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The Present and the Future of Polyethylene Pyrolysis †

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Abstract: Most plastics used in the market are based on petroleum. Because of their chemical inertness and durability, plastics are essentially non-biodegradable. Previously, plastic waste management typically focused on reusing and recycling into valuable products. However, virgin plastic resins and their chemical processing to produce new plastic products are more economical than recycling. As such, most plastic wastes end in dumpsites and sanitary landfills. Waste-to-energy conversion is a viable solution to the alarming rise of plastic proliferation in the Anthropocene age. The conversion of plastic wastes into valuable products such as liquid oils, fuel gas, and solid chars through a high-temperature pyrolytic process could lead to a source of alternative fuels. In this paper, the application of the pyrolysis process for polyethylene was discussed. Several process parameters were seen to influence the characteristics of the final pyrolysis products, such as the operating temperature, type of catalyst, and presence of agitation. Optimizing these key parameters is essential for the industrial adoption of the pyrolysis of plastics.

Keywords: polyethylene; pyrolysis; plastics

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1. Introduction

The discovery of plastics resulted in a great paradigm shift in human activities. For over five decades, the global value chain relied heavily on plastics because of their highly-desirable properties such as ease of manufacturing, flexibility to meet the users' demands, high tensile strength, chemical inertness, durability, high insulative capability, and low cost. Indeed, it has been an integral part of human lives and accelerated our progress as a specie. Moreover, it has been a key driver of innovation s in various sectors such as construction, healthcare, electronics, automotive, packaging, and others.

However, with the rapid population growth, human consumption of commodity plastics also increased unprecedentedly. Plastics are slow to decompose; they require hundreds of years to complete decomposition due to their rigid chemical structure. Because of this, plastic waste has accumulated in the environment. As of 2015, approximately 6300 Mt of plastic waste had been generated worldwide. Of this amount, only a staggering 9% (600 Mt) had been recycled, and only 10% of this amount has been recycled more than once despite efforts by various environmental sectors to promote recycling. Around 12% (800 Mt) of plastics are incinerated, while the remaining 79% (4900 Mt) end up either in landfills or in the natural environment [1]. The share of plastics in municipal solid waste (by mass) increased from less than 1% in 1960 to more than 10% by 2005 in middle- and high-income countries [2]. Moreover, global solid waste generation, strongly correlated with gross national income per capita, has grown steadily over the past five decades [3].

The global plastic pollution cycle is defined as the continuous and complex movement of plastic materials between different abiotic and biotic ecosystem compartments, including humans [4]. Indeed, the continuous generation of plastic waste affects humans and the geologic cycle. In particular, plastic debris has been found in all major ocean basins [5], spending millions of dollars for coastal clean-up operations. In 2010 alone, an estimated 4 to 12 million metric tons (Mt) of plastic waste was generated on land and entering the marine environment [2]. The contamination of freshwater systems and terrestrial habitats has also increased alarmingly [5–7]. Thus, the near-permanent contamination of the natural environment with plastic waste is a growing concern. Plastic waste is now so ubiquitous in the environment that it has been suggested as a geological indicator of the proposed Anthropocene era. Suppose our current waste management practices continue in the years to come. In that case, it is estimated that around 12,000 Mt of plastic waste will be in landfills or the natural environment by 2050 [1].

The amount of mismanaged plastic waste generated by the coastal population of a single country ranges from 1.1 MT to 8.8 million MT per year. The top 20 countries with the most mismanaged plastics encompassed 83% of the total plastic waste in 2010. The Philippines ranked third among these countries, just next to China and Indonesia. Of course, the entire annual waste generation is primarily a function of population size, with the top waste-producing countries having some of the largest coastal populations. However, the percentage of the mismanaged waste is also important when assessing the largest waste contributor available to enter the environment [2]. In particular, although the Philippines produces only 0.5 kg/person/day of solid waste, its inefficient management contributed significantly to the mismanaged plastic waste amounting to 1.83 million MT/year, or 83% of the total plastic waste generated. For comparison, the United States has a relatively large waste generation rate (2.58 kg/person/day) but only ranks 20th among the top mismanaged plastic producers, contributing about 0.9 million MT/year. Sixteen of the top 20 producers are middle-income countries, where fast economic growth is probably occurring, but waste management infrastructure is lacking (the average mismanaged waste fraction is 68%). Only two of the top 20 countries have mismanaged fractions < 15%; here, a relatively low mismanaged rate results in a large mass of mismanaged plastic waste because of large coastal populations [2].

