High Molecular Weight Product Formation in Polyolefin Chemical Recycling: A Comprehensive Review on Primary and Secondary Products

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ABSTRACT

Annually, an enormous amount of plastic waste is produced worldwide. This waste should be appropriately managed to limit the environmental burden. However, only a small part of plastic waste is recycled; the rest is burned, disposed of, or ends up in the environment. In the transition toward a circular economy, chemical recycling has emerged as a promising conversion technique. Much of the research in chemical recycling focuses on producing lightweight liquids and gases. However, it is crucial to emphasize that valuable heavy products, such as waxes and lubricants, can also be obtained through upcycling. This perspective examines the chemical upcycling of polyolefin plastics into high molecular weight products, primarily focusing on waxes and lubricants. The production of heavy fractions from polyolefin plastics has the potential to be a profitable conversion strategy as value-added products are obtained. Favorable life cycle assessments prove it to be a sustainable strategy. Literature shows that different techniques, such as metathesis and hydrogenolysis catalysis or thermal pyrolysis, can be used to obtain heavy fractions from polyolefin plastics. Among these methods, thermal pyrolysis has been the subject of extensive research and is the most mature technology today. Additional chemical reactions can be used to further fine-tune the desired compositional or product properties, to clean the pyrolysis products, or to obtain other secondary products such as fuels and light olefinic gases.

TEXT

Introduction

Plastics have become an integral part of human life and are present in nearly every aspect of human existence. In the last century, plastic production has steadily increased worldwide, reaching a staggering 391 million tons in 2021.[1] The demand for plastic spans various sectors, with the packaging industry significantly contributing – representing over 39% of Europe's sector demand. The plastic is usually of a single-use nature, creating a significant need for plastic recycling. Only 35% of the collected post-consumer waste in Europe was recycled in 2020, whereas 23% was still sent to landfills and 42% was used for energy recovery. Different plastics are produced, of which polyolefins are the most in-demand type. They represent almost half of all resin production, creating a great challenge but an equal opportunity for polyolefin waste recycling. The most common types of polyolefin plastics are high-density polyethylene (HDPE), low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), and polypropylene (PP).[1]

Humanity predominantly operates today within a linear economy model where plastics are produced, used, and thereafter either landfilled or incinerated, with or without energy recovery. The transition to a circular economy, focusing on reuse and recycling, is paramount for reducing our environmental impact. Plastic recycling can be classified into four categories: primary or in-plant recycling of scrap material, only involving clean and non-contaminated plastics; secondary or mechanical recycling, entailing sorting and separation of waste plastics, size reduction and melt filtration; tertiary or chemical recycling, involving the complete or partial depolymerization of the polymer chains toward monomers, oligomers, or other chemicals; and quaternary recycling or energy recovery, this through incineration of plastics, being the most effective way for volume reduction. Nevertheless, quaternary recycling has high environmental impacts as it contributes to the emission of greenhouse gases and potentially releases airborne pollutants.[2]

Primary recycling is limited to clean and uncontaminated plastics, leaving post-consumer waste allocated to the other recycling categories. In transitioning to a circular economy, energy recovery using incineration should be limited due to material loss and possible environmental contamination. Mechanical recycling is the preferred recycling method for post-consumer waste. However, plastic polymers can deteriorate with every re-extrusion cycle, limiting the number of times it can be recycled. Chemical recycling can be used in conjunction with mechanical recycling, especially for polyolefins, which have high chemical stability. Plastics that are not suitable for mechanical recycling can be processed and recycled chemically. The most suitable technologies for polyolefins include thermal pyrolysis and catalytic processes such as catalytic cracking, hydrogenolysis, hydrocracking and gasification.[2,3]

Thermal and catalytic conversion strategies are both extensively researched for polyolefin recycling. Thermal pyrolysis is a promising technology for the chemical recycling of polyolefins, as it is suitable for highly heterogeneous mixtures and is a rather simple technology. Some challenges are the broad product ranges that are obtained, the high volumes that are required for cost-effective operations, the low tolerance for polyvinyl chloride (PVC) as well as the need for a stable waste supply. Catalytic conversions are also of great research interest as they can lower the temperature needed for polymer degradation and narrower product distributions can be obtained. They can, however, suffer from catalyst deactivation, which is caused by organic coke formation and by contaminants still present in the plastic mixture. This issue may lead to higher investment and operational costs.[3] In this review, the different recycling strategies that can transform polyolefin plastics into high molecular weight (MW) products such as waxes or lubricants are addressed and discussed. Additionally, secondary upgrading techniques are considered that can yield a range of different products. For other primary products from plastic waste, such as fuels, light olefins, or hydrogen and carbon nanotubes, we refer to recently published reviews elsewhere.[4–6]

Waxes typically consist of a complex mixture of long-chain hydrocarbons (≥ C18). They vary in terms of molar mass, molar mass distribution, and degree, nature and position of sidechain branching, as well as the potential presence of functional groups. Waxes can be classified according to their origin, with petroleum waxes being the most used waxes nowadays. This review, in contrast, will focus on degradation waxes originating from the depolymerization of polyolefin plastics. Both petroleum and degradation waxes are hydrocarbon waxes, and both mainly comprise of straight, branched, or naphthenic long hydrocarbons.[7] Degradation waxes can be expected to be used for similar applications as petroleum waxes, provided that they are also purified and chemically upgraded. These degradation waxes could partially substitute for the use of fossil-based waxes, making it a transition toward a more circular economy for these product classes.

