Review

Catalytic Pyrolysis of Plastic Waste and Molecular Symmetry Effects: A Review

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Abstract: The present review addresses the latest findings and limitations in catalytic pyrolysis for the processing of plastic waste into valuable fuels. Compared to thermal degradation of plastics, catalytic pyrolysis provides better results in regards to the quality of the obtained liquid hydrocarbon fuel. Different types of catalysts can be used in order to improve the thermal degradation of plastics. Some of the most used catalysts are different types of zeolites (HUSY, HZSM-5, Hβ), Fluid Catalytic Cracking (FCC), silica-alumina catalysts, or natural clays. There is a need to find affordable and effective catalysts in the aim of achieving commercialization of catalytic pyrolysis of plastic waste. Therefore, this study summarizes and presents the most significant results found in the literature in regards to catalytic pyrolysis. This paper also investigates the symmetry effects of molecules on the pyrolysis process.

Keywords: catalyst; pyrolysis; plastic waste; zeolites; symmetry effects

1. Introduction

Plastic is a non-degradable material that can persist in the environment for long periods of time [1]. On the other hand, it is a very special material with a great number of advantages: it is affordable, versatile, light, and resistant [2,3]. Plastic originates from petrochemicals and contains mostly hydrocarbons and some additives, such as antioxidants, flame retardants, and stabilizers, which make the material very bio-undegradable [4]. Thanks to its unvaluable properties, plastic can be used for many different functions [2]. A total of 44.8% of all plastics produced in 2015 were used for packaging purposes, and 18.8% in the building and construction industry [5]. Other big plastic consumers are the textile industry, consumer and institutional products, transportation, and electronics [5]. The exponential growth of plastic production is shown in Figure 1 [6]. Chemical resistance is well known to be one of the most important properties of plastics. As a result, land, water, and oceans become easily polluted by plastic waste, implying serious risks for the survival of living organisms [5] and important impacts on wildlife, natural surroundings, and human health [7–9].

The most used types of plastics are polyethylene (PE), polypropylene (PP), polyvinylchloride (PVC), polyethylene terephthalate (PET), and polystyrene (PS). Usually, their utilization in daily life is in the form of mixtures of monomers, oligomers, and additives [10].

Plastic waste is commonly found as a component in municipal solid waste, with PE and PS as the main components of the heterogeneous mixture [1]. Plastic waste consists of different mixtures of plastic products, such as low- and high-density polyethylene (LDPE and HDPE, respectively), PP, PS, PVC, and PET. Plastic waste is bulkier than other organic residues and therefore a massive space is needed in landfills. This disadvantage is also responsible for the high cost of disposal and incineration of plastic waste. Additionally, plastic waste incineration and disposal lead to abundant emissions of harmful compounds [11,12].

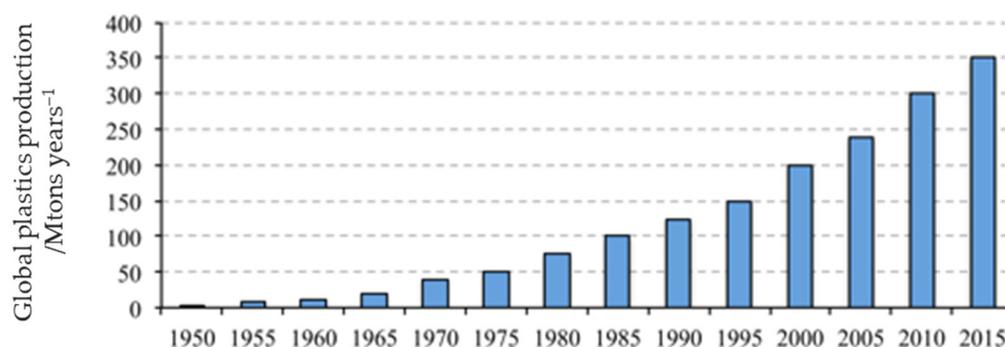As seen in Figure 2, a high percentage of plastic waste was still landfilled across Europe in 2018 [13].

Figure 1. Exponential growth of plastic production over the years (adapted from [6]).
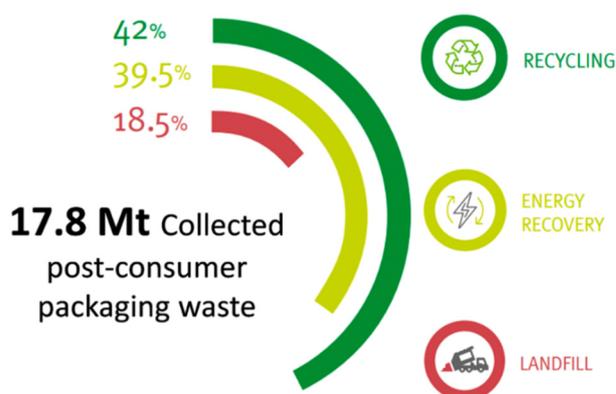

Figure 2. Plastic waste management in Europe in 2018 (taken from [13]).

Waste-to-energy technologies can convert plastic waste into heat, hydrocarbon fuels, and chemicals [14,15]. There are different ways to process plastic waste. Primary or mechanical recycling involves grinding plastics and producing new goods with recycled material. During secondary recycling or incineration, calorific value is generated. Tertiary recycling or pyrolysis is a thermo-chemical process, where the polymer is heated under an inert atmosphere causing polymer cracking [16–21]. In order to limit char formation, pyrolysis should be performed in an oxygen-free or at least oxygen-poor atmosphere [22]. During pyrolysis, plastic is heated to a certain temperature and oxygen is extracted from the reaction chamber. Depending on the working conditions, such as temperature, heating rate, and residence time, there are different types of pyrolysis processes that can be distinguished by hydro-, oxidative, catalytic, steam, vacuum, microwave-, plasma, or electrical heating pyrolysis [23]. Pyrolysis could play an important role in plastic waste management, since it is an environment-friendly solution, allowing for the production of liquid fuels and other products for further applications [24].

Pyrolysis processes have gained a lot of attention in recent times, since they represent a basis to produce a second generation of synthetic fuels, materials, and chemicals [19,25–28]. Pyrolysis is a reaction occurring in the absence of oxygen, whereby organic compounds are decomposed, generating gaseous and liquid products. On the contrary, the inorganic matrix usually remains unaltered [11,29,30].

