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Chapter

Chemical Recycling of Polyolefins (PE, PP): Modern Technologies and Products

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Abstract

Chemical recycling is one of the most intensively developed potential solutions for the global plastic waste issue. This broadly defined term covers several different technologies that lead to many diverse products. Polyolefins (polyethylene and polypropylene) can be chemically recycled by pyrolysis (cracking) or gasification. These polymers' chemical composition and structure make them a great potential source of valuable hydrocarbons or carbon atoms for syngas production. Thermal and catalytic cracking of polyethylene and polypropylene can be optimised to maximise specific types of hydrocarbons that, after optional additional processing, such as hydrotreatment, steam cracking or distillation, can be used as intermediates in petrochemical plants, fuels or fuel components, monomers for polymerisation of new, virgin polymers or as specialty chemicals (final market products). Gasification of plastic waste transforms polymers into a mixture of hydrogen, carbon monoxide and carbon dioxide, which can be further used as a source of these gasses, transformed into chemicals and fuels, or used directly to produce energy. This chapter presents all of these process paths with examples of existing technologies and their level of technology readiness and perspectives for scale-up.

Keywords: polyolefins, polyethylene, polypropylene, chemical recycling, pyrolysis, thermal cracking, catalytic cracking, gasification

1. Introduction

Reduce, reuse, recycle – this is the current strategy to prevent the world from being flooded by plastic waste. There are many initiatives led by governments, regulators, and also companies and entrepreneurs to follow these guidelines: the so-called "Single Use Plastics" Directive (SUP) [1], The Circular Plastics Alliance, and The Alliance to End Plastic Waste – to name a few. Incineration and energy recovery of plastics seem to no longer be the promoted solution due to increasing carbon dioxide emissions and causing the loss of the potential hidden within polymers. Although landfilling of plastics practically does not emit CO_2, it can lead to microplastic release into the environment [2].

Chemical recycling is now more recognised as a potential solution to recycling or ending the life of plastic, as it can potentially treat the waste that cannot be mechanically recycled, keeping "carbon" in the industry loop. But there is no one official understanding of the term "chemical recycling" worldwide. European

regulation defines recycling only at a very general level as any operation that takes waste and makes products, materials, and substances, except fuel components [3]. ISO 15270 is even more precise, limiting chemical (feedstock) recycling to cracking, gasification and depolymerisation processes to convert plastic waste into monomer of new raw materials, excluding energy recovery and incineration [4]. On the other hand, American Chemistry Council (ACC) defines chemical (advanced) recycling as any technology that converts post-use plastics into monomers, specialty polymers, feedstocks and fuels [5]. What is more, the process of waste to value-added chemicals is also known as upcycling [6].

Recycling itself, both mechanical or chemical, can produce two types of products. Suppose the properties of the recycled material are not considerably different from those of the virgin material and can be used in the same application. In that case, the recycling process is called "closed-loop recycling". This approach is difficult for the mechanical recycling of some polymers for specific applications (like food packaging or specialty applications) as, in many cases, the processing of plastic waste causes partial degradation of the polymer structure and a change to its mechanical properties. When recycled material has different properties and is used in different applications to the original one, the recycling process is called "open-loop".

In the current chapter, both types of chemical recycling technologies of polyolefins (polyethylene and polypropylene) – closed-loop and open-loop, will be described.

2. Structure of polyolefins

Polyethylene (PE) and polypropylene (PP) are polymers called polyolefins. These are the two largest plastic resins based on production worldwide. One of the reasons for this is the variety of applications where these plastics are used: mainly in packaging but also in toys, piping, cable covers, automotive parts, ship ropes or even bulletproof vests. Polyolefins are inert, have low thermal conductivity (are good insulators) and are not subject to attack by most chemicals. As thermoplastic resins, most polyolefins can be mechanically recycled; however, thanks to the chemical and hydrocarbon structure, they are also proper materials for chemical recycling via cracking (pyrolysis) and gasification.

Polyethylene is a product of ethylene polymerisation. Depending on the production process and consequent chemical structure and properties, many types of PE are produced. The major ones are:

- low-density polyethylene (LDPE),

- high-density polyethylene (HDPE),

- linear low-density polyethylene (LLDPE),

- crosslinked polyethylene (PEX).