Base oils constitute the bulk of lubricants (approximately 65 to 99+%).[8] Besides the base oil, different chemicals can be found, such as viscosity modifiers and pour point depressants. Like waxes, different sources can be utilized for producing base oils, with mineral sources prevailing as the most employed option. Mineral base oils can differ in their carbon number ranges, starting from C15 or C20 up to C50 or higher.[9] Mineral base oils can be comprised of n-alkanes, iso-alkanes, naphthenes with short or long side chains, and aromatics with short or long side chains. A base oil is typically a mixture of these different types of components. Each type of component has an influence on the base properties of the base oil. Different base oil categories are defined based on their composition and are categorized according to the American Petroleum Institute (API) interchange guidelines. Group I up to Group III base oils are obtained from mineral sources. Group IV are synthetic poly-alpha-olefin (PAO) base oils, and Group V is a miscellaneous group of all other base oils that are not categorized in the previous groups. Within these base oil groups, further differences can be found in the saturation levels, sulfur contents, and viscosity indexes, as well as in the proportion of paraffins, naphthenes, and aromatics.[8]

Typical products from polyolefin degradation are hydrocarbon gases, liquids, and waxes. The high MW products can be present as a side-product or targeted specifically in the degradation process. Considerable attention has been given to the production of the lower MW products, driven by the philosophy of creating the basic buildings for polyolefins. Conversely, less attention has been directed towards the production of higher MW products. This review therefore focuses on the following topics: the catalytic conversion strategies of polyolefins toward high MW products; the thermal pyrolysis conversion strategies of polyolefins toward high MW products; the secondary chemical (catalytic) transformation strategies of these produced high MW products to useful products, including impurity removal; and the techno-economic analysis (TEA) and life cycle assessment (LCA) studies conducted on polyolefin recycling studies toward high MW products, *i.e.*, waxes and base oils (for lubricant production). The latter studies are essential, as achieving positive outcomes for both TEA and LCA renders the recycling strategies appealing, feasible, and viable. To the author's knowledge, no previous perspectives or reviews have been published on the precise topic of this perspective.

1. Catalytic conversion toward high molecular weight products

Whereas catalytic cracking has been studied most extensively within polyolefin catalytic conversion, the majority of the catalytic cracking reactions yield significant quantities of lighter products. This is attributed to the excessive (multiple) cracking of higher MW hydrocarbons by the catalyst, which poses challenges in terms of selectivity control.[10,11] However, some catalytic reaction pathways are reported for producing these higher MW products.

One such catalytic reaction pathway was explored by Jia *et al.*[12] Their study reports PE degradation with a tandem catalytic cross-alkane metathesis (CAM) reaction, as illustrated in Figure 1A. Lighter alkanes, like petroleum ethers, were used as cross-metathesis partners for PE chains. Initially, both alkanes and PE chains undergo dehydrogenation, followed by olefin metathesis forming shorter alkenes, which are then hydrogenated. When an excess of light alkanes is present, this initial CAM product can react further, producing shorter chains and limiting heat and mass transfer issues. A supported pincer-ligated iridium (Ir) complex, which can be seen in Figure 1B, facilitated dehydrogenation/hydrogenation reactions, while Re_2O_7/γ-Al_2O_3 enabled alkane metathesis reactions. Efficient breakdown required Ir complexes to create internal double bonds. Linear alkanes generated straight-chain products, whereas branched alkanes resulted in products with branching, which could potentially improve the liquid properties. Figure 2 illustrates the narrowing polydispersity index (PDI) and MW distributions in function of time. The oil yield only rises significantly after the 24-h time point; before this, waxes are the main product. This catalysis worked across various PE MWs, LDPE, LLDPE, and post-consumer bottles and films, even with stabilizers and additives. Mild conditions (175 °C) sufficed for these reactions. While short times led to waxes, extensive times were needed for producing liquids. Moreover, only milligram-scale PE conversions were carried out so far.[12]