The only way to permanently eliminate plastic waste is by destructive thermal treatment, such as combustion or pyrolysis [1]. Combustion or incineration is being practiced worldwide, but the increasing concerns about its impact on atmospheric chemistry hampered its application in some countries. Take the Philippines, for example, which banned incineration by enacting the Philippine Clean Air Act of 1999 [8]. However, pyrolysis is the only remaining choice to eliminate plastic waste to not lessen landfill congestion, especially in developing countries. This is especially attractive because pyrolysis products, i.e., oils, chars, and gases, can be used as fuels in manufacturing plants, potentially shifting the treatment of used plastics as waste to feedstocks for waste-to-energy solutions [9–11]. As such, the circular economy, which started in the European Union and is slowly being adopted among various countries, can be realized [12].

Herein, we present a short review of pyrolysis using plastics as feedstock. Specifically, we look at the pyrolysis of polyethylene and its future research trends.

2. Pyrolysis of Polyethylene

Pyrolysis generally refers to the thermal degradation of long-chain polymer molecules into smaller, less complex molecules by applying heat and pressure. It requires intense heat for a minimal processing time in the absence of oxygen to produce oil, gas, and char, which are highly valuable and can be used as fuel sources to power several industries, such as petrochemical and chemical manufacturing plants. For example, liquid oil can be used in furnaces, boilers, turbines, and diesel engines without equipment overhaul or retrofitting [13]. Pyrolysis can produce high pyrolysis oil by up to 80 wt.% at around 500 °C [14]. Like any manufacturing plant, the process parameters can be manipulated to optimize the product yield depending on the energy requirements of the end users. Although energy-intensive, it is considered a green technology because the supposed gaseous emissions also have a substantial calorific value that can be used to fill the energy requirement of the pyrolysis plant [15]. Furthermore, compared to recycling, it has more flexibility regarding materials handling because it does not need an intense sorting process, thus less labor-intensive. Because of these advantages, considerable research attention was given to the pyrolysis of different plastics. Research interest continues to grow in the search for improved process conditions to lower energy requirements, maximize product yield and minimize unwanted reactions.

2.1. Polyethylene Terephthalate

Polyethylene terephthalate (PET) is mainly used for packaging various food products such as bottled water and soft carbonated beverages primarily because of their suitability to be molded into lightweight and pressure-resistant containers. PET has an average HHV of 23,090 kJ/kg [16], which is relatively lower than other plastics. Nevertheless, the abundance of waste PET and its high volatile matter content makes it an attractive feedstock for pyrolysis.

Çepelioğullar and Pütün [17] found that the thermal degradation of PET starts at around 360 °C. They found that the maximum degradation of PET occurred at 427.7 °C (79.78% of its initial weight was degraded), which they explained to be due to the decomposition of the PET's structural backbone. On the other hand, Girija et al. [18] found that maximum degradation (approximately 60%) occurred at a relatively higher temperature (440 °C). They also showed that PET undergoes single-stage degradation during thermal pyrolysis. Holland and Hay further explained the detailed mechanism of PET degradation [19]. Accordingly, during pyrolysis, PET undergoes intramolecular backbiting and β-C–H hydrogen transfer which causes its degradation at elevated temperatures. They also found that PET loses more aliphatic parts as the reaction proceeds than aromatic ones.

