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Circular plastics technologies: pyrolysis of plastics to fuels and chemicals

Abstract: Pyrolysis technologies are a staple in plastic chemical recycling because of the robustness to contamination and existing infrastructure. Pyrolysis is already considered to be a reasonably mature technology with numerous pilot plants operating to pyrolyze plastic waste into fuels and chemicals. This chapter will describe the pyrolysis process and important process parameters, the types of plastics that are suitable for pyrolysis recycling, the mechanism of pyrolytic degradation of various plastics, the products derived from different plastics, companies that have successfully scaled pyrolysis recycling, and recent innovations in the technology.

keywords: circularity; degradation; fuels; plastic; pyrolysis; thermolysis.

1 Introduction

One of the fastest scaling and expanding areas in plastic recycling is the conversion of waste plastics to petrochemicals and refined hydrocarbons via pyrolysis. Pyrolysis of plastics (also known as thermolysis or polymer cracking) has been a potential route for plastic waste management since the 1980s but has seen significant growth and expansion over the last five years [1]. Pyrolysis can be simply defined as the degradation of polymers at high temperatures in the absence of oxygen to yield oils consisting of gaseous and liquid hydrocarbon fractions. In other words, plastics can be transformed back into something like the crude oil that was originally pumped from the ground and converted into hydrocarbons in an oil refinery. In the three loops of plastic recycling outlined by the Ellen MacArthur Foundation (EMF), pyrolysis would fall in the molecular loop where the polymer backbone is broken down to a molecular level disparate from the parent monomers and further chemistry is required before re-polymerization back into the original polymer is possible (Figure 1) [2].

Pyrolysis is an energy intensive, robust process that can accommodate common contaminations associated with post-consumer plastic waste such as food, dirt, aluminum laminates, printing inks, oil residues, and more [3]. Because of the high

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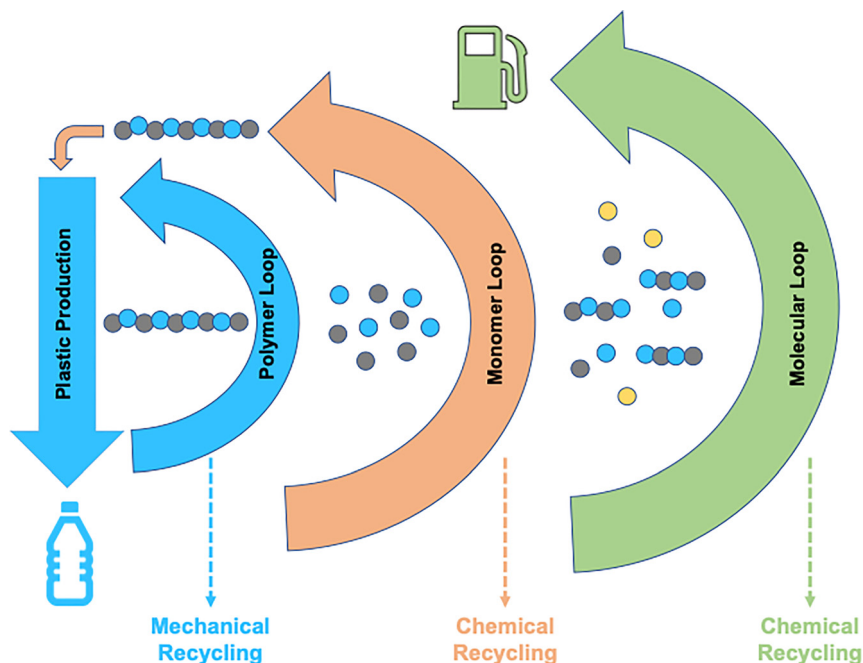


Figure 1: The EMF has broken down plastic recycling into three loops: (1) the polymer loop where the polymer backbone remains unchanged (i.e., mechanical recycling); (2) the monomer loop where polymer is broken down (or “unzipped”) back into the parent monomer that can be directly repolymerized back into the original polymer; and (3) the molecular loop where the polymer backbone is broken down into useful chemicals that can be further processed into monomers or used as fuel (i.e., pyrolysis or gasification).

temperatures, even highly contaminated plastics can be processed without difficulty by pyrolysis [3]. Historically, pyrolysis has been employed at the large scale primarily as either a “waste-to-fuels” process or “waste-to-energy” process when combined with gasification (discussed later in this chapter). However, the current momentum towards a circular economy for plastics has shifted the focus to a “waste-to-plastics” pathway that involves converting the pyrolysis oil into monomers or other chemicals to be used for plastic remanufacturing [1].

Pyrolytic recycling of plastic waste has already been achieved on a commercial scale with new developments to improve the process such as microwaves and catalysts showing great commercial potential. Major polymer producers all around the world have announced strategies that plan to use the output of pyrolysis processes to utilize plastic waste as a raw material to remake plastics [4]. These commitments are likely reactions to the ambitious goals being set by consumer facing companies such as Coca-Cola, PepsiCo, and Unilever to incorporate up to 50% recycled material in their packaging in the next 5–10 years despite low volume outputs from mechanical recycling [4].

Plastic films and flexibles that are used in many types of packaging are very difficult to recycle via conventional mechanical recycling pathways used today as they are not compatible with existing processing equipment (i.e., easily jams during sorting or in hoppers, feeders, and extruders). This limitation, coupled with the rising demand for recycled materials, has led to a rapid growth and expansion of the pyrolysis industry along with new innovations. This chapter will describe the pyrolysis process and important process parameters, the types of plastics that are suitable for pyrolysis recycling, the mechanism of pyrolytic degradation of various plastics, the products derived from different plastics, companies that have successfully scaled pyrolysis recycling, and recent innovations in the technology.

