

**PERFORMANCE OF A CONTINUOUS SCREW KILN REACTOR FOR THE THERMAL AND
CATALYTIC CONVERSION OF POLYETHYLENE - LUBRICATING OIL BASE MIXTURES**

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Abstract

Both thermal and catalytic cracking of mixtures consisting of low-density polyethylene (LDPE) and a lubricating oil base have been investigated in a continuous screw kiln reactor, provided with two reaction zones operating at different temperatures (T_1/T_2). The incorporation of the lubricating oil into the plastic leads to a significant decrease in its viscosity which favours the mixture flow through the reactor. Thermal cracking at 450/500°C of LDPE – lubricating oil base mixtures with compositions ranging from 40/60 to 70/30 w/w % led in all cases to their almost complete conversion (~ 90 %) towards a broad spectrum of $C_1 - C_{40}$ hydrocarbons. Catalytic cracking of a 70/30 (w/w %) LDPE – lubricating oil base mixture over mesoporous Al-MCM-41 catalysts at 400/450°C proceeded with lower activity with regards to the pure LDPE catalytic cracking. This result is related to both the lower reactivity of the oil compared to the pure polyolefin and to the poisoning of the catalyst acid sites by sulphur/nitrogen - containing compounds present in the lubricant oil base. However, at higher temperatures (450/500°C), complete conversion of the mixture was attained over both Al-MCM-41 and nanocrystalline HZSM-5 (n-HZSM-5) catalysts. Al-MCM-41 materials leads mainly to $C_5 - C_{12}$ products (65 % selectivity) whereas lighter hydrocarbons were formed preferentially over n-HZSM-5 (63 % selectivity towards $C_3 - C_5$ compounds). These results demonstrate that the screw kiln reactor is an efficient system for the continuous processing of plastic - lubricant oil mixtures by thermal and catalytic treatments.

Keywords: LDPE, lubricating oil, cracking, Al-MCM-41, nanocrystalline HZSM-5

1. Introduction

The high level of development in the industrialized societies has brought about a huge availability of products that inevitably end their life as a residue. These increasing amounts of wastes have become a matter of concern for they are a true menace to our current high standards of life quality. Among the different wastes, plastics and lubricating oils are worth special attention as their recycling and management is not yet a well established issue. Polyolefins (LDPE, HDPE and PP) are extensively used materials and they account for more than 60 % of the total of plastic wastes present in municipal solid wastes (MSW) [1]. The currently existing strategies to deal with these wastes are based largely on landfilling and energy recovery (roughly 64 % and 23 %, respectively, of the total plastic wastes in Western Europe) [2]. On the other hand, great amounts of lubricating oil wastes are also obtained annually, accounting for about 15 - 20 wt % of those corresponding to plastics ones [3]. Unfortunately, lubricating oil wastes are often either burned off or disposed of by uncontrolled landfilling. These alternatives are unacceptable regarding the environmental damage that can be caused since the used oils contain numerous additives harmful to human health (metals, sulphur, PAH, etc.). For instance, their typical contents of sulphur are within the range 0.1 – 2 wt %, depending on the nature and treatments of the raw petroleum cut, what implies a clear environmental risk in terms of smoke, acid rain, etc.

As in the case of polyolefins, the main components of lubricating oils are carbon-hydrogen based molecules, hence it seems feasible and interesting to explore the joint degradation and processing of both types of wastes. In this respect, catalytic cracking of polyolefins over solid acids (zeolites, silica-alumina, MCM-41, clays, etc.) to yield different hydrocarbon fractions has been proposed by several authors as a promising alternative for feedstock recycling [4-12]. In previous works of our research group [12-14], Al-MCM-41 and nanocrystalline HZSM-5 (crystal size below 100 nm) have shown high performances for the catalytic conversion of polyolefinic plastics. These catalysts have demonstrated to be especially suitable for plastic cracking due to their uniform mesoporous structure (Al-MCM-41) and high proportion of external acid sites (nanocrystalline HZSM-5), that allow surpassing the diffusional and steric constraints resulting from the bulky nature of plastic macromolecules. In addition, the different acid strength and pore structure of both types of catalysts allows tailoring the selectivity towards different products. Thus, Al-MCM-41 led mainly towards liquid C₅ – C₁₂ hydrocarbons, whereas nanocrystalline HZSM-5 gave rise to gaseous compounds.