During the pyrolysis of polymers, macromolecules are broken down into smaller molecules [31]. The advantage of pyrolysis is the production of high energy materials (char, tar, and gas) from low energy solid waste. The conversion depends on the operating conditions used: the heating rate, maximum temperature, processing time at the maximum temperature, pressure, and catalysts used [30,32–34]. The liquid products yield, as well

converting of raw material, which depends on the experimental conditions (process parameters), raw material type (waste or clean, synthetic plastics) and composition (mixture or individual plastic types), reactor type, size of the sample's particles, and time of the reaction. Therefore, for each individual system or pyrolysis plant, it is necessary to clearly define the operating parameters and to investigate the conditions for an adequate yield [35]. Volatile matter, together with ash content, are important factors in determining the liquid yield. When the content in the volatile matter is high, a more abundant production of liquid oils can be obtained. On the contrary, the ash content tends to reduce the amount of liquid oils and increases the formation of char and gases [19].

Pyrolysis can be thermal or catalytic [36,37]. Thermal pyrolysis requires higher temperatures (from 350 to 900 °C), which can lead to a low molecular weight and low quality products [11]. Gases evolved during pyrolysis have a high calorific value, and could be used in different gas machines and engines for the generation of electricity without any other treatments or modifications [38]. The addition of catalysts overcomes the limitations of thermal pyrolysis, by reducing either the reaction temperature or the time [11]. Furthermore, the addition of catalysts improves conversion, reduces activation energy of pyrolysis, and enhances the fuel quality. The most commonly used catalysts for the pyrolysis of plastics are zeolites, polyciliate components, and clays [31,32,39]. Compared to thermal pyrolysis, the catalytic process has the advantage of a lower process temperature, a reduction of solid residues such as carbonized char and volatile fraction, shorter time process, high product selectivity, and high-octane-number products. Zeolite-based catalysts are the best option for the pyrolysis of plastic waste, and for co-pyrolysis of combined plastic waste/biomass [40].

Processing of PVC is not preferred because it leads to the formation of hydrochloric acid (HCl) that can damage process equipment and cause high-temperature corrosion. This drawback can be solved by dechlorination, with an increase of the overall process costs. In addition, PET pyrolysis leads to the formation of oxygenated aromatic hydrocarbons, which cause the lowering of oil quality, decrease of liquid product yield, and damage of the process equipment [41]. Generally, the presence of oxygen and halogen elements in the structure of polymers lead to the reduction of liquid pyrolytic fuel quality [42]. Studies from Li et al. [18] and Fivga and Dimitriou [43] have focused on the economic feasibility of the plastic pyrolysis process. Both studies concluded that the process is economically feasible when the capacity of the facility is scaled up. Another study on the pyrolysis of plastic was reported by Iribarren et al. [44]. This study showed economic and environmental feasibility. Additionally, the production of energy from the process was analyzed, pointing out that, when compared with two traditional waste management approaches such as incineration and landfilling, plastic pyrolysis shows good results.

The aim of this work is to present and analyze the available and current data on the catalytic pyrolysis of waste, with the goal of providing the best examples and suggesting experimental procedures of good practice, and to find gaps and pathways for further development of this topic. The second section of this review explores the thermal pyrolysis of plastic waste, while the third section covers catalytic pyrolysis, with particular reference to the most used catalysts, providing a literature survey of studies on the catalytic pyrolysis of plastic waste. Finally, the fourth section is focused on molecular symmetry effects in pyrolysis processes.

2. Thermal Pyrolysis

Thermal (non-catalytic) pyrolysis of plastic waste is an endothermic reaction which proceeds in the absence of catalysts [1]. In this process, polymer materials are heated to very high temperatures, whereby macromolecules are broken down into smaller molecules. Pyrolysis products are represented by a wide range of hydrocarbons, further classified into a non-condensable gas fraction, liquid fraction (paraffins, olefins, naphthenes, and aromatics), and solid residue. A variety of fuels can be recovered from the liquid fraction—in the range of gasoline (C4–C12), diesel (C12–C23), kerosene (C10–C18), and motor oil (C23–C40).

However, when the process temperature is high, there is an increased production of the non-condensable gaseous fraction and, consequently, a decrease in that of liquid fuels, such as diesel [11,45–48]. A significant yield of the gaseous fraction is obtained by thermal pyrolysis due to the breaking of aliphatic chains in small fragments [49].

In general, the influence of temperature on the distribution of pyrolysis products should be considered together with the influence of other process parameters, such as carrier gas flow and reaction time, as well as other parameters such as the type of plastic, the composition of the plastic mixture, and especially the type of configuration reactor system [35]. Therefore, for each individual system or pyrolysis plant, it is necessary to clearly define the above mentioned parameters, and investigate their effect on the yield [35].

Pyrolysis reactions usually take place in three steps: initiation, propagation, and termination [11]. During initiation, the cracking of large polymer molecules into free radicals occurs. Free radicals and molecular species are cracked into smaller radicals and molecules in the propagation steps. Finally, the generated radicals are combined together during the termination step to obtain stable molecules via the formation of covalent bonds [50].

Thermal analysis can play a crucial role in determining the thermal behavior of thermoplastic and thermoset components in mixtures that simulate real plastic waste. These techniques, which in some cases are coupled with pyrolysis experiments in a pilot scale reactor, can be used for the identification and characterization of polyolefins and multilayer-packaging-based plastic waste or some thermoplastic components of WEEE when they are subjected to a pyrolysis process [51,52].

There are several studies focused on the behavior of different WEEE, such as printed circuit boards, keyboards, video cards, and telephone line at different temperatures. The study of the thermal behavior of mixed plastics from packaging and electric equipment residues revealed the advantages of applying pyrolysis feedstock recycling from an energetic point of view [53].

3. Catalytic Pyrolysis

Catalytic pyrolysis involves the addition of a catalyst, with a higher conversion rate of plastic into oils and higher quality of the products, which is related to the lower temperatures and lower reaction time of the process [1,21]. Catalysts are also used in pyrolysis for the optimization of product distribution and increase of product selectivity, and provide yields similar to the conventional fuels, such as diesel and gasoline [54–57]. Catalysts are usually classified into two groups: homogeneous and heterogeneous. Generally, homogeneous catalysts are in a single phase (reactants, products, and catalysts are in the same phase), i.e., liquid solution, while the heterogeneous catalysts are in solid form [58,59]. The most used homogeneous catalysts for plastic pyrolysis are aluminum chloride ($AlCl_3$), potassium hydroxide (KOH), sodium hydroxide (NaOH), and sodium methoxide (CH_3ONa). Commonly used acidic catalysts are hydrochloric, phosphoric, sulphuric, and organic sulphonic acids. Homogeneous acid catalysts are preferred to base ones, because of the lower activity of the latter [58].