2 Technical scope

Pyrolysis




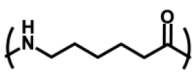
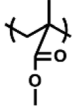
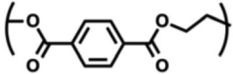
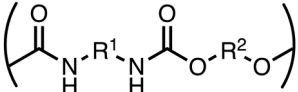
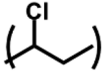
Thermal pyrolysis

Process parameters

Thermal degradation of macromolecules via pyrolysis can be accomplished in the presence of a catalyst (catalytic pyrolysis) or without (thermal pyrolysis) [5]. Thermal pyrolysis of plastics involves the decomposition of polymeric materials by means of high temperatures when it is applied in oxygen-free conditions. Since pyrolysis relies on the endothermic breaking of covalent bonds the supply of heat is essential to efficiently decompose the material [6]. Other key process parameters that influence the end products from pyrolysis are temperature, reactor type, pressure, residence time, and catalyst loading and type [7, 8]. Each of these parameters can be tailored to optimize the product yield and composition as well as reduce the energy requirements. However, temperature and reactor type have the most significant impact on product selectivity [9].

Temperature. Temperature is probably the most significant operating parameter in pyrolysis recycling since it controls the cracking reaction of the polymer backbone. The pyrolysis temperature range can be broad, between 300 and 900 °C for most plastics, and depends on a myriad of factors [10]. When the temperature is high enough, the energy will overcome the enthalpy of the C–C bond and result in a broken bond [11]. Temperature settings are based on the type of polymer being pyrolyzed and the preferred product composition/distribution. Typically, the pyrolysis temperature is dictated by the onset of degradation of the polymer which can be determined by thermal gravimetric analysis (TGA). Pyrolysis, for most plastics, begins at ~300 °C or earlier depending on the polymer structure and types/concentration of heteroatoms [6]. Typically, polymers with robust carbon-carbon bonds, such as polyolefins, require

Table 1: Summary of pyrolysis temperatures, products, and downstream applications for common plastics.

Polymer	Structure	Pyrolysis temperature (°C)	Pyrolysis product	Downstream applications
Polyethylene (PE)		378–539 ^a [14, 15] 360–550 ^b [16–19] 600–800 [3, 20]	Waxes, paraffins, olefins	Oil refinery feedstock for conversion to diesel fuel or chemicals
Polypropylene (PP)		400–500 [15, 21]	Waxes, paraffins, olefins	Oil refinery feedstock for conversion to diesel fuel or chemicals
Polystyrene (PS)		350–500 [3, 18, 20]	Styrene, styrene oligomers	Monomers
Nylon-6		330–400 [22] 760 [23] 410–490 [24]	ϵ -caprolactam	Monomers
Polymethyl methacrylate (PMMA)		450–580 [25–28]	Methyl methacrylate	Monomers
Polyethylene terephthalate (PET)		350–520 [29]	Benzoic acid, vinyl terephthalate, aldehyde	Upgrading to chemicals or fuels
Polyurethane (PUR)		700–760 [23] 250–450 [24]	Benzene, methane, ethylene, NH ₃ , HNC	Upgrading to chemicals or fuels
Polyvinyl chloride (PVC)		220–520 [29]	HCl, benzene	Upgrading to chemicals or fuels

^aHigh density polyethylene (HDPE), ^blow density polyethylene (LDPE).

higher energy inputs and temperatures than other common plastics. Table 1 summarizes reported temperature ranges required for the pyrolysis of the most common plastics found in municipal solid waste (MSW). The pyrolysis temperature can also be influenced by the types of plastic additives in the feedstocks. All plastic formulations contain a complex concoction of additives, such as stabilizers, plasticizers and/or pigments [12]. Most additive types will evaporate during pyrolysis, but certain additives

can affect the kinetics and mechanism of degradation and require additional tuning to the temperature [6]. Furthermore, additives that contain inorganic molecules can result in char formation and reactor fouling over time.

The selected operating temperature also depends on the target products and distribution. In general, when the pyrolysis temperature is high, there is increased production of noncondensable gaseous fractions and lower liquid yields, such as diesel. Higher temperatures increase the yield of hydrogen, methane, acetylene, aromatics, and soot, whereas lower temperatures favor generation of aliphatic compounds and liquid products [13]. Therefore, if a gaseous or char product (e.g., carbon black) is preferred, higher temperatures >500 °C are suggested. If a liquid, fuel-like product is preferred instead, lower temperatures in the range of 300–500 °C are recommended, and this condition is applicable for all plastics [8]. When targeting diesel-like products, the optimal operating range for most common plastics is 390–425 °C according to the review by Sheirs et al. [3]. The high temperature requirements associated with pyrolytic recycling are one of the major limitations considered when scaling the technology as higher temperatures mean higher costs and greenhouse gas (GHG) emissions. Current innovations in pyrolysis focus on strategies to lower the required temperatures for plastic recycling and will be discussed in a later section.

Reactor type. After temperature, the second most important parameter to consider when designing a pyrolysis process is the reactor type. A pyrolysis process design typically consists of a feeding section, reactor unit, and product collection vessels that contain downstream separation lines for product recovery and purification (Figure 2) [30–32]. Reactor type directly affects mixing of the plastics, quality of heat transfer, and final product yield in the pyrolysis process and requires configurations that have excellent mass and heat transfer characteristics. The type of catalyst that can be used in the process also depends on the reactor type applied. Several kinds of reactors can be used for pyrolysis including those involving high heat and mass transfer rates such as fluidized beds (bubbling and catalytic), autoclaves, melting vessels, plasma reactors, and unique designs to enable vacuum pyrolysis [33]. Similarly, it is also possible to find rotating cone [34], cyclonic reactors [35], and ablative process reactors [36] used in pyrolysis processes. At the commercial scale, the most common types of reactors used are fluidized bed reactors (FBRs), fluid catalytic cracking reactors (FCCRs), and screw/Auger kiln reactors (Figure 3) [5, 37, 38]. Emerging technologies are also exploring microwave assisted reactor designs and continuous extrusion designs for pyrolysis processes to lower energy inputs and increase throughput. The various reactors/configurations listed thus far have advantages and disadvantages in terms of technical and economic parameters. The literature contains many reports comparing the operation and performance of pyrolysis reactors [39–46]. Each configuration comes with benefits and trade-offs, as to be expected. Some known advantages and disadvantages of pyrolysis reactors identified in the literature are summarized in Table 2. The remainder of this section will focus on the most common reactor types used at the commercial scale.

