



# Thermal and catalytic degradation of polyethylene wastes in the presence of silica gel, 5A molecular sieve and activated carbon

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## ARTICLE INFO

### Article history:

Received 24 June 2010

Received in revised form 9 December 2010

Accepted 29 December 2010

Available online 5 January 2011

### Keywords:

Polyethylene

Plastic wastes

Pyrolysis

Catalysts

Catalytic degradation

## ABSTRACT

A comparative study of thermal and catalytic degradation of polyethylene wastes has been carried out with the aim of obtaining chemical compounds with potential use in the chemical industry and the energy production. Polyethylene wastes were obtained from polyethylene bags used in supermarkets. Catalysts utilized in the study were silica gel, 5A molecular sieve and activated carbon. The pyrolysis was performed in a batch reactor at 450, 500 and 700 °C during 2 h for each catalyst. The ratio catalyst/PE was 10% w/w and the solid and gaseous products were analyzed by gas chromatography and mass spectrometry. The optimum operation temperature and the influence of the three catalysts are discussed with regards to the products formed. The best temperature for degradation with silica gel and activated carbon as catalysts was 450 °C and with 5A molecular sieve was 700 °C. Degradation products of PE (solid fraction and gas fraction) are depending on temperature and catalyst used. External surface and structure of catalysts were visualized by Scanning Electron Microscopy (SEM) and the contribution on product distribution is commented. All products from different degradations could be used as feed stocks in chemical industry or in energy production based on the value of heat of combustion for solid fraction (45 000 J/g), similar to the heat of combustion of commercial fuels.

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## 1. Introduction

In our modern society the production and consumption of plastics have increased drastically and wastes derived from them have become more difficult to handle. The plastic materials have a significant success in the market due to multiple applications because they have good physical and chemical properties and, in many cases, they replace other materials such as glass or wood. Once plastics have finished their use, these materials form part of urban solid wastes, generating great environmental impact, because such material has a very long period of biodegradation.

Current statistics estimate plastic wastes represent 11.7% of urban wastes in Spain [1,2]. Household and industrial plastic wastes generated in Spain in 2001 and 2006 were 2.59 and 2.79 million tons, respectively. There was a significant increase of recycled plastic wastes in this period of time going from 279 thousand tons in 2001 (10.8%) to 499 thousand tons in 2006 (17.9%). However, the amount of no recycled plastics continues to be very large.

On the other hand, world market energy consumption is projected to increase by 44% from 2006 to 2030 [3]. Total energy demand in the non-OECD countries increases by 73%, compared with an increase of 15% in the OECD countries. This means that

crude oil consumption has to increase from 85 million barrels per day in 2006 to 99 million barrels per day in 2015 and 122 million barrels per day in 2030. Consequence of the high demand of oil, its availability will decrease and its price can become excessively high. An alternative to the energy obtained from crude oil could be the energy obtained from plastic wastes.

Incineration can be applied for this purpose, but this alternative does not have much acceptance, due to the emissions associated: dioxins, greenhouse gases and discharges of ashes [4], as well as the attitude of the population rejecting the construction of incinerators near residential areas.

Pyrolysis is another alternative for obtaining energy from plastic wastes. It is based on the principle that most of organic substances are thermally unstable and they can be broken in an oxygen-free atmosphere [5]. By using pyrolysis process, plastics are transformed into fuel-like products [6,7]. This is a highly endothermic process, but a suitable technology for plastic wastes treatment since fuel-like products obtained from plastic wastes have a calorific power similar to some fuels and natural gas, and higher than coal. They have a high pyrolytic potential due to the energy emitted.

Two different methods for pyrolysis of plastic wastes have been reported: thermal degradation [5] and catalytic degradation [6]. Different solid catalysts can be used for catalytic degradation: molecular sieves [7,8], alumina and aluminosilicates [9–12], silica gel [13,14], activated carbon [15,16] and fluid catalytic cracking (FCC) catalysts [16–18].

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Zeolites are largely used in industry for the separation of hydrocarbons and for catalysis, specially zeolite 5A is used in the separation of linear from branched alkanes [19].

Silica gel, alumina and aluminosilicates can be considered natural acids, since they are able to transfer protons to hydrocarbons which act as weak bases [20]. Aguado et al. [11,12] propose the use of mesoporous aluminosilicates type MCM-41 for liquid fuel production from polyethylene wastes.

Few experimental works with activated carbon have been reported. In some experiments this material has been used as a support for some metals such as platinum, iron, molybdenum or zinc [16,21] but this procedure of catalyst preparation has a high cost.

At present, catalytic degradation of plastic wastes (pyrolysis) is an incipient alternative and articles related to this field are only experimental assays which need a deeper knowledge to be applied in municipal wastes treatment plants.

The objective of this work is to examine the potential of silica gel, 5A molecular sieve and activated carbon as catalysts to improve degradation of polyethylene wastes (plastic bags from supermarkets) under pyrolytic conditions at low temperature. These three catalysts were selected because they show a high mechanical and thermal resistance and low cost. Products obtained are fuel-like products and organic compounds which are proposed to be applied in chemical industry. The effect of temperature on conversion percentage will be studied for the three catalysts. The influence of catalyst structure on the products obtained will be investigated analyzing surface area and surface morphology by microscopic techniques.

## 2. Experimental

### 2.1. Experimental equipment and degradation conditions

Polyethylene wastes obtained from supermarket postconsumer bags were cut in pieces of approximately 1 cm × 1 cm size. Raw material composition was high density polyethylene, 25 μm thickness, 132 °C melting point, dyed with titanium oxide (33% Ti and traces of B, Al, Mg, Fe and Si). Polymer cracking experiments were carried out in a batch fixed bed reactor, under nitrogen atmosphere. 10 g of polymer was used in thermal degradation and 10 g of polymer mixed with 1 g of catalyst were loaded into the reactor in catalytic degradation experiments. Ratio catalyst/PE was in all cases

1:10 in weight (1.0 g catalyst for 10.0 g PE wastes). Previous experiments and data obtained by other authors [8] showed this ratio to be the optimum in the use of catalyst for highest conversion. Ratios 0.1:10 and 3:10 were also assayed, being insufficient first one (conversions lower than 5%) and second one conducted to similar values in conversion of PE.

Degradation time was fixed in 2 h. This time was selected according to previous studies performed by other authors [5,6,15]. Previous experiments were done over this subject, to compare results with those obtained in other articles. Confirmation was obtained with similar conversions at higher degradation times and incomplete degradation at lower degradation times.

Pyrolysis processes are generally classified into low, medium and high temperature processes, based on the range of temperature used to destroy the plastic structure [8,22,23]. Pyrolysis at low temperature is carried out at temperature lower than 550 °C to produce oils and tars and pyrolysis at medium temperature is performed between 550 and 800 °C to produce methane and higher hydrocarbons [4,24]. In high temperature process (higher than 800 °C [25]) the produced gas has a lower calorific power and some catalysts can be affected by a modification of their porous structure [26]. In order to establish the optimal reaction temperature for each catalyst, pyrolysis reactions were performed in triplicate at three different temperatures: 450, 500 and 700 °C.

