Chapter from the book *Material Recycling - Trends and Perspectives*
Downloaded from: http://www.intechopen.com/books/material-recycling-trends-and-perspectives

Interested in publishing with IntechOpen?
Contact us at book.department@intechopen.com
1. Introduction

Nowadays, plastics play a fundamental role in modern life, they are included in all productive chains. Plastics frequently replace more traditional materials such as wood, metal, glass, leather, paper and rubber because they can be lighter, stronger, corrosion resistant, acid and base resistant, durable and a better insulators. Plastics are polymers with high molecular weight and usually synthesized from low molecular weight compounds, although they can be obtained also through the chemical modification of high molecular weight natural materials such as cellulose (Gervet, 2007).

Plastics can be divided into two major groups, according to their thermal behavior: thermosets and thermoplastics. Thermoplastics soften when they are exposed to heat, and they can be molded and shaped, this heating process can be repeated many times. These plastics contribute to the total plastic consumption by roughly 80% and are used as containers, packaging, trash bags and other non-durable goods (Al-Salem et al., 2009). Some examples are high and low density polyethylene (HDPE, LDPE), polystyrene (PS), polypropylene (PP) and polyvinyl chloride (PVC). In contrast, thermosets solidify irreversibly when heated, since an irreversible network of cross-linked covalent bonds is formed, giving a hard, durable, strength and heat resistant products. Such is the case of unsaturated polyurethane (PU), unsaturated polyesters and, alkyd, phenolic and epoxy resins. For that reason, they are used primarily in automobiles, construction adhesives, furniture, kitchenware, inks, and coatings. A third group of plastics, rubber-type, are named elastomers, formed by slightly cross-linked polymer chains; in less proportion than thermosets, giving to these materials elastic properties and relatively good resistance (Morton-Jones, 1993; Aguado & Serrano, 2007, Scheirs & Kaminsky, 2006).

In the last thirty years, plastic industry has raised very quickly, growing around 500%. In 2008, the global plastic production was 245 Mt; the European Community accounts for around 25% of world production, whereas the United States by around 13%; China alone accounts for 15%. Polyethylene has the highest share of production of any polymer type and the packaging and construction sectors represent more than 50% of plastic demand (EC, 2011; USEPA, 2008).
As a consequence of the widespread use of plastics, they represent between 10 to 13% of the municipal solid wastes (MSW) generation in the whole world. In 2008, the total generation of plastic waste in the EU-27, Norway and Switzerland was 24.9 Mt while in the United States was 30.05 Mt. Packaging is by far the largest contributor to plastic waste by 63%. In the United States, the recycling rate for different types of plastic varies greatly, resulting in an overall plastics recycling rate of only 7%. In 2008, however, the recycling rate of some plastics became much higher, for example in 2008, 28% of PET bottles and jars and 29% of HDPE bottles were recycled (USEPA, 2008).

Plastic waste generation imposes negative environmental effects, since these materials are usually non-biodegradable and, therefore, they can remain as waste in the environment for a very long time; they may pose risks to human health as well as to the environment; and they can be difficult to reuse and/or recycle in large-scale practice. An issue of particular concern is that giant masses of plastic waste have been discovered in the North Atlantic and Pacific Oceans, the full environmental impacts of which are not yet fully understood but which may cause severe damage to seabirds, marine mammals and fish (Derraik, 2002, Lavender et al., 2010). Plastic waste in the ocean causes the death of up to one million seabirds, 100 000 marine mammals and countless fish every year (UNEP, 2006).

Once the material enters the waste stream, recycling is the process of using recovered material to manufacture a new product (Hopewell et al., 2009). Recycling, being one of the strategies for minimization of waste, offers three benefits (Edwards, 1999): (i) reduces the demand upon new resources, (ii) cuts down on transport and production energy costs and (iii) uses waste which would otherwise be lost to landfill sites. Plastic wastes are mainly found in MSW mixed with other classes of residues, consequently, their recycling is limited and landfills are the primary destination of these wastes. Recycling plastic waste provides important environmental advantages such as:

1. **Saving space in landfills.** The need to create new landfills and to put more trash in the earth is ever increasing, and recycling is the only sustainable solution to drastically decrease the waste deposited into landfills. In addition, as common plastics are not degradable, they can remain for centuries without space liberation. One ton of plastic bottles free more than 7 cubic yards of landfills, then, recycling plastic means liberating a lot of space unnecessarily used.

2. **Energy conservation.** The recycled material is used as a resource, although most of the times, every recycled piece of plastic changes into something completely different after the process. Recycling can use two-thirds the energy to manufacture from recycled products. One pound of recycled PET can save as much as twelve thousand BTU’s energy (Scheirs, 2001).

3. **Reduction of air pollution and greenhouse gases.** An average net reduction in greenhouse gas emissions (GHG) of around 1.5 ton of CO₂-eq of recycled plastic has been estimated (Department of Environment and Conservation (NSW), 2005). The reduction in pollutant emissions and GHG is mainly due to the substitution of virgin polymer production, decreasing fuel burning.

