42.4	48.4	47.4
α-methyl-styrene	3.8	3.8	4.2	4.7

A similar distribution as that of the previous experiments can be seen: styrene, toluene and ethyl-benzene are the main components. It can be seen that at the longer reaction times (30 and 120 min) more styrene, α-methyl-styrene and dimethyl-heptene while less toluene and ethyl-benzene are produced than at the shorter reaction times (0 and 15 min). Therefore, the decomposition reactions that take place in the later stages of the process yield a comparatively higher proportion of styrene, α-methyl-styrene and dimethyl-heptene than the early stages decomposition reactions.

The elemental composition and higher heating value of the pyrolysis liquids are presented in Table 11.

Table 11. Elemental composition (wt.%) and HHV (MJ kg^{-1}) of the pyrolysis liquids obtained at 0, 15, 30 and 120 min

EXPERIMENT	C	H	Cl	Others[a]	H/C Ratio	HHV
0 min	85.6	11.2	1.0	2.2	1.6	42.5
15 min	87.0	11.1	0.6	1.3	1.5	41.1
30 min	86.5	11.3	0.5	1.5	1.6	43.3
120 min	86.7	11.3	0.7	1.3	1.6	42.5

[a] By difference

It can be seen that there are no significant differences among the elemental compositions of the liquids, which are mainly composed of carbon (85-87 wt.%) and hydrogen (≈11 wt.%). In this case, the highest chlorine content was found in the 0 min experiment liquids, due to the fact that at the early stages of the process all the chlorine has already released from the sample (Figure 2) while the final liquid yield has not achieved yet, being the chlorine proportionally higher in liquid composition under such conditions. As in the case of previous experiments, pyrolysis oils have very high HHV and it does not vary with time.

3.2.3. Gas composition

The composition of the pyrolysis gases is presented in Table 12. It can be observed that the proportion of light hydrocarbons, as methane and ethane, as well as that of the oxygenated compounds CO and CO_2, decrease with time. This fact suggests that these compounds are formed in a greater proportion in the first steps of the pyrolysis process.

Table 12. GC-TCD/FID analysis (wt.%) and HHV (MJ kg^{-1}) of pyrolysis gases obtained at 0, 15, 30 and 120 min

EXPERIMENT	**0 min**	**15 min**	**30 min**	**120 min**
H_2	0.2	0.6	0.4	0.5
CO	1.6	0.9	0.7	0.6
CO_2	5.4	4.6	2.9	2.7
Methane	12.6	11.6	8.3	8.0
Ethane	12.8	12.0	10.0	10.1
Ethene	12.3	10.5	12.2	12.4
C3	28.2	26.0	29.1	29.2
C4	14.9	18.8	17.6	17.9
C5	9.0	9.5	9.5	9.3
C6	2.9	5.5	9.2	9.3
HHV	47.2	48.2	48.6	48.9

On the other hand, the heavier gases (C4-C6) yields clearly show an increase from 0 (26.8 wt.%) to 120 minutes (36.4 wt.%). Such effect was also observed in the fractions of pyrolysis liquids (Figure 5) and it can be explained by the same behavior. The HHV of the 0 min run was a little bit lower than those of the other gases, which may be attributed to its higher CO_2 content. Anyhow, the HHV was in all cases in the range of that of the natural gas.

3.2.4. Pyrolysis solids

The composition of the pyrolysis solids obtained at the different reaction times is presented in Table 13.

Table 13. Moisture, elemental composition (wt.%) and HHV (MJ kg^{-1}) of the pyrolysis solids obtained at 0, 15, 30 and 120 min

EXPERIMENT	**Moisture**	**C**	**H**	**Cl**	**Others[a]**	**H/C Ratio**	**HHV**
0 min	n.d.[b]	83.8	14.0	0.1	2.2	2.0	47.4
15 min	0.4	94.4	3.7	0.2	1.3	0.5	39.4
30 min	0.2	93.7	3.5	0.3	2.3	0.4	38.2
120 min	0.3	94.1	3.5	0.1	2.0	0.4	38.2

[a]By difference; [b]Not determined

It can be seen that the carbon (83.8 wt.%) and hydrogen (14.0 wt.%) contents of the solid obtained in the 0 min run are quite similar to those of polyolefins. Therefore, the unconverted product of such run must be mainly composed of PE and PP; this is corroborated by the TGA analysis of the individual plastics (Figure 2) which showed that the decomposition of these plastics takes place at somewhat higher temperatures than those of the other plastics in the mixture. On the contrary, the solids obtained at 15, 30 and 120 minutes are mainly composed of carbon, which indicates that it is char, the carbonised product that is usually formed in pyrolysis of many plastics; it can also be seen that they hardly differ from one another. Concerning HHV, Table 13 shows that it is higher for the solids of the 0 min run, which is due to the fact that this solid contains a greater proportion of hydrogen, which has a much higher heat of combustion than carbon.

4. Conclusion

Pyrolysis is an attractive alternative for recycling mixed plastic wastes which cannot be recycled by means of mechanical processes. Conversions to valuable gaseous and liquid products higher than 99 wt.% can be obtained. The liquid products obtained may be used as high HHV alternative fuels or as a source of valuable chemicals, such as styrene or toluene. 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 (char) may find applications such as solid fuel, pigment, activated carbon, low quality carbon black, etc.

Temperature is an essential parameter of the process since it has a significant influence in the properties and proportions of the products obtained. At the lowest temperature (460 ºC), total pyrolysis is achieved and the highest liquid yield is obtained, but the high content of long chain hydrocarbons (>C13) in the liquid gives rise to a high viscosity product which may cause operating problems (pipe obstruction) and is somewhat difficult to handle. On the contrary, the highest temperature tested (600 ºC) generated the lowest proportion of liquids, and the maximum of gas; additionally, at this temperature very high contents of aromatics (98 % area) and greater quantities of PAH than at other temperatures are obtained. Consequently, 500 ºC was considered to be the optimal temperature for plastic waste pyrolysis, since total conversion is achieved and a high yield of liquids of better quality than those of higher and lower temperature pyrolysis runs are obtained.

The influence of time in plastic wastes pyrolysis in a semi-batch reactor is only noticeable for very low reaction times (0-15 min), due to the high thermal inertia of these systems. 15-30 min was considered the optimum reaction time range, since total conversion is achieved and longer reaction times did not produced any beneficial effect.

To summarize, 500 ºC and 30 min were considered the most appropriate conditions for plastic wastes pyrolysis in terms of yield and general quality of the liquids obtained. Nevertheless, the modification of these conditions significantly changes the composition of the liquids and this provides the opportunity to obtain specific products depending on the final aim of the process, conferring pyrolysis an attractive versatility which must be taken into account when it comes to design a feedstock recycling process.

Acknowledgements

The authors thank the Spanish Ministry of Education and Science (MEC) (CTQ 2007-67070/PPQ) as well as the Basque Country Government (ETORTEK 2007 IE07-207, GIC 07-09-IT-354-07 and Researchers’ formation program - 2008) for financial assistance for this work.

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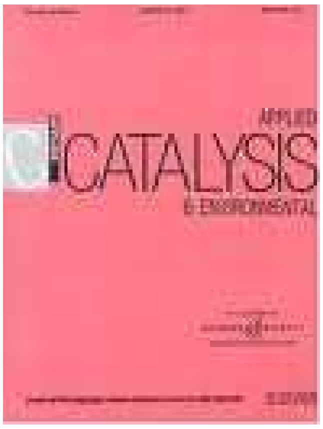
4.2. SIMULATED SAMPLE RUNS

4.2.2. Catalytic pyrolysis (1 of 2)



Article: *Catalytic pyrolysis of plastic wastes with two different types of catalysts: ZSM-5 zeolite and Red Mud*

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Journal: *Applied Catalysis B: Environmental 104, 211-219.*

Year of publication: *2011*

Applied Catalysis B: Environmental 104 (2011) 211–219

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Catalytic pyrolysis of plastic wastes with two different types of catalysts: ZSM-5 zeolite and Red Mud

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ARTICLE INFO

Article history:
Received 11 January 2011
Received in revised form 16 March 2011
Accepted 24 March 2011
Available online 1 April 2011

Keywords:
Feedstock recycling
Catalytic pyrolysis
Plastic wastes
ZSM-5 zeolite
Red Mud

ABSTRACT

The influence of ZSM-5 zeolite and Red Mud in the pyrolysis of plastic wastes has been studied. Both catalysts have been thoroughly characterized; the zeolite shows weak and strong acid sites and great BET surface area (412.0 $m^2 g^{-1}$), while Red Mud contains lower acidity, with also weak and strong acid sites, meso-macropores and BET surface area of 27.49 $m^2 g^{-1}$. Both catalysts have been tested in pyrolysis of a mixture of plastics which resembles municipal plastic wastes, at 440 and 500 °C in a 3.5 dm^3 semi-batch reactor. The results have been compared with those of the thermal process. It has been proved that ZSM-5 zeolite has a strong effect in the characteristics and distribution of pyrolysis products. It generates at both temperatures a greater proportion of gases and liquids with a higher content of aromatics than without catalyst. Red Mud needs higher temperatures than ZSM-5 zeolite to exert a catalytic effect in pyrolysis, since similar results to those obtained without catalyst are obtained at 440 °C, while at 500 °C a higher yield of gases and a greater proportion of aromatics in the liquids is obtained.

1. Introduction

Research on feedstock recycling of plastic wastes is receiving increasing attention in the last years. The unstoppable generation of plastic wastes, the market limitations to some mechanically recycled plastic goods, and the possibility of obtaining valuable products from complex plastic wastes that cannot be recycled by simple mechanical recycling, are some of the driving forces which promote chemical recycling research.

Feedstock recycling includes several techniques such as depolymerisation, thermal and thermo-catalytic decomposition and the utilization of plastic wastes as reducing agents or as secondary fuels in some industrial processes. Pyrolysis is a thermal process which enables to obtain a wide range of hydrocarbons with no need of expensive chemical reagents. Plastic wastes are decomposed by the sole effect of temperature in an inert atmosphere, generating liquid and gaseous products which can be useful as fuels and/or sources of chemicals. It has been reported that the use of catalysts in pyrolysis presents some advantages compared to simple thermal processes [1,2]: i.e., lower energy consumption, shorter reaction time and good selectivity to higher added value products.

Over the past two decades, a large number of results on catalytic pyrolysis of plastics have been published in the literature. A wide range of catalytic materials have been tested: homogeneous catalysts [3,4], acid mesoporous materials [5,6], non-acid mesoporous solids [7,8], FCC catalysts [9,10], zeolites [11,12], metallic oxides [13,14], etc. Zeolites have been found to be particularly efficient catalysts in the degradation of polyethylene [12,15,16]. Most of the previously mentioned studies have been carried out with single plastics or simple mixtures of plastics. Real waste samples or complex mixtures of plastics, which include PVC and PET, have scarcely been studied due to the problems that oxygenated and chlorinated compounds can produce. In this paper, the effect of a zeolite (ZSM-5) in pyrolysis of a complex plastic mixture including PVC and PET (which resembles real plastic wastes) is presented.

On the other hand, from an industrial implementation point of view, the use of expensive catalysts, as those above mentioned, may condition the economy of the process, since high amounts of catalyst would be necessary in a continuous operating plant. Ali et al. [17] concluded that the catalyst cost (type and amount) is a key factor when the economy of both technologies, catalytic cracking and thermal cracking, is compared. Additionally, Cardona and Corma [18] concluded that a plastic waste pyrolysis process could only be supported if the catalyst cost was practically zero. For this reason, the search of "cheap catalysts" for pyrolysis of plastic wastes is of the most interest.

Red Mud, which is a by-product of the alumina production Bayer process, has been used as catalyst mainly to favour hydrogenation reactions, since Fe_2O_3 is its main component [19–22]; however, the presence of other components as SiO_2, Al_2O_3 or TiO_2 may con-

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doi:10.1016/j.apcatb.2011.03.030

tribute to plastic wastes cracking. Up to now, very few studies have been published about the use of Red Mud in pyrolysis [4,23,24].

In a previous work published by the authors [4] a first screening of catalysts in pyrolysis of plastic wastes was performed; the catalysts were tested just at 500 °C and the plastic waste used was a real waste stream which was a very heterogeneous and variable sample, since it came from the rejects of a waste packaging sorting industrial plant. The main conclusion of such study was that it was worthwhile to investigate thoroughly the effect of ZSM-5 and Red Mud on pyrolysis of plastic wastes. For this reason, a thorough study of pyrolysis with these two catalysts is presented in this paper, which includes: (1) a detailed characterization of the catalysts, (2) an exhaustive characterization of the pyrolysis products, and (3) the study of the influence of temperature in the process depending on the catalyst used, with the objective of better understanding the effect of catalysts in the pyrolysis process. Besides, this study has been carried out with a plastic mixture which resembles real wastes but which was prepared by the authors, in order to dispose of a homogeneous and invariable sample which enables to analyse the effect of the catalysts without the distorting effect of the influence of the sample composition.

It is well-known that ZSM-5 zeolite is a suitable catalyst for pyrolysis of plastics while the published information concerning Red Mud is quite limited. The interest of this paper lies mainly in the use of a complex plastic mixture (which resembles real waste streams) and the exhaustive comparison between ZSM-5 zeolite, a very suitable but expensive catalyst, and Red Mud, an inexpensive and scarcely studied material as pyrolysis catalyst.

2. Materials and methods

2.1. Materials

The plastic mixture used for the experiments was composed of 40 wt% polyethylene, 35 wt% polypropilene, 18 wt% polystyrene, 4 wt% poly(ethylene terephthalate) and 3 wt% poly(vinyl chloride). The origin and application of each plastic is showed in Table 1.

The proportions of the plastics in the mixture were established based on the composition of real samples coming from packing and packaging applications which were characterized by the authors in a previous paper [25]. All the materials were used in pellet size (3 mm) for the pyrolysis experiments, while finely ground (<1 mm) samples were prepared for characterization purposes. The characterization results of the plastic mixture are presented in Table 2.

ZSM-5 zeolite, in NH_4^+ cation form and with a SiO_2/Al_2O_3 ratio of 50, was provided by Zeolist International. Red Mud was obtained from a German alumina production company. Its composition is presented in Table 3; it is mainly composed of Fe_2O_3 and Al_2O_3 together with other oxides including titania. Both catalysts were tested as were received, without any activation operation, and were thoroughly mixed with the plastic sample in a proportion of 10 wt% in all the experiments (10 g of catalyst/100 g of plastics).

Table 3
Composition of Red Mud (wt%) (dried basis).

Fe_2O_3	Al_2O_3	TiO_2	SiO_2	CaO	Na_2O	Others[a]
36.5	23.8	13.5	8.5	5.3	1.8	10.6

[a] By difference.

3. Experimental

The pyrolysis experiments were carried out in semi-batch conditions in a laboratory scale installation equipped with an unstirred 3.5 dm^3 reactor and a condensation-separation system (Fig. 1). In a typical run, 100 g of the sample are placed into the reactor and the system is heated at a rate of 20 °C min^{-1} up to the desired temperature, followed by an isothermal step of 30 min. The vapours leaving the reactor are swept away by a 1 dm^3 min^{-1} nitrogen flow to a series of gas–liquid separators cooled by running water. The uncondensed products are passed through an activated carbon column and collected as a whole in Tedlar plastic bags, to be afterwards analysed by gas chromatography.

The collected solids (products in the reactor after pyrolysis) and liquids are weighed, and both solid and liquids yields are calculated as weight percentage with respect to the amount of raw material pyrolysed. Gas yields are as a general rule calculated by difference. Some experiments were specifically devoted to directly quantify the amount of gases by gas chromatography; in such experiments a closure of the mass balance of about 90 wt% was obtained. The results of the pyrolysis yields which are presented in Section 4 of this paper are the mean value of at least three pyrolysis runs carried out in the same conditions and which did not differ more than three points in the percentage.

3.1. Analytical techniques

Both the raw materials and the solid and liquid pyrolysis products obtained were thoroughly characterized using the following analytical techniques. The moisture and ash contents of the samples were determined by thermogravimetric analysis according to D3173-85 and D3174-82 ASTM standards respectively, and the elemental composition with an automatic CHN analyser. Chlorine was determined following the method 5050 of the Environmental Protection Agency (EPA) of the United States. The higher heat-

Table 1
Origin and application of the plastics used in the mixture.

Plastic name	Acronymus	Origin	State	Application
Polyethylene	PE	Repsol Química	Virgin	Household
Polypropylene	PP	Repsol Química	Virgin	General
Polystyrene	PS	Dow Chemical	Virgin	General
Poly(ethylene terephthalate)	PET	Remaplast S.A.[a]	Recycled	Bottles
Poly(vinyl chloride)	PVC	Gaiker[b]	Recycled	Bottles

[a] Spanish Company devoted to municipal plastics recycling.
[b] Spanish Technology Centre dedicated to research and innovation.

Table 2
Moisture, ash, elemental composition (wt%) and HHV (MJ kg^{-1}) of the plastic mixture pyrolysed.

Moisture	Ash	C	H	N	Cl	Others[a]	H/C ratio	HHV
0.1	0.0	84.7	12.5	<0.1	1.1	1.5	1.8	43.9

[a] By difference.

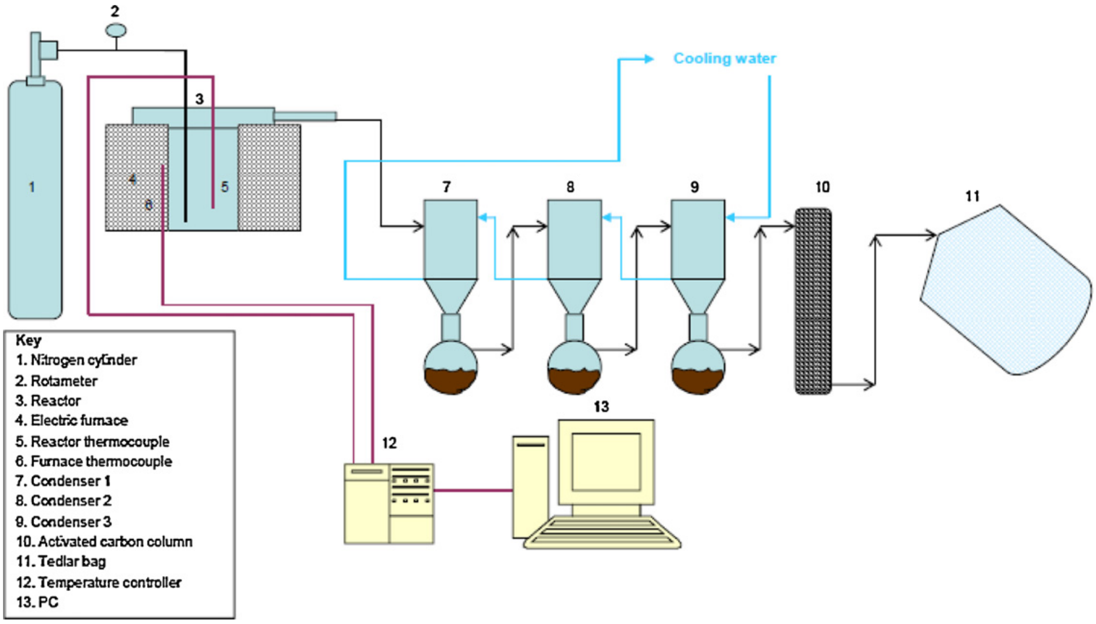

Fig. 1. Flow sheet of the experimental set-up used.

ing value (HHV) was determined with an automatic calorimetric bomb.

Additionally, pyrolysis liquids were also analysed by gas chromatography coupled with mass spectrometry detector (GC–MS), Agilent 6890 and Agilent 5973 respectively. Characteristics of the method used are shown in Table 4. Identification of the constituents was based on comparison of the retention times with those of calibration samples and on computer matching against commercial library of mass spectra (Wiley7n) and MS literature data. The library-matched species which exhibited a degree of match lower than 85% were classified as "Not identified".

Pyrolysis gases were analysed by means of a gas chromatograph coupled with thermal conductivity and flame ionization detectors (GC–TCD/FID). Table 5 shows the characteristics of the method used. Due to the difficulty in distinguishing among isomers from C3 to C6, such discrimination has not been made. The HHV of the gases was calculated according to their composition and to the HHV of the individual components [26].

Table 4
GC–MS method characteristics.

Column	HP5MS
Carrier gas	He
Carrier gas flow	1.0 mL/min
Initial temperature/initial time	40 °C/10 min
Heating rate	8 °C/min
Final temperature/final time	280 °C/10 min
Injection temperature	280 °C
Injection volume	1.0 μL (split 100:1)
Detector temperature (quad/source)	150 °C/230 °C

Table 5
GC–TCD/FID method characteristics.

Columns	Molecular sieve 13X Chromosorb 102
Carrier gas	He/Ar
Carrier gas flow	48 mL/min
Initial temperature/initial time	40 °C/10 min
Heating rate	6 °C/min
Final temperature/final time	200 °C/10 min
Injection temperature	110 °C
TCD detector temperature	110 °C
FID detector temperature	200 °C

The textural properties of the catalysts were determined by means of nitrogen adsorption–desorption isotherms at 77 K in AUTOSORB-1 Quantachrome equipment. Surface areas were calculated by means of BET equation and external surface areas and micropores volume were obtained applying the *t*-plot method. Total pore volume was measured at $P/P_0 = 0.99$.

Acidity of the catalysts was measured by temperature-programmed desorption (TPD) of ammonia on a Micromeritics AutoChem 2910 instrument. Prior to adsorption experiments, the samples (86–300 mg) were first pre-treated in a quartz U-tube in nitrogen stream at 500 °C. Then, they were cooled down at 100 °C in N_2 flow (20 $cm^3\ min^{-1}$) before the ammonia adsorption started. The adsorption step was performed by admitting small pulses of ammonia in Ar at 100 °C up to saturation. Subsequently, the samples were exposed to a flow of argon (50 $cm^3\ min^{-1}$) for 2 h at 100 °C in order to remove reversibly and physically bound ammonia from the surface. Finally, the desorption was carried out from 100 to 500 °C at a heating rate of 10 °C min^{-1} in Ar stream (50 $cm^3\ min^{-1}$). This temperature was maintained for 15 min until the adsorbate was completely desorbed. The amount of ammonia desorbed at a given temperature range was taken as a measure of the acid site concentration, whereas the temperature range at which most of the ammonia was desorbed indicated the acid strength distribution [27,28]. SEM images were obtained in a LEO 1525 electron microscope.

4. Results and discussion

4.1. Catalyst characterization

Fig. 2 shows the N_2 adsorption–desorption isotherms of the catalysts. According to the International Union of Pure and Applied Chemistry (IUPAC) classification of adsorption isotherms, the shape of the adsorption isotherm for ZSM-5 is a combination of the type I (Langmuir) isotherm and type IV isotherm. The adsorption volume at a very low relative pressure ($P/P_0 < 0.1$) is high, indicating the presence of microporous adsorption (type I). With the increase in relative pressure, capillary condensation occurs, showing type IV

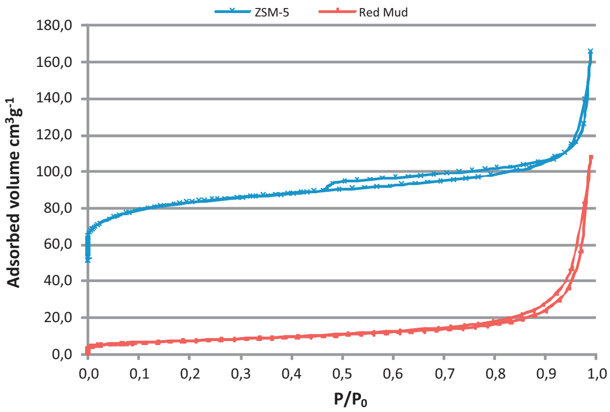

Fig. 2. N2 adsorption–desorption isotherms at 77 K of ZSM-5 zeolite and Red Mud.

Table 6
Textural properties of the catalysts used.

Property	ZSM-5 zeolite	Red Mud
BET surface area ($m^2\,g^{-1}$)	412.0	27.49
External surface area (ESA) ($m^2\,g^{-1}$)	65.88	25.78
Micropore area ($m^2\,g^{-1}$)	346.1	1.71
Micropore volume (MPV) ($cm^3\,g^{-1}$)	0.100	0.009
Total pore volume (TPV) ($cm^3\,g^{-1}$)	0.397	0.184

behaviour. The hysteresis loop, which resembles the H4 type, may be attributed to the mesoporous structure. This type of hysteresis is usually found in solids consisting of aggregates or agglomerates of particles forming slit shaped pores (plates or edged particles like cubes), with uniform size and/or shape. Additionally, the steep jump observed at high relative pressures (>0.9) indicates some macropores existence.

Concerning Red Mud, the adsorption isotherm could suggest that this catalyst is a meso-macroporous material, since the adsorption is very low at low pressures and starts fast increasing from $P/P_0 \approx 0.7$.

Table 6 shows the textural properties of the catalysts. Both catalysts present significant differences in pores distribution. BET surface area of ZSM-5 zeolite is 412 $m^2\,g^{-1}$, with high micropore area (346.1 $m^2\,g^{-1}$) and also high micropore volume (0.100 $cm^3\,g^{-1}$), which indicates the existence of relatively high internal porosity in this catalyst. On the other hand, Red Mud shows BET and ESA of 27.49 and 25.78 $m^2\,g^{-1}$ respectively, which means that in addition to being a low porosity material, most of the pores are macro and mesopores located in the external surface of the catalyst. The BET surface area obtained with Red Mud agrees with the expected value for this material, which has been reported to be in the range 20–30 $m^2\,g^{-1}$ [29,30].

Fig. 3 shows the NH_3 TPD plot of both catalysts. ZSM-5 catalyst shows the typical TPD profile of this zeolite, which consists in two main desorption peaks which prove the presence of both weak and strong acid sites [31,32], the latter corresponding to Brönsted type acid sites [33]. The total acidity of the catalyst was determined to be 0.176 mmol $NH_3\,g^{-1}$ and the quantified area under the two peaks showed a distribution of 37% weak acidity and 63% strong acidity. On the other hand, as expected according to the composition of Red Mud, lower total acidity was obtained for this catalyst (0.094 mmol $NH_3\,g^{-1}$) with 26% weak acidity and 74% strong acidity, which was quantified under an intense peak with a very slow NH_3 desorption at 550 °C. Wang et al. [30] suggested that the desilication product in Red Mud structure, containing Si–O–T units (T = Si or Al), confers this catalyst a zeolitic nature, which could be responsible for the strong acidity measured in this paper.

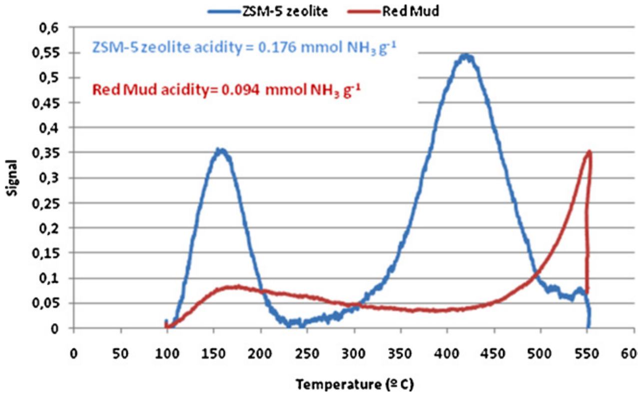

Fig. 3. NH3 TPD plot of ZSM-5 zeolite and Red Mud.

SEM images of both catalysts are presented in Fig. 4. ZSM-5 zeolite is formed by uniform crystals with sizes within the nanometer size (≈100–300 nm), while Red Mud is constituted by different size particles and crystals with also different shapes and morphology, ranging from nanometer size particles to quite big ones formed by agglomeration of the former, which confers it a highly heterogeneous internal structure.

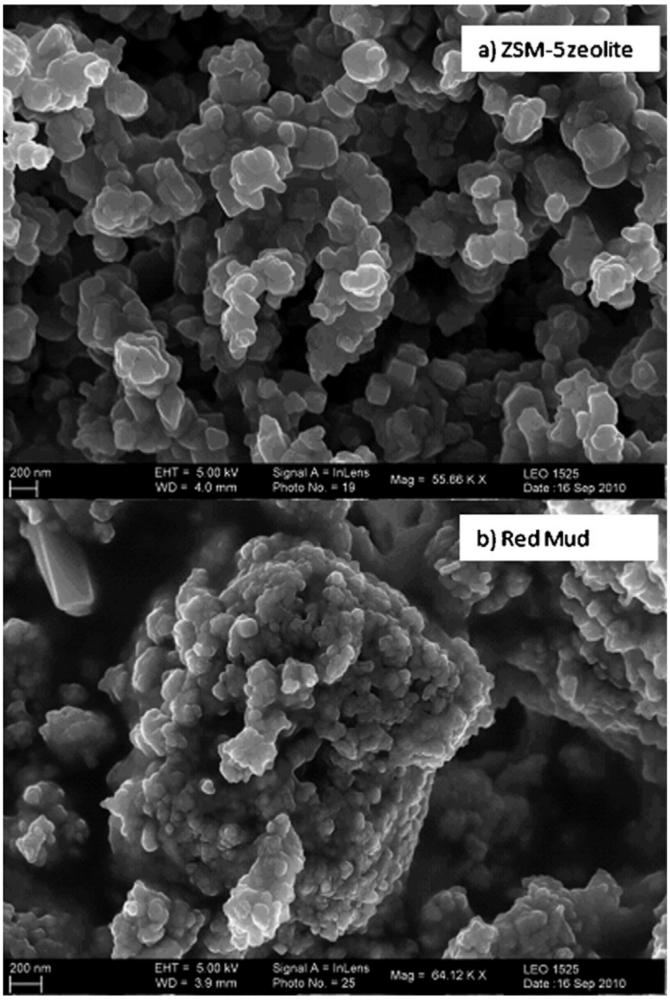

Fig. 4. SEM micrographs of ZSM-5 zeolite (a) and Red Mud (b).

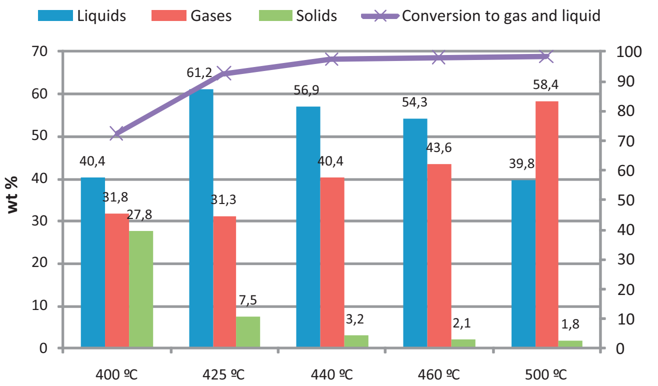

Fig. 5. Pyrolysis yields (wt%) as a function of temperature in the ZSM-5 catalytic experiments.

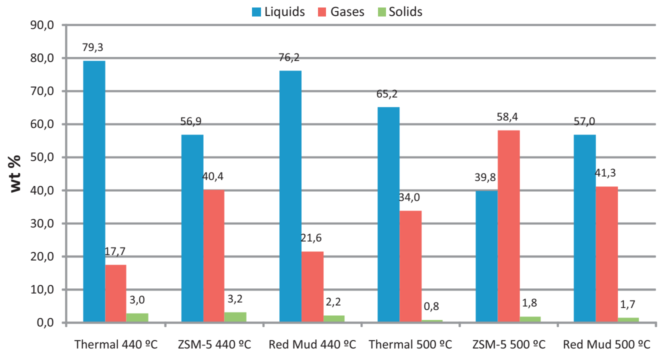

Fig. 6. Pyrolysis yields (wt%) as a function of temperature and catalyst used.

4.2. Influence of temperature on ZSM-5 catalytic pyrolysis yields

A preliminary study of the effect of temperature on catalytic pyrolysis yields was carried out in order to select the most appropriate temperatures to compare the behaviour of both catalysts. The range between 400 and 500 °C was explored using ZSM-5 catalyst. The pyrolysis yields obtained (weight %) are presented in Fig. 5, as well as the conversion to liquid and gas. As it can be seen, 400 °C is a temperature not high enough to decompose the entire sample, since a solid residue (unconverted plastic) near 30 wt% is obtained. On the contrary, at 425 °C more than 90 wt% conversion is achieved, and from 440 to 500 °C the solid fraction yield can be considered more or less constant. At this temperature range, the remaining solid fraction was mainly composed of the char that is produced in pyrolysis of many polymeric materials [e.g. 34–36]. Therefore, 440 °C is a temperature high enough to achieve total conversion of the plastic mixture to gaseous and liquid products when ZSM-5 zeolite is used.

It can also be seen that as temperature is raised from 425 to 500 °C, the liquid yield decreases and consequently the gas production increases. This behaviour has also been reported by many other authors [1,31,37] and it is attributed to the stronger cracking of C–C bonds that takes place at higher temperatures, which gives rise to lighter hydrocarbons with shorter carbon chains. Among the temperatures at which total conversion is achieved, 440 °C is the lowest one and at the same time the one that yields the greatest amount of liquids, while 500 °C is the temperature that leads to the highest gas yield. For this reason, these temperatures (440 and 500 °C) were selected as the most interesting to compare thermal and catalytic (ZSM-5 and Red Mud) pyrolysis.

4.3. Comparison among thermal, ZSM-5 and Red Mud pyrolysis

4.3.1. Pyrolysis yields

The yields of liquid, gaseous and solid products (weight %) obtained at 440 and 500 °C in the thermal and catalytic runs are presented in Fig. 6. As it can be seen, the liquids are the main fraction in thermal pyrolysis, reaching 79.3 wt% at 440 °C and 65.2 wt% at 500 °C. The gas fraction is very low at 440 °C (17.7 wt%) but higher at 500 °C (34.0 wt%), due to the previously mentioned stronger cracking that is produced at higher temperatures. When ZSM-5 zeolite is added to the sample, a great gas production enhancement is observed at 440 °C (40.4 wt% gases and 56.9 wt% liquids) and even higher at 500 °C (39.8 and 58.4 wt% respectively). This significant increase in gas yield produced by ZSM-5 zeolite, which has also been reported by other authors [16,31,38], demonstrates the cracking ability of this catalyst, which is a consequence of its high porosity and strong acidity, as shown in Fig. 3.

The influence of Red Mud in pyrolysis yields is lesser than that of the zeolite; slightly higher gas yields than without catalysts are obtained at both 440 and 500 °C (4 and 7 wt% higher respectively), which indicates that its cracking ability is lower than that of the zeolite, as was expected according to its lower surface area and acidity. Sushil and Batra [29] reported that in hydrogenation and liquefaction applications Red Mud becomes active at 400 °C, which may be the reason why higher increase in gases is obtained at 500 °C than at 440 °C.

The difference in the pyrolysis yields obtained with Red Mud and ZSM-5 zeolite could be explained as follows. Taking into account that the type of contact among catalysts and plastics is solid–solid and comparing the product yields of Fig. 6, it could be suggested that thermal pyrolysis is the first step in the reaction since pyrolysis liquids yield is higher without catalysts at both temperatures. The thermally degraded products could then more easily access to the acid sites into the catalysts porous structure, leading to higher cracking rate (more gases and fewer liquids than in the thermal runs). If the process takes place according to this theory, the additional conversion produced by the catalysts is directly related to their textural and acid properties. Consequently, the higher porosity and acid strength of ZSM-5 zeolite compared to those of Red Mud, produce more gases and fewer liquids than the latter.

Fig. 6 also shows that the solid yields obtained at 440 °C are in every case a little bit higher than those obtained at 500 °C, which implies that at 440 °C some unconverted product remains in the solid fraction mixed with char. The solid yield of the thermal run at

Table 7
Main components of the pyrolysis liquids determined by GC–MS (% area).

Compound	Thermal 440 °C	ZSM-5 440 °C	Red Mud 440 °C	Thermal 500 °C	ZSM-5 500 °C	Red Mud 500 °C
Toluene	8.1	12.3	8.9	8.1	17.5	14.2
Dimethyl-heptene	7.8	1.8	7.8	5.9	0.8	2.1
Ethyl-benzene	5.7	10.6	6.6	5.0	9.6	9.0
Xylenes	n.d.[1]	10.1	1.4	<3.0	13.8	4.2
Styrene	46.3	31.4	46.0	48.4	27.9	42.3
α-Methyl-styrene	3.2	4.5	4.3	4.2	3.4	4.9
Methyl-napththalene	n.d.[a]	3.3	0.7	n.d.[1]	3.5	2.3

[a] Not detected.

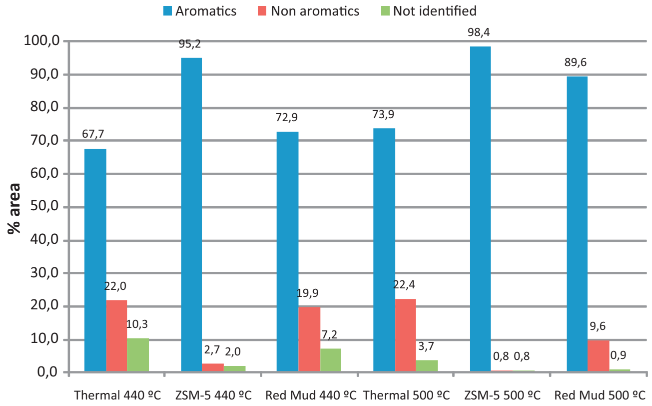

Fig. 7. Aromatics, non-aromatics and not identified compounds in the liquid fractions (% area).

500 °C is lower than those of the catalytic runs, which may be due to the fact that char formation is enhanced by acid catalysts, as it has been reported by other authors [5,39].

4.3.2. *Pyrolysis liquids*

The characterization results of the pyrolysis liquids are presented in Figs. 7 and 8 and Tables 7 and 8. In Fig. 7 total aromatics, non-aromatics and unidentified compounds have been quantified; Fig. 8 shows the pyrolysis liquids compounds grouped according to their carbon number, while the percentage of their main components have been summarized in Table 7. Additionally, the elemental composition and higher heating value (HHV) of the pyrolysis liquids obtained in each experiment are presented in Table 8. Fig. 7 shows that aromatic compounds are the main fraction of the liquids derived from all the experiments at both temperatures. However, it must be mentioned that the values presented in Tables 7 and 8 and Figs. 7 and 8 are % area and not wt%, thus the relative amounts of aliphatic and aromatic products are not straight reflected by these values since different kinds of organic compounds have different responses in MS.

