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Catalytic conversion of low-density polyethylene using a continuous screw kiln reactor

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Abstract

Both thermal and catalytic cracking of low-density polyethylene (LDPE) have been investigated using a screw kiln reactor. Thermal degradation gives rise to a broad product distribution, whereas catalytic cracking over Al-MCM-41 leads mainly to hydrocarbons within the gasoline range (C_5–C_{12}) with selectivities up to 80%. The increase of the screw speed between 3 and 15 rpm in the catalytic experiments allows the plastic feed rate to be varied in the range 20–41 $\mathrm{g\,h^{-1}}$. The changes observed in the TOF values when varying the screw speed point out a decrease of the activity per site with increasing residence times, which may be due to the catalyst deactivation or to a contribution of the degradative extrusion at higher screw speeds. Likewise, a certain increase in the selectivity towards the gasoline fraction is observed at short residence times. On the other hand, PIONA analyses indicate that, regardless of the screw speed, the main components of the gasoline are olefins (50%) and isoparaffins (20%), whereas the aromatic content is always below 6%, with a proportion of benzene lower than 0.1%. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: LDPE; Feedstock recycling; Plastic wastes; MCM-41; Screw kiln reactor

1. Introduction

Feedstock recycling is a promising alternative for the management of plastic wastes, as it may allow these residues to be transformed into valuable products. Moreover, it is favoured by both the increasing amounts of plastic wastes and the problems associated to the currently applied solutions, landfilling and incineration, such as emission of dangerous compounds and social rejection. Accordingly, feedstock recycling of plastic wastes is a very active field of research [1–10]. Among the different processes under study, those dealing with polyolefins are predominant since these type of polymers account for more than 70% of the total plastic content in the municipal solid waste (MSW) stream [11]. In this way, catalytic cracking of low-density polyethylene (LDPE) over Al-MCM-41 has proved to be successful for obtaining both high conversions and selectivities towards gasolines [12]. These results were ascribed to the medium acid strength of Al-MCM-41 and the presence of both high surface area and uniform mesopores (around 2.5 nm) in this material, which makes possible the catalytic degradation of the bulky polyolefinic molecules.

From an industrial viewpoint, continuous reaction systems are preferred for operational reasons rather than batch ones. Accordingly, several continuous reactors such as fixed and fluidized beds have been employed for polyolefin cracking. In this work, a screw kiln reactor has been investigated for the conversion of LDPE through both thermal and catalytic treatments.

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It must be pointed out that in spite of the evident interest of this continuous system for the conversion of plastic wastes, little can be found in the literature about its application [13–15].

2. Experimental

2.1. Catalyst

The catalyst used in the present work is a mesoporous Al-MCM-41 material synthesized using hexadecyltrimethylammonium chloride as template and prepared according to a procedure described in the literature [16]. Prior to the reaction, the catalyst was ground and sieved to get a mesh size below 0.074 mm. Likewise, in order to get a homogeneous mixture between the plastic and the catalyst, the former was cryogenically ground down to 0.25 mm particle size by means of a Retsch ZSM-100 ultracentrifuge mill.

The catalyst has been characterized following conventional techniques: X-ray powder diffraction (XRD), X-ray fluorescence (XRF), ^{27}Al magic angle nuclear magnetic resonance (^{27}Al-MAS-NMR), N_2 adsorption and desorption isotherms at 77 K, transmission electron microscopy (TEM) and scanning electron microscopy (SEM).

2.2. Reaction system and procedure

Both thermal and catalytic cracking experiments of LDPE ($M_w = 416\,000$, REPSOL) have been carried out in a screw kiln reactor described elsewhere [13]. In the case of the catalytic cracking, a plastic and catalyst mixture (250 g of LDPE; plastic/catalyst, 50:1 (w/w)) is loaded into a hopper and flushed with nitrogen for 30 min. Subsequently, it is hermetically closed and heated at 300 °C under nitrogen atmosphere. The molten mixture is fed by gravity into the reaction zone which comprised a motor driven screw placed inside a cylindrical stainless steel reaction chamber (i.d.: 2 cm, length: 52 cm). The residence times and feed rates of the plastic can be modified by adjusting the screw speed within the range 3.0–15 rpm. The reaction chamber is heated by two furnaces (1 and 2) placed sequentially, so the temperatures corresponding to their respective heating zones are T_1 and T_2, respectively. The temperature along the screw is measured and controlled by means of a number of thermocouples inserted in different points of the reactor wall. Thus, radial and axial temperature gradients were observed to be practically negligible.