4. **Oil conservation.** The increase of the price of oil is actually an important economic issue around the whole world; every ton of recycled plastic saves almost 2000 pounds of oil. Savings can be due to the reduction of raw refinery materials in the manufacturing process, to the use of plastics as a source of combustion fuel in incinerators, as well as fuel production from plastics by catalytic desintegration (Aguado & Serrano, 2007).
5. Saving marine life. It has been reported that a plastic raft (bottle caps, toys, bottles, etc.) floats on the Pacific Ocean, trapping and killing marine life, as well as sea birds and turtles, unable to distinguish plastics from food, dying by malnutrition or asphyxia (Derraik, 2002).

Several end-of-life options exist to deal with plastic wastes. Four categories can be considered for the treatment and recycling processes of plastic wastes (Table 1), depending of requirements of every locality or industry; each method presents advantages and disadvantages. Although primary and secondary recycling schemes are well established and widely applied, it has been concluded that many of the PSW tertiary and quaternary treatment schemes appear to be robust and worth of additional investigation (Al-Salem et al., 2009; Hopewell et al., 2009).

<table>
<thead>
<tr>
<th>Method</th>
<th>Description</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-extrusion (Primary)</td>
<td>Involves the reintroduction of clean scrap of single polymer to the extrusion cycle in order to produce products of the similar material.</td>
<td>Re-using plastic is preferable to recycling as it requires less energy and fewer resources. Usually they feed the secondary process.</td>
<td>Limited, since rarely possess the required quality. Sorting must be attempted within a short time. Removing paints is necessary.</td>
</tr>
<tr>
<td>Mechanical Recycling (Secondary)</td>
<td>Involves reprocessing of plastic by melting, shredding or granulation. Separation, washing and preparation of wastes are essential.</td>
<td>It is an economic and viable route for plastic wastes recovery. It is used mainly to manufacture fibers for carpets, apparel and bottles.</td>
<td>Mechanical recycling of PSW can only be performed on single polymer plastic, e.g. PE, PP, PS, etc. Requires intense energy consumption.</td>
</tr>
<tr>
<td>Feedstock or Chemical Recycling (Tertiary)</td>
<td>Refers to techniques used to breakdown plastic polymers into their monomers or small molecules. It is the most sustainable method.</td>
<td>Can be used in petrochemical and chemical production plants; wastes are converted into valuable feedstock chemicals, useful as fuels or raw materials.</td>
<td>Costs of a feedstock plant are still high in comparison with oil plants. Still lacks the proper design and kinetic background to target certain products and chemicals.</td>
</tr>
<tr>
<td>Incineration and energy recovery (Quaternary)</td>
<td>Implies burning waste to produce energy in the form of heat, steam and electricity.</td>
<td>Produce heat, power and/or gaseous fuels. Plastic waste results in a volume reduction of 90–99%, which reduces the reliability on landfilling</td>
<td>Health and environmental concerns due to the production of large amounts of air pollutants.</td>
</tr>
</tbody>
</table>

Table 1. Methods for treatment and recycling of plastic wastes. Modified from (Scheirs & Kaminsky, 2006; Al-Salem et al., 2009; Hopewell et al., 2009) and based on the ASTM classification.
Among the feedstock (tertiary) recycling methods, we should consider:

- Pyrolysis. Thermal decomposition of polymer chains.
- Gasification. Decomposition under oxygen or stream conditions to yield synthesis gas.
- Hydrogenation. Chain breaking with hydrogen.
- Catalytic cracking. Polymer chain breaking through the action of a catalyst.

Scheme 1 shows an overview of the thermal and chemical recycling processes that can be applied to plastic waste (Kumar et al., 2011). We should point out that methanolyis can be included among alcoholysis methods and hydrolysis is also another chemolysis method.

Catalytic polymer cracking is one of the actual alternatives of feedstock recycling since very valuable products can be obtained. These technologies can be applied to HDPE, LDPE and PP, which represent around 60% in plastic wastes, although certain polyamides can be efficiently depolymerized. Moreover, in principle, any kind of plastic may be recycled, providing the right catalyst, the right reaction system and the right operation conditions. The industrial application of the catalytic polymer recycling has been limited more because economic considerations rather than technical considerations. Due to the high price of crude oil, these technologies are receiving renewed attention, (Schiers, 2001).

### 2. Catalytic materials

Nowadays, molecular sieves are the most studied and employed materials for the chemical decomposition of plastic waste. Other catalyst systems may be effective for breaking polymer chains, such as the previously used Friedel-Crafts catalysts, however, they present corrosion and environmental problems (Clark, 1999).
Molecular sieves are a wide range of solid materials of porous microstructure. Many of them possess acid or basic properties, very useful in catalytic reactions. There are several types of molecular sieves, depending mainly, on their chemical composition and their pore system. The catalytic decomposition of plastic waste polymer chains takes place following the same pathways as the hydrocarbon catalytic cracking reactions used in petroleum refinery processes and, catalysts employed by this industry are also useful for polymer decomposition. Alumina, silica, amorphous silica-alumina and crystalline aluminosilicates (mainly zeolites) are widely used in petroleum processes. Hydrocarbon cracking reactions may take place through hydride remotion, promoted by Lewis acid sites, or through a carbocation intermediate, from the carbon protonation by Brønsted acid sites. Fluid Catalytic Cracking (FCC) refinery plants around the world employ faujasite zeolite (FAU), having strong Brønsted acid sites, as the principal component of FCC catalysts. Therefore, our research group, as other researchers, have employed commercial FCC catalysts for the catalytic cracking of plastic waste (Cardona & Corma, 2000, De la Puente et al., 2002, Lin et al. 2010, Ortega et al., 2006, Sanchez et al., 2003). A very promising option, from an economical point of view, is to use waste FCC catalysts (also called equilibrium catalysts) disposed from refinery plants. In addition to faujasite zeolite (or Y zeolite), other zeolites such as mordenite, clinoptilolite, X zeolite or ZSM-5, have also been employed for the catalytic decomposition of plastic waste (Clark, 1999, Huang et al., 2010). Natural zeolites are other very promising option, from an economical point of view, since they are a lot cheaper than synthetic zeolites.