A variety of reactor types has been tested for thermal and catalytic cracking of polyolefins (batch, fixed bed, fluidized beds, etc.) [15-20]. Continuous reactors are preferred at an industrial scale but the high viscosity and low thermal conductivity of the molten plastics make difficult their direct feed with the conventional designs. The possibility of solving this problem by diluting the plastic in oils has been earlier investigated [17]. However, the maximum recommended proportion of plastic in the mixture for a good rheological behaviour was found at best 5 – 10 %, that would make necessary the supply of large amounts of used oils for the processing of plastic wastes at a commercial scale. Recently, we have reported the use of a laboratory screw kiln reactor for the

continuous cracking of polyolefins [19]. With this system, overall outputs up to 100 g/h were obtained in the thermal and catalytic cracking of pure LDPE.

In this work, we have studied the performance of a screw kiln reactor for the thermal and catalytic coprocessing of LDPE-lubricating oil having plastic contents higher than 40 wt %, in order to increase the feasibility of industrial application of these type of processes. As catalysts, Al-containing mesoporous MCM-41 materials and a nanocrystalline HZSM-5 zeolite have been selected, taking into account their excellent catalytic properties for the conversion of polyolefins observed in earlier works [14, 20].

2. Experimental section

2.1. Catalysts preparation

Three samples of mesoporous Al-MCM-41 with Si/Al atomic ratios within the range 19 – 75 have been prepared following a room temperature sol-gel approach earlier reported [21]. Likewise a nanocrystalline HZSM-5 zeolite (n-HZSM-5), having a nanometer crystal size, has been synthesized with Si/Al = 60 according to a procedure published elsewhere [22]. The active form of the catalysts was obtained by calcination of the as-synthesized samples in air at 550°C for 12 h.

2.2. Catalysts characterization

Nitrogen adsorption-desorption isotherms were performed at 77 K in a Micromeritics ASAP 2010 apparatus. The samples were previously outgassed at 200 °C under vacuum for 5 h. Surface areas of the catalysts were calculated according to the BET method. Pore size distributions in the mesopore range were obtained by application of the BJH procedure to the adsorption branch of the isotherm, assuming cylindrical pore shape and using the Jura–Harkins equation to obtain the thickness of the adsorbed layer. External surface area of the nanocrystalline HZSM-5 was calculated by application of the t-plot method to a selected zone of the isotherm.

X-ray diffraction (XRD) patterns were collected in a Philips X'PERT MPD diffractometer using Cu K α radiation. The Si/Al atomic ratios of the samples were determined by X-ray fluorescence (XRF) performed in a Philips PW 1404 spectrometer. ^{27}Al MAS NMR spectra of the calcined catalysts were carried out in a Bruker MSL-400 spectrometer equipped with a Fourier transform unit and using $\text{Al}(\text{H}_2\text{O})_6^{+3}$ as external standard reference. The spectra were recorded at 104.26 MHz with a spinning frequency of 4000 cps under room temperature.

Transmission electron micrographs (TEM) were taken in a JEOL JEM 2000 FX microscope operating under an accelerating voltage of 200 kV. Prior to the observation, the samples were dispersed in acetone, stirred in an ultrasonic bath and finally deposited over a carbon – coated copper grid.

2.3. Raw materials

Both low-density polyethylene (LDPE) and lubricating oil base were provided by REPSOL-YPF. The polymer presents an average molecular weight (M_w) of 416,000 and a mean particle size of roughly 2 μ m. The distribution by carbon atom number of the lubricating oil base (determined by GC) as well as both its sulphur and nitrogen content (calculated by XRF and quimioluminescence, respectively) are shown in Table 1. In order to obtain an homogeneous raw mixture for the cracking experiments, the LDPE particles were first cryogenically ground down to particle sizes below 0.25 μ m by means of a Retsch ZSM-100 ultracentrifuge mill, yielding a fine powder that was subsequently mixed by stirring with the selected amount of lubricating oil base.