Fig. 1 shows the experimental device for the degradation experiments of PE, with nitrogen gas feed and products separators.

Degradation experiments of PE wastes separated products in two fractions: solid fraction and gas fraction. The gaseous products were collected, measured in volume by water displacement and analyzed by gas chromatography–mass spectrometry and gas chromatography. The amount of coke and PE residues mixed with the catalyst was determined by resting the difference in catalyst weight before and after degradation experiments.

The catalysts employed in this research were silica gel (supplied by Rhone Poulenc industries Ltd.), Linde 5A molecular sieve (supplied by Rhone Poulenc industries Ltd.) and activated carbon (supplied by Panreac). Three samples of activated carbon were used: powdered activated carbon, activated carbon of 0.10 mm particle size and washed activated carbon of 0.10 mm particle size.

Activated carbon was decided to be washed because microscopic observation showed dust entrapped in pores constrictions of catalyst. Wash procedure of activated carbon consisted of taken the sample of 0.10 mm particle size and mixed with deionized water

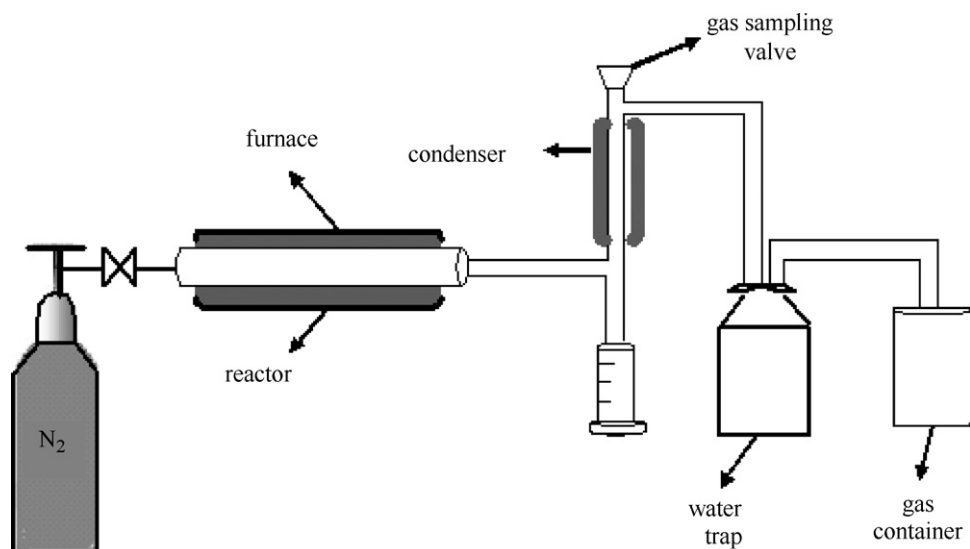


Fig. 1. Experimental device for the degradation experiments of PE.

during 24 h, afterwards the sample was filtered (glass filter) and dried at 120 °C for 3 h.

### 2.2. Gas chromatography–mass spectrometry analysis

Gaseous products were analyzed using a gas chromatograph Shimadzu GC 17A with a mass detector Shimadzu QP5000. The capillary column used was a DB5 (0.25 mm × 30 m). The oven temperature was 40 °C. Detector and injector were set up at 270 °C. Helium was used as carrier gas at constant flow of 1.7 mL/min. The oven temperature program was: 40 °C for 20 min, 50 °C for 5 min and 270 °C for 40 min, raising the temperature at 17 °C/min [27].

### 2.3. Gas chromatography analysis

Perkin-Elmer 8500 gas chromatograph with a flame-ionized detector (FID) was used for the analysis of higher volatile compounds with a molecular weight lower than 40 g/mol. A packed column of Porapak Q (3.6 m) was used. Oven and detector temperature was 250 °C. Nitrogen was used as carrier gas, at constant flow of 30 mL/min.

### 2.4. Specific surface area

The superficial area for each catalyst was measured by BET method of the simple point, adopted when nitrogen adsorption is

very strong due to the nature of the samples [28]. This analysis was carried out by Inorganic Chemistry Department of the University of Salamanca in a Micromeritics Flowsorb II 2300 instrument.

### 2.5. Scanning Electron Microscopy (SEM) analysis

Catalysts samples were analyzed in a 940 DSM Zeiss Digital Scanning Microscope, in order to visualize the structure and morphology of the material. Dried samples were fixed in aluminum supports specially designed for Digital Scanning Microscope using an adherent for this aim.

Samples of silica gel and 5A molecular sieve were sputter-coated with a gold layer in a SEM Coating System of Bio-Rad before SEM-imaging. This treatment was not necessary for activated carbon because of the conductivity of the material. The images were taken at  $10^{-3}$  Pa vacuum by the secondary electrons detector of the microscope [29].

### 2.6. Heat of combustion

The heat of combustion of solid fraction from different polyethylene degradation experiments was determined with a C200 IKA Calorimeter System according to standard method (DIN 51900; ASTM D5865). Calorimeter was calibrated using benzoic acid as a standard (0.5 g pills weight).

Using a hydraulic press, pills made from the samples of solid fraction (approximately 1 g) obtained from different degradations were prepared for use in the calorimeter.