Research attention has also been focused on new molecular sieves with pore sizes larger than those of zeolites, such as MCM-41 or SBA-15, that allow larger molecules inside the pore channels. According to the IUPAC (International Union of Pure and Applied Chemistry), zeolites are considered microporous materials, with pore sizes smaller than 2 nm, whereas MCM-41 and SBA-15 are considered mesoporous materials, with pore sizes falling within the range between 2 and 50 nm. These materials have mostly weak acid properties as such, but they can be functionalized in many different ways. Their acid properties can be greatly enhanced by the introduction of for instance, aluminum, gallium, iron or zirconium atoms during the synthesis (Chen et al., 2007, Chen et al., 2006, Diaz-Garcia et al., 2010), or by the immobilization of sulfonic or heteropolyacid strong acid groups onto the pore channels, after the synthesis (Boveri et al., 2005, Hernández et al., 2010, Schacht et al., 2010, Wang et al., 2009, Wang et al., 2008, Yang et al., 2009). Recent studies have also employed hybrid micro/mesoporous materials (Serrano et al., 2010).

2.1 Microporous materials: Natural and synthetic zeolites

Nanostructured microporous materials have been the focus of much attention because their unique properties, such as a large specific surface by volume unit (many physical and chemical interactions take place on surfaces), electrical and thermal conductivity, ductility or mechanical resistance. Zeolites are a much relevant class of microporous materials that have found application on diverse fields, such as ion exchangers (i.e. water treatment), adsorbents (i.e. for nuclear plants waste), catalysts, or even as food supplement for farm animals (Mravec et al., 2005). Zeolites have become cornerstone and common household in research centers, industry and domestic environments (Masters & Maschmeyer, 2011).
Zeolites are crystalline aluminosilicates of tridimensional structure and with cavities and channels between 0.3 and 1 nm width. The inner structure is very porous and cavities and channels may be occupied by mobile cations and water molecules. The basic structure is formed by $\text{TO}_4$ tetrahedra ($T = \text{Si, Al}$) with oxygen atoms connecting neighboring tetrahedra. Zeolites composition may be described by three components (Auerbach et al., 2005):

$$M^{m+}_{n/m} \cdot [\text{Si}_{1-n} \text{Al}_n \text{O}_2] \cdot n\text{H}_2\text{O}$$

Extra-framework cations framework adsorbed phase

And their chemical formula by (Dyer, 1988):

$$M_{x/n} \text{Al}_x \text{Si}_y \text{O}_{2x+y} \cdot w\text{H}_2\text{O}$$

Zeolites have an inner surface much larger than their external surface. Zeolites microporosity is open and the structure allows matter transfer between the inter-crystalline space and the surrounding media. This transference of matter is limited by the pore diameter and form, allowing the in and out movement of molecules of a specific critic size (ACS Monograph, 1976).

<table>
<thead>
<tr>
<th>ZEOLITE</th>
<th>NUMBER OF TETRAHEDRA</th>
<th>PORE ($\theta$) DIAMETER (nm)</th>
<th>EXAMPLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small pore</td>
<td>8</td>
<td>$0.3 &lt; \theta &lt; 0.5$</td>
<td>Erionite, A</td>
</tr>
<tr>
<td>Medium pore</td>
<td>10</td>
<td>$0.5 &lt; \theta &lt; 0.6$</td>
<td>ZSM-5, ZSM-11</td>
</tr>
<tr>
<td>Large pore</td>
<td>12</td>
<td>$0.6 &lt; \theta &lt; 0.9$</td>
<td>$\gamma$, $\beta$, $\Omega$</td>
</tr>
<tr>
<td>Extralarge pore</td>
<td>18</td>
<td>$0.9 &lt; \theta$</td>
<td>MCM-9, VPI-5</td>
</tr>
</tbody>
</table>

Table 2. Zeolite classification.

There are natural and synthetic zeolites. The structure of a synthetic zeolite is exactly the same as its corresponding natural zeolite. Nowadays, there are a lot more synthetic zeolites than natural zeolites. Most natural zeolites are obtained from volcanic-origin geological regions (Dyer, 1988). The catalytic activity of natural zeolites is limited by impurities and a reduced specific surface (Auerbach et al., 2003).

Even if there are more than 10,000 registered patents dealing with the synthesis of zeolites, most synthetic zeolites have been prepared by simple modifications of the Barrer and Milton method, varying only two parameters: the cation and the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (Mravec et al., 2005).

