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Chemical Catalyzed Recycling of Polymers: Catalytic Conversion of PE, PP and PS into Fuels and Chemicals over H-Y

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Abstract

In the following study the termocatalytic degradation of polyethylene of high and low density, (HDPE, LDPE), polypropylene (PP) and polystyrene (PS) on the H-Y zeolite was performed. The catalytic activity was carried out in a batch reactor at 500 °C. The reaction time was 43,75 min. Liquid product yields ranged from ~42 and ~44% wt% for polyethylenes and PP, while the production of PS showed ~71 wt%. The gaseous products ranged between ~46 and ~52 for PE and PP and ~24 wt% for PS. The PP generated the greatest amount of carbonaceous residues (~10 wt%) whereas the LDPE produced the lowest (~4 wt%).

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1. Introduction

The per capita consumption of plastics in Argentina reached 43 kg in 2012. The consumption of these materials has grown steadily over the last 35 years because of their lighter mass, greater versatility and safety conditions.

A continuous increase in the use of plastics increases their amount in the waste stream. Plastic materials constitute up to 20% of the volume of municipal waste in the metropolitan area of Buenos Aires. More than 55% of

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this fraction consists in polyolefins – low-density polyethylene (LDPE), high-density polyethylene (HDPE) and polypropylene (PP). PE's are the most widely used. HDPE and LDPE are thermoplastic polymers made from petroleum. They have different mechanical properties due to their degree of branching. HDPE is more crystalline than LDPE because it contains fewer branches. Due to their outstanding dielectric properties, their major application is in packaging film, supermarket bags, pipes for gas and telephone cables.

Polypropylene is a thermoplastic polymer that is obtained by polymerization of propylene. The copolymers are formed by adding ethylene over/along the process. PP is a rigid plastic, with high crystallinity and high melting point, excellent chemical resistance and lower density. It is used in a wide variety of applications including packaging and labeling, textiles (e.g., ropes, thermal underwear and carpets), stationery, plastic parts and reusable containers of various types, laboratory equipment, loudspeakers, automotive components, and polymer banknotes.

PS is a polymer of styrene monomer. PS is easily molded. It is used in pots for dairy products (yoghurt, desserts, etc.), ice cream, candy, etc.; packaging: cups, grocery & deli trays; refrigerators: doors and shelves; cosmetics: bottles, disposable razors; bazaar: plates, cutlery, trays, etc.; toys, cassettes, blisters, etc.; insulation: PS foam plates.

Since plastics are of petrochemical origin, they have inherently high calorific value. Thus they can be converted back to useful energy. For example, a kilo of plastic contains energy equivalent to a kilo of diesel, a plastic bag has enough energy to power a 60 W lamp for ten minutes and a container of yogurt can power a low-energy lamp for five hours.

There are several options to recycling plastic materials:

- **Primary treatment:** it is physical recycling. The plastic is ground down and then reprocessed and compounded to produce a new component that may or may not be used for the same purpose as the original.
- **Secondary treatment:** it consists of fusion and mechanical handling. The waste products are converted into various forms with different applications from the original plastic, in an evolutionary process "cascade" to lower benefits. It can only be performed on single-polymer plastic, e.g. PE, PP, PS. Separation, washing and preparation of this waste are all essential to produce high quality, clear, clean and homogenous end products.
- **Tertiary treatment or "chemical recycling":** it pursues the comprehensive utilization of the constituent elements of plastic, producing either fuels or petrochemical feedstock. The methods can be catalytic or thermal, depending on the type of polymer.
- **Quaternary treatment:** because of their high calorific value, they are a convenient source of energy. The quaternary treatment involves incineration to recover energy and results in a volume reduction of 90%–99%, which reduces the reliability on landfilling. However, it is socially challenged due to gas emissions.

An attractive alternative in waste plastic recycling is the catalytic cracking process from which you can obtain liquid and gaseous hydrocarbons of great value added from the addition of catalysts, which improves the purely thermal technology, and the spectrum distribution of products is greatly reduced, allowing one to reach higher selectivity towards certain products based on the characteristics of the catalyst used, reducing reaction times and temperatures of the process to 350–550 °C.

Among many authors who reported results about the catalytic degradation of polyolefin plastics over zeolites. Serrano et al. tested the catalytic activity of different ZSM-5 in the pure and waste LDPE and HDPE cracking. They worked at 340 and 360 °C and the major products were C3–C4 olefins and C5–C12 hydrocarbons (20%–60%), proportion depends on both the polyolefin and the catalyst. Miskolczi et al. investigated the catalytic degradation of waste plastics (polyethylene and polystyrene) in a batch reactor over different catalysts (FCC, ZSM-5 and clinoptillolite).

Serrano et al. studied the catalytic degradation of polystyrene over HMCM-41, amorphous SiO₂–Al₂O₃ and HZSM-5 zeolite at 375 °C. They found thermal cracking and catalytic degradation over HZSM-5 yield mainly styrene. On the contrary, the main products resulting from the catalytic cracking over HMCM-41 and SiO₂–Al₂O₃ are benzene, ethylbenzene and cumene but in proportions lower than 20 wt%.

Recycled tertiary polymer blends have also been reported in the literature: Lin et al. studied the catalyst degradation of a mixture of post-consumer polymer waste (PE/PP/PS) using a fluidizing reaction system similar to the FCC process. They obtained about 53 wt% olefin products in the C3–C6 at 330–450 °C.

Renzini et al. studied the cracking of low-density polyethylene over ZSM-11 modified with H⁺ and Zn²⁺. In this study, they found that Zn²⁺ incorporation favors aromatization due to the higher amount of Lewis acid sites.

Pierella et al. studied the thermal catalytic transformation of HDPE over Zn-, Mo-, and H-, ZSM-11 and MCM-41 materials. These samples could act as an electron-donor–acceptor complex between carbenium intermediate species and the unoccupied molecular orbital (LUMO) of the Zn/Mo sites present in the catalyst by hydride abstraction.

In this paper, we study the catalytic decomposition of different polymers (HDPE, LDPE, PP and PS) over HY and analyze the effect of the different feeds on liquid, gaseous and waste solid yields.

2. Experimental section

2.1. Materials

The commercial polymers used in this work were low density polyethylene (0.922 g/cm³) high-density polyethylene (0.9490 g/cm³), polypropylene (0.946 g/cm³) and polystyrene (0.96-1.04 g/cm³).

The catalyst NH₄-Y (Si/Al=2.47) was provided by Aldrich. The H-zeolite was obtained by means of a thermal treatment under nitrogen flow for 8 h at 500 °C and then calcinations in air at the same temperature during 10 h just before use.

2.2. Methods

Pure polymers were studied by thermal analysis (TG-DSC) a system using differential scanning calorimetry and thermogravimetry 2920 MDSCTA Instruments TGA 2950. Samples were subjected to a constant heating rate of 10 °C/min from room temperature to 600 °C under flow of nitrogen of 50 ml/min.

The catalyst was characterized by different techniques. X-ray powder diffraction (XRD) patterns were collected in air at room temperature on a Phillips PW-1700 equipment, using Cu K α radiation of wavelength 1.54Å. Diffraction data were recorded from 5° to 60° 2 θ angles, with an interval of 0.01° and scanning speed of 2° /min. The assessment of the specific surface areas by the BET method was carried out with N₂ adsorption at 77 K using a Micromeritics ASAP 2000 equipment. Infrared measurements on the zeolite was performed in a JASCO 5300 FTIR spectrometer. For structure characterization in the lattice vibration region (400–1800 cm⁻¹), the sample was mixed with KBr at 0.05% and pressed forming wafers. In order to determine the type and concentration of acidic sites of the fresh catalyst, pyridine (Py) adsorption experiment was carried out on self-supporting wafers (8–10 mg/cm²) using a thermostated cell with CaF₂ windows connected to a vacuum line. Pyridine (3 Torr) was adsorbed at room temperature and desorbed at 250 °C and 10⁻⁴ Torr for 1 h. The numbers of Brønsted and Lewis acid sites were calculated from the maximum intensity of the adsorption bands at 1545 cm⁻¹ and 1450–1460 cm⁻¹, respectively, and quantified using the literature data of the integrated molar extinction coefficients, which are independent of the catalysts or strength of the sites.

2.3. Catalytic system

The experiments of catalytic degradation were carried out in a batch, fixed-bed quartz reactor (9 mm internal diameter and 300 mm height). The particle size of the catalysts was in the 0.9–1.2 μ m range, and the polymers were used as 3.5 mm pellets.

The reactor was heated by an electric furnace, which was connected to a programmable temperature controller. A thermocouple was placed very close to the catalyst bed in order to monitor the temperature of the process (Figure 1). The study of the catalyst activity was performed with 2/1 polymer-to-catalyst mass ratio, chosen according to previous work and each experiment started at 25 °C and was heated to 500 °C, holding this final temperature for 20 min. The reaction time of each tests was 43.75 min. After the reaction time, the reactor was cooled at room temperature before. The reactor was continuously purged with nitrogen carrier gas at a flow of 25 mL/min. The liquid yield was assessed by mass difference of the condenser before and after the experiment. The mass of coke was determined by mass difference in the reactor, and the mass of gas products was determined by means of an overall mass balance of the experiment. The polymer was totally converted to gaseous and liquid hydrocarbons (GHC, LHC), and coke under these conditions, according to the FTIR data of the reactor contents at the end of the experiments, which showed the absence of the band characteristic of polymers.

The gaseous and liquid products were analyzed using a gas chromatograph (HP5890) equipped with a FID detector, using a HP-1 capillary column (30 m × 0.32 mm i.d.). Gas chromatography/mass spectrometry (Shimadzu QP5050 GC-17A) was used for the identification of products, using a 25 m, 0.2 mm i.d. HP-5 capillary column.

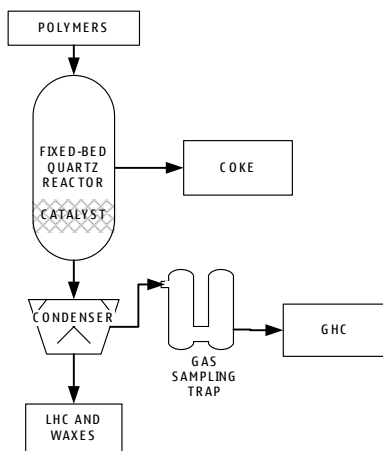


Fig. 1. Catalytic system.

3. Results and discussion

3.1. Characterization of the zeolite

The physicochemical properties of the catalysts are summarized in Table 1.

Table 1. Physicochemical properties of zeolite H-Y.

BET Surface area (m ² /g)	Crystallinity (%)		Total acid sites (mmol Py/mg)	Brönsted/Lewis
	FTIR ^a	XRD		
594	>99	100	0.0374	6.22

^a FTIR (Fourier Transform Infrared Spectroscopy) in the fingerprint zone of the materials (400-1200 cm⁻¹)

Crystallinity, as assessed from both XRD and FTIR techniques is very high, thus confirming that the severe conditions employed during the chemical and thermal treatments did not affect the structural characteristics of the catalyst.

The XRD patterns of the H-Y zeolite show the characteristic signals corresponding to each structure at 2θ of 6.13, 10.09, 11.91, 15.71, 18.61, 20.41, 23.71, 27.07 y 31.43° corresponding to the planes (111), (220), (311), (331), (511), (440), (533), (642) respectively.

3.2. Characterization of the polymers

Figure 2, 3 and 4 shows the mass loss curves obtained in the thermogravimetric analysis (TG curves) and DSC, corresponding to the degradation of LDPE, HDPE and PP.

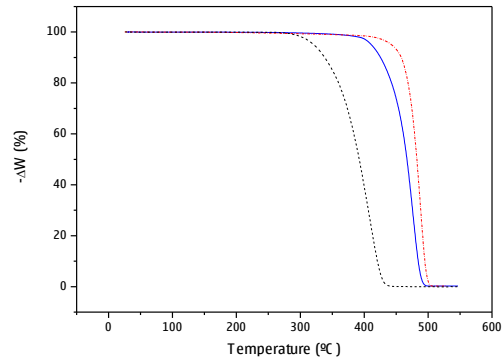


Fig. 2. TG profiles of polyolefin polymers. Symbols: (—) LDPE; (- - -) HDPE and (----) PP.

The results of thermogravimetric analysis (TG) revealed that, the decomposition temperature range for LDPE and HDPE ranged between 450 and 500 °C, while for PP and PS occurred between 350 and 450 °C.

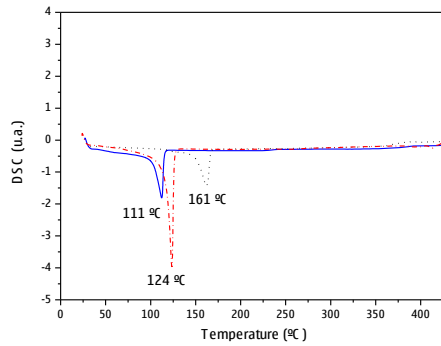


Fig. 3. DSC curve of pure polymers. Symbols: (—) LDPE; (- - -) HDPE and (----) PP.

DSC results (Figure 3 and 4) show an endothermic signal related with the polymers melting point (LDPE: 111 °C; HDPE: 124°C; PP: 161°C) and the glass transition temperature of PS at 100 °C.