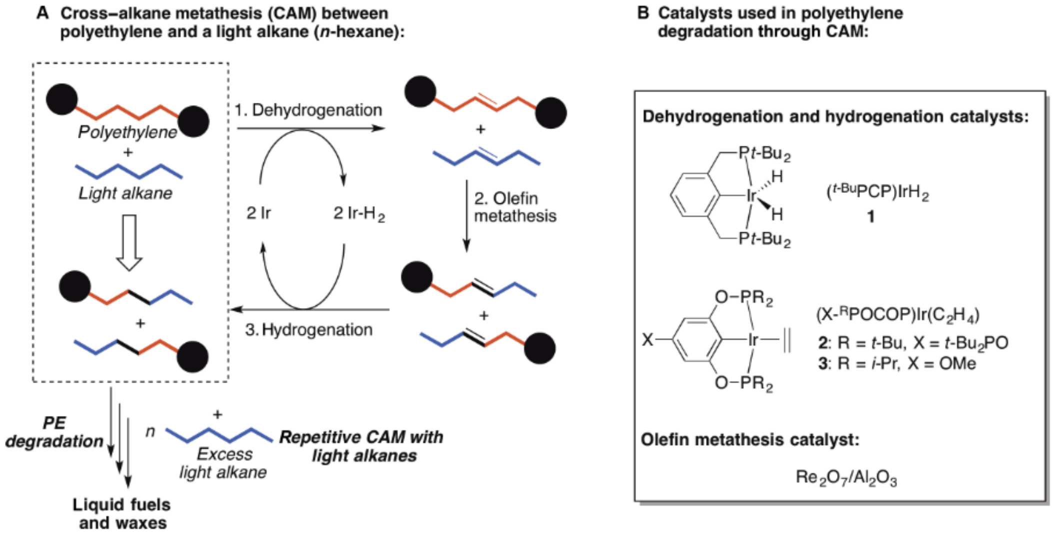

Figure 1. The degradation of polyethylene (PE) chains using the cross-alkane metathesis (CAM) mechanism with light alkanes. (A) The proposed PE degradation pathway using the CAM. (B) The respective structures of the used dehydrogenation and olefin metathesis catalysts. Reprinted with permission from ref 12. Copyright 2016 American Association for the Advancement of Science.

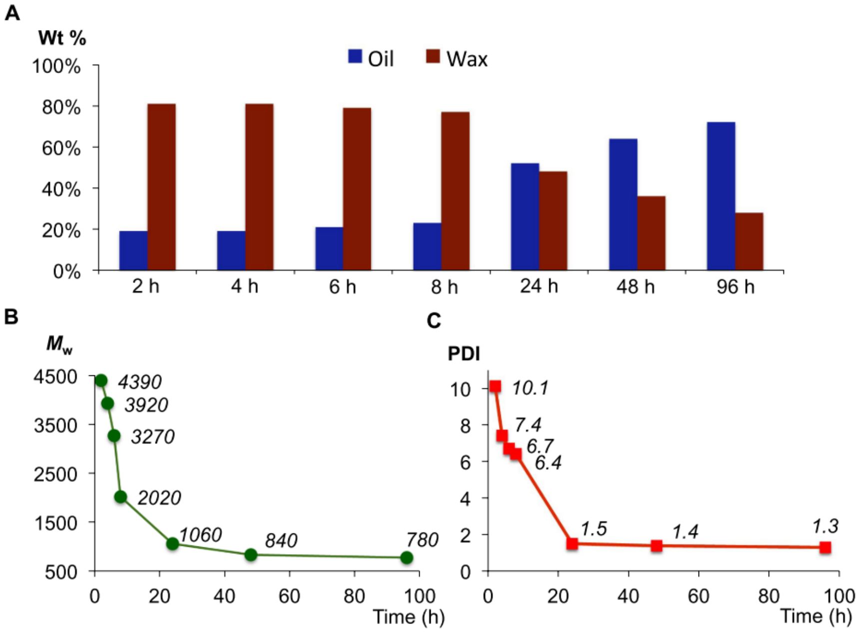

Figure 2. Degradation of HDPE (120 to 135 mg) with n-octane (4 ml) by Ir complex 2 (4.2 mmol Ir) and Re_2O_7/γ-Al_2O_3 (57.0 mmol Re_2O_7) at 175 °C after 2, 4, 6, 8, 24, 48, and 96 h. (A) Distributions of oil and wax products. (B) MW of the isolated PE wax products. (C) Molecular weight distributions of the isolated PE wax products. Reprinted with permission from ref 12. Copyright 2016 American Association for the Advancement of Science.

A more intensively studied catalytic degradation method is catalytic hydrogenolysis. Here the C-C bonds can be cleaved under the action of hydrogen and a metal-supported catalyst. Different products can be obtained, depending on the chosen catalyst and reaction conditions. Here only focus will be given on the production of heavy liquids (C15+) or waxes; lighter product formation can be found elsewhere in other sources.[13–15]

In one study, different PEs and a single-use plastic bag were catalytically transformed into lubricants and waxes.[16] This was done using well-dispersed Pt nanoparticles supported on $SrTiO_3$ perovskite nanocuboids by atomic layer deposition. Reactions were performed at 11.7 bar

H_2 at 300 °C. PE samples (50 mg) with a MW ranging from 17200-420000 g/mol were successfully converted to a liquid product of 625-1130 g/mol after 96 h. This catalyst produced very few light hydrocarbons, contrasting the tested benchmark Pt/Al_2O_3 catalyst. The PE proved to adsorb more favorably at the Pt sites of the SrTiO3 support to suppress over-hydrogenolysis towards undesired light hydrocarbons. This behavior stems from the electronic and geometric properties of the Pt nanoparticles and the SrTiO3 support, where edge sites proved more reactive for hydrogenolysis than Pt facets.[17] The tribological properties of the produced liquid showed comparable results to that of synthetic base oils such as PAO lubricants, surpassing Group III mineral oils.[16]