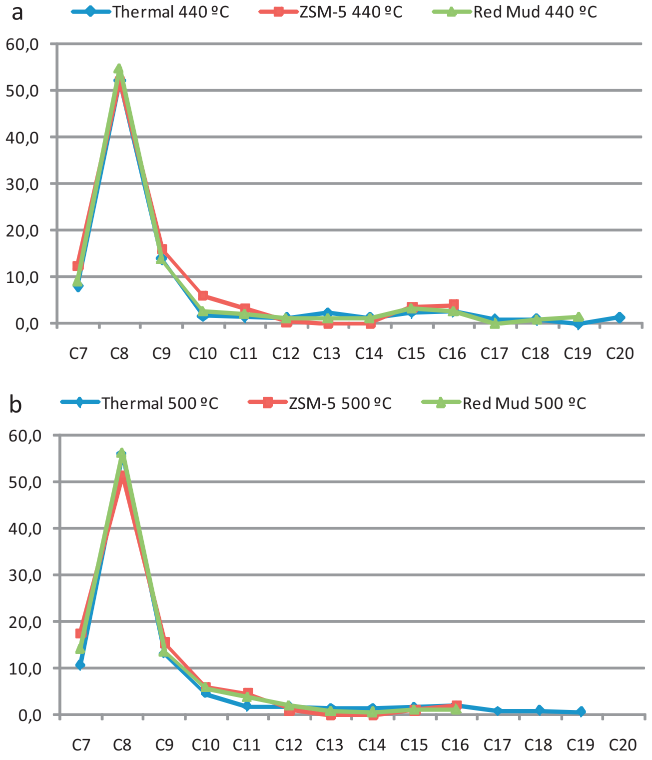

Fig. 8. Pyrolysis liquids characterized by carbon number (% area) at 440 °C (a) and 500 °C (b).

Table 8
Elemental composition (wt%) and HHV ($MJ\,kg^{-1}$) of the pyrolysis liquids.

Experiment	C	H	Cl	Others[a]	H/C ratio	HHV
Thermal 440 °C	86.1	12.3	0.2	1.4	1.7	44.7
ZSM-5 440° C	87.6	11.2	1.2	0.0	1.5	42.2
Red Mud 440 °C	85.4	11.8	0.5	2.2	1.7	44.3
Thermal 500 °C	86.5	11.3	0.5	1.5	1.6	43.3
ZSM-5 500 °C	88.8	9.9	1.3	0.0	1.3	40.6
Red Mud 500 °C	87.5	10.5	1.1	0.9	1.4	40.9

[a] By difference.

At first sight, a general increase in aromatic compounds is observed when temperature is increased from 440 to 500 °C. Therefore, temperature is also a key parameter when catalyst is used, producing more aromatics as a consequence of secondary reactions which are produced to a major extent at high temperatures [40]. The use of ZSM-5 zeolite produces a strong aromatization of the liquid products, which reach 95.2 and 98.4% area aromatics at 440 and 500 °C respectively, while just 67.7 and 73.9% area aromatics are obtained in the same conditions without catalyst. These results show that ZSM-5 zeolite has a great influence in aromatization reactions. Marcilla et al. [41] reported that the high percentage of aromatics obtained with this zeolite could be attributed to the high number of Brönsted acid sites contained in its structure, where aromatization reactions are favoured. Therefore, it can be stated that the strong aromatization obtained with ZSM-5 zeolite in this study is related to the strong acidity of the zeolite used (63% of strong acid sites). It is known that strong acid sites contribute to coke-forming reactions, leading to the fast deactivation of the catalysts. In this sense, the authors have carried out a parallel study concerning the deactivation and regeneration of the ZSM-5 zeolite. Such study has proved that the catalyst is strongly deactivated after one pyrolysis run, but it can be easily regenerated by means of coke combustion.

The aromatics content obtained with Red Mud at 440 °C is only slightly higher than that obtained in the thermal process, but at 500 °C the aromatics content is considerably higher in presence of Red Mud compared to the thermal run. This is in agreement with the theory that Red Mud needs high temperatures to be activated. In fact, the aromatic production reached at 500 °C was 89.6% area, which is 15% higher than that obtained in the thermal run. These results are not in accordance with those reported by Yanik et al. [23] in a work about the catalytic effect of Red Mud in the degradation of a polymer mixture, since they concluded that Red Mud did not show any effect in the cracking process; on the contrary, similar results concerning aromatics formation were obtained by the authors in a previous paper in which plastics were pyrolysed in presence of Red Mud [4]. These differences may be attributed to the fact that the composition of Red Mud varies depending of the specific process from which it is obtained. It has been reported [42] that some Red Mud components such as Na_2O may act as poison, diminishing the catalytic activity. Different Na_2O contents may be the reason for the differences in Red Mud activities found by different authors. In fact, the Red Mud used by Yanik et al. [23] contained a higher proportion of Na_2O (7.1 wt%) than that of the Red Mud of the present study (1.8 wt%).

Fig. 8 shows the pyrolysis liquids compounds grouped according to their carbon number. As it can be seen in Fig. 8a, the pyrolysis liquids obtained at 440 °C are a mixture of C7–C20 compounds in the thermal experiment, of C7–C16 compounds in the ZSM-5 experiment and of C7–C19 compounds in the case of Red Mud. Therefore the cracking ability of ZMS-5 zeolite is also shown in

Table 9
GC–TCD/FID analysis (wt%) and HHV (MJ kg^{-1}) of pyrolysis gases.

Experiment	Thermal 440 °C	ZSM-5 440 °C	Red Mud 440 °C	Thermal 500 °C	ZSM-5 500 °C	Red Mud 500 °C
H_2	0.1	0.8	0.7	0.4	1.0	0.8
CO	0.4	0.7	0.5	0.7	0.7	1.2
CO_2	2.7	4.9	8.5	2.9	1.9	7.5
Methane	9.7	8.8	11.2	8.3	10.6	14.1
Ethane	12.7	6.5	6.3	10.0	8.6	12.4
Ethene	8.8	9.3	8.1	12.2	11.1	17.3
C3–C4	43.8	57.0	39.2	46.7	50.7	41.5
C5–C6	21.7	11.9	25.5	18.7	15.5	5.3
HHV	48.7	46.0	49.1	48.6	49.8	47.1

pyrolysis liquids, leading to lighter compounds production than in thermal decomposition. Similar results have been obtained by other authors before [43,44]. In all cases, most of pyrolysis liquids compounds are in the C7–C10 range, with a sharp peak in C8 fraction; this is a rather convenient result from the point of view of potential applications of these liquids, since C5–C10 is the gasoline carbon number range. A small peak can be also detected in C15–C16 fractions, which corresponds to substituted double ring aromatic compounds. Similar profiles can be found in Fig. 8b, which shows the distribution of pyrolysis liquids compounds at 500 °C. Again, higher Red Mud activity can be observed at this temperature, shortening the pyrolysis liquids carbon range at same extent as the zeolite (C7–C16), while thermal pyrolysis liquids reach C19 compounds.

The main individual components of the pyrolysis liquids are presented in Table 7. For the sake of reduction, only those compounds with a percentage quantified area greater than 3% have been included. Styrene is the most abundant product with percentage areas ranging from 27% to almost 50% area. The next abundant products are toluene (8–17.5% area) and ethyl-benzene (5–10.6% area), and other C8 aromatic compounds like xylenes and α-methylstyrene, which justifies the sharp peak observed in C8 in Fig. 8. It is somewhat surprising that so much styrene is obtained in the pyrolysis liquids, since the initial sample is mainly composed of polyolefins (40 wt% PE and 35 wt% PP) and only contains 18 wt% PS. The authors have confirmed that such GC–MS peak corresponds to styrene using the following procedure: (1) comparison of the mass spectrum of this peak with the theoretical mass spectrums of styrene found in two different databases (Wiley7 and NIST), (2) analysis of pure styrene (standard quality) with the same conditions in order to compare the mass spectra and (3) analysis of the liquids with multidimensional chromatography (GCxGC). All the mass spectra (i.e. the databases ones, that of pure styrene and that of the peak assigned to styrene in the GC–MS analysis of the liquids, both in mono and multidimensional GC–MS), were almost coincident.

In general terms, the production of styrene is higher in the thermal experiments than when catalyst is used. This effect is more pronounced with ZSM-5 zeolite than with Red Mud. At the same time, ZSM-5 zeolite enhances the production of toluene, ethyl-benzene and xylenes. Serrano et al. [5] explained that in the catalytic decomposition of PS, the carbenium nature of the acid catalyzed cracking leads to aromatic products different from styrene, while styrene is the main product in thermal decomposition of PS. The high proportions of styrene obtained in the thermal experiments of this work suggest that styrene is probably formed by other mechanisms (secondary reactions) apart from direct PS decomposition, but the decrease of this compound in the presence of ZSM-5 zeolite could be explained by the above mentioned theory reported by Serrano et al. [5].

Concerning Red Mud, no significant differences with the thermal experiment were found at 440 °C, but there did were differences in the experiments carried out at 500 °C: lower styrene production and higher ethyl-benzene and toluene yields were observed. It is not easy to propose a mechanism to explain these changes, due to the fact that Red Mud is a complex mixture of metal oxides which can influence in different ways in the process. On the one hand, Al_2O_3 and SiO_2 could enhance cracking due to their acid nature, leading to a decrease in styrene yield as it has been exposed above for ZSM-5. However, on the other hand, Fe_2O_3, which is known to have hydrogenation activity, is the main component of Red Mud. The hydrogenation character of Red Mud could be even stronger than that of Fe_2O_3 alone due to the presence of TiO_2 impurity, as it has been reported by Sushil and Batra [29]. If such is the case, the increase in ethyl-benzene could have been produced by direct hydrogenation of styrene, while the increase in toluene could have been produced by hydrocracking of styrene, yielding toluene and methane.

The elemental composition and higher heating value (HHV) of the pyrolysis liquids are presented in Table 8. It can be seen that these liquids are mainly composed of carbon and hydrogen, with small quantities of chlorine which comes from PVC. The lowest H/C ratios are obtained with ZSM-5 zeolite (1.5 at 440 °C and 1.3 at 500 °C) which is in agreement with the greater aromatics content of the liquids produced by this catalyst, as it has been observed in the GC–MS analyses. It is worth mentioning that pyrolysis oils have very high HHV, similar to those of conventional liquid fuels, so they may be considered as an appropriate alternative to fossil fuels. However, it has to be mentioned that the chlorine contained in the liquids could be very detrimental for their application. For this reason, the authors have studied, in a previous work [45], different alternatives to reduce the chlorine content of the pyrolysis liquids and found out that it can be reduced to a high extent if a low temperature dehydrochlorination step is applied prior to the pyrolysis process.

4.3.3. *Gas composition*

Table 9 shows that pyrolysis gases are composed of hydrocarbons ranging from C1 to C6, hydrogen and some carbon dioxide and monoxide. It can be seen that C3–C4 is the main fraction of pyrolysis gases both in thermal and in catalytic pyrolysis. ZSM-5 zeolite increases this fraction especially at 440 °C (from 43.8 wt% without catalyst to 57.0 wt%). This effect of ZSM-5 zeolite has also been reported by other authors [46,47] and it could be related to the shape selectivity of this catalyst (pore size). Once more the effect of Red Mud is noticeable at 500 °C, while it is negligible at 440 °C. At 500 °C Red Mud produces larger quantities of light hydrocarbons (C1–C2) and diminishes the proportion of C3–C6 gases. It is worth noting that Red Mud generates the highest proportion of methane at 500 °C (14.1 wt%), which may be caused by the hydrocracking reaction of styrene (to lead toluene and methane), which has been previously mentioned, proposed in the GC–MS liquid composition discussion (Table 7). Additionally, the great proportions of CO_2 obtained with Red Mud may be attributed to the catalytic activity of Fe_2O_3, since it has been reported [42] that the formation of CO_2 is produced by the stepwise reduction of haematite (Fe_2O_3)

Table 10
Moisture, elemental composition (wt%) and HHV (MJ kg^{-1}) of the pyrolysis solids.

Experiment	Moisture	C	H	Cl	Others[a]	H/C Ratio	HHV
Thermal 440 °C	n.d.[b]	86.6	10.0	<0.1	3.3	1.4	42.7
ZSM-5 440 °C	0.7	23.0	2.2	0.1	74.0	1.1	13.1
Red Mud 440 °C	0.8	13.6	0.7	4.2	80.7	0.6	11.3
Thermal 500 °C	0.2	93.7	3.5	0.3	2.3	0.4	38.2
ZSM-5 500 °C	1.2	13.8	0.9	0.1	84.0	0.8	5.9
Red Mud 500 °C	0.9	13.9	0.7	3.7	80.8	0.6	6.7

[a] By difference.
[b] Not determined.

to wustite (FeO) and metallic iron (Fe) by means of the reaction between hydrocarbons and Fe_2O_3.

It has to be mentioned that both catalyst enhance hydrogen production, which could be attributed to the hydrogen abstraction that takes place during aromatization reactions. Finally, it is also worth noting that the HHV of the gases in all cases is in the range of that of natural gas (48–53 MJ kg^{-1}). For this reason pyrolysis gases may be used as gaseous fuels to supply the energetic demand of the process, and the surplus may be valorised.

4.3.4. *Pyrolysis solids*

The composition of the pyrolysis solids is presented in Table 10. The great differences among the thermal and the catalytic runs derived solids are due to the fact that the catalyst is mixed with the pyrolysis solids. The higher carbon and lower hydrogen contents of the solid obtained in the thermal run at 500 °C (93.7 and 3.5 wt%) in comparison with that obtained at 440 °C (86.6 and 10 wt%) is due to the fact that some unconverted product remained in the solid fraction in the 440 °C experiment. Somehow similar behaviour can be observed in the ZSM-5 experiments, while in the Red Mud runs the composition of the solids obtained at 440 and 500 °C are almost coincident. These results are in agreement with the data in Fig. 6, where it can be appreciated that for thermal and ZSM-5 experiments the solid yields are higher at 440 °C than at 500 °C, showing further degradation, while the solid yield of Red Mud experiments are similar at 440 and 500 °C. Anyway, the pyrolysis solids are in all cases carbonaceous materials with high HHV. They could find applications such as alternative to fossil solid fuels, pigment or carbon black after catalysts separation and recovery.

5. Conclusion

Pyrolysis is a promising alternative for plastic wastes recycling. Poor quality mixed plastics can be converted into valuable liquids with high HHV and significant proportions of chemicals as styrene, ethyl-benzene or toluene; they can be used as an alternative to fossil fuels or as a source of chemicals for petrochemical processes. Additionally, C3–C4 rich gases with very high HHV are generated, which can be used for power generation for the process and/or for external applications. Pyrolysis solids are a minor by-product of the process mainly composed of carbon, with several potential applications (fuel, pigment, etc.).

The use of catalysts in pyrolysis of plastic wastes has a significant influence in both products yields and characteristics of the products. ZSM-5 zeolite is a very active catalyst for plastic waste pyrolysis; on the one hand, it promotes gas production and give rise to lower molecular weight and higher aromatic containing liquids even at low temperatures (440 °C), despite the fact that the initial sample is mostly polyolefinic. On the other hand, it enables to operate at lower temperatures (440 °C), achieving similar yields and product properties than in thermal runs at higher temperatures (500 °C). This implies energy saving and consequently operating costs reduction.

Red Mud shows a noticeable activity in plastic waste pyrolysis. However, it needs higher temperatures than ZSM-5 zeolite to become active in the pyrolysis process. It shows no activity at 440 °C while at 500 °C it increases gas yields, decreases liquids viscosity and promotes liquids aromatization. Taking into account these effects and considering that Al_2O_3 and SiO_2 are components of Red Mud and that it has both weak and strong acid sites in its structure, Red Mud may be considered a solid acid catalyst. However, there are differences in the nature of the liquids and gases obtained with Red Mud and ZSM-5 zeolite, which imply that other reaction pathways, such as hydrogenation and/or hydrocraking reactions take place, probably due to the presence of Fe_2O_3 and TiO_2 among the Red Mud components. The fact that Red Mud, which is an inexpensive by-product of the alumina industry, could help recycling of municipal plastic wastes by pyrolysis is of the most interest not only from the point of view of the economy of the process, but also from a global recycling point of view, since Red Mud is in its turn an industrial waste.

Acknowledgements

The authors thank the Spanish Ministry of Education and Science (MEC) (CTQ 2007-67070/PPQ) as well as the Basque Country Government (ETORTEK 2007 IE07-207, GIC 07-09-IT-354-07 and Researchers' Formation Program – 2008) for financial assistance for this work.

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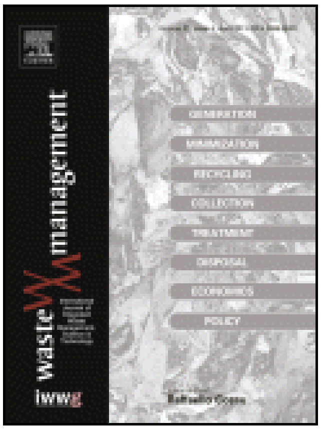
4.2. SIMULATED SAMPLE RUNS

4.2.2. Catalytic pyrolysis (2 of 2)



Article: *Deactivation and regeneration of ZSM-5 zeolite in catalytic pyrolysis of plastic wastes*

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Journal: *Waste Management.*

State: *Accepted Manuscript (In Press).*

Waste Management xxx (2011) xxx–xxx

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Deactivation and regeneration of ZSM-5 zeolite in catalytic pyrolysis of plastic wastes

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ARTICLE INFO

Article history:
Received 17 November 2010
Accepted 4 April 2011
Available online xxxx

Keywords:
Pyrolysis
Feedstock recycling
Catalytic decomposition
Plastic wastes
ZSM-5 zeolite
Regeneration

ABSTRACT

In this work, a study of the regeneration and reuse of ZSM-5 zeolite in the pyrolysis of a plastic mixture has been carried out in a semi-batch reactor at 440 °C. The results have been compared with those obtained with fresh-catalyst and in non-catalytic experiments with the same conditions. The use of fresh catalyst produces a significant change in both the pyrolysis yields and the properties of the liquids and gases obtained. Gases more rich in C3–C4 and H_2 are produced, as well as lower quantities of aromatic liquids if compared with those obtained in thermal decomposition. The authors have proved that after one pyrolysis experiment the zeolite loses quite a lot of its activity, which is reflected in both the yields and the products quality; however, this deactivation was found to be reversible since after regeneration heating at 550 °C in oxygen atmosphere, this catalyst recovered its initial activity, generating similar products and in equivalent proportions as those obtained with fresh catalyst.

1. Introduction

Nowadays, plastic waste management policies are based on energy recovery or elimination processes. In Occidental Europe, about 80 wt.% of the annually generated plastics is landfilled or incinerated (Cimadevila, 2008). However, to fulfil the requirements defined in the European legislation concerning waste management, the application of new recycling processes is an unavoidable task that will have to be carried out in the forthcoming years.

In this sense, ‘‘feedstock recycling’’ includes a very wide range of techniques which offer an opportunity to obtain valuable chemicals from poor quality mixed plastics streams. Broadly speaking, such techniques are focused on producing new non-plastic products from plastic goods, normally monomers or hydrocarbons, and therefore are very different from traditional mechanical recycling processes. Among them, pyrolysis is of the most interest since it is a relatively low cost process from which a broad distribution of products can be 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, while the inorganic material remains unaltered in the solid fraction and free of the binding organic matter, being able to be subsequently recycled.

The use of catalysts confers pyrolysis an additional value since an adequate catalyst can improve the products quality and lead the process towards a good selectivity to more valuable products, even at lower temperatures than in thermal pyrolysis (Buekens and Huang, 1998; Aguado and Serrano, 1999). For this reason, catalytic pyrolysis has been intensively studied in the last years. The catalysts more investigated have been conventional acid solids used in petrochemical feedstocks cracking, as zeolites (e.g., Vasile et al., 2001; Aguado et al., 2009) or FCC catalyst (e.g., Miskolczi et al., 2004; Olazar et al., 2009), as well as non zeolitic mesostructured solids (e.g., Sakata et al., 1999; Aguado et al., 2007). The results reported in the literature show that the cracking ability of the catalysts depends on both their physical (textural properties) and their chemical (acid sites) characteristics. For this reason, one of the most used catalyst is ZSM-5 zeolite, due to its strong acidity and shape selectivity, the latter depending on the particular textural properties (structure and pore size) of each zeolite. These particular properties promote cracking of C–C bonds and determine the chain length of the products obtained (Serrano et al., 2005a; Miskolczi et al., 2006).

However, ZSM-5 zeolite is an expensive catalyst which may condition the economy of the process, due to the high amounts of catalyst which would be necessary in a continuous operating plant. An economic study carried out by Ali et al. (2002) concluded that the catalyst cost (type and amount) is a key factor when it comes to compare the catalytic cracking with thermal cracking technology economics; for this reason, the study of deactivation, regeneration and reuse of catalysts is of the most interest from an industrial implementation point of view.

Up to now, the majority of the studies related to the application of used catalysts in plastic wastes pyrolysis have been carried out with spent FCC catalysts (e.g., Lee et al., 2002; Lin et al., 2010). Some of these studies have shown that the initial activity of such

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doi:10.1016/j.wasman.2011.04.004

Please cite this article in press as: López, A., et al. Deactivation and regeneration of ZSM-5 zeolite in catalytic pyrolysis of plastic wastes. Waste Management (2011), doi:10.1016/j.wasman.2011.04.004

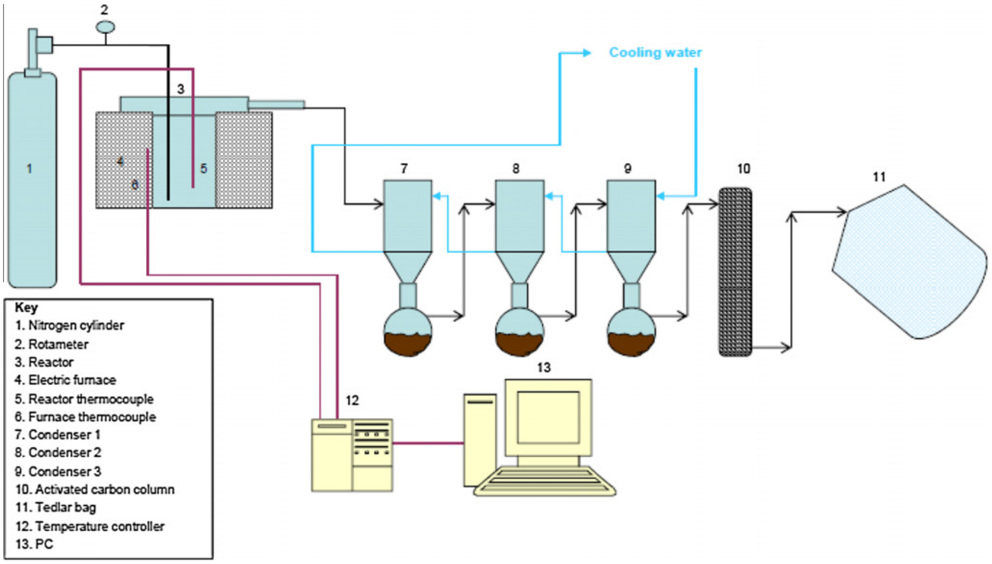

Fig. 1. Flow sheet of the experimental set-up used.

catalysts remains almost unaltered after regeneration and that several regeneration steps can be applied to them without a significant activity loss (Lin and Yang, 2008). There are fewer references in the literature concerning ZSM-5 zeolite regeneration (Serrano et al., 2007; Angyal et al., 2009) and most of them have been carried out in pyrolysis of polyolefins, mainly polyethylene, hindering the problems which can arise due to the interactions among the components when complex plastic mixtures similar to real wastes are pyrolysed.

The objective of this work is to study the loss of activity of ZSM-5 zeolite in order to evaluate if this effective catalyst could be used more than once in pyrolysis of plastic mixtures. With this objective, an exhaustive characterization of the products obtained in thermal pyrolysis and with fresh, regenerated and spent ZSM-5 is presented in this paper.

2. Materials and methods

2.1. Materials

The plastic mixture used for the experiments was composed of 40 wt.% high density polyethylene (HDPE), 35 wt.% polypropylene (PP), 18 wt.% polystyrene (PS), 4 wt.% poly(ethylene terephthalate) (PET) and 3% poly(vinyl chloride) PVC. HDPE, PP and PS were provided by Spanish chemical companies, PVC was provided by a PVC products manufacturing Spanish company, and PET was obtained from a Spanish plastic recycling company. All the plastic materials were used in pellet size ($\approx$3 mm) for the pyrolysis experiments. Additionally finely ground samples ($\leqslant$1 mm) were prepared for characterization purposes. The proportions of the plastics in the mixture were established characterizing real samples coming from packing and packaging applications and rejected from an industrial separation plant located in Amorebieta, in the north of Spain (López et al., 2010). The characteristics and composition of the plastic mixture are presented in Table 1. The term "others" in this Table is determined by difference and it includes all elements except carbon, hydrogen, nitrogen and chloride, which are specifically analysed; it must be mainly oxygen coming from PET. As it can be seen, carbon and hydrogen are the main components (84.7 and 12.5 wt.%, respectively) as a consequence of the high HDPE, PP and PS content of the sample (93 wt.%), since these materials are just composed of carbon and hydrogen; this fact also explains its great higher heating value (HHV). It must be mentioned that the sample also contains 1.1 wt.% of chlorine, due to the presence of PVC in the mixture.

A commercial ZSM-5 zeolite provided by Zeolist International was used for the catalytic experiments. The catalyst has a SiO_2/Al_2O_3 ratio of 50 and a total acidity of 0.17 mmol NH_3 g^{-1}; it was used as was received, without any activation operation. In all the experiments, 10 g of zeolite were mixed with the 100 g plastic sample at the beginning of the experiment (liquid phase contact).

2.2. Experimental procedure

The pyrolysis experiments were carried out using a 3.5 dm^3 semi-batch reactor. In a typical run, 100 g of the sample were placed into the reactor which was sealed and heated at a rate of 20 °C min^{-1} up to 440 °C; this temperature was maintained for 30 min, a standard time which was established on the basis of previous studies carried out by the authors with other polymeric wastes in the same installation (Legarreta et al., 1995; de Marco et al., 1995; Torres, 1998). The parameters used in this paper (440 °C, 30 min) are optimized operating conditions as far as energy efficiency, conversion and liquid yields is concerned. These optimized conditions were established by the authors after specific research concerning this topic.

Nitrogen was passed through during the whole experiment at a rate of 1 dm^3 min^{-1} to sweep the decomposition products from the

Table 1
Moisture, ash and elemental composition (wt.%) and HHV (MJ kg^{-1}) of the plastic mixture.

Parameter	Moisture	Ash	C	H	N	Cl	Others[a]	H/C ratio	HHV
Value	0.1	0.0	84.7	12.5	<0.1	1.1	1.5	1.8	43.9

[a] By difference.

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reaction medium. The evolved products flowed to a series of running water cooled gas–liquid separators where the vapours were condensed and collected as liquids. The uncondensed products were passed through an activated carbon column and collected as a whole in Tedlar plastic bags. A study about the appropriate configuration for condensation and cleaning of the pyrolysis gases was reported by the authors in a previous paper (de Marco et al., 2009). The optimised experimental set-up is presented in Fig. 1.

The amount of solids (products in the reactor after pyrolysis) and liquids obtained in each pyrolysis run were weighed, and the pyrolysis yields were calculated as weight percentage with respect to the amount of raw material pyrolysed. In the catalytic experiments, the solid yield was calculated in a free catalyst basis. Gas yields were, as a general rule, calculated by difference. Some experiments were specifically devoted to directly quantify the amount of gases by gas chromatography; in such experiments a closure of the mass balance of about 90 wt.% was obtained. The results of the pyrolysis yields which are presented in Section 3 of this paper, are the mean value of at least three pyrolysis runs carried out in the same conditions and which did not differ each other more than three points in the percentage.

2.3. Analytical techniques

Moisture and ash contents of the samples were determined by thermogravimetric analysis according to D3173-85 and D3174-82 ASTM standards, respectively, and the elemental composition with an automatic CHN analyser. Chlorine was determined following the method 5050 of the Environmental Protection Agency (EPA) of the United States. The higher heating value (HHV) was determined with an automatic calorimetric bomb.

Additionally, pyrolysis liquids were also analysed by gas chromatography coupled with mass spectrometry detector (GC–MS). When the match quality of the identification result provided by the MS search engine was lower than 85%, the result was not considered valid and such compounds were classified as “No identified”. The compounds names included in the tables of this paper correspond to the tentative assignments provided by the MS search engine and have been contrasted, as far as possible, with bibliographic data and occasionally with calibration standards. Pyrolysis gases were analysed by means of a gas chromatograph coupled with thermal conductivity and flame ionization detectors (GC-TCD/FID). Due to the difficulty in distinguishing among isomers from C3 to C6, such discrimination was not made. The HHV of the gases was calculated according to their composition and to the HHV of the individual components.

The textural properties of the fresh, the regenerated and the used catalyst were determined by means of nitrogen adsorption–desorption isotherms at 77 K in an AUTOSORB-1 Quantachrome equipment. Surface areas were calculated by means of BET equation and external surface areas were obtained applying the *t*-plot method. Total pore volume was measured at $P/P_o = 0.99$. The regeneration of the used catalyst was carried out in two steps in a LECO TGA-500 thermobalance, which is capable of handling at the same time 19 crucibles of 1–5 g capacity each. In the first step the catalyst was heated under nitrogen flow up to 550 °C and maintained there for 30 min and then coke was eliminated by combustion under oxygen flow at the same temperature until no longer weight loss was detected. SEM images were obtained in a LEO 1525 electron microscope and the amount of carbon deposited in the catalyst was determined with the LECO elemental analyser.

3. Results and discussion

3.1. Catalysts characterization

The textural properties of the fresh, regenerated and spent ZSM-5 zeolite are presented in Table 2. With the aim to study the influence of char-coke particles in the spent ZSM-5 characteristics, the textural properties of char obtained with similar conditions in a thermal pyrolysis run have been included in Table 2. BET surface area of ZSM-5 zeolite is 412.0 $m^2 g^{-1}$, with high micropore area (346.1 $m^2 g^{-1}$) and also high micropore volume (0.1 $cm^3 g^{-1}$), which indicates the existence of relatively high internal porosity in this catalyst. The spent ZSM-5, which was characterized after one pyrolysis experiment, showed quite low micropore area (3.0 $m^2 g^{-1}$). This fact may be explained by the relatively high content of carbon which was deposited in the zeolite surface during pyrolysis (23.0 wt %); this carbon is supposed to be the char which is formed during the process, so it most probably has the same properties as the char of thermal pyrolysis, which are presented in Table 2. The micropore area and micropore volume values for char indicate that char is not a microporous material, and deposited in the zeolite drastically decreases the micropore area of that.

The deposited carbon is also responsible for the higher total pore volume (TPV) obtained in the zeolite after pyrolysis (0.6 $cm^3 g^{-1}$) compared to the fresh catalyst (0.4 $cm^3 g^{-1}$), as well as for the noticeable increase in the external surface area (ESA, from 65.9 $m^2 g^{-1}$ in fresh catalyst to 288.6 $m^2 g^{-1}$ in spent one). This external area is about 99% of the total surface area (BET, 291.6 $m^2 g^{-1}$) of the spent ZSM-5, which indicates that almost all micropores have been blocked by coke during the pyrolysis run.

These results are corroborated by the characteristics of the regenerated ZSM-5 zeolite, since after burning the coke (regeneration), the BET surface area of the catalyst was practically the same as that of the fresh one (411.1 and 412.0 $m^2 g^{-1}$, respectively), and the same occurs with the TPV (0.4 $cm^3 g^{-1}$ in both samples). Such was not the case of the ESA, which remained higher than in the fresh catalyst (124.3 and 65.9 $m^2 g^{-1}$, respectively). These data suggest that some changes in the physical structure of the catalyst may have taken place during the regeneration of the zeolite, since the carbon which remains after regeneration (0.7 wt.%) is too low to be responsible for such a high difference in ESA. On the other hand, it cannot be stated that this carbon content corresponds to coke; they could be not removable stable coke species which are formed during pyrolysis of plastic wastes (Serrano et al., 2007), but also carbon from carbonates formed during the regeneration process.

Table 2
Textural properties of the catalysts and of char.

Property	Fresh ZSM-5	Spent ZSM-5	Regenerated ZSM-5	Char
BET surface area ($m^2 g^{-1}$)	412.0	291.6	411.1	4.7
Ext. surface area ($m^2 g^{-1}$) (ESA)	65.9	288.6	124.3	4.7
Micropore volume ($cm^3 g^{-1}$) (MPV)	0.1	1.0E-03	0.1	0.0
Total pore volume ($cm^3 g^{-1}$) (TPV)	0.4	0.6	0.4	9.5E-03
Micropore area ($m^2 g^{-1}$)	346.1	3.0	286.8	0.0
Carbon (wt.%)[a]	–	23.0	0.7	94.1

[a] Determined by CHN analysis.

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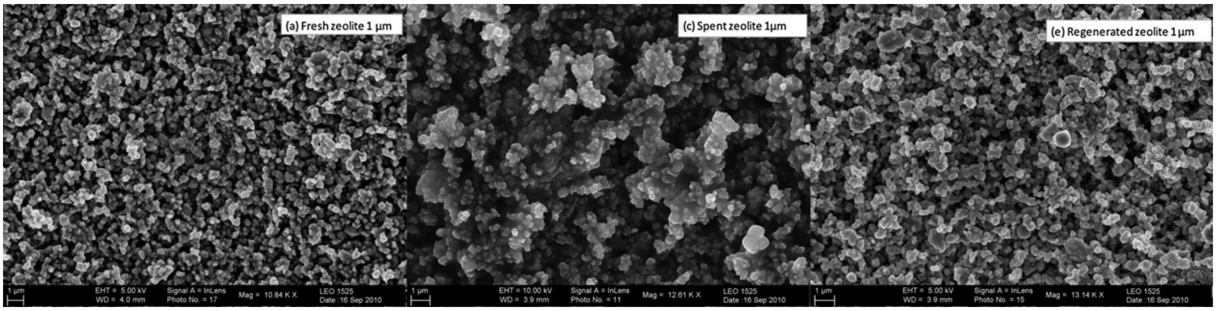

Fig. 2. SEM photographs of the fresh, spent and regenerated zeolite.

SEM photographs of the fresh, spent and regenerated zeolite are presented in Fig. 2 in order to see the effect of deposited coke and regeneration in the surfaces of the catalysts. Fig. 2 shows that fresh ZSM-5 zeolite is formed by uniform crystals with sizes within the nanometer size (≈100–300 nm). Quite higher particles can be observed in the spent zeolite as a consequence of some kind of agglomeration produced by the deposited coke. On the contrary, the SEM photograph of the regenerated zeolite is very similar to that of the fresh one, which indicates that it recovers its textural appearance after the regeneration process.

3.2. Pyrolysis yields

The pyrolysis yields obtained in the thermal and catalytic experiments are shown in Fig. 3. The liquid fraction was the main product in all cases, reaching almost 80 wt.% in the thermal pyrolysis run, followed by gases. The solid fraction, which was practically equivalent in all the experiments (≈3 wt.%), corresponds to char formed during pyrolysis (Grittner et al., 1993; Williams and Williams, 1997; Van Krevelen and Te Nijenhuis, 2009).

The use of fresh ZSM-5 produced a strong increase in the gas yield, which was about 40 wt.% while less than 20 wt.% of gases was obtained in the thermal run. As a consequence fewer liquids were obtained with the fresh catalyst than in the thermal run. This is a well known effect which has been reported before by other research groups (e.g., Miskolczi et al., 2006; Williams and Bagri, 2004) as well as by the authors (de Marco et al., 2009), and it is attributed to both the textural properties of the zeolite and the presence of Brönsted and Lewis acid sites in this catalyst.

After one pyrolysis experiment, the zeolite was recovered and spent directly in the following pyrolysis run; the yields obtained are shown in Fig. 3. These results clearly show that the catalyst has lost its activity, yielding liquids and gases almost in the same proportions as in the thermal run. This quick deactivation has also been observed by other authors and it has been associated with coke deposition, which seems to block the zeolite pores as well as the acid sites (Angyal et al., 2009).

On the contrary, after the regeneration of the zeolite, the yields obtained were very similar to those obtained with the fresh catalyst, showing the effectiveness of the regeneration process and the possibility of using the zeolite more than once if it is properly regenerated. These results are quite in accordance with those obtained by Serrano et al. (2007), who studied the regeneration of two nanocrystalline ZSM-5 catalysts in pyrolysis of PE.

3.3. Pyrolysis liquids

A summary of the GC–MS analyses applied to pyrolysis liquids is shown in Table 3. Aromatic compounds were the main fraction in the liquids, ranging from 67.7% to 97.4% area. It is worth mentioning the aromatization ability of the ZSM-5 zeolite, which produced a great increase in such compounds if compared to the thermal experiment. The capacity of this catalyst to increase aromatics in the liquid fraction has been reported before in the pyrolysis of plastic mixtures (Vasile et al., 2001) as well as in the pyrolysis of pure PE (Serrano et al., 2005b; Marcilla et al., 2009), and it is explained by the presence of high number of Brönsted acid sites (strong acid sites) within this zeolite, where aromatization reactions are favoured. It is also worth noting that the use of ZSM-5 led to the generation of higher quantities of C5–C9 compounds and lower quantities of long chain chemicals (>C13), which is quite in accordance with the well known shape selectivity of this catalyst.

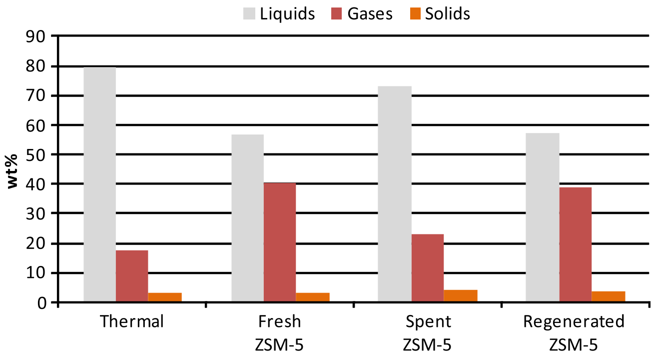

Fig. 3. Pyrolysis yields obtained in the thermal and catalytic experiments.

When the spent ZSM-5 was used, the aromatic content of the liquids drastically decreased from 95.2% to 78.4% area, due to the fact that most of strong acid sites responsible for the aromatization reactions have probably been blocked by coke and char particles; however, the total aromatic content of the liquid obtained in this experiment (78.4% area) was still higher than that obtained in the thermal experiment (67.7% area) which indicates that the zeolite still retains some catalytic activity; this fact can also be observed in the carbon number of liquid fractions, where the decrease in the C5–C9 fraction of the liquids obtained with the spent zeolite is not as high as the mentioned decrease in aromatics. As observed before in the yields discussion, the results obtained with the regenerated ZSM-5 are very similar to those obtained in the fresh catalyst experiment, both in aromatics content and in the carbon number of liquid fractions, indicating that the zeolite has effectively been regenerated.

Table 4 shows the main individual components of the pyrolysis liquids. All of them are aromatic compounds except for dimethylheptene, a branched olefin which has also been obtained by other authors as one of the main products of the cracking of polypropylene (Kaminsky and Zorriqueta, 2007). The products yields confirm the tendency observed in the results presented above, showing similar behaviours for the experiments carried out with fresh and regenerated ZSM-5 and a somewhat intermediate behaviour

Table 3
Aromatic and non-aromatic compounds found in the pyrolysis liquids (% area).

Experiment		Thermal	Fresh ZSM-5	Spent ZSM-5	Regenerated ZSM-5
Total aromatics		67.7	95.2	78.4	97.4
Total non aromatics		22.0	2.7	13.9	1.8
Unidentified		10.3	2.0	7.8	0.8
C5–C9	Aromatics	63.4	78.7	69.4	77.2
	Non aromatics	10.6	2.7	8.1	1.8
	Total	74.1	81.4	77.5	79.0
C10–C13	Aromatics	n.d.[a]	9.5	2.3	12.7
	Non aromatics	5.4	n.d.[a]	5.2	n.d.[a]
	Total	5.4	9.5	7.5	12.7
>C13	Aromatics	4.3	7.5	6.6	6.6
	Non aromatics	5.9	n.d.[a]	0.6	0.6
	Total	10.2	7.5	7.2	7.2

[a] Not detected.