2.4. Reaction system

Thermal and catalytic cracking experiments were carried out in a continuous screw kiln reactor, shown in Figure 1, and earlier described in the literature [19]. The reaction system consists of a hermetically heated hopper wherein the LDPE – lubricating oil base mixture is loaded either alone (thermal cracking experiments) or with the suitable amount of catalyst (catalytic cracking experiments). Then, the hopper is heated at 300°C under a nitrogen flow to ensure an inert atmosphere. The reacting mixture is fed by the screw into the reactor which is divided into two sequentially placed reaction zones heated at temperatures T_1 and T_2 , respectively. The screw speed rate can be varied within the range 0.7 – 11.0 rpm which allows both modifying the residence time and controlling the product output. Once the system has reached steady state, the reaction is left running for 1 h, the products being separated at the outlet by an ice trap into gases and condensed liquids and/or waxes. 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 of the liquid fraction ($C_5 - C_{12}$) were carried out in a Varian 3800 GC equipped with a 100 m length x 0.25 mm i. d. chrompack capillary column. The conversion was defined as the weight of collected products with $C_n \leq C_{40}$ in regards to the mass of LDPE + oil mixture fed to the reactor. In all experiments, mass balances were closed with an error within the range $\pm 5\%$.

3. Results and discussion

3.1. Thermal cracking of LDPE – lubricating oil base mixtures

3.1.1. Effect of the raw mixture composition

Thermal cracking experiments were carried out using different LDPE – lubricating oil base mixtures prepared with relative proportions within the range 70/30 – 40/60 w/w %. The reaction temperatures of the two heating zones ($T_1/T_2 = 450/500^\circ\text{C}$) and the screw speed (8.5 rpm) were chosen according to previous experiments with pure LDPE, since these values led to almost total conversion towards the desired products (hydrocarbons with carbon atom number below 40) [19]. The results obtained in the thermal cracking of the plastic-oil mixtures are summarized in Table 2. As it occurred in the aforementioned experiments with pure LDPE, conversions around 90 % and higher were always attained irrespective of the lubricating oil proportion in the mixture. In addition, it can be appreciated that a significant enhancement in the product output takes place with increasing proportions of the lubricating oil base in the mixture. Thus, the overall product output increased from 64.0 up to 244.4 g/h. The data shown in Table 2 indicate that, not only the overall product output, but also the LDPE feed rate, calculated taken into account the plastic proportion in the raw mixture, is

increased with the amount of lubricating oil base. These results can be interpreted as a consequence of the progressively lower viscosity of the mixture with increasing contents of lubricating oil base, which gives rise to a much faster feeding from the hopper to the screw, confirming that the addition of oils to plastics is a convenient method to favor the flow and continuous feeding of polyolefins.

Selectivity by groups, shown in Table 2, point out that the major products of the thermal cracking were the $C_{13} - C_{22}$ and $C_{23} - C_{40}$ fractions, being always obtained in a 35 – 40 wt% proportion, irrespective of the mixture composition. Likewise, the selectivity towards $C_5 - C_{12}$ remained almost constant for the different raw mixtures (~ 22 %). However, the yield of gaseous compounds tends to decrease with increasing contents of the lubricant oil base in the mixture while the opposite is observed for the $C_{23} - C_{40}$ fraction. Figure 2 shows the selectivity by carbon atom number corresponding to the experiments with the two limiting compositions (70/30 and 40/60 w/w %, respectively), together with that obtained in the pure LDPE thermal cracking under the same conditions. The selectivity patterns for the pure LDPE and the 70/30 LDPE - oil mixture cracking show a broad product distribution within the range $C_1 - C_{40}$, being fairly similar above C_{14} hydrocarbons. However, the thermal cracking of the 40/60 LDPE - oil mixture presents higher amounts of hydrocarbons in the range $C_{30} - C_{40}$ coming from slightly cracked lubricant oil (see Table 1). These results indicate that a lower extension of the cracking reactions takes place with increasing lube oil amounts, which may be related to the lower residence time of the raw mixture within the screw reactor as a consequence of its faster feeding, although it can be also explained assuming that the lubricating oil base is more stable against thermal cracking than the LDPE polymer. On the other hand, n-paraffins and 1-olefins account for more than 70 % of the selectivity in the $C_5 - C_{12}$ fraction, their relative proportion being within the range 0.8 – 1.2. This is in agreement with the expected

radical cracking mechanism typical of the thermal degradation, which favours the formation in close amounts of a broad spectrum of both 1-olefins and n-paraffins and shows that both the polyolefin and the lubricating oil base are extensively degraded.

