

Fuels from Waste Plastics by Thermal and Catalytic Processes: A Review

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Feedstock recycling of plastic waste by thermal and catalytic processes is a promising route to eliminate this refuse (which is harmful to the environment) by obtaining, at the same time, products that are useful as fuels or chemicals. During the past decade, this option has undergone an important evolution from a promising scientific idea to an alternative that is very close to reality with commercial opportunities. Thus, several commercial processes have been developed worldwide, most of them especially addressed toward the preparation of diesel fuel. The present review highlights the most remarkable achievements of the field, providing a fundamental insight into this fascinating area and highlighting the main milestones that should be achieved in the next future for this alternative to become applied commercially on a large scale.

1. Introduction

Plastic waste constitutes a growing social problem, because of the loss of natural resources, the environmental pollution, and the depletion of landfill space. The management of plastic waste is intended to follow a hierarchical approach, to decrease the environmental impact according to the ensuing order: waste minimization, reuse, recycling, energy recovery, and landfilling. Waste minimization and reuse are options with limited applicability. Hence, recycling and energy recovery are alternatives to be also considered.¹ Energy recovery by incineration, a priori, seems to be a suitable solution that takes advantage of the high energy content of plastics (similar to oil, roughly 2-fold of that of coal) but presently is largely questioned, because of the possible emission of toxic compounds (e.g., dioxins, furans). Recycling accounts for a more suitable environmental solution, because it allows for the retrieval of either plastics (mechanical recycling) or fuels/raw chemicals (feedstock recycling) from waste plastics. The situation for recycling recently has improved, so we are slowly but steadily evolving into a recycling-oriented society. The involvement of government through different laws (e.g., EU Directive 94/62/CE, Japan Containers and Packaging Recycling Law²), the cooperation of civil society, and the increased technological development in the field³ has opened up new ways of plastic waste recycling.

The magnitude of the problem can be roughly estimated by examining several figures.⁴ The total world production of plastic in 2005 was ~230 million tonnes, having overtaken the consumption of steel. In Western Europe, 47.5 million of tonnes were consumed in the same year and the equivalent amount of generated post-consumer waste accounted for 22 million tonnes. The main components of the household plastic waste streams include the following five families of plastics: polyethylene (low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), high-density polyethylene (HDPE)), polypropylene (PP), poly(vinyl chloride) (PVC), polystyrene (PS), and polyethylene-terephthalate (PET), which account entirely for 74% of all plastic wastes. Figure 1 shows the distribution of the different end-of-life treatments for plastic waste in Western

Europe in 2005.⁴ Landfilling is still the main treatment (53%), although its share is dropping at a rate of 2% annually, which highlights the growing success of recycling/energy recovery options. Two types of recycling can be distinguished: mechanical recycling, which recovers the plastic material for similar or lower-quality applications for such plastics, and feedstock recycling, which turns the plastic waste by means of chemical reactions into chemical raw materials or fuels. Presently, feedstock recycling only represents 2% of the total recycling effort, while mechanical recycling is the preferred recycling strategy (16%). In Japan, the share of feedstock recycling is fairly similar to that observed in Europe (2.7%).⁵ The current unfavorable situation of feedstock recycling is mostly based on the high investments costs of recycling treatments.⁶ For instance, the cost of the use of plastic waste in blast furnaces and coke oven furnaces is estimated to be 50–80 yen/(kg plastic), whereas, for liquefaction, the cost is ~80–100 yen/(kg plastic).⁷ However, liquefaction, which converts plastics into hydrocarbon mixtures that are useful as fuels, via thermal and/or catalytic cracking, is gaining growing interest. Thus, the economics turns out to be favorable for liquefaction when treating larger volumes of plastic, as well as considering the growing price of a barrel of oil. Thus, in Poland, several plastics cracking installations

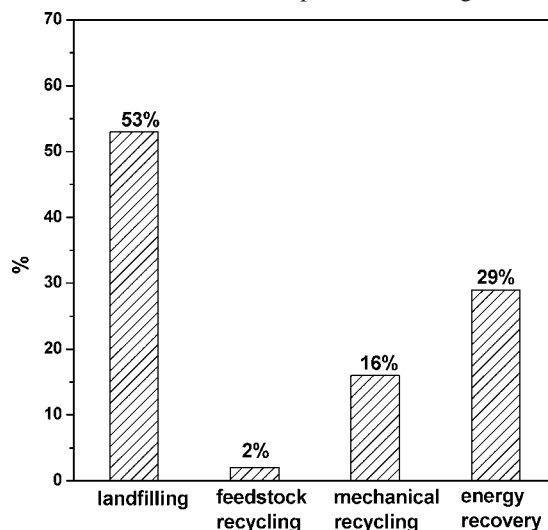


Figure 1. Distribution of waste plastics among the different management options in Western Europe (2005 data; from ref 4).

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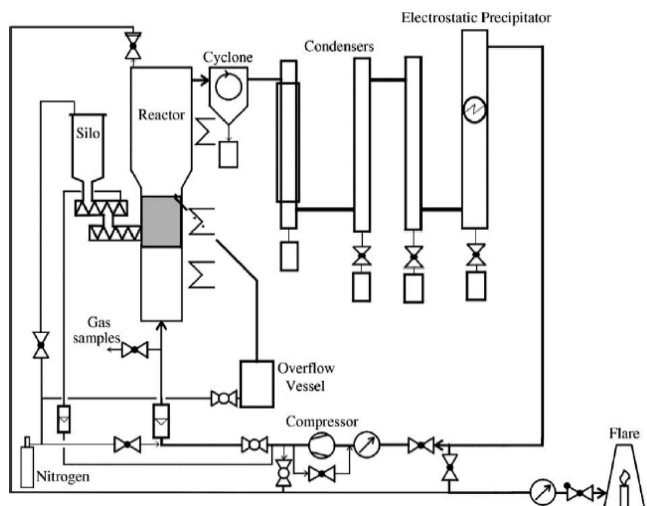


Figure 2. Flow scheme of the Hamburg process. (Reprinted with permission from ref 15. Copyright Elsevier, 2004.)

have been built, the largest of them being located in Zabrze, with an estimated capacity of 145000 t/yr.⁸ Similarly, two plants are currently operated in Japan: the first is located in Niigata (6000 t/yr)⁹ and the second one is located in Sapporo (14800 t/yr).⁵ The technology currently is mature enough to be provided commercially by several companies, H.SMART, Inc.⁸ and Ozmotech,¹⁰ respectively. Consequently, liquefaction technology using thermal/catalytic pyrolysis toward fuels shows a promising future in the forthcoming years, especially considering the different technical solutions that exist to solve the problem of chlorine from residual PVC in the waste. The present review is aimed at providing an insight in the field of plastics recycling via thermal/catalytic pyrolysis toward fuels/chemicals, highlighting the main progress that has been achieved recently.

2. Thermal Processes

This category of processes comprises the thermal treatment of the plastic waste at 400–800 °C under an inert atmosphere. One point to be taken into consideration is the high viscosity and low thermal conductivity of plastics, which lead to problems with heat and mass transfer. Accordingly, the adequate choice of reactor is a subject of utmost importance. Thermal degradation leads usually (e.g., HDPE, LDPE, PP) to a broad hydrocarbon distribution of reaction products, except for certain plastics, wherein the recovery of the monomer is feasible (poly(methyl methacrylate) (PMMA), PS, polytetrafluoroethylene (PTFE)). The most-known thermal treatment is the Hamburg process, which was developed by Kaminsky and co-workers;^{11–15} this flow scheme is shown in Figure 2. The core of the process is comprised of a fluidized-bed reactor, which promotes mass and heat transfer, ensuring a uniform temperature throughout the reactor. This system avoids the appearance of temperature gradients inside the reactor, in contrast to that it occurs, e.g., when rotary kilns are present, which usually promotes a wider product distribution. The process is designed for laboratory scale with an output of 1–2 kg/h. The reactor consists in a 1.5-m-wide stainless steel tube with a height of 6.7 m, which is filled with millimeter-grain-size sand. The reactor is heated with a filament, and the fluidizing gas enters at the bottom, through a steel plate distributor. Two screw conveyors feed the plastics into the reactor, wherein they are quickly converted. The products are caught in separation units that consist of a cyclone, coolers, and an electrostatic precipitator.