Table 4
Main components of the pyrolysis liquids determined by GC–MS (% area).

Compound	Thermal	Fresh ZSM-5	Spent ZSM-5	Regenerated ZSM-5
Toluene	8.1	12.3	9.9	13.2
Dimethyl-heptene	7.8	1.8	5.4	1.2
Ethyl-benzene	5.7	10.6	9.0	11.2
Xylenes	n.d.[a]	10.1	2.0	13.1
Styrene	46.3	31.4	42.9	23.7
α-Methyl-styrene	3.2	4.5	4.4	3.8
Methyl-napththalene	n.d.[a]	3.3	4.9	4.9

[a] Not detected.

among these ones and the thermal run when spent zeolite was used. Anyway, styrene was found to be the main product in the liquid fraction in all the experiments, followed by toluene and ethylbenzene.

It is somewhat surprising that so much styrene is obtained in the pyrolysis liquids, especially in the thermal and spent ZSM-5 experiments (46.3% and 42.9% area, respectively), since the initial sample is mainly composed of polyolefins (40 wt.% PE and 35 wt.% PP) and only contains 18 wt.% PS. However, previous studies carried out by the authors with the same installation and with plastic samples with similar PS contents, styrene was also the main component of pyrolysis liquids (de Marco et al., 2009; López et al., 2011). The authors have confirmed that such GC–MS peak corresponds to styrene by comparing the mass spectrum of this peak with the theoretical mass spectrums of styrene found in two different databases (Wiley7 and NIST) and by analysing pure styrene (standard quality) with the same conditions in order to compare the result. All the mass spectra (i.e., the databases ones, that of pure styrene and that of the peak assigned to styrene in the GC–MS analysis of the liquids) were almost coincident. This result is almost equivalent to that obtained by Miskolczi et al. (2006), who obtained 53.4% styrene in the pyrolysis liquids of a 90%PE-10%PS mixture at 410 °C.

It is really a difficult task to propose a possible mechanism for styrene formation in such a complex system (five polymeric input materials and many more decomposition products). Concerning thermal decomposition, styrene is formed at a great extent from direct depolymerisation of PS and, as the other aromatic compounds, from secondary reactions among the primary products of the other polymers decomposition, e.g., Diels–Alder type reactions followed by dehydrogenation.

When catalysts are added to the process, it has to bear in mind that both thermal and catalytic decomposition take place at the same time, so both mechanisms are produced simultaneously. In presence of zeolite type catalysts, styrene is formed by thermal mechanisms on the one hand, but on the other hand the "thermally" formed styrene decomposes into other aromatic compounds as a consequence of the secondary reactions that take place to a greater extent in presence of such catalysts. This is the reason why styrene yield is usually lower in catalytic pyrolysis compared to thermal pyrolysis, as it can be seen in Table 4, i.e., the yield of styrene was lower in the fresh and regenerated zeolite runs (31.4% and 23.7% area, respectively) than that obtained in the thermal and spent ZSM-5 experiments (46.3% and 42.9% area, respectively).

This fact is in accordance with the reported by Serrano et al. (2000), who suggested that the lower styrene formation during PS catalytic decomposition with zeolites is produced since the carbenium nature of the acid catalyzed cracking leads to aromatic products different from styrene. The higher yields of toluene, ethyl-benzene and xylenes in the fresh and regenerated catalytic runs may indicate that such compounds are involved in styrene decomposition reactions. Similar behaviour concerning styrene yield was found in thermal and catalytic decomposition over ZSM-5 zeolite by Williams and Bagri (2004) and Miskolczi et al. (2006), when they pyrolysed PS and PS-PE blends, respectively.

The liquids characterization was completed with elemental and HHV analysis; the results are shown in Table 5. The elemental composition of the liquids hardly differ one another, except for slight variations in the carbon and hydrogen contents. These variations are related to the aromatics content of such liquid: the higher the aromatic content, the higher the carbon and the lower the hydrogen content and consequently the H/C ratio, due to the insaturation of the aromatic ring. Taking into account the high aromatics content (67–98% area) it seems, at first, somewhat surprising that in all cases the H/C ratio are around 1.5 instead of close to 1. The explanation to this fact is that H/C = 1 corresponds to non-substituted or lowly-substituted aromatics, but when aromatics are linked to paraffinic or olefinic chains, H/C ratios are higher than 1.

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Table 5
Elemental composition (wt.%) and HHV (MJ kg^{-1}) of the pyrolysis liquids.

Parameter	Thermal	Fresh ZSM-5	Spent ZSM-5	Regenerated ZSM-5
C	86.1	87.6	86.4	87.1
H	12.3	11.2	11.6	11.0
Cl	0.2	1.2	0.3	0.6
Others[a]	1.4	0.0	1.7	1.3
H/C ratio	1.7	1.5	1.6	1.5
HHV	44.7	42.2	44.2	42.9

[a] By difference.

It is also important to mention that the HHV of the liquids is very high and similar to that of conventional liquid fuels, showing their potential application as alternative fuels; in this sense, the chlorine contained in these liquids, coming from the PVC of the plastic mixture, could condition their application as liquid fuels. The problem of chlorine may be overcome by stepwise pyrolysis, as it has been demonstrated by the authors in a previous paper (López et al., 2011) which showed that the chlorine content of the liquids coming from PVC containing plastic mixtures can be drastically reduced by carrying out a previous low temperature dechlorination step.

3.4. Pyrolysis gases

The composition of the pyrolysis gases is presented in Table 6. They are composed of hydrocarbons from C1 to C6, carbon dioxide and monoxide and small quantities of hydrogen. The use of fresh catalyst enhanced the production of C3 and C4 fractions compared to the thermal experiment; in the case of spent and regenerated ZSM-5, the production of C4 fraction was even higher than in the fresh zeolite experiment, while the C3 fraction was lower in the former cases. Once more, despite the distribution between C3 and C4 fractions was not the same, the addition of both was similar in the thermal and spent catalyst runs (43.8 and 42.6 wt.%, respectively) and lower than those obtained with fresh and regenerated ZSM-5 (57.0 and 57.1 wt.% respectively), which shows that ZSM-5 promotes the production of such fractions.

It is worth noting that the use of catalysts also increased the production of H_2; this fact has also been reported by other authors (Marcilla et al., 2009; Shah et al., 2010) and may be due to the hydrogen abstraction that takes place during the aromatization reactions, which are favoured by ZSM-5 catalyst.

Table 6
GC-TCD/FID analysis (wt.%) and HHV (MJ kg^{-1}) of pyrolysis gases.

Compound	Thermal	Fresh ZSM-5	Spent ZSM-5	Regenerated ZSM-5
H_2	0.1	0.8	0.7	0.9
CO	0.4	0.7	0.7	0.7
CO_2	2.7	4.9	6.5	4.8
C1–C2				
Methane	9.7	8.8	10.1	9.7
Ethane	12.7	6.5	9.1	6.8
Ethene	8.8	9.3	12.1	9.1
Total	31.2	24.6	31.3	25.6
C3–C4				
C3	26.1	32.4	11.7	21.4
C4	17.7	24.6	30.9	35.7
Total	43.8	57.0	42.6	57.1
C5–C6				
C5	17.4	7.0	13.1	6.7
C6	4.3	4.9	5.1	4.2
Total	21.7	11.9	18.2	10.9
HHV	48.7	46.0	45.8	47.1

Table 7
Moisture (wt.%), elemental composition (wt.%) and HHV (MJ kg^{-1}) of the pyrolysis solids.

Parameter	Thermal	Fresh ZSM-5	Spent ZSM-5	Regenerated ZSM-5
Moisture	n.d.[2]	0.7	0.5	0.6
C	86.6	23.0	31.4	25.9
H	10.0	2.2	2.5	2.6
Cl	<0.1	0.1	0.2	0.1
Others[a]	3.3	74.0	65.4	70.8
H/C ratio	1.4	1.1	1.0	1.2
HHV	42.7	13.1	11.6	14.2

[a] By difference; [2]Not determined.

It has to be mentioned that pyrolysis gases may also contain some chlorine (in HCl form) as it can be deduced from the chlorine mass balance. However, in a potential industrial process such HCl would be absorbed in alkaline solutions by means of wet scrubbers, so that a usable HCl free gas stream would be obtained.

3.5. Pyrolysis solids

Table 7 shows the elemental composition of pyrolysis solids. The great differences among the values of the thermal experiment solid and those of the catalytic ones (specially “others” content) are due to the fact that in the latter the catalysts are mixed with the pyrolysis solids. Concerning the solids of the thermal run, it can be seen that they have quite a high hydrogen content (10 wt.%), which indicates that total decomposition has not been achieved and some unreacted polymer remains in the solid.

There are no significant differences among the solids obtained in the catalytic experiments except for their carbon content. The fresh catalyst showed the lowest carbon content (23.0 wt.%), and the regenerated zeolite a somehow higher carbon content (25.9 wt.%), which indicates that, despite the regeneration process was very effective in terms of yields and products quality, the regeneration process slightly promotes char formation. The highest carbon content was obtained in the solid of the spent ZSM-5 zeolite (31.4 wt.%), quite a high value which justifies the lack of activity of this catalyst due to the strong blockage caused by coke deposition.

4. Conclusions

ZSM-5 zeolite is a very interesting catalyst for pyrolysis of mixed plastic wastes, since high conversions of the samples can be obtained at low temperatures. When it is used, higher conversions than 95 wt.% and liquid fractions with high quantities of valuable aromatic compounds as styrene or toluene are generated, as well as C3–C4 rich gases. The liquid fraction can be used as an alternative to fossil fuels or as a source of valuable chemicals, while the gaseous fraction could be used for power generation for the process itself. Solid yields are lower than 4 wt.%, they are mainly composed of carbon and they can be eliminated from the catalyst by burning them in air.

When using ZSM-5 zeolite in pyrolysis, it is quickly deactivated to a great extent by coke deposition, losing its capacity to produce liquid and gaseous fractions of the same quality of those obtained with the fresh catalyst experiments, although somewhat better quality than that obtained in a thermal run. A regeneration process consisting of burning the deposited coke in an air stream at 550 °C enables the catalyst to recover its initial activity and to produce liquids and gases almost equivalent to those obtained with the fresh catalyst. This is a key factor in the pyrolysis of plastic wastes with ZSM-5 zeolite since having the chance of reusing this catalyst with its whole activity is essential for the economics of a potential industrial pyrolysis process.

Please cite this article in press as: López, A., et al. Deactivation and regeneration of ZSM-5 zeolite in catalytic pyrolysis of plastic wastes. Waste Management (2011), doi:10.1016/j.wasman.2011.04.004

Acknowledgements

The authors thank the Spanish Ministry of Education and Science (MEC) (CTQ 2007-67070/PPQ) as well as the Basque Country Government (ETORTEK 2007 IE07-207, GIC 07-09-IT-354-07 and Researchers' formation program – 2008) for financial assistance for this work.

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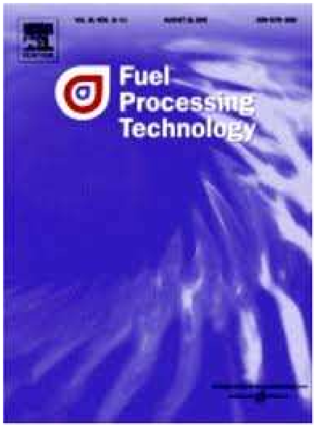
Please cite this article in press as: López, A., et al. Deactivation and regeneration of ZSM-5 zeolite in catalytic pyrolysis of plastic wastes. Waste Management (2011), doi:10.1016/j.wasman.2011.04.004

4.2. SIMULATED SAMPLE RUNS

4.2.3. Dechlorination of products (1 of 2)



Article: *Dechlorination of fuels in pyrolysis of PVC containing plastic wastes*

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Journal: *Fuel Processing Technology 92, 253-260.*

Year of publication: *2011*

Fuel Processing Technology 92 (2011) 253–260

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Dechlorination of fuels in pyrolysis of PVC containing plastic wastes

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ARTICLE INFO

Keywords:
Stepwise pyrolysis
PVC
Feedstock recycling
Thermal decomposition
Plastic wastes
$CaCO_3$

ABSTRACT

The objective of this work is the study of several dechlorination methods devoted to reduce the chlorine content of the liquids obtained in pyrolysis of PVC containing plastic wastes. A mixture of polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET) and polyvinyl chloride (PVC) has been pyrolysed in a 3.5 dm^3 semi-batch reactor at 500 °C for 30 min. Stepwise pyrolysis carried out at several temperature and time conditions, the addition of $CaCO_3$ for chlorine capture and a combination of both methods have been studied. Additionally, some thermogravimetric analyses have been carried out in order to establish the best conditions for PVC dehydrochlorination in the presence of other plastics. It has been proved that the application of dehydrochlorination methods plays a significant role in the characteristics of pyrolysis liquids. Stepwise pyrolysis is an effective method for reduction of the chlorine content of pyrolysis liquids; additionally, heavier hydrocarbons and lower quantity of aromatics in the liquids than in conventional pyrolysis are obtained. The addition of $CaCO_3$ leads to the retention of a significant amount of chlorine in the solid, but more chlorine than in a conventional run is found in the liquids, which contains a higher amount of aromatics.

1. Introduction

Plastics consumption has drastically increased in the last few decades. Annual consumption of plastics in Occidental Europe is about 60 million tons, yielding almost 23 million tons of plastic 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 [1]. Pyrolysis may be an alternative for increasing the chemical recycling percentage and an opportunity to obtain valuable liquid fuels from plastic wastes.

The presence of some PVC in real streams of municipal plastic wastes is still very common. Due to the low consumption of PVC in commodity applications, it is a minority product which is not recovered in the industrial separation and classification plants and therefore usually forms part of the rejected streams of such plants [2,3]. These rejected streams, composed by very different and intermingled plastics, cannot be mechanically recycled. In the pyrolysis process (heating in an oxygen free atmosphere), the organic components of the material are decomposed generating liquid and gaseous products, which can be useful as fuels and/or sources of chemicals. The inorganic ingredients (fillers, metals, etc.) remain practically unaltered and free of the binding organic matter, and therefore metals could be separated and the remaining solid may be reused (additive, fillers, pigment, etc) or as a last resort, it would be a minimum waste to be landfilled. Pyrolysis is an especially appropriate recycling technique for waste streams containing different plastics for which mechanical recycling is not feasible. The study of the fate of chlorine in pyrolysis of PVC containing plastic wastes is of a great interest since chlorinated compounds can be formed in the pyrolysis liquids and this is very detrimental either in order to supply such liquids to an oil refinery or to use them directly as fuels.

The objectives of this paper are on the one hand to study and compare several dechlorination methods in the pyrolysis of PVC containing plastic wastes, and on the other hand to analyse the influence of these methods not only on the chlorine content of the pyrolysis products but also on the characteristics of such products. There are many references in the literature about the thermal decomposition of PVC since it is a polymer which produces hydrogen chloride (HCl) when it is moderately heated, creating toxic and corrosive conditions. Consequently its sustainability has been under discussion for many years [4] and for this reason the thermal behaviour and pyrolysis kinetics of both virgin and waste PVC, either alone or mixed with other plastics, have been widely studied and discussed by many authors [5–12].

The dechlorination attempts proposed until now can be divided in three groups: stepwise pyrolysis, catalytic pyrolysis and pyrolysis with adsorbents added to the sample. In stepwise pyrolysis, a previous low temperature step is carried out in order to remove the chlorine of

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doi:10.1016/j.fuproc.2010.05.008

the original sample as HCl, which evolves as a gas; then the sample is pyrolysed in a conventional run [13,14]. In catalytic pyrolysis, some metal containing catalysts have been studied in order to prove their potential dual use, as pyrolysis catalysts and as HCl formation inhibitors. Blazsó et al. [15] studied the inhibition of HCl formation by using several metal containing catalysts in liquid phase contact (LPC). Recently some research on catalytic dechlorination in vapour phase contact (VPC) has also been done [16]. Finally, the addition of adsorbents to the sample reduces the HCl emission since the evolved HCl is trapped by means of physical and/or chemical adsorption and retained in the solid fraction. Several materials as biomass constituents [17,18], petrochemical residues [19] and alkaline adsorbents ($CaCO_3$, CaO, $Ca(OH)_2$, Na_2CO_3, $NaHCO_3$) [20] have been used as HCl adsorbents.

However, most of these studies have been done pyrolysing PVC alone or simple polymer mixtures; only a few authors have applied dehydrochlorination methods to mixtures as complex as that used in this paper [21,22]. Additionally most of the studies focus only on the chlorine content of the pyrolysis products and no information is given about the influence of the dechlorination methods on the complete properties and characteristics of the liquid fuels obtained. In this paper two of the dechlorination methods (stepwise and addition of adsorbents) have been studied, applying them to a PVC containing plastic mixture which simulates the composition of complex real plastic waste streams. The distribution of chlorine among the products is presented and also a detailed characterization of such products. Additionally, the thermal behaviour of PVC has been studied by means of thermogravimetric analyses in order to determine the best conditions for the dehydrochlorination of the PVC containing plastic mixture.

2. Materials and methods

2.1. Materials

The following materials were used to prepare the plastic mixture for the experiments: virgin PS, PE and PP provided by Spanish chemical companies, a type of PVC typically used for rigid transparent applications provided by a PVC products manufacturing Spanish company and waste PET coming a Spanish plastic recycling company. All the plastic materials were used in pellet size (≈3 mm) for the pyrolysis experiments; additionally finely ground samples (≤1 mm) were prepared both for the thermogravimetric studies and for characterization purposes. Commercial $CaCO_3$ powder with a purity grade >98.5% was used as adsorbent.

The proportions used in the plastic mixture can be seen in Table 1. This composition was established characterizing real samples rejected from an industrial plant located in Amorebieta, in the north of Spain [2,3], and based on the composition proposed by other authors as representative of municipal plastic wastes in Europe [23–25]. The characterization results of both PVC alone and the plastic mixture are presented in Table 2. The chlorine content of the PVC sample is 36.3 wt.%, which is somewhat lower than the theoretical expected value according to the PVC chemical formula (56.8 wt.%); this is most probably due to the fact that the PVC sample is not a PVC pure resin but a PVC product which contains several additives apart from the PVC polymer.

Table 1
Composition of the plastic mixture pyrolysed.

Material	wt.%
PE	40
PP	35
PS	18
PET	4
PVC	3

Table 2
Moisture, ash and elemental composition (wt.%) and GCV (MJ kg^{-1}) of PVC and the plastic mixture pyrolysed.

Sample	PVC	Plastic mixture
Moisture	0.2	0.1
Ash	0.0	0.0
C	44.4	84.7
H	5.7	12.5
N	0.2	<0.1
Cl	36.3	1.1
Others[a]	13.2	1.5
H/C ratio	1.5	1.8
GCV	26.0	43.9

[a] By difference.

2.2. Experimental

The thermal behaviour of PVC alone was studied using a Mettler Toledo TGA/SDTA851 analyser. The analyses were conducted with 7.5 mg samples, which were heated under nitrogen flow (50 mL min^{-1}) to 600 °C at a rate of 20 °C min^{-1}. The temperatures of the maximum degradation rates ($T\max_1$ and $T\max_2$) were determined from the derivative thermogravimetric (DTG) plot. The thermal behaviour of PVC in the mixture (in presence of all the other plastics) was studied with a LECO TGA-500 analyzer since larger samples were necessary for chlorine determination after the dehydrochlorination step. In this case, a total sample mass of 0.5 g was heated at a rate of 20 °C min^{-1} to the dehydrochlorination temperature and nitrogen was passed through at a rate of 50 mL min^{-1} during the analysis.

The pyrolysis experiments were carried out at 500 °C in nitrogen atmosphere, using an unstirred stainless steel 3.5 dm^3 reactor. Previous studies carried out by the authors [26,27] with other polymeric wastes (scrap tyres, automobile shredder residues, etc.) indicated that in the mentioned installation, 500 °C was the optimum temperature for treating such type of wastes by pyrolysis, since at lower temperatures complete decomposition of the organic matter was not achieved, and at higher temperatures the slight increase in gas yield was indeed counterbalanced by a detrimental effect on the liquid yield, so that 500 °C was chosen as the process optimal temperature for the samples under investigation.

Three types of experiments have been carried out. 1) A conventional experiment in which 100 g of the sample were placed into the reactor, which was then sealed. Nitrogen was passed through at a rate of 1 dm^3 min^{-1} and the system was heated at a rate of 20 °C min^{-1} to 500 °C, and maintained there for 30 min. It has been proved by the authors that in the mentioned installation at 500 °C after 30 min no more pyrolysis products evolve from the reactor [28–30]. During each run the vapours leaving the reactor flowed to a series of running water cooled gas–liquid separators where the condensed liquids were collected. The uncondensed products were passed through an activated carbon column and collected as a whole in Tedlar plastic bags, to be afterwards tested by gas chromatography. The experimental set-up can be seen in Fig. 1. 2) Stepwise pyrolysis, in which a previous dehydrochlorination step was carried out at 275 °C or at 300 °C during 30, 60 and 120 min and then the temperature was raised at 20 °C min^{-1} to 500 °C to complete the pyrolysis process. 3) Adsorption experiments in which 4.65 g $CaCO_3$ were added to the sample and then a conventional run was carried out. The reason why $CaCO_3$ was chosen as adsorbent was that it is a cheap product which could be appropriate to be used in an industrial scale. The amount of $CaCO_3$ used corresponds to an stoichiometric relation Ca:Cl of 3:1, which has been proposed by other authors [20,31] as enough to achieve an efficient HCl capture.

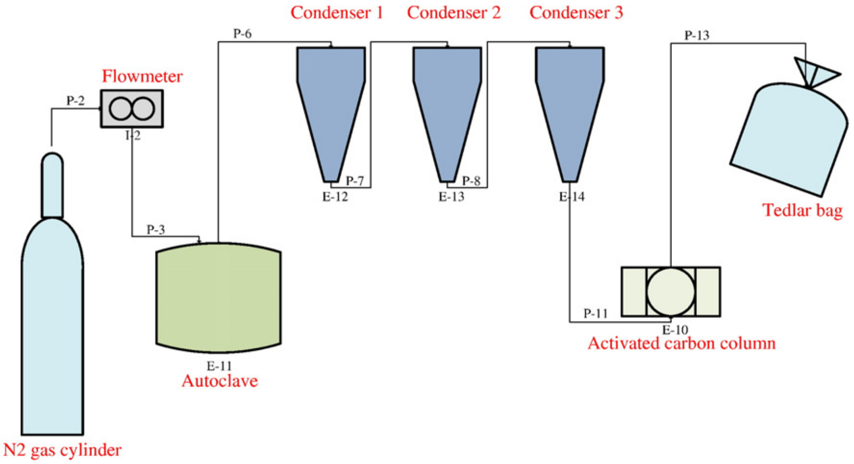

Fig. 1. Flow sheet of the experimental set-up used.

The amount of solids (residues in the reactor) and liquids obtained were weighed and the pyrolysis yields were calculated as weight percentage with respect to the raw material pyrolysed. In the experiments carried out with $CaCO_3$ the amount of input $CaCO_3$ was subtracted from the amount of total solids remaining in the reactor and the yield was calculated with respect to input plastic material (without $CaCO_3$); although some $CaCO_3$ may have been converted to $CaCl_2$, this calculation was considered accurate enough to estimate the solid pyrolysis yields. Gas yields were normally determined by difference. In some experiments specifically devoted to directly quantify the amount of gases, a closure of the mass balance of about 90 wt.% was obtained.

2.3. Analytical techniques

Both the raw materials and the solid and liquid pyrolysis products obtained were thoroughly characterized using the following analytical techniques. The moisture and ash contents of the samples were determined by thermogravimetric analysis according to D3173-85 and D3174-82 ASTM standards respectively, and the elemental composition with an automatic CHN analyser. Method 5050 of the Environmental Protection Agency (EPA) of the United States was used for chlorine determination. The gross calorific value (GCV) was determined with an automatic calorimetric bomb. Additionally, pyrolysis liquids were also analysed by gas chromatography coupled with mass spectrometry detector (GC–MS). Concerning pyrolysis gases, they were analysed by means of a gas chromatograph coupled with a thermal conductivity and a flame ionization detectors (GC-TCD/FID). The GCV of the gases was theoretically calculated according to their composition and to the GCV of the individual components.

3. Results and discussion

3.1. Thermogravimetric analyses

The thermal degradation of PVC takes place by means of “side group elimination”, a two-stage process in which the polymer chain is first stripped of molecules attached to the backbone of the polymer, leaving an unsaturated chain that is further degraded. The first stage takes place around 300 °C and the second one at around 470 °C [e.g. 31–33]. In this paper similar decomposition temperatures are obtained.

In order to study the quantitative loss of chlorine of PVC depending on the dehydrochlorination temperature and time, additional TG analyses with greater samples, whit which chlorine could be determined after dehydrochlorination, were conducted; the results are presented in Table 3.

Table 3 shows the quantitative chlorine loss at different temperatures and times. It can be seen that almost all the chlorine (≈99 wt.%) is lost at 300 °C while lower chlorine removal is achieved at lower temperatures even when greater times were used. It can be seen that after 30 minutes at 300 °C, PVC weight loss was 54.1 wt.%, which is greater than the chlorine content of the original sample (36.3 wt.%). It has been reported in the literature that the dehydrochlorination of PVC is accompanied by the formation of benzene, toluene, naphthalene and other aromatic compounds [6,33,34]. Jiang et al. [31] found also some H_2O and CO_2 among the products of the first decomposition stage of PVC, so this may be the reason why a greater loss than the expected one was obtained in this study at 300 °C and 30 min. These same conditions (300 °C and 30 min) were applied to each of the individual plastics and to the plastics mixture. The results, total weight loss with respect to input material and Cl loss with respect to total chlorine, are presented in Table 4. It has been included in this table the theoretical losses calculated based on the results of the individual losses.

Table 4 shows that the total weight loss as well as the chlorine loss of the plastics mixture is lower than the theoretical calculated value. Therefore, there must be some kind of interaction among the plastics when they are decomposed together. It has been reported by many authors [11,12,14,33,35] that during thermal degradation of plastics interactions among the components take place. Wang et al. [16] studied the dehydrochlorination of PVC/PE, PVC/PP and PVC/PS mixtures and concluded that the dehydrochlorination rate of PVC depends on the presence of other polymers, obtaining the lowest dehydrochlorination yield when PVC is pyrolysed together with polystyrene. It can also be seen in Table 4 that the weight loss of the other plastics was very low, being PS the plastic component which experimented the highest weight loss (3.3 wt.%); this is in agreement with the findings of other authors [36] who have reported that PS decomposition starts at temperatures quite close to 300 °C. These results show that a previous low temperature dehydrochlorination step can be applied previous to pyrolysis without a significant loss of sample.

Table 3
Effect of time and temperature on PVC dehydrochlorination in TGA.

Temperature (°C)	Time (min)	Total weight loss[a] (wt.%)	Cl loss[b] (wt.%)
250	90	41.1	94.0
250	120	43.7	94.8
275	60	50.4	96.9
300	30	54.1	99.2

[a] With respect to the sample weight.
[b] With respect to chlorine.

Table 4
Weight and chlorine loss of the individual plastics and of the mixture (TGA 300 °C, 30 min).

Sample	Weight loss (wt.%)	Chlorine loss (wt.%)
PE	0.7	–
PP	0.3	–
PS	3.3	–
PET	0.8	–
PVC	54.1	99.2
Mixture	2.5	97.9
Theoretical mixture loss	2.7	99.2

3.2. Pyrolysis experiments and characteristics of the products obtained

3.2.1. Pyrolysis yields

The liquid, gas and solid yields (weight %), obtained with the different dehydrochlorination alternatives are presented in Table 5. The results are the mean value of three pyrolysis runs carried out in the same conditions and which did not differ more than three points in the percentage. In the table, the two numbers after "stepwise" are the temperature and the time of the dehydrochlorination step respectively. The results obtained in a conventional run have also been included in order to analyse the influence of the dehydrochlorination methods in the products yields.

It can be seen that a decrease in liquid yields and an increase in gas yields was produced when stepwise pyrolysis was applied. This is in accordance with a study carried out by Janik et al. [37] who pyrolysed PE/PVC, PP/PVC and PS/PVC mixtures in stepwise mode. They concluded that the increase in gas yield was due to the greater HCl evolution; however, in this study the chlorine content in the gas fraction after stepwise pyrolysis was not high enough to produce such gas yield increase; therefore it can be suggested that, although no significant weight loss is produced in the previous low temperature step, some partial thermal cracking of the polymers and subsequent reorganization of their structures is produced, and this promotes the gas generation in the subsequent pyrolysis step.

The addition of $CaCO_3$ to the sample had even a greater influence on the gas yield, probably as a result of the stronger cracking that is produced due to the hot spots generated in the reaction between HCl and $CaCO_3$, yielding calcium chloride ($CaCl_2$) which remains in the solid fraction; the reaction between HCl and Ca-based additives has been reported by several authors [20,31,34]. However, Table 5 shows that when $CaCO_3$ was combined with the dehydrochlorination step almost no gas increase was produced, probably because in this case the reaction between HCl and $CaCO_3$ took place in the previous 300 °C step, so that such hot spots are not produced in the following pyrolysis step when the other plastics are being cracked and the system is more sensitive to small changes in the pyrolysis conditions.

Table 5 shows that in all the cases, a small quantity (0.6–1.3 wt.%) of solid residue was obtained although no inorganic material was contained in the original sample (see Table 2); this is attributed to char formation, due to secondary repolymerization reactions among the polymer derived products. Char formation in pyrolysis of polymeric wastes is a well documented fact which has been reported and studied before by the authors [2,3,26,27] as well as by many other research groups [38–41].

Table 5
Pyrolysis yields (wt.%).

Method	Liquids	Gases	Solids
Conventional	65.2	34.0	0.8
Stepwise 275/30	58.6	40.1	1.3
Stepwise 300/30	61.7	37.7	0.6
Stepwise 300/60	58.2	40.2	1.6
Stepwise 300/120	59.5	39.3	1.2
$CaCO_3$	46.6	54.4	1.2
Stepwise 300/60 + $CaCO_3$	62.4	36.6	1.0

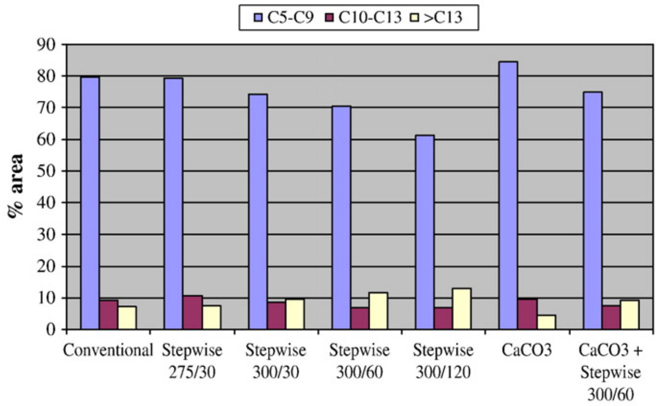

Fig. 2. Pyrolysis liquids separated by atom carbon number (% area).

3.2.2. Characteristics of the liquids

The results obtained in GC–MS analyses of the pyrolysis liquids are presented in Figs. 2 and 3. Since liquids from pyrolysis of plastic wastes are usually a complex mixture of many hydrocarbons and with the aim of better analysing the effect of dehydrochlorination methods on the characteristics of pyrolysis liquids, all the compounds identified by GC–MS have been grouped in three categories according to their number of carbons: C5–C9, C10–C13 and >C13 (Fig. 2); additionally total aromatics, saturated and unsaturated compounds, and no identified compounds have been quantified (Fig. 3). When the match quality of the identification result provided by the MS search engine, was lower than 85%, the result was not considered valid and these compounds have been classified as "No identified" in Fig. 3. It has also to be mentioned that the maximum injection temperature of the GC equipment was 300 °C, so the products with higher boiling point were not determined. Thermogravimetric analyses at 300 °C showed that the liquids of the four samples contain about 20 wt.% of products with a boiling point higher than 300 °C. Therefore, the following discussion concerning GC–MS results corresponds only to the 80 wt.% of products with boiling points lower than 300 °C.

As it can be seen in Fig. 2, C5–C9 was the main fraction of the pyrolysis liquids obtained in all the pyrolysis experiments; this is a rather convenient characteristic with a view to potential applications liquids, since C5–C9 is the gasoline range atom carbon number. It can also be seen that dehydrochlorination methods played an important role in the quality of the liquids. Stepwise pyrolysis at 275 °C during 30 min hardly affected the liquids quality compared to those of the

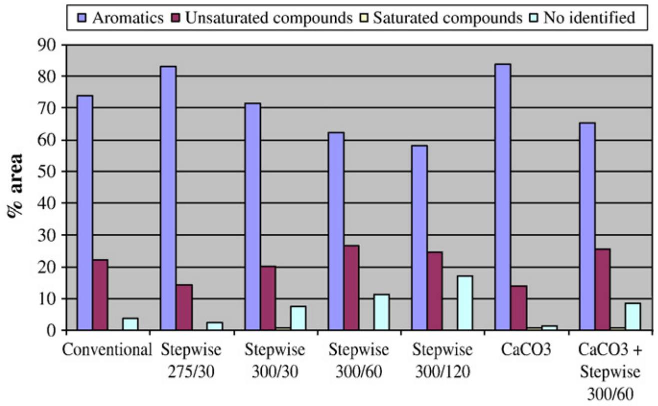

Fig. 3. Aromatics, saturated and unsaturated compounds and no identified compounds of pyrolysis liquids (% area).

Table 6
Main components of the pyrolysis liquids by means of GC–MS analysis (% area).

Method	Toluene	2,4-dymethylheptene	Ethylbenzene	Xylenes	Styrene	α-methylstyrene
Conventional	8.1	5.9	5.0	<3.0	48.4	4.2
Stepwise 275/30	11.6	3.5	6.3	<3.0	47.8	4.0
Stepwise 300/30	6.7	4.9	4.0	–	52.9	3.4
Stepwise 300/60	6.8	7.6	3.2	–	46.8	2.8
Stepwise 300/120	5.0	6.4	<3.0	–	43.4	2.7
CaCO3	12.5	4.1	7.1	3.1	46.2	4.6
Stepwise 300/60 + CaCO3	8.0	7.1	3.8	<3.0	47.0	3.2

conventional run; however, the stronger the dehydrochlorination conditions used (higher temperatures and times), the heavier the liquids obtained, ranging from 79.5 wt.% of C5–C9 and 7.6 wt.% of >C13 under stepwise 275/30 to 61.4 wt.% of C5–C9 and 13.2 wt.% of >C13 under stepwise 300/120. In fact, the liquid products obtained after pyrolysis when any of the 300 °C previous dehydrochlorination steps was performed, were semi-solid products at room temperature, while when stepwise 275/30 was used the products were low viscosity liquids. These results suggest again that although no visible effect was observed during the dehydrochlorination steps, plastic wastes may suffer partial degradation and/or reorganization of structures during these previous steps, which produces changes in the liquids generated in the subsequent pyrolysis step.

Concerning the addition of $CaCO_3$ to the plastic mixture, it leads to the generation of more C5–C9 compounds than in the conventional run. This may indicate that $CaCO_3$ has some type of catalytic effect on the pyrolysis process since more gases (see Table 5) and lighter and more aromatic liquids (see Figs. 2 and 3) were produced; the same influence on the pyrolysis process has been observed by the authors in a previous study about catalytic decomposition of plastic wastes [2]. The combination of stepwise pyrolysis and $CaCO_3$ addition produced less quantity of C5–C9 and more of >C13 than when $CaCO_3$ was used alone and the results were quite similar to those obtained when stepwise 300/30 was used. So when both methods were combined, the increase in C5–C9 and the decrease in >C13 fraction produced by $CaCO_3$ was counterbalanced by the decrease in C5–C9 and the increase in >C13 caused by the dehydrochlorination step at 300 °C and 60 min.

Fig. 3 shows that the pyrolysis liquids were mainly composed of aromatics and unsaturated hydrocarbons, while saturated compounds hardly appeared in this fraction. It has to be mentioned that although the plastic sample used in the experiments was mainly composed of polyolefins (PE and PP), the pyrolysis oils obtained in the conventional run had more than 70% area of aromatics. There are many references in the literature which report that aromatics are produced in the pyrolysis of polyolefins (e.g. [24,41–43]) although not in such a high proportion as in this study. On the contrary, Pinto et al. [44] obtained a quite high proportion of aromatics (35%) in the pyrolysis of polyolefin rich samples in a closed batch reactor even though the temperature used was rather low (430 °C), and Kaminsky and Kim [21] did obtain oils with an aromatic content similar or even higher than that obtained in this work when pyrolysed municipal plastic wastes in a fluidized bed reactor at high temperatures (715–730 °C). Additionally, in previous studies carried out by the authors [2,3] about pyrolysis of polyolefin rich samples in a batch reactor at 500 °C, proportions of aromatics as high as those presented in this paper were obtained. Therefore, it can be stated that aromatics are frequently formed in pyrolysis of polyolefin rich samples and that their proportion strongly depends on the reactor design and the operating conditions.

It has to be mentioned that the aromatic content of the liquid products was again influenced by the dehydrochlorination method used. In all the stepwise experiments, except 275/30, a lower proportion of aromatics and a greater proportion of unsaturated compounds than in the conventional experiment were obtained. This influence was more pronounced as stronger were the dehydrochlorination conditions. On the contrary, when $CaCO_3$ was used, a higher proportion of aromatics and a greater proportion of unsaturated compounds than in the conventional experiment were obtained. When both dechlorination methods were combined a halfway effect between both effects was observed. So these results indicate again that the dechlorination methods play important role in the characteristics of pyrolysis liquids.

The main individual components of the liquids obtained can be seen in Table 6. For the sake of reduction only those compounds with a percentage quantified area greater than 3% have been included. The compounds names correspond to the tentative assignments provided by the MS search engine and have been contrasted, as far as possible, with bibliographic data and occasionally with calibration standards.

Table 6 shows that in every case, styrene was the most abundant product with percentage areas ranging from 43% area when stepwise 300/120 was applied to almost 53% area when stepwise 300/30 was used. The next abundant products were toluene (5–12.5%) and 2,4-dymethylheptene (3–7.6%). The possibility of obtaining valuable hydrocarbons, such as styrene or toluene, from the plastic sample used, confers pyrolysis a potential attractive, even though it is known that the achievement of an efficient separation of such chemicals is not easy. It is difficult to analyse the effect of the dechlorination methods on the proportions of the individual components, however it can be seen that broadly speaking all the aromatics in Table 6 decreased when the time in the 300 °C dechlorination step was increased while 2,4-dymethylheptene (aliphatic) increased, and this is in agreement with the tendencies, concerning aromatics, previously presented in Fig. 3.

The elemental composition and gross calorific value of the pyrolysis liquids obtained in each experiment are presented in Table 7. Nitrogen has not been included since as it can be seen in Table 2 the original sample contained less nitrogen than the detection limit of the CHN analyzer.