Later hydrogenolysis studies achieved plastic conversion at lower temperatures, albeit with higher hydrogen pressures. Nakaji *et al.*, detailed a gram-scale (3.4 g) conversion of virgin LDPE, HDPE, PP, commercial bags, and waste PE in an autoclave reactor at 60 bar H_2 and 240 °C.[18] Various catalysts were developed and tested: metals on a CeO_2 support (Ru, Ir, Rh, Pt, Pd, Cu, Co, and Ni); Ru on diverse supports (C, TiO_2, MgO, ZrO_2, and SiO_2); and Pt/H-USY. The Ru/CeO_2 alone displayed activity, yielding 76% conversion with 9.8%, 71% and 19% selectivity for gas (C1-C4), liquid (C5-C21) and wax (C22-C45), respectively. The other used metals demonstrated extremely low catalytic activity (≤ 5% conversion). Among Ru-supported catalysts, Ru/CeO_2 produced fewer non-valuable gases (C1-C4, primarily C1) due to inner (instead of outer) C-C bond dissociation. The authors state that Ru dispersion on CeO_2 was high owing to the high basicity of the metal oxide support and the basic properties of CeO_2. Pt/H-USY exhibited lower conversions at 240 °C (7%) despite longer reaction times (24 *vs.* 5 h for Ru/CeO_2), requiring 250 °C and 42 h for complete conversions and showing lower selectivity for liquids and waxes (82 *vs.* 90% for Ru/CeO_2). Besides, it was noted that higher MW LDPEs needed longer reaction times (8-24 h). Reaction times can be ranked: HDPE (10h) < LDPE (8-24 h) < PP (72 h), which can be explained by polymer-catalyst surface hindrance. This was observed even though the molecular weight of the used polymers could be ranked as following: PP < LDPE < HDPE. Wax production followed a similar pattern as the reaction times: HDPE (4.1%) < LDPE (5.4-6.8%) < PP (10%). The commercial bag product yields mirrored virgin LDPE but took 30 hours, while waste PE reacted yet required 48 hours reaction time for obtaining high yields.[18]

Similarly, another study focused on the conversion of isotactic PP (i-PP) toward lubricants using hydrogenolysis.[19] Various metals (Pd, Rh, Ir, Ni, Pt, and Ru) were tested with TiO_2 as the initial support. Reactions, conducted on a gram-scale (2g i-PP), took place at 250 °C at 30 bar H_2 in a stirred autoclave reactor. Almost no activity was noticed with the tested catalysts, except for the use of the Ru metal, yielding 28% gas (C1-C6) and 66% liquid. Furthermore, different supports were explored (SiO_2, C, Al_2O_3, CeO_2, and TiO_2) using the Ru metal, all proving highly active, except for Al_2O_3. Notably, all catalysts, except for the Ru/TiO_2, produced significant gas fractions (C1-C4), with up to an 82% methane yield, emphasizing the critical role of proper metal-catalyst support choice. The methane yield decreased in the following order: Ru/C > Ru/CeO_2 > Ru/SiO_2 > Ru/Al_2O_3 ≈ Ru/TiO_2, accordingly, the highest liquid yield was achieved with the latter Ru/TiO_2 catalyst. Additional testing with different isotactic and amorphous PPs revealed comparable results, however, with varying kinetics due to the different MWs and microstructures. Comparison of physical properties (*e.g.*, pour point, kinematic viscosity, and viscosity index) of the products with commercial lubricants showed similar values.[19] The Ru/C catalyst was also tested in other studies using HDPE and single-use PP.[20,21] High methane yields were obtained, especially at the elevated temperatures and longer reaction times.[20]

This undesired methane formation was suppressed by Wang *et al.*, using a Ru-supported tungstated zirconia (Ru-WZr) catalyst.[22] In their study, 2 g of LDPE was converted at 250 °C under 50 bar H_2 for a maximum of 2 hours. Other Ru-supported catalysts like Ru-HY and Ru-Al-MCM-41 proved to be less active (56 and 68% conversion, respectively) and produced more methane (36 and 52%, respectively). The introduction of WO_x in a Ru-Zr catalyst reduced the methane yield from 16 to 4.6% and increased the C20-C35 fraction from 22 to 35%. The authors attribute this enhanced performance to $(WO_x)_n$ clusters storing hydrogen as surface hydroxyls, facilitating the spillover effect. The stored hydrogen then enhances reverse hydrogenation and desorption of the long alkyl intermediates, preventing further chain scission, as can be seen in Figure 3.[22]