Niksiar et al. [20] designed a spouted bed to study the kinetics of the pyrolysis of PET in the temperature range of 450–560 °C. They found that the thermal degradation of PET follows a first-order kinetic model, and its reaction rate constant follows the Arrhenius equation. Internal conduction resistances were negligible due to the excellent mixing of the particles and the high gas flow rate in the spouted bed reactor. Their study showed that kinetic constraints only limit the pyrolysis of PET. PET yields mostly gaseous products upon undergoing pyrolysis. In particular, Fakhrhoseini and Dastania [14] obtained yields of 29.14–38.89 wt.% liquid oils, 5.74–8.98 wt.% solids, and 52.13–65.12 wt.% gaseous products depending on the heating rate used during pyrolysis. Analysis of the pyrolysis products of PET by Dimitrov et al. [21] showed that the main decomposition products are carbon dioxide, acetaldehyde, benzoic acid, and 4-(vinyloxycarbonyl) benzoic acid. They found that the composition of the pyrolysis products varies depending on the contaminants initially present in waste PET.

2.2. High-Density Polyethylene

HDPE is known for its high tensile strength because of its long linear polymer chains and lower branching than LDPE. It is typically used to make bottles, other containers, toy parts, and corrosion-resistant piping. In addition, HDPE has a very high volatile matter content and low ash content.

The catalytic conversion of HDPE to useful products was investigated by Ahmad et al. [22] in the presence of $BaTiO_3$-based catalysts in a micro steel reactor at 350 °C and 30 min reaction time. Their results showed that the type of catalysts used during pyrolysis affects the conversion and the composition of the products in terms of the carbon range (C_6 to C_{30}) and hydrocarbon group types (paraffin, olefins, naphthenes, and aromatics) produced. Among the catalysts used, Pb-Co/$BaTiO_3$ gave the maximum yield of liquid products (86%) when used in 1 wt.% loading. Undoped $BaTiO_3$ led to the formation of C_6–C_{12} and C_{13}–C_{16} range of hydrocarbons while doping it with Pb or Co enhanced the yields of C_{17}–C_{20} and C_{20}–C_{30} hydrocarbons, respectively. Regardless of the catalysts used in the reactor, they showed that catalytic pyrolysis increases the formation of paraffin and reduces the formation of olefins and naphthenes obtained in the pyrolysis products.

Aboulkas et al. [23] performed a kinetic study of the thermal degradation of HDPE at four heating rates (2, 10, 20, and 50 K/min) using isoconversional methods (Friedman, Kissinger– Akahira–Sunose, Flynn–Wall–Ozawa) for the analysis of their activation energies. Their results showed that activation energy is practically constant in the 0.1–0.9 conversion range, which suggests that the pyrolysis of HDPE occurred in a single-step process. Furthermore, they calculated the activation energy of HDPE to be 238–247 kJ/mol. They established that a "contracting sphere" model could be used to explain the reaction mechanism of the thermal degradation of HDPE.

Obeid et al. [24] studied the pyrolysis of HDPE waste products using thermal and catalytic cracking in a packed bed reactor operating under an inert atmosphere at 450 °C. They obtained pyrolysis products ranging from paraffin ($\leq C_{44}$), olefins ($\leq C_{22}$), aromatics ($\leq C_{14}$), and alcohols (C_{16} and C_{17}). In addition, they studied several reactor bed materials: the yield of paraffin increases in the order of Cement > White clay > Silica Sand, whereas the yield of olefins was in the reverse order. Because of the high paraffin produced, they concluded that HDPE oils are more suited to be used as a fuel rather than a chemical feedstock. Interestingly, the product distribution, i.e., carbon-chain length, was narrowed to C_{10}–C_{28} when the zeolitic catalysts were used with a significant aromatics yield. This shows that, again, depending on user demands, the product composition of pyrolysis products can be altered by using different bed materials.

2.3. Low-Density Polyethylene

LDPE was first produced in 1933 by Imperial Chemical Industries (ICI) using a high-pressure process via a free radical polymerization reaction. Compared to HDPE, LDPE has more branching, resulting in lower tensile strength and hardness. However, LDPE has better resilience than HDPE, thus making it easier to be molded to the desired applications. In addition, it has excellent water resistance and is therefore widely used for producing plastic bags and packaging materials. Because of the wide use of LDPE in the packaging industry, it is one of the most common wastes seen in municipal solid wastes.