It can be seen that there are no significant differences among the elemental compositions of the liquids, which are composed mainly of carbon (86–89 wt.%) and hydrogen (9–12 wt.%). The same tendency which was observed in the GC–MS analysis can be seen in the hydrogen content of the liquids, which contained more hydrogen as the stepwise conditions were stronger; as a consequence, the H/C ratio increases with the same tendency since carbon content was more stable. This fact is quite in concordance with the decrease in aromatics observed in Fig. 3. Chlorine content and evolution will be commented in the Section 3.3.

It is worth mentioning that pyrolysis oils have very high GCV, similar to those of conventional liquid fuels, so they may be considered as an

Table 7
Elemental composition (wt.%) and GCV (MJ kg^{-1}) of the pyrolysis liquids.

Method	C	H	Cl	Others[a]	H/C ratio	GCV
Conventional	86.5	11.3	0.5	1.5	1.6	43.3
Stepwise 275/30	87.7	11.0	0.3	1.0	1.5	42.7
Stepwise 300/30	86.2	11.5	0.3	2.0	1.6	42.7
Stepwise 300/60	87.0	12.0	0.2	0.8	1.6	43.6
Stepwise 300/120	86.4	12.2	0.2	1.2	1.7	43.9
CaCO3	87.7	10.9	0.6	0.8	1.5	42.7
Stepwise 300/60 + CaCO3	86.9	12.0	0.3	0.8	1.7	43.8

[a] By difference.

Table 8
GC-TCD/FID analysis (wt.%) and GVC (MJ kg^{-1}) of pyrolysis gases.

Method	Conventional	Stepwise 275/30	Stepwise 300/30	Stepwise 300/60	Stepwise 300/120	CaCO3	CaCO3 + stepwise 300/60
H_2	0.4	0.4	0.8	1.2	1.0	0.5	0.4
CO	0.7	1.2	1.1	0.9	1.0	1.3	1.2
CO_2	2.9	2.5	2.6	2.8	2.7	4.3	4.2
Methane	8.3	7.9	8.0	7.7	7.4	10.1	7.3
Ethane	10.0	8.1	9.7	9.8	9.1	10.3	9.3
Ethene	12.2	14.5	13.9	11.9	11.4	12.5	11.8
C3	29.1	28.5	33.0	28.3	28.7	26.2	28.0
C4	17.6	19.5	20.3	17.9	18.3	21.5	18.3
C5	9.5	8.0	8.7	10.6	11.8	7.4	10.4
C6	9.2	9.6	1.9	8.9	8.6	5.8	9.1
GCV	48.6	48.4	49.6	47.4	47.7	47.9	48.8

appropriate alternative to fossil fuels, since although in terms of energy efficiency the GCV of the oils is comparable to that of the original samples (see Table 2), the advantage of pyrolysis is that it transforms a solid plastic waste into more valuable and easily handled fuels.

3.2.3. Gas composition

Table 8 shows that pyrolysis gases are composed of hydrocarbons ranging from C1 to C6, hydrogen and some carbon dioxide and monoxide. Due to the difficulty in distinguishing among isomers from C3 to C6, such discrimination has not been made. The composition of the gases obtained is presented in a free chlorine basis, since in a potential industrial process the evolved HCl would be absorbed in alkaline solutions by means of wet scrubbers. It can be seen that there are no important differences among the gas compositions of all the experiments; in all cases, C3 and C4 fractions are the predominant ones, which is in agreement with the results of other authors who have proved that C3 and C4 are the main fractions of the gases of pyrolysis of LDPE, HDPE and PP [35,41,45]. Concerning the influence of the dechlorination method in gas composition, Table 8 shows that there is not a clear effect. Obviously there do is an effect in HCl content, which has not included in this table; it will be discussed in Section 3.3.

It is also worth noting that the GCV of all the gases is higher than that of natural gas (44 MJ kg^{-1}). For this reason pyrolysis gases may be used as gaseous fuels to supply the energetic demand of the process, and the surplus may be valorized.

3.2.4. Pyrolysis solids

The composition of the pyrolysis solids obtained is presented in Table 9. The solids obtained after the stepwise experiments hardly differ one another, and are composed by carbon, which corresponds to the carbonaceous product (char) previously mentioned, which is formed during pyrolysis, some hydrogen and a slightly variable quantity of other elements. Table 9 shows that the solids obtained when $CaCO_3$ was used were quite different, obviously because such solids contain CaCO3 and products derived from it, such as $CaCl_2$. It was concluded that such solid probably contained some $CaCl_2$ due to its high moisture content, since $CaCl_2$ is a very hygroscopic compound. The pyrolysis solids were in all cases, except when $CaCO_3$ was added, a carbonaceous material with very high GCV which could be used as an alternative to fossil solid fuels.

Table 9
Moisture, elemental composition (wt.%) and GCV (MJ kg^{-1}) of the pyrolysis solids.

Method	Moisture	C	H	Cl	Others[a]	H/C ratio	GCV
Conventional	0.2	93.7	3.5	0.3	2.3	0.4	38.2
Stepwise 275/30	0.3	90.4	3.4	0.3	5.6	0.4	39.0
Stepwise 300/30	0.2	91.7	2.8	0.1	5.2	0.4	37.5
Stepwise 300/60	0.8	92.0	3.4	0.1	3.7	0.4	38.9
Stepwise 300/120	0.9	91.8	3.3	0.2	3.8	0.4	38.6
CaCO3	9.7	22.7	1.7	6.7	59.2	0.9	7.8
Stepwise 300/60 + CaCO3	10.1	24.5	2.2	0.3	62.9	1.1	9.4

[a] By difference.

3.3. Distribution of chlorine in the pyrolysis products

Table 10 shows the percentage of chlorine in the products obtained after each experiment. It can be seen that the chlorine content of the liquids after a conventional pyrolysis run is 0.5 wt.%; this chlorine content in the liquid fraction is quite higher than that obtained by Sakata et al. [32] in the pyrolysis of PE/PP/PS/PVC mixtures, however, other study carried out by the same research group [22] concluded that the formation of chlorinated compounds in the liquid fraction is higher when the plastic mixture also contains PET; such is the case of the sample studied in this paper. In fact, the chorine content obtained in this paper in the conventional pyrolysis is quite similar to that obtained by Sakata et al. [46] in the pyrolysis experiments with real plastic waste samples which contained PET.

When the dehydrochlorination step at 300 °C during 60 min was used the lowest liquids chlorine content (0.2 wt.%) was obtained; a reduction of more than 50% of the liquids chlorine content of the conventional pyrolysis was achieved. In these conditions, the chlorine content in the solid fraction was also the lowest (0.1 wt.%) while gases chlorine content was as high as 2.5 wt.%. The chlorine content in the gases has been calculated by difference and corresponds to the chlorine which evolves as HCl in the first dehydrochlorination step; as it has be mentioned before, in an industrial process HCl could be absorbed in alkaline solutions by means of wet scrubbers and the gases generated in the subsequent pyrolysis step would be free of chlorine.

Concerning experiments with addition of $CaCO_3$, Table 10 shows that it is an effective method to trap chlorine in the solid, retaining up to 6.7 wt.% of chlorine in this fraction; on the other hand, in this case, the lowest chlorine content in the gases was obtained. This is quite in agreement with other authors who have used adsorbents in pyrolysis experiments [20,47]. However, the liquids chlorine content was the highest; therefore, unfortunately, the adsorbent does not hinder chlorine from going to the liquids. Yanik et al. [37] obtained similar results using Red Mud as a solid adsorbent of HCl; they concluded that the adsorbed HCl reacted with the degradation products of the polymers and became part of the liquids.

In order to find out if such effect could be avoided, a combination of both methods was carried out. This experiment gave rise to the

Table 10
Chlorine in the pyrolysis fractions (wt.%).

Method	Chlorine in liquids	Chlorine in gases[a]	Chlorine in solids
Conventional	0.5	2.2	0.3
Stepwise 275/30	0.3	2.3	0.3
Stepwise 300/30	0.3	2.4	0.1
Stepwise 300/60	0.2	2.4	0.1
Stepwise 300/120	0.2	2.5	0.2
CaCO3	0.6	0.9	6.7
Stepwise 300/60 + CaCO3	0.2	1.7	7.5

[a] By difference.

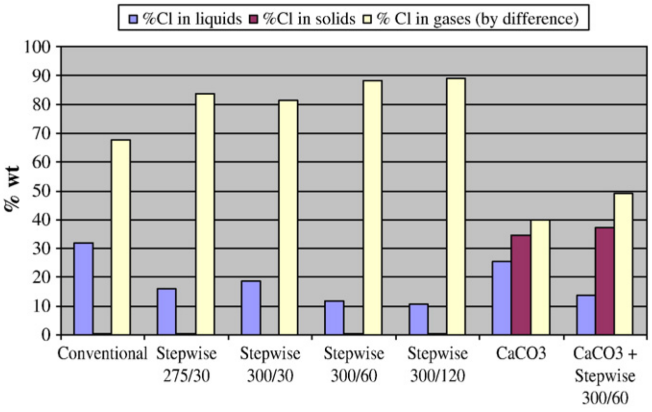

Fig. 4. Chlorine distribution among the pyrolysis fractions (wt.%).

highest adsorption of chlorine in the solid fraction (7.5 wt.%), probably because in the previous dehydrochlorination step there was time enough to adsorb HCl as it was being generated. Therefore in the combined method, liquids with chlorine content as low as in simple stepwise pyrolysis were obtained and less HCl went to the gaseous fraction. Beckmann et al. [20], who had also carried out pyrolysis experiments with adsorbents, concluded that if calcium chloride is formed in the char, it can be easily leach out by simple washing, avoiding chlorinated compounds generation in potential applications of char such as energy valorisation.

The chlorine weight % distribution among the pyrolysis fractions has been presented in Fig. 4. The figure shows that in the conventional pyrolysis run most of the chlorine (≈68 wt.%) went to the gaseous fraction as HCl; however, a significant quantity of this chlorine (≈32 wt.%) formed organochlorinated compounds that appeared in the liquid fraction. It can also be seen that stepwise pyrolysis enabled to remove almost 90 wt.% of the chlorine as HCl, decreasing the percentage of chlorine that went to the liquids to just 10 wt.%. When $CaCO_3$ was added to the plastic mixture, the percentage of chlorine that went to the gaseous fraction was drastically reduced but the percentage of chlorine which went to the liquids was only slightly reduced compared to the conventional run (≈25 wt.%). When both methods were combined, the chlorine distribution was similar to that of the $CaCO_3$ alone experiment but the percentage of chlorine that went to the gaseous and solid fractions was somewhat increased, while the percentage of chlorine that went to the liquids was reduced.

So at first sight, the combination of both methods seems to be the most effective alternative since liquids with chlorine content as low as in simple stepwise pyrolysis and gases with the lowest chlorine content are produced. However, it must be taken into account that whenever stepwise is used, most of the gaseous HCl is evolved in the previous dehydrochlorination step, so that in the subsequent pyrolysis step a HCl-free gas would be generated. Therefore, since the liquids chlorine contents are equivalent when stepwise is combined with $CaCO_3$ and when only stepwise is used, it is not worthwhile to add $CaCO_3$ since more solids, which in addition are contaminated with chlorine, are obtained.

4. Conclusion

Pyrolysis is an attractive alternative for recycling mixed plastic wastes. The liquid products obtained may be used as high GCV alternative fuels or as a source of valuable chemicals, such as styrene or toluene. 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 (char) may find applications such as solid fuel, pigment, activated carbon, low quality carbon black, etc.

Stepwise pyrolysis and/or addition of adsorbents can be used to reduce the chlorine content of the products generated in PVC containing plastic wastes pyrolysis. However, it must be taken into account that these alternatives also modify the characteristics and quality of the liquids obtained in the process.

The liquids chlorine content can be reduced more than 50 wt.% compared to conventional pyrolysis by means of a previous low temperature dehydrochlorination step. The higher the temperature and the time of such step is, the lowest the chlorine content of the liquid and solid fractions. Nevertheless, it was concluded that 300 °C and 60 min were the most appropriate conditions for the dehydrochlorination step, since increasing time from 60 to 120 min did not enhance the results. On the other hand, stepwise pyrolysis leads to the generation of liquids with heavier hydrocarbons and less aromatics, and this effect is greater as higher are the temperature and time.

Concerning the addition of $CaCO_3$, it was found to be an efficient method to retain the chlorine in the solid and it gave rise to the lowest generation of gaseous HCl. However, unfortunately, higher levels of chlorine were obtained in the liquids compared to conventional pyrolysis. On the other hand, $CaCO_3$ seems to have some kind of catalytic effect, yielding more gases, less liquids and a higher proportion of aromatics and C5–C9 fraction in the liquids.

The combination of both methods, although at first sight looks as the most effective alternative (low chlorine content in the liquids and the lowest HCl generation), is not worthwhile compared to simple stepwise pyrolysis since 1) liquids chlorine content are equally low in both cases, 2) HCl generation, though lower, is not avoided, so an absorption and neutralization unit will be anyway required, and 3) greater amounts of solids, which in addition are contaminated with chlorine, are obtained.

To summarize, the main conclusion is that a previous low temperature (300 °C) dehydrochlorination step, complemented with an appropriate HCl capture and neutralization unit, is a required stage of pyrolysis process whenever plastic wastes might contain PVC. Such step eliminates chlorine but in addition it has a significant influence on the characteristics of the pyrolysis oils. So when it comes to designing the process with the aim of obtaining liquids of a given quality, the operating conditions of both the pre-stage and the pyrolysis process itself should be taken into account.

Acknowledgements

The authors thank the Spanish Ministry of Education and Science (MEC) (CTQ 2007-67070/PPQ) as well as the Basque Country Government (ETORTEK 2007 IE07-207, GIC 07-09-IT-354-07 and Researchers' formation program — 2008) for financial assistance for this work.

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4.2. SIMULATED SAMPLE RUNS

4.2.3. Dechlorination of products (2 of 2)

Article: *Dechlorination of PVC in catalytic pyrolysis of packaging plastic wastes*

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Journal: *Journal of Hazardous Materials.*

State: *Under review.*

Abstract

PVC is frequently present in plastic wastes giving rise to the presence of chlorine in pyrolysis products, which is rather detrimental for their potential applications mainly due to chlorine environmental hazards. The use of zeolites has been proved to be beneficial for the pyrolysis process and it has been demonstrated that a low temperature dechlorination step prior to the pyrolysis process significantly reduces the chlorine content in the liquid products. In this paper the combination of both, catalyst and dechlorination step, is explored. A mixture of polyethylene (PE), polypropylene (PP), polystyrene (PS), poly(ethylene terephthalate) (PET) and poly(vinyl chloride) (PVC) has been pyrolysed in a 3.5 dm^3 semi-batch reactor at 440 ºC for 30 min using a ZSM-5 zeolite as catalyst. A previous low temperature (300 ºC) dechlorination step has been carried out both with and without catalyst. It has been proved that the application of such dechlorination gives rise to a 75 wt.% reduction of chlorine in the liquid fraction. However, such step has a negative influence on the catalyst, which loses some catalytic activity. The optimum procedure in terms of quality and Cl content of the products is first a low temperature step and then the catalytic pyrolysis step.

Keywords: stepwise pyrolysis, feedstock recycling, catalytic decomposition, plastic wastes, ZSM-5 zeolite, dechlorination.

1. Introduction

PVC is one of the most widely used polymers. Its polar nature, provided by the chlorine atom in its repeat unit, enables to combine this polymer with a much wider range of additives than any other polymer, yielding a wide range of plastic compounds with very different properties. Consequently, it can be used in a significant number of applications, ranking second in total thermoplastic worldwide production, just following polyolefins [1]. However, it is also the presence of chlorine in the PVC backbone the key concern when it comes to waste PVC management, due to the chlorinated compounds which can arise during waste treatment operations as a consequence of the molecular instability of PVC towards heat and light [2].

Nowadays PVC is mainly used in the construction sector, followed by electronic equipment and automotive applications. Although the use of this material for packaging applications has decreased during the last years, 4% of total packaging goods were estimated to be made of PVC in 2007, including thin-wall containers, small bottles, film, sheets and lids [3]. Since PVC is a minority product in packaging wastes, it is not specifically recovered from such wastes for recycling, as it is in the case of the construction PVC wastes [4]. For this reason the presence of PVC in rejected packaging wastes streams is still very common [5]. These rejected streams are the fractions of packaging wastes which cannot be mechanically recycled since they are composed of different and much intermingled plastic materials, and consequently, they are nowadays incinerated or landfilled.

Pyrolysis is a process which has received renewed attention in the last years for recycling plastic wastes, converting them in potentially useful liquids and gases. In the pyrolysis process (heating in an oxygen free atmosphere), the organic components of the material are decomposed generating liquid and gaseous products while the inorganic ingredients (fillers, metals, etc.) remain practically unaltered and free of the binding organic matter, allowing their separation to be recovered and reused. Therefore, pyrolysis is an attractive and alternative recycling technique for rejected plastics waste streams, provided that the formation of chlorinated compounds is prevented, since they are very detrimental for using pyrolysis products as fuels or chemical reactants.

The pyrolysis process can be improved by means of dechlorination methods which prevent the generation of chlorinated compounds when PVC containing samples are pyrolysed. The dechlorination methods more frequently reported in the literature are stepwise pyrolysis and pyrolysis with adsorbents. In stepwise pyrolysis, a previous low temperature step is carried out in order to remove chlorine from the original sample as HCl, which evolves as a gas at temperatures around 300 ºC; in a second step the sample is pyrolysed as in a conventional run. On the other hand, the addition of adsorbents to the sample reduces the HCl emission since the evolved HCl is trapped by means of physical and/or chemical adsorption and is retained in the solid fraction.

In a previous paper [6], the authors investigated these two dechlorination methods and applied them to the same sample as that used in this paper but in non-catalytic pyrolysis. The results obtained showed that with stepwise pyrolysis the lowest chlorine content in the liquid fraction was achieved. On the other hand, it is well known that the use of catalysts enhances the quality of pyrolysis products. Therefore, the objective of this paper is to study the effectiveness of the previous dechlorination step when catalyst is used in the pyrolysis process.

There is plenty of information in the literature about dechlorination in the thermal decomposition of PVC either alone or mixed with other plastics [e.g. 7-12]; on the other hand, zeolites (as catalysts in the pyrolysis of polymeric materials) have been reported to be effective for improving the quality of pyrolysis products as well as to enable to operate at milder pyrolysis conditions (lower temperatures and reaction times) compared to thermal pyrolysis [e.g. 13-16]. On the contrary, it is not easy to find information in the literature about the combined effects of both the dechlorination step and the catalyst together in the pyrolysis process. Most of the dechlorination studies of PVC mixtures carried out with catalysts up to now have focused on using the catalysts as adsorbents for the evolved HCl [17-18] or as HCl formation inhibitors [19-21]. To the best of our knowledge, only two papers, published by Zhou et al. [22] and Yanik et al. [23], have shown the combined effect of a previous low temperature step and the catalytic action, but using simple binary mixtures (PP/PVC, PE/PVC, PS/PVC) and with catalysts different from zeolites. Consequently, the novelty of this paper is the report of the behavior of zeolites in stepwise pyrolysis when the process is applied to a complex plastic mixture similar to real packaging waste streams, including an exhaust characterization of all the products obtained in the process.

2. Materials and methods

2.1. Raw materials and catalyst

A mixture of plastics which simulates the composition of real plastic waste streams rejected from industrial sorting plants was prepared for the pyrolysis experiments. The origin, application and proportions of each plastic in the mixture are presented in Table 1.

Table 1. Origin, application and proportions of the plastics used in the mixture

Plastic name	**Acronymus**	**Origin**	**State**	**Application**	**Proportion (wt.%)**
Polyethylene	PE	Repsol Química	Virgin	Household	40
Polypropylene	PP	Repsol Química	Virgin	General	35
Polystyrene	PS	Dow Chemical	Virgin	General	18
Poly(ethylene terephthalate)	PET	Remaplast S.A.[a]	Recycled	Bottles	4
Poly(vinyl chloride)	PVC	Gaiker[b]	Recycled	Bottles	3

[a] Spanish Company devoted to municipal plastics recycling
[b] Spanish Technology Centre dedicated to research and innovation

The composition of the sample was established based on the composition of real samples rejected from an industrial plant located in the north of Spain (Amorebieta), where the packaging wastes of the province of Biscay are sorted [5]. All the plastic materials were used in pellet size (≈3 mm) for the pyrolysis experiments. Additionally finely ground samples (≤1 mm) were prepared for characterization purposes; the composition and characteristics of the sample used for the pyrolysis experiments are shown in Table 2.

Table 2. Moisture, ash and elemental composition (wt.%) and HHV (MJ kg^{-1}) of the plastic mixture

Parameter	**Moisture**	**Ash**	**C**	**H**	**N**	**Cl**	**Others[a]**	**H/C ratio**	**HHV**
Value	0.1	0.0	84.7	12.5	<0.1	1.1	1.5	1.8	43.9

[a] By difference

The catalyst used for the pyrolysis experiments was a commercial ZSM-5 zeolite provided by Zeolist International; in all the experiments it was used as received and in a plastic/catalyst ratio of 10/1. Its main characteristics are presented in Table 3. The textural properties of the catalyst were determined by means of nitrogen adsorption-desorption isotherms at 77 K in AUTOSORB-1 Quantachrome equipment. Surface areas were calculated by means of BET equation and external surface areas were obtained applying the t-plot method. Total pore volume was measured at $P/P_o = 0.99$. The acidity of the catalyst was measured by temperature-programmed desorption (TPD) of ammonia with a Micromeritics AutoChem 2910 instrument.

Table 3. Textural and acid properties of the ZSM-5 zeolite

BET surface area ($m^2\ g^{-1}$)	412.0
External surface area (ESA) ($m^2\ g^{-1}$)	65.88
Micropore volume (MPV) ($cm^3\ g^{-1}$)	0.100
Total pore volume (TPV) ($cm^3\ g^{-1}$)	0.397
Total acidity (mmol $NH_3\ g^{-1}$)	0.176

2.2. Experimental

The pyrolysis experiments were carried out using an unstirred stainless steel 3.5 dm^3 reactor in semi-batch operation. In all the experiments, 100 g of plastic sample were placed into the reactor; nitrogen was passed through at a rate of 1 $dm^3\ min^{-1}$ through all the run, and the vapors leaving the reactor flowed to a series of running water cooled gas-liquid separators where the condensed liquids were collected. The uncondensed products were passed through an activated carbon column and collected as a whole in Tedlar plastic bags. The experimental set-up used in the experiments is presented in Figure 1.

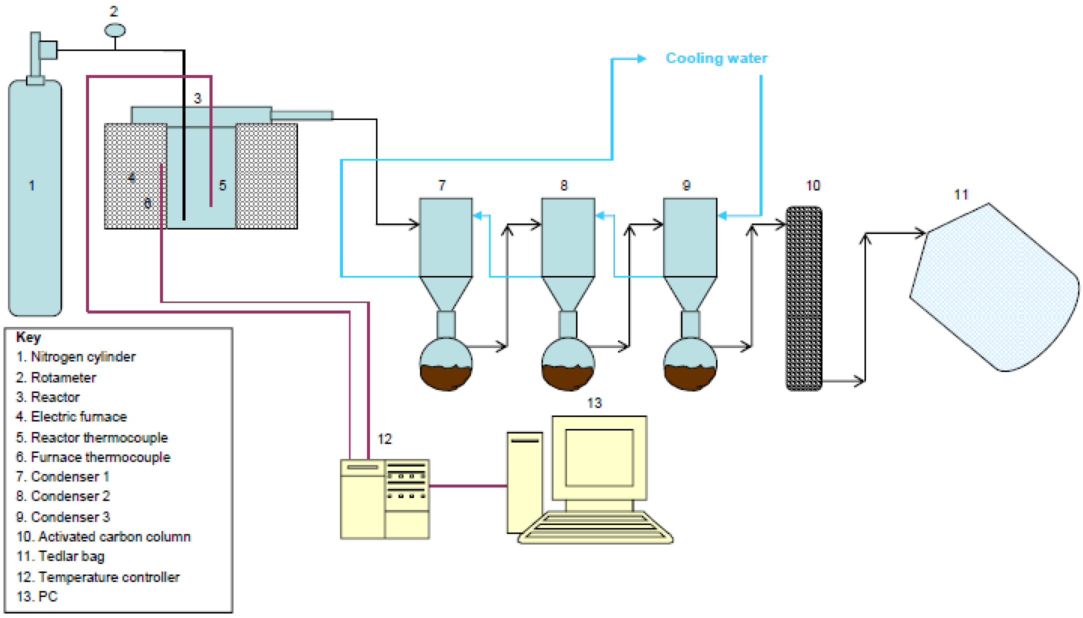

Figure 1. Flow sheet of the experimental set-up used

Three different pyrolysis methods were explored. 1) “Conventional catalytic pyrolysis”, in which the plastic sample was mixed with the catalyst and the system was heated at a rate of 20 ºC min^{-1} to 440 ºC, and maintained there for 30 min. 2) “Catalytic stepwise pyrolysis”, in which the plastic sample was mixed with the catalyst, a previous dechlorination step was carried out at 300 ºC during 60 min and then the temperature was raised at 20 ºC min^{-1} to 440 ºC to complete the pyrolysis process. 3) “Non catalytic dechlorination step + catalytic pyrolysis”, in which the dechlorination step was applied to the plastic sample alone (without catalyst) and then the catalyst was added, carrying out the final pyrolysis as in the other methods. In order to add the catalyst it was necessary to cool down the system with the plastic sample to room temperature after the dechlorination step, extract the dechlorinated melted sample, freeze it in liquid nitrogen, grind it in a mill, mix it with the catalyst and place them together again in the reactor, to carry out a conventional experiment. Additionally, the results obtained in a “conventional thermal pyrolysis” (which consisted in heating the plastic sample without catalyst at a rate of 20 ºC min^{-1} to 440 ºC followed by a dwell of 30 min) have been included in Tables 4 and 8 in order to satisfactory explain the results obtained in the three pyrolysis methods explored in this paper.

The amount of solids remaining in the reactor and the liquids condensed in the gas-liquid separators were weighed after pyrolysis and the pyrolysis yields were calculated as weight percentage with respect to the raw material pyrolysed. The amount of input zeolite was subtracted from the amount of total solids remaining in the reactor and the solid yield was calculated with respect to input plastic material (without catalyst). Gas yields were normally determined by difference; in some experiments specifically devoted to directly quantify the amount of gases, a closure of the mass balance of about 90 wt.% was obtained. The results of the pyrolysis yields which are presented in "Results and Discussion" section of this paper are the mean value of at least three pyrolysis runs carried out in the same conditions and which did not differ more than three points in the percentage.

2.3. Analytical techniques

Both the raw material and the solid and liquid products obtained were characterized using the following techniques. The moisture and ash contents of the samples were determined by thermogravimetric analysis according to D3173-85 and D3174-82 ASTM standards respectively, and the elemental composition with an automatic CHN analyzer. Method 5050 of the Environmental Protection Agency (EPA) of the United States was used for chlorine determination. The higher heating value (HHV) was determined with an automatic calorimetric bomb.

Additionally, pyrolysis liquids were also analyzed by gas chromatography coupled with mass spectrometry detector (GC-MS). When the match quality of the identification result provided by the MS search engine was lower than 85%, the result was not considered valid and these compounds are classified as "Not identified" in this paper. Concerning pyrolysis gases, they were analyzed by means of a gas chromatograph coupled with a thermal conductivity and a flame ionization detector (GC-TCD/FID). The HHV of the gases was theoretically calculated according to their composition and to the HHV of the individual components.

3. Results and Discussion

3.1. Pyrolysis yields

The liquid, gas and solid yields (weight %), obtained with the three mentioned pyrolysis methods and those of the conventional thermal run are presented in Table 4.

Table 4. Pyrolysis yields (wt.%)

METHOD	Liquids	Gases	Solids
Conventional thermal pyrolysis	79.3	17.7	3.0
Conventional catalytic pyrolysis	56.9	40.4	3.2
Catalytic stepwise pyrolysis	69.0	29.0	2.0
Non-catalytic dechlorination step + catalytic pyrolysis	56.8	41.2	2.0

If the conventional thermal and conventional catalytic pyrolysis experiments are compared, it can be stated that the catalyst plays an important role in pyrolysis products distribution, producing more gases and fewer liquids than in the thermal run. A more thorough discussion about the effect of ZSM-5 zeolite in pyrolysis of plastic wastes has been presented elsewhere [24]. When the previous dechlorination step is carried out in presence of the catalyst, a somehow intermediate behavior in pyrolysis yields can be observed, producing an increase in liquid yield and a decrease in gas yield compared with the conventional catalytic experiment. This fact suggests that the zeolite losses some activity during the dechlorination step.

In the previous paper published by the authors about dechlorination in thermal pyrolysis [6], the effect of the previous step was just the opposite; it promoted gas generation to the detriment of liquid production. In that work it was suggested that some partial thermal cracking of the polymers and subsequently some reorganization of their structures was produced in the previous step, leading to a greater gas generation in the later pyrolysis step.

This partial cracking of the polymers together with the fact that the plastic sample is melted during the dechlorination step could be the reason why the catalyst activity is lost in the actual work, since the cracked and melted fragments may physically block the catalyst pores during the dechlorination step. Consequently, the catalytic effect of the zeolite in the subsequent pyrolysis step could be hindered. In addition, Table 4 shows that when the catalyst is added to the sample after the dechlorination step, almost the same yields as in the conventional catalytic experiment are obtained, which confirms that the dechlorination step caused the loss of activity of the zeolite.

Table 4 shows that in every case, a small quantity (2.0-3.2 wt.%) of solid residue was obtained. The solid residues were a mixture of unconverted plastic and char, a carbonized product formed during the pyrolysis process. The formation of char in pyrolysis of polymeric materials is a very well documented fact which has been reported before by the authors [25-26] as well as by other research groups [27-28]. The solid residue in the conventional catalytic run is somewhat higher than in the other runs, which may indicate that the previous low temperature step somewhat prevents the formation of char.

3.2. Characteristics of the pyrolysis liquids

The results obtained in GC-MS analyses of the pyrolysis liquids are presented in Figures 2, 3 and 4. Figure 2 shows all the compounds identified by GC-MS grouped in three categories according to their carbon number: C5–C9, C10–C13 and >C13; total aromatics, no aromatics and no identified compounds are presented in Figure 3 and the main components of pyrolysis liquids are shown in Figure 4.

Figure 2 shows that in a conventional catalytic experiment, C5-C9 is the main fraction of the pyrolysis liquids ranging more than 80% area. The formation of light hydrocarbons in the pyrolysis of polyolefinic plastic wastes in presence of ZSM-5 zeolite has been reported before [29-30]; Serrano et al. [30] suggested that in the pyrolysis of polyolefins this catalyst leads the reaction through an end-chain scission pathway, yielding light hydrocarbons as primary products, instead of the typical polyolefinic random scission pathway which is followed in thermal pyrolysis.

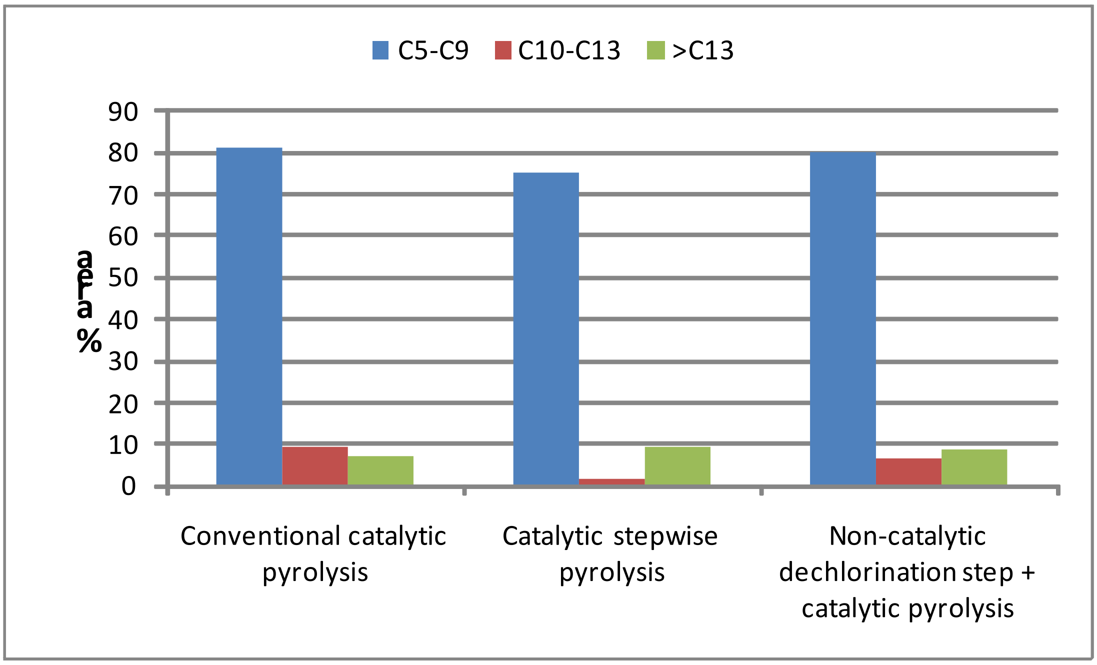

Figure 2. C5-C9, C10-C13 and >C13 fractions of the pyrolysis liquids (% area)

When the dechlorination step is carried out in presence of the zeolite, the percentage of light (C5-C9) and medium (C10-C13) hydrocarbons significantly decrease (75.5 and 1.5% area respectively), and the yield of heavy hydrocarbons increases up to 9.5% area. This fact is in agreement with the previously mentioned loss of activity of the catalyst that is produced during the previous step. In fact, when the catalyst is added after the dechlorination step, the C5-C9 yield is quite similar to that of the conventional catalytic run. However, a small difference can be observed in the C10-C13 and >C13 fractions between those two experiments, since after the dechlorination step the heavy hydrocarbons fraction is higher than in the case of the conventional catalytic pyrolysis (8.9 and 7.0% area respectively). The very same occurred in the previous study of the authors [6], when stepwise pyrolysis was compared to conventional pyrolysis but both without using catalyst. It was then suggested that some degradation and reorganization of polymer structures takes place during the previous step, leading to different pyrolysis pathways and consequently to different pyrolysis products. Whenever previous step is used, higher >C13 yield is obtained. It seems plausible that such incipient degradation enables larger molecules to evolve from the reactor in the subsequent pyrolysis step. This reasoning may explain also the fact previously mentioned that lower solid residue is obtained when the previous dechlorination step is carried out.

In Figure 3 the compounds in pyrolysis liquids have been grouped in aromatics, non-aromatics and not identified. Figure 3 shows that ZSM-5 conventional catalytic pyrolysis liquids have a highly aromatic nature (>90% area). This seems at first sight quite surprising since the plastic sample used in this work is mainly composed of polyolefins; however, it is a consequence of the strong aromatization power of the zeolite used. Many other authors [e.g. 15, 31], as well as the authors in a previous work [24], have obtained liquids with high levels of aromatics when ZSM-5 zeolite is used, which is attributed to the high number of Brönsted acid sites contained within this zeolite, which promote aromatization reactions.

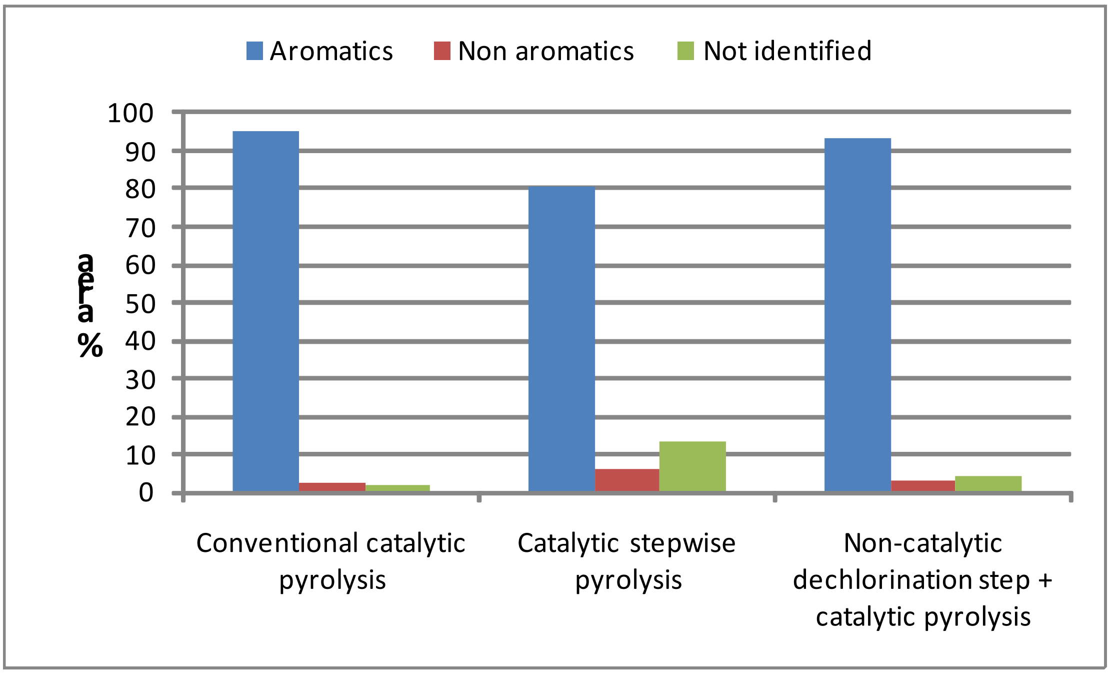

Figure 3. Aromatic, non aromatic and not identified compounds in pyrolysis liquids (% area)

Figure 3 also shows that when the dechlorination step is carried out with the catalyst mixed with the sample, the production of aromatics is lower than in conventional catalytic pyrolysis. But when the catalyst is added after the previous dechlorination step is almost as high as in the conventional catalytic run. It is also remarkable that the application of the dechlorination step produces higher “not identified” compounds yield than in the conventional pyrolysis run, especially in the stepwise catalytic experiment (13.4% area). Quite similar results were obtained by the authors in their previous paper about dechlorination in thermal pyrolysis [6], in which the yield of “not identified” compounds after dechlorination step at the same conditions was also higher than 10% area. This may be because, as it has been mentioned before, when the previous step is used, somewhat larger molecules evolve from the reactor and the match quality of the identification provided by the MS search engine is probably less reliable for larger molecules.

The main components of the pyrolysis liquids are presented in Figure 4.