LDPE is a type of polyethylene with the most branched structure and a density lower than that of HDPE. HDPE is a polymer with a linear structure with a low degree of branching. LLDPE is produced by the polymerisation of ethylene with other olefins with longer hydrocarbon chains, like 1-butene, 1-hexene or 1-octene. The result, a linear backbone with short and uniform branches. Finally, PEX is a polymer obtained by crosslinking the process of polyethylene. This crosslinking
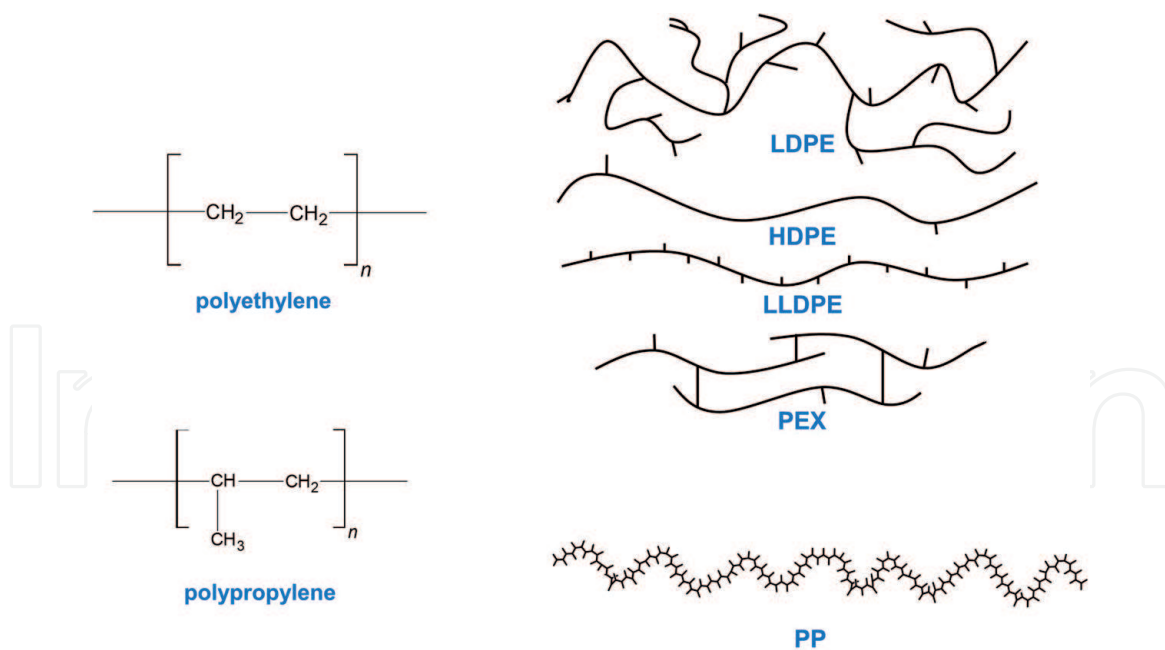
Figure 1.
Structures of polyethylene and polypropylene.

changes the properties of polyethylene significantly – increased temperature, pressure, or corrosion resistance. Thermoplastic polyethylene becomes thermoset which limits the possibility of mechanical recycling of this material significantly.

Polypropylene is a product of the polymerisation of propylene. It means that every monomer has a methyl side group. Due to the presence of asymmetric carbon atoms in the chain, stereoisomerism is observed for this polymer.

Differences in the structures are presented in **Figure 1**. These differences influence the polymer's mechanical properties and the cracking or gasification process conditions, and the composition of products from chemical recycling processes.

It should be noted that many different additives are used to change the properties of the polymer during the production of plastic items. For example, pigments and dyes are added to change the colour; glass fibres can be added to alter the mechanical properties of the polymer, and talk is sometimes added to reduce the price of the final goods. Stabilisers (like UV stabilisers), flame retardants, lubricants and plasticisers are other types of additives commonly used in the plastic industry. The quantity of these additives may be vast, from parts of a percent up to 60–70%. What is more, in many cases, polyolefins are used together with other polymers. For example, in multilayer films used for packaging, PE is used together with poly(ethylene terephthalate) (PET). What is more, flexible packaging is often highly printed. The final yield and composition of chemical recycling products will depend on the type and quantity of all of the impurities.

3. Cracking (pyrolysis)

The cracking of polymers is a process where long polymer chains are broken into products with shorter chains. During heating (at around 350–600°C), molecules start to vibrate until the vibrations are intense enough to overcome van der Waals forces. The short-chain molecules then evaporate. When the energy of the van der Waals force is higher than the enthalpy between carbon atoms in the molecule, the bond in the molecule will break instead of evaporating. In polyolefins' chains, the most unstable bonds will be the first to break, leading to the creation of radicals.

The dissociation energy needed to break the bond between carbon atoms lowers with the order of carbon classification: primary > secondary > tertiary, which means that the first place in a polymer molecule where the bond will break is at the branching. This already indicates that polypropylene cracks at lower temperatures than polyethylene because all carbons in the structure (apart from terminal ones) are tertiary. It also means that LDPE cracks easier than HDPE because of higher branching. All types of polyethylene and polypropylene can be cracked, including those that are challenging for mechanical recycling, like PEX.

3.1 Mechanism of cracking reaction

In general, the following steps of the cracking reaction can be identified:

- initiation – free-radical creation,

- propagation – products and secondary radicals creation, isomerisation,

- termination – recombination, disproportionation, cyclisation, arenes creation, polycondensation.