As previously mentioned, at the beginning of the Catalytic Materials Section, several zeolites have been employed for the catalytic decomposition of plastic waste, and our research group has experience with synthetic zeolites (Torres et al., 2011, Torres et al., 2008). However, considering that natural zeolites are a lot cheaper and ready available in Mexico, we selected natural Mexican mordenite (MOR), Figure 1, and natural Mexican clinoptilolite (HEU) for the catalytic decomposition of low-density polyethylene. Zeolites can be identified by their characteristic XRD pattern and this technique also allows assessing the purity of natural zeolites (Figure 2).
2.2 Mesoporous materials: MCM-41

Among the newly developed mesoporous synthetic materials (MCM, SBA, HMS, MSU or FDU labels), MCM-41 has received special attention for catalytic cracking reactions. Nanostructured MCM-41 mesoporous materials are constituted by an ordered network of hexagonal channels and they have promising applications in adsorption, ion exchange, water treatment and catalysis. These mesoporous materials are synthesized through a templating mechanism employing ammonium surfactants. The ammonium surfactants can form lyotropic liquid crystals with lamellar, cubic or hexagonal mesophases, and, at the right precursors concentration, the mesoporous MCM materials can attain the same geometries (Figure 3). The mesopores have a typical length of 3 nm but it can be varied by using surfactant molecules of different size. MCM-41 materials are essentially silicates but the composition can be modified by the introduction of many other different elements that confer these materials specific properties. The materials can be modified during the synthesis procedure or after the synthesis procedure.
Fig. 3. MCM-41 of hexagonal microstructure (a), MCM-48 of cubic microstructure (b), MCM-50 of lamellar microstructure (c).

The MCM-41 hexagonal channel system has a characteristic XRD pattern (Figure 5) and, it can actually be seen by transmission electron microscopy (Figure 4).

Fig. 4. Transmission electron microscopy image of MCM-41 (Wang et al. 2009).

Fig. 5. XRD of siliceous MCM-41 and zirconium-modified MCM-41 (Chen et al., 2006).
Table 3 shows the Si/Al molar ratio and the textural properties of several catalysts we have employed for the catalytic decomposition of low-density polyethylene, which include commercial fresh and waste FCC refinery plant catalyst (with faujasite zeolite as main cracking agent), natural mordenite zeolite and Al-MCM-41 and Ga-MCM-41 mesoporous materials. FCC catalysts were provided by the Mexican Petroleum Institute (IMP).

<table>
<thead>
<tr>
<th>CATALYST</th>
<th>Si/Al Ratio</th>
<th>Unit Cell Parameter (nm)</th>
<th>Specific Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCC-Fresh</td>
<td>24.5 *</td>
<td>24.30</td>
<td>300.34</td>
</tr>
<tr>
<td>FCC-Equilibrium</td>
<td>25 *</td>
<td>24.46</td>
<td>166.15</td>
</tr>
<tr>
<td>Al-MCM-41</td>
<td>9</td>
<td>41.75</td>
<td>800</td>
</tr>
<tr>
<td>Ga-MCM-41</td>
<td>25 **</td>
<td>46.18</td>
<td>900</td>
</tr>
<tr>
<td>Natural Mordenite</td>
<td>5.5</td>
<td>18.1</td>
<td>280</td>
</tr>
</tbody>
</table>

1 By XRD, 2 By BET method
* Of the zeolite, ** Si/Ga Ratio

Table 3. Composition and textural properties of catalysts employed for the catalytic cracking of polyethylene (Ortega et al., 2006).

We have studied Al-MCM-41 and Ga-MCM-41 nanostructured mesoporous materials for the catalytic cracking of polymers, because the introduction of Al and Ga within the material’s framework during the synthesis procedure, results in enhanced Brönsted acidity. We have also immobilized tungstophosphoric acid, $H_3WPW_{12}O_{40}$, onto the MCM-41 surface (after the synthesis) for the same reason.

The pore size, pore volume, pore size distribution and specific surface area of most molecular sieves is often calculated from nitrogen (or other gases) adsorption-desorption isotherms. Such isotherm is shown in Figure 6, for a tungstophosphoric acid-MCM-41 material employed in the catalytic cracking of polyethylene (Hernandez et al., 2010).

Fig. 6. Nitrogen adsorption-desorption isotherm and pore-size distribution (insert) of the tungstophosphoric acid-MCM-41 material employed in the catalytic cracking of polyethylene (Hernandez et al., 2010).
material. The shape of the isotherm corresponds to a type IV isotherm, according to the Brunauer-Emmet-Teller (BET) classification, typical of mesoporous materials. The pore size distribution (insert) confirms, from the main peak, that the pores are of approximately 3 nm, within the mesoporous range.

The introduction of the heteropolyacid reduces the surface area and the pore volume of the support, but strongly enhances the Brönsted acidity of the material (Table 4).

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET Surface area (m^2/g)</th>
<th>Pore volume (cm^3/g)</th>
<th>Pore size (Å)</th>
<th>Acidity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-MCM-41</td>
<td>420.0731</td>
<td>0.445895</td>
<td>22</td>
<td>0</td>
</tr>
<tr>
<td>HPA25</td>
<td>340.6419</td>
<td>0.3332</td>
<td>27</td>
<td>41</td>
</tr>
<tr>
<td>HPA50</td>
<td>191.4937</td>
<td>0.2373</td>
<td>23</td>
<td>74</td>
</tr>
<tr>
<td>HPA70</td>
<td>204.0907</td>
<td>0.1923</td>
<td>26</td>
<td>94</td>
</tr>
</tbody>
</table>

*Brönsted acidity, **Lewis acidity
25, 50 and 70 denote the w/w proportion of H$_3$PW$_{12}$O$_40$ with respect to MCM-41

Table 4. Textural and acidic properties of MCM-41 and tungstophosphoric acid-MCM-41 employed in the catalytic cracking of polyethylene (Hernandez et al., 2010).