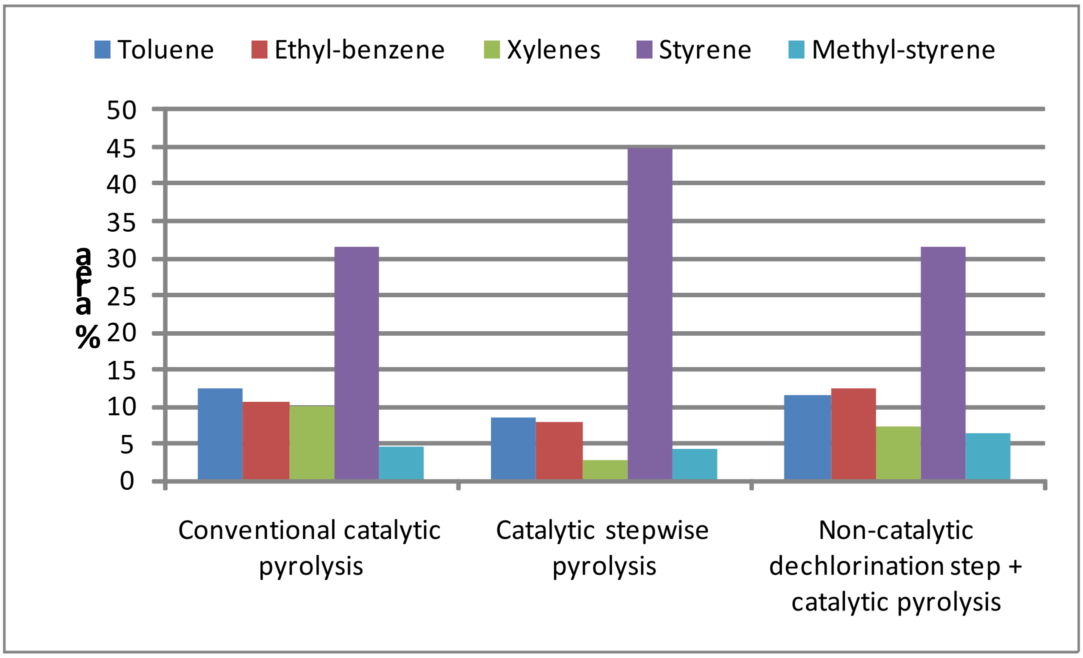

Figure 4. Main components of the pyrolysis liquids (% area)

It can be seen that once more, the liquids derived from the conventional catalytic pyrolysis and the non-catalytic dechlorination step + catalytic pyrolysis experiments produced quite similar results. Both yielded more than 30% area of styrene and around 10% area of toluene and ethyl-benzene. On the contrary, the catalytic stepwise pyrolysis experiment yielded much more styrene (≈45% area) and smaller quantities of the other components compared to the two other experiments. Serrano et al. [32] have reported that in the acid catalyzed cracking of PS different products like ethyl-benzene or methyl-benzenes can be formed instead of styrene due to the carbenium nature of the process, while when no catalyst is used styrene and its corresponding dimers and trimers are the main products. In accordance with Serrano, the tendency shown in the stepwise catalytic experiment of producing more styrene and lower quantities of monoaromatics could be due to the fact that the catalyst has lost its activity during the dechlorination step. Anyhow, the yield of styrene and monoaromatics is rather high in all the cases, and this possibility of producing valuable chemicals from plastic wastes confers pyrolysis an added value as recycling process.

The elemental composition and higher heating value of the pyrolysis liquids obtained in each experiment are presented in Table 5.

Table 5. Elemental composition (wt.%) and HHV (MJ kg^{-1}) of the pyrolysis liquids

EXPERIMENT	**Conventional catalytic pyrolysis**	**Catalytic stepwise pyrolysis**	**Non-catalytic dechlorination step + catalytic pyrolysis**
C	87.6	87.7	83.9
H	11.2	11.9	11.9
Cl	1.2	0.3	0.3
Others[a]	0.0	0.1	3.9
H/C Ratio	1.5	1.6	1.7
HHV	42.2	44.4	43.3

[a] By difference

It can be seen that there are no significant differences among the elemental compositions of the liquids, which are mainly composed of carbon (84-88 wt.%) and hydrogen (9-10 wt.%). It is also worth noting that surprisingly the carbon content of the liquid obtained in the non-catalytic dechlorination step + catalytic pyrolysis experiment was lower than that obtained in the other two experiments, and consequently the H/C ratio is higher. This is an unexpected result which is in conflict with the aromatics contents reported in Figure 3, since the liquids of this experiment have similar contents of aromatics as the conventional catalytic experiment and therefore they should have similar H/C ratios. No explanation to this fact has been found at the moment.

It is worth mentioning that in all the cases pyrolysis oils have very high HHV, similar to those of conventional liquid fuels, so they may be considered as an appropriate alternative to fossil fuels. Obviously, the presence of chlorine in the liquids is rather detrimental for this application. A thorough discussion concerning chlorine content and its evolution will be commented in the section 3.5.

3.3. Gas composition

The composition of the pyrolysis gases is presented in Table 6. It has been calculated in a free chlorine basis, since in a potential industrial process the evolved HCl should be separated before the application of the gases. The chlorine content of the gases will also be discussed in section 3.5.

Table 6. GC-TCD/FID analysis (wt.%) and HHV (MJ kg^{-1}) of pyrolysis gases

EXPERIMENT	**Conventional catalytic pyrolysis**	**Catalytic stepwise pyrolysis**	**Non-catalytic dechlorination step + catalytic pyrolysis**
H_2	0.8	0.6	0.7
CO	0.7	0.3	0.4
CO_2	4.9	2.9	2.6
C1-C2	24.6	10.9	31.6
C3-C4	57.0	60.4	61.7
C5-C6	11.9	25.0	3.0
HHV	46.0	48.4	49.4

Table 6 shows that pyrolysis gases are mainly composed of hydrocarbons ranging from C1 to C6, together with some hydrogen and some carbon dioxide. The hydrocarbons have been separated in three fractions (C1-C2, C3-C4 and C5-C6) in order to better analyze the effect of the different pyrolysis methods used. C3-C4 hydrocarbons are the main fraction and have comparable yields in all the experiments, which is in agreement with the results of other authors who have also proved that C3 and C4 are the main fractions of the gases of pyrolysis of polyolefins when ZSM-5 zeolite is used [33-34].

Concerning the influence of the different dechlorination methods in gas composition, Table 6 shows that the lowest proportions of light hydrocarbons (C1-C2) and the highest of heavy hydrocarbons (C5-C6) were obtained in the stepwise catalytic pyrolysis run (10.9 wt.% and 25 wt.% respectively). This is quite in accordance with the previous results concerning the characteristics of the liquids, and it is attributed to the fact that the zeolite losses its activity during the dechlorination step. When the catalyst is added after such step (non-catalytic dechlorination step + catalytic pyrolysis), the highest C1-C2 fraction proportion (31.6 wt.%) and the lowest C5-C6 hydrocarbons proportion (3.0 wt.%) is obtained, therefore even stronger cracking than in the conventional catalytic process is produced, so the previous step somehow facilitates the subsequent cracking action of the catalyst.

It has to be mentioned that in this case, more than 90 wt.% of pyrolysis gas is composed of C1-C4 hydrocarbons, which confers this gas fraction a remarkable HHV (49.4 MJ kg^{-1}). Anyway, the gases obtained in all the pyrolysis runs have a HHV comparable to that of the natural gas (48-53 MJ kg^{-1}), therefore pyrolysis gases have a great potential for power generation.

3.4. Pyrolysis solids

The composition of the pyrolysis solids is presented in Table 7.

Table 7. Moisture, elemental composition (wt.%) and HHV (MJ kg^{-1}) of the pyrolysis solids

EXPERIMENT	**Conventional catalytic pyrolysis**	**Catalytic stepwise pyrolysis**	**Non-catalytic dechlorination step + catalytic pyrolysis**
Moisture	0.7	1.0	0.9
C	23.0	14.4	13.8
H	2.2	0.9	1.0
Cl	0.4	0.4	0.4
Others[a]	73.7	83.3	83.9
H/C Ratio	1.1	0.8	0.9
HHV	9.4	4.9	6.3

[a]By difference

In all the cases the solids are mixed with the catalyst and this is the reason for the high “others” content. The carbon and hydrogen contents of the solids of the experiments carried out with dechlorination step are lower than when such step is not performed, which could be in relation with the slightly lower solid yields obtained in these experiments (showed in Table 4) and which could indicate that the dechlorination step contribute to complete the pyrolysis process which may not be completed in the conventional catalytic experiment. As it has been mentioned for the other pyrolysis products, the discussion concerning chlorine content and distribution will be included in section 3.5.

3.5. Distribution of chlorine in the pyrolysis products

Table 8 shows the percentage of chlorine in the products obtained after each experiment. In order to compare the chlorine distribution as a function of the addition of catalyst, the chlorine content of the liquids obtained in the conventional thermal pyrolysis run at 440 ºC has been included in Table 8.

Table 8. Chlorine in the pyrolysis fractions (wt.%)

METHOD	Cl in liquids	Cl in gases[a]	Cl in solids
Conventional thermal pyrolysis	0.2	5.3	<0.1
Conventional catalytic pyrolysis	1.2	1.0	0.4
Catalytic stepwise pyrolysis	0.3	3.0	0.4
Non-catalytic dechlorination step + catalytic pyrolysis	0.3	2.2	0.4

[a] Calculated by difference taking into account that there is 1.1 wt.% chlorine in the original sample

It can be seen that the chlorine content of the liquids after a conventional catalytic pyrolysis run is 1.2 wt.%, which is quite higher than in a conventional thermal run (0.2 wt.%) and it may condition the potential application of such liquids. Yanik et al. [23] studied the chlorine content of oils derived from catalytic pyrolysis with different types of catalysts and did obtain the highest concentration of chlorine in pyrolysis oils after using a SiO_2-Al_2O_3 nature catalyst, as is the one used in this work. They suggested that the solid acid catalyst could somehow retain the evolved HCl in the reaction medium during enough time to allow the reaction among this and the organic vapors derived from the polymeric sample, and so yielding chlorinated compounds. Therefore, the effect of the catalyst concerning chlorine content in liquids follows the same tendency as in the case of Yanik. This result indicates that the quality of pyrolysis liquids, in terms of chlorine content, is lower in catalytic pyrolysis than in thermal pyrolysis. For this reason, the dechlorination step is an unavoidable task in this case.

When the dechlorination step is applied, the chlorine content of the liquids decreases in both cases (from 1.2 to 0.3 wt.%), which is equivalent to a 75% reduction of chlorine in the liquids with respect to the conventional catalytic pyrolysis liquids. Since chlorine evolves as HCl (mainly generated in the first step), Table 8 shows higher contents of chlorine in the gases when the previous dechlorination step is used (2.2 - 3.0 wt.%) than that obtained in conventional catalytic pyrolysis (1.0 wt.%). As it has been mentioned before, the objective of this previous step is precisely to separate the chlorine as HCl, since in an industrial process HCl could be absorbed in alkaline solutions by means of wet scrubbers and the gases generated in the subsequent pyrolysis step would be free of chlorine.

The effect of the dechlorination step can be clearly seen in Figure 5, where the chlorine weight % distribution among the pyrolysis fractions is presented.

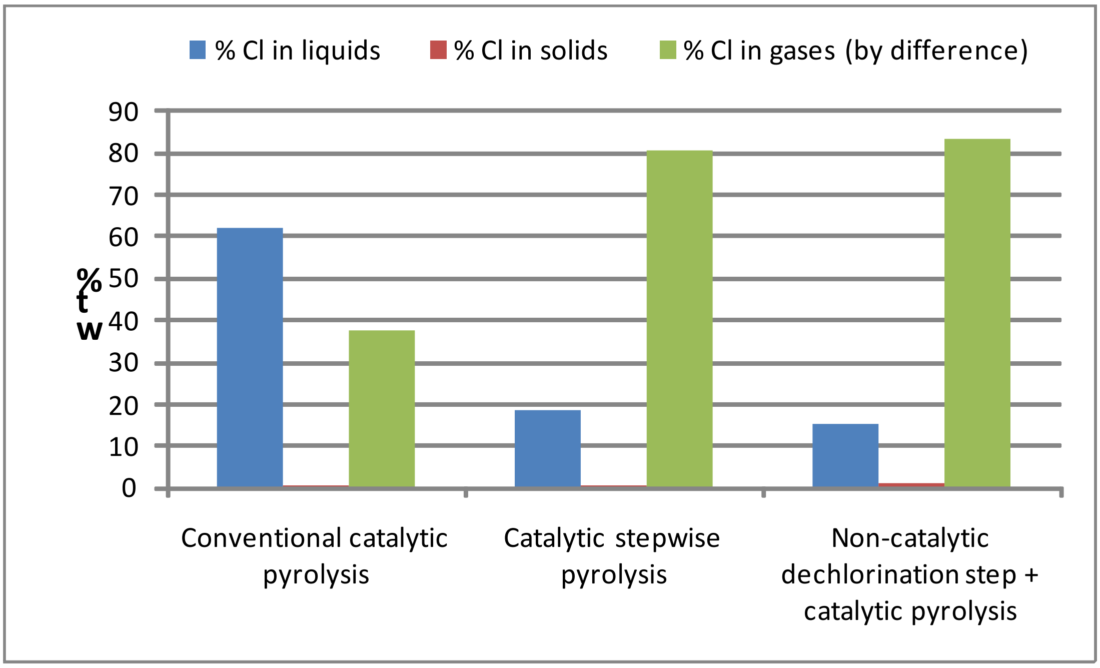

Figure 5. Chlorine distribution among the pyrolysis fractions (wt.%)

The figure shows that in the conventional catalytic pyrolysis run the chlorine preferentially formed organochlorinated compounds that appeared in the liquid fraction (more than 60 wt.% of chlorine), being just around 35 wt.% of this chlorine in HCl form in the gas fraction. This relation is strongly counterbalanced by means of stepwise pyrolysis, which enabled to transfer 83.5 wt.% of the chlorine to the gas fraction if a dechlorination step is carried out prior to catalytic pyrolysis.

4. Conclusions

Catalytic pyrolysis is an attractive alternative for recycling mixed plastic wastes. ZSM-5 zeolite is an effective catalyst which enhances the production of lighter and more aromatic liquid products and C3-C4 rich gas fractions from polyolefinic feedstocks.

Pyrolysis products may be used as high HHV alternative fuels or as a source of valuable chemicals. However, the presence of PVC in the original sample leads to the generation of chlorinated chemicals which are part of the pyrolysis liquids, and this is very detrimental for their potential applications.

The liquids chlorine content can be reduced up to more than 75 wt.% compared to conventional catalytic pyrolysis by means of a previous dechlorination step at 300º C during 60 min. However, the authors have proved that when the catalyst is mixed with the sample from the beginning of the process, the previous dechlorination step significantly decreases the catalyst activity, giving rise to liquids with a higher content of heavier hydrocarbons and a lower content of aromatics. On the other hand, the addition of the catalyst after the thermal dechlorination step has been found to be an efficient method to obtain almost the same results as in the conventional catalytic process, in terms of products yield and quality, and at the same time the high reduction in the chlorine content of the liquids.

To summarize, the main conclusion is that the optimum configuration for recycling plastic wastes by pyrolysis whenever the income material contains PVC is a previous low temperature (300º C) dechlorination step, complemented with an appropriate HCl capture and neutralization unit, and then a higher temperature catalytic step. The addition of catalyst should be done after the dechlorination step, since otherwise the catalyst is deactivated during such step.

Acknowledgements

The authors thank the Spanish Ministry of Education and Science (MEC) (CTQ 2007-67070/PPQ) as well as the Basque Country Government (ETORTEK 2007 IE07-207, GIC 07-09-IT-354-07 and Researchers’ formation program - 2008) for financial assistance for this work.

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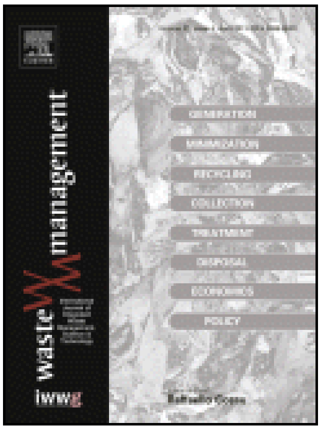
4.3. REAL SAMPLES RUNS

4.3.1. Thermal pyrolysis



Article: *Pyrolysis of municipal plastic wastes: Influence of raw material composition*

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Journal: *Waste Management 30, 620-627.*

Year of publication: *2010*

Waste Management 30 (2010) 620–627

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Pyrolysis of municipal plastic wastes: Influence of raw material composition

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ARTICLE INFO

Article history:
Accepted 20 October 2009
Available online 18 November 2009

ABSTRACT

The objective of this work is the study of pyrolysis as a feedstock recycling process, for valorizing the rejected streams that come from industrial plants, where packing and packaging wastes are classified and separated for their subsequent mechanical recycling. Four real samples collected from an industrial plant at four different times of the year, have been pyrolysed under nitrogen in a 3.5 dm^3 autoclave at 500 °C for 30 min. Pyrolysis liquids are a complex mixture of organic compounds containing valuable chemicals as styrene, ethyl-benzene, toluene, etc. Pyrolysis solids are composed of the inorganic material contained in the raw materials, as well as of some char formed in the pyrolysis process, and pyrolysis gases are mainly composed of hydrocarbons together with some CO and CO_2, and have very high gross calorific values (GCV).

It has been proved by the authors that the composition of the raw material (paper, film, and metals contents) plays a significant role in the characteristics of pyrolysis products. High paper content yields water in the pyrolysis liquids, and CO and CO_2 in the gases, high PE film content gives rise to high viscosity liquids, and high metals content yields more aromatics in the liquid products, which may be attributed to the metals catalytic effect.

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, which in a very short period are converted to wastes, yielding about 15 million tons of such wastes per year (Cimadevila, 2008). 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 (Cimadevila, 2008).

The Packing and Packaging Waste Directive (2004/12/CE) obliges to valorize (energy recovery + recycling) 60% of the packing and packaging wastes, with at least 55–85% of recycling. For this to be possible, in many European countries, on the one hand municipal (yellow) containers for municipal plastic and metallic packing wastes have been set out 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 (>25 wt% cannot be properly classified or separated and is rejected. The rejected fractions 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 landfilled.

The general objective of this paper is to study experimentally the suitability of the pyrolysis process as an alternative for the valorisation of real streams of plastic wastes rejected from a packaging waste separation and classification industrial plant. In the pyrolysis process (heating in an oxygen free atmosphere), the organic components of the material are decomposed generating liquid and gaseous products, which can be useful as fuels and/or sources of chemicals. The inorganic ingredients (fillers, metals, etc.) remain practically unaltered and free of the binding organic matter, and therefore metals could be separated and the remaining solid may be reused (additive, fillers, pigment, etc.) or as a last resort, it would be a minimum waste to be landfilled. Pyrolysis is especially appropriate for products or streams which contain different plastics and other ingredients both organic and inorganic, for which mechanical recycling is not feasible; such is the case of the fraction that has been studied in this work.

There are many references in the literature about the thermal decomposition of plastics. Different experimental procedures have been used including thermogravimetric analysers (e.g. Aguado et al., 2007; Ghoshal et al., 2008) fixed bed reactors (e.g. Williams and Badri, 2004; Serrano et al., 2009), fluidized bed pyrolysis units (e.g. Berrueco et al., 2007; Marcilla et al., 2007), vacuum pyrolysis

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doi:10.1016/j.wasman.2009.10.014

units (e.g. Roy et al., 1999; Karaduman et al., 2001), spouted bed reactors (e.g. Olazar et al., 2009), etc. The study presented in this paper has been carried out in a fixed bed reactor, however, results from different reactor geometries are many times difficult to compare since pyrolysis yields and characteristics of the products obtained depend not only on the feedstock and operating conditions used for the experiments, but also on the specific characteristics of the system used, such as the size and type of reactor, the efficiency of heat transfer, and the residence time.

On the other hand, most of the pyrolysis studies have been carried out with individual plastics, to get information about the decomposition kinetics (e.g. Faravelli et al., 2001; Broadbelt and Levine, 2009) or about the products obtained (e.g. Williams and Williams, 1999; Kaminsky et al., 2004), and with mixtures of commodity plastics (e.g. Angyal et al., 2007; Demirbas, 2004; Kiran et al., 2000). Only a few studies have been published concerning pyrolysis of real municipal plastic wastes (Kaminsky et al., 1997; Kaminsky and Kim, 1999; Sakata et al., 2003; Lee, 2007) and there is no information about the influence of the variability of the plastic waste composition in the pyrolysis process and the products obtained. Obviously there are considerable differences among the compositions of the rejects of different industrial waste separation plants, due to differences both in the separation processes and in the raw materials reaching the plants. Moreover, it has been proved by the authors that the composition of the rejects of a specific industrial waste separation plant may significantly vary in the course of time. Therefore, different samples obtained from a Spanish industrial plant have been pyrolysed, in order to (1) evaluate the feasibility of pyrolysis as a feedstock recycling technique and (2) determine the influence of the raw material composition on the characteristics of the process products.

2. Experimental

2.1. Origin of the samples

Four real samples coming from the rejects of a waste separation and classification industrial plant located in Amorebieta, in the north of Spain, have been pyrolysed. In the plant, the plastic wastes are passed through two rotating trommel screens (opening sizes of 200 mm and 80 mm) and ballistic separators, which separate fine materials and other small parts. Metals are then mechanically separated using a magnetic unit for ferric metals and an eddy current unit for aluminium. Then, plastics are separated by means of autosorters, optical readers which identify the different materials arriving on the conveyor belts and separate them using air currents. After the whole process, seven reusable streams are obtained: steel, HDPE, LDPE, PET, Tetrabrik® cartons, mixed plastic and aluminium containers. These are then transferred to different containers for each type of material and send to the corresponding material recyclers. About 27 wt% of the income raw material cannot be recovered and is at present being sent to incineration. This rejected stream is the sample used in the pyrolysis experiments.

2.2. Pyrolysis experiments

The pyrolysis experiments were carried out at 500 °C in nitrogen atmosphere, using an unstirred stainless steel 3.5 dm^3 autoclave. Previous studies carried out by the authors (Caballero et al., 2004, 2007, 2009) with other plastic wastes (SMC of polyester and fibreglass, scrap tyres, automobile shredder residues, etc.) indicated that in the mentioned installation, 500 °C was the optimum temperature for treating polymeric wastes by pyrolysis, since at lower temperatures complete decomposition of the organic matter was not achieved, and at higher temperatures no significant improvement of pyrolysis yield (i.e., amount and properties of the products) was observed; the observed slight increase in gas yield was indeed counterbalanced by a detrimental effect on the liquid yield, so that 500 °C was chosen as the process optimal temperature for the samples under investigation.

In a typical run, 100 g of the sample with a particle size of 8 mm were placed into the reactor, which was then sealed. Nitrogen was passed through at a rate of 1 $dm^3\,min^{-1}$ and the system was heated at a rate of 20° C min^{-1} to 500 °C, and maintained there for 30 min. It has been proved by the authors that in the mentioned installation after 30 min no more pyrolysis products evolve from the autoclave (de Marco et al., 1995; Legarreta et al., 1995). During each run the vapours leaving the reactor flowed to a series of running water cooled gas–liquid separators where the condensed liquids were collected. The uncondensed products were passed through an activated carbon column and collected as a whole in Tedlar plastic bags, to be afterwards tested by gas chromatography. A flow sheet of the experimental setup is presented in Fig. 1.

The amount of solids (residues in the autoclave) and liquids obtained were weighed and the pyrolysis yields were calculated as weight percentage with respect to the raw material pyrolysed. Gas yields were normally determined by difference. In some experiments specifically devoted to directly quantify the amount of gases, a closure of the mass balance of about 90 wt% was obtained.

2.3. Analytical techniques

Samples of about 25 kg were collected at the plant. Then, representative samples of 6 kg were selected by successively dividing the sample into fourths and those samples were used for the composition determination. Visual inspection as well as simple identification techniques (flame colour, density, and in doubtful cases FTIR analysis) were used for the composition determination. Once the components were identified and quantified, the samples were ground using a cutting mill suitable for plastics with a sieve grate of 8 mm, which generates a particle size small enough ($\leqslant$8 mm) to be able to extract homogeneous samples for the experiments. Additionally, 100 g of the sample with a particle size $\leqslant$ 8 mm were more finely ground ($\leqslant$1 mm) for characterization purposes under cryogenic conditions using a small cutting mill.

Both the raw materials and the solid and liquid pyrolysis products obtained were thoroughly characterized using the following analytical techniques. The moisture and ash contents of the samples were determined by thermogravimetric analysis according to D3173-85 and D3174-82 ASTM standards, respectively, and the elemental composition with automatic CHN and S analysers. Method 5050 of the Environmental Protection Agency (EPA) of the United States was used for Cl determination. The gross calorific value (GCV) was determined with an automatic calorimetric bomb. Additionally, pyrolysis liquids were also analysed by gas chromatography coupled with mass spectrometry detector (GC–MS).

Concerning pyrolysis gases, they were analysed by means of a gas chromatograph coupled with a thermal conductivity and a flame ionization detectors (GC–TCD/FID). The GCV of the gases was theoretically calculated according to their composition and to the GCV of the individual components.

3. Results and discussion

3.1. Composition and characteristics of the samples coming from the industrial plant

The amount and type of components contained in the four real samples coming from the rejects of the packaging waste separation and classification industrial plant are presented in Table 1. The

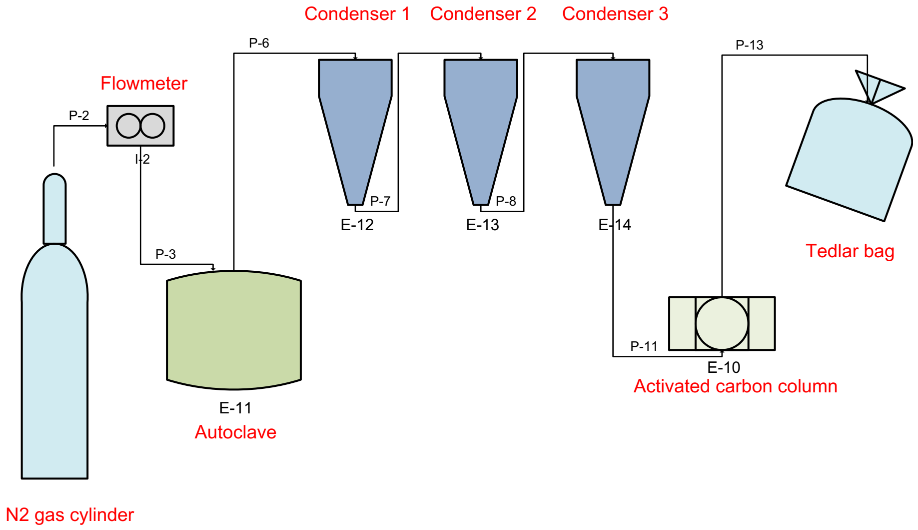

Fig. 1. Flow sheet of the experimental set-up used.

components of the sample have been classified in three groups. Packaging plastics, which are in all cases the most abundant fraction, are mainly composed of PE and PP together with some PS, PET and PVC. Other packaging materials which are not plastic goods are also used in the packaging industry; in this fraction, metallic materials (iron, aluminium) as well as complex packages, composed of more than one material, are included. The third group, which has been called inappropriate materials, contains those materials which should not have been deposed in the yellow container since they are not packaging materials; in this fraction all kinds of municipal solid wastes (paper, clothes, wood, glass, gardening...) can be found. A picture of one of the samples pyrolysed can be seen in Fig. 2.

Table 1 shows that there are important differences among the compositions of the four samples. Samples 1 and 2 contain more than 90 wt% packaging plastics while such materials are much less abundant in samples 3 and 4, which contain more than 30 wt% of inappropriate materials. It can be seen that sample 1 contains about 98% packaging materials while samples 2, 3 and 4 have unusually high film, paper and glass contents. Paper and glass are inappropriate materials which are normally separated to a great extent in the separation and classification plant. PE film is also a material that can be easily separated in the plant, provided that the plant is properly working. These results demonstrate that the composition of the rejected streams of a municipal plastic wastes separation plant is not constant; it depends not only on the type of industrial separation plant, but also on several factors such as a potential miss-function of any of the stages of the nominal process of the plant, or fluctuations in the raw material due to changes in the citizen habits or to seasonal variations.

Finely ground samples (<1 mm) of the four samples were characterized and the results are presented in Table 2. All the samples have rather low moisture content. The paper rich sample is the one which contains more water (2 wt%) due to its hygroscopic character. On the other hand, sample 1 and the film rich sample hardly contain inorganic materials (2.4 wt% ash in both cases) while the paper rich sample and especially the glass rich sample, have rather high inorganic contents, mainly metals and inappropriate materials such as glass. The ash content of paper based materials depends on the specific kind of paper (newspaper, magazine, cardboard). The paper contained in the paper rich sample came mainly from magazines, and it has been proved by the authors that magazine papers have a high ash content (up to 26 wt%) which probably comes from the inks and additives of the paper. This fact explains the high ash content of the paper rich sample. Consequently, carbon and hydrogen contents (≈60 wt% and ≈9 wt%, respectively) are significantly lower than those of sample 1 and the film rich sample (≈82 wt% carbon and ≈13 wt% hydrogen). With respect to Cl content, coming from PVC, it is quite low in all cases (≈2 wt%) since this material is less and less used in packaging. Concerning "others", which was calculated by difference, they contain oxygen and all the other elements that have not been determined. It is worth noting that this percentage is rather higher in the paper rich sample, which is attributed to the high content of cellulose since this is a high oxygen containing polymer. The H/C atomic ratio is around 1.7 for all the samples except for the film rich one, whose H/C ratio is 2; this is a consequence of its high PE and PP contents, since the H/C ratio corresponding to the molecular formula of polyolefins (C_nH_{2n}) is exactly 2. Concerning the GCVs, samples 1 and the film rich sample have very high GCV (≈41 MJ kg^{-1}) while the GCV of the paper and glass rich samples is much lower (≈30 MJ kg^{-1}), which is mostly due to the great proportion of paper, and glass and inert materials they contain.

3.2. Results of the pyrolysis experiments

The mean value of the liquid, gas and solid yields, obtained in three pyrolysis runs carried out with each sample and which did not differ more than three points in the percentage, are presented in Table 3. It can be seen that sample 1 and the film rich sample reached the highest conversions to liquids and gases, in both cases more than 90 wt%, while the solid fraction was a minority by-product of the process. On the contrary, when the paper and the glass rich samples were pyrolysed, the solid yields were higher (26.6 and 33.5 wt%, respectively), mostly due to their greater ash contents.

In the four cases, the solid yield was higher than the original inorganic content of the sample (% ash in Table 2); this is attributed to char formation, due to secondary repolymerization reactions among the polymer derived products. The amount of char formed has been included in Table 3. The authors (Caballero et al., 2004, 2007, 2009) and also other research groups (Grittner et al. 1993; Williams and Williams, 1997; Sakata et al., 2004) have obtained a certain amount of char in the pyrolysis of many polymeric materials. Table 3 shows that the paper rich sample is the one that gives rise to a higher char yield (15.2 wt%); this is attributed to its high

Table 1
Composition of the samples pyrolysed (wt%).

	Material	Sample 1	Sample 2 (film rich sample)	Sample 3 (paper rich sample)	Sample 4 (glass rich sample)
Packaging plastics	HDPE	39.50	13.44	5.26	18.77
	PP	34.17	9.63	8.19	21.94
	PS	9.33	4.07	8.78	8.36
	Expanded PS	6.93	2.53	1.01	3.02
	PET	2.94	2.88	7.33	3.23
	PVC	4.16	4.28	1.42	0.79
	PE film	–	50.55	9.40	2.14
	PP film	–	4.92	2.07	1.73
	Subtotal	**97.03**	**92.30**	**43.46**	**59.98**
Other packaging materials	Complex	0.02	0.64	2.97	0.22
	Blister	–	–	0.21	–
	Tetra-Brik	0.17	2.73	7.82	–
	Al film	0.19	0.64	1.53	2.50
	Aluminium	–	0.42	1.12	1.35
	Iron	–	0.20	1.25	1.27
	Subtotal	**0.38**	**4.63**	**14.90**	**5.34**
Inappropriate materials	ABS	2.24	–	2.30	2.39
	PMMA	–	–	0.48	0.55
	PUR	–	–	0.07	0.18
	PA	–	–	0.36	0.25
	PC	–	0.11	0.04	0.83
	Elastomer	–	–	0.08	2.42
	Latex	–	–	0.37	0.97
	Medical waste	–	0.07	0.38	0.98
	Paper	0.35	2.80	33.25	4.19
	Clothes	–	–	2.15	0.08
	Gardening	–	0.01	0.24	0.56
	Wood	–	0.07	0.28	3.32
	Glass	–	0.01	0.60	16.18
	Inerts	–	–	1.04	1.78
	Subtotal	**2.59**	**3.07**	**41.66**	**34.68**
	Total	**100**	**100**	**100**	**100**

Fig. 2. A picture of one of the samples pyrolysed.

Table 2
Moisture. ash and elemental composition (wt%) and GCV (MJ kg^{-1}) of the samples pyrolysed.

Sample	Sample 1	Film rich sample	Paper rich sample	Glass rich sample
Moisture	0.1	0.6	2.0	1.0
Ash	2.4	2.4	11.4	28.2
C	82.8	81.0	61.1	58.7
H	11.9	13.7	8.9	8.7
N	0.2	0.1	0.3	0.5
S	0.4	<0.1	<0.1	<0.1
Cl	1.6	0.7	2.4	1.0
Others[a]	0.7	1.4	13.8	1.8
H/C ratio	1.7	2.0	1.7	1.8
GCV	41.6	41.4	29.4	30.6

[a] By difference.

Table 3
Pyrolysis yields (wt%).

Fraction		Sample 1	Film rich sample	Paper rich sample	Glass rich sample
Liquids	Organic phase	53.0	65.7	35.1	40.9
	Aqueous phase	0.0	0.0	12.4	0.0
Gases		41.5	26.5	26.0	25.6
Solids	Original inorganic	2.4	2.4	11.4	28.2
	Char	3.1	5.4	15.2	5.3

content in cellulose based materials which, as has been proved by many authors in previous studies (e.g. Badri, 2008; Jones et al., 2008; Fabbri et al., 2009), has a great tendency to form char. A study carried out by Van Kravelen and Te Nijenhuis (2009) 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 –OH and =O, which is the case of cellulose based materials. This is corroborated by a previous work carried out by the authors (de Marco et al., 2002) about pyrolysis of many different materials, which showed that cardboard yields about 26 wt% char. According to these data the paper rich sample, which contains about 34 wt% of cellulose based materials, should yield ≈9 wt% char. The result obtained in this paper is somewhat higher (15.2 wt% char); the 6 wt% in excess can be attributed to those plastics in the sample with char forming tendency, such as PET or PVC. In fact, sample 1, which hardly contains paper, does yield

Table 4
GC–MS analysis of the pyrolysis liquids (organic phases) (% area).

t_R (min)	Molecular formula	Assignment	Sample 1	Film rich sample	Paper rich sample	Glass rich sample
5.06	C_6H_{12}	Methyl-pentene or cyclohexene	1.3			
12.84	C_7H_8	Toluene	12.0	6.9	11.5	14.9
13.98	C_8H_{16}	Octene	1.0			
16.10	C_9H_{18}	Dimethyl-heptene	5.4	1.4		1.2
16.89	C_8H_{10}	Ethyl-benzene	10.4	6.3	17.8	16.4
17.17	C_8H_{10}	Xylenes	2.1	2.1	3.4	4.1
17.85	C_9H_{18}	Nonene	1.0	2.0		
17.92	C_8H_8	Styrene	40.9	16.4	27.2	33.5
18.80		–	1.4			
18.98	C_9H_{12}	Methylethyl-benzene	<1.00		1.6	1.5
20.63	C_9H_{10}	α-Methyl-styrene	4.8	2.2	6.1	7.0
20.75	$C_{10}H_{20}$	Decene	1.9	3.7	<1.0	1.0
22.30	C_9H_8	Indene	<1.0		2.0	1.6
22.74	C_8H_8O	Phenyl-ethanone			1.7	
23.14	$C_{11}H_{22}$	Undecene	1.4	3.6	<1.0	<1.0
24.60	$C_7H_6O_2$	Benzoic acid			1.3	
24.67	$C_{10}H_{10}$	Methyl-indene			1.7	1.3
25.22	$C_{12}H_{24}$	Dodecene	1.3	3.1		<1.0
25.48	$C_{10}H_8$	Naphthalene	<1.0	2.5	4.2	3.1
27.11	$C_{13}H_{26}$	Tridecene	1.3	3.5	1.1	1.0
27.24	$C_{13}H_{28}$	Tridecane		1.3		
27.43		–	1.2			
27.61	$C_{11}H_{10}$	Methyl-naphthalene			4.5	3.1
28.86	$C_{14}H_{28}$	Tetradecene	1.3	3.9	<1.0	<1.0
28.98	$C_{14}H_{30}$	Tetradecane		1.4		
29.06	$C_{12}H_{10}$	Phenyl-benzene			2.6	1.4
30.50	$C_{15}H_{30}$	Pentadecene	1.2	3.6	<1.0	<1.0
30.61	$C_{15}H_{32}$	Pentadecane		1.4		
32.04	$C_{16}H_{32}$	Hexadecene	1.1	3.6		<1.0
32.14	$C_{16}H_{34}$	Hexadecane		2.8		
33.37	$C_{15}H_{16}$	Propanediyl-benzene	1.0		1.5	<1.0
33.50	$C_{17}H_{34}$	Heptadecene	1. 8	3.5		
33.58	$C_{17}H_{36}$	Heptadecane		1.9		
34.88	$C_{18}H_{36}$	Octadecene	1.1	5.6		
34.96	$C_{18}H_{38}$	Octadecane		1.7		
35.48	$C_{14}H_{10}$	Anthracene			1.4	
36.20	$C_{19}H_{38}$	Nonadecene		5.6		
36.26	$C_{19}H_{40}$	Nonadecane		2.0		
37.45	$C_{20}H_{40}$	Eicosene		2.6		
37.51	$C_{20}H_{42}$	Eicosane		3.6		
37.88	$C_{16}H_{12}$	Phenyl-naphthalene	1.3		3.0	1.2
38.70	$C_{21}H_{44}$	Heneicosane		1.8		
Total			96.2	100.0	92.6	92.3

about 3 wt% char which must come from the char forming plastics. The paper rich sample contains higher quantities of these plastics (PET + PVC) as well as of tetra-brik, which is also composed of cardboard; this justifies its higher char forming tendency.

It is also worth noting that the paper rich sample generated a high proportion of aqueous liquid phase while the other samples did not generate water at all. The water generation is again a consequence of the high cellulose content of this sample; several authors (e.g. Demirbas, 2007; Luik et al., 2007; Xi-Feng et al., 2009) have also reported that water is formed in the pyrolysis of cellulose rich samples. In the same way, the authors (de Marco et al., 2002) obtained more than 90 wt% water in the liquids of the pyrolysis of cardboard, result that is quite in accordance with the water yield obtained in this work.

The results obtained in GC–MS analyses of the organic phase of the pyrolysis liquids are presented in Table 4. For the shake of reduction only those compounds with a percentage quantified area greater than 1% have been included. When the match quality of the identification result provided by the MS search engine, was lower than 85%, the result was not considered valid and no name is specified in Table 4. The compound names correspond to tentative assignments provided by the MS search engine and contrasted as far as possible with bibliographic data and sometimes with standards. It has also to be mentioned that the maximum injection temperature of the GC equipment is 300 °C, so the products with higher boiling point are not determined. Thermogravimetric analysis at 300 °C showed that the liquids of the four samples contain about 20 wt% of products with a boiling point higher than 300 °C. Therefore, the following discussion concerning GC–MS results corresponds only to the 80 wt% of products with boiling points less than 300 °C.