Heterogeneous catalysts are mostly in the solid form, and they are added to solid or liquid or gaseous compounds in the mixture [59]. Heterogeneous catalysts are of more common use, because of their easy separation from the liquid pyrolysis product, which allows the catalyst to be reused and regenerated [60]. Another important advantage of heterogeneous catalysts over homogeneous ones is that they are non-corrosive. The surface area, porosity, arrangement of functional groups, and acidity are important features for the pyrolysis process [58,61]. Most used catalysts are the following: zinc oxide—ZnO; magnesium oxide—MgO; calcium-carbonate—$CaCO_3$; calcium carbide—CaC_2; silicon dioxide—SiO_2; aluminum oxide—Al_2O_3; silicon dioxide alumina doped—SiO_2-Al_2O_3; zeolite Socony mobil-5—ZSM-5; zeolite; red mud; and fluid catalytic cracking—FCC [54,55]. The FCC catalysts are widely used in petroleum refineries for the cracking of heavy oils into gasoline and liquid oil petroleum [1,60]. The FCC contains three parts: zeolite crystals and a non-zeolite

acid matrix that is made of silica-alumina with a binder in the structure [61]. Silica-alumina catalysts have Lewis acid sites, acting as electron acceptors, and Brönsted acid sites with ionizable hydrogen atoms. Acidity of these catalysts influences the production of liquid oils from the pyrolysis of waste plastics. When the acidity is very high, the production of liquid oils is reduced [1]. The presence of open pores in zeolites is the most important feature of this type of catalyst. Zeolites with high acidity are more active in the cracking process, thus increasing the production of light olefins and decreasing the heavy fractions [1,62].

3.1. Catalyst Structure and the Pyrolysis Mechanism

Zeolite catalysts have a crystalline structure that contains primary structural TO4 tetrahedron units. T represents the central atom, mostly Si or Al, surrounded by O atoms connecting the units to each other. Interconnection between the building units leads to three-dimensional microporous structures with different geometries and structural characteristics [62]. Zeolites also promote hydrogen transfer reactions, due to the presence of many acid centers [8]. Silica-alumina catalysts and zeolites result in an increase of the gaseous yield. Lighter molecules, supporting gas formation, are obtained as a consequence of the increased cracking reactions and acidity [62]. Compared with zeolites, silica-alumina catalysts can be assumed not to contain stable crystalline structures with pore volumes larger than those in zeolites, which are microporous [63]. Many studies have been published on the pyrolysis of plastic waste polymers due to the advantageous microporous structure of ZSM-5 zeolite [42,64–66]. These papers also provide exhaustive surveys of the studies performed on the catalytic pyrolysis of plastic waste in the presence of zeolites (ZSM-5).

The activation energy is known to decrease in the presence of catalysts, thus suggesting an increase of the reaction rate, although no information is available on the value of the pre-exponential factor. As a consequence, the use of catalysts reduces the optimum temperature needed for the pyrolysis process allowing for energy saving, therefore reducing the most relevant cost for industries [19].

Catalysts can be placed either in the pyrolysis reactor (in situ) or in a separate catalytic bed (in-line). Catalysts, such as the protonated (H^+) form of ZSM-5 orHZSM-5, protonated form of Y zeolite (HY), protonated form of beta zeolite (Hß), and hierarchical H-style ultra-stable Y HUSY zeolite, promote the carbocationic cracking of pyrolysis volatiles and isomerization, oligomerization-cracking, and hydrogen transfer. The main properties of catalysts that influence the cracking performance are strength and porosity. During the catalytic processing of plastics, the polymer matrix melts upon heating and is dispersed over the catalyst surface. Mechanisms of catalytic pyrolysis also include chain scission, isomerization, oligomerization, H-transfer, and aromatization. The first step of polymer cracking is ascribed to adsorption of the reactant molecule on the acid site, where it undergoes protonation with the formation of carbonium ions. This intermediate promotes the cracking of molecules. As a consequence, the reaction rate is mostly affected by acid site strength, density, and distribution. A catalyst's acid active site promotes cracking of olefinic compounds and hydrogen transfer reactions. When catalyst sites are strongly acidic, the formation of olefins (via end-chain scission) is favored, whereas, when the catalyst sites are weakly acidic, the formation of waxes (random scission) is enhanced. The obtained products (olefins or waxes) undergo further reactions to produce low-molecular-weight compounds [62]. In the study carried out by Cai et al. [67], the catalytic pyrolysis of various plastic types with Fe/Al_2O_3 was studied in order to obtain high value hydrogen, aromatic chemicals, and carbon nanotubes as reaction products. This work showed that plastic polymers tend to decompose through a random scission mechanism, and ethylene obtained from PE decomposition was more involved in the catalytic coke deposition with respect to propylene (from PP decomposition), which further increased the amount of solid carbon. Furthermore, high impact polystyrene (HIPS) and general-purpose polystyrene (GPPS) deposited more carbon than that produced during the catalytic pyrolysis of polyolefin plastics. This is explained by the difference in the molecular structure of the different plastic types, because of the presence of benzene rings in the HIPS and GPPS structures. When

GPPS and HIPS are heated to their degradation temperatures, the large polymer moiety breaks up into smaller aromatic compounds such as styrene or styrene oligomers. When the catalysts are used, the ethenyl group in the styrene molecule is removed and benzene rings are accessible to produce high value hydrogen, aromatic chemicals, and carbon nanotubes as reaction products. At the same time, C-C and C-H bonds in the ethenyl groups are broken. On the catalyst, carbon atoms are dissolved and suddenly recombined by melting iron, thus forming graphitic carbon. The residual hydrogen atoms are responsible for the formation of low-molecular-weight gases. The heavier aromatic hydrocarbon compounds are decisive for the carbon-generating process in comparison to micro alkane and olefin molecules. Due to the higher degree of conversion into solid carbon, the amount of gaseous products obtained from PS is lower than that produced from PE and PP [67].

Paula et al. [6] have performed thermal and catalytic pyrolysis of plastic waste (PE, PP, PS) with ZSM-5 zeolites and modified mordenite (MOR). Mordenite was treated with NaOH in order to improve the pore volume. By treatment with alkali, a mesoporous morphology can be produced in the catalyst, thus preserving its acidity. Mordenite has an irregular pore size, which could contribute to the occurrence of secondary reactions taking place on the catalyst surface. Reactions on the catalyst surface may contribute to bimolecular secondary processes and the production of aromatic compounds, which further lead to lower conversion rates and increase light fraction hydrocarbons. Low conversion rates can also be related to mono-dimensional channel systems and low mesoporosity, which limited the catalyst's access to polymer chains on the active sites. However, the treated ZSM-5 catalyst showed better performance in the catalytic processing of plastics compared to mordenite. Another study where the effect of small pores of the ZSM-5 catalyst was discussed is reported in [42].