3.1.2. Influence of the screw speed

The effect of the screw speed upon the thermal cracking at 450/500 °C was studied using a standard mixture made up of 60 % LDPE and 40 % lubricant oil base, the results obtained being shown in Figure 3. Almost complete conversion (around or higher than 90 %) was attained for all the studied screw speeds (0.7 – 11 rpm) while the overall product output increased from 34 up to 125 g/h. Selectivity by groups, also depicted in Figure 3, shows that the main product was the C₁₃ – C₂₂ fraction (roughly 35 – 40 %), whose proportion abates slightly with increasing screw rates, whereas the amount of gases (C₁ – C₄) can be regarded as negligible (< 5 %). A certain trend towards heavier products can be observed with increasing screw speeds, since the share of the C₂₃ – C₄₀ fraction enhances continuously from 25 % (0.7 rpm) up to 35 – 40 % (8.5 - 11 rpm), which can be assigned to the lower residence times of the mixture with increasing screw rates. Figure 4 shows the selectivity by carbon atom number for the two limiting screw speeds (0.7 and 11 rpm). As expected, a broad product distribution was obtained for both cases. The higher proportion of products within the C₂₈ – C₄₀ range for the experiment carried out at 11 rpm confirms again a somewhat lower degradation of the mixture due to the shorter residence time corresponding to this experiment.

3.2. Catalytic cracking of the LDPE – lubricant oil mixture

3.2.1. Physicochemical properties of the catalysts

The main physicochemical properties of the catalysts used for promoting the conversion of the LDPE - lubricating oil base mixture are shown in Table 3. The three Al-MCM-41 samples present Si/Al atomic ratios varying in the range 19 – 75, hence they possess different concentration of acid sites, which in turn should be responsible for the cracking activity. Likewise, N₂ adsorption isotherms at 77 K confirm that these materials show high BET surface areas (> 1000 m²/g) and uniform mesopores with sizes in the range 2.2 – 2.5 nm, values which are typical of MCM-41 materials.

On the other hand, the second selected catalyst type is a nanocrystalline HZSM-5 zeolite, which presents a microporous structure (pore size ~ 0.55 nm) and a nanometer crystal size (60 nm). As a consequence, this sample exhibits a high proportion of external surface area (81 m²/g), and therefore of external acid sites, which play an essential role in the degradation and conversion of the bulky molecules present in both plastics and lubricating oils.

The state of the aluminum in the four catalysts has been checked by ²⁷Al MAS NMR applied to the calcined samples. The obtained spectra (not shown) indicate that in all cases the aluminum is incorporated into tetrahedral positions, as indicated by a major peak present at 54 ppm, while the proportion of extraframework aluminum (peak at 0 ppm) is always below 15 % of the total area.