Table 4 shows that the plastic waste pyrolysis liquids are composed of a mixture of organic compounds of 6–21 carbons. Several differences can be found among the compositions of the liquids of the four different samples pyrolysed. The liquids derived from sample 1, and from the paper and glass rich samples were dark brown-coloured, rather fluid products, which resembled petroleum fractions and contained large quantities of aromatics. On the contrary, the liquids obtained from the film rich sample, were a semisolid product which, as it can be seen in Table 4, contained significant quantities of long chain alkanes and alkenes of up to 21 carbon number. This high content of long chain compounds is directly attributed to the high polyethylene (PE) content of the original sample. The thermal degradation of PE occurs through a random scission that results in the formation of free radical fragments. Subsequent hydrogen chain transfer reactions transform the radical fragments into unsaturated and saturated straight chain molecules, alkenes and alkanes. Several authors have also obtained

Table 5
Fractions of interest in pyrolysis liquids (% area).

Fractions		Sample 1	Film rich sample	Paper rich sample	Glass rich sample
C5–C9	Aromatics	71.0	32.6	75.1	80.7
	No aromatics	8.7	3.3	0.0	1.2
	Total	79.7	35.9	75.1	81.9
C10–C13	Aromatics	1.6	2.5	15.6	10.6
	No aromatics	5.9	15.1	2.1	3.3
	Total	6.5	17.6	17.7	13.9
>C13	Aromatics	2.3	0.0	5.9	2.0
	No aromatics	6.4	46.5	1.3	2.1
	Total	8.7	46.5	7.2	4.1
Total aromatics		74.9	36.5	96.6	93.4
Total unsaturated compounds		21.0	38.9	3.4	4.7
Total saturated compounds		0.0	24.6	0.0	1.93
No identified		4.1	0.0	0.0	0.0

this type of products in pyrolysis of pure PE and PE rich samples, among others Sakata et al. (1996) using a batch reactor and Vasile et al. (2001) using an extruder type reactor (continuous feed). This fact demonstrates that long chain hydrocarbons are obtained when pure PE or PE rich samples are pyrolysed whatever the reactor geometry is. However, this is not the case of the pyrolysis yields, which shows a strong dependence on the reactor geometry; the same sample can produce more than 80 wt% of condensates in a fixed bed reactor and around 30 wt% in a fluidized bed one, probably due to significant differences in the nitrogen–polymer contact and heat transfer rate (Aguado and Serrano, 1999). For this reason only same reactor geometries pyrolysing the same sample can be properly compared.

Table 4 shows that in every case, styrene was the most abundant product with percentage areas ranging from 16% with the film rich sample to almost 41% when sample 1 was pyrolysed. The next compounds in abundance are toluene (7–15%) and ethyl-benzene (6–18%). The possibility of obtaining valuable aromatic hydrocarbons, such as styrene, toluene, and ethyl-benzene, from the waste plastic samples used, confers pyrolysis a potential attractive, even though it is known that the achievement of a efficient separation of such chemicals is not easy.

In order to better analyse the effect of raw material composition on the characteristics of pyrolysis liquids, all the compounds identified by GC–MS, including those with % area <1%, have been grouped in three categories according to their number of carbons: C5–C9, C10–C13 and >C13; additionally total aromatics have been quantified. The results are presented in Table 5, which shows that the organic liquids derived from sample 1, the paper rich sample and the glass rich sample have a high content of aromatics. It has been reported (Williams and Williams, 1999; Bockhorn et al., 1999; Sablier et al., 2006) that one of the mechanisms of formation of aromatics is via Diels–Alder reactions and subsequent dehydrogenation to form aromatic rings and it is probably related to the specific composition of the sample pyrolysed. The film rich sample, which contains the highest proportion of polyolefins in plastic fraction (85.1 wt%), yields the lowest proportion of aromatics (36.5% area), while the paper rich sample, which contains the lowest proportion of polyolefins in plastic fraction (57.3 wt%), gives rise to the highest aromatics contents (96.6% area). The same tendency was observed with sample 1. It contains 75.9 wt% polyolefins in plastic fraction and yields 74.9% area aromatics. On the contrary, the glass rich sample, which has very similar polyolefin content, gives rise to a much higher content of aromatics (93.4% area). The reason why the glass rich sample yields liquids with higher proportions of aromatics may be attributed to its higher metals content (5.12 wt%), since it has been proved by other research groups (e.g. Buekens and Huang, 1998; Siddiqui et al., 2004; Aguado et al., 2007) as well as by the authors (Caballero et al., 2009) that the formation of aromatics in pyrolysis of plastics is catalysed by metal-containing catalysts. Concerning the number of carbon atoms, again, the liquids derived from sample 1, the paper rich sample and the glass rich sample contain more than 75% area of gasoline range products (C5–C9), which together with their high aromatic contents contributes to the low viscosity of the liquids. On the other hand, the high viscosity product obtained from the film rich sample yields ≈46% area of heavy oils (>C13) which justifies its semisolid consistency.

Table 6
GC–MS analysis of the aqueous phase of the paper rich sample derived liquid (% area).

t_R (min)	Molecular formula	Assignment	Paper rich sample
3.06	H_2O	Water	86.1
15.77	$C_5H_4O_2$	Furancarbaldehyde	2.7
20.41	C_6H_6O	Phenol	3.7
24.57	$C_7H_6O_2$	Benzoic Acid	3.6
27.90	$C_8H_4O_3$	Isobenzofurandione	3.9
Total			100.0

Table 7
Elemental composition (wt%) and GCV (MJ kg^{-1}) of the organic pyrolysis liquids.

Sample	Sample 1	Film rich sample	Paper rich sample	Glass rich sample
C	85.5	83.9	89.1	77.3
H	11.5	12.1	9.3	9.5
N	0.2	<0.1	<0.1	0.3
Cl	0.8	1.3	n.d.	0.2
Others[a]	2.1	2.6	1.5	12.7
H/C ratio	1.6	1.7	1.2	1.5
GCV	41.2	41.8	Not determined	36.6

[a] By difference.

Table 6 shows the GC–MS analysis of the aqueous phase obtained in the pyrolysis of the paper rich sample. It can be seen that it is mainly composed of water together with some oxygenated compounds. Similar proportions of water were obtained by Luik et al. (2007) in the pyrolysis of air-dried pine bark, a cellulose based material which contains a proportion of oxygen similar to that contained in paper. The presence of oxygenated compounds in the pyrolysis liquids of cellulose rich materials has also been reported by other authors (Luik et al., 2007; Demirbas, 2007; Xi-Feng et al., 2009).

The elemental composition and gross calorific value of the pyrolysis organic liquids obtained with the four different samples pyrolysed are presented in Table 7. It can be seen that there are no significant differences among the results obtained with sample 1,

Table 8
GC–TCD/FID analysis (wt%) and GVC (MJ kg^{-1}) of pyrolysis gases.

Sample	Sample 1	Film rich sample	Paper rich sample	Glass rich sample
H2	0.0	0.9	0.5	0.5
CO	2.4	6.8	11.6	7.4
CO2	4.9	11.8	33.1	21.0
Methane	15.2	26.2	9.4	6.7
Ethane	15.7	17.9	5.5	8.0
Ethene	25.7	9.4	11.4	16.7
C3	32.1	14.2	15.5	23.1
C4	1.6	12.8	10.3	15.9
C5	0.0	0.0	2.7	0.7
C6	0.0	0.0	0.0	0.0
GCV	47.5	43.8	29.7	37.2

Table 9
Moisture, elemental composition in wet basis (wt%) and GCV (MJ kg^{-1}) of pyrolysis solids.

Sample	Sample 1	Film rich sample	Paper rich sample	Glass rich sample
Moisture	n.d.	0.0	2.8	2.3
C	48.0	46.0	42.7	29.3
H	1.9	1.9	1.9	1.2
N	0.9	1.0	0.8	1.1
Cl	3.7	5.5	5.1	4.7
Ash + Others[a]	45.5	45.6	46.7	61.4
H/C ratio	0.5	0.5	0.5	0.5
GCV	n.d.	16.9	15.6	11.5

[a] By difference.

the film rich sample and the paper rich sample. On the contrary, the glass rich sample liquids are quite different. They have the lowest carbon content and the highest contents of other elements; possibly oxygen coming from oxygenated compounds which were identified by GC–MS though were not included in Table 4 since they were in proportions lower than 1% area. Such compounds are probably derived from cellulose based materials contained in this sample (paper + gardening + wood).

It is worth mentioning that pyrolysis oils have very high GCV, similar to those of conventional liquid fuels, so they may be considered as an appropriate alternative to fossil fuels, since although in terms of energy efficiency the GCV of the oils is comparable to that of the original samples, the advantage of pyrolysis is that it transforms a solid plastic waste into more valuable and easily handled fuels. However, it has to be mentioned that these liquids contain chlorine to some extent (≈1 wt% in sample 1 and the film rich sample and ≈0.2 wt% in glass rich sample). Chlorine is derived from PVC and it can be seen that the higher the PVC content of the raw material, the higher the percentage of chlorine in the pyrolysis liquids. The presence of chlorine is rather detrimental for the immediate use of these liquids as fuels. Nevertheless, there are several alternatives to avoid the transference of chlorine to the liquids, such as carrying out a first low temperature dehydrochlorination step (Hornung et al., 1999; Siddiqui and Ali, 2005) or using absorbents, e.g. Red Mud or calcium and sodium-based absorbents (Beckmann et al., 2001; Yanik et al., 2006), mixed with the raw material in order to retain chlorine in the solid fraction.

Concerning gases, Table 8 shows that they are composed of hydrocarbons ranging from C1 to C6, hydrogen and some carbon dioxide and monoxide. Due to the difficulty in discriminating among isomers from C3 to C6, such discrimination has not been made. The gases from the film rich sample contained the highest quantities of H_2 and CH_4 which is attributed to the high PE content of this sample. Aguado and Serrano (1999) did also obtain high proportions of H_2 and CH_4 in pyrolysis of PE rich samples. The paper rich sample produced significant quantities of CO and CO_2 which is most probably due to its high paper content, since cellulose is a high oxygen containing polymer. The formation of CO_2 in pyrolysis of cellulose based materials has also been reported by other authors (Fontana et al., 2000; Ahmed and Gupta, 2009; Couhert et al., 2009). Li et al. (2001) and Banyasz et al. (2001) investigated gas evolution and the mechanism of cellulose pyrolysis in a two heating zone pyrolysis system. The two heating zone experiments indicated that a large proportion of CO is formed from the decomposition of primary volatile products (aldehydes) during secondary reactions, while CO_2 is formed at the early stages of cellulose pyrolysis during the primary reactions. As a consequence of the higher CO_2 content, the paper rich sample gas has lower GCV than the other gases.

The GCV of all the samples except the paper rich one is similar to, or in the case of sample 1 higher than, that of natural gas (44 MJ kg^{-1}). For this reason pyrolysis gases may be used as energetic source for the process, and the surplus may be valorized.

The composition of pyrolysis solids is presented in Table 9. The solids obtained with the four samples hardly differ one another, and are composed by carbon, which corresponds to the carbonaceous product (char) previously mentioned, which is formed during pyrolysis, and the inorganic matter contained in the original sample, obviously more abundant in the glass rich sample. The pyrolysis solids are at first sight a useless product of the pyrolysis process, which most probably would have to be landfilled. At best, the inorganic material could be recovered for recycling processes and the organic fraction could be used for energy recovery. For this to be possible it has to be mentioned the need for (1) evaluating the inorganic pollutants (i.e., heavy metals) and organics concentration and leachability and (2) assessing the mineralogical stability of the solids which are formed at high temperatures and are likely to be metastable under ambient conditions since leachability and metastability of the solid stream might hinder utilization or might pose the need of a pre-treatment step aimed at improving the material quality. Anyhow, if the solid could not be valorized it would be a minority by-product of the pyrolysis process, since the weight of the original plastic waste is reduced by more than 90%.

4. Conclusion

Pyrolysis is a promising technique for feedstock recycling of packing and packaging plastic wastes. When the separation process in the plastic waste classification plant is properly carried out, a rejected non-usable waste stream is left, which in the pyrolysis process yields conversions to liquid and gas as high as 90 wt%.

The composition of the raw material plays a very important role in the distribution and quality of the pyrolysis products. On the one hand, paper leads to the generation of a high proportion of aqueous liquid phase and to great percentages of CO and CO_2, and consequently to gases with lower GCV. On the other hand, high PE film contents give rise to high viscosity paraffinic/olefinic liquids. And finally, the presence of inorganic materials, especially metals, may have a catalytic effect yielding lighter and more aromatic liquids, but obviously leaves a higher amount of solids in the autoclave.

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, metals and glass of the solid fraction may be recovered for recycling processes and the remaining solid (mainly char) may find applications such as solid fuel, pigment, activated carbon, and low quality carbon black.

Acknowledgements

The authors thank the Spanish Ministry of Education and Science (MEC) (CTQ 2007-67070/PPQ) as well as the Basque Country Government (ETORTEK 2007 IE07-207 and Researchers' formation program - 2008) for financial assistance for this work.

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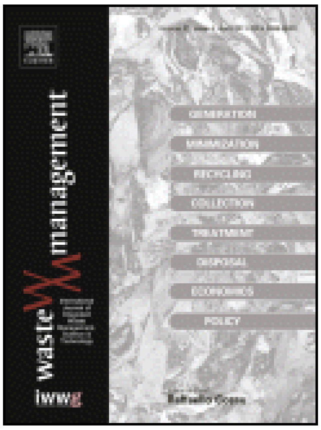
4.3. REAL SAMPLES RUNS

4.3.2. Catalytic pyrolysis



Article: *Pyrolysis of municipal plastic wastes II: Influence of raw material composition under catalytic conditions*

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Journal: *Waste Management*

State: *Minor revision.*

Abstract

In this work, the results obtained in catalytic pyrolysis of three plastic waste streams which are the rejects of an industrial packing wastes sorting plant are presented. The samples have been pyrolysed in a 3.5 dm^3 reactor under semi-batch conditions at 440 ºC for 30 minutes in nitrogen atmosphere. Commercial ZSM-5 zeolite has been used as catalyst in liquid phase contact. In every case, high HHV gases and liquids which can be useful as fuels or source of chemicals are obtained. A solid fraction composed of the inorganic material contained in the raw materials and some char formed in the pyrolysis process is also obtained. The zeolite has shown to be very effective to produce liquids with great aromatics content and C3-C4 fraction rich gases, even though the raw material was mainly composed of polyolefins. The characteristics of the pyrolysis products as well as the effect of the catalyst vary depending on the composition of the raw material. When paper rich samples are pyrolysed, ZSM-5 zeolite increases water production and reduces CO and CO_2 generation. If stepwise pyrolysis is applied to such sample, the aqueous liquid phase can be separated from the organic liquid fraction in a first low temperature step.

Keywords: pyrolysis, feedstock recycling, catalytic decomposition, packaging wastes, plastic wastes, ZSM-5 zeolite.

1. Introduction

Packaging waste management is at present a key concern in Europe. The growing waste generation has forced the European Union (EU) to face the problem, taking specific policies which have tried to boost sustainable development since the 1970s (Alwaeli, 2010). The Council Directive 94/62/EC established for the first time the levels to be recycled concerning packaging wastes and these levels were re-established and hardened by the Council Directive 2004/12/EC, which amended the former. Although this Directive aims at reducing the production of packaging waste, a general increase in per capita quantities of packaging being put on the European market was reported in the period 1997-2007, which lead to the corresponding increase in packaging waste generation in the EU-27 Member States (European Environment Agency, 2010).

There are large differences in the management of packaging wastes among Member States, depending mainly on the use and generation of these wastes. In Spain, packaging wastes are collected in specific municipal containers and then sent to industrial separation and classification plants, where the wastes are separated in different fractions (PE, PET, mixed plastics fraction, steel, tetra-brick, aluminum cans, etc.) for their subsequent mechanical recycling. In such plants, a significant amount of the income materials cannot be properly classified or separated and it is rejected. Although it is mainly composed of plastics, many different intermingled packaging materials are found in this rejected fraction and therefore it cannot be mechanically recycled; for this reason, the rejected fraction is nowadays incinerated or landfilled. The average rejected percentage of the income materials in Spanish separation plants is around 45 wt.% (Ecoembalajes España, 2009).

Pyrolysis could be an alternative to landfill or incineration for these rejected streams. In the pyrolysis process (heating in an oxygen free atmosphere), the organic components of the material are decomposed generating liquid and gaseous products, which can be useful as fuels and/or sources of chemicals. The inorganic ingredients (fillers, metals, etc.) remain practically unaltered and free of the binding organic matter; therefore metals could be separated, and the remaining solid (non-metallic inorganic compounds + char) may be reused as additive, filler for plastics, pigment, etc., although its potential applications strongly depend on the specific composition of the raw material which directly conditions the pyrolysis solids composition. Anyhow, as a last resort, it would be a minimum waste to be landfilled.

Although a lot of papers have been published in the last years concerning thermal and catalytic decomposition of plastics (e.g. Kaminsky et al., 1976, 1991, 2004; Williams et al., 1996, 2004; Serrano et al., 1998, 2009), it is difficult to find information in the literature about pyrolysis of real fractions of plastic wastes coming from packaging applications (Kaminsky et al., 1997; Kaminsky and Kim, 1999), and even more difficult papers concerning catalytic degradation, since catalysts can be deactivated by the presence of inert materials and heteroatoms (Cl, N, S) which form usually part of these type of wastes (Ding et al., 1997; Aguado and Serrano, 1999).

In a previous work (López et al., 2010) the authors studied the variability and behavior in thermal pyrolysis at 500 ºC of the rejected stream of a packaging classification and separation plant. The authors proved that the composition of the rejects of a specific industrial waste separation plant may significantly vary in the course of time and this variability has a strong influence in the pyrolysis process and in the products obtained. The objective of this paper, which is the second part of the author's previous work, is to study the catalytic degradation of these real samples in presence of ZSM-5 zeolite, an acid solid catalyst which has been reported to be especially appropriate in the cracking of plastic feedstocks (e.g., Serrano et al., 2000; Miskolczi et al., 2004; Aguado et al., 2007). The influence of the catalyst in the process and products quality as a function of the composition of the raw material will be discussed, and some results will be compared with those obtained in the first part of the work (thermal pyrolysis) in order to better understand the possibilities of the pyrolysis process. The discussion will be supported with the complete characterization of the pyrolysis products.

2. Experimental

2.1. Samples and catalyst

Three real samples coming from the rejects of a packaging separation and classification industrial plant located in Amorebieta, in the north of Spain, have been pyrolysed. This industrial plant sorts the packaging wastes of most of the province of Biscay.

Information about the process of the separation plant has been given elsewhere, together with the complete characterization of the samples and the discussion about their composition and characterization (López et al., 2010). In order to provide enough information to follow this paper, a summary of the main components as well as the characterization results of the samples are presented again in this paper in Tables 1 and 2.

Table 1. Composition of the samples pyrolysed (wt.%)

	Material	**Sample 1** (Film rich sample)	**Sample 2** (Paper rich sample)	**Sample 3** (Glass rich sample)
Packaging plastics	HDPE	13.44	5.26	18.77
	PP	9.63	8.19	21.94
	PS	6.60	9.79	11.38
	PET	2.88	7.33	3.23
	PVC	4.28	1.42	0.79
	PE film	50.55	9.40	2.14
	PP film	4.92	2.07	1.73
	SUBTOTAL	**92.30**	**43.46**	**59.98**
Other packaging materials	Tetra-Brik	2.73	7.82	-
	Others	1.90	7.08	5.34
	SUBTOTAL	**4.63**	**14.90**	**5.34**
Inappropriate materials	Paper	2.80	33.25	4.19
	Wood	0.07	0.28	3.32
	Glass	0.01	0.60	16.18
	Inerts	-	1.04	1.78
	Others	0.21	6.49	9.21
	SUBTOTAL	**3.07**	**41.66**	**34.68**

Table 2. Moisture. ash and elemental composition (wt.%) and HHV (MJ kg^{-1}) of the samples pyrolysed

SAMPLE	**Film rich sample**	**Paper rich sample**	**Glass rich sample**
Moisture	0.6	2.0	1.0
Ash	2.4	11.4	28.2
C	81.0	61.1	58.7
H	13.7	8.9	8.7
N	0.1	0.3	0.5
S	<0.1	<0.1	<0.1
Cl	0.7	2.4	1.0
Others[1]	1.4	13.8	1.8
H/C ratio	2.0	1.7	1.8
Gross formula[2]	$CH_{2.02}$	$CH_{1.75}Cl_{0.01}O_{0.17}$	$CH_{1.78}O_{0.02}$
HHV	41.4	29.4	30.6

[1] By difference; [2]Considering others=oxygen

The catalyst used in the experiments was a commercial ZSM-5 zeolite provided by Zeolist International; its main characteristics are shown in Table 3.

Table 3. Textural and acid properties of the ZSM-5 zeolite

BET surface area (m^2 g^{-1})	412.0
External surface area (ESA) (m^2 g^{-1})	65.88
Micropore area (m^2 g^{-1})	346.1
Micropore volume (MPV) (cm^3 g^{-1})	0.100
Total pore volume (TPV) (cm^3 g^{-1})	0.397
Total acidity (mmol NH_3 g^{-1})	0.176

In all the experiments it was used as was received in a plastic/catalyst ratio of 10/1 and in liquid phase contact mode. In this catalytic configuration the catalyst is mixed with the sample in the pyrolysis reactor; liquid phase contact mainly differs from vapor phase contact (in this configuration the catalyst is placed in a secondary reactor where pyrolysis vapors are reformed) in the fact that the catalyst directly influences in the pyrolysis reactions. Although sometimes the consumption of catalyst is higher in liquid phase contact, this configuration was used in this work with the aim of studying the effect of catalyst in the pyrolysis reactions.

2.2. Thermogravimetric analyses and pyrolysis experiments

The thermal behavior of the samples was studied using a Mettler Toledo TGA/SDTA851 analyzer. The analyses were conducted with 7.5 mg samples, which were heated under nitrogen flow (50 mL min^{-1}) to 600 ºC at a rate of 20 ºC min^{-1}. The temperatures of the maximum degradation rates were determined from the derivative thermogravimetric (DTG) plot. The thermogravimetric analyses were carried out without catalyst since they were used to obtain analytical information.

The pyrolysis experiments were carried out at 440º C in nitrogen atmosphere, using an unstirred stainless steel 3.5 dm^3 reactor in semi-batch operation. In a typical run, 100 g of sample with a particle size of 8 mm are mixed with 10 g of catalyst and placed into the reactor. Nitrogen is passed through at a rate of 1 dm^3 min^{-1} and the system is heated at a rate of 20º C min^{-1} to 440º C, and maintained there for 30 minutes. 440 ºC is the final temperature of the process but pyrolysis begins below that temperature; in the catalytic experiments, the first pyrolysis vapors can be seen between 270 and 300 ºC. The parameters used in this paper (440 ºC, 30 min) are optimized operating conditions as far as energy efficiency, conversion and liquid yields is concerned. These optimized conditions were established by the authors after specific research concerning this topic.

During each run the vapors leaving the reactor flow to a series of running water cooled gas-liquid separators where the condensed liquids are collected. The uncondensed products are passed through an activated carbon column and collected as a whole in Tedlar plastic bags. Some tests carried out by the authors with and without the activated carbon column (de Marco et al., 2009) showed that such column retained all the aromatic products as well as some liquid products which otherwise passed to the Tedlar bag. A rather small proportion of C4-C6 compounds were also retained, but there was not a significant difference between the composition and HHV of the pyrolysis gases obtained with and without the activated carbon column.

The flow sheet of the experimental setup is presented in Figure 1. As it can be seen in the Figure, the thermocouple which measures and controls the process is placed in the middle of the reactor chamber. This means that although the reactor is an unstirred one and plastics have low thermal conductivity, it is guaranteed that the whole plastic sample reaches at least the preset temperature. On the other hand and concerning N_2 carrier gas distribution, there is a diffusion plate inside the reaction chamber (in the bottom of the reactor) which distributes nitrogen all around the reaction chamber.

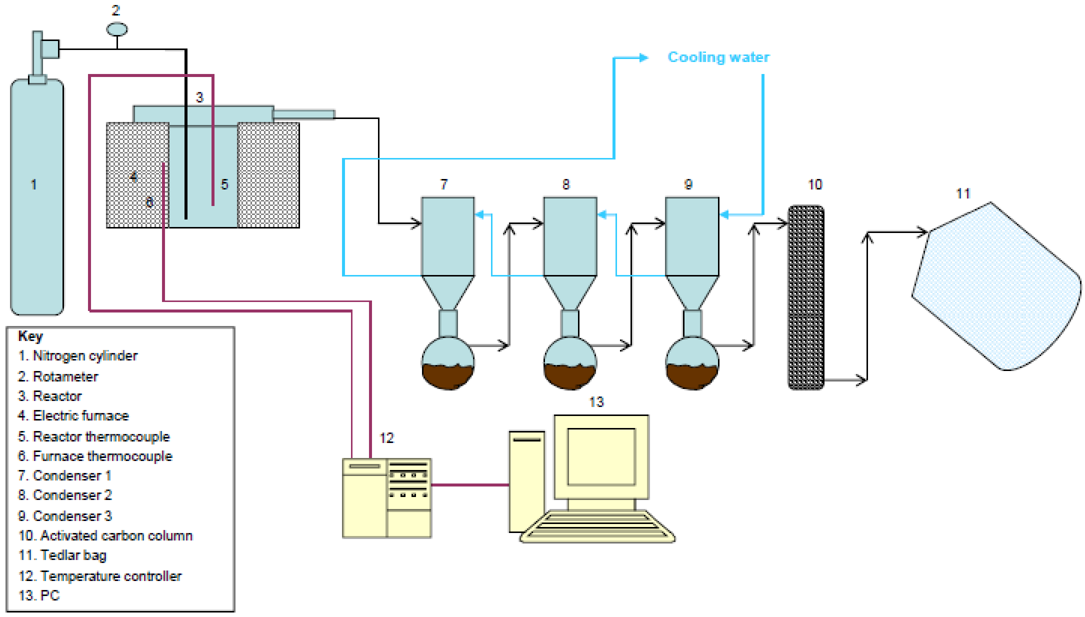

Figure 1. Flow sheet of the experimental set-up used

The amount of solids (products left in the reactor) and liquids obtained are weighed and the pyrolysis yields calculated as weight percentage with respect to the raw material pyrolysed (100 g). The amount of input zeolite is subtracted from the total amount of solids and the yield is calculated with respect to input plastic material (without catalyst). Gas yields are normally determined by difference. In some experiments specifically devoted to directly quantifying the amount of gases, a closure of the mass balance of about 90 wt.% was obtained. In such experiments, total gas quantification was made as follows: (1) mass quantification (mg mL^{-1}) of each gaseous component was determined by GC-FID/TCD; (2) total pyrolysis gas volume was measured and (3) the gaseous compounds quantities were extrapolated to the total volume.

The results of the pyrolysis yields which are presented in the “Results and Discussion” section of this paper are the mean value of at least three pyrolysis runs carried out in the same conditions and which did not differ more than three points in the percentage.

2.3. Analytical techniques

Samples of about 25 kg were collected at the industrial sorting plant. Then, representative samples of 6 kg were selected by cone and quartering procedure and those samples were used for the identification and quantification of components. Visual inspection as well as simple identification techniques (flame color, density, and in doubtful cases FTIR analysis) were used for the composition determination. Once the components were identified and quantified, the samples were ground using a cutting mill suitable for plastics with a sieve grate of 8 mm, which generates a particle size small enough (≤8 mm) to be able to extract homogeneous 100 g samples for the experiments. Additionally, 100 grams of the sample with a particle size ≤8 mm were more finely ground (≤ 1 mm) for characterization purposes under cryogenic conditions using a small cutting mill.

Both the raw materials and the solid and liquid pyrolysis products obtained were thoroughly characterized using the following analytical techniques. The moisture and ash contents of the samples were determined by thermogravimetric analysis, according to D3173-85 and D3174-82 ASTM standards respectively, and the elemental composition with automatic CHN and S analyzers. Method 5050 of the Environmental Protection Agency (EPA) of the United States was used for Cl determination. The higher heating value (HHV) was determined with an automatic calorimetric bomb.

Additionally, pyrolysis liquids were also analyzed by gas chromatography coupled with mass spectrometry detector (GC-MS). When the match quality of the identification result provided by the MS search engine was lower than 85%, the result was not considered valid and these compounds are classified as “Not identified” in the corresponding tables in this paper. The compound names correspond to the tentative assignments provided by the MS search engine, contrasted as far as possible with bibliographic data and sometimes with standards. Concerning pyrolysis gases, they were analyzed by means of a gas chromatograph coupled with a thermal conductivity and a flame ionization detectors (GC-TCD/FID). The HHV of the gases was theoretically calculated according to their composition and to the HHV of the individual components.

The textural properties of the catalyst were determined by means of nitrogen adsorption-desorption isotherms at 77 K in AUTOSORB-1 Quantachrome equipment. Surface areas were calculated by means of BET equation and external surface areas were obtained applying the t-plot method. Total pore volume was measured at $P/P_o = 0.99$. Acidity of the catalysts was measured by temperature-programmed desorption (TPD) of ammonia on a Micromeritics AutoChem 2910 instrument.

3. Results and discussion

3.1. Thermogravimetric analyses

For a better understanding of the thermal behavior of the samples, their TGA plots have been included in Figure 2; Figure 2a shows the weight loss of the samples as a function of temperature and Figure 2b the first derivative of the weight loss. It can be seen in Figure 2a that all of them reach their final weight loss at temperatures over 500 ºC, being this weight loss different from one sample to another due to the differences in composition shown in Table 1. In general terms, the lower proportions of inorganic and char forming materials in the film rich sample make this sample have the highest weight loss (≈95 wt.%). On the contrary, the paper and glass rich samples reach lower weight loss, i.e., 80 and 70 wt.% respectively.

Figure 2b gives more information about the composition of the samples. The paper rich sample shows a quite higher peak near 500 ºC than the other samples, which indicates that this sample contains higher quantities of polyolefins than the other ones, which is in good agreement with the data reported in Table 1. On the contrary, the paper and glass rich samples shows a more noticeable peak at around 440 ºC than the film rich sample, which is indicative of the higher amount of PS and PET in the composition of the formers. Additionally, a small peak around 300 ºC can be seen in all the samples. This corresponds to PVC first decomposition but also to paper decomposition; this is the reason this peak is the highest one for the paper rich sample.

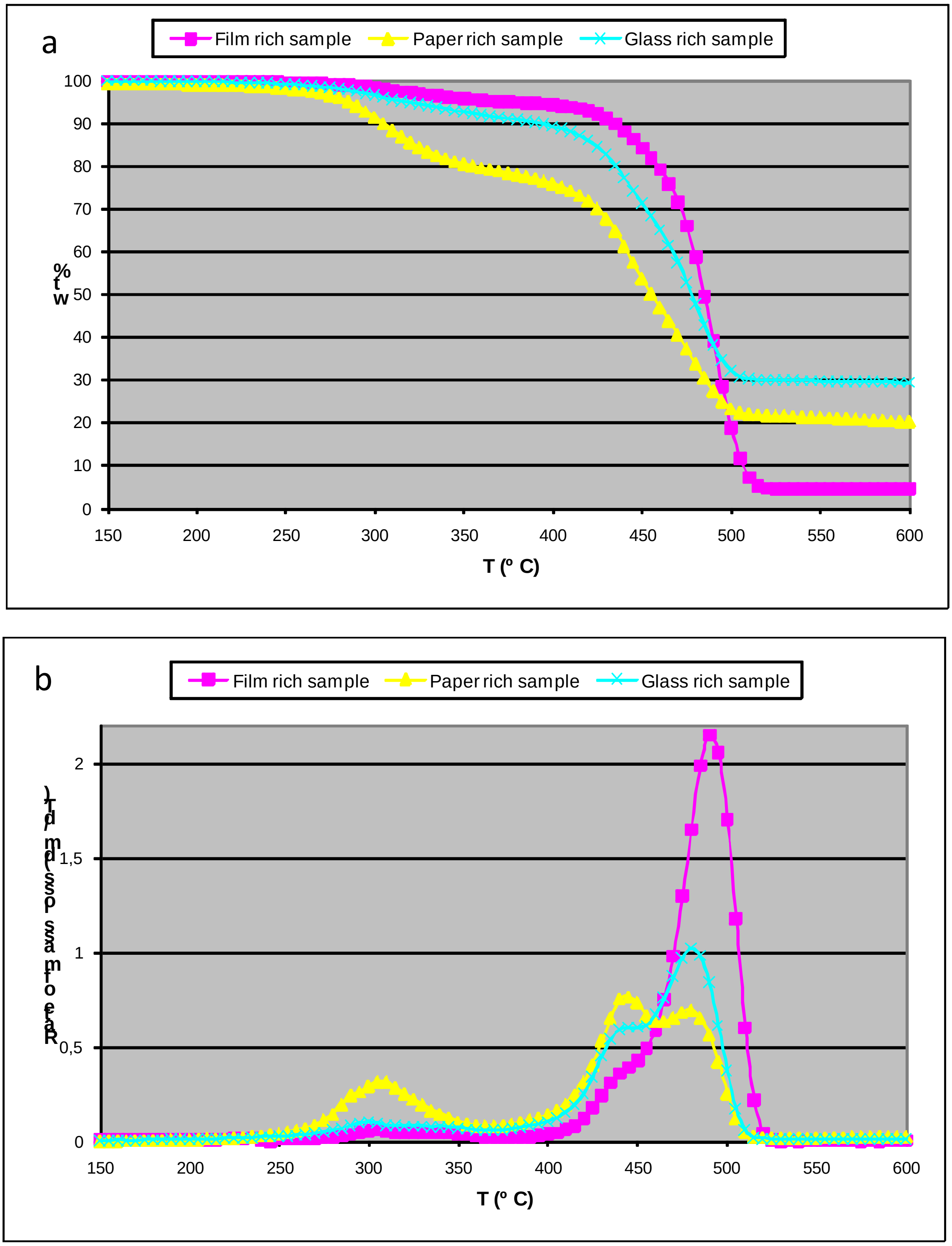

Figure 2. TG and DTG plots of the samples pyrolysed

3.2. Pyrolysis yields

The pyrolysis yields obtained with the three samples tested are presented in Table 4. It can be seen that the yields highly vary depending on the sample pyrolysed. The film rich sample yields 49.9 wt.% of gases and 41.5 wt.% of organic liquids, which means that in spite of the low temperature used (440 ºC), more than 90 wt.% of the plastic waste has been converted. This is an interesting result since 65 wt.% of this sample is PE, and it has been reported that the maximum thermal degradation rate of PE is achieved between 470 and 480º C (Serrano et al., 2005). In the previous paper of the authors (López et al., 2010) very similar conversion (92.2 wt.%) was obtained with the very same sample at 500 ºC without catalyst. Therefore, pyrolysis can be carried out at lower temperatures than thermal runs when ZSM-5 zeolite is used as catalyst, obtaining quite similar results. The particular effect of this catalyst has also been reported by other authors (Aguado et al., 2007).

Table 4. Pyrolysis yields (wt.%)

FRACTION		**Film rich sample**	**Paper rich sample**	**Glass rich sample**
Liquids	Organic phase	41.5	25.5	39.2
	Aqueous phase	0.0	17.1	3.3
Gases		49.9	29.4	13.8
Solids	Inorganics	2.1	11.2	30.8
	Char	6.5	16.9	12.9

The paper rich sample produced lower quantities of organic liquids (25.5 wt.%) and gases (29.4 wt.%) than the film rich sample and it generated an aqueous phase in the liquid fraction and the highest char yield (16.9 wt.%). These effects were also observed in non-catalytic pyrolysis in the previous work published by the authors (López et al., 2010) and they are attributed to the high content in cellulose based materials of this sample. The aqueous liquid fraction obtained in this paper (17.1 wt.%) is higher than that obtained then (12.4 wt.%), due to the greater water generation which is produced in presence of acid solid catalysts during cellulose based materials pyrolysis (Aho et al., 2007; Pan et al., 2010). This also explains the aqueous phase generation in the pyrolysis of the glass rich sample (3.3 wt.%), which did not yield aqueous fraction in the thermal experiments but which also contains a relatively high proportion of cellulose based materials (paper + wood >7 wt.%).

It is also worth noting that the glass rich sample produced quite a high char yield (12.9 wt.%) compared to that obtained in the previous paper of the authors (5.3 wt.%). So the zeolite strongly promotes char formation with this sample, which is in agreement with what has been reported by Serrano et al. (2000) and Williams and Badri (2004), that zeolitic catalysts contribute to char formation. With the other samples, however, char production is only slightly higher than in the thermal experiments (6.2 wt.% now and 5.4 wt.% in the previous work with the film rich sample; 16.9 wt.% now and 15.2 wt.% then with the paper rich sample). So it seems that some kind of interaction among the materials of the glass rich sample and the catalyst itself takes place. It may be suggested that the great quantities of non volatile components (glass, other inert materials and catalyst) which are mixed with the polymeric materials in such sample contribute to char formation just because there is some physic or steric hindrance in the normal release of the polymer derived vapors. Consequently, longer residence time of the vapors in the reactor could lead to higher generation of secondary and tertiary products, which most probably lead to char formation. However, no references have been found in the literature to confirm this theory.

3.3. Pyrolysis liquids

The results obtained in the GC-MS analyses of the organic phase of the pyrolysis liquids are presented in Table 5. For the sake of reduction, only the identified compounds with a percentage quantified area greater than 1% are shown. Nevertheless, all the identified compounds have been considered in the total quantifications (aromatic hydrocarbons, alkanes, alkenes, etc.) and in the C5-C9, C10-C13 and C13-C16 fractions.