When the bond between hydrogen and carbon atom is broken, a radical is created (initiation step). In the second step of the process, polymer bond breaks at the β position, creating one unsaturated molecule and another radical. Depending on the type of polymer, this cracking can follow one of these types of reactions:

- unzipping – the chain break at the β position of the molecule (β-scission) with monomer's creation;

- backbiting – intramolecular transfer of a hydrogen atom from one part of the molecule to the other part of the same molecule and then β-scission in the middle part of the molecule with the creation of specific molecules with shorter chains;

- random scission – intermolecular transfer of hydrogen atom and then β-scission in the middle part of the molecule with the creation of products with shorter chains (**Figure 2**) [8].

In the case of polyolefins, cracking occurs mainly by random scission and backbiting reactions.

In the last step of the process, the radical can react with another radical, creating saturated alkane (recombination), one alkane and one alkene (disproportionation), create cyclic structure (cyclisation), dehydrogenate and condensate and take part in other reactions. In the end, a mixture of different types of hydrocarbons with varying chain lengths is created. When condensation and dehydrogenation reaction progress, polycyclic aromatic hydrocarbons (PAH) are created, which still react and finally create a coke, that is reach in carbon.

3.2 Product composition

As mentioned before, the cracking of polyolefin chains produces different hydrocarbons. In general, three types of streams are created during the pyrolysis of polyethylene and polypropylene: gas fraction that consists of hydrocarbons with the lowest molecular weights, a liquid or semisolid fraction (pyrolysis oil) that consists
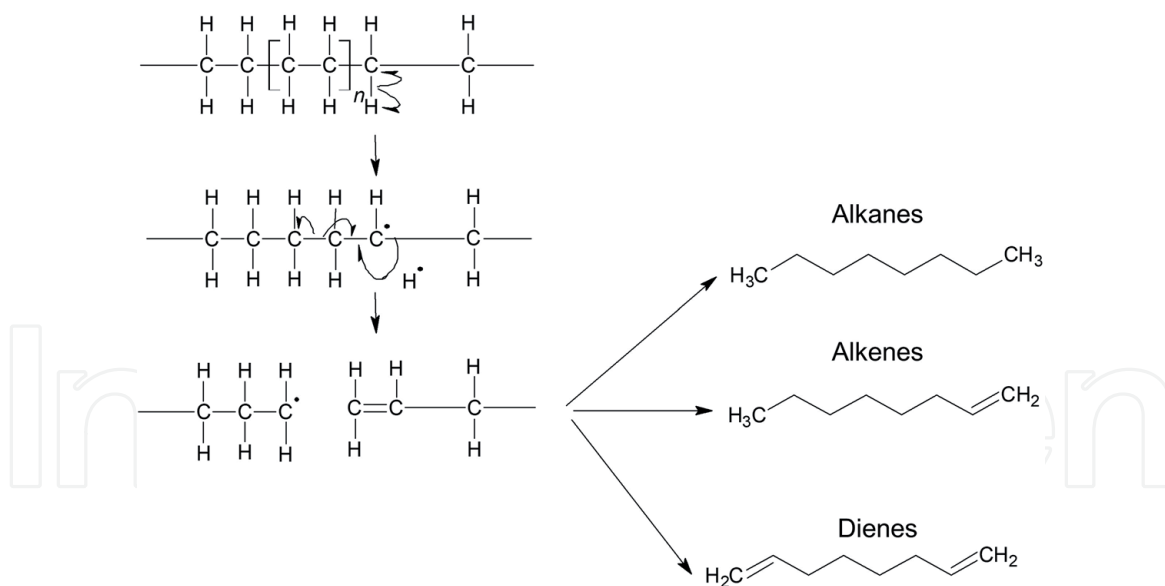
Figure 2.
Cracking of polyolefins by random scission reaction, redrawn from [7].

of hydrocarbons that were created in the form of vapours which after cooling were condensed and the process residue (char), that consists of plastic's additives and coke, which was created during the process. The composition and yields of each of these products depend on the feedstock's composition and process conditions such as temperature, pressure, residence time, and catalyst used.

For example, during the process in a rotary kiln reactor with quartz sand used as a heat carrier, pyrolysis oil consisting of 43,1% of aliphatic hydrocarbons and 55,5% of aromatic hydrocarbons were obtained from polyethylene. Pyrolysis oil from polypropylene consisted of 44,7% aliphatic and 52,9% aromatic hydrocarbons [9]. On the other hand, during thermal cracking of PE and PP in a microreactor at different temperatures gave products consisting of 59,7% alkanes, 31,90% alkenes, 8,40% cycloalkanes and 66,55% alkanes, 25,7% alkenes and 7,58% cycloalkanes, respectively. No aromatics were identified [10]. These two examples already indicate how different products can be obtained, depending on the process conditions.

In general, it can be observed that raising the temperature and residence time can increase arenes creation and can also raise the alkane to alkene ratio in the product, for example, in [11]. Aromatics content can also be significantly raised by the use of certain catalysts, like zeolites. The type of catalyst also influences the alkane/alkene ratio [12]. It should be noted that catalysts can be rapidly deactivated, limiting their use in continuous processes [13]. An increase in the temperature can increase the yield of long-chain hydrocarbons due to reduced residence time. However, it can also favour increased gas and lower molecular weight product formation by increasing the number of secondary reactions if the residence time is long enough. The majority of cracking processes are conducted at atmospheric pressures. However, some investigations present that higher pressure can increase the gas formation at lower temperatures, but with the increase of the temperature, the effect was diminished. A decrease of double bonds formation with the pressure increase was also observed [14]. What is more, different polymers can have a synergistic effect on co-pyrolysis [15]. Polystyrene (PS) is also a valuable feedstock for pyrolysis. The product of PS cracking is almost fully aromatic, with styrene monomer as a major product [16]. It can also be co-pyrolysed with polyolefins. Poly(methyl methacrylate) (PMMA) is another polymer that can be pyrolysed [17]. Poly(vinyl chloride) (PVC) produces large quantities of corrosive hydrogen chloride and can contaminate all – gas, liquid, and residue. PET gives low yields of

oil, and the thermal cracking of polyurethanes provides products reach in organic nitrogen components [18]. Pyrolysis of biomass converts waste into oil with high oxygen content and increase coke formation [19]. That is why most of the research and developed technologies are based on polyolefins, optionally with the addition of polystyrene, while other plastics and biomass are treated as impurities.

Pyrolysis of plastics is a complex process with many variables that produce hydrocarbons from polyolefin feedstock. It makes the process difficult but flexible at the same time. That is why many different solutions are used (other types of reactors), but also different product types for different applications are obtained.

3.3 Product applications

As described in the previous section, cracking of polyethylene and polypropylene can lead to many different products. The composition of the products – hydrocarbon type and chain length – will determine their application.

3.3.1 Plastic-to-intermediate

Pyrolysis oil obtained during thermal or thermocatalytic cracking of polyolefins is a complex mixture of hydrocarbons with different chain lengths (5 to 30 and more carbon atoms). Linear and branched paraffins and olefins, together with aromatics: mono and polyaromatics – with and without aliphatic side chains, are obtained. Such a complex mixture does not have a direct application without additional treatment. However, as a hydrocarbon product, it can be mixed with refinery and petrochemical streams and processed together with crude. The process is simple, consisting of only a cracking reactor, product cooling system, residue discharge system and gaseous product burning unit (for energy production).

However, the capacity of commercial chemical recycling plants is limited due to plastic waste availability and the process itself – polymers have a low thermal conductivity which makes the scale-up of the pyrolysis reactor challenging. The biggest pyrolysis plants have a capacity of about 100 000 tons per year which is very small compared to the standard refinery size of about 4–10 million tons per year. This means that the recycled stream is highly dissolved in the refinery. As a result, the product can be contaminated, so there is no need for expensive detailed sorting and washing of the plastic waste or purification of the pyrolysis oil. Even though this makes the process much cheaper, the solution is not economically feasible.

Cracking is an endothermic process that requires a lot of energy to melt the plastic and break polymer bonds, as plastics are excellent insulators. The residue obtained from cracking is usually a high-calorific by-product and contains a high level of contamination, limiting its use in incinerators, especially if the raw material used for pyrolysis was not properly separated and cleaned. For example, the presence of PVC significantly raises the chlorine content, which is limited in incinerators' feedstock specifications. Special treatment of this residue increases the overall cost of operations.

Pyrolysis of plastic waste into feedstock for refineries was very popular a couple of years ago. For example, in Poland until 2007, many commercial (Technology Readiness Level, TRL = 9) plants were operated, but their profitability was based on relief in excise tax. When regulation changed, they were all bankrupted. Low prices of crude oil caused the closure of other companies worldwide, or they changed their profile. For example, Agilyx from the US had to shut down its flagship plant in Tigard in 2016, later changing its activity profile to polystyrene recycling [20].

3.3.2 Plastic-to-fuel

The most popular application for products from the chemical recycling of polyethylene and polypropylene are fuels and fuel components. Hydrocarbon product can be separated into more narrow fractions like gasoline, diesel, light and heavy fuel oil. Hydrocarbons with the highest molecular weights (waxes) can be circulated back to the cracking reactor or cracked in an additional catalytic process. Proper process parameters can also limit the quantity of waxy hydrocarbons, but it usually causes high gas yields. Pyrolysis reactors are followed by distillation units. The ratio between different products depends on technology. An example of two companies' products slates are presented in **Table 1** [21].

From one side, fuels obtained from the pyrolysis of polyolefins are characterised by low concentrations of sulphur (less than 0,1%) and are easily burned as hydrocarbon fractions. On the other hand, high olefin content reduces oxidation stability. Furthermore, reactive alkenes relatively easily undergo polymerisation reaction creating gums with high molecular weights. That is why products from PE and PP cracking should not be stored for a longer time. This tendency to polymerisation can also cause issues in distillation units where resins deposit at surfaces of elevated temperatures, reducing heat transfer coefficient in heaters and heat exchangers, also plugging the distillation columns and reducing mas flow in these units. Foaming during distillation is also observed [22, 23].

Hydrotreatment (catalytic reactions with hydrogen) of the products from pyrolysis could be a solution – olefins can be saturated into paraffins, stabilising the product. But it would raise the total cost of the process as it usually carries out at elevated pressures and requires special, separate units. What is more, products reach in linear paraffins may have high pour point of diesel and light fuel oil fractions. Unsuitable gasoline fraction octane number and cold-temperature behaviour of heavier fractions limit their use in combustion. To keep proper fuel parameters, blends of hydrotreated fractions from chemical recycling of plastics and commercial fuels can be prepared. But to keep proper parameters, a maximum of 1% of gasoline fraction, 10% of diesel fraction and 20% of light fuel fraction from polyolefins' cracking can be used [24]. If the process is controlled to produce a highly aromatic product, then higher octane gasoline and lower cetane diesel could be obtained.

Fuels and fuel components obtained from plastic waste compete in price with fossil fuels, making the profitability of the process challenging. Also, this type of application in European regulation is seen as energy recovery, so it is not considered chemical recycling. Nevertheless, there are several companies that are focused on the production of fuels. For example, Bightmark Energy is building a 100 000 t/a commercial facility (TRL 9) in Ashley (US), which is planned to be commissioned in 2021. Braven Environmental is planning a 65 000 t/a plant in Virginia. Nexus Fuels commercial-scale plant's capacity is 50 t/d, similar to one module of Integrated Green Energy Solutions' plant constructed in Amsterdam.

Type of product	Cynar	PK Clean
Kerosene, %	10	—
Diesel, %	70	66
Light fuel oil/Naphtha, %	20	33
Wax, %	—	re-circulated

Table 1.
Product slate examples [21].

Polish company Handerek Technologies develops technology for fuels production by pyrolysis of plastics and further hydrotreatment at atmospheric pressure, using syngas (mixture of hydrogen and carbon oxide). The process at an early stage of commercialisation, presenting only a small scale pilot plant (TRL 4–5) with plans to build commercial plants with a capacity of 10 000 t/a.

3.3.3 Plastic-to-monomer

The production of monomers that would be firther used for polymerisation could be the only solution for closed-loop recycling of PE and PP waste. Depolymerisation of polyolefins is not easy as bonds between carbon atoms in the chain are relatively strong. As described before, thermal or thermocatalytic cracking leads to a mixture of hydrocarbons with different chain lengths. Gas fraction is produced, but alkenes content in it is usually low. A research was conducted to maximise the gas fraction and olefin content, but the highest ethylene concentration in the gas stream achieved was 25%. Still, a minimum of 40% of liquid product was obtained [7]. In other research, steam was used in a fluidised bed reactor for pyrolysis of plastic waste to maximise olefin yields. 20–31% ethene and 14–18% propene were obtained. Additionally, 19–23% gasoline was produced. These yields are similar to standard naphtha steam cracker's product, but the research was run at lab-scale, and no information about scale-up is available [25].

The most extensively investigated process currently is the production of feedstock for commercial steam crackers. Plastic waste is cracked thermally or catalytically into a liquid fraction with proper boiling range and further mixed with fossil feedstock. Some research presented that it would be possible to use liquid from plastic pyrolysis only, receiving results similar to use naphtha [26]. But to avoid coking of the colder section of the steam cracking reactor and contamination of created streams with heteroatoms present in pyrolysis oils, co-cracking with standard feeds is preferred. Purification of the pyrolysis oil by hydrotreatment upfront steam cracking could be a solution that increases the total cost of the process. Considering the capacities of chemical recycling plants and current steam crackers (millions of tons of ethylene), significant dissolution of pyrolysis oil in fossil-based feedstock might be a solution for this issue, as pyrolysis oil can be only a small part of the inlet stream to the steam cracker.

Although making monomers and then polymers from polyolefin waste look like a very promising route for closed-loop recycling of polyethylene and polypropylene, several concerns should be considered. First, the basic question mark is about yields of the process. If it is assumed that pyrolysis oil has similar properties to commercial naphtha, then yields of ethylene and propylene that can be used for further polymerisation is limited, as presented in **Table 2** [27]. In the case of higher boiling fractions (like gasoil or diesel fraction) or oils reach in branched or aromatic

Product	% wt.
Residual gas (methane, hydrogen)	16,0
Ethylene	35,0
Propylene	15,0
C4 fraction	8,5
Fraction >C4 (C5, pyrolysis gasoline, residual oil)	25,5

Table 2.
Products of steam cracking of naphtha [27].

hydrocarbons, yields of ethylene and propylene are lower, and the yield of liquid products rises [28]. These products can be used as feedstock for chemical processes but are currently used primarily as fuels, which is not considered as recycling according to European regulations.

As the plastic-based liquid has to be blended with naphtha or other steam cracking fossil-based feeds, it is challenging to trace the flow of materials along the supply chain. For that purpose, a mass balance accounting system is required. It is a set of rules for allocating the recycled content to different products in order to be able to claim the recycled content. Products can be accredited by the independent scheme, for example, the International Sustainability and Carbon Certification Plus (ISCC) scheme. NGOs challenge the currently used calculation method as requiring more clarification and a more strict approach as it can be misused, claiming incorrect recycled contents [29]. It is understandable as long as detailed and correct data is not shared. For example, in one of the published Life Cycle Assessments (LCA) for the process, the considered amounts of naphtha from chemical recycling that is needed to produce 1 kg of LDPE were 1,2–2,0 kg with the baseline of 1,5 kg of naphtha per 1 kg of LDPE produced. These numbers are not in line with ethylene yields from fossil naphtha (as presented in **Table 2**) and require a broader explanation [30].

The final consideration is about the overall environmental impact of the process. For evaluating the influence of the process or product, a systematic analysis of the environmental impacts, called Life Cycle Assessment (LCA), is used. Currently, only two executive summaries of LCA were published, which were also criticised by NGOs [31]. As not enough data is publicly available, it is difficult to evaluate these concerns. What is sure, the process chain is very long and complex, as presented in **Figure 3**, and requires the use of fossil-based feedstocks and only part of the plastic pyrolysis oil is converted back to a polymer. The yield of the fraction that can be processed in a steam cracker in the plastic pyrolysis process is unknown. In this case, LCA analysis should consider yields and processing of other products from plastic pyrolysis and steam cracking to present the whole impact. Lastly, the feasibility of these processes are a matter of concern, especially if hydrotreatment is used for pyrolysis oil purification.
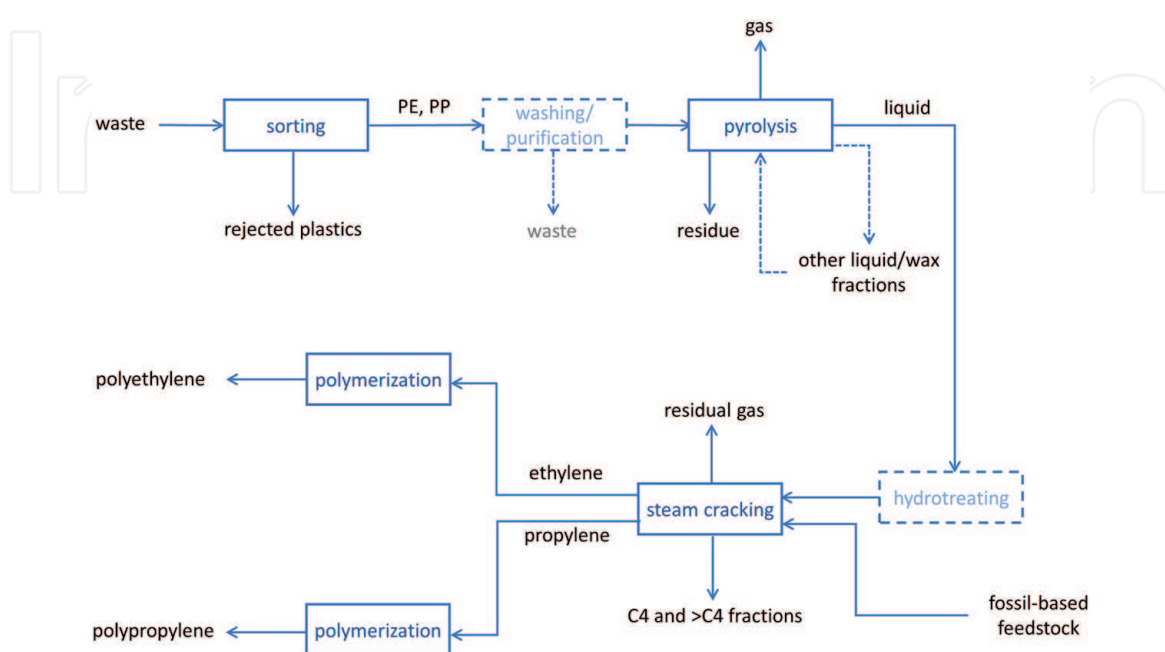

Figure 3.
Scheme of polyethylene and polypropylene from the plastic waste production process.

Currently, big polyolefin producers are involved in projects for the chemical recycling of plastics into monomers, like BASF, SABIC, Borealis or Chevron Philips Chemical, cooperating with companies experienced in pyrolysis, like Plastic Energy, Quantafuel or Nexus Fuels. In Geleen, the Netherlands, a plant for cracking of polyolefins is constructed and a hydrotreating system for purification of pyrolysis oil, which will later be fed to a steam cracker. This project is a joint investment of Plastic Energy and SABIC [32]. The plant is expected to have a capacity of 15–20 000 t/a and to become operational in 2022.

3.3.4 Plastic to chemicals (upcycling)

The production of valuable chemicals from waste, called upcycling, is an interesting alternative. The mixture of hydrocarbons obtained from polyolefins' pyrolysis can be upgraded or separated into different hydrocarbon types. What is more, the flexibility of the cracking process enables the maximisation of target fractions.

The major advantage of plastic-to-chemicals processes is that most of the proposed solutions offer final market products that do not require further processing in petrochemical plants. In this case, a mass balance approach is not required as products are based entirely on plastic waste. As products are not dedicated to be burned for energy production, these technologies can be classified as open-loop recycling also under European regulations. What is more, special, niche applications enable higher margin than compared to naphtha or fuel. On the other hand, these applications are limited when products are produced from waste, require high purity (virgin) polymers or complex pre- or post-treatment and purification, which may significantly influence the feasibility.

Benzene, toluene and xylenes (BTX) are important aromatics used by petrochemical industry to produce valuable chemicals like polystyrene, nylons, methacrylates, polyurethanes, plasticisers and many more. The pyrolysis process of polyethylene and polypropylene can be controlled to maximise aromatic hydrocarbons. A presence of polystyrene in the raw material could increase yields of BTX fraction. Nevertheless, it is possible to obtain 53% and 32% BTX from PP and PE, respectively [33–35]. These aromatics have to be further separated from the pyrolysis oil.

Encina from the US is an example of a company that provides a technology of catalytic cracking for BTX and propylene production but is currently not at a commercial scale. The planned unit will produce about 90 000 t/a of chemicals [36].

Polyolefin waxes can also be produced by the cracking of polymers. These kinds of waxes are widely used in PVC production, surface modifiers, additives to other waxes etc., and can be produced as a by-product of polyolefins production. Some companies, like Mitsui Chemicals America, Hana Corp., EPChem or Merlob, crack virgin polymers for the purpose of wax production. In this case, an issue of contamination by additives does not exist. If polyolefin wastes are considered, then a proper purification process should be implemented, or the application range would be significantly limited to those where colour and presence of inorganics is not an issue.

GreenMantra Technologies from Canada produces waxes by catalytic pyrolysis of plastic wastes at elevated pressure (4,5–25 bar). Wax products under the name of Ceranovus can be used for bitumen and asphalt modification, polymer processing or adhesives production. As an addition, fuel oil is produced. The current plant (TRL 9) has a capacity of 5 000 t/a [37]. Another company producing waxes ("EnviroWax") from plastic waste through pyrolysis is Trifol from Ireland. The by-products are fuels: diesel/kerosene and naphtha. The company has a pilot plant (TRL 6–7) with plans for scale-up to 37 000 t/a [38].

Figure 4.
Clariter products.

Clariter carries out the most complex process for plastic waste conversion into chemicals. Aliphatic solvents ("Solventra"), white oils ("Oilter") and paraffin waxes ("Clariwax") of high purity are produced from polyolefin waste via thermal cracking, hydrotreatment, and distillation and are alternatives to similar fossil-based products available in the market (**Figure 4**). To maximise on profit, target products are deeply purified from heteroatoms and hydrogenated so they can potentially be used in the cosmetic industry. Other applications are: paints, inks, degreasers, wax emulsions, paper and wood impregnation, lubrication, car or furniture polishes, silicone sealants and others. The company owns a pilot plant in Poland (TRL 5) and an Industrial-scale Plant in South Africa (TRL 7) with scale-up plans for 60 000 t/a facilities. Most interestingly, the company claims to achieve a net negative carbon footprint which is unique compared to other LCA's published [39].

4. Gasification

Gasification is a well-established process for the conversion of many non-renewable sources, like petroleum resids, petcoke or coal. In general, it can process any carbonaceous material into a valuable mixture of hydrogen, carbon monoxide and carbon dioxide – called syngas (synthetic gas). Syngas itself is a source of hydrogen and carbon monoxide used for various chemical processes or as fuel when separated into pure streams, or as a high calorific fuel or feedstock for chemical synthesis into other chemicals, like methanol, ethylene glycol, acetic anhydride and hydrocarbons (via Fischer-Tropsch synthesis) when not separated. Examples of syngas applications are presented in **Figure 5**. As polyolefins consist of carbon and hydrogen, these can be very good feedstock for gasification.

4.1 Gasification reaction

Gasification is a complex process with several reactions taking place between carbon-based material, oxygen and steam at high temperatures (700–1500°C). Examples of reactions that take place during gasification are presented in **Table 3**.