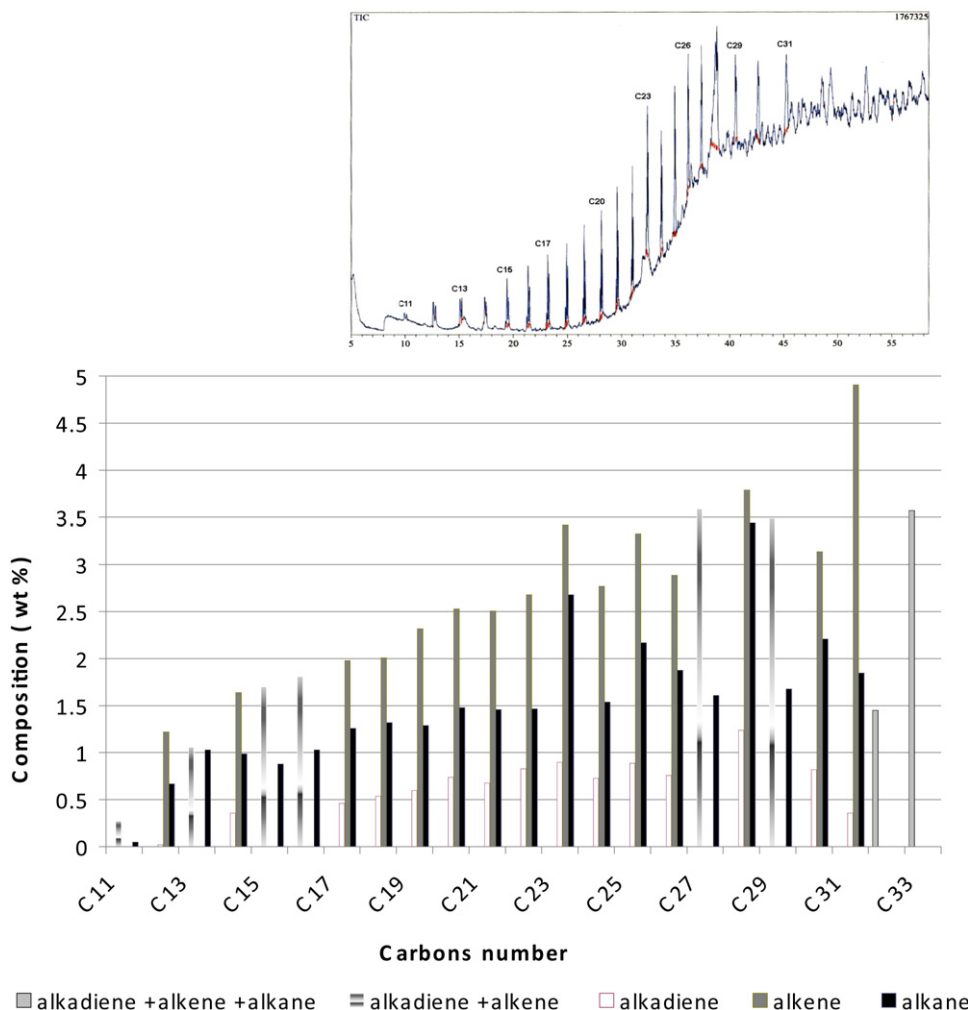


Fig. 2. Solid fraction composition of products from thermal degradation ( $T=450$  °C). GS MS data are recorded in the top of the figure.

**Table 1**  
Average conversion percentage of catalytic degradation of polyethylene wastes with different catalysts.

Temperature (°C)	Silica gel (0.56 mm)		5A molecular sieve (0.65 mm)		Powdered activated carbon	
	Average conversion (%)	*S	Average conversion (%)	*S	Average conversion (%)	*S
450	43.9	1.5	25.1	2.5	49.2	1.4
500	34.2	0.9	37.2	0.6	27.3	1.2
700	37.0	1.0	49.7	1.1	27.0	1.0

\* Standard deviation.

### 3. Results and discussion

#### 3.1. Solid fraction

Conversion was calculated as:

$$\text{Conversion (\%)} = \frac{W_0 - W_R}{W_0} \times 100$$

where  $W_0$ , weight of initial polyethylene waste and catalyst in reactor and  $W_R$ , weight of final solid waste and catalyst in reactor.

##### 3.1.1. Thermal degradation

Thermal degradation was carried out at 450 °C [30] to compare these results with the results of catalytic degradation at the lowest temperature. Conversion percentage for thermal degradation was 23.3% with a standard deviation of 1.4.

For thermal degradation of PE wastes the solid fraction is composed by products of high molecular weight (number of carbons from 11 to 33) and alkenes predominate (Fig. 2).

##### 3.1.2. Catalytic degradation with silica gel

Average conversion of PE wastes in catalytic degradation using silica gel as catalyst is clearly higher than thermal degradation (Table 1). Conversion decreased as temperature increased from 450 to 700 °C and the maximum average conversion was obtained at 450 °C.

The decrease of conversion percentage with the increase in temperature can be attributed to several factors. One of them is due to the fact that when silica gel is warmed up to high temperatures, it loses water firstly from the mesopores and finally from hydroxyl groups of the surface. This phenomenon happens in the range of temperatures from 200 to 1000 °C and it is accompanied by a loss

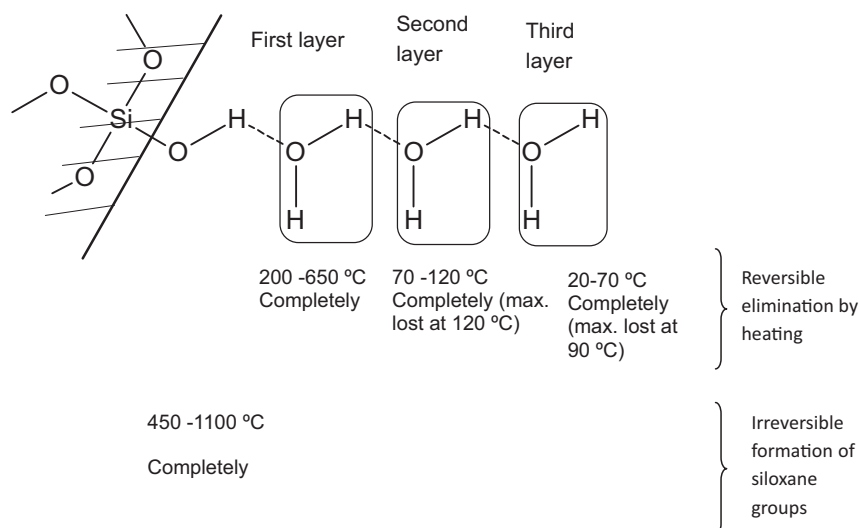
in the superficial area [31]. Silica gel is a siloxane and silanol groups structure and when it is warmed up to temperatures below 150 °C, physically eliminates the absorbed water (third and second layers in Fig. 3). Over 200 °C water entrapped by hydrogen bonds begins to be eliminated from the first layer. This process is completed at 650 °C. From 450 °C the formation of siloxane bonds by dehydration of two silanol neighbouring groups and the deactivation of the polar surface character can take place. This process is completed at high temperatures, originating a very hydrophobic surface which conducts weak and nonspecific adsorptions. The behaviour is explained in Fig. 3 [32].

Fig. 4 shows distribution of solid products from PE wastes degradation using silica gel as catalyst. Majority compounds were found in the range  $C_{15}$ – $C_{23}$  and the alkenes predominated over alkanes and alkadienes.

##### 3.1.3. Catalytic degradation with 5A molecular sieve

Conversion versus temperature is increasing in Table 1 for catalytic degradation of polyethylene wastes using 5A molecular sieve as catalyst. This behaviour is contrary to the one obtained using silica gel as catalyst and reaches a higher value (49.7% at 700 °C). Molecular sieve is not affected by temperature in external surface structure like silica gel. On the other hand, increasing temperature can produce thermal vibrations in the crystalline structure of this catalyst and in polymer molecules, favouring diffusion of the PE into the microporous system of the molecular sieve.

Fig. 5 shows a uniform distribution of products from degradation of polyethylene wastes with 5A molecular sieve, attending number of carbons. Although proportion of alkenes is clearly higher, also mixtures of alkadiene, alkene and alkane were found, but only in compounds of high molecular weight, between  $C_{31}$ – $C_{34}$ .