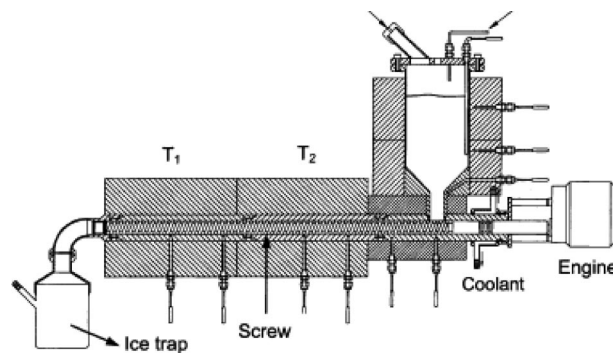


Figure 3. Scheme of the screw kiln reactor used in the thermal and catalytic degradation of LDPE. (Reprinted with permission from ref 17. Copyright Elsevier, 2001.)

Different strategies have been applied with this system:

- (1) The cracking of plastics at 500–650 °C to produce waxes and oils, that constitute potential feedstocks in refineries.
- (2) Pyrolysis of plastics in a steam stream at 650–800 °C to attain mostly light olefins, such ethene, propene, and butadiene.
- (3) Pyrolysis at 600–800 °C, using liquid-free pyrolysis gases as a fluidizing agent and leading mainly to BTX oils.
- (4) Monomer recovery from certain plastics (such as PS, PMMA, and PTFE) by heating at 450–550 °C.

Thus, in the pyrolysis of mixed plastics (polyolefin, polystyrene, and PVC)¹² at 685–740 °C with a residence time of 2–3 s, a composition of 44 wt% of gases and 50 wt% of oil was obtained, with the latter containing 40% of BTX (~10% of benzene). In contrast, the pyrolysis at 510 °C of a plastic mixture of PP, PE, and PS led to 90 wt % of oil/waxes with a low aromatic content (0.1–0.3 wt %),¹³ showing the role of temperature in promoting the aromatic formation.

The use of steam as fluidizing medium allows one to obtain high yields of ethene and propene. Thereby, at temperatures of ~700–750 °C, high yields of olefins were achieved (21–29 wt % ethene, 16–21 wt % propene, and 5.6–6.6 wt % butadiene).¹³ On the other hand, poly(methyl methacrylate) (PMMA) was depolymerized at 450 °C into >98% of the monomer. Similarly, for the case of polystyrene at 520 °C, a 75% of styrene was achieved, as well as 10% of oligomers. However, the presence of fillers (such as alumina trihydrate) in PMMA was observed to decrease the amount of recovered monomer (just 58%).¹⁵

Williams at al.¹⁶ also performed the pyrolysis of low-density polyethylene in fluidized-bed reactors, which led to a mixture of wax, oil, and gas products. An increase of reaction temperature improved the yield of gases, reaching 71% at 700 °C, and their main components were methane (11.7%), ethene (26.8%), and propene (18.6%). Similarly, the share of aromatics in oils was augmented in parallel with the temperature.

Another devices used for the thermal cracking of plastics are screw extruders or screw-kiln reactors such as that depicted in Figure 3,¹⁷ which was developed in our laboratory. It consists of a hopper wherein the raw plastics are melted and fed into the screw under a nitrogen atmosphere. The screw is located into a 52-cm-long stainless steel tube with an internal diameter (id) of 2 cm. Two furnaces are placed along the tube to heat the plastics, creating two different heating areas (T_1/T_2). For $T_1/T_2 = 450\text{ °C}/500\text{ °C}$, the thermal degradation of LDPE leads mostly to gasoline-range hydrocarbons (C_5 – C_{12}) and middle distillates (C_{13} – C_{33}), with selectivities of ~25 and 55 wt %, respectively, with the *n*-paraffin and the corresponding 1-olefin being the main products of each fraction. The screw reactor

herein described has the advantage over conventional batch reactors of a lower production of gases and higher yields of heavy products (C_{34} – C_{55}). This is ascribed to the intimate contact along the extruder among light and heavy products, favoring recombination reactions which lower the yield of highly reactive gaseous olefins. A similar design constitutes the so-called moving bed reactor, developed by Kodera et al.,¹⁸ which consists of a horizontally placed tubular reactor with a screw conveyor, a feed hopper, a pyrogas outlet, and a residue/oil receiver. The internal diameter and length of the tube are 70 and 1200 mm, respectively, which is surrounded by an electric heater. The plastic (PP) was mixed with sand (at a ratio of 0.8 kg plastic to 7.2 kg sand) and heated at 700 °C for 10 min, leading to a composition of 82 wt % gaseous hydrocarbons, with their main components being methane (18.7%), ethylene (19.5%), and propylene (24.2%). In this regard, the obtained gaseous product constitutes a flue gas, having an economical value 2–3 times higher greater than that of fuel oil (Japanese data).

One point that must be taken into account is to ensure the absence of polymers from waste electronic–electric equipment (WEEE), e.g., epoxy and polycarbonate resins, high-impact polystyrene, and ABS, because they contain different flame retardants with halogen functions in their makeup, which are harmful, considering the future application of the cracking products for fuels. Bozi et al.¹⁹ observed, in the thermal treatment at 550 and 700 °C, the decomposition of polycarbonates that contained tetrabromobisphenol A (TBBA) as a flame retardant and the formation of >20 bromine-containing products, among them being numerous brominated phenol derivatives, bromobenzenes, and bromo-4-alkylbenzenes.

An alternative to decrease the plastic viscosity and to increase the mass- and heat-transfer rates involves mixing the plastic with an oil or solvent. In addition, the oil/solvent itself may modify the cracking mechanism, because the solvent may be included in it. Thereby, mixtures of LDPE and vacuum gas oil (VGO) (0–100 wt %) were thermally cracked by Marcilla et al.²⁰ in a fluidized-bed reactor at 350–400 °C. They observed that the C_1 – C_8 yield at 400 °C increased almost linearly, with the percentage of LDPE in the blend varying from 30.0% (0% LDPE) to 67.1% (100% LDPE). In addition, a certain amount of heavy hydrocarbons that remained adhered to the walls of the reactor was not considered in the mass balance (16%–20%) when using high shares of LDPE. For a blend that contained 25 wt % LDPE, the amount of dry gas (C_1 – C_2) was 14.4%, whereas the LPG (C_3 – C_4) content was 11.3%, with their major components being ethene (9.8%) and propene (6.8%), respectively. Serrano et al.²¹ performed a thermal degradation of mixtures of LDPE and lubricating oil (LDPE:oil ratios from 70:30 to 40:60) at $T_1/T_2 = 450$ °C/500 °C in the screw kiln reactor that was previously described.¹⁷ In all cases, ~90% conversions to C_1 – C_{40} hydrocarbons were attained. The major components were the C_{13} – C_{22} and C_{23} – C_{40} fractions in a proportion within a range of 35%–40%, whereas the yield of gas decreased as the base content of lubricating oil increased (from 6.3 to 0.9 for LDPE:oil ratios of 70:30 and 40:60, respectively).