3.2.2 Catalytic cracking experiments

Catalytic cracking experiments were performed in the screw kiln reactor using a LDPE-lubricant oil mixture with a composition of 70/30 (w/w %), which approximately resembles the relative proportion in which both residues are actually generated by the market. This makeup leads to a viscous mixture as the lubricating oil base is completely absorbed by the plastic forming a sort of unique rheological phase. The first experiments were carried out under similar conditions to those previously applied for pure LDPE ($T_1/T_2 = 400/450^\circ\text{C}$, 8.5 rpm) with a ratio (mass of plastic + lubricant oil) / (mass of catalyst) = 50. Initially, two catalysts were tested, Al-MCM-41(1) and Al-MCM-41(3). The output was quite similar for both cases (~ 84 g/h) but the corresponding conversions into gaseous and liquid fractions were fairly different: 29.6 and 1.3 %, respectively. By comparison, the output obtained in pure LDPE cracking over the same catalysts and under the same conditions was roughly the half (40 g/h), which agrees well with the higher viscosity of the pure molten plastic. However, the conversions obtained with pure LDPE were far superior: 40.7 (Al-MCM-41(1)) and 80.4 % (Al-MCM-41(3)). Especially remarkable is the drop in conversion observed for the Al-MCM-41(3) sample, which present the lowest concentration of acid sites. The presence of lubricant oil leads practically to a complete loss of its activity, since the reported value (1.3 %) corresponds to the one obtained in the blank test reaction, without catalyst, under these experimental conditions. The Al-MCM-41(1) catalyst is not so sensitive to the presence of lubricant oil in the mixture, although its activity is also decreased. However, its selectivity pattern is similar to that obtained in the catalytic cracking of pure LDPE, leading towards 70 % of $\text{C}_5 - \text{C}_{12}$ hydrocarbons.

In a second series of catalytic cracking experiments, a combination of higher reaction temperatures ($T_1/T_2 = 450/500^\circ\text{C}$) were tested in the cracking of the mixture over both types of catalysts (Al-MCM-41 and n-HZSM-5). Under these conditions, the outputs obtained over all the

catalysts are within the range 90 – 100 g/h. The results of conversion and selectivity by groups are shown in Figure 5. As inferred from this figure, high conversions were obtained over the four catalysts investigated. The lowest activity was again observed for the Al-MCM-41(3) sample, although in this case with a high conversion, which shows that the temperature increase has been very effective in promoting the activity of this catalyst.

Selectivity by groups, bears out that a carbocationic catalytic cracking and not a thermal cracking of the LDPE – lubricant oil mixture is responsible for the product distribution obtained at $T_1/T_2 = 450/500^\circ\text{C}$. Thus, for all the Al-MCM-41 catalysts, the $C_5 - C_{12}$ fraction was the major product (> 65 %) whereas the share of the other fractions was always below 15 %. In addition, a slight trend in this series towards heavier products with decreasing aluminum content in the Al-MCM-41 materials can be appreciated.

A completely different behaviour is observed in the mixture conversion over the n-HZSM-5 zeolite. In this case, the catalytic cracking takes place chiefly by an end-chain cracking pathway due to its high external surface area, acid strength and microporous structure, leading to a low formation of products heavier than C_{12} . Consequently, the main products obtained over the zeolite are $C_1 - C_4$ (43 %) and $C_5 - C_{12}$ (55 %) fractions, the presence of heavier products being practically negligible.

Figure 6 compares the selectivities by carbon atom number obtained over both Al-MCM-41(2) and n-HZSM-5 catalysts, as well as that corresponding to the blank thermal cracking reaction. The selectivity patterns exhibited by both catalysts are the expected ones for a carbocationic catalytic cracking pathway according to their respective acid strength and pore structure and clearly different

from that corresponding to the thermal cracking. Likewise, these results show clearly that both LDPE and lubricating oil base are effectively converted and cracked over the Al-MCM-41 and n-HZSM-5 catalysts. Catalytic cracking over n-HZSM-5 zeolite leads to a narrow product distribution with a major maximum placed at the C₄ fraction (25 %) and a second one at C₇ – C₈ (10 %). Especially interesting is the high selectivity towards the C₃ – C₅ fraction (63%) exhibited by the n-HZSM-5 zeolite. The Al-MCM-41(2) catalyst presents a wider product distribution with two close maxima placed at C₅ and C₇ (~ 14 %), respectively, the proportion of hydrocarbons heavier than C₃₀ being negligible. In contrast, thermal cracking gives rise to the broadest product distribution, having also the highest amounts of heavy hydrocarbons. These results confirm that catalytic cracking present the advantage of leading to products with higher commercial value.