3.2. Application of Zeolites for the Catalytic Pyrolysis of Plastic

PE, PP, PS, and PET were pyrolyzed in the presence of HZSM-5 zeolite in a tandem micro-pyrolyzer. Pyrolysis was conducted in situ and ex situ. The in situ catalytic pyrolysis of plastics gave a higher amount of solid residue and led to the production of aromatic hydrocarbons, with the exception of PS. During the ex situ catalytic pyrolysis of PS, a high amount of aromatics was produced compared to the in situ catalytic pyrolysis, with a large production of styrene. In the case of PET, in situ catalytic pyrolysis generated a large amount of CO_2 and a small amount of CO, compared to the ex situ catalytic pyrolysis. Pyrolysis of PE and PP yielded comparable amounts of alkenes and alkanes in ex situ and in-situ catalytic pyrolysis, with the amount of produced alkene higher than the alkane yield during ex situ catalytic pyrolysis. These results show that in situ and ex situ catalytic pyrolysis of plastics have different reaction mechanisms [14]. Another study that also confirmed catalytic pyrolysis of the polymers to depend on the chemical and physical characteristics of the catalysts, and on the chemical and structural nature of polymers, was reported by Marcilla et al. [16].

Colantonio et al. [68] investigated the pyrolysis of plastic residue from a material recovery facility. The goal of this study was to investigated the effect of the HUSY catalyst and hydrogen zeolite socony mobil-5 (HZSM5) catalyst on the quality of the pyrolysis products. The plastic residue used as a feed was composed of 45 wt.% of PE, 30 wt.% of PP, 20 wt.% of PS, and 5 wt.% of PET. Thermogravimetric analysis showed that HUSY reduces the degradation temperature of all plastic polymers, with the highest effect on polyolefins. HZSM5 showed a significant effect on the degradation of PE. The pyrolysis reaction was carried out in a laboratory semi-batch reactor at 370, 450, and 650 °C, on the basis of TG analysis. The use of zeolites resulted in a reduction of the heavy oil fraction and inhibition of wax formation. HUSY showed the best results in regards to the monoaromatic yield, whereas, HZSM5 influenced the production of gases.

A noticeable improvement in the production of light oil to the detriment of tar was obtained in a recent study [68], which carried out catalytic pyrolysis of thermoplastics extracted from waste electrical and electronic equipment (WEEE) using various catalysts

prepared from fly ash. The pyrolytic degradation of common polymers found in packaging materials was recently studied in [69]. The cracking temperature affects the type and number of the segments produced, with higher temperatures favoring the conversion of the polymer chains to monomers and the release of smaller molecules, and lower temperatures are more likely to produce oligomers. Faujasite (FAU) zeolites typically induced the formation of char due to their large cavity volume where secondary reactions can take place [70].

The pyrolysis of multilayered plastic and mixed resin plastic waste in the presence of the iron-modified zeolite ZSM-5 catalyst was examined in the study carried out by Kremer et al. [71]. The FTIR analysis showed that PET was present in the exterior part of the packaging, mixed with PE and PP. Some packaging also contained small amounts of PA. The study showed how the activation energy of pyrolysis decreases in the presence of a catalyst and that the catalyst lowered the content of polyaromatic compounds. Kinetic analysis of the pyrolysis of non-recyclable plastics and its influence on the product yield was studied by Kremer et al. [41]. In this study, plastic waste that was not mechanically recyclable was used. The plastic waste was separated from PVC, so that the main components of the used feedstock were PE, PET, PA, PP, and a very small amount of PS. Two different catalysts were employed in the pyrolysis process. The first catalyst was FCC, and the second one was iron (III) oxide (Fe_2O_3) loaded on the zeolite support ZSM-5 (Fe-ZSM). Pyrolysis was conducted in a fixed-bed reactor, and TG and DTG analyses were carried out at 5, 10, and 15 °C. The study concluded that the order of polymer degradation was PS < PET < PP < LDPE < HDPE. The decomposition temperature of pure PS was in the range between 350 and 450 °C. PET degradation occurs in the temperature range between 390 and 470 °C, whereas PP, LDPE, and HDPE require the highest temperatures (450–510 °C) for degradation. In the presence of catalysts, the pyrolysis of plastic waste is faster and the formation of wax is evidently reduced [41]. Another kinetic study on the pyrolysis of waste plastic polymers (PP, PE, PET, and PS) and three synthetic mixtures, representing commingled post-consumer plastic waste output from recovery facilities, was reported by Tuffi et al. [72]. Volatilization that occurs in one step of mass loss is complete for all polymers tested, with the exception of PET, because of the formation of complex aromatic compounds [72].

Nanoporous MCM-41 (mobil composition matter no. 41), which has suitable properties for catalytic applications of polymers, such as the specific area and pore size, can be used for the degradation of PET [73]. The effect of pore shape on the catalytic performance of zeolites during HDPE degradation was investigated in the presence of several zeolites with different pore sizes. Good results (high conversion rates of HDPE) were obtained using BEA and MFI zeolites, due to their bent pores, which slowed down catalytic deactivation because of carbon deposit, defeating the formation of longer molecules. Sudden blocking of linear pores by a small amount of carbon deposit decreased the MOR zeolite's activity. FAU zeolite had large pores connected through supercages, leading to better mass transfer and a high yield of liquids. On the other side, MWW zeolite had numerous large pores that influenced the slow diffusion of cracked products, enhancing yields of small hydrocarbons. By taking all these findings into account, it can be concluded that the pore shape of the studied zeolites was a crucial parameter for the determination of catalytic activity and product selectivity in the degradation of polymers [74].

Catalytic pyrolysis of HDPE on HZSM-5 and iron-alumina pillared montmorillonite (FAMO) was performed in a conical spouted bed reactor. The acid sites of catalysts affect the activity and the cracking products. When the acid site is stronger, the produced hydrocarbon mixture is lighter. In view of the bulky nature of polymers, another important factor for the activity of catalysts is the availability of the acid sites. In the pyrolysis performed with the HZSM-5 catalyst, the high activity and high selectivity for gases could be explained by the strong acidity of the zeolite, related to the easy and full access to acid sites located on its outer surface. On the other hand, FAMO showed low selectivity towards gases, because of the lower acid strength of catalyst site. However, when pyrolysis

is performed at a temperature of 550 °C, the catalyst showed a better performance in the production of diesel-range products [75].

Garforth et al. [76] have investigated the catalytic pyrolysis of HDPE at temperatures between 290 and 430 °C in a fluidized-bed reactor using HZSM-5, H-mordenite zeolite HMOR, HUSY, and SAHA catalysts. This study showed that initial cracking of HDPE has to be restricted to the outer surface and pore entrances of the zeolite, and the subsequent initial cracked products are decomposed within the catalyst. Zeolite catalysts, namely HZSM-5, HMOR, and HUSY, were more effective in the conversion of polymers into volatile hydrocarbons than SAHA. Another study focused on the influence of the zeolite catalyst (ZSM-5) and red mud was carried out by Lopez et al. [77]. ZSM-5 and red mud were tested on a plastic mixture simulating the municipal plastic waste. Pyrolysis was performed in semi-batch reactor at 440 and 500 °C, respectively. ZSM-5 produced a higher proportion of gases and liquids with aromatics compared to the thermal process. Red mud also showed positive results in plastic waste degradation, although higher temperatures were required than in the process with ZSM-5 [77].