Table 5. GC-MS analysis of the pyrolysis liquids (organic phases) (% area)

Molecular formula	**Assignment**	**Film rich sample**	**Paper rich sample**	**Glass rich sample**
C_5H_{10}	Methyl-butene	2.0	n.d.[1]	n.d.[1]
C_7H_8	Toluene	8.5	7.5	7.3
C_7H_5N	Benzonitrile	n.d.[1]	1.4	<1.0
$\mathbf{C_8H_8}$	**Styrene**	**29.8**	**25.3**	**40.2**
C_8H_{10}	Ethyl-benzene	7.1	24.8	14.8
C_8H_{10}	Xylenes	11.7	3.5	1.8

C_8H_8O	Phenyl-ethanone	n.d.[1]	1.3	n.d.[1]
C_9H_8	Indene	1.0	1.9	<1.0
C_9H_{10}	α-methyl-styrene	3.6	6.0	6.9
C_9H_{12}	Ethylmethyl-benzene	3.9	<1.0	n.d.[1]
C_9H_{12}	Trimethyl-benzene	2.8	1.4	n.d.[1]
C_9H_{18}	Dimethyl-heptene	1.9	<1.0	3.8
C_9H_{18}	Propyl-cyclohexane	n.d.[1].	n.d.[1]	1.7
TOTAL C5-C9[2]		***75.5***	***76.0***	***78.6***
$C_{10}H_8$	Naphthalene	1.1	4.8	n.d.[1]
$C_{10}H_{10}$	Methyl-indene	1.2	2.1	n.d.[1]
$C_{11}H_{10}$	Methyl-naphthalene	2.7	4.0	n.d.[1]
$C_{11}H_{24}$	Undecane	1.5	n.d.[1]	n.d.[1]
$C_{12}H_{10}$	Ethenyl-napththalene	n.d.[1]	2.0	n.d.[1]
$C_{12}H_{26}$	Dodecane	1.1	n.d.[1]	n.d.[1]
TOTAL C10-C13[2]		***8.5***	***12.9***	***0.6***
$C_{14}H_{10}$	Phenanthrene	n.d.[1]	1.4	n.d.[1]
$C_{14}H_{30}$	Tetradecane	1.0	n.d.[1]	n.d.[1]
$C_{15}H_{14}$	Phenylcyclopropyl-benzene	1.2	n.d.[1]	1.1
$C_{15}H_{16}$	Propanediyl-benzene	2.0	2.0	2.7
$C_{16}H_{12}$	Phenyl-naphthalene	n.d.[1]	3.2	1.9
$C_{16}H_{16}$	Phenylbuthenyl-benzene	1.6	n.d.[1]	1.4
TOTAL C13-C16[2]		***5.8***	***7.3***	***7.2***
TOTAL AROMATIC HYDROCARBONS		**78.3**	**92.5**	**79.8**
TOTAL ALKANES		**4.5**	**n.d.[1]**	**n.d.[1]**
TOTAL ALKENES		**0.8**	**n.d.[1]**	**n.d.[1]**
TOTAL BRANCHED ALKENES		**3.9**	**0.9**	**3.8**
TOTAL NAPHTHENES		**n.d.[1]**	**n.d.[1]**	**1.7**
TOTAL HETERO-COMPOUNDS (Cl, N, O)		**2.2**	**2.7**	**3.2**
NOT IDENTIFIED		**10.3**	**3.9**	**11.5**

[1]Not detected; [2]This classification includes all compounds in this range, not only those reported in the upper part of the table

Table 5 shows that the liquids obtained in catalytic pyrolysis of packaging wastes are a mixture of hydrocarbons from C5 to C16 for the film rich sample and from C7 to C16 for the paper and glass rich samples; they have a very high content in aromatics (78-93 % area) and an important proportion of products in the C5-C9 carbon atom number range. It is worth mentioning that the film rich sample yielded 78.3 % area of aromatics, in spite of being composed mainly of polyolefins (80 wt.%). In the previous paper of the authors, the amount of aromatics obtained in the corresponding non-catalytic pyrolysis run was just 36.5 % area (López et al., 2010). Therefore, ZSM-5 zeolite clearly promotes aromatization reactions, which has also been reported by other authors (e.g., Vasile et al. 2001; Marcilla et al., 2009). Most of the aromatics found in the liquids derived from polyolefin rich samples pyrolysis are formed by secondary reactions. Aromatics formation is attributed to secondary reactions among the primary aliphatic products (Diels-Alder reactions and/or cyclation of olefin structures followed by dehydrogenation reactions) and these secondary reactions are favored by catalysts as that used in this study.

Concerning the carbon atom number fractions, the film rich sample yielded 75.5 % area of C5-C9 products, while in the corresponding non-catalytic run only 35.9 % area of such products and up to 46.5 % area of >C13 products were obtained, even though the thermal run was carried out at higher temperatures than the catalytic one (500 and 440 ºC respectively). Even though the liquid yield in the catalytic run is lower than in the thermal run, the absolute value of C5-C9 percentage is higher than in the thermal run. Therefore, ZSM-5 zeolite is a very effective catalyst for polyolefin rich samples cracking, increasing the C5-C9 fraction which is of the most interest since such fraction resembles gasoline like fuels.

Table 5 also shows that the liquids obtained with the film rich sample contain 4.5 % area of alkanes but only 0.8 % area of alkenes (and none among the main components of the liquids), which are normally the main primary products generated in PE decomposition at low temperatures (Predel and Kaminsky, 2000; Ueno et al., 2010). This fact may be explained as follows; the main mechanisms proposed up to now to explain the formation of aromatics in pyrolysis of polyolefin rich samples are (1) Diels-Alder type reactions followed by dehydrogenation (Williams and Williams, 1999) and (2) direct cyclation of olefinic structures (Ji et al., 2006). Both processes, apart from contributing to olefin transformation, generate high quantities of hydrogen, which can be adsorbed in the surface of the zeolite, and so it is readily available to saturate olefins, leading to alkanes production.

The liquids obtained with the paper rich sample contain a very high proportion of aromatics (92.5 % area). Such content is quite similar to that obtained by the authors in the previous thermal experiment (96.6 % area) (López et al., 2010). Table 5 shows that with this sample the C5-C9 fraction is also, as with the film rich sample, the most abundant one (76.0 % area), and it is also as abundant as in the corresponding thermal run (López et al., 2010). It must not be inferred from these facts that the catalyst has almost no effect with this sample since it must be borne in mind that the thermal experiments were carried out at 500º C while the experiments with ZSM-5 catalyst have been carried out at 440º C, so the catalyst enables to lower 60ºC the process temperature keeping the quality of the products.

Finally, the liquids derived from the glass rich sample contained 79.8 % area of aromatics, while in the thermal experiments carried out at 500º C aromatics amounted up to 93.4 % area (López et al., 2010), so it seems that with this sample the catalyst is less effective than with the other samples. A plausible explanation to this fact is that fine inorganic particles derived from brittle materials as glass, which are especially abundant in this sample, may block the zeolite pores leading to its deactivation. In addition to this, it must be also taken into account that in the previous paper (López et al., 2010) the authors concluded that the inorganic materials of this sample may have some kind of catalytic effect, and consequently there is no margin for the zeolite to highlight its effect. On the other hand, the proportion of C5-C9 hydrocarbons is the highest among the three samples (78.6 % area) but it is also lower than that obtained in the previous non-catalytic runs (81.9 % area) (López et al., 2010).

Table 5 shows that in every case, styrene is the most abundant product with percentage areas ranging from 25 % with the paper rich sample to more than 40 % with the glass rich sample. Since the PS contents of the samples is rather low (6-11 wt.%), styrene must be generated not only by direct depolymerization of PS, but also by secondary reactions that take place in the course of pyrolysis. It is a really difficult task to propose a possible mechanism for styrene formation. First of all, it has to bear in mind that in catalytic pyrolysis of plastics both thermal and catalytic decomposition take place at the same time, so both mechanisms can be produced simultaneously. Concerning thermal decomposition, styrene is formed at a great extent from direct depolymerization of PS but also by reactions among the primary products derived from the other polymers decomposition. On the other hand, it has been reported (Serrano et al., 2000) that styrene formation during PS catalytic decomposition with zeolites can be lower than in thermal decomposition since the previously formed styrene decomposes into other aromatic compounds as a consequence of the secondary reactions that takes place to a greater extent in presence of zeolites. This is the reason why styrene yield is usually lower in catalytic pyrolysis compared to thermal pyrolysis. As a consequence, to elucidate a possible mechanism for styrene formation in such a complex system (many difficult input materials and many more decomposition products) is not an easy task.

The second most abundant product in the liquids derived from the paper and glass rich samples is ethyl-benzene (24.8 and 14.8 % area respectively), while xylenes isomers are the second compound in abundance in the film rich sample liquids (11.7 % area). The proportion of toluene in the three liquids is also significant (7.3–8.5 % area). A relationship between styrene and ethylbenzene yields can be inferred from the data. For the paper and glass rich samples, which contain similar quantities of PS, the total sum of styrene and ethylbenzene is almost the same (50.1 and 55 % area respectively). In the case in which the zeolite has stronger effect (with paper rich sample), the yield of ethylbenzene is higher than that of the glass rich sample. These data could indicate that ethylbenzene is one of the products of the secondary reactions of styrene.

This composition confers pyrolysis liquids a potential use as raw chemicals source, even though it is known that the achievement of an efficient separation of such chemicals is not easy. On the other hand, although aromatics proportion is limited in commercial fuels, some oil refinery processes (e.g. catalytic reforming process) are focused on producing light aromatic hydrocarbons from naphthenes and alkanes, with the aim of obtaining high-octane reformates for gasoline blending. A highly aromatic liquid fraction coming from plastics pyrolysis may be used in such blending operations without the needing of catalytic reforming processes.

The GC-MS analysis of the aqueous phases obtained in the pyrolysis of the paper and glass rich samples is shown in Table 6; this time all the identified compounds have been included. In both cases, the aqueous phase is a mixture of oxygenated compounds in water solution, being water by far the main component. The proportion of water in the aqueous phase of the paper rich sample liquid (92.4 % area) is higher than that obtained in the previous work of the authors (86.1 % area) (López et al., 2010), when no catalyst was used. Other research groups (Sharma and Bakhshi, 1993; French and Czernik, 2010) have reported that ZSM-5 zeolite is a good catalyst to convert oxygenated organic compounds derived from the primary decomposition of cellulose based materials into short chain hydrocarbons, which will be detected in gaseous phase. This could be the reason why there is less quantity of oxygenated compounds in the aqueous phase of the catalytic experiment compared to the thermal one. Therefore, it could be concluded that one of the roles of ZSM-5 zeolite in pyrolysis of cellulose based materials is to decrease oxygenated organic compounds generation, increasing as a consequence water production.

Table 6. GC-MS analysis of the pyrolysis liquids (aqueous phases) (% area)

Molecular formula	Assignment	Paper rich sample	Glass rich sample
H_2O	**Water**	**92.4**	**87.0**
$C_3H_6O_2$	Methyl acetate	n.d.[1]	0.1
C_3H_8O	Propanol	1.1	0.2
C_4H_6O	Dihydrofuran	0.3	0.2
$C_3H_6O_2$	Propanoic acid	0.5	0.8
C_5H_8O	Cyclopentanone	n.d.[1]	0.2
C_4H_6O	Oxolanone	0.7	1.0
$C_5H_4O_2$	Furfural	0.5	n.d.[1]
C_6H_6O	Phenol	0.9	2.0
C_2H_4	Butadiene	n.d.[1]	0.2
$C_7H_6O_2$	Benzoic Acid	0.3	0.2
$C_6H_6O_2$	Benzenediol	0.2	0.2
$C_6H_{11}NO$	Caprolactam	n.d.[1]	2.0
$C_9H_{10}O$	Methylphenyl-ethanone	n.d.[1]	0.1
$C_8H_4O_3$	Isobenzofurandione	0.4	0.4
TOTAL IDENTIFIED		**97.3**	**94.6**
TOTAL NOT IDENTIFIED		**2.7**	**5.4**

[1] Not detected

Since the zeolite has promoted the formation of water, in this work it has been possible to detect and quantify an aqueous phase in the liquid fraction of the glass rich sample. It has to be mentioned that in the previous work of the authors the carbon content of the glass rich sample derived liquids was 77.3 wt.%, which is quite low compared with the usual values which are obtained in plastics pyrolysis derived organic liquids (84-90 wt.%). The low carbon and high “others” content were probably produced due to the presence of an oxygenated phase (water included) dispersed in the organic liquid. It was not possible to separate such oxygenated phase from the organic phase, not even centrifuging the liquids, which indicates that it was in the form of an emulsion; other methods such as changing the ionic strength of the water phase would be needed in order to achieve such separation.

The elemental composition and higher heating value of the organic phase of the pyrolysis liquids are presented in Table 7.

Table 7. Elemental composition (wt.%) and HHV (MJ kg^{-1}) of the organic pyrolysis liquids

SAMPLE	**Film rich sample**	**Paper rich sample**	**Glass rich sample**
C	84.6	87.4	84.7
H	12.9	10.2	11.5
N	< 0.1	0.1	0.2
Cl	0.3	0.9	0.2
Others[1]	2.3	1.5	3.4
H/C ratio	1.8	1.4	1.6
HHV	44.4	38.4	41.9

[1] By difference

The results are quite in agreement with the GC-MS analyses and show that the liquid obtained from the paper rich sample has the highest carbon content (87.4 wt.%), as well as the lowest hydrogen content (10.2 wt.%), which corresponds to the great proportion of aromatics showed in Table 5. This is the reason why its H/C ratio and HHV are also the lowest ones (1.4 and 38,4 MJ kg^{-1} respectively). On the contrary, the H/C ratio and HHV of the liquid derived from the film rich sample are the highest ones (1.8 and 44.4 MJ kg^{-1} respectively), corresponding to the higher proportion of non-aromatic compounds in its composition. It is worth mentioning that the three liquids have very high HHV, similar to those of conventional liquid fuels, so they can be considered as an appropriate alternative to fossil fuels. Table 5 also shows that some of the chlorine coming from PVC ends in the liquid fraction; the amount of chlorine is especially high in the liquid derived from the paper rich sample (0.9 wt.%), which is the consequence of the high chlorine content of this sample. The presence of chlorine is a handicap to make use of pyrolysis liquids. A method for preventing transferring chlorine to pyrolysis oils is presented in Section 3.6.

The results in this section have shown that ZSM-5 zeolite has a strong effect in the pyrolysis liquids. However, the quantity and cost of the catalyst is a key factor in the economy of the process. The authors have studied at the same time of this work (unpublished yet) the regeneration capacity of ZSM-5 zeolite after plastic wastes pyrolysis process. The results obtained in such study have proved the possibility of zeolite regeneration, leading to the same results as those obtained in the pyrolysis runs carried out with fresh ZSM-5 zeolite. These results make ZSM-5 zeolite be a very interesting catalyst for plastic wastes pyrolysis.

3.4. Pyrolysis gases

Table 8 shows that pyrolysis gases are composed of hydrocarbons ranging from C1 to C6, hydrogen and some carbon dioxide and monoxide.

Table 8. GC-TCD/FID analysis (wt.%) and GVC (MJ kg^{-1}) of pyrolysis gases

SAMPLE	**Film rich sample**	**Paper rich sample**	**Glass rich sample**
H2	0.5	1.2	0.7
CO	0.6	8.7	3.7
CO2	1.4	20.4	11.7
Methane	1.4	11.0	4.3
Ethane	1.4	4.9	4.9
Ethene	5.1	12.5	5.8
C3	29.6	24.3	27.3
C4	32.0	15.2	25.2
C5	19.8	1.8	15.1
C6	8.3	<0.1	1.2
HHV	48.3	36.7	42.6

In all the cases, C3 and C4 are the main components of the gases. In the non-catalytic pyrolysis runs carried out by the authors in the previous work (López et al., 2010), noticeable lower proportions of C3 and C4 compounds were obtained. Therefore, ZSM-5 zeolite promotes C3-C4 fractions formation. Wei et al. (2010) and Huang et al. (2010) have also reported that C3 and C4 fractions are the main gaseous components in ZSM-5 catalytic pyrolysis of PE and PP rich samples.

The paper rich sample generated high quantities of CO and CO_2, which was also reported in the first part of this work (López et al., 2010) and it is most probably due to its high paper content, since cellulose is a high oxygen containing polymer. It has to be mentioned that the proportions of CO and CO_2 obtained in this work (8.7 and 20.4 wt.% respectively) are lower than those obtained in the non-catalytic experiments in the previous paper (11.6 and 33.1 wt.% respectively). This may be because some of the oxygen has been used to form water which condensed in the aqueous liquid fraction, which, as it has been mentioned before, is more abundant in the catalytic than in the non-catalytic experiment. It is also worth noting that the paper rich sample generated the highest quantity of H_2 in the gases, probably due to the fact that the liquids of this sample are the ones that contain the highest quantity of aromatics, and aromatization reactions are normally accompanied by H_2 production.

The glass rich sample showed behavior halfway between those of the other two samples; it generated more quantity of C3-C4 fraction than the paper rich sample and less than the film reach sample, due to its proportions of PE and PP, which are halfway between those of the other samples. Similarly, it also generated less CO and CO_2 than the paper rich sample and less than the film rich sample, probably due to the relatively high proportion of cellulose based materials that this sample contains.

The HHV of the gases depends on the CO_2 content and consequently the paper rich sample, which is the one with the highest content of CO_2, has the lowest HHV (36.7 MJ kg^{-1}). Anyway, the HHV of any of the pyrolysis gases is quite high, close than that of natural gas (48-53 MJ kg^{-1}). For this reason pyrolysis gases may be used as energetic source for the process.

3.5. Pyrolysis solids

The composition of pyrolysis solids is presented in Table 9.

Table 9. Moisture, elemental composition in wet basis (wt.%) and HHV (MJ kg^{-1}) of pyrolysis solids

SAMPLE	Film rich sample	Paper rich sample	Glass rich sample
Moisture	5.0	6.5	2.2
C	26.8	27.4	14.5
H	3.6	2.4	1.2
N	0.5	0.6	0.8
Cl	3.7	5.5	4.0
Ash	57.7	56.2	75.9
Others[1]	2.7	1.4	1.4
H/C ratio	1.6	1.1	1.0
HHV	14.5	10.4	11.0

[1] By difference

Given that it was not possible to separate the catalyst from the pyrolysis solid products, the latter were characterized mixed with the catalyst. The catalyst and the inorganic material coming from the original samples are the reason why the “ash” classification is the highest one in all the cases (56-76 wt.%), especially in the solid of the glass rich sample. Comparing to the results obtained in the previous paper of the authors in experiments without catalyst (López et al., 2010), a much higher H/C ratio has now been obtained (1-1.6 now and 0.5 then). This is probably due to the fact that the thermal runs were carried out at 500 ºC, while the catalytic runs were performed at 440 ºC; at this lower temperature small quantities of the raw material may have not been decomposed.

The film rich sample derived solid is the one with the highest H/C ratio, which may indicate that more unconverted plastic matter is present in this solid than in the other ones. Finally, it must to be mentioned that the pyrolysis solids have a significant chlorine content (3.7-5.5 wt.%), the highest one that obtained in the solid coming from the paper rich sample, which is in accordance with some published results which report that cellulose based materials are capable of fixing the chlorine in the solid fraction of the pyrolysis process (Fontana et al., 2000; Kuramochi et al., 2008).

The pyrolysis solids may look at first sight as a useless product of the pyrolysis process, which most probably would have to be landfilled. At best, the inorganic material and the catalyst could be recovered and the organic fraction could be used for energy recovery. Bernardo et al. (2009 and 2010) have recently published some works warning about the potential ecotoxicology of pyrolysis derived chars due to their content in heavy metals and organic contaminants. So whatever the final use of these solids is, a pre-treatment step aimed to improving the material quality would probably be necessary prior to their final disposal.

3.6. Avoiding water and chlorine in pyrolysis liquids by means of stepwise pyrolysis

Stepwise pyrolysis is an alternative to avoid transferring the chlorine that comes from PVC containing plastic mixtures to pyrolysis liquids. It consists in a previous low temperature step in which the PVC is partially decomposed generating HCl, which is removed from the reaction medium and therefore cannot react with the pyrolysis organic vapors (Hornung et al., 1999; Sakata et al., 2004). In a previous paper (López et al., 2011), the authors obtained quite good ratios of dechlorination of the liquids of a PVC containing plastic mixture by means of a 300 ºC-60 min step previous to pyrolysis.

As it has been discussed above, the presence of paper in packaging waste samples leads to the generation of an aqueous phase in the liquid fraction; this involves that a separation process will be required to remove water after pyrolysis. In order to know the behavior of paper under pyrolysis conditions, a paper sample coming from magazines was analyzed by thermogravimetric analysis. The first derivative plot of the weight loss of the sample as a function of temperature is shown in Figure 3.

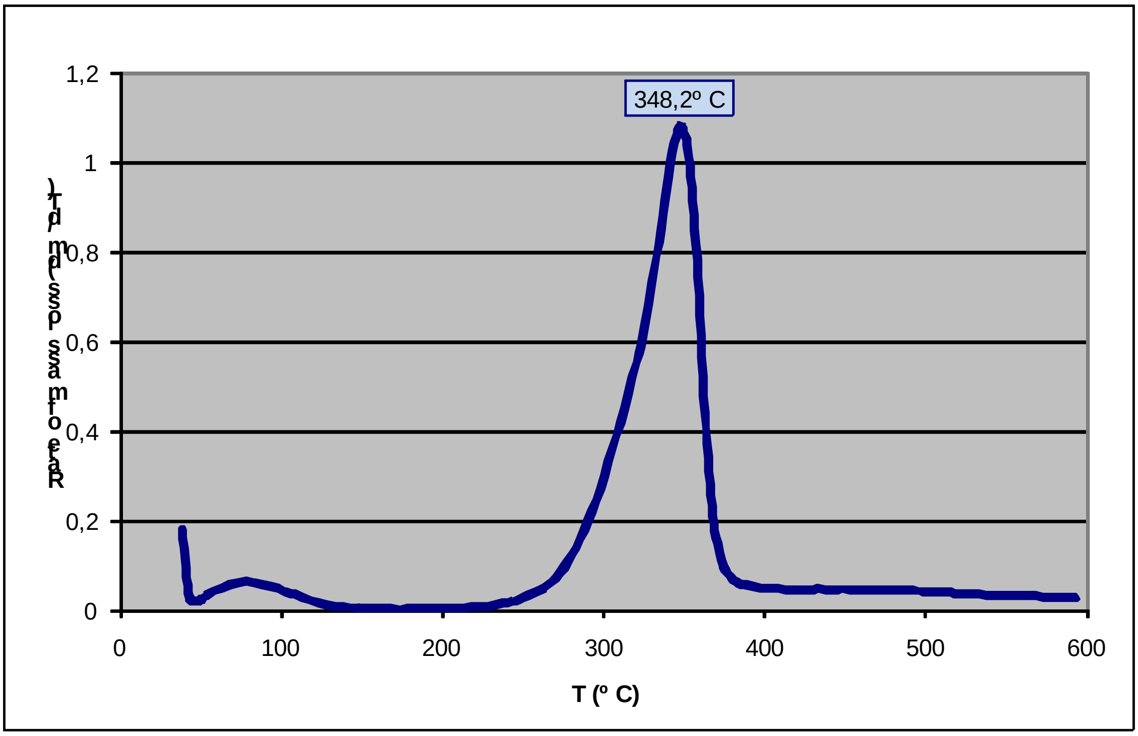

Figure 3. DTG plot of a sample of magazine paper

It can be seen that the maximum degradation rate of paper takes place at around 350º C, which is quite close to the temperature at which the maximum degradation rate of PVC first decomposition takes place (≈300º C), and far enough from the temperature at which the maximum degradation rates of the main packaging plastics takes place (≈425 ºC for PS, ≈450 ºC for PET, ≈475 ºC for PP and ≈485 ºC for PE), as it has been proved by the authors and other research groups (e.g. Bhaskar et al., 2005). Additionally, Korkmaz et al. (2009) have reported in a study about pyrolysis of tetrapack that the temperature at which the maximum degradation rate of the cardboard takes place is about 360º C. Therefore, paper-like materials which are usually found in packaging wastes decomposed in a relatively low temperatures range.

A stepwise pyrolysis experiment with a previous step at 300 ºC during 60 min was carried out with the paper rich sample in order to know if it is possible to remove water previous to the pyrolysis process itself. Since the objective of this experiment was just water removal, it was carried out without catalyst and at 500 ºC, which are the same conditions as those used in the previous paper of the authors (López et al., 2011). The pyrolysis yields and the characteristics of the liquids are presented in Tables 10 and 11.

Table 10. Pyrolysis yields obtained in stepwise pyrolysis with paper rich sample (wt.%)

FRACTION		Previous step (300º C)	Pyrolysis step (500º C)
Liquids	Organic phase	0.0	35.0
	Aqueous phase	16.7	0.0
Gases		20.9	
Solids	Inorganics	11.4	
	Char	16.0	

Table 10 shows that complete removal of water is achieved if stepwise pyrolysis is applied. As expected, the organic liquid yield was higher and the gas yield lower than those obtained in the catalytic experiment (Table 4), while char yields were very similar (16.0 wt.% in stepwise and 16.7 wt.% in the catalytic experiment). It has to be mentioned that the aqueous phase yield obtained in stepwise pyrolysis was lower (16.7 wt.%) than in the case of catalytic pyrolysis (19.2 wt.%), which can be explained as follows.

Table 11. Elemental composition (wt.%) and HHV (MJ kg^{-1}) of the organic pyrolysis liquids obtained in stepwise pyrolysis of the paper rich sample

SAMPLE	Paper rich sample
C	60.9
H	10.2
N	0.2
Cl	0.2
Others[1]	28.7
H/C ratio	1.4
HHV	41.5

[1] By difference

Table 11 shows that the carbon content of the organic liquid obtained in stepwise pyrolysis is quite lower than that obtained in the catalytic experiment (60.9 and 87.4 wt.% respectively), which produces a great “others” content in the former, probably due to high proportions of oxygen solved in the organic fraction. Although this high oxygen content could be a limitation for liquid fraction applications, quite a similar elemental composition can be found in the bio-oils coming from biomass pyrolysis (Demirbas, 2007; Bhattacharya et al., 2009), for which a wide range of applications and purification processes are being developed nowadays (Mohan et al., 2006).

Additionally, the low temperature previous step produced a high ratio of dechlorination of the sample, leading to an organic liquid fraction with only 0.2 wt.% of chlorine instead of the 0.9 wt.% which was obtained in the conventional catalytic pyrolysis run with this same sample (Table 7). This is a promising result since almost 80 wt.% of dechlorination has been achieved. Therefore, a previous low temperature step is an effective way of avoiding both chlorine and water in the pyrolysis liquids, when PVC and/or paper containing packaging wastes are pyrolysed.

Conclusions

The results presented in this paper have been obtained at lab scale with three plastics-rich residues coming from a waste packaging sorting industrial plant. Since the composition of the samples is intrinsically fluctuating and the installation used is not an industrial one, the results must be considered as an interesting approach for developing new plastic waste management solutions. Pyrolysis is an attractive alternative for chemical recycling of complex plastic wastes and the use of catalyst can significantly enhance the process.

The main conclusions that can be drawn from the results of this work are the following. ZSM-5 zeolite is a suitable catalyst for obtaining C3-C4 rich gases and liquids with high aromatic content at relatively low temperatures (≈440º C) even if the raw material contains great quantities of polyolefins. However, when there are high proportions of inorganic components in the raw materials, physical blockage and subsequent loss of the catalyst activity takes place, and no effect in the pyrolysis products is observed. In such cases, a thermal process at higher temperatures would probably be a more effective way of obtaining valuable products. When the waste sample contains significant quantities of paper and cellulose based materials, the formation of a two-phase liquid fraction can be avoided by means of a previous low temperature step (≈300º C), in which the oxygen rich aqueous phase is removed. In these cases, an organic liquid which resembles bio-oils coming from biomass pyrolysis is obtained, which contains less carbon and more oxygen than the usual in pyrolysis liquids. ZSM-5 zeolite promotes the formation of water, so it should be added to the process after the separation of the aqueous phase in the previous low temperature step. In any case, stepwise pyrolysis is recommended to reduce the chlorine content in the liquid fraction when PVC is one of the raw materials.

The pyrolysis liquids and gases obtained in pyrolysis of packaging wastes are high HHV products which can be used as alternative fuels for heat and power generation. Additionally, the liquid fraction can be considered a source of valuable chemicals, since styrene, xylenes, toluene or ethyl-benzene are obtained in high proportions. Finally, metals and glass of the solid fraction may be recovered for recycling processes.

This and the previous paper of the authors, both devoted to analyze the behavior of different real packaging samples in pyrolysis, have shown that such process is a promising technique for feedstock recycling of packaging plastic wastes. It is a versatile process which can be adapted to the nature and composition of the raw material in order to make the most of the pyrolysis products. Variations in the process, such as the use of catalyst and carrying out the process in more than one step, enable to produce good quality fuels and chemicals from poor-valued mixed packaging wastes.

Acknowledgements

The authors thank the Spanish Ministry of Education and Science (MEC) (CTQ 2007-67070/PPQ) as well as the Basque Country Government (ETORTEK 2007 IE07-207, GIC 07-09-IT-354-07 and Researchers' formation program - 2008) for financial assistance for this work.

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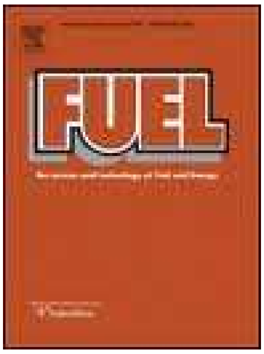
4.4. PYROLYSIS YIELDS PREDICTION TOOL AS A FUNCTION OF SAMPLE COMPOSITION



Article: *Pyrolysis of municipal packaging wastes: Pyrolysis yields prediction tool*

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Journal: *Fuel*

State: *Under review.*

Abstract

The yield and characteristics of packaging wastes pyrolysis products depend on the composition of the input material. The aim of this study is to predict the yield of the different pyrolysis fractions (organic liquid, aqueous liquid, gas, char, inorganics) as a function of the input waste composition. Nine real municipal packaging waste samples and four mixtures of pure materials prepared by the authors have been pyrolysed in a 3.5 dm^3 semi-batch reactor at 500 ºC. The pyrolysis yields obtained in these experiments, together with some data about the pyrolysis yields of specific materials taken from the literature, have been used as raw data for developing the prediction model. The model parameters have been obtained by means of multiple lineal regression of the experimental data. The accuracy of the predicted values is influenced by the nature of the specific sample; the predicted values are more accurate when mixtures of pure materials are studied than when real complex samples are considered. Anyway, the predicted values are acceptable enough to be a useful tool for designing industrial processes. Additionally, the model is easily used since it only requires a few composition data.

Keywords: pyrolysis, feedstock recycling, empiric model, packaging wastes, yields prediction.

1. Introduction

Pyrolysis is an alternative process for recycling polymeric waste streams. By this technique fuels and chemicals are produced by means of thermal cracking of the polymeric feedstocks. The pyrolysis process consists in heating the sample in an oxygen free atmosphere; the organic components of the material are decomposed and evolve from the reactor generating liquid and gaseous products, while the inorganic materials remain unaltered in the reactor together with a carbonaceous solid formed in the process called char. Pyrolysis is an especially appropriate recycling technique for waste streams containing different polymers and other materials, since no separation operations are needed prior to the process. This confers pyrolysis an advantageous position with respect to mechanical recycling, which requires quite pure polymers to be successfully used.

Semi-industrial pyrolysis processes which have been developed up to now have spent much time on trials looking for the ideal waste composition to optimize the process design and economics [1]. However, previous studies carried out by the authors have proved that the composition of municipal packaging wastes varies depending on several factors such as the technology of the sorting plants, seasonal variations, citizen habits etc. [2]. Therefore, if pyrolysis is to be considered an alternative to recycle municipal packaging wastes, it has to be assumed that working with real waste streams means that the input material is going to have a changeable composition and that the process must be versatile enough to be capable of treating wastes of different composition and the products derived from them.

Modeling can be a useful tool to help to design industrial processes. Models of different complexity can be implemented depending on the nature and the accuracy of the prediction desired. Broadly speaking and concerning thermal sciences, the following models types have been proposed: (1) Empiric models, where a collection of experimental data are computationally optimized in order to obtain a general model which explains the empirical results and predicts future ones [3-5]. (2) Kinetic models, where a global kinetic behavior of the process is inferred from experimental data, usually obtained in TGA analyses [6-8]. (3) Chemical equilibrium based models, where the concentration of some process products is predicted from the proximate and ultimate analysis of the sample, taking into account some species which will be formed during the process but not considering the representative reactions [9-11]. (4) Mechanistic models, where all the species and reactions are considered (up to the desired precision) and a differential equations system is mathematically solved in order to obtain products concentration [12-13]. All the above mentioned models present drawbacks and advantages; a resumed compilation of them is showed in Table 1.

Table 1. Major advantages and drawbacks of different types of models

Model type	Major advantages	Major drawbacks
Empiric	-Model simplicity -Accuracy in the specific application	-Need of lots of experimental work -Limited validity
Kinetic	-Low experimental requirements	- Description of a complex phenomenon using a global kinetic scheme
Chemical Equilibrium	-Simple experimental input -Independent of the reactor design	-Errors derived from assuming equilibrium state -Kinetic is not considered
Mechanistic	-Detailed and accurate compounds prediction	-Computational and theoretical difficulties

At first sight, chemical equilibrium and mechanistic models seem to provide more detailed information about the process; however, the former can lead to big errors due to the assumption of chemical equilibrium state condition, which is especially difficult to fulfill at low temperatures and when kinetic constraints become the major factor [14]. On the other hand, the hundreds or high number of species and reactions that take place in mixed packaging wastes pyrolysis make it computationally difficult or almost impossible to implement a mechanistic model; Levine and Broadbelt [13] reported 151 species and more than 11000 reactions in the mechanistic model of single PE pyrolysis. Consequently, the development of an empiric model to predict pyrolysis yields based on experimental data, has been considered the best option in this study.

The objective of the model is to predict the different pyrolysis fractions as a function of the raw material composition. To the best of our knowledge, there is no published information in the literature about a prediction tool of this type. It is of special worth since it has been derived based on pyrolysis data of real municipal packaging wastes and provides valuable previous information rather useful for designing/operating packaging wastes industrial pyrolysis processes.

2. Raw materials and experimental procedure

2.1. Samples pyrolysed

The real municipal packaging waste samples used in this study come from an industrial classification and separation plant which sorts the municipal packaging wastes of the province of Biscay (north of Spain). Such plant is specifically designed to separate metallic packages (tins, aluminum film, etc.) and plastic packages (HDPE, film PE, PET, PP-PS, etc.); therefore, the rest of materials which reach the plant, together with small size materials of the desired fractions, are rejected. Such rejected stream, which is at present sent to incineration, is the sample studied in this paper.

Six different 30-kilogram samples were collected directly from the rejected fraction of the sorting plant between 2007 and 2010 (these 6 samples are named in this paper as “real sample” 1 to 6). Representative 6 kg samples were extracted from the 20 kg-samples by cone quartering procedure in order to determine their composition. Visual inspection as well as simple identification techniques (flame color, density, and in doubtful cases FTIR analysis) were used for this purpose. The real sample 6 was in turn fractionated in three other samples selecting some materials of interest: a commodity plastics-rich sample (named in this paper real sample 7), a cellulose-based materials-rich sample (named real sample 8) and the very same whole sample 6 but without the majority of its inorganic materials (named real sample 9). The detailed composition of these 9 real samples is presented in Table 2.

Table 2. Detailed composition of the real samples pyrolysed (wt.%)

MATERIAL	**REAL SAMPLE 1**	**REAL SAMPLE 2**	**REAL SAMPLE 3**	**REAL SAMPLE 4**	**REAL SAMPLE 5**	**REAL SAMPLE 6**	**REAL SAMPLE 7**	**REAL SAMPLE 8**	**REAL SAMPLE 9**
COMMODITY PLASTICS									
PE	39.50	13.44	5.26	13.35	9.59	5.69	17.24	-	8.42
PE film	-	50.55	9.40	1.52	1.84	0.68	2.06	-	1.01
PP	34.17	9.63	8.19	15.61	6.07	8.29	25.11	-	12.27
PP film	-	4.92	2.07	1.23	0.95	1.26	3.82	-	1.86
PS/HIPS	9.33	4.07	8.78	5.95	9.92	10.80	32.72	-	15.98
EPS (Expanded PS)	6.93	2.53	1.01	2.15	1.52	0.71	2.15	-	1.05
PET	2.94	2.88	7.33	2.30	1.33	2.91	8.81	-	4.31
PVC	4.16	4.28	1.42	0.56	0.67	2.67	8.09	-	3.95
SUBTOTAL	**97.03**	**92.30**	**43.46**	**42.67**	**31.89**	**33.01**	**100.0**	**-**	**48.85**
OTHER THERMOPLASTICS & THERMOSETS									
SAN	-	-	-	-	0.92	0.47	-	-	0.70
POM	-	-	-	0.03	0.74	0.25	-	-	0.37
PC	-	0.11	0.04	0.59	0.35	0.85	-	-	1.26
PMMA	-	-	0.48	0.39	0.24	0.43	-	-	0.64
Foam (PUR)	-	-	0.07	0.16	0.32	0.04	-	-	0.06
PA	-	-	0.36	0.18	0.22	-	-	-	-
ABS	2.24	-	2.30	1.70	0.20	0.38	-	-	0.56
Thermoset resin	-	-	-	0.13	0.05	0.28	-	-	0.41
Elastomer	-	-	0.08	1.72	0.48	0.13	-	-	0.19
Latex	-	-	0.37	0.69	-	-	-	-	-
SUBTOTAL	**2.24**	**0.11**	**3.70**	**5.59**	**3.52**	**2.83**	**-**	**-**	**4.19**

CELLULOSE-BASED MATERIALS									
Paper / Cardboard	0.35	2.80	33.25	2.98	8.26	20.82	-	77.48	30.81
Wood / Cork	-	0.07	0.28	2.36	0.68	1.42	-	5.28	2.10
Tetra-brik	-	1.50	7.82	-	-	1.89	-	7.03	2.80
Gardening waste	-	0.01	0.24	0.40	0.35	2.56	-	9.53	3.79
Clothes	-	-	2.15	0.06	0.22	0.18	-	0.68	0.27
SUBTOTAL	**0.35**	**4.38**	**43.74**	**5.80**	**9.51**	**26.87**	**-**	**100.0**	**39.77**
INORGANICS									
Glass	-	0.01	0.60	34.01	39.48	19.81	-	-	-
Arid / Ceramic	-	-	1.04	5.51	6.15	5.96	-	-	-
Aluminium film	0.19	0.64	1.53	1.78	3.29	4.18	-	-	-
Magnetic metal	-	0.20	1.25	0.90	1.82	0.04	-	-	-
No magnetic metal	-	0.42	1.12	0.96	0.25	2.44	-	-	-
Battery	-	-	-	2.08	-	-	-	-	-
SUBTOTAL	**0.19**	**1.27**	**5.54**	**45.24**	**50.99**	**32.43**	**-**	**-**	**-**
COMPLEX MATERIALS (ORGANIC + INORGANIC)									
ABS + Aluminium	-	-	-	-	1.26	-	-	-	-
PP film+ Aluminium film	0.17	-	-	-	0.78	0.16	-	-	0.24
PVC + Aluminium (blister)	-	-	0.21	-	0.41	0.24	-	-	0.35
PE + Aluminium	-	1.23	-	-	-	0.66	-	-	0.98
Printed circuit board	-	-	0.02	-	-	0.32	-	-	0.47
Complex packaging	0.02	0.64	2.95	-	0.23	3.48	-	-	5.15
Medical waste	-	0.07	0.38	0.70	1.41	-	-	-	-
SUBTOTAL	**0.19**	**1.94**	**3.56**	**0.70**	**4.09**	**4.86**	**-**	**-**	**7.19**
TOTAL	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**

Table 2 shows that there are significant differences among the samples even though they have been collected from the same stream of the same industrial plant. These results evidence that the rejected fraction of the separation and classification plant includes high proportions of materials which should have either not reached the plant (glass in samples 4,5 and 6; paper in samples 3 and 6) or should have been separated in the process itself (PE film in sample 2). Therefore, the composition of this rejected stream depends on several factors, such as a potential miss-function of any of the stages of the nominal process of the plant, or fluctuations in the raw material due to changes in the citizen habits or to seasonal variations.