The above commented experiments indicate that the presence of the lubricating oil in the raw mixture causes a negative effect at T₁/T₂ = 400/450°C on the catalytic activity of the mesoporous Al-MCM-41 materials. The lubricant oil base is essentially made up of paraffins and naphthenes with a reduced aromatic content and it possesses a high amount of organic bound sulphur (~ 4000 ppm) in addition to a significant content of nitrogen (85 ppm), which are known to poison acid catalysts by strong chemisorption on their acid sites [23]. Therefore, the reduced activity caused by the presence of the lubricating oil base in the raw mixture can be assigned to the coupling of two effects: lower reactivity for cracking of the hydrocarbons in the lube oil compared to the LDPE chains and partial poisoning of the catalyst acid sites mainly by sulphur and nitrogen containing compounds. However, both effects can be overcome by increasing the reaction temperature since all the studied catalysts, even those with lower aluminum content, degrade almost completely the LDPE/ lubricant oil mixture at T₁/T₂ = 450/500°C.

PIONA analyses of the C₅ – C₁₂ fraction, shown in Figure 7, point out that olefins are the main products obtained over the Al-MCM-41 samples (> 40 %), whereas isoparaffins were also obtained in significant proportions (13 – 18 %). The remaining components (n-paraffins, aromatics and naphthenes) were present in much lower amounts, clearly below 10 %. In addition, over these catalysts, the olefinic content tends to enhance continuously with increasing Si/Al atomic ratios while the opposite is observed with the isoparaffins. This is likely due to a progressively higher extent of isomerization reactions with increasing contents of acid sites. In contrast, n-HZSM-5 zeolite shows a quite different PIONA product distribution. Also in this case, olefins are the main products but with a fairly lower selectivity (30 %) than that corresponding to Al-MCM-41 catalysts due to the formation of high amounts of aromatic hydrocarbons (26 %). This high aromatic selectivity exhibited by n-HZSM-5 has been earlier observed in the cracking of polyolefins, being assigned to the preferential end-chain cracking reactions which take place over the strong acid sites located on the external surface or the pore mouth of this zeolite [20]. The primary products of this cracking pathway are C₃ – C₅ olefins, which subsequently undergo oligomerization, cyclization and aromatization reactions. The occurrence of these secondary reactions is favored in the screw kiln reactor due to the continuous contact among the different fractions as they move along the reactor with similar residence times. In contrast with semi-batch reactors having continuous nitrogen flow that removes the lighter products, typically used for the conversion of polyolefins, gaseous olefins are not removed in the screw reactor, which promotes their further conversion by secondary reactions.

Conclusions

Thermal and catalytic cracking of LDPE - lubricating oil base mixtures with plastics contents higher than 40 wt % has proved to be feasible using a continuous screw kiln reactor. The presence of the lubricant oil base contributes to an enhancement in the mixture fluidity, giving rise to increasingly higher product outputs (up to 244 g/h). The usage of this sort of reactors would enable the coprocessing of LDPE-oil waste mixtures with compositions within the range they are actually generated.

Thermal cracking of LDPE – lubricant oil base mixtures, with compositions in the range 70/30 to 40/60 w/w %, at 450/500°C leads to their almost complete degradation (conversions around 90 %), the products being chiefly C₁₃ – C₂₂ and C₂₃ – C₄₀ fractions. Their main components are n-paraffins and 1-olefins, as expected from a radical thermal cracking mechanism. Increasing the screw speed gives rise to higher outputs (125 g/h at best for 11 rpm) with almost complete conversion in all cases, as well as to slightly higher selectivities towards heavier compounds (C₂₃ – C₄₀).

Catalytic cracking of a 70/30 w/w % LDPE – lubricant oil base mixture has been studied over two types of acid catalysts: mesoporous Al-MCM-41 and nanocrystalline HZSM-5 zeolite (n-HZSM-5). When the reaction is carried out at low temperatures ($T_1/T_2 = 400/450^\circ\text{C}$) over Al-MCM-41 catalysts, a significant decrease in their activity is observed with regards to the cracking of pure LDPE, which has been ascribed to the lower reactivity of the lube oil as well as to the presence of both sulphur and nitrogen containing organic compounds, causing a partial poisoning of the catalyst. However, when the reaction temperature is increased up to 450/500°C, high conversions (> 85 %) were obtained over all the catalysts, probably due to both the higher activity of the acid sites and the weaker chemisorption of both nitrogen and sulphur containing compounds. The selectivity patterns