3.3. Application of Natural Catalysts for Plastic Pyrolysis

In order to make the catalytic pyrolysis more affordable, catalyst costs need to be reduced, because scaling up the process on the continuous scale requires a large amount of catalysts that further influences the overall cost of the process [58]. Naturally occurring silica-rich zeolites (clinoptilolite and mordenite) can be used for plastic pyrolysis [64]. Several studies closely examined the application of natural zeolites [78–81]. Natural zeolites frequently have impurities such as Na, Mg, Ca, K, Ti, and Fe that can promote further reactions, therefore, could not be used for the process on a larger scale [64].

Clays may be used as catalysts for plastic degradation. However, they require higher temperatures for pyrolysis than zeolites. Clays act like solid acid catalysts and they have been used in the petroleum industry before zeolites were discovered. Because of their affordable price and availability, clays were extensively studied and applied for the plastic pyrolysis process. The acidity and activity of clays can be enhanced by pillaring them (PILC) and, subsequently, by applying an acid treatment. Layered clay forms a two-dimensional porous network, with a microporous size larger than zeolites. PILC have a grid of voids and they are not as flexible as the parent clays [82]. Mixed plastics (HDPE, PS, PP, and PET) have been pyrolyzed in the presence of modified pillared clays (PILC) and Al-PILC [83]. Budsaereechai et al. [54] have investigated the application of pelletized bentonite clay as a catalyst for the pyrolysis of PS, PP, LDPE, and HDPE. As previously stated, PS contains mainly aromatic hydrocarbons (gasoline-range), whereas longer aliphatic hydrocarbons (for diesel engines) are present in PP, LDPE, and HDPE. The pelletized form of catalysts eliminates the pressure drop and reduces the pyrolysis processing time. Furthermore, due to the high acidity of the bentonite catalyst, no wax is formed during the process.

Experiments were carried out by Auxilio et al. [84] on five zeolitic and clay-based catalysts (pelletized and powdered zeolite-based catalysts and clay) for the pyrolysis of virgin HDPE, HDPE waste, and mixed plastic waste. A two stage thermo-catalytic process was detected and monitored in a bench scale reactor, with a continuous feeding system. This work outlined important information for the possible upscaling process: diesel fuel can be produced by two-stage thermo-catalytic cracking, by optimizing the waste plastic composition. The acid strength of the catalysts is crucial for reaching a good selectivity of the hydrocarbon fraction, since a higher acidity leads to gasoline formation, whereas a lower-to-mild acidity leads to the formation of diesel. In addition, mesopore volume is an important factor for avoiding catalyst coking, especially when the mesopore volume is small and the coke formation is more prominent; a pelletized form of the catalyst is favorable over a powder form, because it avoids the large pressure drop in the reactive distillation column [84].

Five different plastic types (HDPE, LDPE, PP, PS, and PET) were mixed and pyrolyzed in a fixed-bed reactor (temperature up to 400 °C, 90 min). Natural catalysts (clays and dolomite) and a synthetic catalyst (pelletized zinc oxide) were used for the plastic pyrolysis. Based on the calculations of liquid and gas yields, the study has concluded that the use of natural catalysts does not give a significantly different amount of fuel yields compared to synthetic catalysts [31]. Thermal and catalytic pyrolysis of PP, LDPE, and HDPE, as well as mixtures of these three materials, were carried out in a batch reactor, in the presence of calcium bentonite. The presence of a catalyst had accelerated the reaction and improved the quality of the condensable fraction. Furthermore, the reaction time decreased with the increase of the catalyst concentration. This means that the reaction rate increased with increasing the catalyst concentration, due to the high surface area and the catalyst's acidity. The ideal catalyst-to-plastic ratio is found to be 1:3 at 500 °C [17]. By using this optimal ratio, the highest yields of liquids were obtained: 88.5 wt.% for PP, 82 wt.% for LDPE, 82.5 wt.% for HDPE, and 81 wt.% for mixed plastics [17].

An interesting study was carried out by Nguyen et al. [85] in which the pyrolysis of PP waste plastics in the presence of natural-clay-mineral NCM, with $LaFeO_3$ nanoparticles, was studied. The degradation of PP was investigated using thermogravimetry (TG) and differential scanning calorimetry (DSC). The results showed that pyrolysis of PP takes place between 460 and 480 °C, and the formation of coke was observed on the surface of the catalyst. The study also reported that in the presence of the catalyst the cracking component consisted of 49.3% and 34.4% of alkenes and alkanes, respectively. Recently, a comprehensive overview of polystyrene pyrolysis was reported in the literature [86]. The effects of temperature, reactor type, and catalysts on the oil yield were also discussed. When bentonite catalysts are used for the pyrolysis of PS, mostly styrene compounds were formed. On the other hand, zinc catalysts promoted better selectivity of the end products, while the spent FCC catalyst was highly efficient in the production of liquid yields. Calcium oxide represents an economical and very effective catalyst in the depolymerization of PS into styrene compounds.

A modified natural zeolite was used by Miandad et al. [87] as a catalyst for the pyrolysis of plastics containing PP, PS, PET, and PE. In order to improve the catalytic properties, natural zeolites from Saudi Arabia were treated in a novel thermal activation process followed by an acid treatment with HNO_3. The degradation of PET and PE require higher temperatures compared to other types of plastic. PE is a long chain branch structure and its degradation occurs via random chain scission, which requires a high temperature. The decomposition of PET follows the ester link random scission, where oligomers are formed as the resulting compounds. The highest amount of liquid oil is obtained via the catalytic pyrolysis of PS in comparison with those obtained through the catalytic degradation of PE and PP. Liquid oil produced from the catalytic pyrolysis with two selected catalysts showed high aromatic content with aliphatic and other hydrocarbon compounds. The obtained liquid oils had higher heating values (HHV) in the range of conventional diesel.

3.4. Application of Other Types of Catalysts for the Catalytic Pyrolysis of Plastic

An interesting study was conducted by Cocchi et al. [88], where the plastic film residue (PFR) from plastic waste recycling (polyolefin mixture residual) was pyrolyzed in the presence of coal fly ash (CFA) and CFA-derived zeolites, aiming at investigating the catalyst's effect on yields and the quality of the obtained oils. CFA-derived zeolites were produced from CFA by melting in the presence of NaOH, followed by a hydrothermal method NaX/CFA, and by a further acidification HX/CFA. The best results were achieved with HX/CFA, since it reduced the endothermic contribution, and, at the same time, improved the gas and oil yield, as well as the selectivity towards the gasoline-range products.