Gaseous and liquid products leaving the reactor are separated by means of an ice trap. The gaseous products are collected in a sampling bag and their volume is obtained from volumetric displacement measurements, whereas the amount of condensed products is obtained by weighing. GC analyses of the gaseous and condensed products were performed in a Porapak Q packed column and an MXT capillary column, respectively. PIONA analyses of the gasoline fraction were carried out on a 100 m length × 0.25 mm i.d. Chrompack capillary column. Conversion was calculated from the mass of hydrocarbons with $C_n \leq C_{55}$ which are recovered during a period of 1 h after achieving the steady state operation, referred to the total LDPE mass being fed during that period. The remaining products, made up of a mixture of heavy waxes and partially cracked polymer, were not included in the conversion. Mass balances were closed with an error within the range ±5%.

3. Results and discussion

3.1. Comparison between thermal and catalytic cracking in the screw kiln reactor

The sample of Al-MCM-41 used in the catalytic experiments presents a BET surface area of 1565 $m^2\,g^{-1}$, a Si/Al atomic ratio of 40 and mean pore diameter according to the BJH method of 2.15 nm. These physicochemical parameters are in agreement with those typically reported in the literature for this type of materials. Moreover, the ^{27}Al-NMR-MAS spectrum (data not shown) of the as-synthesized Al-MCM-41 exhibits just one peak at 53 ppm corresponding to tetrahedral aluminium. After calcination to remove the occluded surfactant molecules, a second peak of lower intensity at 0 ppm is observed, showing the formation of extra-framework octahedral Al species during this treatment. Nevertheless, more than 80% of the Al atoms remain with tetrahedral coordination in the calcined Al-MCM-41.

Catalytic cracking of LDPE over Al-MCM-41 was performed at $T_1/T_2 = 400/450\,^{\circ}C$ using a screw

Table 1
Thermal and catalytic cracking of LDPE in the screw kiln reactor

Experiment[a]	Screw speed (rpm)	T_1/T_2 (°C)	Output ($g\,h^{-1}$)	Conversion (wt.%)	TOF[b] (s^{-1})	Selectivity (wt.%)			
						C_1–C_4	C_5–C_{12}	C_{13}–C_{23}	C_{24}–C_{55}
ST	3.0	450/550	38.0	100.0	–	9.4	28.9	35.7	26.0
SC1	3.0	400/450	19.6	69.1	0.291	21.4	66.4	4.6	7.6
SC2	6.0	400/450	26.9	64.9	0.374	18.1	69.3	9.7	2.9
SC3	15.0	400/450	41.2	51.4	0.454	18.3	77.7	2.0	2.0

[a] ST, SC: thermal and catalytic cracking experiments in the screw kiln reactor, respectively.

[b] TOF values calculated as mass of converted LDPE/mass of Al in the catalyst/s.

speed of 15 rpm. Under these conditions, the thermal cracking only led to a slightly cracked polymer with a negligible conversion towards C_1–C_{55} products (<1%). Owing to this, a thermal cracking experiment previously reported [13], done under more severe experimental conditions ($T_1/T_2 = 450/550\,°C$, screw speed = 3 rpm) and with similar product output to that obtained in catalytic cracking ($40\,g\,h^{-1}$), was chosen for a proper comparison. Table 1 shows the conversions and selectivities by groups obtained for both thermal (ST) and catalytic cracking (SC3) reactions, while Fig. 1 illustrates their corresponding selectivities by carbon atom number. Al-MCM-41 leads mainly to hydrocarbons in the gasoline range