The hydrogen to carbon oxide ratio in obtained syngas varies significantly (from 0,7 to 6 for different fossil fuels) depending on the type of the raw material and technology. For different applications, different ratios are required. It is technically possible to obtain every required syngas composition from every feedstock, but it has economic limitations [28].
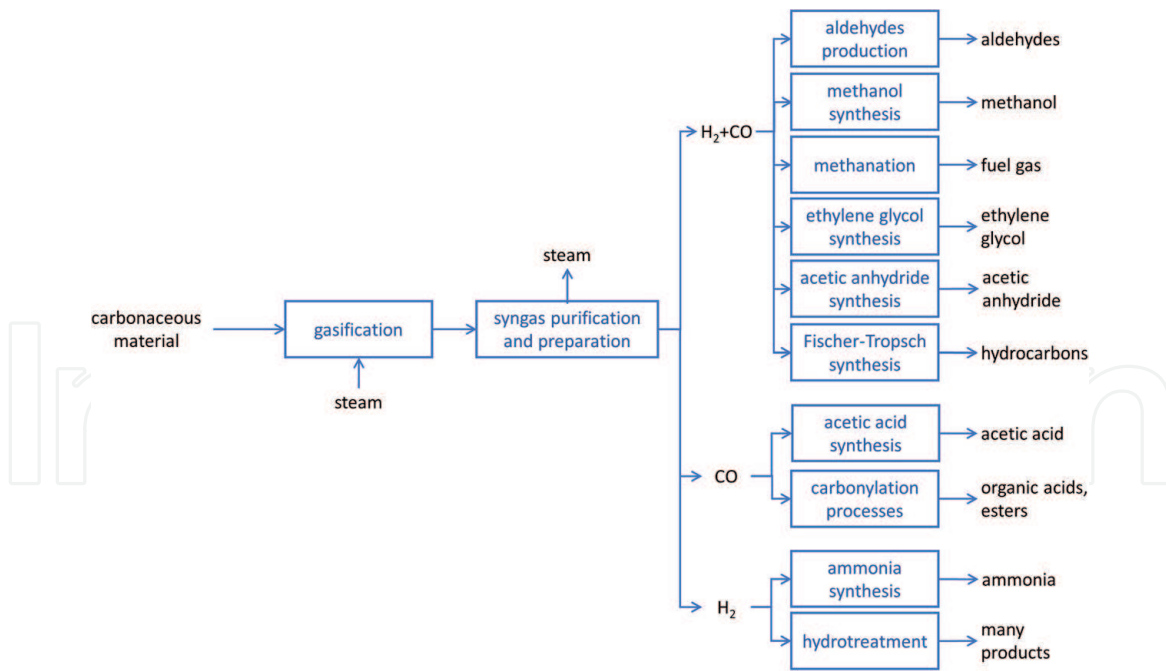
Figure 5.
Overview of potential syngas applications [28].

Reaction	ΔH, kJ/mol
Primary reactions	
$C + H_2O \rightleftarrows CO + H_2$	+118,9
$C + CO_2 \rightleftarrows 2CO$	+160,9
$C + 2H_2 \rightleftarrows CH_4$	−87,4
$2C + O_2 \rightleftarrows 2CO$	−246,3
Secondary reactions	
$C + H_2O \rightleftarrows H_2 + CO_2$	−42,3
$CO + 3H_2 \rightleftarrows CH_4 + H_2O$	−205,8

Table 3.
Examples of gasification process reactions [28].

4.2 Gasification of plastic waste

Polyolefin waste is potentially a very good source of carbon for gasification. What is more, as biomass and other plastic wastes are also reach in carbon, mixed wastes streams can be used. Gasification of waste has the following steps: drying, pyrolysis, cracking and reforming, char gasification. Drying of plastics has an insignificant role but might be important when plastics are processed with biomass, unlike the pyrolysis step, which is key in the gasification of plastics. The poor heat conductivity, sticky nature, high content of volatiles created during pyrolysis of polyolefins, and relative low char and high tar yields make the process different from coal or biomass gasification challenging but also promising. Air and steam gasification processes are proposed with different pros and cons. Finally, co-gasification with fossil-based feedstock or other waste streams is possible, expanding the flexibility of the process. The variability of quality and composition of the feedstock is a significant problem [40].

Gasification seems to be a promising alternative to pyrolysis for chemical recycling of plastic waste, which can produce chemicals or fuels without detailed

separation and washing of the feedstocks. It is attractive due to the versatility of potential products. On the other hand, it is related to high capital and operational costs [41]. What is more, currently, only fuels are produced, which might be related to instability of the waste streams, which may cause problems with keeping proper hydrogen to carbon oxide ratio.

Canadian company Enerkem provides the most advanced waste pyrolysis technology. The company currently operates a commercial (TRL 9) plant in Edmonton with a capacity of 38 000 m^3/a of methanol and ethanol used as a fuel. Another plant in Canada for fuels and chemicals production with a capacity of 125 000 m^3/a is under construction, and two more projects with capacities of 270 000 m^3/a of methanol each are developed currently in Europe [42]. Ebara Environmental Plant and Ube Industries from Japan provide gasification of plastic waste through partial oxidation by oxygen and steam. 70 000 tons of plastic waste is processed at Showa Denko's Kawasaki Plant since 2003. Currently, a feasibility study for the next plant in South Korea is being processed [43].

5. Conclusions

Chemical recycling of polyethylene and polypropylene gained much attention over the last years due to the rising plastic waste issue. Many projects of demonstration or commercial facilities are currently being developed. Although the definition of chemical recycling is inconsistent worldwide, four main types of products can be identified: intermediates for further chemical processing, fuels and fuel components, monomers and final chemical products. Pyrolysis and gasification are processes that can be used for polyolefins providing mainly open-loop recycling solutions. These technologies require deep feasibility and environmental impact analyses due to their complexity, different values of products, need for co-processing with fossil-based feedstock or high capital cost. Nevertheless, intensive growth of plastic waste volumes is an opportunity for these technologies to be further developed, optimised and commercially used.

Conflict of interest

The author declares no conflict of interest.

Thanks

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