Dai et al. [89] have studied the conversion of polyolefin waste into low aromatic naphtha in a microwave pyrolysis reactor. Various catalysts were screened in order to choose the best one for the conversion of HDPE into shorter-chain olefins with the smallest aromatic selectivity. Mesoporous silica SBA-15(SiO$_2$)-supported metal catalysts (Al, Co, Ni, Zn, etc.) were tested for the pyrolysis process. Among the tested catalysts, Zn/SBA showed to be the most promising candidate for the pyrolysis of polyolefins. Integration of ZnO altered the mesoporous structure of SBA-15 (Santa Barbara Amorphous) catalyst and increased its acidity. This led to higher catalytic activity for the conversion of polyolefins into shorter hydrocarbon chains with a low aromatic selectivity. In the same study, zeolites were also tested and their performances compared with that of SBA-15 for the pyrolysis of polyolefins. In particular, USY and ZSM-5 were chosen for this reaction. In comparison to SBA-15 catalysts, zeolites seem to have a better cracking performance, but the main constituents in the liquid oil were aromatic hydrocarbons, which are not suitable for converting naphtha into plastic monomers [89].

Hydrocracking of LDPE was monitored over commercial zirconia nano powders with a fixed amount of sulfate and various amounts of Pt [65]. The addition of Pt on sulfated zirconia resulted in an increase in the catalyst's acidity and reduction in the crystallinity of ZrO$_2$. As a consequence, when higher concentrations of Pt were used, gasoline production was increased.

4. Comparison between Thermal and Catalytic Pyrolysis

Many examples were found in the literature where thermal and catalytic pyrolysis of plastic waste were considered and their performances compared. In this section, a short survey of some of the most relevant results is reported.

Thermal pyrolysis of PP and HDPE were investigated by Ahmad et al. [90], by carrying out the pyrolysis reaction in a steel microreactor. The conversion for PP was 98.66% (liquid: 69.82%, gas: 28.84%, and residue: 1.34%) at 300 °C, while the conversion for HDPE at 350 °C was also high, 98.12% (liquid: 80.88%, gas: 17.24%, and residue: 1.88%). Both liquids obtained by pyrolysis of PP and HDPE showed fuel-like criteria.

Thermal degradation and catalytic pyrolysis of real-world waste plastics and single plastic components (PE, PP, PS, and PET) were studied by Muhammad et al. [91]. Pyrolysis was conducted in fixed-bed reactor, and zeolite HZSM-5 was used as a catalyst. Feedstock sample of the real-world plastic contained mostly PE, PP, and PET. The thermal pyrolysis of waste plastic yielded a high amount of oil/wax (81–97 wt.%). By addition of a catalyst the amount of oil/wax decreased to between 44 and 51 wt. %. The TG analysis of individual plastic polymers showed that the degradation temperature of PS is around 420 °C, which is lower than those of PET and PP (around 480 °C). Thermal and catalytic pyrolysis of HDPE waste was studied under an inert atmosphere at 450 °C in a packed bed reactor [92]. Various bed materials (sand, cement, and white clay) were tested to investigate the thermal cracking of HDPE. Sodium hydroxide, HUSY, and Hß zeolite were used to enhance the pyrolysis of HDPE. The highest yield of liquids during thermal degradation of HDPE (82%) was obtained by using a powder bed reactor. In the catalytic pyrolysis, each catalyst was examined with each type of reactor bed. The yield of the products changed when HUSY or Hß were used as a catalyst, with changing of the reactor bed material. Another study where plastics were processed by thermal and catalytic pyrolysis was reported by Saeaung et al. [93]. In this study, HDPE, LDPE, PP, and PLA were obtained. The effect of pyrolysis temperature and catalyst on the liquid composition and yield were studied. Thermal pyrolysis of HDPE and LDPE yielded high amounts of waxes. On the other side, the thermal degradation of PP and PLA led to the formation of liquids and waxes. The TG curves of HDPE, LDPE, and PP showed only one step of mass loss occurring between 400 and 500 °C, because of the similar chemical bonds between the molecular structures. In addition, only one step is expected in the TG curve of PLA, but at lower temperatures (300–400 °C). The maximum degradation temperatures were found at 490, 473, 454, and 371 °C for HDPE, LDPE, PP, and PLA, respectively. The difference in the degradation

temperatures can be ascribed to the chemical structure of each plastic type. HDPE has a linear structure, whereas LDPE is more branched. As a consequence, the heat transfer can be favored within the latter matrix. In another study [37], the authors used polyethylene film waste and different catalysts, aiming to investigate the influence of their presence on the formation of high-quality liquid oil. The best results, in terms of the reduction of wax consistency, were obtained by using HUSY, Zeocelcliopilolite, HBEA, and Na-Y-Geace.

Thermal and catalytic pyrolysis of LDPE, HDPE, and PP, and mixtures of LDPE and PP, were performed under a nitrogen atmosphere in a laboratory-scale batch reactor at 460 °C. For the catalytic pyrolysis run, a zeolite-type catalyst was used. The application of a catalyst reduced the degradation temperature of the polymers, which implied a reduction of the energy consumption of the process. Thermal cracking of PP yielded about 86 and 94 wt.% of liquids for PP and LDPE, respectively [36]. The effect of the catalyst fraction (powdered acidic ultrastable Y zeolite—HUSY) on the pyrolysis of HDPE was also investigated [94]. The study showed how the conversion to volatile products changes with the catalyst fraction in the system with two different reactor temperatures (693 and 643 K), under a nitrogen atmosphere for 25 min. It was found that at 643 K the catalyst fraction of 11 or 20% was not enough for the complete reaction of the polymer. When the temperature was increased to 693 K, the conversion decreased when the catalyst fraction was increased. At this temperature, 11% of catalyst was enough to accomplish the whole polymer conversion. Adding more catalyst would lead to the negative effect of converting more polymer into coke. Secondary reactions took place when the strength of the acid sites of higher catalyst fractions was high. Furthermore, the overcracking of primary products into smaller molecules was found, owing to the secondary reactions, so that more gaseous products were obtained. Consequently, the product distribution was shifted towards lighter hydrocarbons. Raveh-Amitet et al. [95] have examined thermal and catalytic pyrolysis of HDPE with ZSM-5 and Zeolite Y. The decomposition of HDPE was also monitored with and without catalysts using TG. Among the tested zeolites, ZSM-5 [25] led to the most significant decrease of the decomposition temperature. This result is worth noting, since a decrease of temperature leads to a lower energy consumption. Susatriawan et al. [96] have investigated the effects of zeolite size during the occurrence of the pyrolysis of LDPE. It was concluded that the smaller size of the zeolite influenced the rates of both heat transfer and pyrolysis, the pyrolysis temperature, the reaction rate, and the yield of oil.