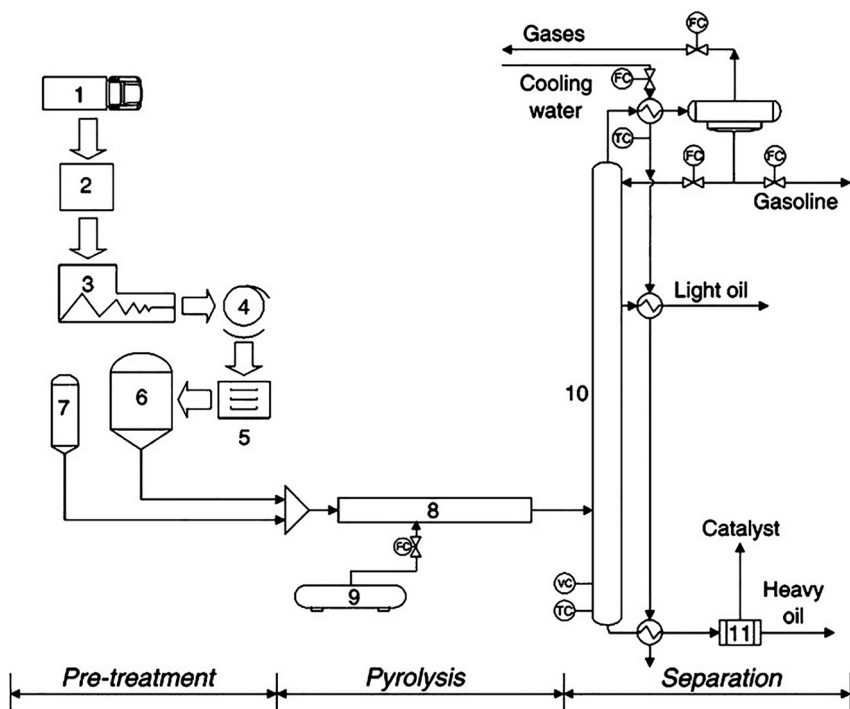


Figure 2: Schematic of a small-scale pyrolysis pilot plant. The configuration includes (1) transportation of the waste to the facility; (2) selective collection and sortation of target feedstocks for pyrolysis; (3) shredding of the plastic; (4) washing; (5) drying; (6) waste storage; (7) catalyst storage; (8) reactor unit; (9) heating gas storage; (10) separation unit; and (11) catalyst filter. Reprinted with permission from miskolczi et al. (Source: Miskolczi 2009) [32].

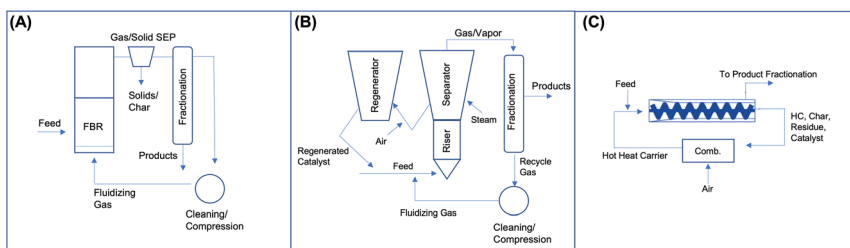


Figure 3: Common reactors used for pyrolytic recycling of plastics: (A) fluidized bed reactor; (B) fluid catalytic cracking reactor; and (C) screw/Auger kiln reactor.

Fluidized bed reactors. FBRs (Figure 3A) are the most widely used reactor type for plastic pyrolysis [8, 46]. In this type of reactor configuration the plastic waste is melted (i.e., converted to a “fluid”) and passed through a solid granular material (sand or solid

Table 2: Comparing advantages and disadvantages of common pyrolysis reactors (red = poor; yellow = satisfactory; green = good) [28, 39–46]

Reactor Type	Temp. Control	Heat Transfer	Residence Time Flexibility	Thermal Mode	Catalytic Mode	Product Quality	Ease of Scale-Up	Economics (Costs)
Fixed Bed	Red	Red	Green	Yellow	Yellow	Green	Red	Yellow
Bubbling Fluidized Bed	Yellow	Green	Yellow	Green	Green	Green	Yellow	Yellow
Catalytic Fluidized Bed	Yellow	Green	Yellow	Green	Yellow	Green	Yellow	Red
Screw/Auger Kiln	Red	Red	Green	Green	NA	Yellow	Yellow	Yellow
Melting Vessel	Red	Red	Green	Green	NA	Yellow	NA	Yellow
Extruder	Yellow	Red	NA	NA	Yellow	Green	Green	Yellow

catalyst) at high enough speeds to suspend the solid and yield fluid-like properties [47]. This process, known as fluidization, imparts many important advantages to an FBR over other pyrolysis reactors. FBRs are characterized by excellent heat and mass transfer rates, resulting in consistent temperature control throughout the reactor and highly uniform products [31]. In a catalytic FBR, the catalyst sits on a distributor plate and is well mixed with the fluid in the bed providing a large surface area for reaction to occur [48]. From an economic point of view, FBRs are very attractive as they have low operating costs, can be operated in continuous mode, and the catalysts (when used) can be recovered and recycled in the process several times [8, 10]. Some disadvantages to using FBRs can be the complexity in the reactor design, solid fraction attrition, and bed defluidization which can lead to frequent shutdowns [49]. Solid fraction attrition is attributed to the solid/solid collisions in the hot solid media leading to attrition phenomena and producing fine particles in the resulting solid fraction [50]. These small particles hinder the separation process resulting in higher solids concentrations in the liquid fraction. This promotes aging, erosion, blockage, and combustion problems in the FBR design [41].