Solvents have also been used in the thermal degradation of HDPE.^{22,23} Serrano et al.²² thermally degraded mixtures of 4 g of HDPE and 40 g of solvent at 400 °C and 20 bar, with the solvent being chosen among compounds with different hydrogen-donating capabilities (9,10-dihydroanthracene, tetralin, decalin, and 1-methyl naphthalene). They observed that poor-hydrogen-donating solvents (decalin, 1-methyl naphthalene) gave the

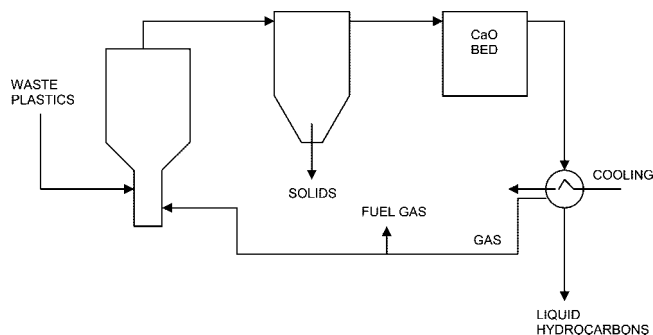


Figure 4. Scheme of the BP thermal cracking pilot plant.

highest C_5 – C_{32} yields, with 1-olefins as the main components. The role played by the solvent is to enhance the content of 1-olefins in the final product through the suppression of the secondary reactions between intermediate radicals and 1-olefins. In this regard, the HDPE conversion increased with the decalin content and the amount of C_5 – C_{32} olefins increased with both time and temperature, reaching a selectivity of 76% after 5 h at 425 °C.²³ On the other hand, Oh et al.²⁴ degraded polystyrene in supercritical acetone, obtaining the kinetic parameters. They found that the activation energies of polystyrene degradation in supercritical acetone were within a range of 73.3–200.7 kJ/mol, which is lower than those of thermal degradation under a nitrogen atmosphere.

Regarding commercial applications of thermal cracking technology, it must be said that a plant based on the Hamburg process with a capacity of 5000 t/yr was built in Germany. Other thermal cracking processes are closely related to the Hamburg process, such as the BP process,²⁵ which is depicted in Figure 4 and has been developed on a pilot-plant scale (50 kg/h) in Grangemouth, U.K. The first stage consists of a size reduction and the elimination of metal refuse from the plastic mixture, which is composed of polyolefins (80%), PS (15%), PET (3%), and PVC (2%). This mixture is fed to a hopper and loaded into a fluidized bed cracking reactor that is operating at 500 °C with an inert gas. The gas flow that results from the reactor is introduced into a cyclone that separates the solid particles. The process incorporates a calcium oxide bed, wherein hydrogen chloride from PVC is neutralized, which leads to products with just ~10 ppm of chlorine. Finally, the gas is cooled and liquid hydrocarbons are condensed. The yield of liquid hydrocarbons is 85%, which can be subsequently added to the refinery streams while the remainder are gases, mostly ethylene and propylene.

3. Catalytic Processes

The use of catalysts allows the plastic degradation pathway to be modified, with regard to pure thermal cracking. Initially, two positive effects are to be expected by the incorporation of a catalyst into the reaction medium: (i) a reduction of the cracking temperature, and (ii) suitable control of the selectivity, which enables the formation of more-valuable products. Herein, the main aspects related to catalytic processes of plastic cracking are revised. These include the catalyst itself, the reactor type, the effect of chlorine from PVC, and the different pilot-plant and commercial-scale processes.

3.1. Catalysts. Catalysts for plastic cracking may be either homogeneous or heterogeneous, although the former are rather more the exception than the rule. Homogeneous systems are mostly based on classic Lewis acids, such as aluminum trichloride and metal tetrachloroaluminates.²⁶ The catalytic degradation of polyethylene²⁶ with $AlCl_3$ at 370 °C mostly

Table 1. Physicochemical Properties of Catalysts Used in the Cracking of Low-Density Polyethylene (LDPE), High-Density Polyethylene (HDPE), and Polypropylene (PP)^a

catalyst	Si/Al	surface area, S_{BET} (m^2/g)	pore volume, V_p (cm^3/g) ^b	pore size, D_p (nm)	acidity (mmol/g) ^c	T_{max} ($^{\circ}\text{C}$)	NH_3/Al ratio
Al-MCM-41	42.7	1327	1.51	2.9	0.30	314	0.79
$\text{SiO}_2\text{-Al}_2\text{O}_3$	35.6	261	0.97	10.0	0.24	302	0.53
HZSM-5	31.0	362	0.18	0.55	0.52	470	1.00

^a Data taken from ref 62. ^b Total pore volume measured at $p/p_0 = 0.995$. ^c Determined by NH_3 TPD measurements.

resulted in the formation of gaseous hydrocarbons (88%), whose main components were isobutane (42%) and isobutene (22%), with negligible amounts of hydrocarbons heavier than C_5 . Ionic liquids such as 1-ethyl-3-methylimidazolium chloride have also been used as solvents for the catalytic cracking of polyethylene with AlCl_3 .²⁷ Low working temperatures (90–250 $^{\circ}\text{C}$) and long reaction times (1–6 days) were reported, which led to the formation of light alkenes ($\text{C}_3\text{--C}_5$), with branched and cyclic alkanes as the major components. However, homogeneous systems pose the problem of the difficult recovery and separation of the catalysts from the products. This is not the case for heterogeneous catalysts.

Accordingly, a great variety of heterogeneous catalysts have been used for the catalytic cracking of plastics: (a) silica–alumina,^{28–32} (b) conventional zeolites (HZSM-5, HBeta, HY, etc.),^{28,29,32–52} (c) fresh and spent FCC catalysts,^{53–59} (d) meso-structured catalysts (MCM-41, FSM-16, Al-SBA-15, AlUTD-1),^{60–70} (e) nanocrystalline and hierarchical zeolites,^{71–73} (f) superacid solids ($\text{ZrO}_2/\text{SO}_4^{2-}$),⁷⁴ (g) gallosilicates,⁷⁵ (h) aluminum pillared clays,⁷⁶ (i) metal-based catalysts,⁷⁷ and (j) basic oxides (BaO , K_2O).^{78,79}

Zeolites are, by far, the most-used catalysts. They are microporous aluminosilicates that are formed by the linkage of SiO_4 and AlO_4 tetrahedra. Zeolites show a monodimensional, bidimensional, or tridimensional pore channel system with pore sizes in the range of 0.4–1.0 nm, which turns them into molecular sieves (shape selectivity). On the other hand, the presence of aluminum provides the zeolites with acid properties (Brönsted and Lewis) that vary from one zeolite to another, according to their topology. The zeolite structures HY, HZSM-5, and HBeta are the catalysts that are used industrially for the cracking of petroleum fractions.

Plastics pose certain specific problems for their catalytic cracking, because of both their bulky nature and high viscosity, which create mass-transfer constraints. Consequently, mesoporous catalysts with high accessibility of the plastic molecules and small-crystal-size catalysts (high external surface area) are expected to lead to enhanced catalytic activities in the cracking of plastic. This approach was proved by Aguado et al.⁶² in the catalytic cracking of three pure polyolefins (LDPE, HDPE, and PP) over mesoporous Al-MCM-41, $\text{SiO}_2\text{-Al}_2\text{O}_3$, and HZSM-5 catalysts in a batch reactor. The physicochemical properties of these catalysts are summarized in Table 1. Al-MCM-41, which is a uniformly mesoporous aluminosilicate with pore sizes of ~ 2.9 nm, showed a lower conversion than HZSM-5 zeolite in the cracking of both polyethylenes, because of its inferior acidity. In contrast, in the cracking of PP, 99.2% conversion was achieved over Al-MCM-41, while only 11.3% was obtained over HZSM-5. This phenomenon was ascribed to the steric hindrances shown by the bulky PP, which is unable to enter into the HZSM-5 zeolite micropores. Only the acid sites located over the zeolite external surface are accessible to the PP molecules, and there is a minimum number of these, because of the micrometer-scale particle size (7 μm) in this zeolite sample. Another point of interest comes from the distribution of the obtained products over different catalysts (that is, the