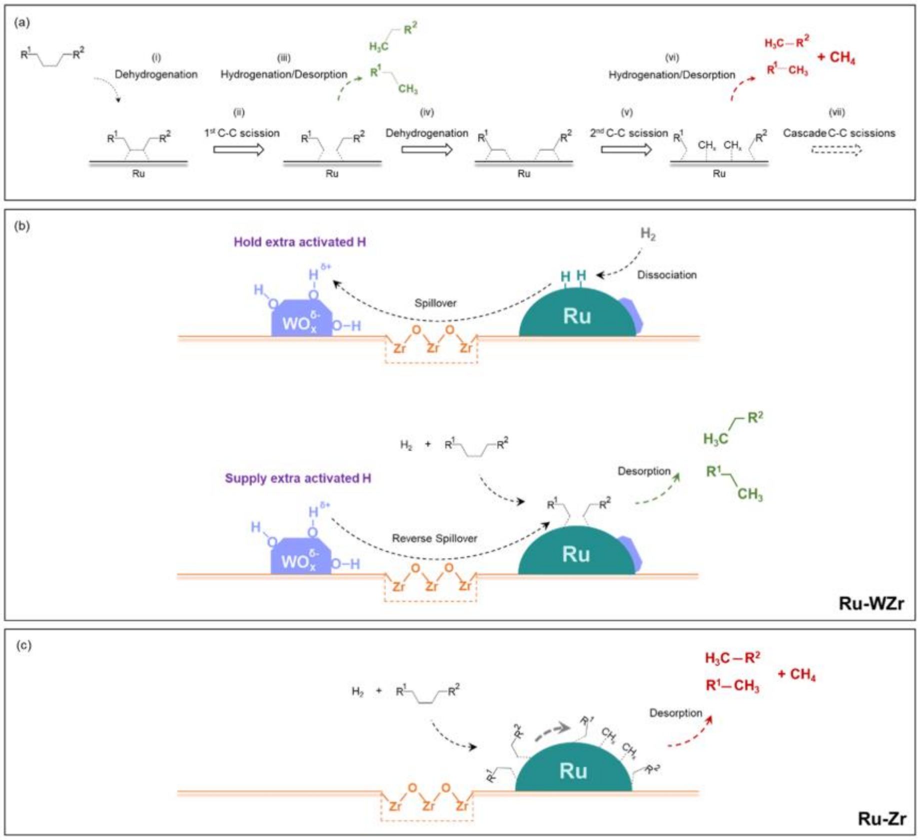

Figure 3. The proposed alkane hydrogenolysis mechanism with the effect of the different catalyst compositions. (a) General hydrogenolysis mechanism over Ru-metal. (b) Selective hydrogenolysis reaction over Ru-WZr using the spillover and reverse spillover effects. (c) Non-selective hydrogenolysis mechanism over Ru-Zr. Reprinted with permission from ref 22. Copyright 2021 American Chemical Society.

Kots *et al.* explored the hydrocracking and hydrogenolysis of PVC-contaminated plastic waste toward lubricants, waxes, and fuel-range hydrocarbons, as illustrated in Figure 4.[23] The presence of PVC contamination in plastic waste is concerning due to the potential poisoning of Ru and Pt active sites by chlorine. Additionally, during PVC decomposition, HCl is produced, which is highly corrosive and toxic. Lubricants and fuels containing several ppm of HCl or chlorinated organics are unsuitable for use. While extensive sorting might solve this issue, removing trace amounts from waste mixtures is labor-intensive. To circumvent this, the researchers employed a two-stage conversion strategy. In the first stage, Cl-contaminated PP underwent treatment with a magnesia-alumina mixed oxide at 30 bar H_2 at 250 °C. This resulted in the formation of a solid chloride, leading to the near-complete removal of the chlorine in the polyolefin melt. Subsequently, the researchers successfully processed up to 10 wt% PVC content into lubricants using Ru-based catalysis in the second stage.[23]

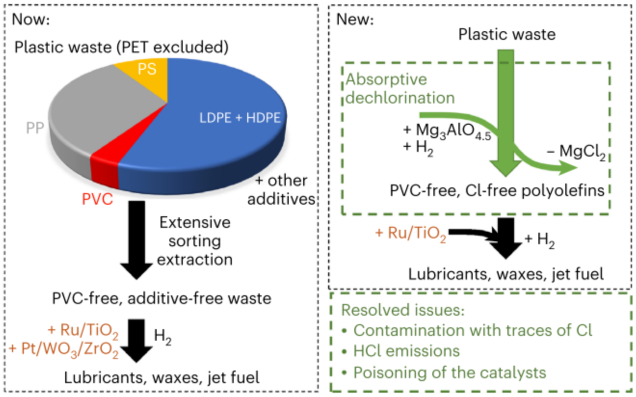

Figure 4. A schematic representation of the hydrotreatment of PVC-contaminated plastic waste and proposed scheme for adsorptive dechlorination. Reprinted with permission from ref 23. Available under a CC-BY 4.0. Copyright 2023 Springer Nature.