Plastics from waste electrical and electronic equipment, namely WEEE, can be also pyrolyzed in order to obtain oil yields. In the study by Santella et al. [70], this type of waste was pyrolyzed in a bench-scale semi-batch reactor. Plastic was thermally and catalytically pyrolyzed. HUSY and HZSM-5 were used as catalysts in the catalytic run, at a temperature of 400 °C. The thermal run was conducted at 400, 600, and 800 °C. The highest oil yields were obtained in the presence of HZSM-5, and at 600 and 800 °C without catalysts. More solid particles were collected when HUSY was used. The presence of catalysts contributed to reach higher yields of lighter and viscous oil yields, and the products contained a higher concentration of monoaromatics under catalytic conditions, when compared to the oil produced in the thermal pyrolysis run. Waste polypropylene plastic was treated with pyrolytic (thermal and catalytic) processes using a batch reactor and FCC as a catalyst. Thermal pyrolysis gave the maximum amount of liquid oil, while the catalytic pyrolysis reduced its yield, and increased that of gas [97]. Finally, Onwudili et al. [98] used FCC, Y, and ZSM-5 zeolites for the catalytic pyrolysis of a plastic mixture containing HDPE, LDPE, PP, PS, and PET that simulated municipal solid waste. The application of catalysts resulted in an increase of the gas yield and a decrease in that of oil.

Finally, all the information gathered for thermal and catalytic pyrolysis are summarized in the Table 1.

Table 1. Comparison between thermal and catalytic pyrolysis.

Thermal Pyrolysis	Catalytic Pyrolysis
Requires high temperatures	Lower reaction temperature
Resulting oils have low quality	Better conversion rate, with reduction in reaction time, temperature, and activation energy
Gases from the process can be used for different gas engines	Improved oil quality and better distribution of hydrocarbons
Production of a wide range of HC and solid residues	Smaller fractions of solid residue
	Homogeneous or heterogeneous catalysts

5. Molecular Symmetry Effects in Pyrolysis Processes

No studies are available in the literature specifically focused on the relevance of molecular symmetry in the pyrolysis of plastics. However, some conclusions can be drawn on the basis of the research carried out on the effects of molecular symmetry and steric and geometrical issues caused by different molecules that are subjected to pyrolysis process, especially in the presence of catalysts. In this section, relevant examples are presented and the results critically discussed.

Several studies have explored the different aspects of molecular symmetry of certain molecules when pyrolysis takes place under different experimental conditions. In the study by Serinyel et al. [99], pyrolysis of the four symmetric ethers, diethyl ether (DEE), di-n-propylether (DPE), di-isopropylether (DIPE), and di-n-butyl ether(DBE),was performed in a jet-stirred reactor, and the main products were CO, CH_4, H_2, and C_2H_4. Furthermore, all ethers produced the n/2 alcohol and olefin as the result of a molecular reaction (to a small extent). This study aimed to give new kinetic information on the product analysis of the four symmetric ethers. Another study dealt with pyrolytic decompositions of symmetrical and unsymmetrical organotellurium (II)-compounds: Pr_2Te, di-*tert*-butyl telluride Bu_2Te, $(allyl)_2Te$, $(2-metylally)_2Te$, and $(3-metyl-3-butenyl)_2Te$. A combination of gas chromatography and gas chromatography/mass spectroscopy were applied and it was found that the pyrolytic decomposition occurs via bond homolysis [100]. In recent years, many authors focused their attention on the analysis of degradation kinetics of polymers and plastic waste [101,102]. In the study by Tian et al. [103], the kinetic behavior and release of evolved gases during the pyrolysis of waste tea was investigated by the TG-FTIR technique. As far as the kinetic analysis was concerned, three model-free, and three model-fitting models were selected for describing the mechanism of the pyrolysis process. The results showed that the three-dimension diffusion (spherical symmetry) model (D3) fits well to model the pyrolysis mechanism of waste tea. Diffusion mechanisms were also determined for the reaction kinetics of the degradation of nanocomposite materials based on copolymers of styrene and n-butyl methacrylate with either graphene oxide or functionalized graphene oxide [104].

Haas and Ring [105] have examined the thermal degradation of SiH_4 and Si_2H_6 in the presence of C_2H_2. This decomposition was studied with orbital symmetry considerations. The activity of a catalyst is mainly determined by its structures. Since the catalysts have a certain degree of porosity, and the pores have an irregular shape, it is difficult in this case to analyze the symmetry effects of catalysts.

In the pyrolysis of macromolecules such as waste plastic or any other material, where the aim is to produce diesel or oil, the size of the zeolites pores is crucial, since it does (or does not) allow the diffusion of heavy compounds. As already noted, (Section 3.2), zeolites are microporous, but there is the possibility of forming mesopores in order to overcome this limitation. One possibility is to use organic surfactants during the synthesis of zeolites. Another option is dealumination, which comes together with damaging of the crystal matrix and the decrease of active acid sites [42]. The size of the pores is an important factor in determining the products and reactants that can reach the active sites of the catalyst [106].

A basic scheme of polymer degradation in the presence of an acid catalyst is presented in Figure 3. Thermal cracking takes place on the outer surface of the solid catalyst, while the internal pores behave as channels for selective passage and further breakdown of larger hydrocarbons. As a consequence, gases are mainly produced in the small pores, while waxes are produced on the outer side of the catalyst. At the catalyst surface, low-molecular-weight hydrocarbons are produced that are volatile at the reaction temperature and can diffuse through the molten polymer film as final products, or can react further within the pores. The catalytic reaction is improved by microporous catalysts, producing gases and lowering the liquid product yield, with a better quality than in the case of catalytic pyrolysis with macropores [107].
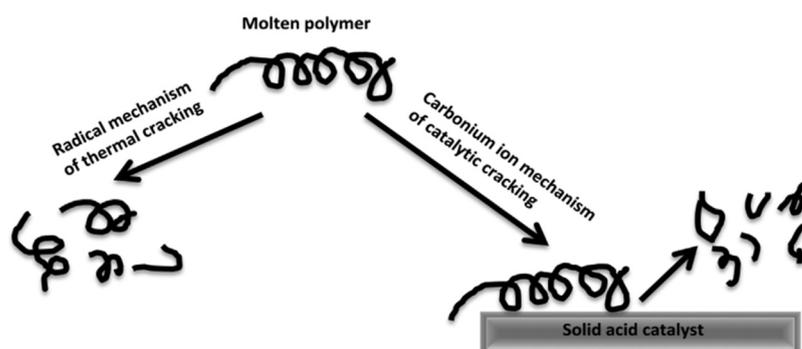

Figure 3. Polymer cracking over a solid acid catalyst [107].