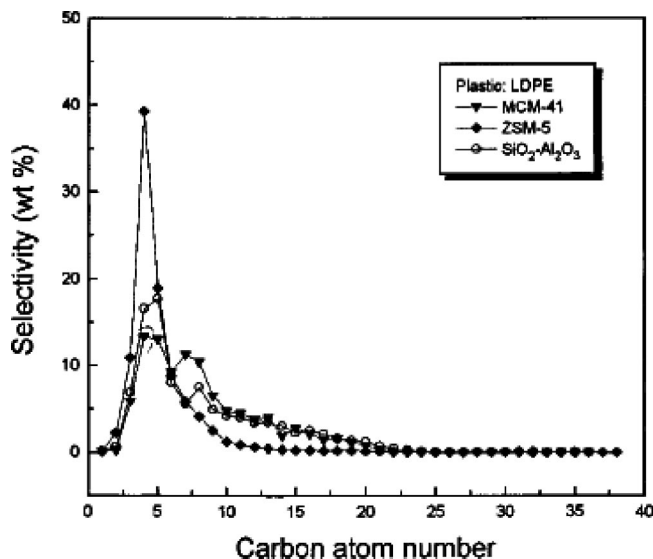


Figure 5. Carbon atom number distribution in the products of the LDPE catalytic cracking over Al-MCM-41, $\text{SiO}_2\text{-Al}_2\text{O}_3$, and HZSM-5 catalysts (400 $^{\circ}\text{C}$, 0.5 h, plastic:catalyst = 18 (w/w)). (Reprinted with permission from ref 62. Copyright American Chemical Society, 1997.)

selectivity). For the case of LDPE, the strong acid sites of HZSM-5 zeolite leads mainly to $\text{C}_3\text{--C}_5$ olefins, which yield a composition of 52.6% gaseous $\text{C}_1\text{--C}_4$ hydrocarbons, 44.6% gasoline-range hydrocarbons ($\text{C}_5\text{--C}_{12}$), and a negligible amount (2.8%) of middle distillates ($\text{C}_{13}\text{--C}_{40}$). In contrast, Al-MCM-41 and $\text{SiO}_2\text{-Al}_2\text{O}_3$, because of their medium acid strength, yielded just 20%–25% gases, 54%–66% gasoline-range compounds, and 16%–20% middle distillates. Figure 5 shows the carbon atom number distribution of the obtained products with a clear maximum at the C_4 fraction, especially for HZSM-5, and a second one at $\text{C}_7\text{--C}_8$ for Al-MCM-41 and $\text{SiO}_2\text{-Al}_2\text{O}_3$.

The presence of mesopores in the catalyst is intended to play a positive role in plastic cracking. In this regard, Sakata et al.⁶⁸ claimed that KFS-16, which is a pure silica mesoporous material without acid sites, was even capable of cracking polyethylene as fast as silica–alumina, yielding higher amounts of liquids. This finding was ascribed to the mesopores acting as a flask that stores the radical species for a long time, so long-lived radicals may accelerate plastic degradation. Similarly, Seddegi et al.⁶⁷ indicated that all-silica MCM-41-catalyzed HDPE cracking through a carbenium mechanism was mediated by the acidity of the surface silanol groups.

Nanocrystalline zeolites have also shown remarkable properties for the cracking of plastics, because of their high share of external acid sites that are fully accessible to the bulky polymer molecules. Serrano et al.⁷¹ tested a nanocrystalline HZSM-5 zeolite (crystal size of <100 nm, external surface area = 78 m^2/g , Si:Al ratio = 30) in the catalytic cracking of HDPE, LDPE, and PP at temperatures within 340–380 $^{\circ}\text{C}$, using a plastic:catalyst mass ratio of 100. The reference micrometer-scale HZSM-5 catalyst (crystal size = 1.5 μm , Si:Al ratio = 31) yielded 43.8% conversion in the HDPE cracking at 360 $^{\circ}\text{C}$

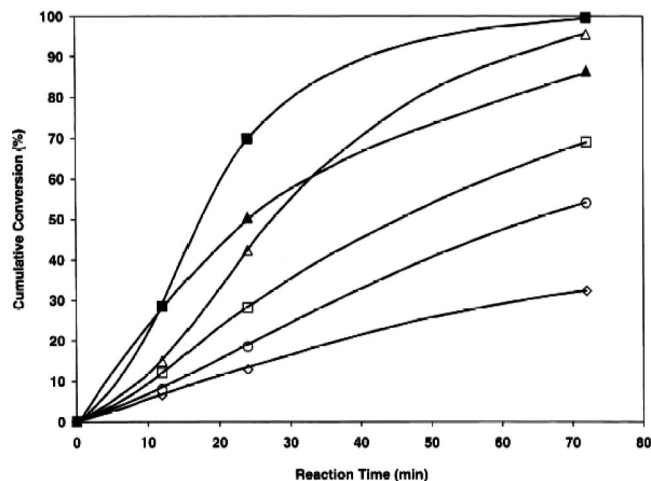


Figure 6. Catalytic cracking of PP at 380 °C with spent FCC catalyst using various plastic:catalyst ratios (w/w): (\diamond) 35:1, (\circ) 35:1.5, (\square) 35:1.75, and (\triangle) 35:2. Silica-alumina and USY results (denoted by solid squares (\blacksquare) and triangles (\blacktriangle), respectively) are shown for comparison purposes (plastic: catalyst = 35:1.5 (w/w)). (Reprinted with permission from ref 54. Copyright Elsevier, 2000.)

for 3 h, while the value corresponding to nanocrystalline HZSM-5 was ~ 2 -fold (92.8%). Note that this catalyst was capable of cracking the plastics at temperatures as low as 340 °C. On the other hand, nanocrystalline HZSM-5 exhibited a high resistance to deactivation. Other materials of catalytic interest include hierarchical zeolites, which have at least two levels of ordered porosity (usually mesopores, in addition to the zeolite micropores). These hierarchical mesoporous-microporous materials present improved accessibility and remarkable mass-transfer properties, which is especially interesting for the processing of plastics molecules, because of their bulky nature. In this way, García et al.⁷² used a hybrid ZSM-5/MCM-41 material for the catalytic degradation of HDPE at 380 °C, using a plastic:catalyst mass ratio of 100 in a batch reactor. The conversion of HDPE over the hybrid ZSM-5/MCM-41 was much higher (68%) than those over Al-MCM-41 (0%) and micrometer-scale HZSM-5 (5%). Also, within this alternative of hybrid catalysts, Serrano et al.⁷³ used a hierarchical zeolite that was obtained from silanized seeds of ZSM-5 zeolite in the cracking of PP at 360 °C with a plastic/catalyst mass ratio of 50 (w/w), obtaining total conversion (100%) of this plastic, while nanocrystalline HZSM-5 zeolite led only to 27.3% conversion.

Another interesting approach to the feedstock recycling of plastics consisted of performing the cracking of the polyolefins, using a spent FCC catalyst. This was tested by Cardona et al.⁵⁴ in the catalytic cracking of PP in a semibatch stirred reactor at 380 °C. The cost of the catalyst is practically zero, because it is initially a residue, so this constitutes an added advantage. Figure 6 shows the performance of different amounts of the spent FCC catalyst in the cracking of PP at 380 °C, compared with silica-alumina and USY. Although the spent FCC catalyst is less active than silica-alumina and USY, this inconvenience can be override by working with higher catalyst:polymer ratios. According to the authors, working with a polymer:catalyst ratio of ~ 10 :1 yields 100% conversion after 1 h of contact time. In this line, Lin et al.⁸⁰ used a spent fluidized catalytic cracking (FCC) catalyst in the conversion of a commingled polymer waste ($\sim 38\%$ HDPE, $\sim 24\%$ LDPE, $\sim 30\%$ PP, $\sim 7\%$ PS, and $\sim 1\%$ PVC) in a fluidized bed reactor at 340–460 °C. When the temperature was increased, the gas and coke yields became enhanced and the liquid yields decreased, which produced 56 wt % olefins in the C₃–C₇ range at 400 °C. These authors also

studied the effect of the flow rate of the fluidizing gas and the polymer:catalyst mass ratio. The enhanced formation of secondary products (benzene, toluene, and xylene (BTX)) was observed at low flow rates of the fluidizing gas, whereas upon increasing the polymer:catalyst mass ratio, lower C₅–C₉ gasoline yields and higher liquid product yields were appreciated.

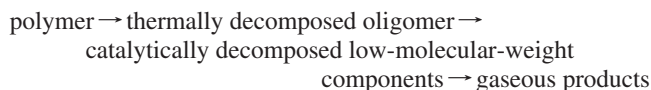
A fundamental aspect to be considered for industrial application of a catalyst is its deactivation performance. Uemichi et al.⁸¹ studied the deactivation of HZSM-5, HY, and HMordenite zeolites and silica-alumina in the degradation of polyethylene in a fixed-bed reactor at 375–526 °C ($W/F = 7$ –23 g catalyst min/(g polyethylene)). HZSM-5 exhibited extremely low coke formation and slight deactivation, because of its three-dimensional network of micropores. Silica-alumina, despite accumulating a considerable amount of coke, did not show severe deactivation, likely because of the presence of large pores. In contrast, fast deactivation occurred over both HY and HMordenite. For HY zeolite, the occurrence of a three-dimensional network with large cavities (supercages) allows the deposition of coke, because of the conversion of aromatics to polyaromatics that fill the pores. In the case of HMordenite, the unidimensional channels of the zeolite underwent pore blocking by coke. On the other hand, Marcilla et al.⁸² modeled the deactivation behavior of HZSM-5 in the catalytic cracking of LDPE, taking into account the effect of coke formation, and the acid and surface properties of the zeolite, on the decay in activity. Marcilla et al.⁴⁷ also studied the influence of the temperature in the nature of the coke obtained in the cracking of LDPE over USY and HZSM-5 zeolites, and they observed an enhancement in the polyaromatic nature of the coke when the temperature was increased, as well as a different composition of the coke that was produced over both zeolites.

Other heteroatoms (different from aluminum) can be incorporated into the zeolite framework, providing the zeolite with specific acid properties. In this regard, Uemichi et al.⁷⁵ describes a H-gallosilicate catalyst that degrades polyethylene at 425 °C in a flow reactor yielding 63.6% of liquids with a remarkable share of BTX aromatics (35.7%), that could be applied as raw chemicals.

Aluminum pillared clays⁷⁶ have also been investigated in the catalytic pyrolysis of polyethylene in a semibatch reactor. They showed high selectivity toward liquid hydrocarbons with low coking levels, because of their mild acidity. In addition, the aluminum pillared clays may be regenerated, holding similar conversions and selectivities. On the other hand, metals (platinum, iron, molybdenum, zinc, cobalt, nickel, and copper) supported over activated carbon⁷⁷ increased the activity for the production of aromatics in the catalytic degradation of polyethylene, in comparison with the metal-free catalyst. Solid superacids⁷⁴ ($\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$, $\text{Al}_2\text{O}_3/\text{SO}_4^{2-}$, $\text{ZrO}_2/\text{SO}_4^{2-}$) were also tested in the degradation of mixtures of commingled waste plastics and coal in the presence of hydrogen. However, these catalysts showed lower cracking activities than conventional silica-alumina and HZSM-5 zeolites. On the other hand, basic oxides (BaO , K_2O)^{78,79} were successfully used in the degradation of polystyrene, which led to high selectivity to the monomer styrene.

3.2. Influence of the Type of Reactor and Operation Conditions. As previously mentioned, the type of reactor plays a key role, because of the low thermal conductivity and high viscosity of plastics, which may lead to the appearance of mass- and heat-transfer constraints. This factor, along with the operation conditions, influences the product distribution.

The first and most straightforward alternative consists of feeding the plastic directly into a fixed-bed reactor such as that described by Ishihara et al.³⁰ The plastic sample was melted at 230 °C, and it was fed directly into the top of the reactor with nitrogen as the carrier gas and silica–alumina as the catalyst. An increase in temperature from 390 °C to 475 °C led to a parallel augmentation of gaseous hydrocarbons, from 30.9% to 74.0%. On the other hand, the decrease in residence time created a lower yield of gases. The authors proposed the following scheme of reactions:



However, this option of direct reaction polymer–catalyst in fixed beds usually causes both a pressure drop and contact problems.

In several works, the decomposition of the polymers has been performed via a combination of thermal and catalytic treatments. In the first thermal cracking step, liquid products are attained, with them being subsequently reformed in catalytic fixed-bed reactors. Thus, Songip et al.²⁹ obtained a heavy oil via the thermal pyrolysis of polyethylene at 450 °C that was used as feed in the catalytic fixed-bed reforming reactor. Five catalysts were tested: zeolite REY, HY, SiO₂–Al₂O₃, HZSM-5 (Si:Al = 65), and HZSM-5 (Si:Al = 1000). Rare-earth-metal-exchanged Y zeolite was the best catalyst for the reforming of polyethylene oil to gasoline with a research octane number (RON) of 67, which adds low amounts of coke. In contrast, HZSM-5 yielded the highest amount of gaseous hydrocarbons and the lowest of gasoline. The remarkable performance of REY zeolite was explained in terms of their large pores, which allow heavy oil to penetrate, as well as its proper acid properties that decrease coke formation and enhance gasoline yield. Bagri et al.⁴⁶ upgraded the gases obtained from the polyethylene pyrolysis at 500 °C in a secondary reactor that contained either zeolite Y or ZSM-5. The oils obtained over zeolite Y showed greater concentrations of aromatic hydrocarbons than those of zeolite ZSM-5.

Fluidized beds have also been tested in the catalytic cracking of polymers. The uniformity in temperature throughout the bed is meant to yield narrower and more-valuable product distributions. Sharratt et al.³³ performed the catalytic pyrolysis of HDPE over HZSM-5 (Si:Al = 17.5) in a fluidized-bed reactor operating at ambient pressure with fluidizing gas velocities of 1.5–4 cm/s. The major products of HDPE cracking over HZSM-5 were C₃–C₅ olefins (>65 wt %), with minor amounts of methane and ethane, which were only detected at higher temperatures. These products were obtained mostly via carbocationic mechanisms of the following types: β -scission, hydrogen transfer, and oligomerization. The yield of smaller cracked products, BTX, and coke increased with temperature. On the other hand, when the polymer:catalyst mass ratio was enhanced, lower amounts of C₁–C₄ hydrocarbons and coke were achieved and higher liquid yields were obtained. Similarly, in the results of Lin and Yang,⁸⁰ the flow rate of the fluidizing gas also has an important role, because its increase led to primary cracking products (olefins), whereas low flow rates created secondary products (BTX).

Kaminsky et al.¹⁴ tested the Hamburg process (fluidized bed) using a FCC catalyst with polyethylene and PS at temperatures in the range of 370–515 °C and an output of 1 kg/h. The presence of the catalyst changes the product distributions, when compared to thermal degradation. Thus, for the catalytic degradation of PS, ethylbenzene (18%–26%), benzene (9%–22%), and toluene

(3%–5%) were obtained primarily, instead of styrene (61%), which is the major product of thermal cracking. In the polyethylene case, gases (48%–52%) and low boiling oils (38%–39%) were the main products, instead of the waxes that were yielded in the noncatalytic experiments. Similarly, Lin and Yang³⁷ compared the performance of several catalysts (HZSM-5, USY, HMOR, MCM-41, and SiO₂–Al₂O₃) in the degradation of HDPE and PP in a fluidized-bed reactor operating at 360 °C with a polymer:catalyst mass ratio of 0.4:1. The highest mass of unconverted polymer was observed over Al-MCM-41 and SiO₂–Al₂O₃, whereas the highest coke yields were measured over USY and HMOR. HZSM-5 and HMOR produced similar C₁–C₄ and C₅–C₉ yields (~60% and ~30%, respectively), whereas, over USY, the yields were 35% and 54%, respectively. SiO₂–Al₂O₃ and Al-MCM-41 led to similar product distributions with a wide molecular range and a high olefinic yield (>85%). In addition, the larger pore zeolites (HMOR, USY) showed quick deactivation, unlike HZSM-5 and the nonzeolitic catalysts (SiO₂–Al₂O₃, MCM-41).

A two-stage catalytic process for the degradation of polyethylene was investigated by Uemichi et al.,⁴² to obtain a better-quality gasoline than that obtained with single-stage operation. Two catalysts (silica–alumina and HZSM-5) were placed sequentially in a tubular reactor wherein the plastic was fed previously from a melter through a capillary tube heated at 340 °C. The tested temperatures were 375–425 °C using W/F values in the range of 4–18 g catalyst min/(g polyethylene). The degradation over HZSM-5 produced a low gasoline yield with high aromatic content, whereas silica–alumina produced a low-quality liquid. In contrast, the two-stage degradation that combined both silica–alumina and HZSM-5 led to improved gasoline yields and a high octane number, because of the proper combination of mesoporosity and acidity for the reaction. The best results were achieved when the weight ratio of silica–alumina to HZSM-5 was 9:1, which produced a gasoline with 58.8% C₅–C₁₂, RON = 94, and a total aromatic content of 25.2 (0.9% benzene). The relative share of HZSM-5 is critical, as may be seen in Figure 7, wherein the changes of aromatics, benzene, liquid yields, and RON value with HZSM-5 content are depicted. The enhancement in HZSM-5 content increased the amount of benzene, aromatics, and RON and diminished the liquid yields.

Another alternative is the processing of plastic waste that has been mixed and diluted with hydrocarbon fractions. An important problem in this option involves the plastic viscosity, because percentages above 10 wt % plastics increases the viscosity to levels that might cause pipe clogging and transportation problems. Ng⁸³ studied the cracking of blends of 5–10 wt % of HDPE and VGO in a fixed-bed reactor at 510 °C and weight hourly space velocity (WHSV) of 20 h^{−1}, using a FCC catalyst. The product distribution is dependent on the plastics share. A 5 wt % HDPE yielded only gaseous hydrocarbons and coke, while 10 wt % plastic produced a significant amount of gasoline-range hydrocarbons. This fact was ascribed to a lower over-cracking of gasoline at inferior catalyst:HDPE ratios.

To avoid viscosity limitations, Arandes et al.⁸⁴ performed a fast pyrolysis of PP to obtain waxes that were subsequently degraded in a riser simulator with a commercial FCC catalyst. The diagram of the riser simulator is shown in Figure 8. This system basically consists of an internal recycle reactor operating at 1 atm and 500–550 °C, with a catalyst:feed ratio of 5.5 and a contact time of 3–12 s; these are conditions that are similar to those of industrial FCC units. The catalyst is situated in a basket, and the gases are impelled by a turbine located upward, passing through the basket. These authors indicated that a

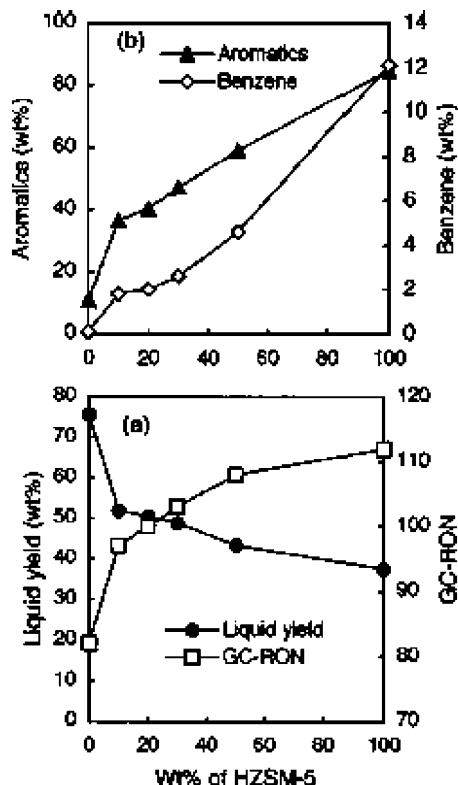


Figure 7. Catalytic degradation of polyethylene over HZSM-5 and silica-alumina, showing the evolution in the yield, GC-RON, and aromatics and benzene contents of the liquid products with the silica-alumina/HZSM-5 weight ratio ($T = 400\text{ }^{\circ}\text{C}$, $W/F = 7\text{ g catalyst min/(g polyethylene)}$). (Reprinted with permission from ref 42. Copyright American Chemical Society, 1999.)

mixture of VGO (80 wt %) + waxes (20 wt %) is especially interesting, because a synergetic effect, which increased the yields of gasoline and liquefied petroleum gas (LPG), was appreciated, because of the reactivity of the primary $\text{C}_2\text{--C}_4$ radicals. In addition, the conversion and relative yields were very sensitive to the contact time and temperature. In this regard, the gasoline share accounts for 42 wt % at $500\text{ }^{\circ}\text{C}$ after 12 s, with the amount of coke being within acceptable ranges (2.8–5.0 wt %).

Following this strategy of decreasing the viscosity of plastic wastes, mixtures of lubricating oil bases and LDPE with compositions ranging from 40:60 to 70:30 (w/w) were cracked in a screw kiln reactor at $400\text{--}500\text{ }^{\circ}\text{C}$ over Al-MCM-41 and nanocrystalline HZSM-5.²¹ Complete conversions were attained at $450\text{ }^{\circ}\text{C}/500\text{ }^{\circ}\text{C}$ over both catalysts. Al-MCM-41 produced mostly $\text{C}_5\text{--C}_{12}$ products (65%), whereas over nanocrystalline HZSM-5, the main components were hydrocarbons in the $\text{C}_3\text{--C}_5$ fraction (63%). Figure 9 shows the PIONA analyses of the $\text{C}_5\text{--C}_{12}$ hydrocarbon fraction obtained over three Al-MCM-

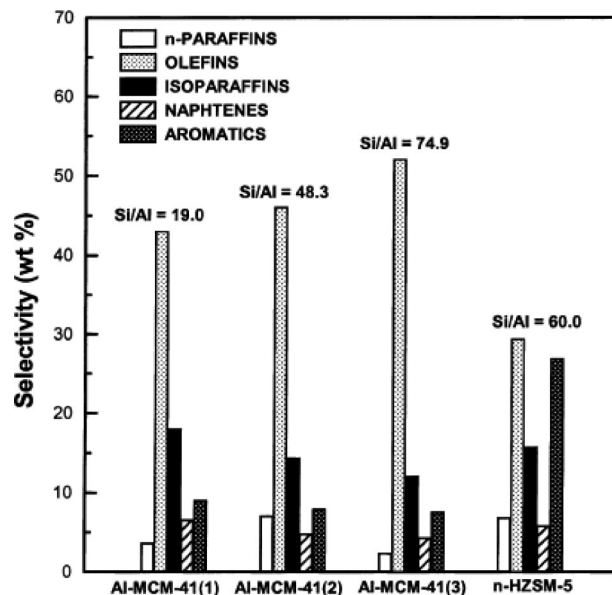


Figure 9. PIONA analyses of the $\text{C}_5\text{--C}_{12}$ fraction obtained in the catalytic cracking of a LDPE-lubricant oil mixture over $n\text{-HZSM-5}$ and three Al-MCM-41 catalysts in a screw kiln reactor ($T_1/T_2 = 450\text{ }^{\circ}\text{C}/500\text{ }^{\circ}\text{C}$, 8.5 rpm, LDPE-lubricant oil base = 70:30 (w/w)). (Reprinted with permission from ref 21. Copyright Elsevier, 2003.)

41 catalysts with different Si:Al atomic ratios and a nanocrystalline HZSM-5 zeolite. Over Al-MCM-41 catalysts, olefins were always the major products (>40%), followed by isoparaffins (13%–18%). The remaining components (naphthenes, aromatics, and n -paraffins) were present in lower amounts (<10%). In contrast, over nanocrystalline HZSM-5, similar contents in aromatics and olefinic hydrocarbons (~30%) were attained.

3.3. Effect of Chlorine from PVC. One of the most important problems for the commercial implementation of the feedstock recycling technologies is the presence of PVC into the makeup of plastic waste. Although sorting systems allow for its removal from the main wastestream, in many cases, a residual concentration of PVC still remains in its composition. Note that 1% PVC means >0.5 wt % chlorine. PVC decomposes thermally at temperatures of $\sim 260\text{ }^{\circ}\text{C}$,⁸⁵ which produces a huge amount of hydrogen chloride (HCl). In addition to the corrosion problems, the fuels obtained may incorporate chlorine-containing hydrocarbons, which turns the product practically useless. Uddin et al.⁸⁶ performed a degradation of mixtures of PP/PVC, PE/PVC and PS/PVC (8 g/2 g) at $360\text{--}430\text{ }^{\circ}\text{C}$ in a batch reactor. They determined that 91–96 wt % of chlorine was removed as HCl, 3–12 wt % in the liquid product fraction, and <0.5 wt % as solid residue, with the chlorine content in oil being within the range of 2800–12700 ppm. These halogenated hydrocarbons are likely produced by the reaction between the HCl formed from PVC and the hydrocarbons obtained from the degradation

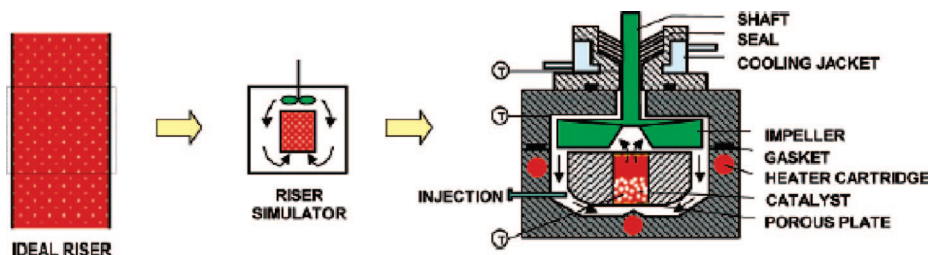


Figure 8. Diagram of the riser simulator used in the catalytic cracking of the waxes obtained in the fast pyrolysis of PP. (Reprinted with permission from ref 84. Copyright American Chemical Society, 2007.)

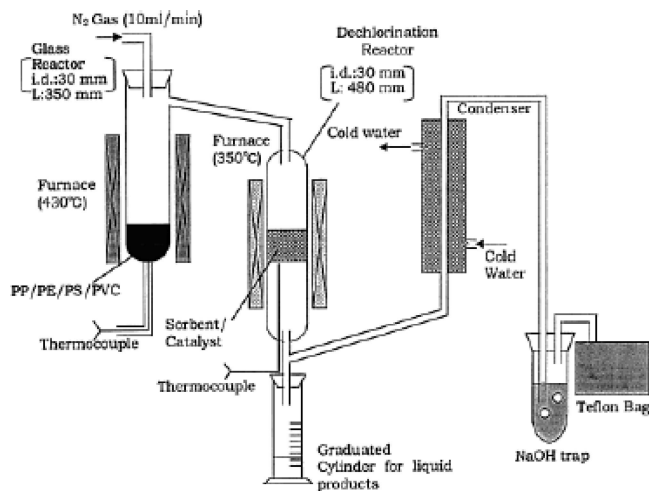


Figure 10. Experimental setup used for the degradation of PP/PE/PS mixed with PVC at 430 °C and dechlorination at 350 °C over a calcium carbonate-based carbon composite. (Reprinted with permission from ref 89. Copyright American Chemical Society, 2003.)

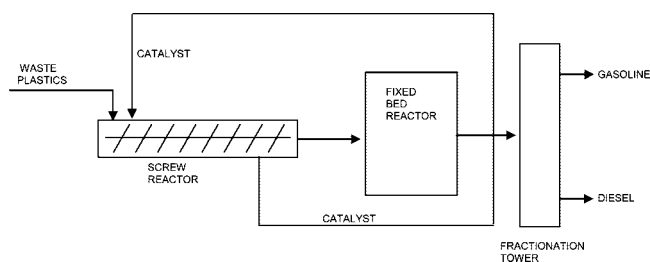


Figure 11. Scheme of the Li's process for the direct catalytic cracking of plastic wastes.

of PE, PP, and PS. The addition of FeOOH , Fe_2O_3 , or Fe_3O_4 as sorbents allows one to decrease the chlorine content (up to 1100 ppm with FeOOH), by fixing the chlorine as iron compounds such as ferrous chloride. However, the traditional way to address this situation consists of adding $\text{CaO}/\text{Ca}(\text{OH})_2$, either in a previous thermal step or even in the catalytic treatment, to neutralize the released HCl , forming CaCl_2 as a byproduct. In this line, Fujimoto et al.⁷ added $\text{Ca}(\text{OH})_2$ with the FCC catalyst, which eliminated the release of HCl and reduced the halogenated content of the liquids from 4000 ppm to <100 ppm. Another procedure to remove the PVC, called mechanochemical dechlorination, was reported by Mio et al.⁸⁷ The method involves the grinding of PVC with CaO , using a planetary ball mill, followed by washing with water, which does not require any heating operation and enables, under certain conditions, the complete elimination of chlorine. On the other hand, Bhaskar et al.⁸⁸ tested several calcium-, iron-, and potassium-based carbon composite sorbents for the capture of HCl that evolved from the PVC. The sorbents were prepared by mixing 90 wt % metal carbonate with 10 wt % phenol resin and 20 wt % water, followed by their calcination at 500 °C for 1 h under a nitrogen atmosphere. The calcium carbonate-based carbon composite showed the best performance, while the optimum temperature for adsorption was determined to be 350 °C. In a continuation of that work, Bhaskar et al.⁸⁹ tested the calcium carbonate-based carbon composite not only in the dechlorination of the gases but also in the dechlorination of the liquids from the thermal cracking of the plastics. The experimental setup is shown in Figure 10. The system involves a reactor to perform the thermal cracking of a PP/PE/PS/PVC mixture at 430 °C, followed by a dechlorinating reactor that contains the composite sorbent operating at 350 °C.

This setup allows one to decrease the chlorine content in oils from 360 ppm (without sorbent) to 0 ppm, working continuously for four runs.

3.4. Pilot Plant and Commercial Processes. Several commercial processes are currently available to catalytically crack plastic waste.⁹⁰ In the Thermofuel process, molten plastics are thermally cracked at 350–425 °C in a first reactor under a nitrogen gas atmosphere. Subsequently, the pyrolytic gases pass through a catalytic reaction tower that has been heated at 220 °C, and finally the products are condensed in a two-stage system. The final product is a hydrocarbon mixture that is approximately equivalent to a diesel. The most essential stage in the process is the catalytic reaction tower, because it contains a catalyst (Nickel Raney) that changes the initial composition of the pyrolytic gases. Thereby, hydrocarbons heavier than C_{25} are cracked, whereas those lighter than C_6 are reformed, which creates a mixture similar to a diesel fuel. The catalyst has the additional advantage of not undergoing meaningful poisoning. In addition, the Thermofuel diesel yields less SO_x , NO_x , and particulates than conventional diesel.

Another interesting process that involves direct catalytic cracking was developed by Li,⁹¹ and its flow diagram is shown in Figure 11. The process is intended to obtain both gasoline and diesel from waste plastic, and it is comprised of two stages. In the first stage, a catalyst formed by alumina powder, water glass, and HZSM-5 zeolite is added to the waste plastic in a screw reactor at 600–700 °C. The second stage is a fixed bed with a catalyst that is composed of ZSM-5, flokita, and REY zeolite working at temperatures of 300–600 °C. The reaction products are subsequently separated in a fractionation column into gasoline and diesel. The obtained yields indicate that, from 1400 kg of waste plastic (50% PE, 25% PP, and 25% PS), one can obtain 630 kg of gasoline, 420 kg of diesel, 140 kg of inorganic residue, and 210 kg of flammable gas.

The Smuda process⁹² also deserves attention. This is a continuous catalytic cracking process wherein the mixed plastics are fed, using an extruder, into a catalytic vessel operating at 350 °C under a nitrogen atmosphere. The gaseous products are separated subsequently in a distillation column. A variety of catalysts have been proposed, preferentially nickel or iron silicates, added in a 5%–10% ratio. The final product is a fuel that is composed of 85% diesel and 15% gasoline. The largest plastic cracking plant, which is located in Zabrze, Poland, operates with six cracking reactors with a capacity of 20 m³ that are equipped with agitators and internal heat exchangers. In this plant, the catalyst is silica–alumina, which reduces coke formation, with regard to thermal cracking.

Another catalytic process for obtaining diesel from waste plastic is the Nanofuel process.⁹⁰ It consists of a catalytic depolymerization at 270–370 °C, using a NaY zeolite catalyst, that is performed in a stirred reactor. To ensure good thermal conductivity, the process uses hot oil as the pyrolysis medium. The catalyst and the plastic are fed into the reactor and the gaseous products are fractionated in a distillation column. The process produces very high liquid fuel yields (93%–95%) and a diesel with a cetane index (CI) above 56.

In a different line of work, the Reentech process uses several sequential catalytic stages for the continuous preparation of gasoline, kerosene, and diesel from waste plastic.⁹³ First, melted plastics are decomposed and dehydrogenated over a nickel-based catalyst at 350–370 °C. Subsequently, they are cracked in a moving-bed reactor, using a silica–alumina catalyst at 500–550 °C, with steam also being introduced to remove the heavy oils that are present over the catalyst surface. Afterward, the different

fractions are separated in a fractionation column. The process results in 75% liquid fuels (55% gasoline, 25% kerosene, 20% diesel), 15% gas, and 10% carbon.

4. Conclusions

Currently, it can be stated that the cracking of plastic waste constitutes a mature field of research with commercial opportunities and a promising future in the forthcoming years. This fact proves today the feasibility of profitable catalytic cracking technology, especially in the current context of high prices of crude oil. The bounds of this technology are known: high investment costs, a need for plastic sorting, and improved catalytic systems capable of addressing the complex makeup of plastic waste. Its research is not a closed field, because there is still room for improvement in the existing technologies, in reference to both the catalyst and the process itself. In this regard, catalytic systems with improved tolerance to heteroatoms, higher activities, and improved selectivities toward diesel are subjects of interest.

In summary, the following concluding remarks may be stated, regarding the thermal and catalytic cracking of plastic waste to produce fuels:

(1) The thermal cracking processes of plastics mostly result in wide hydrocarbon distributions that require subsequent treatment to obtain valuable products. Only with certain plastics (polystyrene (PS), poly(methyl methacrylate) (PMMA), polytetrafluoroethylene (PTFE)) does thermal cracking lead to a meaningful share of the starting monomers.

(2) Regarding the product distribution, the content of gaseous hydrocarbons (mostly olefins) and aromatics in the pyrolytic oils resulting from thermal cracking increases at temperatures above 650–700 °C. In contrast, oils with scarce amounts of aromatics are chiefly attained at temperatures of ~500 °C.

(3) Thermal cracking has been performed in a variety of reactors, such as batch, fluidized-bed, and screw kiln reactors. The fluidized-bed reactor allows one to achieve uniform temperatures, which leads to narrower and more-valuable product distribution. On the other hand, under the same conditions, the use of a screw kiln reactor leads to smaller content of gaseous hydrocarbons and a greater share of liquid hydrocarbons, especially in the range of gas oils, because it favors recombination reactions of the gaseous olefins.

(4) The use of solvent/oils along with the plastics allows one to decrease the viscosity, augmenting the heat- and mass-transfer rates. In addition, the solvent may modify the cracking mechanism, which leads to changes in the product distribution. Accordingly, for oil/plastics mixtures, the yield of gases decreases when the oil content is augmented. Similarly, the use of poor-hydrogen-donating solvents in the cracking increases the share of liquid hydrocarbons in the range of C₅–C₃₂, and it also increases the 1-olefin content.

(5) The presence of a suitable catalyst decreases the cracking temperature and increases the plastic conversion, in comparison with thermal processes. The most-used catalysts are zeolites (e.g., HZSM-5, HY), mesoporous materials (Al-MCM-41), and silica–alumina. Regarding the selectivity, catalysts with strong acid sites (e.g., HZSM-5 zeolite) primarily lead to C₃–C₅ olefins, whereas catalysts with medium acid sites (Al-MCM-41, SiO₂–Al₂O₃) result in gasolines and middle distillates.

(6) Because of the bulky nature and high viscosity of plastics, catalysts with highly accessible acid sites show improved performances. Thus, the use of nanocrystalline and hierarchical mesoporous–microporous zeolites as catalysts lead to higher conversions than that observed over conventional zeolites.

(7) Deactivation of the catalysts could be an important limitation in the direct catalytic cracking of plastic waste. The deactivation rate is dependent on the acidity and pore structure of the catalysts. Hence, the cracking over large-pore HMOR and HUSY zeolites showed quicker deactivation than that over HZSM-5, SiO₂–Al₂O₃, and Al-MCM-41. The use of two-stage processes, including thermal cracking followed by a catalytic reforming, is an easy way to avoid the deactivation of catalysts, because it may prevent direct contact of the catalyst with impurities that are present in the raw plastic waste. In these combined processes, zeolite REY was the best reforming catalyst for yielding gasolines, whereas HZSM-5 resulted in a larger share of gaseous hydrocarbons.

(8) Catalytic fluidized beds are especially adequate reactors, considering their uniform temperature. The influence of the main operation variables indicates that the enhancement in polymer/catalysts mass ratio results in smaller amounts of gases and coke and larger amounts of liquid. Similarly, the increase of the flow of the fluidizing gas augments the yield of primary cracking products (olefins).

(9) Two-stage catalytic processes result in better gasoline than that formed with just one catalyst. Thus, the use of two catalysts in series (SiO₂–Al₂O₃ + HZSM-5) in a fixed bed allows one to obtain high yields of gasoline with a good octane number. In addition, upon increasing the HZSM-5 share, the yield of aromatics and RON increases while the yield of liquids decreases.

(10) To reduce the viscosity, mixtures of plastic/vacuum gas oil can be prepared and cracked catalytically over fluidized catalytic cracking (FCC) catalysts. The composition of the cracking products is dependent on the plastic share, so only gaseous products are obtained for mixtures with a plastics content of 5% and mainly gasoline for mixtures with a plastics content of 10%. Another way to decrease the viscosity of the reaction medium is to perform a fast pyrolysis of the plastic to give waxes and crack them subsequently using catalytic processes.

(11) The presence of poly(vinyl chloride) (PVC) is a serious drawback, because of the release of HCl at temperatures above 260 °C. The removal of the HCl released from PVC degradation can be attained via the addition of CaO/Ca(OH)₂, iron oxides (FeOOH, Fe₂O₃, or Fe₃O₄) or calcium carbonate-based carbon composite sorbents to the reaction mixture.

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