Onwudili et al. [25] studied the composition of the pyrolysis products of pure LDPE over a temperature range from 300 to 500 °C in a closed batch reactor. They observed that at a temperature of 350 °C, only 0.7 wt.% of gas is formed, but as the temperature increases to 400 °C, LDPE decomposed and yielded 94.7 wt.% of tar. Conversion to oil only started at temperatures above 410 °C, and the total conversion of LDPE was accomplished at 425 °C and above. Pyrolysis of LDPE yields 89.5 wt.% liquid oil and 10.0 wt.% gas at 425 °C. Further increase in the pyrolysis temperature decreased the oil yield due to cracking and secondary reactions, increasing the gas yields and char formation. For example, at 500 °C, significant char formation occurred (15.5 wt.%), and gas production increased (47.0 wt.%) with a corresponding decline in oil yield. Here we see that the product composition can easily change depending on the temperature profile inside the pyrolysis reactor.

Shah et al. [26] catalytically pyrolyzed waste LDPEs in a home-assembled batch reactor under atmospheric pressure. LDPE decomposition was a single-step process between 175.5 °C and 400 °C. In typical thermal pyrolysis, the maximum conversion was obtained at 400 °C, yielding 12.0 wt.% liquid oil and 13.36 wt.% gas. The optimum conditions, with respect to LDPE conversion, are as follows: SiO2 (1 g catalyst/5 g LDPE, 180 min residence time, 350 °C, liquid yield = 69.73 wt.%) and CaC_2 (1 g catalyst/5 g LDPE, 60 min residence time, 350 °C, liquid yield = 79.10 wt.%). They found that CaC_2 is the best catalyst choice if shorter pyrolysis time is desired, while SiO_2 is the best choice if maximum LDPE conversion to pyrolysis products is desired. Furthermore, CaC_2 is selective toward forming aliphatic products, while SiO_2 is selective towards polar and aromatic products. Analysis of the liquid products showed that SiO_2-derived oil is gasoline-like while CaC_2-derived oil is diesel-like. Here we have seen that catalyst type affects the selectivity of the pyrolysis products, thus affecting the end-use of these fuels. This means that by modifying the catalyst, we can fine-tune the product distribution, properties, and yield to meet the demands of the end users. Furthermore, this study showed that varying the reactor conditions affect the conversion of LDPE to high-value pyrolysis oil. Thus, optimizing the reactor conditions is necessary to achieve maximum value from plastic waste.

3. Research Gaps

While studies on the pyrolysis of plastics date back to the early 1970s, most studies are focused on investigating the effect of several process parameters on the yield and quality of pyrolysis-derived products. Table 1 summarizes the performance of various plastics that have undergone pyrolysis. Since pyrolysis is a thermal-activated process, temperature dramatically affects product distribution and speciation. In general, increasing the temperature increases the overall degradation of plastics. Depending on the type of plastic, the minimum temperature to activate pyrolysis also varies. High yields of char and gaseous products are formed at very high temperatures. Catalyst type affects the species present in each product and alters the required residence time for pyrolysis. By designing the catalyst, a wide variety of products can be formed to meet the demands of the end users. Agitation also affects the overall kinetics of pyrolysis because it controls the temperature profile across the reactor, especially for highly-viscous plastic melts. Some researchers optimized the process parameters to maximize the liquid oil yield. However, these "optimization studies" does not capture the interaction across several parameters because only one-factor-at-a-time studies were done. While this may capture the local optimum, operating the process at the global optimum is desired to maximize yields. Moreover, economic constraints have not been considered in their "optimization studies", something which should have been done to balance the trade-off between process efficiency and process economics.

Table 1. Summary of Studies on the Pyrolysis of Plastic Wastes.