Zhang *et al.*, converted PE using a Pt/γ-Al2O3 catalyst without hydrogen in an unstirred mini-autoclave reactor.[24] Here, long-chain alkyl aromatics and alkyl naphthenes were produced, which can be used in lubricants and other products. The authors propose a tandem reaction of PE hydrogenolysis, followed by aromatization *via* dehydrocyclization, as can be seen in Figure 5. In this mechanism, exothermic hydrogenolysis was coupled with endothermic aromatization, rendering the reaction thermodynamically accessible at the used temperature of 280 °C. In this way, up to 80 wt% PE could be converted. However, also here long reaction times were used (24 h) on a small scale (8.4 mmol initial polymer).[24]

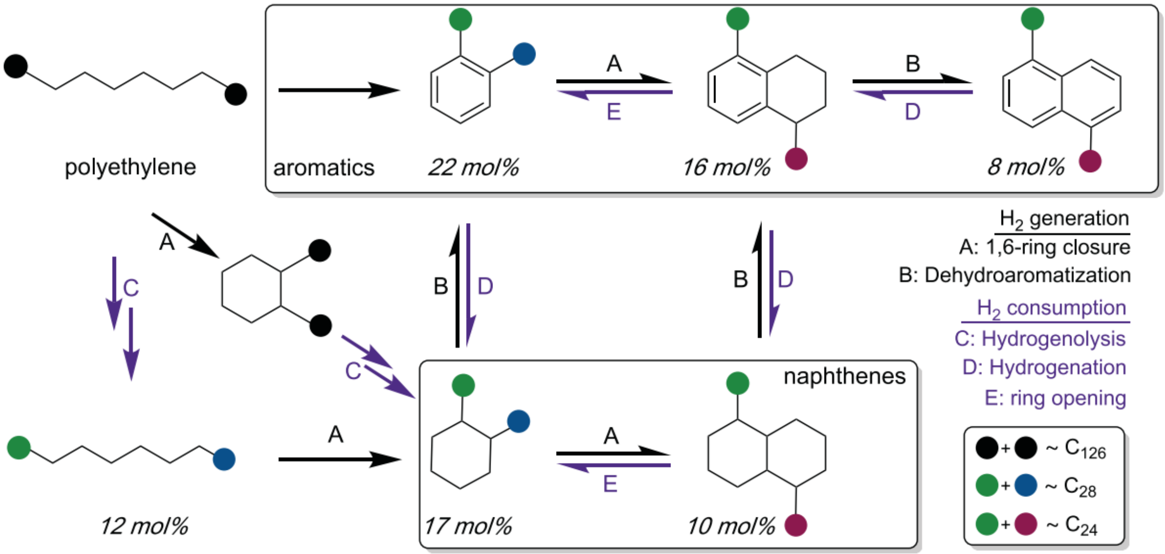

Figure 5. The proposed tandem PE hydrogenolysis, followed by aromatization *via* dehydrocyclization. Reprinted with permission from ref 24. Copyright 2020 American Association for the Advancement of Science.

The aforementioned studies highlight that catalytic depolymerization is a promising method for heavy hydrocarbon production, demonstrating the feasibility of generating base oils and, to a lesser extent, waxes. Noteworthy is the utilization of relatively low temperatures. However, it is crucial to note the use of expensive noble metals, coupled with longer reaction times, particularly when comparing it to the thermal pyrolysis reaction (as discussed in Section 2). It should be noted that these studies were conducted on the gram-scale or lower, whereas many thermal degradation studies have been successfully implemented on a pilot or industrial scale. Replicating these results on a larger scale is imperative to validate this technology as a viable plastic conversion method. Avoiding deeper cracking towards smaller molecules additionally proves to be challenging in the catalytic conversion pathways. Lastly, catalyst poisoning is an important issue that should be circumvented.

2. Thermal pyrolysis toward high molecular weight products

Thermal pyrolysis entails breaking polyolefin chains by applying external heat, typically under an inert nitrogen atmosphere. This technique can produce high MW products, as well as liquids and gases, depending on the process severity in terms of contact time, temperature, and reactor type. This review focuses solely on wax production, as producing gases and liquids has been studied more widely.[5,25–27] Unfortunately, many thermal pyrolysis papers omit wax yield details, despite the product's significance. Besides, the definition of the 'wax fraction' may vary (causing confusion) and characterization of the wax product is frequently absent.

The thermal pyrolysis reaction mechanism is characterized by a complex sequence of reactions, starting with random chain scission on the polymer chain. This process generates free radicals, leading to inter- and intramolecular hydrogen transfers and β-scissions, resulting in secondary radicals and shorter hydrocarbons. In the PE pyrolysis mixture, alkanes are predominantly straight and stable; olefins are mostly present as α-olefins, iso-olefins and diolefins (α,ω-olefins). The olefin/paraffin ratio generally decreases with increasing carbon number. In both PE and PP, long-chain olefins can be subjected to random scission, intermolecular hydrogen transfer, and β-scission. In PP chains, the tertiary carbons form weak branching links, explaining why it requires less activation energy to break compared to the carbon chains in PE.[28,29] Further literature about reaction mechanism, modelling, and kinetics can be found in other sources.[30,31]

The product composition in thermal pyrolysis is strongly influenced by reaction conditions, reactor type, and feed composition. Various reactor types, as shown in Figure 6, are commonly employed.[32] Thermal pyrolysis can give rise to a broad product distribution, with the specific product depending on factors such as heating rate, temperature, and residence time for a given polymer or mixture.[33–36] Calculating solid and gas residence times can be challenging and is often omitted in studies, complicating literature comparison. Figure 7 illustrates wax yields from literature, highlighting variations with changes in reaction temperature for different plastic types and reactors. Studies with single data points were excluded from the figure.