Fig. 7. Scanning electron micrographs of a representative H$_3$PW$_{12}$O$_{40}$–MCM-41 material (Hernandez et al., 2010).

From Figure 7, image a) describe the morphology and surface features of the sample, image b) belong to the oxygen atoms distribution, image c) belong to the silicon atoms distribution, while images d) and e) correspond to tungsten atoms distribution from K and L transition signals, respectively. These microscopy images indicate a uniform distribution of the heteropolyacid without cluster formations.

Figure 8 shows the FTIR spectra of the heteropolyacid-impregnated MCM-41 materials, exhibiting the characteristic H$_3$PW$_{12}$O$_{40}$ absorption bands at 1080, 982, 893 and 822 cm$^{-1}$. The IR absorption bands in Figure are assigned as: 1080 cm$^{-1}$ belonging to P-O vibrational symmetrical stretching, 982 cm$^{-1}$ to W=O$_4$ stretching coordination, 893 cm$^{-1}$ to W-O$_6$-$\ W$ bridge stretching mode (inter-bridges between corner-sharing octahedra) and 799 cm$^{-1}$ to W-O$_6$-$\ W$ stretching mode (intra-bridges between edge-sharing octahedra) These absorption bands were retained in the HPW/MCM-41 materials, indicating the preservation of the heteropolyacid Keggin structure. The preservation of the Keggin structure of H$_3$PW$_{12}$O$_{40}$ was further confirmed by 31P-MAS-NMR (Hernandez et al., 2010).
Fig. 8. FTIR spectra of heteropolyacid-MCM-41 materials. 25, 50 and 70 denote the w/w proportion of H₃PW₁₂O₴₀ with respect to MCM-41.

2.3 Key catalyst properties

Most catalysts employed for the catalytic polymer cracking are acid micro- or meso-porous solids. Several gas or liquid products are obtained, in different proportions, depending on the catalyst selection. Key factors under consideration are the nature of the acid sites, the acid strength and textural properties, such as the pore size and the specific surface area. Alumina is widely used in industrial catalytic processes and has Lewis-type acid sites; Lewis sites are also characteristic of several types of silica. Aluminosilicates, such as zeolites or amorphous silica-alumina have a combination of Brönsted and Lewis acid sites. Increasing the aluminum content in the catalyst framework increases the total number of Brönsted acid sites, however, a reduced content of aluminum leads to stronger Brönsted acid sites. The purely siliceous MCM-41 has a medium Lewis acidity and weak Brönsted acidity, but the latter can be greatly enhanced by introducing Al, Ga, Fe, or Zr (among other) atoms within the material’s framework, or by anchoring strong acids on the MCM-41 channels, such as heteropolyacids or sulfonic groups. In general terms, strong Brönsted acid sites lead to catalysts with high cracking activity. Strong Brönsted acid sites also tend to produce a larger proportion of gas products (rather than liquid products) and may produce larger amounts of coke.
In order to have relatively more control over the products obtained, it is convenient a catalyst with a regular pore structure and a uniform pore size distribution. Materials with pores of many different sizes tend to produce much more different products and byproducts. In general terms, mesoporous materials favor liquid products, while microporous materials produce a larger proportion of gas products. The catalytic cracking of polymer chains starts at the outer surface of the microporous materials, but once the chain fragments enter the pores, where many active sites are located, small gas molecules come out from them. Zeolites with very small crystal size (of nanometers, instead of micrometers) and large external surface area, may produce less amount of gas molecules while having high cracking activity (Covarrubias et al., 2010). We should point out, that both, gas or liquid products are useful, for chemical industrial processes or as fuels; we may wish to favor certain products depending on the intended application.

3. Reaction mechanism

The reaction mechanism of the catalytic cracking of polymer chains follows similar pathways of those of the hydrocarbon catalytic cracking in petroleum refinery plants. These mechanisms have been studied for a number of years. The catalytic cracking process takes place at temperatures high enough to have parallel thermal cracking reactions (Kumar et al., 2011). Some of the efforts for elucidating the thermal cracking mechanism of polyethylene go back to the end of the 1940’s (Oakes and Richards, 1949). The thermal cracking reactions follow a free radical mechanism, by breaking covalent bonds by the action of heat, producing free radical species. Catalytic cracking reactions undergo either by the protonation of carbon atoms in the polymer chain (protons coming from Brönsted acid sites), or by the abstraction of a hydride ion from the polymer chain, by Lewis acid sites.

Protonation:

Hydride abstraction:

The resulting ions can be stabilized by β-scission, isomerization or hydrogen transfer reactions. Scheme 2 shows different reactions that can take place, each one more or less favored depending on the temperature (Kumar et al., 2011). The surface area and the porous structure of the catalyst also play an important role. The breaking down of polymer chains starts at the external surface of the catalyst. Small enough fragments may get inside the pores, where additional cracking reactions take place, resulting in small-size gas molecules. Unlike thermal cracking, a certain catalyst may promote the selectivity towards specific products (Pinto et al., 1999).
Scheme 2. Reactions involved in the thermal and catalytic cracking of polymer chains (Kumar et al., 2011).