Regardless of the challenges associated with FBRs, they are considered robust and scalable reactors that are widely employed in demonstration and commercial pyrolysis plants [46]. An example of a successful commercial pyrolysis operation using an FBR is Recycling Technologies in the United Kingdom (UK). Recycling Technologies claim they can process up to 20 tons per day (TPD) of plastic waste into Plaxx™, a low sulfur heavy fuel oil, via their FBR pyrolysis configuration. Another example is the BP process that used an FBR to pyrolyze up to one TPD of plastic waste into light and heavy waxes, although this plant is no longer operational.

A variant of the FBR is the conical spouted bed reactor (CSBR) that is designed with more intense mixing in the bed to prevent defluidization events and reduce shutdowns. While CSBRs have not been demonstrated on a large scale, this type of reactor has been applied for the thermal pyrolysis of polyolefins on a laboratory scale, reporting very high yields of wax up to 80 wt% [51]. Other studies have reported successful conversion of polyolefin feedstocks to gasoline and diesel range products [52–54].

Fluid catalytic cracking reactors. FCCRs are common reactors found in conventional refineries and have historically been applied to convert vacuum gas oil (VGO) to gasoline. A primary challenge in achieving a continuous process for plastic pyrolysis is the continuous feeding of the feedstock in solid form into the reactor [55]. Fluid catalytic cracking reactors (FCCR) offers a solution to this problem by dissolving the plastic feed in a suitable solvent, followed by pyrolysis of the solution [55–57]. A common FCCR configuration is outlined in Figure 3B. First, a hot particulate catalyst is contacted with the dissolved plastic feedstock, creating cracking products and a coked catalyst. The plastic is cracked into gaseous components and separated to fuel gas [31]. The coked catalyst is separated, stripped of residual oil products, and regenerated by burning the coke. The hot catalyst is then recycled to the riser for additional cracking [58]. FCCRs are characterized by good solid polymer mixing, but some disadvantages associated with this type of reactor are high energy requirements (compared to other pyrolysis reactors), the costs associated with use of solvent, and very dilute feed streams [59]. One example of a large-scale operation using an FCCR is Reentech in South Korea. This process applies an FCCR pyrolysis configuration cracking of plastic wastes [3].

Screw/auger reactor. Screw/Auger Kiln reactors are a relatively simple design that overcome some of the problems of conveying heat for pyrolyzing plastics. Auger reactors are typically made up of a tubular reactor and a screw conveyer as shown in Figure 3C. The screw is used to convey a single feedstock or a blend with solid heat carriers down the length of a reactor tube. This is a continuous process where the residence time can be varied by the varying the speed of the screw and length of the reactor [60]. Typically, metal or ceramic spheres are added to the conveyer line that help avoid coke build-up and improve the heat transfer during the pyrolysis process. Some key benefits to using an Auger reactor for pyrolysis is the continuous operation, ability to purge through the length of the reactor (i.e., efficient chlorine removal), and selective zone heating [60]. Auger reactors have been historically used to pyrolyze tires and thermoset based waste electrical and electronic equipment (WEEE). Two well-known examples of commercial scale use of screw/Auger reactors to pyrolyze plastic waste are Agilyx and Renewlogy. Agilyx is currently operating a pilot facility using a continuous, dual screw reactor design to process 10 TPD of plastic waste. Renewlogy is also operating a pilot plant facility at 10 TPD using an Auger/kiln reactor design. Brassard et al. recently reviewed auger reactor designs and the effect of various operational parameters on their performance [61].

Pressure and residence time. Pressure and residence time are both temperature dependent factors that can influence product distribution and yield from plastic pyrolysis. Typically, in a pyrolysis process, applying higher pressures can shift the molecular weight of the product distribution and shifts the product yields to more gaseous products. However, this trend is only apparent at high temperatures and shows less impact at lower temperatures. The residence time can be defined as the average amount of time that the molten or dissolved plastic spends in the reactor [62]. Shorter residence times will yield longer carbon products and longer residence times will increase the overall yield of lighter hydrocarbons and noncondensable gases [63]. Studies applying auger reactors in pyrolysis processes have highlighted the importance of short residence time for obtaining a high yield of light olefins [3]. However, this affect is also temperature dependent as seen by Mastral et al. who studied the effect of residence time and temperature on product distribution of HDPE thermal cracking in an FBR. It was found that a higher liquid yield was obtained at longer residence times when the temperature was less than 685 °C. However, at higher temperatures, the residence time had less influence on the liquid and gaseous yield [62].

Degradation mechanisms and products

The pyrolytic degradation mechanisms of plastics depend on the parent polymer. There are four types of degradation mechanisms that can occur: random-chain scission, end-chain scission, chain-stripping, and crosslinking. These different mechanisms are related to the bond dissociation energies, the chain defects of the polymers, the aromaticity, and the presence of halogen and other hetero-atoms in the polymer chains. The products obtained from pyrolysis vary based on the parent polymer and are summarized for common plastics in Table 1. This section will discuss the different types of plastics that can be recycled by pyrolysis and their respective products. Additionally, companies that have demonstrated pilot scale pyrolysis recycling operations are summarized in Table 3 along with the respective primary feedstocks and products.