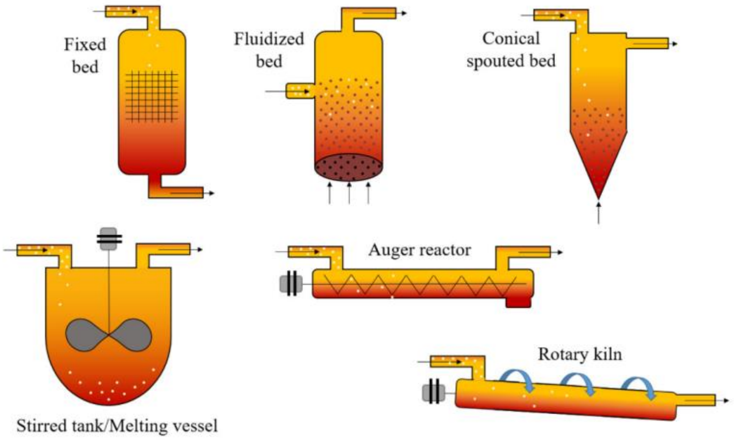

Figure 6. Commonly used thermal pyrolysis reactor types. Reprinted with permission from ref 32. Available under a CC-BY 3.0. Copyright 2022 Royal Society of Chemistry.

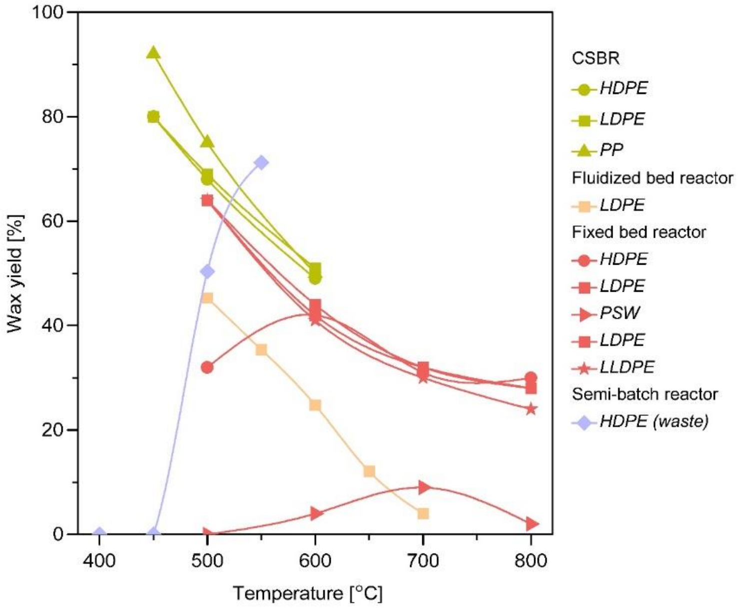

Figure 7. Different wax yields are plotted as a function of the reactor temperature for different reactors and polymer types. Data references: conical spouted bed reactor (CSBR) from ref 37, fluidized bed reactor from ref 38, fixed bed reactor from ref 39,40, and semi-batch reactor from ref 41.

Conical spouted bed reactors (CSBR) demonstrated the highest wax yields. Among plastic types, PP showed the highest wax yield (92%), followed by HDPE and LDPE with nearly identical yields. The elevated yield of PP at lower temperatures is attributed to its more branched chain structure, causing initial cracking at the branch of the chain rather than on the principal chain. Cracking of this principal chain is low due to the short residence times in the CSBR. Despite LDPE's more branched structure compared to HDPE, similar wax yields were achieved, although LDPE produced lighter waxes.[37] The high wax yields in this type of reactor can be attributed to some specific advantages of the reactor. Firstly, the cyclic movement of the particles is suitable for fast and uniform coating of the sand or catalyst particles with the melted plastic, which improves the heat and mass transfer between the two phases. Secondly, more vigorous particle movement minimizes defluidization issues compared to bubbling fluidized bed reactors. Thirdly, the reactor boasts very short volatile residence time, ranging from 30 to 500 milliseconds, minimizing secondary reactions.[42–46] A schematic representation of the reactor can be found in Figure 8, while Figure 9 depicts the product distribution for the 500-700 °C temperature range, showing that higher cracking temperatures result in fewer heavy products.[47]

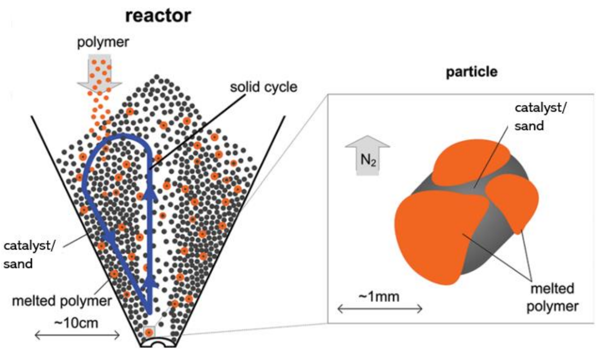

Figure 8. Schematic representation of the conical spouted bed reactor. Adapted with permission from ref 47. Available under a CC-BY 3.0. Copyright 2017 IntechOpen.