4. Reaction systems

4.1 Reaction system design

For the catalytic cracking reaction we have built a semiautomatic reaction system (Figure 9), initially based on a design reported by Uemichi (Uemichi et al., 1998). The reaction system has (1) a loading section, where the polymer melts, (2) a capillary tube for controlling the polymer feed, employing nitrogen as carrier gas, (3) a fixed bed stainless steel reactor, (4) a condenser and (5), recipients for liquid and gas products. It employs valves (HV), thermopars (TIC) and manometers (PI). The reaction system is heated with electric resists inside a ceramic refractory brick. The temperatures of the 1, 2 and 3 heating zones are automatically controlled via Field Point electronic modules from National Instruments; working in an integrated way, through the Labview Professional Development System 6.1 software (Table 5).
Fig. 9. Reaction system employed in our laboratory (Hernandez et al., 2010, Ortega et al., 2006).

<table>
<thead>
<tr>
<th>Software</th>
<th>Hardware</th>
</tr>
</thead>
<tbody>
<tr>
<td>Labview professional development system v.6.1</td>
<td>Field Point Modules from National Instruments:</td>
</tr>
<tr>
<td>Field Point v.3.0.2.</td>
<td>• 1FP-1000 RS-232/RS-485, Network interphase.</td>
</tr>
<tr>
<td>Toolset Software, NI Developer Suite</td>
<td>• 1FP-TC-120 (temperature reading).</td>
</tr>
<tr>
<td></td>
<td>• 1FP-PWM-520 (power output).</td>
</tr>
<tr>
<td></td>
<td>3 Solid-state Relevators, 40 A, 24-240 V AC.</td>
</tr>
<tr>
<td></td>
<td>1 Power Source, 24 V.</td>
</tr>
<tr>
<td></td>
<td>1 Thermal Fuse, 20 A.</td>
</tr>
<tr>
<td></td>
<td>4 Thermopars, K type.</td>
</tr>
<tr>
<td></td>
<td>1 Interphase, RS-232.</td>
</tr>
</tbody>
</table>

Table 5. Description of the reactor instrumentation.

We have recently improved the reaction system through a stronger built reactor, better ceramic refractory thermal insulation and better instrumentation, employing National Instruments NI9211 thermocouple differential input modules, NI9472 sourcing digital output modules and a CDAQ-9174 CompactDAQ chassis.
Besides a fixed-bed reactor, several other reactor types have been employed for the thermal and catalytic cracking of polymer waste, such as fluidized-bed, batch or semi-batch reactors, or screw kilns. Main problems for operating reactors are the low thermal conductivity and the high viscosity of plastics. Figure 10 shows a fluidized-bed reactor aimed at limiting the contact between primary volatile products and the polymer/catalyst mixture (Lin et al., 2010).

Fig. 10. Fluidized-bed reactor (Lin et al., 2010) (1) feeder, (2) furnace, (3) sintered distributor, (4) fluidized catalyst, (5) reactor, (6) condenser, (7) deionized water trap, (8) 16-loop automated sample system, (9) gas bag, (10) GC, and (11) digital controller for three-zone furnace.

Figure 11 shows the diagram of a continuous spouted bed reactor, aimed at handling sticky, viscous polymer/catalyst mixtures, also looking for reducing residence time, which would favor the formation of light olefins, instead of secondary products such as methane, aromatics or coke (Elordi et al., 2011).

Fig. 11. Continuous spouted bed reactor (Elordi et al., 2011).
4.2 Reaction conditions

Prior to carrying out the reaction, we activated the catalysts at 400 °C for 1 h inside our reactor. The reactor had fitted glass fiber in order to keep the catalyst in place. For every test, we employed 0.9 g of polymer (LDPE). The polymer was melt at 290 °C and then introduced into the reactor (0.04 cc/min) The temperature of the capillary tube was set at 330 °C and the reactor temperature at 450 °C (Table 6).

<table>
<thead>
<tr>
<th>Polymer (LDPE) feed</th>
<th>0.9 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>15 psi</td>
</tr>
<tr>
<td>Loading section temperature</td>
<td>290 (°C)</td>
</tr>
<tr>
<td>Capillary tube section temperature</td>
<td>330 (°C)</td>
</tr>
<tr>
<td>Reactor temperature</td>
<td>450 (°C)</td>
</tr>
<tr>
<td>Condenser temperature</td>
<td>-2 (°C)</td>
</tr>
<tr>
<td>Reaction time</td>
<td>30 min</td>
</tr>
<tr>
<td>N₂ flow (carrier gas)</td>
<td>10 (ml/min)</td>
</tr>
</tbody>
</table>

Table 6. Catalytic cracking reaction conditions (Hernandez et al., 2010, Ortega et al., 2006).

4.3 Product composition determination

Reaction products can be classified as gas products (C1-C4) and liquid products (C5-C44). Gas products were analyzed by gas chromatography. Identification of some specific compounds can be carried out by coupling gas chromatography to mass spectrometry. Liquid products were analyzed by simulated distillation (ASTM method D-2887), corresponding to gasoline, turbosine (or jet fuel or naphtha), kerosene, gas oil and fuel oil fractions, as described in Table 7.