Polyolefins. Of the most common waste plastics, polyolefins are probably the most ideal feedstocks for pyrolysis recycling due to their lack of hetero-atoms. Polyolefins include high density polyethylene (HDPE), low density polyethylene (LDPE), linear low-density polyethylene (LLDPE), and polypropylene (PP). In high temperature environments, polyolefins degrade via random chain scission of carbon-carbon bonds where the polymer is broken randomly along the backbone into smaller molecules of varying chain lengths. As an example, the pyrolytic degradation mechanism of HDPE is outlined in Figure 4. Initiation consists of homolytic breaking of the carbon-carbon bonds by random chain scission, resulting in the formation of two radicals. This is followed by depropagation and the release of olefinic monomeric fragments from primary radicals. This mechanism perpetuates with hydrogen chain transfer occurs leading to the formation of olefinic species and polymeric fragments. Moreover, secondary radicals can also be formed from hydrogen abstraction through an intermolecular transfer reaction

Table 3: Select pyrolysis companies, primary feedstocks, and primary products as listed on company websites.

Company	Primary feedstock	Primary product
Brightmark Energy (formerly RES Polyflow)	HDPE LDPE PP PS	Diesel, naphtha, wax
VadXX	HDPE LDPE PP PS	Diesel, naphtha, syngas, carbon black
Agilyx (formerly Plas2Fuel)	HDPE LDPE PP PS	Light synthetic crude oil; styrene monomers
Pyrowave Nexus Fuels LLC	PS HDPE LDPE PP PS	Styrene monomer and oligomers Light crude, diesel, gasoline, kerosene, wax
Renewlogy	HDPE LDPE PP PS	Crude oil and kerosene
Recycling Technologies UK New Hope Energy	NA ^a HDPE LDPE PP PS	Low sulphur hydrocarbon Plaxx™ Synthetic fuels
Plastic Energy	HDPE LDPE PP PS	Diesel, naphtha
Quantafuel	HDPE LDPE PP	Purified diesel
Fuenix Ecology Blest	NA ^a HDPE LDPE PP PS	Naphtha, paraffin and LPG
Climax Global Energy EcoFuel Technology	NA ^a HDPE LDPE PP PS	Crude oil, diesel Purified diesel and kerosene
Enval	Plastic Aluminum Laminates	Aluminum, crude oil

Table 3: (continued)

Company	Primary feedstock	Primary product
Braven (formerly Golden Renewable Energy)	PET	Braven PyChem (Naphtha)
	HDPE	
	LDPE	
	PP	
	PS	
Reentech	PE	Diesel, kerosene, gasoline
	PP	
	PS	

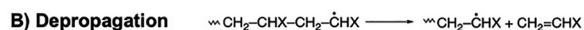
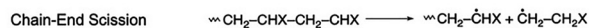
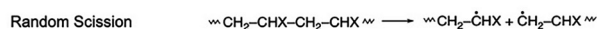
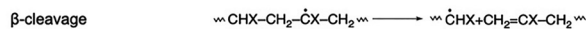
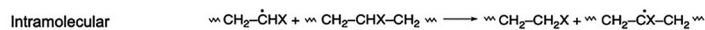
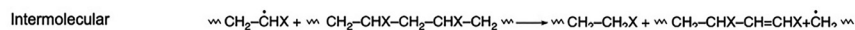
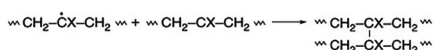
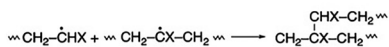
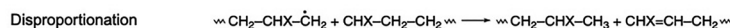
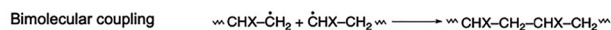
A) Initiation**C) Hydrogen Chain Transfer****D) Branching****E) Termination**

Figure 4: HDPE pyrolysis degradation steps and corresponding mechanisms.

between a primary radical and a polymeric fragment. β -cleavage of secondary radicals leads to an end-chain olefinic group and a primary radical which can ultimately lead to chain branching. Termination occurs in bimolecular mode with the coupling of two primary radicals or by disproportion of the primary macroradicals. The final pyrolysis product from polyolefins consists of a mixture of waxes, paraffins, and olefins that can be converted to diesel fuel or sold to an oil refinery as feedstock. The pyrolysis oil can be

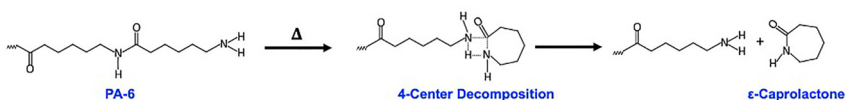
further refined to via hydrotreatment to produce olefins and other polymer precursors for remanufacturing of plastics similar to the process for purifying naphtha for plastic production [64].

The pyrolysis of polyolefins is not a trivial process and requires a considerable amount of energy. It has been reported that at temperatures above 250 °C, the activation energies required for depolymerization of polyolefins range from 150 to 300 kJ/mol [1, 65]. This clearly demonstrates the energy intensiveness of these processes. As a result, many efforts focus on lowering the temperatures required for pyrolyzing polyolefins (as discussed in later sections) and improving the value of the pyrolysis product.

Unzipping polymers. Some common plastics undergo an “unzipping” mechanism in a pyrolysis process in which the polymer depolymerizes directly into parent monomers under pyrolysis conditions. These plastics include polystyrene (PS), polymethyl methacrylate (PMMA), and polyamide-6 (PA-6 or Nylon-6). The unzipping mechanism occurs by end-chain scission where the polymer is broken up from the end groups yielding the corresponding monomers (Scheme 1). Since the resulting pyrolysis oil is made up of mostly the original monomers, these types of plastic pyrolysis fall into the monomer loop (Figure 1) and will be discussed in more detail in Chapter 2 of this book.