Four additional samples prepared by the authors mixing pure materials were also pyrolysed in order to obtain information of the pyrolysis yields generated by known materials of different nature which are present in significant proportions in the real samples. The materials used to prepare these samples were: (1) recycled paper coming from sheet, (2) recycled cardboard coming from packaging boxes, (3) virgin PE (PE-017/PE-071) provided by Repsol Química S.A. and used for household applications, (4) virgin PP (PP-040) provided by Repsol Química S.A. and used for general applications, (5) virgin PS (HIPS-DL471) provided by Dow Chemical, (6) waste PET, washed and milled, coming from recycled bottles and provided by Remaplast S.A., a Spanish company devoted to municipal plastics recycling and (7) waste PVC coming from a variety of bottles and provided by Gaiker, a Spanish Technology Centre dedicated to research and innovation in recycling and recovery of plastics among other research areas.

The composition of these prepared samples is presented in Table 3. A five component sample which simulates real samples was prepared with the main plastics contained in the real samples (sample 1). Sample 2 contains only polyolefins (PE+PP) since these polymers decompose following mainly a random scission mechanism [15-16] and therefore they have their particular pyrolysis behavior. Sample 3 is just pure PS since this polymer is a model compound of end-chain scission type decomposition [17-18]. Sample 4 was prepared with cellulose-based materials (paper and cardboard) as representative of materials which generate an aqueous liquid phase [19-20]; the proportion of paper to cardboard was established based on the proportion that had been observed in the real wastes.

Table 3. Composition of the samples prepared by the authors (wt.%)

MATERIAL	SAMPLE 1	SAMPLE 2	SAMPLE 3	SAMPLE 4
PE	40.0	50.0	-	-
PP	35.0	50.0	-	-
PS	18.0	-	100.0	-
PET	4.0	-	-	-
PVC	3.0	-	-	-
Paper	-	-	-	86.5
Cardboard	-	-	-	13.5
TOTAL	**100.0**	**100.0**	**100.0**	**100.0**

A sample composed of the two left plastics (PET + PVC) was not prepared, since it was decided not to pyrolyse such polymers alone because they cause important operating problems such as corrosion (PVC) and pipeline obstructions due to condensation of previously sublimed products (PET) [19].

2.2. Pyrolysis experiments

The pyrolysis experiments were carried out at 500 ºC in nitrogen atmosphere, using an unstirred stainless steel 3.5 dm^3 reactor. Previous studies carried out by the authors [21-23] with other plastic wastes (SMC of polyester and fiberglass, scrap tires, automobile shredder residues, etc.) indicated that in the mentioned installation, 500 ºC was the optimum temperature for treating polymeric wastes by pyrolysis.

In a typical run, 100 g of the sample with a particle size of 8 mm were placed into the reactor, which was then sealed. Nitrogen was passed through at a rate of 1 dm^3 min^{-1} and the system was heated at a rate of 20 ºC min^{-1} to 500 ºC, and maintained there for 30 min. During each run the vapors leaving the reactor flowed to a series of running water cooled gas–liquid separators where the condensed liquids were collected. The uncondensed products were passed through an activated carbon column and totally collected in Tedlar plastic bags, to be afterwards tested by gas chromatography. A flow sheet of the experimental setup is presented in Fig 1.

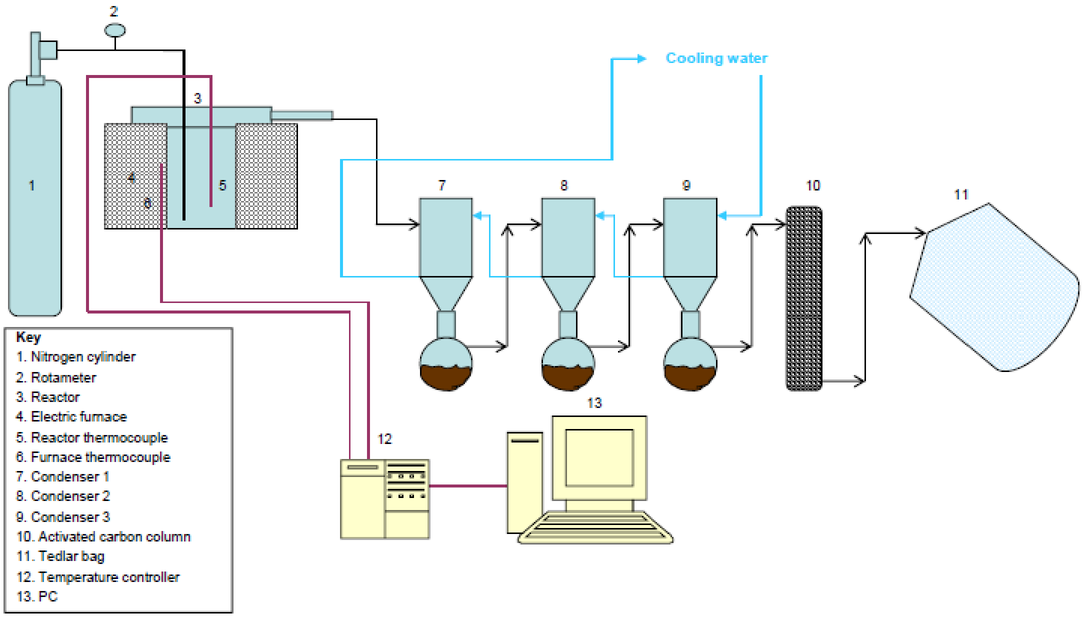

Figure 1. Flow sheet of the experimental set-up used

The amount of solids (residues in the reactor) and liquids obtained were weighed and the pyrolysis yields were calculated as weight percentage with respect to the raw material pyrolysed. Gas yields were normally determined by difference. In some experiments specifically devoted to directly quantify the amount of gases, a closure of the mass balance of about 90 wt.% was obtained. The results of the pyrolysis yields which are presented in “Results and Discussion” section of this paper are the mean value of at least three pyrolysis runs carried out in the same conditions and which did not differ more than three points in the percentage.

2.3. Thermogravimetric analyses (TGA)

Two different thermobalances were used in this study. A LECO TGA-500 thermobalance (which is capable of handling at the same time 19 crucibles of 1-5 g capacity each) and a Mettler Toledo TGA/SDTA851 thermobalance (which works with microsamples and whose results are more accurate due to the smaller sample size). The former was used to carry out the ash determination of the samples pyrolysed, following the ASTM D3174-82 standard. The latter was used to obtain the char yield of PET and PVC. In this case, the analyses were conducted with 7.5 mg samples, which were heated under nitrogen flow (50 mL min^{-1}) to 600 ºC at a rate of 20 ºC min^{-1}.

3. Model description

The objective of the model is to predict the yields of the different pyrolysis fractions (organic liquid, aqueous liquid, gas, char, inorganics) as a function of the raw material composition.

3.1. Model assumptions

Based on the authors' experience, the materials which compose the municipal packaging wastes have been classified into 5 different groups based on their behavior in the pyrolysis process: (1) polyolefins (PO), (2) plastics which produces significant quantities of char in pyrolysis (char forming plastics, CFP), (3) plastics which do not produce char in significant proportions (non char forming plastics, NCFP), (4) cellulose-based materials (CEL) and (5) inorganic materials (INOR). Table 4 shows the materials which have been included in each group.

Table 4. Materials which have been classified in each group

GROUP	**MATERIALS**
Polyolefins (PO)	PE, PP, PE film, PP film
Char forming plastics (CFP)	PET, PVC, POM, PC, Foam, Thermosets, Elastomer, Latex
No char forming plastics (NCFP)	PS/HIPS, EPS, SAN, PMMA, PA, ABS
Cellulose-based materials (CEL)	Paper/cardboard, Wood/cork, Tetra-brik, Gardening waste, clothes
Inorganic materials (INOR)[a]	Glass, ceramics, metals

[a] Determined by TGA according to ASTM D3174-82 standard

The char forming tendency of the plastics has been established following the theory reported by Van Krevelen and Te Nijenhuis [24]. This theory concludes that the char forming tendency depends on the chemical structure of the polymer; such tendency increases with the aromaticity of the polymer, with the substitution of hydrogen atoms of the aromatic units by non-aliphatic chains and when the polymer contains groups capable of reacting with hydrogen atoms of the polymeric structure, such as –OH, =O or –Cl. As it can be seen, there are some materials in Table 2 which have not been specifically included in any of the groups of Table 4, i.e., the complex packaging goods composed of inorganic and organic materials. Since these packaging goods are normally a mixture of different plastics and metals, the proportion of them (which is less than 5 wt.% in all cases) has been proportionally distributed among the other groups in order to take into account their contribution to the yields produced by each group.

On the other hand, it has to be mentioned that the total content of inorganic materials has not been determined by visual inspection of the samples, as it has been done with the other materials. The reason is that if such determination is done visually, it is not possible to quantify the inorganic content of the materials which are included in the other groups (wood, cardboard, fillers in plastics, etc.). The inorganic content of the samples to be used with the model in this study was quantified determining the ash content of the pyrolysis solid generated in their corresponding pyrolysis experiment, since this is the way to determine the exact proportion of inorganic materials that has been introduced in the reactor in each experiment.

Since PVC and PET were not pyrolysed, the pyrolysis yields of PVC and PET used for the development of the model were theoretically determined based on bibliographic data [24-30]; the char yield was additionally experimentally determined by the authors by means of TGA characterization. The PVC and PET pyrolysis yields extracted from the bibliography are presented in Table 5.

Table 5. Bibliographic pyrolysis yields of PET and PVC (wt.%)

MATERIAL	REFERENCE	ORGANIC LIQUID	GAS	CHAR
PET	Authors (TGA)	-	-	15
	Van Krevelen and Te Nijenhius [24]	-	-	17
	Artetxe et al. [25]	41	47	7
	Yoshioka et al. [26]	50	38	12
	Yoshioka et al. [27]	35	37	28
	Mean values	**42**	**41**	**16**
PVC	Authors (TGA)	-	-	21
	Van Krevelen and Te Nijenhius [24]	-	-	22
	Ali and Siddiqui [28]	18	51	31
	Ali and Siddiqui [28]	17	55	28
	Fontana et al. [29]	31	53	16
	Fontana et al. [30]	33	53	14
	Mean values	**25**	**53**	**22**

According to the classification presented in Table 4 and with the inorganics data experimentally determined (TGA) after the pyrolysis runs, the compositions of the real and prepared samples was "re-defined" by grouping all their components according to such classification. The results are shown in Table 6, which gathers the information (input data) which the model will require to make the pyrolysis yields prediction.

Table 6. Composition of the samples defined according to the model input requirements

SAMPLE	**PO**[a]	**CFP**[b]	**NCFP**[c]	**CEL**[d]	**INOR**[e]
Prepared sample 1	75.0	7.0	18.0	0.0	0.0
Prepared sample 2	100.0	0.0	0.0	0.0	0.0
Prepared sample 3	0.0	0.0	100.0	0.0	0.0
Prepared sample 4	0.0	0.0	0.0	100.0	0.0
PET/PVC sample	0.0	100.0	0.0	0.0	0.0
Real sample 1	71.7	7.0	17.8	0.4	3.1
Real sample 2	78.3	7.2	6.6	4.4	3.5
Real sample 3	23.2	8.6	12.1	41.0	15.1
Real sample 4	43.9	8.4	14.0	7.9	25.8
Real sample 5	20.2	4.3	14.3	10.4	50.8
Real sample 6	16.0	7.0	12.9	27.1	37.0
Real sample 7	42.7	18.7	34.3	0.0	4.3
Real sample 8	0.0	0.0	0.0	87.0	13.0
Real sample 9	22.9	10.0	18.4	38.7	10.0

[a] Polyolefins; [b] Char forming plastics; [c] Non-char forming plastics; [d] Cellulose-based materials; [e] Inorganics

3.2. Model calculations

The base equations of the model for any of the samples are the following:

$$\text{Organic liquid yield (OLY)} = a_1*(\%PO) + b_1*(\%CFP) + c_1*(\%NCFP) + d_1*(\%CEL) + e_1*(\%INOR) \quad (1)$$

$$\text{Aqueous liquid yield (ALY)} = a_2*(\%PO) + b_2*(\%CFP) + c_2*(\%NCFP) + d_2*(\%CEL) + e_2*(\%INOR) \quad (2)$$

$$\text{Gas yield (GY)} = a_3*(\%PO) + b_3*(\%CFP) + c_3*(\%NCFP) + d_3*(\%CEL) + e_3*(\%INOR) \quad (3)$$

$$\text{Char yield (CY)} = a_4*(\%PO) + b_4*(\%CFP) + c_4*(\%NCFP) + d_4*(\%CEL) + e_4*(\%INOR) \quad (4)$$

$$\text{Inorganics yield (IY)} = a_5*(\%PO) + b_5*(\%CFP) + c_5*(\%NCFP) + d_5*(\%CEL) + e_5*(\%INOR) \quad (5)$$

where a_1-a_5, b_1-b_5, c_1-c_5, d_1-d_5, e_1-e_5 are the coefficients which define the contribution of each group of materials (PO, CFP, etc.) to the specific pyrolysis yield (OLY, ALY, etc.). The samples prepared with pure materials (samples 2 to 4) were pyrolysed in order to know the exact contribution of PO, NCFP and CEL to the pyrolysis yields. Additionally, the bibliographic data of the PET/PVC sample were used to evaluate the contribution of CFP. The pyrolysis yields obtained with the prepared samples are presented in Table 7. The NCF pyrolysis yields to be used for the model were calculated assuming a PET/PVC proportion equal to 60/40 wt.% (mean value of the relative proportion of PET and PVC in the real samples) and taking as PET and PVC yields the mean values of the data presented in Table 5.

Table 7. Pyrolysis yields of the samples prepared with pure materials (wt.%)

SAMPLE	**OLY**[a]	**ALY**[b]	**GY**[c]	**CY**[d]	**IY**[e]
Prepared sample 2 (PO)	55.2	0.0	44.8	0.0	0.0
Prepared sample 3 (NCFP)	97.5	0.0	1.8	0.7	0.0
Prepared sample 4 (CEL)	5.0	29.8	31.1	34.1	0.0
PET/PVC sample (CFP)[f]	36.1	0.0	45.6	18.3	0.0

[a]Organic liquid yield; [b]Aqueous liquid yield; [c]Gas yield; [d]Char yield; [e]Inorganics Yield

[f]Yields extracted from bibliography (see table 5)

As it can be seen, some of the samples do not contribute to some of the pyrolysis yields; in fact, the aqueous liquid yield is only produced by the CEL sample, and the PO sample does not generate char. These results, together with the fact that the inorganic materials remain unaltered in the process and do not produce any organic fraction bring about some simplifications to the base equations, which are transformed in the following:

Organic liquid yield (OLY) = a_1*(%PO) + b_1*(%CFP) + c_1*(%NCFP) + d_1*(%CEL) (6)

Aqueous liquid yield (ALY) = b_2*(%CEL) (7)

Gas yield (GY) = a_3*(%PO) + b_3*(%CFP) + c_3*(%NCFP) + d_3*(%CEL) (8)

Char yield (CY) = b_4*(%CFP) + c_4*(%NCFP) + d_4*(%CEL) (9)

Inorganics yield (IY) = (%INOR) (10)

Equation 10 needs no calculation, since the inorganics pyrolysis yield (wt.%) must coincide with the inorganic content (wt.%) of the initial sample. The coefficients in equations (6)-(9) were calculated by means of least squares method, following a simple lineal regression in the case of equation 7 and using the Solver Function of Microsoft Excel 2007 to find the independent coefficients of equations 6, 8 and 9 by multiple lineal regression. For this to be possible, for each equation (6) to (9) a series of sub-equations prepared with the pyrolysis yields obtained with each of the samples shown in Table 6 must be set up and solved together. For instance, in order to calculate the coefficients (a_1, b_1, c_1, d_1) of equation (6), 14 sub-equations (9 for the real samples and 5 for the prepared samples) which give the real organic liquid yield as a function of the sample composition (%PO, %CFP, %NCFP and %CEL) must be set up. The input data, the calculated coefficients and mathematical factors provided by Microsoft Excel 2007 Solver Function for each equation are shown in Appendix A of this paper.

4. Results and discussion

The real and predicted pyrolysis yields of all the samples studied are presented in Table 8. This table includes the absolute error of each prediction.

Table 8. Real and predicted pyrolysis yields (wt.%)

SAMPLE	Pyrolysis fraction	Real yield	Predicted yield	Absolute error
Prepared sample 1	Organic liquid	65.2	63.2	2.0
	Aqueous liquid	0.0	0.0	0.0
	Gas	34.0	35.2	-1.2
	Char	0.8	1.7	-0.9
	Inorganics	0.0	0.0	0.0
	Organic liquid + gas	*99.2*	*98.4*	*0.8*
Prepared sample 2	Organic liquid	55.2	57.9	-2.7
	Aqueous liquid	0.0	0.0	0.0
	Gas	44.8	42.1	2.7
	Char	0.0	0.0	0.0
	Inorganics	0.0	0.0	0.0
	Organic liquid + gas	*100.0*	*100.0*	*0.0*
Prepared sample 3	Organic liquid	97.5	95.7	1.8
	Aqueous liquid	0.0	0.0	0.0
	Gas	1.8	2.3	-0.5
	Char	0.7	2.0	-1.3
	Inorganics	0.0	0.0	0.0
	Organic liquid + gas	*99.3*	*98.0*	*1.3*
Prepared sample 4	Organic liquid	5.0	6.0	-1.0
	Aqueous liquid	29.8	30.0	-0.2
	Gas	31.1	33.6	-2.5
	Char	34.1	30.4	3.7

	Inorganics	0.0	0.0	0.0
	Organic liquid + gas	*36.1*	*39.6*	*-3.5*
PET/PVC sample	Organic liquid	36.1	35.8	0.3
	Aqueous liquid	0.0	0.0	0.0
	Gas	45.6	45.3	0.3
	Char	18.3	18.9	-0.6
	Inorganics	0.0	0.0	0.0
	Organic liquid + gas	*81.7*	*81.1*	*0.6*
Real sample 1	Organic liquid	53.0	61.1	-8.1
	Aqueous liquid	0.0	0.1	-0.1
	Gas	41.5	33.9	7.6
	Char	2.4	1.8	0.6
	Inorganics	3.1	3.1	0.0
	Organic liquid + gas	*94.5*	*95.0*	*-0.5*
Real sample 2	Organic liquid	65.7	54.5	11.2
	Aqueous liquid	0.0	1.3	-1.3
	Gas	26.5	37.9	-11.4
	Char	4.3	2.8	1.5
	Inorganics	3.5	3.5	0.0
	Organic liquid + gas	*92.2*	*92.4*	*-0.2*
Real sample 3	Organic liquid	35.1	30.6	4.5
	Aqueous liquid	12.4	12.3	0.1
	Gas	26.0	27.7	-1.7
	Char	11.4	14.3	-2.9
	Inorganics	15.1	15.1	0.0
	Organic liquid + gas	*61.1*	*58.3*	*2.8*
Real sample 4	Organic liquid	40.9	42.3	-1.4
	Aqueous liquid	0.0	2.4	-2.4
	Gas	25.6	25.3	0.3
	Char	7.7	4.3	3.4
	Inorganics	25.8	25.8	0.0
	Organic liquid + gas	*66.5*	*67.6*	*-1.1*
Real sample 5	Organic liquid	26.1	27.5	-1.4
	Aqueous liquid	1.4	3.1	-1.7
	Gas	13.8	14.3	-0.5
	Char	7.9	4.3	3.6
	Inorganics	50.8	50.8	0.0
	Organic liquid + gas	*39.9*	*41.8*	*-1.9*
Real sample 6	Organic liquid	29.3	25.7	3.6

	Aqueous liquid	2.8	8.1	-5.3
	Gas	22.2	19.3	2.9
	Char	8.7	9.8	-1.1
	Inorganics	37.0	37.0	0.0
	Organic liquid + gas	*51.5*	*45.0*	*6.5*
Real sample 7	Organic liquid	60.4	64.2	-3.9
	Aqueous liquid	0.0	0.0	0.0
	Gas	29.1	27.2	1.8
	Char	6.3	4.2	2.1
	Inorganics	4.3	4.3	0.0
	Organic liquid + gas	*89.5*	*91.4*	*-1.9*
Real sample 8	Organic liquid	4.4	5.2	-0.8
	Aqueous liquid	30.1	26.1	4.0
	Gas	29.4	29.2	0.2
	Char	23.1	26.4	-3.3
	Inorganics	13.0	13.0	0.0
	Organic liquid + gas	*33.8*	*34.4*	*-0.6*
Real sample 9	Organic liquid	32.9	36.8	-3.9
	Aqueous liquid	7.1	11.6	-4.5
	Gas	35.9	27.6	8.3
	Char	14.1	14.0	0.1
	Inorganics	10.0	10.0	0.0
	Organic liquid + gas	*68.8*	*64.4*	*4.4*

As it can be seen in Table 8, there are significant differences in the prediction accuracy of the model depending on the fact that the sample is a real waste or a prepared and well-defined sample. The prediction of the pyrolysis yields of the prepared samples is quite accurate and all the absolute errors are lower than 3.7, which are quite acceptable results especially if it is taken into account that the experiment error of the pyrolysis yields is ≈3 wt.%. The accuracy of the pyrolysis yields predicted for the real samples strongly depends on the nature and specific composition of the sample under consideration. This may be attributed to two facts; on the one hand, to the heterogeneity and consequent obvious lack of precision when grouping the components of such samples in families (PO, CFP, NCFP, CEL...), and on the other hand to the potential interactions that may take place among the real samples components.

Since most of the real samples are plastics-rich samples, organic liquids and gases are as a general rule the predominant products; as a consequence they show the greatest absolute errors. The highest deviations can be found in the prediction of the organic liquid and gaseous fractions of real samples 1 and 2 (absolute errors between 7.6 and 11.4) and in the prediction of the gas yield of real sample 9 (absolute error=8.3). On the contrary, the prediction for other samples is really accurate, with errors that lie within the experimental error of the pyrolysis yields determination. For instance, the predicted organic liquid and gas yields for real sample 4 only differ 1.4 and 0.3 respectively from the real values, for real sample 5 only 1.4 and 0.5 respectively and for real sample 8 only 0.8 and 0.2 respectively. These are really good results taking into the complexity of the waste samples (Table 2) and the experimental error of the pyrolysis tests.

The values that results from adding organic liquid and gas yields have been included in Table 8. These added yields represent the conversion of the polymer to the desired valuable products. As a general rule there is a complementarity between gases and organic liquids, so that when liquids are cracked they are most probably converted to gases. Therefore the ratio liquids/gases depends very much on operating factors such as temperature, heating rate or time [21-23]. Table 8 shows that in general terms the prediction of the liquids + gas yields is better than the individual predictions of organic liquid and gas yields for all the samples; it can be seen that when the prediction of the organic liquid yield shows a positive deviation, it is counterbalanced with a negative deviation in the prediction of the gas yield and vice versa, from which it may be inferred that in the real experiments some kind of variation in the extent of cracking has taken place modifying the organic liquid / gas proportion.

In fact, the prediction of organic liquid + gas yield for real samples 1 and 2 only differs 0.5 and 0.2 respectively from the real values, while such samples show significant deviations in the individual yields. No explanation has been found for the differences in the prediction accuracy of the model among the real samples. It may be attributed to some operating or experimental factor or to the intrinsic characteristics of the sample. For instance sample 2, which is one of the samples with the highest error in the organic liquid and gas yields prediction, contains high quantities of PE film. It seems plausible that PE film has not the same pyrolysis behavior as virgin PE grain; PE film is thinner and occupies more volume than PE grains, so the former is probably more quickly and homogeneously heated generating products that leave the reactor sooner (being cracked to a lesser extent), giving as a result a higher liquid and lower gas yield.

Table 8 also shows that as a general rule, the predicted values for the aqueous liquid yields are higher than the real ones for the plastics rich samples. This fact can be due to experimental limitations in the quantification of the aqueous phase, which is carried out separating and weighing such aqueous phase. This procedure is only executed with the pyrolysis liquid collected in the separators. Some additional pyrolysis liquid is retained in the installation pipes and is quantified by weighing the pipes before and after the test. However, it is obviously not possible to collect such liquid and even more to quantify the aqueous phase in it, so it is considered totally organic liquid, and consequently, the total aqueous liquid yield quantified is as a general rule lower than the real one. This is the main reason for the positive deviations of the predicted aqueous liquid yield when plastics-rich samples are considered. On the contrary, if the sample is mainly composed of cellulose-based materials, the predicted values for the aqueous liquid fraction are lower than the real ones, as is the case of real sample 8 (87 wt.% CEL) and real sample 3 (41 wt.% CEL).

Table 8 shows that the predicted values of char yield are higher than the real ones when the initial samples contain high proportions of cellulose-based materials. This is the case for real samples 8, 6 and 3, which contain 87.0, 27.1 and 41.0 wt.% respectively of cellulose-based materials. On the contrary, with the prepared sample 3, which is only composed of paper and cardboard, the result is just the contrary; the model predicts lower proportions of char than the real yield obtained. The explanation to this fact may be that cellulose-based materials different from paper in the real samples (Tetra-brik, wood, etc.) contain other materials (PE in brik, lignin in wood) that yield less char than paper and cardboard. Therefore, since the model minimizes the differences squared, with some samples the difference is positive and in the others negative.

Concerning real samples 4, 5 and 7, which have a rather low proportion of cellulose-based materials (7.9, 10.4 and 0.0 wt.% respectively), the predicted char yield is also lower than the real char. The explanation in these cases may be that due to the low content of cellulose-based materials their contribution to the predictive model loose significance, while the effect of the char forming plastics (CFP) becomes more evident and it may be possible that the char forming tendency of such plastics has been undervalued in the model. It has to be mentioned that CFP content of real sample 5 is rather low (4.3 wt.%), so the above mentioned explanation does not justify the results of this sample; an explanation in this case may be that this sample contains the highest proportion of inorganics (50.8 wt.%) and they may interfere in the process either physically (products retention) or chemically (coke forming reactions), favoring the formation of char and leading to higher char yields than those predicted by the model.

5. Conclusions

The rejects of packaging wastes sorting plants should be mainly composed of packaging plastics (PE, PP, PS, Pet and PVC). However, significant quantities of inappropriate materials such as paper, glass, metals and non-packaging plastics are often present in such wastes. The composition of such rejects varies with the specific conditions of the sorting plant and with the time of the year. The mentioned inappropriate materials yield products other than organic liquid and gases in the pyrolysis process, such as char and water, whose yields vary with the composition of the input material.

An empiric model for the prediction of the pyrolysis yields (organic liquid, aqueous liquid, gas, char and inorganics) as a function of the input material composition has been developed. The model quite well predicts such pyrolysis yields. The only input data required for the model is the proportion of groups of materials of the same nature contained in the wastes sample (polyolefins, char forming plastics, non-char forming plastics, cellulose-based materials, inorganics).

The accuracy in the prediction of pyrolysis yields depends on the complexity of the samples. Very accurate results are predicted when samples prepared by mixing pure materials are considered. The prediction for real samples is more irregular; some real samples are quite well predicted while others show noticeable deviations. The prediction of the valuable desired products (organic liquid + gas) of plastics-rich samples has been found to be quite satisfactory even when significant deviations in the individual prediction of each of these yields are obtained. The predicted values for aqueous liquid yield are higher than the real ones when cellulose-based materials are in the samples in minority proportions, while they are lower than the real ones when the sample contains a high proportion of cellulose-based materials. The char predicted values are lower than the real ones when plastics-rich samples are considered while they are higher for samples with high content of cellulose-based materials.

The simplicity of the proposed empiric model and the low input data requirements make this model an interesting prediction tool for pyrolysis of complex packaging wastes. The values can predicted by the model are acceptable enough to be helpful for the design of industrial processes and will enable to reduce the number of preliminary trials needed for the implementation of the process.

Acknowledgements

The authors thank the Spanish Ministry of Education and Science (MEC) (CTQ 2007-67070/PPQ) as well as the Basque Country Government (ETORTEK 2007 IE07-207, GIC 07-09-IT-354-07 and Researchers' formation program - 2008) for financial assistance for this work.

Appendix A. Model calculation

As it has been described in the text, the equations to be solved for each sample are the following:

Organic liquid yield (OLY) = a_1*(%PO) + b_1*(%CFP) + c_1*(%NCFP) + d_1*(%CEL) (6)

Aqueous liquid yield (ALY) = b_2*(%CEL) (7)

Gas yield (GY) = a_3*(%PO) + b_3*(%CFP) + c_3*(%NCFP) + d_3*(%CEL) (8)

Char yield (CY) = b_4*(%CFP) + c_4*(%NCFP) + d_4*(%CEL) (9)

Inorganics yield (IY) = (%INOR) (10)

The calculation of each coefficient has been made as follows. The results will be shown from the easiest calculation to the most complex one.

A.1. Calculation of the aqueous liquid coefficient: b_2

This equation only requires a simple lineal regression by least squares, which can be easily done with Microsoft Excel. The data must be regressed to an equation in the form $Y=b_2X$; the input data for such regression are shown in Table A.1.

Table A.1. Data for b_2 coefficient calculation (wt.%)

SAMPLE	%CEL (X)	ALY (Y)
Real sample 3	41.0	12.0
Real sample 6	27.1	2.8
Real sample 8	87.0	30.1
Real sample 9	38.7	7.1
Prepared sample 4	100.0	29.8

The value for b_2 was 0.300, with a R^2 value of 0.9196.

A.2. Calculation of the char coefficients: b_4, c_4 and d_4.

The equation of char yield corresponds to a lineal equation of three independent variables ($Y=b_4X_1 + c_4X_2 + d_4X_3$). This calculation was made using the Solver function of Microsoft Excel 2007. The data to be regressed are shown in Table A.2.

Table A.2. Data for b_4, c_4 and d_4 coefficients calculation (wt.%)

SAMPLE	%CFP (X_1)	%NCFP (X_2)	%CEL (X_3)	CY (Y)
Real sample 1	7.0	17.8	0.4	2.4
Real sample 2	7.2	6.6	4.4	4.3
Real sample 3	8.6	12.1	41.0	11.4
Real sample 4	8.4	14.0	7.9	7.7
Real sample 5	4.3	14.3	10.4	7.9
Real sample 6	7.0	12.9	27.1	8.7
Real sample 7	18.7	34.3	0.0	6.3
Real sample 8	0.0	0.0	87.0	23.1
Real sample 9	10.0	18.4	38.7	14.1
Prepared sample 1	7.0	18.0	0.0	0.8
Prepared sample 3	0.0	100.0	0.0	0.7
Prepared sample 4	0.0	0.0	100.0	34.1
PET/PVC sample	100.0	0.0	0.0	18.3

The obtained values were: b_4=0.189, c_4=0.020 and d_4=0.304.

A.3. Calculation of the organic liquid coefficients: a_1, b_1, c_1 and d_1.

The equation of organic liquid yield corresponds to a lineal equation of four independent variables ($Y=a_1X_1 + b_1X_2 + c_1X_3 + d_1X_4$). This calculation was made using the Solver function of Microsoft Excel 2007. The data to be regressed are shown in Table A.3.

Table A.3. Data for a_1, b_1, c_1 and d_1 coefficients calculation (wt.%)

SAMPLE	%PO (X_1)	%CFP (X_2)	%NCFP (X_3)	%CEL (X_4)	OLY (Y)
Real sample 1	71.7	7.0	17.8	0.4	53.0
Real sample 2	78.3	7.2	6.6	4.4	65.7
Real sample 3	23.2	8.6	12.1	41.0	35.1
Real sample 4	43.9	8.4	14.0	7.9	40.9
Real sample 5	20.2	4.3	14.3	10.4	26.1
Real sample 6	16.0	7.0	12.9	27.1	29.3
Real sample 7	42.7	18.7	34.3	0.0	60.4
Real sample 8	0.0	0.0	0.0	87.0	4.4
Real sample 9	22.9	10.0	18.4	38.7	32.9
Prepared sample 1	75.0	7.0	18.0	0.0	65.2

Prepared sample 2	100.0	0.0	0.0	0.0	55.2
Prepared sample 3	0.0	0.0	100.0	0.0	97.5
Prepared sample 4	0.0	0.0	0.0	100.0	5.0
PET/PVC sample	0.0	100.0	0.0	0.0	36.1

The obtained values were: a_1=0.579, b_1=0.358, c_1=0.957 and d_4=0.059.

A.4. Calculation of the gas coefficients: a_3, b_3, c_3 and d_3.

The equation of gas yield corresponds to a lineal equation of four independent variables ($Y=a_3X_1 + b_3X_2 + c_3X_3 + d_3X_4$). This calculation was made using the Solver function of Microsoft Excel 2007. The data to be regressed are shown in Table A.3.

Table A.3. Data for a_3, b_3, c_3 and d_3 coefficients calculation (wt.%)

SAMPLE	**%PO (X_1)**	**%CFP (X_2)**	**%NCFP (X_3)**	**%CEL (X_4)**	**GY (Y)**
Real sample 1	71.7	7.0	17.8	0.4	41.5
Real sample 2	78.3	7.2	6.6	4.4	26.5
Real sample 3	23.2	8.6	12.1	41.0	26.0
Real sample 4	43.9	8.4	14.0	7.9	25.6
Real sample 5	20.2	4.3	14.3	10.4	13.8
Real sample 6	16.0	7.0	12.9	27.1	22.2
Real sample 7	42.7	18.7	34.3	0.0	29.1
Real sample 8	0.0	0.0	0.0	87.0	29.4
Real sample 9	22.9	10.0	18.4	38.7	35.9
Prepared sample 1	75.0	7.0	18.0	0.0	34.0
Prepared sample 2	100.0	0.0	0.0	0.0	44.8
Prepared sample 3	0.0	0.0	100.0	0.0	1.8
Prepared sample 4	0.0	0.0	0.0	100.0	31.1
PET/PVC sample	0.0	100.0	0.0	0.0	45.6

The obtained values were: a_3=0.421, b_3=0.462, c_3=0.039 and d_3=0.336.

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CHAPTER 5

CONCLUSIONS

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The main conclusions that can be drawn from this Ph.D. thesis about pyrolysis of rejected streams of municipal packaging waste are the following:

- Pyrolysis is a promising chemical recycling process which converts mixed packaging waste in valuable products: Pyrolysis liquids, which are a complex mixture of C6-C20 hydrocarbons, can be used as high HHV alternative fuels or as source of valuable chemicals as styrene or toluene. Pyrolysis gases are mainly composed of C3-C4 hydrocarbons and have HHV comparable to that of natural gas. They can supply the energy requirements of the process and the surplus can be used for additional power generation. Pyrolysis solids are composed of a small amount of char, derived from polymeric materials, and the inorganics of the input material.

- The composition of the rejected streams coming from industrial separation and classification plants of municipal packaging waste varies depending on the characteristics of the sorting plant and on the time of the year. Such rejects, which should contain mainly plastic waste, contain other inappropriate materials such as glass, metals and cellulose-based materials.

- The composition of the waste samples has a great influence on the distribution and quality of the pyrolysis products. Cellulose-based materials lead to the generation of an aqueous liquid phase, to great percentages of CO and CO_2 in the gas fraction (which consequently have lower HHV) and to a significant amount of char. On the other hand, high PE film contents give rise to high viscosity wax-like liquids.

- Temperature is an essential parameter of the process. The minimum temperature over which total decomposition of packaging waste is achieved when no catalyst is used is 460 ºC. At this low temperature, high viscosity liquids with high contents of long chain hydrocarbons (>C13) are obtained. As the pyrolysis temperature is raised, lower liquid yields and higher gas yields are obtained, and the liquids are lighter and with a greater content of aromatics. The optimum temperature for pyrolysis of packaging waste when no catalyst is used, in terms of both, yields and quality of the products is 500 ºC.

- Catalysts have a significant influence on pyrolysis of packaging waste. ZSM-5 zeolite enables to operate at lower temperatures (440 ºC), achieving similar yields and product properties than in thermal runs at higher temperatures (500 ºC). Red Mud, which is a cheap byproduct of the aluminum industry, has a noticeable effect in packaging waste pyrolysis, although it has lower activity than ZSM-5 zeolite and its effect does not become evident until higher temperatures (500 ºC).

- ZSM-5 zeolite is quickly deactivated in pyrolysis of packaging waste, but it can be easily regenerated by simple combustion of the deposited coke, which is a key factor for the economics of a potential industrial pyrolysis process.

- Although the use of PVC as packaging material is almost negligible, a small amount of PVC is usually found in the rejects of waste packaging sorting plants. When the raw material contains PVC, pyrolysis liquids include chlorinated compounds and this is very detrimental for their potential applications. The chlorine content of pyrolysis liquids can be significantly reduced by means of a previous low temperature dechlorination step (300 ºC, 60 min), which should be complemented with a unit to capture and neutralize the HCl generated in such step. If the raw material also contains cellulose-based materials, a significant amount of aqueous phase is also separated in this previous step.

- The previous low temperature dechlorination step reduces the activity of the ZSM-5 zeolite in the subsequent pyrolysis step. Therefore, the catalyst should be added after the previous dechlorination step.

- A simple empiric model, which enables to acceptable predict pyrolysis yields as a function of the packaging waste composition, has been developed. It requires few input data and may be a useful tool for designing industrial processes.

- Finally, it has been concluded that a complete and versatile pyrolysis process capable of treating complex and variable plastic packaging waste should include: (1) a first low temperature dechlorination step, (2) the pyrolysis step itself, in which catalyst should be added, if it is used, (3) a condensation unit to collect the pyrolysis oils, provided with a water-oil separation system, and (4) a gas purification system, including a HCl absorption unit to remove HCl from the gaseous fraction both in the dechlorination step and after pyrolysis.

CHAPTER 6

FUTURE RESEARCH LINES

FUTURE RESEARCH LINES

This Ph.D. thesis provides the opportunity to work in parallel or in new research lines concerning feedstock recycling of municipal packaging waste. Some of them are presented below.

- Study of catalytic pyrolysis in vapor phase contact using a second reactor with an independent temperature controller for catalytic treatment of the vapors generated by thermal cracking.

- Upgrading pyrolysis liquids by different processes (e.g. distillation, thermal and catalytic pyrolysis, hydrotreatment), in order to obtain marketable liquids.

- Study of alternatives to make use of pyrolysis solids which enable to recover reusable metals, glasses or char.

- Study in depth the possibilities of Red Mud as pyrolysis catalyst, including pretreatment and activation processes.

- Study of the pyrolysis process in continuous operation in order to better extrapolate the results to an industrial application, including the study of different industrial reactor geometries appropriate for solid materials, such as fluidized bed reactors and screw rotary kiln reactors.

- Study of other alternative chemical recycling techniques for packaging waste which compete with pyrolysis, such as gasification or hydrocracking.

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SYMBOLS LIST

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ABS: Acrylonitrile-Butadiene-Styrene
EPA: Environment Protection Agency
FID: Flame Ionization Detector
GC: Gas Chromatography
GC-MS: Gas Chromatography-Mass Spectrometry
HDPE: High Density Polyethylene
HHV: Higher Heating Value
HIPS: High Impact Polystyrene
IMS: Integrated Management System
LDPE: Low Density Polyethylene
MSW: Municipal Solid Wastes
PA: Polyamide
PC: Polycarbonate
PE: Polyethylene
PET: Poly(ethylene terepththalate)
PMMA: Poly(methyl methacrylate)
POM: Poly(oxymethylene)
PP: Polypropylene
PS: Polystyrene
PUR: Polyurethane
PVC: Poly(vinyl chloride)
SAN: Styrene-Acrylonitrile
SS-304: Stainless Steel 304
TCD: Thermal Conductivity Detector
TGA: Thermogravimetric Analysis
THF: Tetrahydrofuran