<table>
<thead>
<tr>
<th>REFINERY FRACTION</th>
<th>NUMBER OF CARBONS</th>
<th>BOILING POINT (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline</td>
<td>C5-C12</td>
<td>39-220</td>
</tr>
<tr>
<td>Turbosine (naphtha, jet fuel)</td>
<td>C13-C14</td>
<td>221-254</td>
</tr>
<tr>
<td>Kerosene</td>
<td>C15-C17</td>
<td>255-300</td>
</tr>
<tr>
<td>Gas oil</td>
<td>C18-C28</td>
<td>301-431</td>
</tr>
<tr>
<td>Fuel oil</td>
<td>C29-C44</td>
<td>432-545</td>
</tr>
</tbody>
</table>

Table 7. Liquid products corresponding to refinery fractions.

5. Results and discussion

We present results we have obtained for the catalytic cracking of low-density polyethylene. Our research group has established a collaboration project with the industrial group ALFA (via its IDDEA Office) for the decomposition of several other polymers. ALFA’s chemical division is based in Monterrey, Mexico, and has several polymer-precursor industrial plants in different countries. Those results are not presented here.

5.1 Gas products

Several compounds can be obtained among the gas products, such as methane, ethane, ethylene, propane, propylene, n-butane, i-butane, 1-butene or iso-buthylene. The
composition of the gas products strongly depends on the catalyst. The gas products distribution obtained with HPA-modified MCM-41 materials can be seen in Figure 12. The gas product consisted of mainly a mixture of ethane, propane and pentane, with very small amounts of ethylene and propylene. The main gas products obtained with Al-MCM-41 and Ga-MCM-41 at the same reaction conditions, were isobutene and propylene (Ortega et al., 2006, Hernandez et al., 2010). We consider that the strong acid sites provided by the HPA resulted into obtaining the smaller ethane molecules. Pentane was propelled into the gas stream by the heated carrier gas.

Fig. 12. Gas products distribution obtained from the catalytic cracking of low-density polyethylene employing heteropolyacid-MCM-41 materials (Hernandez et al., 2010).

5.2 Liquid products

Figure 13 shows the relative proportion of liquid products obtained from the catalytic cracking of low-density polyethylene, corresponding to refinery oil fractions (ASTM D-2887 method), employing modified mesoporous MCM-41 (Al-MCM-41 and Ga-MCM-41), Mexican Natural Mordenite and used and fresh commercial FCC (FCC-Eq and FCC-F) catalysts (Ortega et al., 2006) FCC catalysts were provided by the Mexican Petroleum Institute (IMP). Unlike the thermal cracking of polyethylene (pyrolisis), the catalytic cracking of polyethylene produced a high proportion of liquid products, for the several catalysts tested. A relatively higher yield of heavier liquid fractions was obtained with the Al-MCM-41 and Ga-MCM-41 mesoporous materials, whereas zeolite microporous materials produced a larger amount of lighter gasoline fractions, in agreement with discussion in Section 2.3. The smaller proportion of heavier fractions together with the larger proportion of the gasoline fraction was obtained with the fresh commercial FCC catalyst, however, this catalyst also produced a high proportion of gas products. As we pointed out before, from an economical perspective, promising options are the equilibrium (disposal) FCC catalyst and natural mordenite.
Fig. 13. Liquid products distribution obtained from the catalytic cracking of low-density polyethylene employing different porous solid catalysts (Ortega et al., 2006).

While Al-MCM-41 and Ga-MCM-41 produced a relatively large gasoline yield (Figure 13), the HPA-MCM-41 catalyst at the same reaction conditions, produced a large proportion of heavier hydrocarbon fractions, as gas oil, followed by fuel oil and then, gasoline and kerosene (Figure 14). We consider that even if the HPA70 has a large number of initial
Brönsted acid sites, the high proportion of relatively large hydrocarbon molecules obtained (C18-C44) is due to the impaired, formerly strong acidity of the heteropolyacid, at the considerably high reaction temperature, and to the reduced surface area of the material; therefore a small part of active sites can be reached by the polymer chains.

5.3 Solid products

When we have carried out the polyethylene catalytic decomposition, a small proportion of solid products have been obtained, in the form of waxes. For comparison, we run the same polymer decomposition at the same reactor conditions without any catalyst, being in fact, the pyrolysis of the polymer. The pyrolysis test yield a large proportion of solid products, 90.67% w/w (Ortega et al., 2006).

For the particular case of the catalytic cracking of poly(ethylene terephthalate), we have obtained a large proportion of solid terephthalic acid.

5.4 Relationship between reaction conditions and products

The products distribution varies at different reaction temperatures, in general terms (for zeolites as well as for other acid solids) high reaction temperatures increase the yield of gas products and middle boiling point components (C5-C12 gasolines) whereas lower reaction temperatures increase the yield of heavier components (C13-C18) (Gulab et al., 2010).

As the polymer to catalyst mass ratio increases, the system becomes less active (Gulab et al., 2010), however, this effect can be compensated by higher temperatures or larger reaction times. This relative loss of activity also tends to produce a higher yield of liquid products.