Polymers containing hetero-atoms. Ideal conditions for pyrolyzing plastics require the absence of oxygen. As a result, polymers containing hetero-atoms in the backbone are not ideal feedstocks for pyrolysis recycling. Common plastics that contain hetero-atoms are polyethylene terephthalate (PET), polyurethanes (PURs), polyamides, and polyvinyl chloride (PVC). Other hetero-atoms found in common plastics include bromine and fluorine. Under pyrolysis conditions hetero-atom containing plastics can yield hazardous and corrosive products such as ammonia, hydrogen cyanide, hydrogen chloride, hydrogen bromide, bromine, hydrogen fluoride, and others [3]. If these types of plastics are used as feedstocks for pyrolysis then careful selection of methods to neutralize or inhibit the effects of hazardous compounds formed are required. This imparts high costs and energy input for the overall recycling process and has significantly limited the widespread adoption of pyrolysis considering the large volumes of PET and PVC found in MSW.

If pyrolyzed, the degradation of mechanism of PET, which contains oxygen and aromatic groups, degrades by random scission of the ester links in the main chain that form carboxylic acid and olefinic end groups [66]. The carboxylic acid end groups



Scheme 1: Schematic of end-chain scission of PA-6 producing ϵ -caprolactam

undergo decarboxylation to yield phenyl end group compounds. Subsequently, benzoic acid and vinyl benzoate are formed by scission of the phenyl end group compounds. During pyrolysis, other volatile products are formed from vinyl benzoate and benzoic acids including benzene, toluene, styrene, and ethyl benzene. The final pyrolysis oil consists mostly of benzoic acid and vinyl terephthalate which can be upgraded to useful chemicals or fuel [10].

PURs are an incredibly complex group of plastics in that are either thermoplastics or thermosets (i.e., crosslinked) and can be synthesized from numerous types of monomers. PURs are classified based on a urethane linkage in the backbone, but in reality, this makes up a small percentage of the actual polymer structure. As a result of this complexity, several different types of degradation mechanisms can occur during pyrolysis such as random chain scission, chain stripping, and crosslinking. Overall, studies show that pyrolyzing PURs results in a complex mixture of compounds in the pyrolysis oil such as benzene, methane, ethylene, amines, and hydrogen cyanide [3].

PVC breaks down via chain stripping under pyrolysis conditions. In this mechanism, the reactive substituents or side groups on the polymer chain are eliminated, leaving an unsaturated chain. This polyene then undergoes further reaction, including β -scission, aromatization, and coke formation. This results in very little monomer recovery and the pyrolysis oil consists mostly of benzene and hydrochloric acid (HCl). The presence of HCl leads to corrosion of the reactor and formation of organochlorine compounds [67]. Additionally, the presence of chlorine limits the application of the pyrolysis oil as fuel. As a result, pyrolysis plants typically avoid PVC feedstock unless it has undergone a dichlorination pretreatment [7].

The presence of halogens is a particular problem in pyrolytic recycling as they can lead to the formation of highly toxic and dangerous compounds. Halogens can be present on the polymer backbone, such as the case with PVC, or in the additives such as brominated flame retardants used in many plastic formulations (present in some cases as high as 60% by mass of the polymer). As a result, dehalogenation has been a major focus in pyrolysis innovations. Dehalogenation technologies have been developed as a pretreatment step, using solvents or thermal treatment to remove halogens. Dehalogenation of liquid products using catalysts or antimony has also been studied. Scrubbing gas effluents from the pyrolysis process to remove HCl and HBr is also employed. Additionally, some efforts have even focused on capturing the bromine released during pyrolysis for reuse in flame retardants [68, 69].

Mixed plastic feedstocks. Pyrolysis is often presented as a solution for recycling of highly mixed, heterogeneous waste. Pyrolysis recycling of mixed waste plastics may be one avenue for recovering value from unwashed, commingled plastics and lowering the costs and logistics of plastic sortation typically required for recycling [3]. However, as demonstrated in the previous section, pyrolyzing different plastics can lead to varying compositions, yields, and quality of pyrolysis oil products. As a result, most commercial facilities have focused on single stream feedstocks. Several researchers have studied the

resulting pyrolysis oil from mixed plastic waste streams [13, 20, 23, 48, 70]. These studies have focused primarily on mixtures of PE, PP, and PS, with low levels of PVC contaminations. Overall, the pyrolysis of mixed plastics produces lower liquid yields of target products liquid when compared to the pyrolysis of single plastic waste streams. Despite the lower liquid yield the quality of pyrolysis oil produced is typically comparable to the single plastic feedstocks. These studies have shown that the oil composition is still acceptable for further processing in petrochemical refineries. The challenge then becomes the techno-economics. Pyrolyzing mixed plastic streams will save on costs in the sorting steps. However, there is still the question on whether these cost savings justify the high energy and costs of pyrolysis when only 50% of the pyrolysis oil can be recovered.

Assisted pyrolysis technologies

Microwave assisted technology

As noted, one of the major drawbacks to pyrolysis is the high energy inputs required to break the robust bonds in common plastics. Additionally, plastic feedstock has very low thermal conductivity which leads to a low rate of heat transfer through the materials and thus requires long residence times to achieve target yields [71]. In electric-heated pyrolysis, the plastic waste is heated by an external heating source which heats everything in the pyrolysis reactor, including the evolved volatiles. This results in significant energy losses and can also promote undesired side reactions that can lead to the formation of toxic compounds, increased production of char, and fouling of the reactor [72, 73]. Microwave heating can be applied as a more efficient means of heating the reactor. Microwave-assisted pyrolysis offers a lower energy pathway for breaking carbon bonds and recovering high quality pyrolysis oil. Microwave-assisted pyrolysis uses microwave heating to thermally crack the plastic waste. In this process, the waste material is mixed with a microwave-absorbent substance such as particulate-carbon. This substance absorbs microwave energy which then generates sufficient thermal energy to achieve the temperatures required for pyrolysis to occur [71]. Microwave radiation offers several advantages over conventional pyrolysis methods such as rapid heating, lower residence times, and lower production costs [8]. Unlike conventional methods, microwave energy is supplied directly to the material through the molecular interaction with the electromagnetic field, thus no energy is wasted to heat up the surrounding area of the pyrolysis chamber. One limitation to microwave-assisted pyrolysis is the lack of sufficient data to quantify the dielectric properties of various plastic waste streams [8]. The efficiency of microwave heating significantly depends on the dielectric properties of the material, which can vary depending on the plastic feedstock [71]. Therefore, most studies focus on single waste streams. Nevertheless, microwave-assisted pyrolysis continues to be explored, with some companies demonstrating the process at the pilot-scale such as Pyrowave, a startup company that uses microwave-assisted technologies to pyrolyze PS into styrene monomer. In-depth

reviews of microwave-assisted pyrolysis have been presented by Lam and Chase [71] and Undri et al. [74].