The porous structure is important when catalysts are used in situ [108]. If the catalyst is used directly, the material recovery, which is one of the main goals [109], is difficult, because the catalyst pores are blocked, since plastic feedstock becomes sticky [1]. However, when catalysts are used directly, the quality of the obtained liquid oils is improved, but formation of coke or impurity is more greatly favored. The tridimensional porous structure of the ZSM-5 catalyst results in less coke deposition because of the circulation of aromatic coke, forerunner to the outer part of zeolite micropores. The increase in the surface area improves the interaction between the catalyst and pyrolysis gas, which results in cracking to gaseous products. Y zeolite has a high surface area and it contributes to the formation of gaseous products, while a natural catalyst with a low surface area favors the formation of liquid products [58]. Polyethylene can diffuse into the HZSM-5 pores in contrast to that observed for other polymers such as polypropylene. In addition, polyethylene's branches and chain ends can diffuse into the HZSM-5 pores and make contact with the acid sites, thus causing an increase in the catalytic reactivity. HZSM-5 has strong and weak acid sites, while HUSY has only weak acid sites. Strong acid sites are able to favor the degradation and cracking of heavy hydrocarbons [63].

Small pores influence the diffusion of vapors and small molecules into the cavities, with subsequent conversion of these molecules into aromatic compounds. The bigger size of the catalyst cavities is an advantage for the conversion of macromolecules into smaller species and for the reduction of mass transfer resistance of the intermediate compounds. However, long-chain or branched structures cannot enter cavities and they crack on the catalyst surface. Unfortunately, this cracking process leads to coke formation and the deactivation of catalysts.

A study on the connections between polymers (polyethylene) and the contact surface of zeolites as catalysts with different characteristics (hierarchical and standard Beta zeolites, Y zeolite, ZSM-5, ZSM-12, and MCM-22) was conducted by Calderia et al. [108]. The hierarchical Beta zeolite resulted to have a superior external area because of the use of a bulky silanized agent in the synthesis. In the cracking reactions, the polymeric macromolecules mostly interacted in the outer surface of the catalysts because of diffusional limitations. Zeolites with bigger external area values—hierarchical Beta, standard Beta, ZSM-5, and MCM-22—required lower temperatures for degradation, with a high conversion efficiency.

Microporous zeolite material shows high thermal stability and stronger acid sites. However, the selection of the zeolite has to be focused on target selectivity, which further implies that HZSM-5 zeolite enhances the production of olefins, whereas hierarchical Beta and HY zeolites promote the production of middle distillates [110]. In addition, the kinetics of the plastic pyrolysis reaction, in the presence of the ZSM-5 zeolite catalyst, modified with iron (III) oxide, was recently investigated [111]. The improvement of the reactivity on the catalyst's surface is due to the doping of the zeolite with iron.

Plastic degradation in the presence of heterogeneous catalysts experiences mass-transfer limitations because of the bulky and viscous origin of the plastic polymers. In order to overcome this constraint, very structured mesoporous silica can be used as a catalyst. The ordered mesopores allow better diffusion of the polymers, and they can also improve plastic cracking by speeding up the degradation rate and increasing the yield of liquid products [62]. A number of studies have examined the catalytic pyrolysis of plastics with mesoporous catalysts [64,112–116].

Y zeolites were found to positively affect the selectivity and thermal stability of catalytic plastic degradation. They increased the formation of light hydrocarbons, and moved the selectivity towards gasoline and diesel fuels with lower olefin concentration. Furthermore, this specific type of catalyst allows a high number of reuses, and shows effective performances in plastic conversion at lower temperatures (<500 °C) compared to other catalysts. Thus, less acidic Y zeolites with lower alumina content (higher Si/Al ratio) reduces the cracking activity, while Y zeolites with a lower Si/Al ratio produce high yields of aromatic hydrocarbons such as benzene and toluene. This is due to the combination of different factors, such as high surface area, large pores, and strong acid sites, as the most important [72].

The use of catalysts leads to the production of valuable liquid fuels with a narrow hydrocarbon distribution in the petrol range ($C_5 \sim C_{12}$) [58]. Furthermore, the decrease of the reaction temperature reduces the energy supplied as heat for the extremely endothermic reactions involved in the process. A better conversion of plastic is obtained by using an acid catalyst with meso- and micropores. Polymer cracking occurs in mesopores and further cracking is favored by the presence of micropores [58].

Structure–property relationships can be used to assess the potential applications of symmetrical and unsymmetrical azoalkanes of the general formula $R'-N = N-R$ and related azoxy, hydrazone, as well as azine, derivatives as novel flame retardants for polypropylene, either alone or in combination with commercially available flame retardants [117]. Although bromine-containing compounds—in combination with antimony oxide—are very efficient flame retardants [118,119], attention is given to monitor the Br content [118,119] and to try to reduce its amount, in the effort to develop more environment-friendly systems [117].

6. Conclusions

Plastic utilization is increasing all over the world, and the problem of plastic waste generation is a growing concern. Plastic waste pyrolysis seems to be a promising method for plastic waste reduction. Pyrolysis of plastic waste is an oxygen-free process, which results in polymer cracking with the formation of gaseous and liquid products that can be used as valuable chemicals or fuels.

Plastic pyrolysis can be thermal or catalytic. However, the results of many studies available in the literature lead to conclude that the latter presents more benefits compared with the former. Some of the most important advantages include the supposed increase of the pyrolysis rate due to the reduction of activation energy, narrow hydrocarbon distribution in the products, and the decrease of reaction time.

Catalysts can be homogeneous or heterogeneous, with the latter more often applied due to their easy separation from the liquid products. The most commonly applied catalysts for plastic pyrolysis are zeolites, natural clays, and silica-alumina catalysts. However, the reaction products depend on the type of applied catalyst. The activity of the catalyst

depends on its structure. Therefore, as far as the pyrolysis of plastic polymers is concerned, the size of the catalyst pores is an important factor influencing the pyrolysis outcome. The presence of ordered mesopores provides a more effective diffusion of the polymer molecules leading to better cracking, with the polymer cracking taking place in the mesopores, and further cracking enhanced by micropores.

Although molecular symmetry is not usually considered in the literature addressing the pyrolysis of plastics, some conclusions were drawn in the present investigation by taking into account some case studies on the pyrolysis of molecular substances different from plastics. In these examples, the effects of molecular symmetry and steric and geometrical issues, especially in the presence of catalysts, have been critically discussed.

This paper shows that thermal and catalytic pyrolysis of plastic wastes are extensively studied processes, and that the number of publications investigating this topic is strongly increasing, thus demonstrating the intensive academic and business attention for this matter in recent years. An improvement of the investigation on catalytic pyrolysis with particular reference to the composition and morphology of the catalysts used seems to be expected in the foreseeable future.

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