confirm that both polyolefin and lubricating oil base are effectively converted and cracked by the Al-MCM-41 and n-HZSM-5 catalysts. Thus, selectivities towards the C₅ – C₁₂ fractions higher than 65 % were obtained over all Al-MCM-41 samples whereas roughly 50 % was measured over n-HZSM-5. On the other hand, PIONA analyses point out that olefins were the main products over Al-MCM-41 catalysts (> 40 %) whereas both olefins and aromatics were formed in significant amounts over n-HZSM-5 (25 – 30 %).

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Table 1. Composition of the lubricating oil base.

C_n	(wt%)	C_n	wt (%)	C_n	(wt%)
C ₂₈	2.0	C ₃₃	18.5	C ₃₈	3.6
C ₂₉	4.1	C ₃₄	8.0	C ₃₉	3.0
C ₃₀	0.6	C ₃₅	12.0	C ₄₀	2.5
C ₃₁	13.6	C ₃₆	6.0	C ₄₁	3.0
C ₃₂	9.6	C ₃₇	13.5	S (ppm)	4000
				N (ppm)	85

Table 2. Thermal cracking of the LDPE-lubricating oil base mixtures with different plastics/oil ratios.

LDPE/oil (w/w %)	Conversion (wt %)	Overall Output (g/h)	Plastic feed rate (g/h)	Selectivity (wt %)			
				C ₁ – C ₄	C ₅ – C ₁₂	C ₁₃ – C ₂₂	C ₂₃ – C ₄₀
70/30	96.8	64.0	44.8	6.3	22.6	36.2	34.9
60/40	90.2	114.6	68.7	3.3	22.0	36.6	38.1
50/50	89.1	177.2	88.6	2.4	22.4	36.1	39.1
40/60	96.3	244.4	97.8	0.9	21.9	36.6	40.6

T₁/T₂ = 450 / 500°C, screw speed = 8.5 rpm

Table 3. Physicochemical properties of the catalysts.

Catalyst	Si/Al	S_{BET} (m²/g)	D_p (nm)	Crystal size (nm)
Al-MCM-41(1)	19.0	1170	2.40	-
Al-MCM-41(2)	48.3	1205	2.50	-
Al-MCM-41(3)	74.9	1270	2.20	-
n-HZSM-5	60.0	435 ^(*)	0.55	60

^(*) External surface area = 81 m² g⁻¹

Figure Captions

Figure 1. Scheme of the screw kiln reactor.

Figure 2. Selectivity by carbon atom number obtained in the thermal cracking of different LDPE - lubricant oil base mixtures ($T_1/T_2 = 450/500^\circ\text{C}$, 8.5 rpm).

Figure 3. Conversion, overall output, and selectivity by groups obtained in the thermal cracking of the LDPE - lubricant oil mixture with different screw speeds ($T_1/T_2 = 450/500^\circ\text{C}$, LDPE – lubricant oil base: 60/40 w/w %).

Figure 4. Selectivity by carbon atom number obtained in the thermal cracking of the LDPE - lubricant oil mixture ($T_1/T_2 = 450/500^\circ\text{C}$, LDPE – lubricant oil base: 60/40 w/w %).

Figure 5. Conversion and selectivity by groups obtained in the catalytic cracking of the LDPE - lubricant oil mixture ($T_1/T_2 = 450/500^\circ\text{C}$, 8.5 rpm, LDPE – lubricant oil base: 70/30 w/w %).

Figure 6. Selectivity by carbon atom number obtained in the thermal and catalytic cracking of the LDPE - lubricant oil mixture ($T_1/T_2 = 450/500^\circ\text{C}$, 8.5 rpm, LDPE – lubricant oil base: 70/30 w/w %).

Figure 7. PIONA analyses of the $C_5 - C_{12}$ fraction obtained in the catalytic cracking of the LDPE - lubricant oil mixture ($T_1/T_2 = 450/500^\circ\text{C}$, 8.5 rpm, LDPE – lubricant oil base: 70/30 w/w %).