Hydrothermal liquefaction

Another method for improving the energy efficiency and yield in plastic pyrolysis is by incorporating subcritical or supercritical water and is known as hydrothermal liquefaction (HTL) [75]. When under subcritical or supercritical conditions water contains enough energy to break carbon-carbon bonds making it a useful solvent for advanced oxidation processes, including degradation and thermochemical conversion of plastic waste [76]. Super critical water (SCW) exists at a temperature above 374 °C and pressure higher than 22.1 MPa, and the physical and chemical properties are dramatically different compared to water at ambient/atmospheric conditions [77]. The high density and ionic product of SCW promotes the solvation of compounds, while the high diffusivity and low viscosity promotes faster mass transfer during pyrolysis [75, 78, 79]. The HTL pyrolysis process contains a series of reactions including hydrothermal cracking, hydrolysis, free radical, nucleophilic substitutions, and cyclization that converts plastics into monomers or chemical feedstock [80]. The SCW can serve as a solvent, catalyst, or reactant [81, 82]. Hydrocarbon yields and distributions are highly dependent on the residence time, but unlike conventional pyrolysis, the heating rate in HTL was reported to have an insignificant effect on product distribution [75]. HTL is not as heavily studied as conventional pyrolysis, but has started to attract more interest in recent years. Some challenges associated with using SCW-assisted pyrolysis are the high costs of equipment and operation and the corrosive effects of SCW on the reactor [5, 83]. One industrial scale example of an HTL process is the ReNew ELP technology that uses SCW to process plastic waste. ReNew ELP's catalytic hydrocracking (Cat-HTR) technology uses SCW to break down plastic feedstocks and harvest hydrogen from the water for use in the creation of new, stable hydrocarbons.

Catalytic cracking

Over the years, various types of pyrolysis have been developed based on the kinetics of the degradation and are categorized as fast, catalytic fast, intermediate, slow, and vacuum pyrolysis [37]. Adding catalysts to the pyrolysis process can facilitate lower temperatures and shorter residence times [51, 67, 84, 85], increase the yield and selectivity of the pyrolysis oil [85, 86], and limit side reactions and the formations of undesired products [51]. Catalysts will impart better control over the product selectivity, but the reactor choice and operating conditions still have a significant effect on the product distribution and yields. Additionally, catalyst properties such as the acidity and pore structure also play a major role in the product distribution obtained [55–57]. Multiple studies have revealed that using catalysts can modify the selectivity towards the production of light olefins, gasoline, or diesel based on the type of catalyst used [31, 51–53, 56, 87]. Homogeneous and heterogeneous catalysts have been investigated with heterogeneous catalysts being the most common in industrial practice due to the ease of

separation and recovery associated with these kinds of catalysts [88]. Homogenous catalysts include Lewis acids and fused metal tetrachloroaluminates ($M(\text{AlCl}_4)_n$), where the metal can be lithium, sodium, potassium, magnesium, calcium, or barium [88, 89]. A wide variety of heterogeneous catalysts can be used including conventional solid acids (such as zeolites, silica–alumina, alumina, and other FCC catalysts), mesostructured catalysts, nanocrystalline zeolites (such as n-HZSM-5), and several others [88, 90]. FCC catalysts are the best choice for maximizing liquid oil production from plastics as they have the highest catalytic activity [8]. Additionally, FCCs can be recovered and reused and are economically attractive. FCC catalysts are typically made of zeolite crystals and a non-zeolite acid matrix known as silica–alumina. FCC catalysts are normally used in the petroleum refining industry to crack heavy oil fractions from crude petroleum into gasoline and liquid petroleum gas (LPG) fractions where aromatic and naphthenic compounds are selectively formed [6].

Catalysts are primarily used to reduce the overall costs of the process while also improving the value and selectivity of the products. Several reports show that the use of an acid catalyst may reduce the pyrolysis temperature, overall energy consumption, and total operating cost of the process [67, 91–95]. Catalysts can improve the hydrocarbon distribution to yield pyrolysis oil that resembles conventional fuel such as gasoline and diesel (e.g., C2–C4 olefins) without requiring further refining [8]. Schirmer et al. showed that the catalytic cracking of PE increases the gasoline yield when compared to conventional pyrolysis [96].

Catalytic cracking also involves several drawbacks. Catalysts can be easily deactivated by carbonaceous deposits, inorganic materials, and chloride and nitrogen-containing species making the process highly sensitive to contamination typically associated with plastic waste streams [55–57, 97]. Finally, many chemical recyclers have struggled to find an optimum catalyst that is ideal for cracking multiple types of plastic waste streams [57]. As a result, intensive pre-treatment steps are often required to limit deactivation of the catalyst. Furthermore, the required catalyst regeneration increases the process complexity and total operating cost [5].

Gasification

Gasification is another important plastic recycling process that is typically classified in the same category as pyrolysis recycling and is the preferred route for heavily contaminated and otherwise unusable, waste streams [5]. Gasification applies high temperatures to convert organic solid material (coal, biomass, plastics, and organic waste) into a gaseous mixture (syngas) of carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2), and methane (CH_4). Gasification consists of heating plastics with a sub-stoichiometric amount of oxygen or air, and steam at temperatures of 700–1500 °C and atmospheric pressure [98, 99]. Process parameters such as temperature, $\text{O}_2/\text{H}_2\text{O}$ ratio, and residence time can be tailored to target a specific H_2/CO ratio in the resulting

syngas. For example, more steam yields more H_2 in the syngas when compared to pure oxygen or pure air gasification. The syngas produced from gasification can be used in Fischer–Tropsch processes (FTS) to produce fuels and chemicals or converted to methanol via catalytic hydrogenation [100]. Methanol can be further converted to olefins via downstream catalytic processes and used to produce new polymers from chemically recycled intermediates [5].

Gasification can be done in air which decreases the costs of gas separation compared to steam gasification, however, the presence of N_2 in such a high-temperature environment triggers the production of harmful nitrogen oxides (NO_x) which are 300X more damaging GHGs than CO_2 . Air gasification also requires higher volumes than steam processes, thus negatively impacting investment costs. Additional challenges associated with the gasification of plastic waste are the high amount of energy required and high production of char that occurs during the process. Typically, dual-stage gasification reactors are required to mitigate char production and reactor fouling, increasing the overall investment costs of the process [101]. Another key challenge is the high yields of toxins and aromatics that limit the direct use of the syngas in downstream processes.

Overall, gasification is a well-established technology and the recent momentum towards a circular economy has led to the development of increasingly viable and sustainable solutions, such as the combination of gasification with pyrolysis or combustion and the cogeneration of different products (e.g., syngas, heat, and power) as summarized by Heidenreich and Foscolo [102]. Eastman has pioneered gasification as recycling technology for carpet waste feedstocks. Eastman's gasification plant in Kingsport, TN uses plastic waste and coal feedstocks to generate syngas which they then feed into other processes at the Kingsport site in a completely integrated design. On a pilot scale, Texaco Inc. and Shell developed a proprietary gasification process, in which petroleum feedstocks were replaced by plastics (Figure 5) [6]. Ube Industries in Japan gasifies plastics in a pressurized FBR, developed jointly by Ube and Ebara Co.

Plasma pyrolysis/gasification

Plasma assisted pyrolysis combines pyrolysis with the thermochemical properties of plasma. The process is similar to gasification and uses extremely high temperatures, ranging between 1730 and 9730 °C, to convert plastic waste into syngas. Plasma assisted

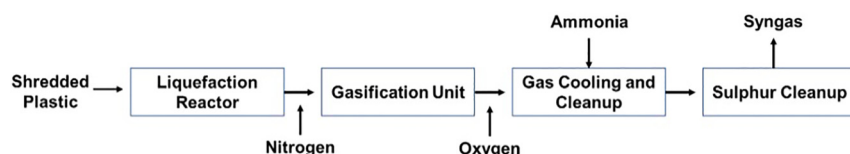


Figure 5: Basic schematic of Texaco gasification process [6].

pyrolysis is extremely fast, lasting between 0.01 and 0.5 s, depending on the process temperature and type of waste feedstock [103]. The resulting syngas is composed mainly of CO, H₂, and small amounts of higher hydrocarbons. Plasma pyrolysis has several advantages over conventional pyrolysis and gasification. Plasma pyrolysis is very fast leading to lower emissions and is suitable for mixed plastic feedstocks [97, 103]. The high temperatures decompose any toxic compounds in the syngas and limit the formation of HCl from PVC. The produced gas has a low tar content and high heating value which makes it suitable for electricity generation in turbines or hydrogen production in an integrated process.

There are still several technical challenges to be addressed before the technology can meet plastic waste management requirements and become commercially available. The challenges differ depending on the specific plasma technology [104]. Thermal plasma technology is a well-established technology in metallurgy processing or material synthesis, but not in waste management [103]. For now, due to economic and legal aspects, the most important application of the technology is the destruction of hazardous waste rather than recycling, but some stakeholders predict that plasma assisted gasification of plastics may soon be commercialized [97].

3 Summary and future perspectives

Pyrolysis technologies are leading the way in chemical recycling because of the robustness to contamination and existing infrastructure. Pyrolysis is already considered to be a reasonably mature technology with numerous commercial plants operating to pyrolyze plastic waste (Table 3). However, current energy requirements, variability of the waste streams, poor life cycle assessment metrics, and techno-economics have presented limitations to implementation of pyrolysis as a major recycling route for plastic waste. At large scales (e.g., tons per day), using pyrolysis and/or gasification technologies to produce fuels and/or chemicals from plastic can address the challenges of waste management and increasing global energy demand simultaneously. Overall, pyrolysis is considered a relatively simple, flexible, and suitable process for recycling plastic waste streams that are difficult to depolymerize. However, many still agree that an improved understanding of the chemistry and more innovative reactor designs are required to realize the full potential of pyrolysis and to achieve lower GHG emissions. Additionally, the absence of an optimum reactor technology to employ catalytic fast pyrolysis is another major bottleneck in industrial applications.

Despite the drawbacks, consumer product companies are making big commitments to use recycled content in their packaging. Governments are also pushing companies to use more recycled plastic. California wants plastic packaging to contain 50% recycled content by 2030. The European Union is pushing for 30% by the same date. Shifting the endgame of pyrolysis to a waste-to-plastics model can help companies and governments achieve these goals. This will require collaborative efforts between the recyclers and oil

refineries that are willing to purchase the pyrolysis oil for conversion into chemical feedstocks for plastics. The feed flexibility of thermal processes supports the potential of pyrolysis and gasification; however, the strong variability in plastic waste streams calls for further assessments through fundamental experiments and models. Additionally, innovations to lower the energy requirements and costs are needed to minimize the environmental footprint and provide an economically viable pathway to a circular plastics economy via pyrolysis recycling.

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