It is not uncommon to observe some condensation in gas containers after the reaction, which can be avoided by reducing the flow rate of the carrier gas. Inside the reaction chamber, the heated carrier gas can cause the evaporation of liquid products and also transports them out of the system.

6. Economic considerations

The most important economic issues that influence the viability of primary and secondary (mechanical) plastic recycling are the price of the recycled polymer compared with virgin polymer and the cost of recycling compared with alternative forms of acceptable disposal (Hopewell et al., 2009).

More individuals, organizations, business, and government agencies are collecting materials for recycling than ever before. The number of curbside recycling programs has grown during the last decade and new economic opportunities allow the birth of new markets. Recycling also creates new businesses that haul, process, and broker recovered materials, as well as companies that manufacture and distribute products made with recycled content. By recycling 1 ton of plastic, you can help save the same amount of energy that two people use in one year, or almost 2,000 pounds of oil (USEPA, 2009).

According to the American Chemistry Council, about 1,800 US business handle or reclaim post-consumer plastics. Plastics from MSW are usually collected from curbside recycling.
bins or drop-off sites. Then, they go to a material recovery facility, where the materials are sorted into broad categories (plastics, paper, glass, etc.). The resulting mixed plastics are sorted by plastic type, baled, and sent to a reclaiming facility. A Mexican study reported that the average cost of one ton of trash is around 350 US Dollars (USD), but if plastics are reduced, the cost would be around 4 USD less (Cortinas, 2009). The investment for recycling of 150 ton could be 300,000 USD producing a monthly utility of 30,000 USD.

The price of virgin plastic is influenced by the price of oil, which is the principle feedstock for plastic production. As the quality of recovered plastic is typically lower than that of virgin plastics, the price of virgin plastic sets the ceiling for prices of recovered plastic. The net heat generation from the use of crude oil in plastic making is roughly $0.4 \times 10^{14}$ kWh from 1939 to 2000. It corresponds to 1.3% of the missing heat and contributes to 0.5% of the global warming (Gervet, 2007).

The profitability of feedstock, chemical recycling methods depends on three key factors: the degree of separation required in the raw wastes, the capital investment involved in the processing facilities and the value of the products obtained (Clark, 1999). For most of feedstock recycling methods, some pretreatment or separation operations are unavoidable. Feedstock recycling methods can be ordered according to the separation steps required (Clark, 1999):

Gasification < thermal cracking < hydrogenation < catalytic cracking < chemical depolymerization

Whereas the value of the products obtained by the feedstock recycling methods follows the opposite order:

Thermal oils < synthesis gas < hydrogenation oils < catalytic olefins and paraffins < monomers

Important benefits of the catalytic cracking of polymer waste with respect to other chemical feedstock recycling methods is the possibility of controlling the selectivity towards desired products and the possibility of reducing energy consumption. The use of cheap catalysts is central under the actual circumstances and some of the current best options are natural materials and waste catalysts from other industries. To use existing industrial facilities is a way for much cost reduction. Since the catalysts and the reaction mechanism of the polymer catalytic cracking are about the same as for the hydrocarbon fluid catalytic cracking (FCC), it is possible to incorporate plastic waste into the FCC refinery feed, with the added benefit that plastic waste has almost no sulfur content and no heavy metals content.

7. Concluding remarks

Active plastic waste catalytic cracking materials involve Brönsted acid sites, present in zeolite catalysts and which we introduced in MCM-41 mesoporous materials by (i) the incorporation of Al and Ga and (ii), by impregnation of the MCM-41 surface with tungstophosphoric acid. The several solid acid catalysts we tested yield gas and liquid products from the LDPE cracking reaction. The gas products consist of a mixture of ethane, propane, butane and pentane, all of them of interest for petrochemical industries or as domestic energy source. Liquid products consist of gasoline, turbosine, kerosene, gas oil,
and fuel oil, corresponding to fuel fractions obtained in industrial petroleum refinery plants. The selectivity towards particular products depends mainly on the choice of catalyst and reaction conditions. The study of the catalytic cracking of plastic waste has led to relevant scientific knowledge and to the development of innovative technologies.

The large-scale application of these processes has been limited by economical and profitability reasons. Previous stages involve plastic separation from municipal waste and, since different mixtures of products are obtained, end stages involve product separation processes. Up to now, it is hard to compete with the still cheap option of producing fuels from natural gas and crude oil and to produce plastics from new raw materials. However, worldwide growing concerns about preserving our environment give plenty of room for imaginative ideas on how to scale up these processes to industry level.

8. References


The presently common practice of wastes' land-filling is undesirable due to legislation pressures, rising costs and the poor biodegradability of commonly used materials. Therefore, recycling seems to be the best solution.

The purpose of this book is to present the state-of-the-art for the recycling methods of several materials, as well as to propose potential uses of the recycled products. It targets professionals, recycling companies, researchers, academics and graduate students in the fields of waste management and polymer recycling in addition to chemical engineering, mechanical engineering, chemistry and physics. This book comprises 16 chapters covering areas such as, polymer recycling using chemical, thermo-chemical (pyrolysis) or mechanical methods, recycling of waste tires, pharmaceutical packaging and hardwood kraft pulp and potential uses of recycled wastes.

How to reference
In order to correctly reference this scholarly work, feel free to copy and paste the following: