

FEEDSTOCK RECYCLING OF AGRICULTURE PLASTIC FILM WASTES BY CATALYTIC CRACKING

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Abstract

Feedstock recycling by catalytic cracking of a real plastic film waste from Almeria greenhouses (Spain) towards valuable hydrocarbon mixtures has been studied over several acid catalysts. The plastic film waste was mostly made up of ambient degraded low-density polyethylene (LDPE) and ethylene-vinyl acetate copolymer (EVA), the vinyl acetate content being around 4 wt %. Nanocrystalline HZSM-5 zeolite (crystal size \sim 60 nm) was the only catalyst capable of degrading completely the refuse at 420°C despite using a very small amount of catalyst (plastic / catalyst mass ratio of 50). However, mesoporous catalysts (Al-SBA-15 and Al-MCM-41), unlike it occurred with virgin LDPE, showed fairly close conversions to that of thermal cracking. Nanocrystalline HZSM-5 zeolite led to 60 wt % selectivity towards C₁ - C₅ hydrocarbons, mostly valuable C₃ - C₅ olefins, what would improve the profitability of a future industrial recycling process. The remarkable performance of nanocrystalline HZSM-5 zeolite was ascribed to its high content of strong external acid sites due to its nanometer dimension, which are very active for the cracking of bulky macromolecules. Hence, nanocrystalline HZSM-5 can be regarded as a promising catalyst for a feasible feedstock recycling process by catalytic cracking.

Keywords: Feedstock recycling, plastic wastes, catalytic cracking, nanocrystalline ZSM-5 zeolite

1. Introduction

Plastic wastes have become a subject of increasing worldwide environmental concern. According to 2000 data [1], the total plastic consumption in Western Europe increased to 35.8 million tonnes (Mt). The plastic wastes collected this same year amounted to 18.8 Mt, the great majority ending up their lifetime as a part of the municipal solid waste stream (MSW). In 1994, the European Union, aware of this problem, launched the 94/62/CE directive on waste packaging that established minimum rates of recycling per material (15 %). Since then, the percentages of recycling and energy recovery have increased to 12.6 % and 20.2 % respectively, but the preferred management strategies of plastic wastes is still landfilling (64 %).

The development of recycling procedures for polyolefins such as low-density polyethylene (LDPE), high-density polyethylene (HDPE) and polypropylene (PP), is highly encouraged since they account for roughly 60 % of the total plastic wastes [2]. In practice, these polyolefin refuse can be recycled either mechanically towards a new plastic with similar / lower applications, or chemically to obtaining chemical raw materials or fuels. However, mechanical recycling should be regarded as an intermediate procedure due to their inherent bounds (progressive loss of plastic properties through melting, saturation of potential end-markets, etc.) [3]. Thus, sooner or latter, mechanically recycled plastics should be treated by other procedures such as feedstock recycling, energy recovery or landfilling.

Feedstock recycling is becoming an increasingly promising alternative [4]. Several polyolefin feedstock recycling procedures have been proposed based on gasification [5,6], hydrogenation [7], thermal pyrolysis [8], catalytic cracking [9], and also recently, its usage as coke substitute in steel making industry. Among them, catalytic cracking towards valuable

hydrocarbons mixtures with controlled compositions useful either as fuels or even raw chemicals, is a matter of increasing research [10 - 16]. In this regard, conventional cracking catalysts (silica-alumina, zeolites, FCC catalysts) [10, 13] as well as new ones with a high share of fully accessible acid sites over its huge external surface (nanocrystalline ZSM-5) or inside the mesopores (AlMCM-41) have been tested [14]. The latter have exhibited a remarkable performance since they were capable of surpassing the steric hindrances posed by the bulky nature of the polymer macromolecules. In addition, selectivity can be tailored by a judicious choice of both the acid properties and porous structure of the catalysts [14].

However, the great majority of catalytic cracking studies have been carried out with virgin plastics so there are some reasonable doubts about their behavior in case of using real plastic wastes. The presence of different polymers in the real plastic waste makeup, additives, fillers, pollutants, dirt and also the unavoidable degradation of the polymer main chain caused by their usage in the environment (mostly UV and air exposure) is supposed to influence heavily both the activity and selectivity of the catalysts. Accordingly, the present work is aimed at studying the performance of several acid catalysts (nanocrystalline HZSM-5, Al-MCM-41, Al-SBA-15, and TiAl-Beta zeolite) for the cracking of a real agriculture film waste coming from Almeria greenhouses (Spain). Some of these catalysts showed previously a high activity in the cracking of a polyethylene-rich polyolefin mixture [14]. The experimental results reported in this work point out that nanocrystalline HZSM-5 exhibits a highly remarkable performance for the cracking of these kind of residues whereas mesoporous materials (Al-MCM-41, Al-SBA-15), unlike it occurred in the cracking of virgin polyolefins, show similar activity to thermal cracking.

2. Experimental Section

2A. Catalysts. The catalysts used in the present research were Al-SBA-15, Al-MCM-41 and both nanometer size HZSM-5 (n-HZSM-5) and TiAl-Beta zeolites. All these catalysts were synthesized in our laboratory according to procedures published in literature [17-19]. The prepared materials were characterized by means of a number of conventional techniques. XRF fluorescence analyses were performed in a Philips PW 1404 spectrometer. XRD measurements were taken in a Philips X'PERT MPD diffractometer using Cu K α radiation with step size and a counting time of 0.02° and 10 s, respectively. Nitrogen adsorption isotherms were obtained in a Micromeritics ASAP 2010 sorptometer recording both adsorption and desorption branches of the isotherms. Previously, the samples were outgassed at 250° C under vacuum for 5 h. The total surface area values were obtained by application of the BET equation whereas the external surface of the samples were calculated by the t-plot procedure. The pore size distributions were determined by application of the Barrett-Joyner-Halenda method (BJH) to the adsorption branch of the isotherm assuming cylindrical pore geometry. NH₃ TPD measurements were carried out in a Micromeritics 2910 (TPD/TPR) equipment. Previously, the samples were outgassed under a He flow (50 Nml min⁻¹) by heating with a rate of 15°C min⁻¹ up to 550°C. An ammonia flow of 35 Nml min⁻¹ was passed through the sample for 30 min at 180°C. The physisorbed ammonia was removed by flowing He (180°C, 90 min) and subsequently, the chemically adsorbed ammonia was desorbed by increasing the temperature up to 550°C (heating rate ~ 15°C min⁻¹), measuring its concentration by a thermal conductivity detector. ²⁷Al-MAS-NMR spectra of the calcined catalysts were obtained at 104.26 MHz using a Bruker MSL-400 spectrometer equipped with a Fourier Transform unit with [Al(H₂O)₆⁺³] as external standard. All the measurements were carried out at ambient temperature with a spinning frequency of 4000 cps and time intervals of 5 s between

successive accumulations. TEM measurements were carried out in a JEOL 2000 electron microscope operating at 200 kV.

2B. Plastics. The plastics employed in the present research were the following: polymeric wastes coming from used greenhouses films of Almeria (Spain), virgin low density polyethylene (LDPE, $(-\text{CH}_2 - \text{CH}_2 -)_x$, $M_w = 416,000$) and virgin ethylene-vinyl acetate copolymer (EVA, 33 wt % vinyl acetate content, $(-\text{CH}_2 - \text{CH}(\text{OCH}_3)_2 -)_x - (\text{CH}_2 - \text{CH}_2 -)_y$). Both commercial polymers were provided by Repsol-YPF. In addition, an homogenous mixture of commercial LDPE (86 wt %) and EVA copolymer (14 wt %) was prepared by grinding them cryogenically. The plastics were characterized by Inductively Coupled Plasma spectroscopy (ICP), Thermogravimetric Analyses (TGA) and Differential Scanning Calorimetry (DSC). ICP measurements were performed with a VARIAN VISTA AX apparatus. TGA were carried out in a SDT 2960 TA instrument heating the sample with a rate of $5\text{ }^\circ\text{C min}^{-1}$ under a 100 Nml min^{-1} nitrogen flow up to $600\text{ }^\circ\text{C}$. DSC analyses were taken using a DSC822e METTLER-TOLEDO device. The sample was heated from -20 to $250\text{ }^\circ\text{C}$ with a rate of $10\text{ }^\circ\text{C min}^{-1}$.

2C. Reaction system. Before being loaded into the reactor, the plastic wastes were washed, dried and ground cryogenically below 1 mm particle size. In addition, the catalysts were also ground and sieved (mesh size below $75\text{ }\mu\text{m}$). The reaction system used in the thermal and catalytic cracking experiments is illustrated in Figure 1. It consists of a stainless steel batch reactor provided with a helicoidal stirrer swept by a continuous nitrogen flow (25 Nml min^{-1}). In a typical experiment, 10 g of plastic film wastes were introduced into the reactor together with 0.2 g of the catalyst (plastic / catalyst mass ratio = 50). Thereafter, the reactor is heated up to the reaction temperature ($380 - 420\text{ }^\circ\text{C}$) with a ramp rate of $6\text{ }^\circ\text{C min}^{-1}$ under inert atmosphere, the reaction temperature being maintained for 2 h. The products leaving the reactor were driven to a

glass condenser cooled by an ice trap. The liquid products were separated and weighed whereas the gaseous products were collected in a gas sampling bag. Gaseous products were analyzed in a Hewlet Packard 5880 GC equipped with a Porapak Q column. Condensed products were analyzed in a Varian 3800 GC equipped with a 10 m MXT capillary column. PIONA analyses (Paraffins, Isoparaffins, Olefins, Naphtenes and Aromatics) were carried out in a Varian 3800 GC provided with a 100 m length x 0.25 mm i. d. Chrompack capillary column. The conversion was defined as follows: $(\text{mass of collected hydrocarbons } C_n, n \leq 40 + \text{mass of acetic acid released}) / (\text{mass of loaded film waste})^{-1} * 100$. The remaining residue into the reactor after the reaction was not regarded as product. The mass balances were closed within a 5 % error range.

3. Results and discussion

3A. Plastic film waste characterization. The plastic film waste recovered from Almería greenhouses (Spain) is mostly made up of both degraded LDPE and EVA copolymer. As a result of the exposure to the ambient light and air of the film throughout its lifetime (2-3 years), it has undergone several degradation processes such as oxidation and crosslinking. TGA of the plastic film waste and both virgin polymers (LDPE and EVA) under inert atmosphere are shown in Figure 2. TGA of the EVA copolymer shows two distinct peaks in the differential curve placed at 340 and 459 °C, respectively. The former (25 wt %) corresponds to the complete elimination of the vinyl acetate present in the polymer, that is released as acetic acid whereas the latter (75 wt %) has been ascribed to the decomposition of the remaining polyethylene-like residue [20], which agrees well with the position of the main peak of virgin LDPE degradation (463 °C). TGA of the film waste shows one main peak in the differential curve situated at the same temperature (463 °C) of the aforementioned, confirming the polyethylenic nature of the film waste. A second small peak placed at 340 °C and corresponding to the acetic acid release also appears, indicating that the

vinyl acetate content of the plastic film waste is roughly 4 wt %. DSC analyses of the plastic film waste as well as of both virgin polymers (LDPE and EVA) are shown in Figure 3. LDPE exhibits only one endothermic peak placed at 110°C corresponding to the polyethylene melting point while EVA copolymer shows solely a broad one centered at 56°C with a shoulder at roughly 72°C. DSC of the plastic film waste presents a main peak at 110°C corresponding to the major component of the refuse, polyethylene. This peak is wider than that of pure LDPE, probably due to the different degradation processes it has undergone during usage. In addition, a second small peak placed at 57°C is appreciated that is associated to the small amount of EVA copolymer present in the plastic residue.

The plastic film waste also contains different inorganic fillers usually loaded in its composition as well as dirt coming from its agriculture usage. ICP analyses of the film waste indicated the presence of the following elements: Al (0.1 wt %), Ni (0.05 wt %), Ca (0.07 wt %), Mg (0.05 wt %), K (0.01 wt %), Fe (0.03 wt %) and S (0.17 wt %). According to the TGA measurements, the total amount of inorganic fillers and dirt, estimated as the final weight above 550 °C, is quite low (about 1-2 wt %).

3B. Catalyst characterization. The main physicochemical properties of the catalysts used in this work are shown in Table 1. Al-SBA-15 and Al-MCM-41 are uniform mesoporous aluminosilicates with pore diameters of 4.7 and 2.0 nm respectively. Al-SBA-15 differ from Al-MCM-41 not only in pore size but also in both its thicker pore wall (> 3.0 nm) and the presence of certain amount of micropores (completely absent in Al-MCM-41) [21]. Titanium aluminum Beta (TiAl-Beta) and nanometer size HZSM-5 (n-HZSM-5) zeolites are crystalline microporous aluminosilicates with a 3D porous structure and a mean pore diameter of 0.63 and 0.55 nm, respectively. n-HZSM-5 has been prepared with a small crystal size so as to obtain a high proportion of external acid sites,

fully accessible to the bulky polymer macromolecules. Thus, the external surface area of this material represents almost 20 % of the total surface. All the catalysts have been synthesized with Si/Al atomic ratios within the 40 - 50 range. Aluminum incorporation into the framework was borne out by ^{27}Al -MAS-NMR measurements, as the share of tetrahedral aluminum after calcination in all the catalysts was roughly 90%. The strength of the catalyst acid sites, determined from the temperature maxima of ammonia programmed desorption (TPD) measurements (see Table 1), follows the order: n-HZSM-5 > TiAl-Beta > Al-MCM-41 ~ Al-SBA-15.

3C. Catalytic conversion of the plastic film waste. Figure 4 shows the conversions obtained at 420°C in the cracking of the plastic film waste over the different catalysts as well as that corresponding to the blank test reaction of thermal degradation. In addition, the results obtained in both thermal and catalytic cracking of the virgin LDPE at 420°C have also been included for establishing a better comparison. As inferred from the figure, the conversion obtained in the thermal cracking of the film waste is slightly lower than that of the LDPE, despite the release of a meaningful amount of acetic acid (~ 3 wt %) around 350 - 400°C. This fact suggests that the plastic film waste is more difficult to be cracked thermally than the commercial LDPE. On the other hand, catalytic cracking of the plastic film waste over the mesoporous materials (Al-SBA-15 and Al-MCM-41) gave rise to similar or even slightly lower conversions than that of the thermal cracking. These results are especially striking compared to those obtained in the cracking of the LDPE since 100 % conversion was attained over both mesoporous catalysts under identical experimental conditions. In contrast, n-HZSM-5 zeolite was able to degrade completely the film waste leading to almost 100 % conversion. Consequently, n-HZSM-5 zeolite seems not to be affected by the plastic film waste composition in contrast with the mesoporous Al-SBA-15 and Al-MCM-41 catalysts. TiAl-Beta zeolite also shows higher activity (60 %) than thermal cracking and mesoporous catalysts but still far from that corresponding to n-HZSM-5 zeolite.

The selectivity by groups obtained with the catalytic cracking of the plastic film waste over the different catalysts as well as that corresponding to the blank test reaction at 420°C are shown in Figure 5. n-HZSM-5 zeolite shows a remarkable high selectivity towards C₁ - C₅ hydrocarbons (60 wt %), the great majority of them being valuable C₃ - C₅ olefins, whereas both thermal and catalytic cracking over the other catalysts led to 20 -30 % selectivity towards this hydrocarbon fraction. The highest selectivity towards C₆ - C₁₂ hydrocarbons was obtained over TiAl-Beta zeolite (> 55 %) and the lowest over n-HZSM-5 zeolite. In addition, both zeolites provided the lowest amount of heavier C₁₃ - C₄₀ hydrocarbons, unlike the mesoporous catalysts and the thermal cracking that show selectivities around 30 %. Figure 6 illustrates the selectivity by carbon atom number obtained in the thermal and catalytic cracking of the plastic film waste over the different catalysts. n-HZSM-5 zeolite presents a main maximum placed at the C₄ hydrocarbon fraction (28 %), the total selectivity towards the valuable C₃ - C₅ hydrocarbon fractions being above 55 %. On the other hand, the product distribution by carbon atom number obtained over both Al-SBA-15 and Al-MCM-41 catalysts is quite similar to that corresponding to the thermal cracking.

PIONA analyses of the C₆ - C₁₂ hydrocarbon fraction are shown in Figure 7. Cracking over Al-MCM-41 and Al-SBA-15 point out the presence of a high and similar content of 1-olefins and n-paraffins, which are the main products expected from a radical cracking mechanism of the polyethylene backbone, typical of the thermal degradation [22]. Both activity and selectivity data indicate that, in the cases of Al-SBA-15 and Al-MCM-41 catalysts, thermal cracking is the major responsible for their respective product distribution. In contrast, the selectivity results obtained over both zeolites (TiAl-Beta and n-HZSM-5) are more in line with those reported in the commercial LDPE cracking [2, 23] and bear out that a carbocationic cracking mechanism is

taking place [24,25]. Selectivity data can be explained in terms of the respective acid strength, external surface and microporous structure of the zeolites. In the case of n-HZSM-5 zeolite, and due to its small micropore size (~ 0.55 nm), the initial cracking steps mainly proceeds on the strong acid sites present over its large external surface ($82 \text{ m}^2 \text{ g}^{-1}$), giving rise to the primary cracking products ($\text{C}_3 - \text{C}_5$ olefins) through a carbocationic end-chain cracking mechanism. Instead, TiAl-Beta zeolite leads mostly to $\text{C}_6 - \text{C}_{12}$ hydrocarbons due to its both lower acid strength and external surface as well as slightly higher micropore size (0.63 nm). In this case, less intense cracking reactions occur whereas secondary $\text{C}_3 - \text{C}_5$ olefin oligomerization reactions takes place inside the micropores leading to higher hydrocarbons.

The performance of both n-HZSM-5 and TiAl-Beta zeolite for the cracking of the plastic film waste within the $380\text{-}420^\circ\text{C}$ temperature range is shown in Figure 8. n-HZSM-5 zeolite was always the most active catalyst regardless of the studied temperature. In addition, it gave rise to a meaningful cracking conversion (15%) even at a temperature as low as 380°C and despite the low amount of used catalyst (under these conditions, the conversion of the thermal cracking reaction was roughly 3 %). By contrast, at this same temperature, TiAl-Beta zeolite provides practically the same activity of the bottom thermal cracking reaction.

On the other hand, in order to check the deactivation of n-HZSM-5 zeolite, its activity evolution with the time was followed at 380°C , showing conversions of 14, 26 and 39 wt % after 2, 4 and 6 h of reaction, respectively. Hence, its cracking performance proceeds with practically no decay in activity with the time. In addition, the obtained products at 380°C are also valuable $\text{C}_2 - \text{C}_5$ hydrocarbons (selectivity above 70 wt %), mostly olefins (ratio olefins / paraffins > 4).

In a previous work [26], the presence of EVA copolymer in a virgin LDPE / EVA copolymer mixture (86/14 w/w) with a vinyl acetate content (~ 4%) similar to that of the film waste here studied, was observed to be detrimental for the cracking over mesoporous catalysts (Al-MCM-41, Al-SBA-15). This behaviour has been ascribed to the occurrence of crosslinking reactions after the release of acetic acid, leading to the catalyst deactivation by coke fouling on the unhindered mesoporous structure of both Al-SBA-15 and Al-MCM-41. A similar phenomenon may also occur in the cracking of the film waste explaining the low activity of the mesoporous catalysts. In addition, the medium acid strength of these materials is not probably high enough for promoting the cracking of the refuse. By contrast, the observed remarkable performance of n-HZSM-5 can be mostly ascribed to both its great content of strong and accessible external acid sites, and high resistance to coke deactivation.

Conclusions

The results reported in this work prove that the direct catalytic cracking of a real plastic film waste is a feasible feedstock recycling procedure provided that a suitable catalyst is used. Mesoporous solids (Al-MCM-41 and Al-SBA-15), that had shown remarkable performance in the cracking of the raw low-density polyethylene (LDPE), were practically inactive with the plastic film waste, probably due to its medium acid strength along with a deactivation phenomenon caused by the presence of EVA copolymer in the raw refuse. However, n-HZSM-5 zeolite was able to degrade completely the film waste using a very small amount of catalyst (plastic / catalyst mass ratio of 50). In addition, more than 55 wt % of C₃ - C₅ hydrocarbons were obtained over this catalyst at 420°C, the majority of them being valuable olefins. Consequently, n-HZSM-5 zeolite shows remarkable properties for the cracking of plastic film wastes, being capable of surpassing the problems posed by its complex makeup.

Acknowledgments

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References

- [1] Association of Plastics Manufacturers in Europe (APME), Summary Report: An analysis of plastics consumption and recovery in Western Europe 2000, (2002).
- [2] J. Aguado, D. P. Serrano, Feedstock Recycling of Plastic Wastes, Royal Society of Chemistry, Cambridge, 1999.
- [3] S. Babinchak, CHEMTECH 21(12) (1991) 728.
- [4] G. L. Nelson, CHEMTECH 25(12) (1995) 50.
- [5] M. R. Kahn, C. C. Albert, S. J. De Canio, WO Patent 9903 (1995).
- [6] H. K. Mucha, U. Drost, R'02 6th World Congress on Integrated Resources Management, Geneve, 2002.
- [7] H. P. Wenning, J. Anal. Appl. Pyrolysis 25 (1993) 301.
- [8] J. Kim, W. Kaminsky, B. J. Schlesselmann, J. Anal. Appl. Pyrolysis 40-41 (1997) 365.
- [9] Plastic Waste Management Institute Newsletter (Japan), Liquefaction Technology 15(3) (1998) 1.
- [10] A. Corma, S. Cardona, Appl. Catal. B 25 (2000) 151.
- [11] G. Manos, I. Y. Yusof, N. Papayannakos, N. H. Gangas, Ind. Eng. Chem. Res. 40 (2001) 2220.
- [12] W. Kaminsky, J. Kim, J. Anal. Appl. Pyrolysis 51 (1999) 127.
- [13] A. R. Songip, T. Masuda, H. Kuwahara, K. Hashimoto, Appl. Catal. B 2 (1993) 153.
- [14] D. P. Serrano, J. Aguado, J. M. Escola, Ind. Eng. Chem. Res. 39 (2000) 1177.
- [15] S. Ali, A. A. Garforth, D. H. Harris, D. J. Rawlence, Y. Uemichi, Catal. Today 75 (2002) 247.
- [16] R. Bagri, P. T. Williams, J. Anal. Appl. Pyrolysis 63 (2002) 29.
- [17] R. Van Grieken, J. L. Sotelo, J. M. Menéndez, J. A.. Melero, Microporous Mesoporous Mater. 39 (2000) 135.

- [18] D. P. Serrano, M. A. Uguina, G. Ovejero, R. Van Grieken, M. Camacho, J. A. Melero, J. Mater. Chem. 9 (1999) 2899.
- [19] J. Aguado, D. P. Serrano, R. Van Grieken, J. M. Escola, E. Garagorri, Stud. Surf. Sci. Catal. 135 (2001) 273.
- [20] A. Marcilla, A. Gómez, J. A. Reyes-Labarta, Polymer 42 (2001) 8103.
- [21] K. Miyazawa, S. Inagaki, Chem. Commun. (2000) 2121.
- [22] T. P. Wampler, J. Anal. Appl. Pyrolysis, 15 (1989) 187.
- [23] J. Aguado, J. L. Sotelo, D. P. Serrano, J. A. Calles, J. M. Escola, Energy Fuels 11 (1997) 1225.
- [24] Bohdan W. Wojciechowski, Ind. Eng. Chem. Res. 36 (1997) 3323.
- [25] A. Corma, Chem. Rev. 95(3) (1995) 475.
- [26] D. P. Serrano, J. Aguado, J. M. Escola, J. M. Rodríguez, L. Morselli, R. Orsi, J. Anal. Appl. Pyrolysis 68-69 (2003) 481.

Table 1. Physicochemical properties of the catalysts

Catalyst	Si/Al	BET surface area (m ² g ⁻¹)	External surface area (m ² g ⁻¹) ^a	Pore Volume (cm ³ g ⁻¹) ^b	Pore Diameter (nm)	Crystal size (nm)	T _{max} (°C) ^c	Acidity (mmol g ⁻¹) ^c
Al-SBA-15	49	623	-	0.65	4.70	-	242	0.260
Al-MCM-41	40	1240	-	0.83	2.10	-	254	0.254
TiAl-Beta	41	653	22	0.25	0.63	230	329	0.276
n-HZSM-5	45	428	82	0.16	0.55	60	357	0.324

^adetermined by the t-plot method; ^bmeasured at p/p₀ = 0.95; ^ccalculated by ammonia TPD measurements

FIGURE CAPTIONS

Figure 1. Scheme of the experimental cracking installation.

Figure 2. TGA under inert atmosphere of the plastic samples.

Figure 3. DSC analyses of the plastic samples.

Figure 4. Conversions obtained with the thermal and catalytic cracking of both plastic film waste and virgin LDPE ($T = 420^{\circ}\text{C}$; $t = 2 \text{ h}$).

Figure 5. Selectivity by groups obtained with the thermal and catalytic cracking of the plastic film waste ($T = 420^{\circ}\text{C}$; $t = 2 \text{ h}$).

Figure 6. Selectivity by carbon atom number obtained with the thermal and catalytic cracking of the plastic film waste ($T = 420^{\circ}\text{C}$; $t = 2 \text{ h}$).

Figure 7. PIONA analyses of the $\text{C}_6 - \text{C}_{12}$ hydrocarbon fraction obtained in the thermal and catalytic cracking of the plastic film waste at 420°C .

Figure 8. Evolution with the temperature of the cracking conversion of the plastic film waste over TiAl-Beta and n-HZSM-5 zeolites ($t = 2 \text{ h}$; plastic / catalyst mass ratio = 50).

FIGURE 1

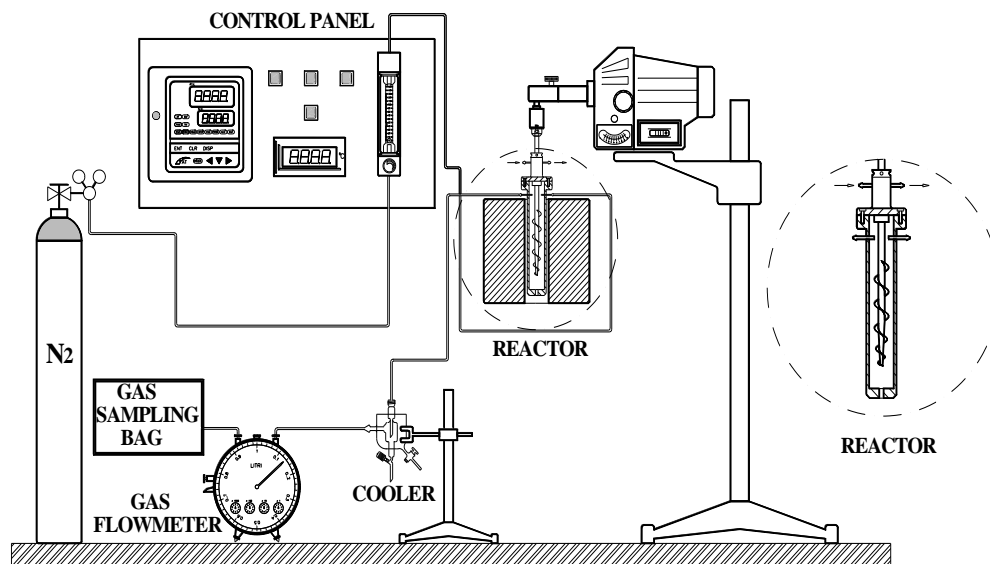


FIGURE 2

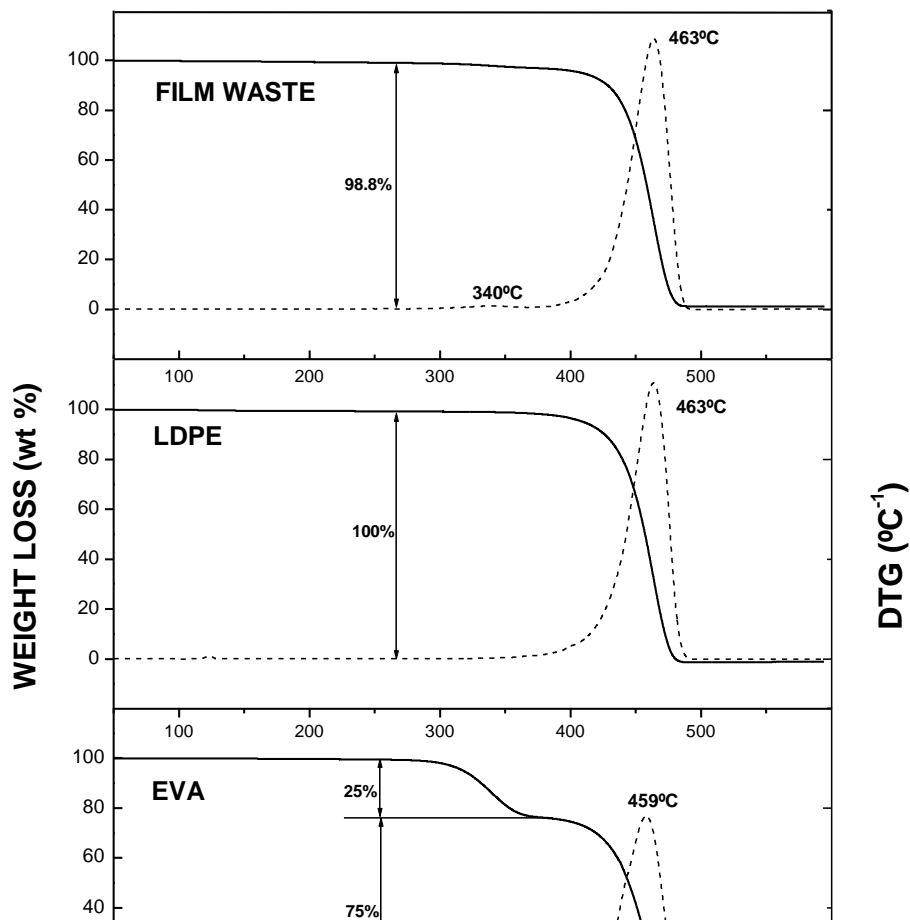


FIGURE 3

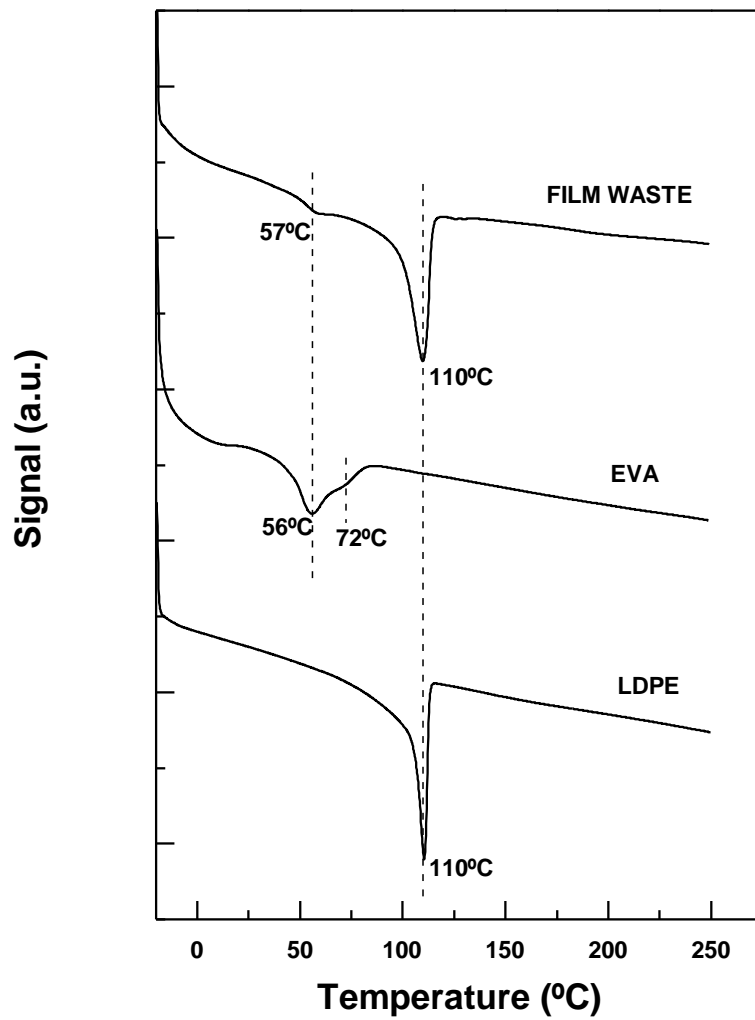


FIGURE 4

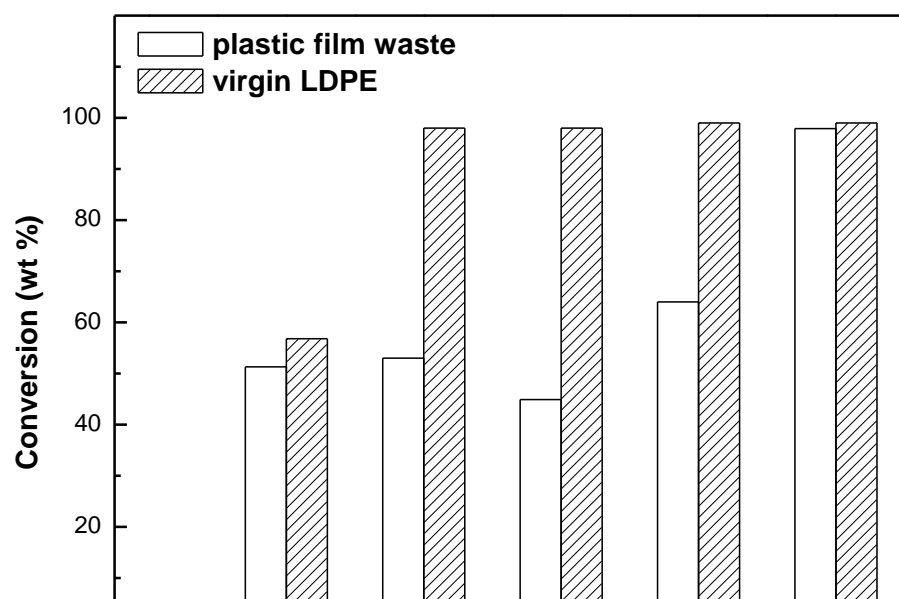


FIGURE 5

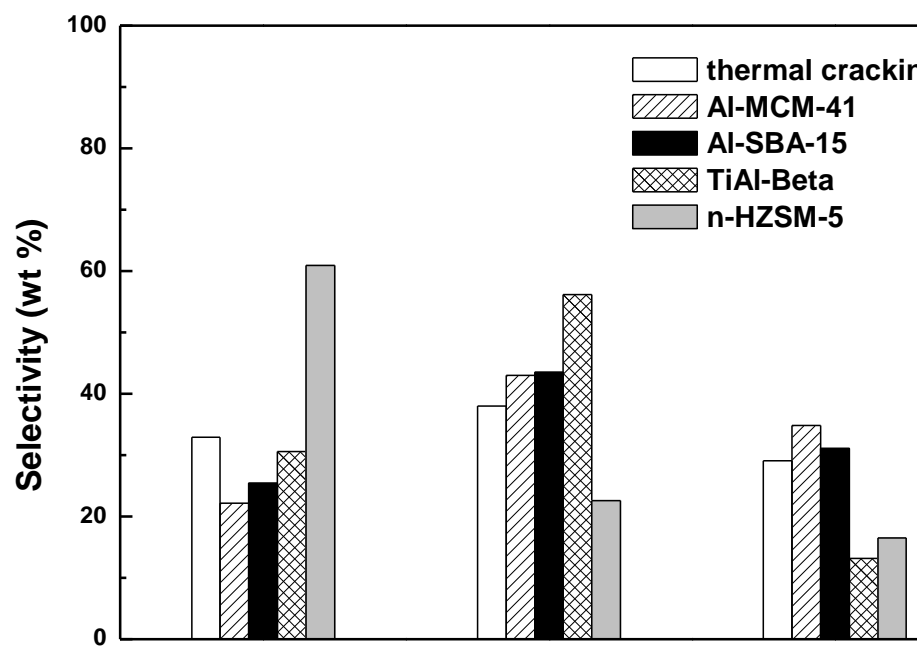