Plastic	Pyrolysis Conditions	Results	Reference
PET	550 °C and 850 °C	Maximum gas yield using of Ni/ZSM-5 catalyst: 550 °C = 30.6% and 850 °C = 70.6%	[27]
	450–600 °C	ZSM-5 zeolite enhanced gas production but caused a decrease in waxy products. The yield of solid residue is lower when using nickel chloride as a catalyst than ZSM-5	[28]
	400–400 °C	Best quality of reformed oils: 5% catalyst loading, 10% nickel loading, and at 450 °C	[29]
HDPE	500 °C	Pyrolysis oil yield: WCE (80%) > CaO (78%) > WCE/HZSM-5 (63%) > HZSM-5 (61%) > Ni-WCE/HZSM-5 (50%) > Ni/HZSM-5 (44%)	[30]
	550 °C	For oxidative pyrolysis, the yield of light olefins increased from 18.6% (ER = 0) to around 30% (ER = 0.1–0.2), but the C_5–C_{11} and heavy oil fraction yields decreased	[31]
	600 °C	Cold plasma pyrolysis = 44 wt% gas yield vs. catalytic pyrolysis with 5 wt% of HZSM-5 = 77 wt% and conventional pyrolysis = 15 wt%	[32]
LDPE	300–600 °C	Char yield at 300 °C = 34.016% compared to at 600 °C = 16.12%; Gas yield at 300 °C = 28.27% compared to 600 °C = 39.51%	[33]
	340 °C	1% of catalysts resulted in 77.97% pyrolysis oil, 14.23% residue, and 7.79% gas 2% of catalysts resulted in 69.6% pyrolysis oil, 24.01% residue, and 6.12% gas	[34]
	2–10 bar at 450 °C	There is enhanced conversion at higher pressures, as evidenced by increased light product occurrence and reduced unreacted feed amount.	[35]

Many studies performed kinetic studies to understand the relation between several operating parameters and the conversion towards pyrolysis products. Some developed kinetic models and obtained kinetic parameters for each plastic type. While these studies provide valuable information necessary for designing a pyrolysis reactor, studies on transport effects and transport modeling are non-existent. Understanding the transport phenomena inside the reactor is essential, especially for non-Newtonian fluids like plastic melts, because it dictates how to design reactor accessories such as agitators and heaters/coolers and how to control the process to achieve the desired products. Furthermore, thermodynamic studies have been limited to determining the activation energy of the process. However, this may not be adequate to capture the complex equilibrium relationship between liquid oils, solid char, and gaseous products. Moreover, energy and material balances are rarely done because time-series information on the evolution of the species within the reactor is rarely obtained in the literature. Knowledge of product speciation is essential, especially if we want to tailor our process to meet the demands of potential end-users.

Most studies characterized the properties of pyrolysis products. Some even compared the properties of the pyrolysis products to the existing fuel standards using a series of standard tests. While these studies can be lauded for their attempt to consider the potential applications of the obtained pyrolysis products, studies on the actual performance testing of these fuel alternatives are absent in the literature. Lastly, as we have seen in the review, the type of plastic used affects the products formed after pyrolysis. Few studies tackled the co-pyrolysis of several plastic blends and the co-pyrolysis of plastics with biomass. However, only very few studies are conducted that use actual plastic wastes obtained from landfills.

4. Future Research

Global interest in the pyrolysis of plastics is growing continuously in the coming years as we search for the best option to eliminate plastic waste from the planet's surface. Numerous research areas are still unexplored, which will continue to drive the field forward. Future areas worthy of investigation include detailed modeling of the transport phenomena occurring inside pyrolysis reactors, thermodynamic studies to model effectively the phase equilibrium between the solid char, liquid oils, and the gaseous products, and development of a rigorous kinetic model that includes mass transfer aside from kinetic effects to fully understand the requirements in the proper design of new catalysts and eventual scale-up into large reactors. Moreover, process intensification studies involving optimizing process parameters such as temperature, pressure, agitation speed, flow rate, particle size, and catalyst size, among others, are worth studying. Multi-objective optimization studies should include maximizing the conversion rate, minimizing process costs, and minimizing the undesired products. Pilot studies should be done to assess the techno-economic feasibility of putting up pyrolysis plants, especially in developing countries where plastic wastes are abundant, and yet the resources are limited. The commercial acceptability of pyrolysis products should also be studied.

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