**Fig. 3.** Characteristics of surface hydration in silica gel and loss of water molecules relative to heating [32].

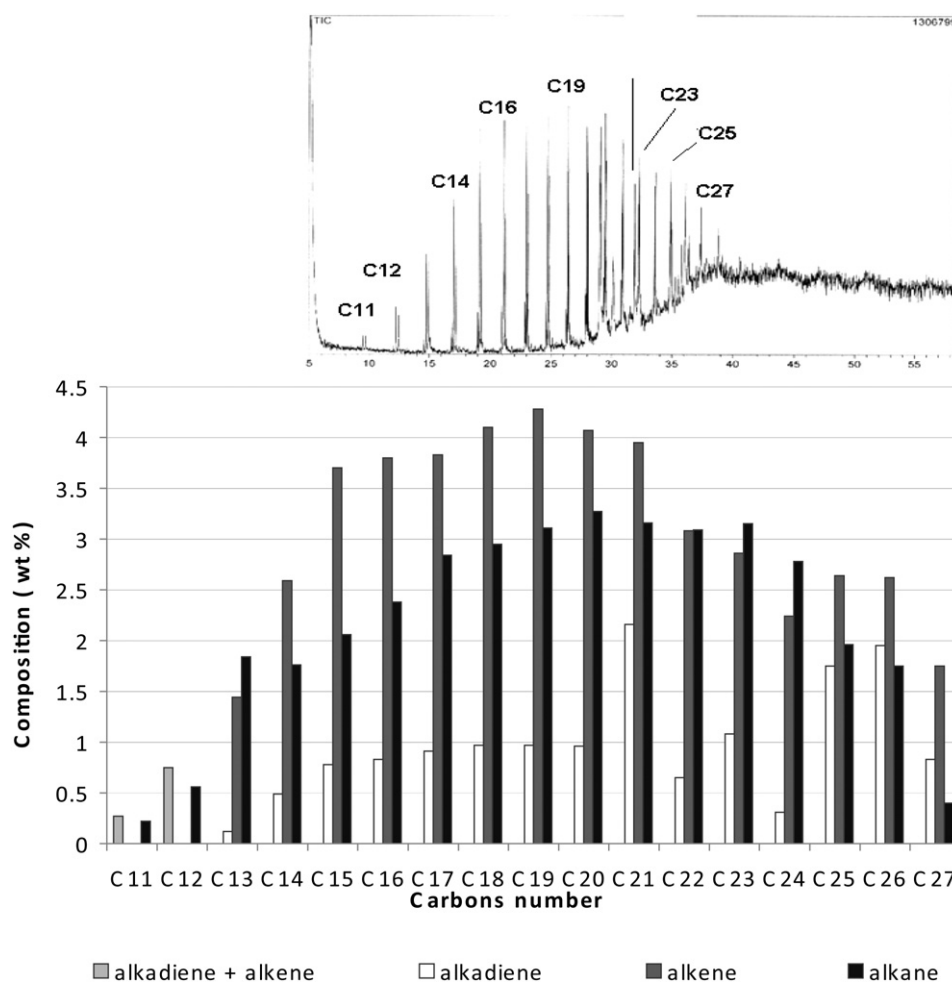


Fig. 4. Solid fraction composition of products from degradation of PE wastes using silica gel as catalyst ( $T=450^{\circ}\text{C}$ ). GS MS data are recorded in the top of the figure.

### 3.1.4. Catalytic degradation with activated carbon

Optimum temperature for the polyethylene degradation with powdered activated carbon as catalyst was  $450^{\circ}\text{C}$ . The highest conversion percentage was obtained at this temperature according to Table 1 (49.2%). This conversion is comparable to the one obtained with 5A molecular sieve (Table 1,  $700^{\circ}\text{C}$ ), but in a much lower temperature value. Conversion obtained using silica gel as catalyst is 43.9% at  $450^{\circ}\text{C}$  (Table 1), lower than the one obtained with activated carbon.

According to literature, activated carbon can be deactivated at high temperature by formation of carbonous deposits or poisoning due to strong adsorption of some compound [33].

Activated carbon can be selected as the best catalyst for PE wastes catalytic degradation. Optimum temperature for catalytic reaction is  $450^{\circ}\text{C}$ . In order to improve PE degradation conversion, particle size of activated carbon was selected and the catalyst was washed with water (Section 2.1). Improvement of conversion can be shown in Table 2, in which results are compared for powdered activated carbon (without particle size selection), activated carbon of 0.10 mm particle size and washed activated carbon (0.10 mm particle size). The use of washed activated carbon makes average conversion of PE wastes to be higher than 60% (62.6%).

The solid fraction composition of products from degradation of PE wastes using activated carbon of particle size 0.10 mm can be seen in Fig. 6 in which alkanes predominated especially between  $\text{C}_{22}$  and  $\text{C}_{31}$ .

Distribution of solid products from PE wastes degradation attending to the number of carbons using washed activated carbon (0.10 mm) is shown in Fig. 7. This solid fraction is enriched by hydrocarbons with lower molecular weight compared to the ones obtained with the other catalysts and thermal degradation. In this case this fraction was a very viscous liquid and not solid as a result of lighter mixture of hydrocarbons.

This catalyst had good catalytic activity for producing aromatic compounds which were not present in other degradations (Table 3), since it is known that the reactivity of activated carbon depends on the access to the active sites where chemical compounds can be adsorbed [34]. Due to its greater surface area, higher conversion percentages were obtained with this catalyst.

With regards to linear hydrocarbons, high presence of alkanes can be observed in Fig. 7, and this could be attributed to alkenes hydrogenation by hydrogen release from the cyclization reactions, which are present in the formation of aromatics (Table 3).

Table 2

Average conversion percentage of catalytic degradation of PE wastes with different samples of activated carbon as catalyst at  $450^{\circ}\text{C}$ .

Activated carbon	Average conversion (%)	Standard deviation
Powdered	49.2	1.4
0.10 mm particle size	56.0	0.9
0.10 mm particle size and washed	62.6	1.9

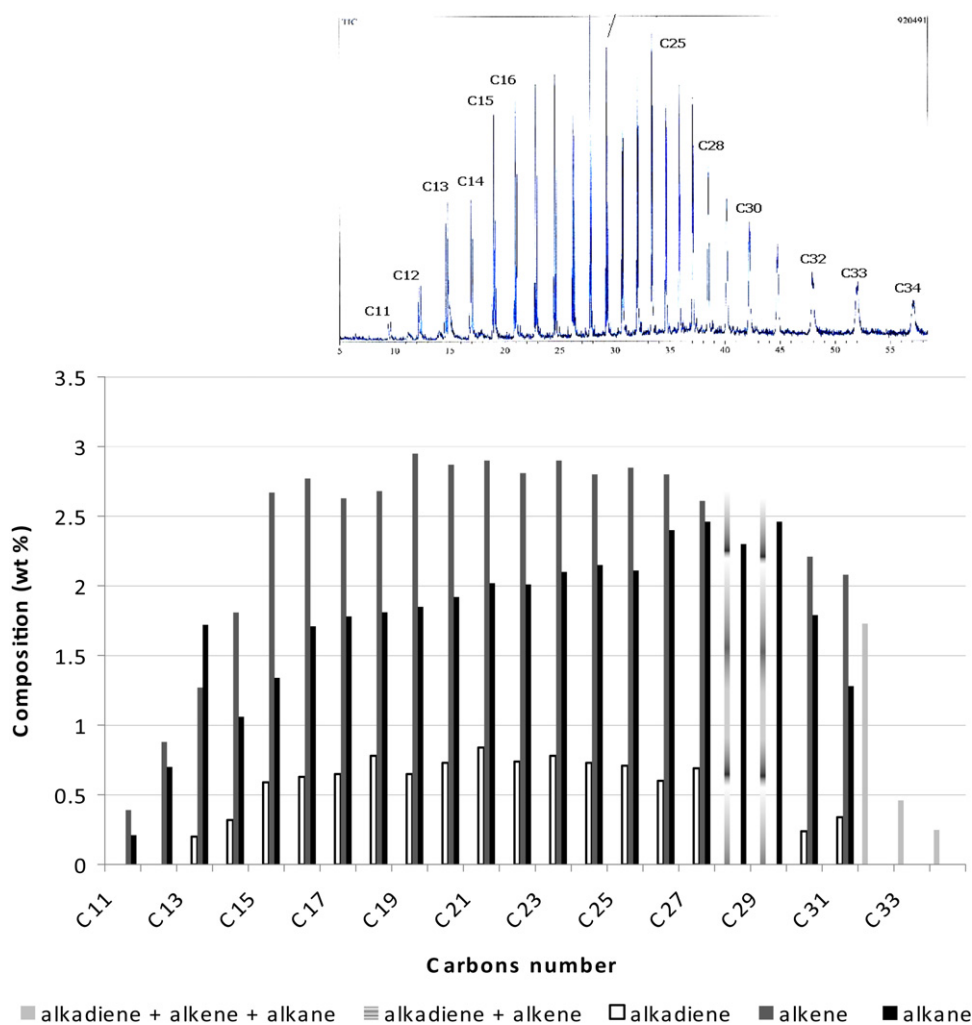


Fig. 5. Solid fraction composition of products from degradation of PE wastes using 5A molecular sieve as catalyst ( $T=450^{\circ}\text{C}$ ). GS MS data are recorded in the top of the figure.

### 3.1.5. Comparative study

The distribution of products in solid fraction attending the number of carbons obtained from different polyethylene wastes degradations are shown in Fig. 8.

In thermal degradation hydrocarbons with high molecular weight predominated from  $\text{C}_{23}$ . Catalytic degradation using silica gel as catalyst clearly shows trend to smaller hydrocarbons, between  $\text{C}_{16}$  and  $\text{C}_{21}$ .

For degradations with activated carbon (0.10 mm) and 5A molecular sieve as catalysts a similar behaviour was observed,

Table 3

Chemical aromatic compounds identified in solid fraction from PE wastes degradation using washed activated carbon (0.10 mm particle size) at  $450^{\circ}\text{C}$ .

Compound	% weight
Ethyl-benzene	0.71
o-Xylene	0.11
m-Xylene, p-xylene + styrene	0.76
Propyl-benzene	0.12
Cumene	0.14
1-Ethyl-2-methyl-benzene	0.25
2-Propyl-benzene	0.19
Indene	0.47
C9	0.53
Naphthalene	1.91
Methyl-naphthalene	0.53
C11	0.30
Total	6.02

increasing the amount of hydrocarbons between  $\text{C}_{24}$  and  $\text{C}_{28}$  with activated carbon.

The use of washed activated carbon as catalyst increased the number of small organic compounds, between  $\text{C}_8$  and  $\text{C}_{12}$ . Due to its abundance (percentage in Fig. 8), some of them are considered to be aromatic compounds (Table 3).

### 3.1.6. Heat of combustion

Heat of combustion was determined for different solid fractions obtained from catalytic degradation of PE wastes (Table 5).

In general, a similar value can be observed for all the different catalysts and higher than  $45000\text{J/g}$ , which is the value for some commercial fuels [35].

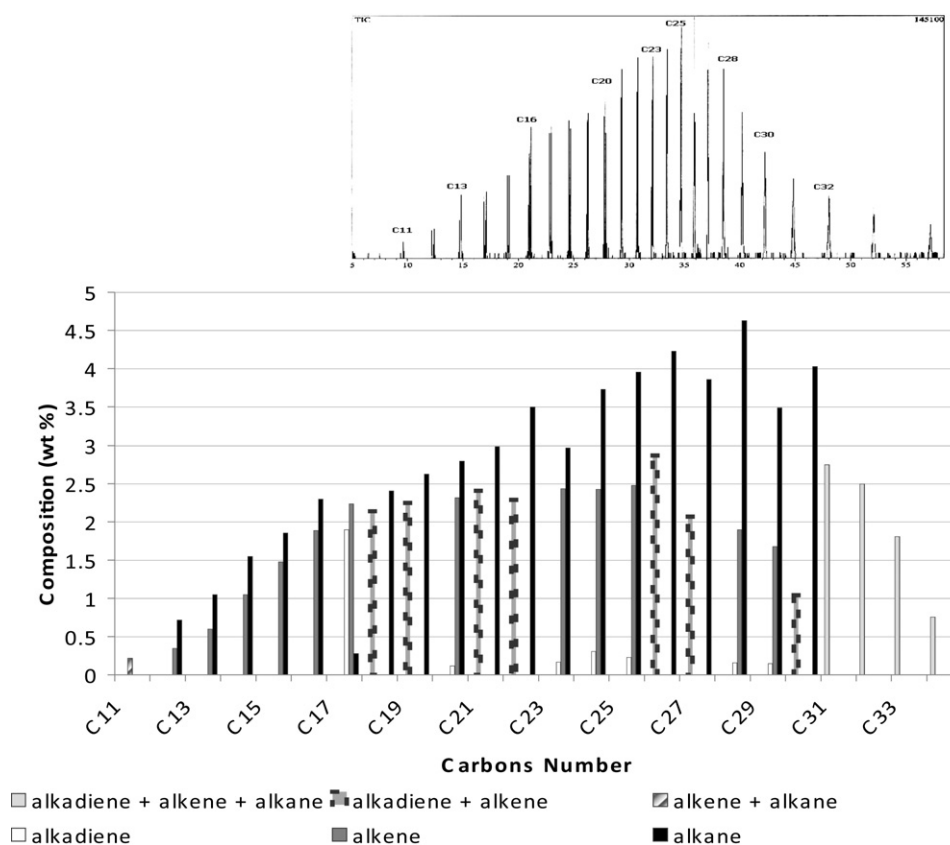
In view of these results, solid fraction of catalytic PE wastes degradation has good qualities for been used as a fuel.

## 3.2. Gas fraction

Methane was detected in catalytic degradation of PE wastes (gas chromatography) and the following results were obtained for the different catalysts assayed:

Silica gel	34%
5A molecular sieve	20%
Activated carbon (0.10 mm)	22%

Other products of higher molecular weight obtained from different PE degradations were analyzed in the gas phase by



**Fig. 6.** Solid fraction composition of products from degradation of PE wastes using activated carbon of particle size 0.10 mm as catalyst ( $T=450^{\circ}\text{C}$ ). GS MS data are recorded in the top of the figure.

gas chromatography–mass spectrometry. Results are shown in Table 4.

Thermal and catalytic pyrolysis of polyethylene conducts to a wide range of products [16]. Depolymerization of polyolefins occurs by means of a radical mechanism [36] and some factors such process selectivity depends on uncatalyzed and catalyzed degradation [37]. In this study molecular structure of products obtained in gas fraction from different degradations of PE wastes was proven to be dependent on catalyst used.

In gas fraction from thermal degradation a wide range of compounds can be found with number of carbons in the range  $\text{C}_4$ – $\text{C}_{10}$ , linear and branched hydrocarbons and benzene appear (Table 4). For degradation of PE wastes using silica gel as catalyst, compounds between  $\text{C}_3$  and  $\text{C}_7$  were obtained and unsaturated products predominate (Table 4). There is a diversity of compounds: linear, branched and aromatic hydrocarbons are present.

5A molecular sieve is clearly selecting gas products to linear hydrocarbons and benzene (Table 4), where structure of linear hydrocarbons is very similar, presenting in some cases an unsaturated carbon on first position of organic chain. Benzene is present in all degradation experiments and branched compounds formation did not take place.

Using activated carbon as catalyst in PE wastes degradation, only four products, besides methane, were observed. Hexane and heptane can be found and benzene and isobutene appeared (Table 4).

According to the results obtained with washed activated carbon (0.10 mm particle size), the products in gas fraction are shown in Table 4. Aliphatic and aromatic compounds between 5 and 7 carbons were present. Also it is observed that the number of unsaturated and branched compounds increases with regards to the experiment with unwashed activated carbon. Formation of aromatic products is attributed to catalytic effect of activated carbon

**Table 4**

Compounds identified in gas fraction from PE wastes degradations with different catalysts.

Degradation	Compounds
Thermal	2-Butene
	n-Pentane
	n-Hexane
	5-Methyl-1-hexene
	3,4,5-Trimethyl-heptane
Silica gel	Benzene
	1-Propene
	1-Pentene
	1-Hexene
	Isobutane
5A molecular sieve	3-Methyl-hexane
	5,5-Dimethyl-1,3-ciclopentadiene
	Benzene
	1-Butene
	1-Hexene
Powdered activated carbon	1-Heptene
	n-Pentane
	1-Heptane
	Benzene
	Isobutane
Washed activated carbon (0.1 mm)	Benzene
	n-Hexane
	n-Heptane
	1-Pentene
	n-Hexane
	1-Heptene
	Isobutane
3-Methyl-hexane	
2-Methyl-pentene	
Benzene	
Toluene	

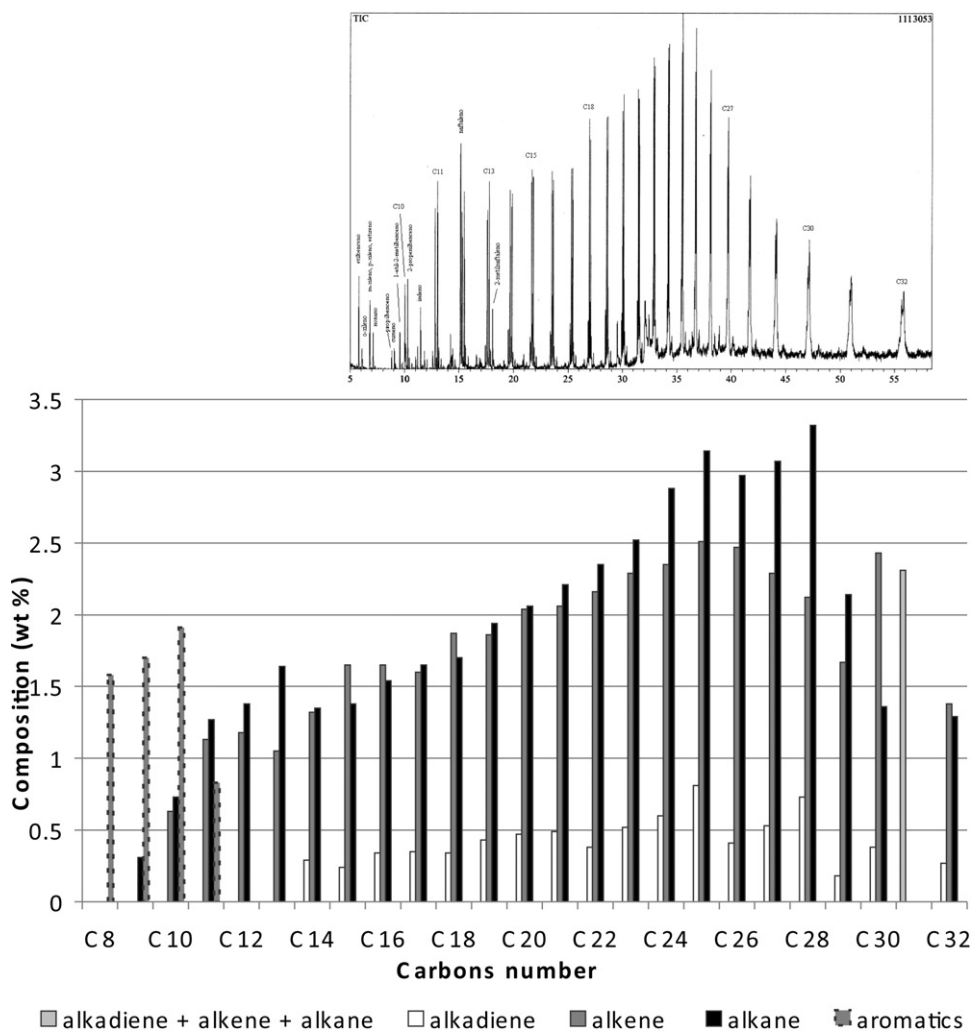


Fig. 7. Solid fraction composition of products from degradation of PE wastes using washed activated carbon of particle size 0.10 mm as catalyst ( $T=450^{\circ}\text{C}$ ). GS MS data are recorded in the top of the figure.

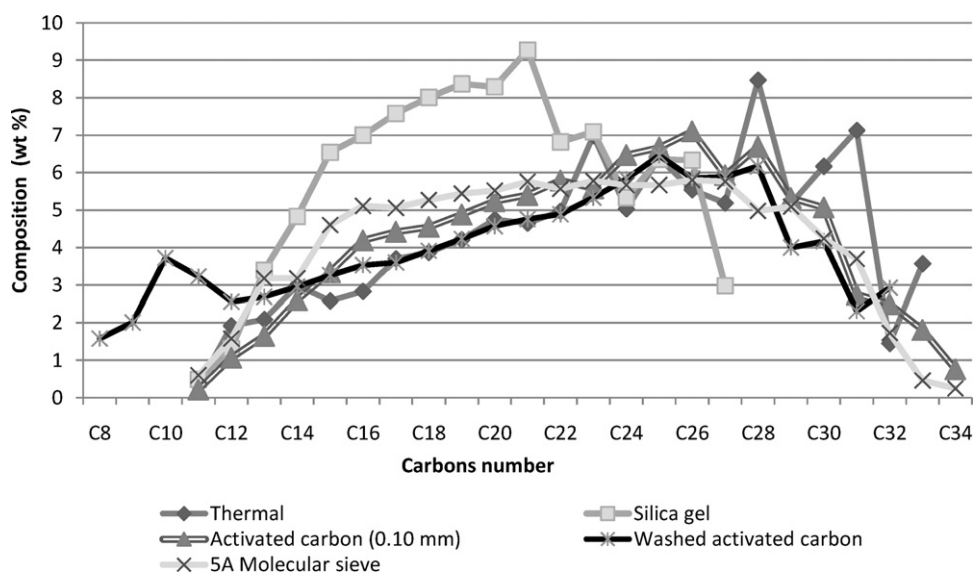


Fig. 8. Comparison of products distribution for the solid fraction of PE wastes degradation in thermal degradation and catalytic degradation ( $T=450^{\circ}\text{C}$ ).



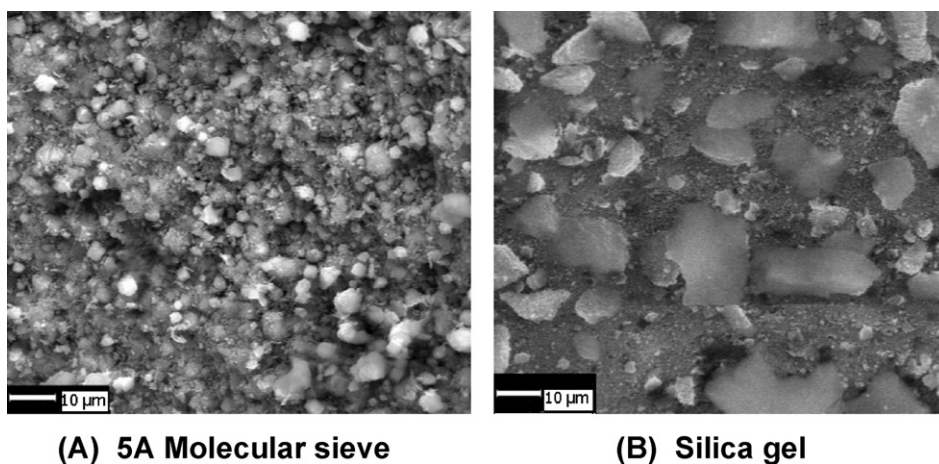


Fig. 9. SEM microphotographs of 5A molecular sieve and silica gel.

on the breakdown of C–C bounds of polyethylene and cyclization reactions from straight chain intermediates.

In general, it could be said that depending on the desired type of product, different catalyst can be selected. As well as in the petrochemical industry, depending on the fraction desired and the use for petroleum derivatives, a different catalyst is used.

### 3.3. Structures of catalysts

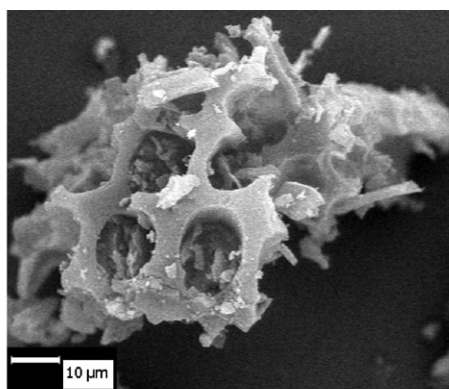
#### 3.3.1. Specific superficial area

Since adsorption is a surface phenomenon, the efficient adsorbents are those which display great surfaces by mass unit and have

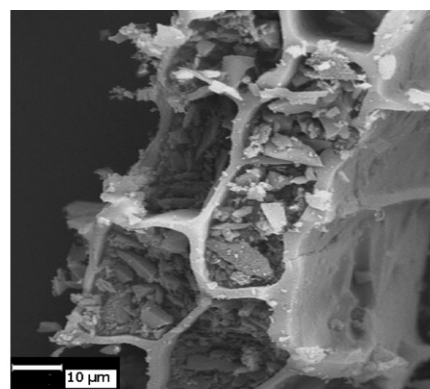
great attractive forces. Table 5 lists the results of surface area for the different catalysts used in this work. Activated carbon has a much greater superficial area and therefore has greater adsorption capacity. Surface area of activated carbon is about three times the surface area for the other two catalysts.

#### 3.3.2. Surface study of catalysts by Scanning Electron Microscopy

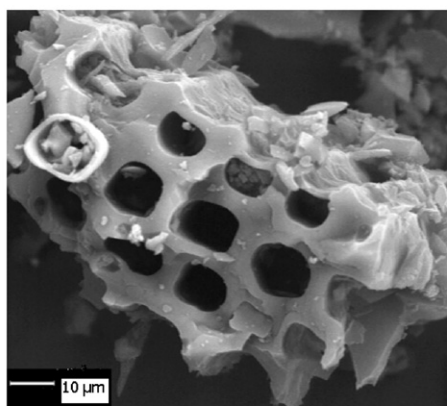
Fig. 9(A) shows the structure of 5A molecular sieve which is an agglomeration of geometric forms constituting a particle. Sifted material presents an irregular particle size. Silica gel morphology is similar to 5A molecular sieve (Fig. 9(B)). Porous structure is due to hollows resulted by agglomeration of geometric forms (macrop-



(A) Powdered activated carbon



(B) Activated carbon (0.10 mm particle size)



(C) Washed activated carbon (0.10 mm particle size)

Fig. 10. SEM microphotographs of activated carbon.

**Table 5**  
BET specific surface area and heat of combustion (HC) of solid fraction of PE wastes degradation with different catalysts used.

Catalyst	BET specific surface area (m <sup>2</sup> /g)		HC (J/g)
	Before reaction	After reaction	
Powdered activated carbon	622	302	45980
Activated carbon (0.10 mm)	664	343	46362
Silica gel (0.54 mm)	163	124	45535
5A molecular sieve (0.65 mm)	197	119	45245

orous). In this material the hollows are obstructed by particle dust. Microporous structure is not observed by SEM.

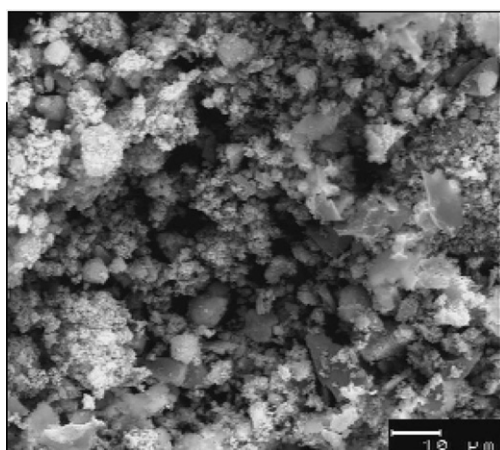
Fig. 10 shows SEM microphotographs of activated carbon. Porous structure of activated carbon visualized by SEM shows specific superficial area to be much greater in this catalyst (Table 5) due to macroporous structure and this could explain why product distribution is not very different to the experiments with molecular sieve, because mesoporous and microporous structure can be related in these two catalysts. In first analysis, activated carbon was observed to have the pores obstructed by many small particles of material dust (A), attributed to vegetal remainders that were not released during activation process of the carbon, and also did not reveal a great change after sifted process (B).

As a result of the washing treatment of activated carbon (Fig. 10(C)) the pores are unoccupied almost completely. This allows a better interaction of polyethylene with the activated carbon, and molecules can flow freely through carbon channels, which explains the increase in the yield of the reaction (higher conversion for washed activated carbon, Table 2).

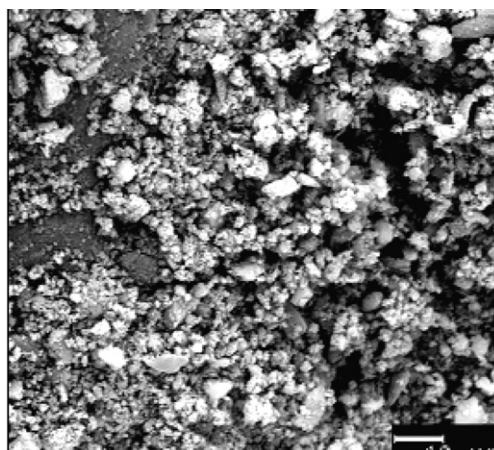
After catalytic degradation of PE wastes, catalysts exhibit an appreciable change in the surface texture and morphology (Fig. 11), related to previous microphotographs before reaction (Figs. 9 and 10). Comparison of 5A molecular sieve (Figs. 9 and 11(A)) and silica gel (Figs. 9 and 11(B)) shows deposits of reaction products on the surface of catalysts.

This situation is repeated in the case of activated carbon (comparison of Figs. 10 and 11) in which some degradation products and catalyst powder are present on the surface of the catalyst (Fig. 11(C) and (D)).

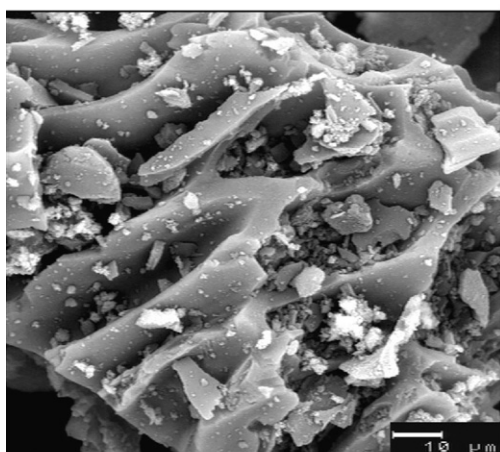
In view of these results, catalysts were regenerated and analysis of BET surface area was performed to evaluate activity of catalysts in further reactions (Table 5). Regeneration of catalysts was done in the experimental device for PE degradations (Fig. 1). Silica gel was treated at 500 °C during 5 h in the presence of air, 5A molecular sieve was heated at 500 °C during 5 h and later at 700 °C during 2 h under air atmosphere and activated carbon (powdered and 0.10 mm particle size) was regenerated at 600 °C with water



(A) 5A Molecular sieve

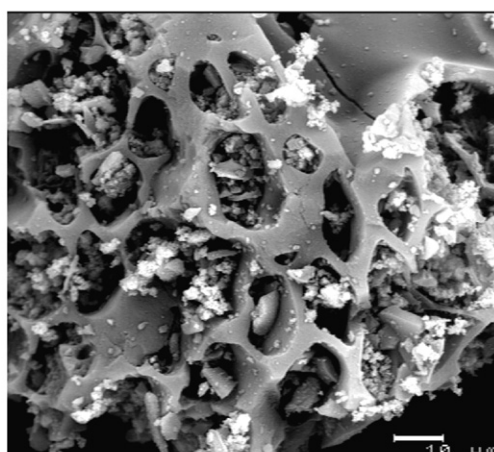


(B) Silica gel



(C) Activated carbon

(0.10 mm particle size)



(D) Washed activated carbon

(0.10 mm particle size)

Fig. 11. SEM microphotographs of the different catalysts after degradation of PE wastes.

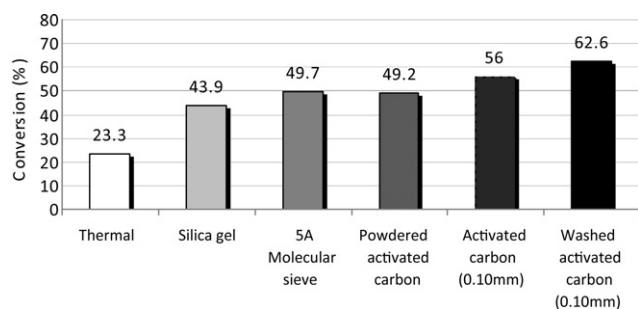


Fig. 12. Conversion percentages of degradation of PE wastes for the different catalysts.

vapour during 2 h under nitrogen flux. In the case of activated carbon, water was boiled passing nitrogen flux for 1.5 h and next 0.5 h nitrogen flux was passed without water vapour to dry the catalyst samples.

In Table 5, BET specific surface area decreased after reaction and regeneration of the catalyst 24% in the case of silica gel, 40% in 5A molecular sieve and between 48% and 51% in activated carbon. With these results showing not very significant decrease in surface area (in terms of catalysis), catalysts are considered to be active for further reactions.

#### 4. Conclusions

In degradation of PE wastes, optimal temperatures depend on catalysts used in this work and are the following:

- Silica gel: 450 °C
- 5A molecular sieve: 700 °C
- Activated carbon: 450 °C

In Fig. 12 conversion percentages for different catalysts are shown, and washed activated carbon exhibit the highest conversion.

Activated carbon is an efficient catalyst for this type of degradations and can produce higher quantity of aromatic compounds.

In solid fractions obtained for thermal and catalytic degradations, with silica gel and 5A molecular sieve, alkenes predominated. In solid fractions for catalytic degradations using powdered, sifted and washed activated carbon alkanes were predominant.

In gas fractions obtained for thermal and catalytic degradations, the highest content in methane was obtained using silica gel as catalyst (34%). 5A molecular sieve and activated carbon (0.10 mm) produce similar results (20% and 22% respectively). Thermal degradation conducts to a wide range of compounds in the range C<sub>4</sub>–C<sub>10</sub>. Silica gel is not selective to linear or branched hydrocarbons and majority of unsaturated compounds between C<sub>3</sub> and C<sub>7</sub> were produced. 5A molecular sieve was selective towards linear hydrocarbons between 4 and 7 carbons, saturated and with an unsaturated bond in first carbon position. Powdered activated carbon as catalyst produces a very selective results only to 4 gas products: hexane, heptane, isobutane and benzene. Sifted and washed activated carbon extent the range of products besides those ones (heptene instead of heptane) to toluene, pentene and methylpentene and hexene.

Observation by SEM of structural relieves of the different materials shows activated carbon to have a much more porous structure than the other two catalysts, with long longitudinal hollows which seems to favor diffusion of organic molecules inside, improving reaction yield. Washed activated carbon has clean hollows increasing catalytic reaction rate.

The main conclusion of this work is the proposal of the use of washed activated carbon as catalyst for the degradation of plastic wastes by pyrolysis at low temperature (450 °C). By this methodology, in ratio catalyst/waste 10% the residue can be degraded in 62.6% (Fig. 12) and products obtained in gas and solid phases could be used in chemical industry.

#### Acknowledgements

The authors would like to thank to Mr. Juan González Julián (University of Salamanca) for assistance in SEM microphotographs and Mr. César Alberto Raposo for technical support in the General Service of Mass Spectrometry (University of Salamanca). We also thank to Professor Vicente Rives Arnau and Mr. Agustín Montero Rozas from Inorganic Chemistry Department (University of Salamanca) for assistance in surface area analysis.

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