FIGURE 6

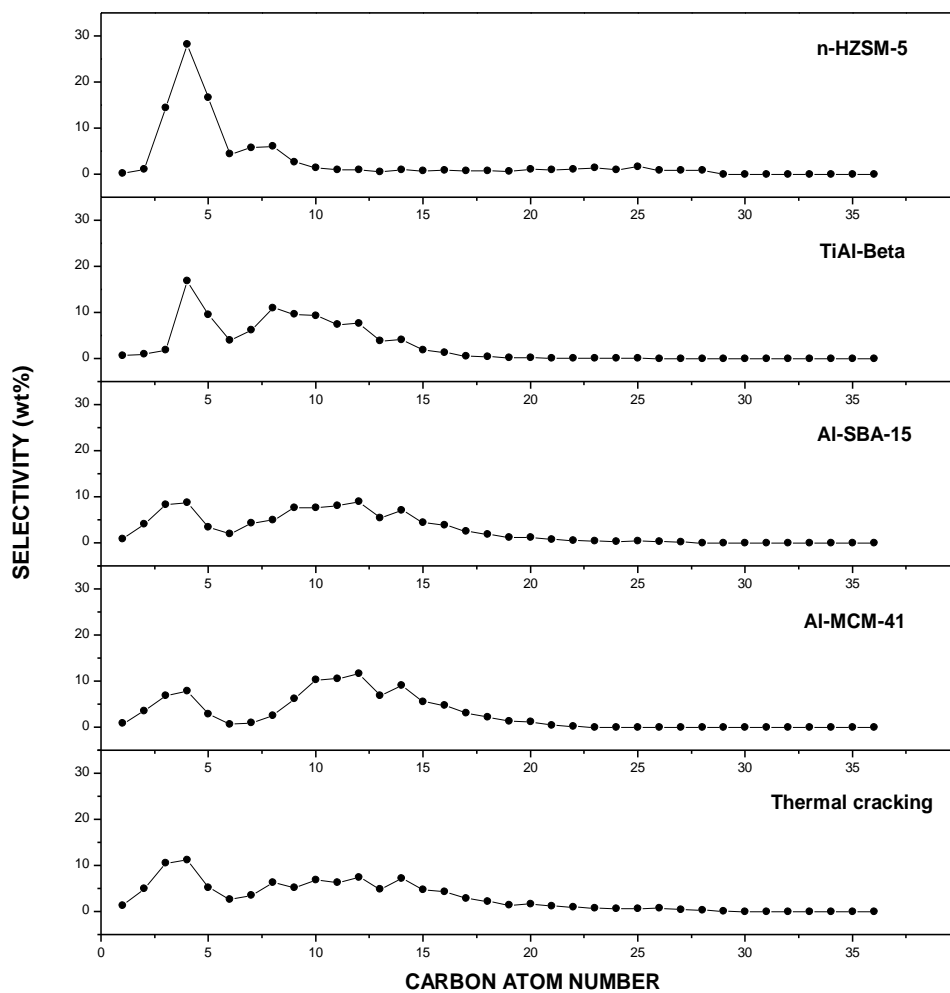


FIGURE 7

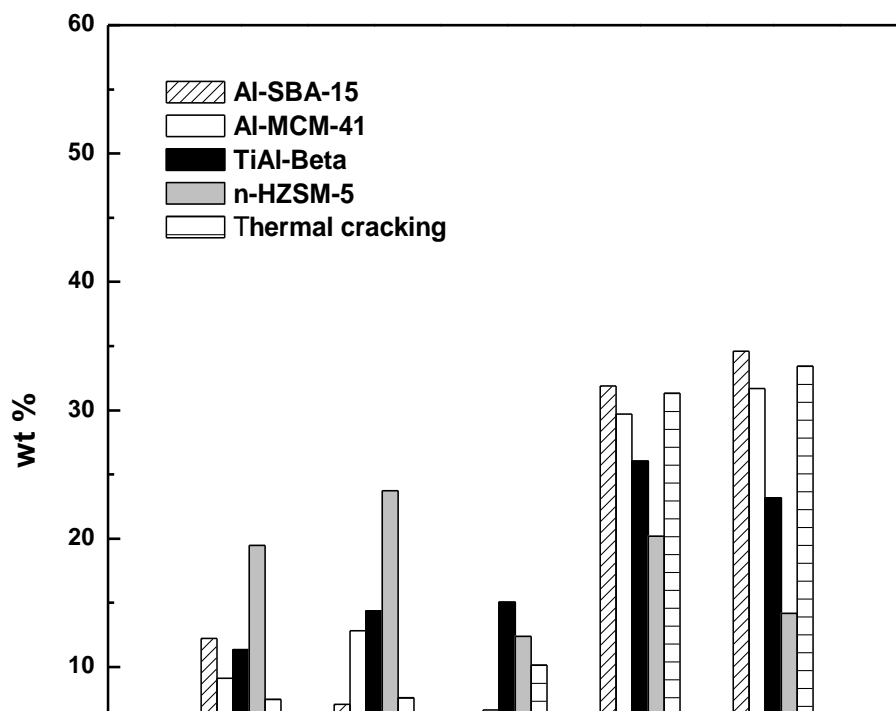


FIGURE 8