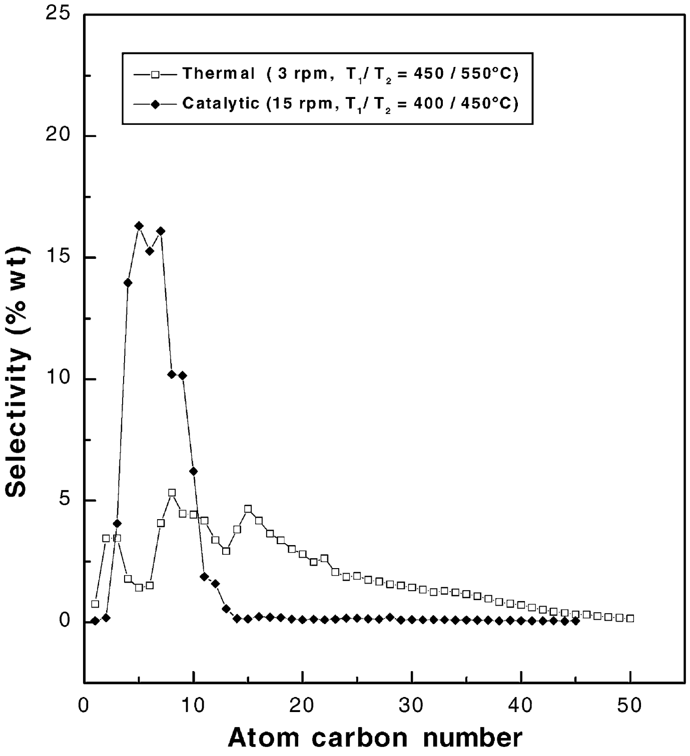

Fig. 1. Comparison of the selectivity by carbon atom number obtained in the thermal and catalytic cracking of LDPE in the screw kiln reactor.

(C_5–C_{12}) with a selectivity in the SC3 experiment close to 80%. Likewise, a remarkable proportion of gases is also obtained (18%), whereas the share of heavier fractions (C_{13}–C_{50}) is virtually negligible (4%) which shows that they undergo an intense overcracking within the screw kiln reactor. The situation is quite different for the thermal cracking since similar amounts of gasoline and gasoil fractions are obtained (30–35%). Similar conclusions can be drawn from the selectivities by carbon atom number depicted in Fig. 1. A narrow product distribution is observed for the catalytic cracking over Al-MCM-41 with two maxima placed at C_5 and C_7 fractions, respectively. It is interesting to note that the overall selectivity for C_4–C_7 hydrocarbons is around 60%. On the contrary, thermal cracking gives rise to a broad product distribution wherein each fraction is mostly formed by the corresponding 1-olefin and *n*-paraffin. These results can be interpreted in terms of the different mechanisms corresponding to thermal (radical) [17] and catalytic cracking (carbocationic) [18].

3.2. Effect of the screw speed on the LDPE catalytic cracking

Table 1 summarizes the results obtained in the catalytic cracking of LDPE over Al-MCM-41 when the screw speed is varied in the range 3–15 rpm. The product output increases from 19.6 up to 41.2 $g\,h^{-1}$ with the screw speed, which shows that this variable is effective for controlling both the plastic feed rate and the residence time within the reactor.

A trend to lower conversions is observed as the screw speed is increased, which is in agreement with the progressively shorter residence times. However, if the results are rationalized in terms of turnover frequency, TOF (data shown in Table 1) a drop off in the TOF values with decreasing screw speeds is obtained. Thus, when the TOF results corresponding to SC1 and SC2 reactions are compared, a great difference is observed. This fact may be due to the existence of deactivating phenomena that would cause a loss of catalytic activity at long residence times.

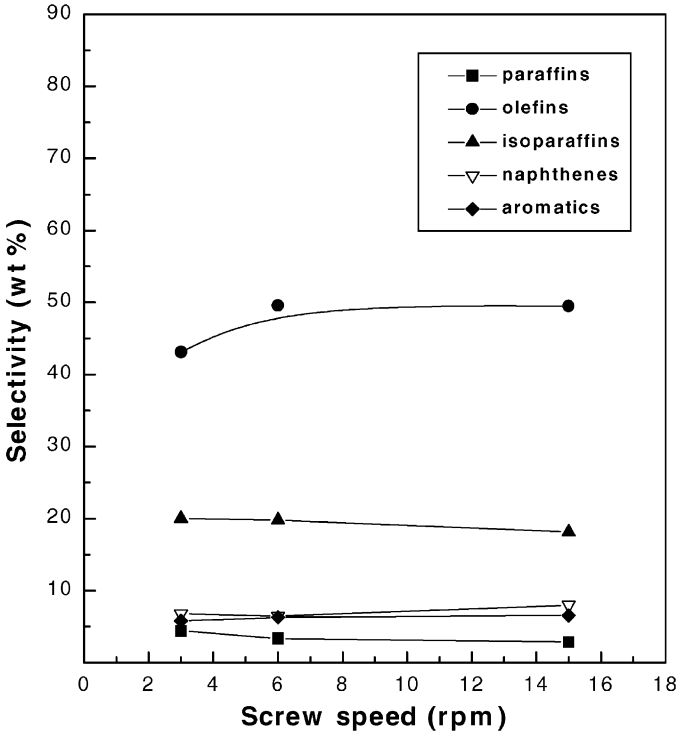

Fig. 2. PIONA analyses of the gasoline fractions obtained in the LDPE catalytic degradation.

Due to its uniform mesoporosity, Al-MCM-41 is a material with fully accessible acid sites, which makes feasible the formation and growth of coke molecules inside this unhindered porous structure. However, other explanation of the increase in the TOF values at shorter residence times is the possible contribution of the extrusion to the polymer degradation, which is expected to be favoured at higher screw speeds.

In regards to the changes in the selectivities by groups with the screw speed, a decrease in the gasoline fraction occurs with slower speeds whereas the proportion of heavier fractions ($>C_{13}$) increases. This results can be interpreted as a consequence of a higher extent and contribution of thermal cracking reactions at longer residence times, which favour non-selective random cracking pathways, as shown in Fig. 1.

The nature and type of the hydrocarbons formed in the LDPE catalytic cracking have been determined by means of PIONA analyses of the gasoline fractions. Fig. 2 illustrates the results of the PIONA measurements obtained in the reactions carried out with different screw speeds. The main products are olefins, with a proportion close to 50 wt.%, and isoparaffins, around 20 wt.%. It is noteworthy that the amount of aromatics is below 7%, whereas the presence of benzene is virtually negligible ($<0.1\%$), which is in agreement with the current trends to limit its presence in fuels below 1%. The content of naphthenic hydrocarbons is in all cases similar to that of aromatics. No great variations are observed in the hydrocarbon types with the screw speed. The most significant change is a decrease in the amount of olefins at lower screw speeds, which is accompanied by a parallel increase in the formation of isoparaffins and *n*-paraffins. These results indicate that hydrogen transfer reactions are somewhat promoted at lower screw speeds, i.e. at longer residence times.

4. Conclusions

Catalytic cracking of LDPE over Al-MCM-41 can be carried out in a screw kiln reactor with high conversion and product outputs. Compared to the thermal degradation, the catalytic conversion is quite faster and shows a completely different selectivity pattern. Thus, thermal cracking gives rise to a broad product distribution, whereas catalytic cracking leads mainly to hydrocarbons within the gasoline range (C_5–C_{12}) with selectivities up to 80%. The modification of the screw speed allows both the plastic feed rate and the residence time to be varied. Increasing the screw speeds in the catalytic experiments causes a certain decrease in the overall plastic conversion, although higher TOF values are obtained. This fact may arise from the catalyst deactivation, enhanced at long residence times, or from the contribution of degradative extrusion at high screw speeds. Selectivity by groups shows a decline of the gasoline share with decreasing screw speeds. Likewise, PIONA analyses of the gasoline fraction point out that, regardless of the screw speed, olefins and isoparaffins are the main products (50 and 20%, respectively), while the aromatics proportion is below 6% with a benzene content lower than 0.1%.

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