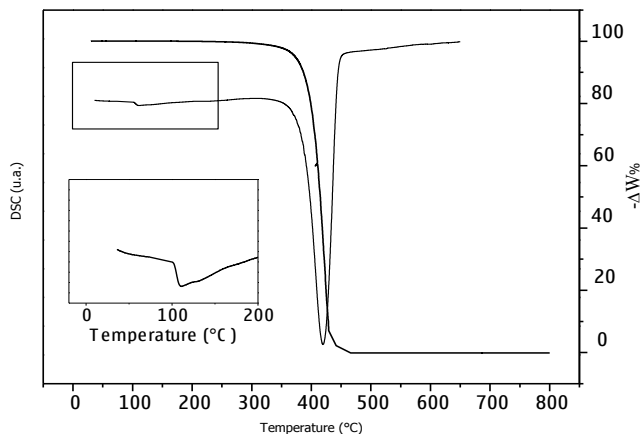


Fig. 4. Thermal analysis (TG and DSC) of PS.

3.3. Catalytic Activity

Figure 5 shows the yield (wt%) of GHC (C1–C6), LHC (C5–C16) and coke obtained in the polymer degradation over H-Y.

Polyolefin feeds showed bigger GHC yields, while polystyrene mostly produced LHC. This can be explained because of the polymer structure. The benzene ring in the PS structure is very stable and decreases cracking reactions.

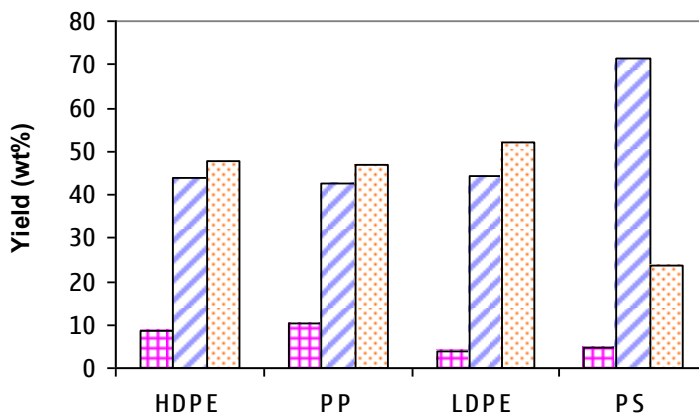


Fig. 5. Yields of the products obtained of thermodegradation of polymers over H-Y zeolite. Symbols: (blue hatched) LHC; (orange dotted) GHC and (pink checkered) coke

The cracking rate of PS to gaseous products is the lowest since the benzene ring in the PS structure is very stable. The yields to gaseous products are in the following order: LDPE > HDPE > PP > PS. However, although PP degradation should be easier since all PP carbons are tertiary, in this polymer cracking (to obtain GHC) H-Y zeolite showed much lower activity than polyethylene. This fact may be explained by the cross-section of PP molecules. So, while the differences in the cracking of HDPE and LDPE are mainly due to the stability of the carbocations formed in each case, the greater difficulty in PP cracking is attributed to its larger cross-section and to the steric hindrance

caused by lateral methyl groups along the chains. The solid wastes obtained were: HDPE, 8.44 wt%; PP, 10.3 wt%; LDPE, 3.75 w%; PS, 4.59 wt%.

It is worth pointing out that the catalytic degradation using zeolite gave very good results, since a noticeable reduction in the yields to solid wastes in favor of liquid and gaseous products was achieved, except for PS that gave yields of ~1% of solid wastes (Table 2).

Table 2. Yields (wt%) obtained from the thermal degradation of the different plastics.

Yields (wt%)	LDPE	HDPE	PP	PS
LHC				95,80
GHC	57,57	50,63	70,79	3,21
Waxes	42,18	48,61	27,72	
Solid wastes	0,25	0,76	1,49	0,99

As regards product distribution, polyolefins yielded similar amounts of the C5-C6 fraction, with 45 wt% on average. The degradation of HDPE yielded a higher percentage of heavier fractions (C11-C16) with 39 wt%, while the cracking of LDPE and PP yielded about 8 wt%.

It is worth noting that the degradation of PS did not yield waxes but a liquid fraction that consists mainly of styrene (81 wt%) and the C10-C16 fraction (12 wt%).

4. Conclusions

The results reported in this work show that the catalytic decomposition of LDPE, HDPE, PP and PS to hydrocarbons of greater value added can be performed using H-Y zeolite in a reaction system designed for the operation conditions tested.

Polyolefins yielded higher percentages of gaseous products (in the range 42 wt% – 45 wt%), while PS yielded a greater amount of liquids (~72 wt%). The catalytic cracking led to the formation of liquid products, gases and coke as reaction products, whereas the purely thermal cracking of polyolefins produced waxes rather than the liquid fraction. In the case of PS, the purely thermal cracking increased the amount of the liquid fraction with higher yields to styrene than in the catalytic test.

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