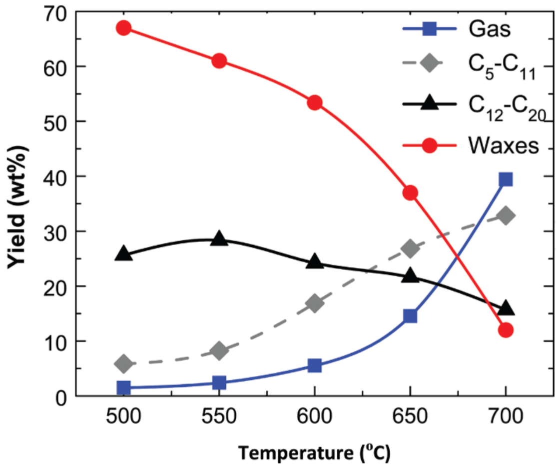

Figure 19. The obtained yields of the different products of the thermal pyrolysis of HDPE in a conical spouted bed reactor. Reprinted with permission from ref 47. Available under a CC-BY 3.0. Copyright 2017 IntechOpen.

CSBRs, despite their efficiency, exhibit high nitrogen consumption, contributing to increased energy consumption, as can be seen below in Section 4. However, the use of a pressure swing adsorption system can mitigate this nitrogen usage. Implementing a draft tube in the CSBR setups can reduce the minimum spouting velocity, consequently lowering the required gas flow for fluidization.[48]

Other high yields of waxes were obtained in fixed bed (batch) type reactors (64% max) by Al-Salem *et al.*, as can be seen in Figure 7.[39,40] Also here, a higher branching in the polymer chain resulted in a higher wax yield at 500 °C, but this effect diminished at higher temperatures. A noticeable difference in the wax yield can be found for plastic solid waste (PSW) pyrolysis, obtained from an active landfill site. The authors attribute this to the mildly branched feedstock (presence of PP) and crystallinity of the PSW, requiring a higher temperature and residence time than the other tested feeds.[39,40,49,50]

Fluidized bed systems have also been studied. Williams *et al.*, reported a notably lower wax yield for LDPE conversions compared to CSBR reactions (45 *vs*. 69% max).[38] In contrast, Predel and Kaminsky achieved high wax yields (84% for HDPE).[51] Comparison with the CSBR system is challenging due to the differences in reactor configuration. Complete description of the operation conditions, like the nitrogen flow rate, were not provided in both studies. Other fluidized bed studies did not represent isolated wax yields, making comparison impossible.[52,53]

The semi-batch reactor, another type explored for polyolefin pyrolysis, operates by collecting pyrolysis products in a separate vessel. Kumar and Singh observed an increase in wax yield with rising reaction temperature (up to 78%).[41] This contrasts with the other discussed reactor studies where an increase in temperature resulted in a decreased wax yields. The authors attribute this phenomenon to the lower primary cracking that takes place at lower temperatures, these formed products are not volatile enough to escape the reactor at the given reaction temperature, leading to increased residence times. This extended residence time enhances secondary cracking reactions, producing lighter products. In contrast, at higher temperatures, the formed waxes are more volatile, allowing them to escape the reactor more easily, reducing residence time.[41]

Continuous stirred tank reactors, studied by Abbas-abadi *et al*., achieved relatively high wax yields (up to 70%).[54,55] The study examined the effects of pressure, temperature, and waste composition, revealing a significant influence of pressure on the amount and composition of pyrolysis products. Generally, an increase in temperature and pressure led to lighter products due to increased chain scissions, generating more olefins and (conjugated) dienes. The formation of linear olefins also elevated the production of aromatic and other secondary products, thereby intensifying coke formation. In the case of PP pyrolyzates, steric hindrance of the branched olefins reduces Diels-Alder reactions, lowering the content of cyclic components. Waste plastics resulted in a higher proportion of naphthenes and (poly)aromatics, along with increased coke formation, likely attributed to the presence of PS, biomass, and metals.[54,55] Similarly, the influence of pressure and temperature was observed in stirred tank reactors.[56–58] A low-temperature reaction (330-385 °C) for LDPE conversion achieved a high wax yield of 80 wt%. However, at these low temperatures, a pressure of 21 bar was necessary. When no external pressure is applied, a temperature of 410 °C is typically required to initiate the thermal conversion of LDPE. However, at higher pressures, more molecular and radical collisions occur, leading to more primary and secondary reactions.[56–58]

In another study, a molten metal reactor was employed to convert HDPE, where tin was melted at 460 °C.[59] The introduction of plastics led to the formation of heavy waxes, once enough waxes accumulated in the reactor, plastic pyrolysis occurred in the wax phase itself. Wax products comprised of chain lengths ranging from C21 to C100, with the majority towards the higher range. However, no information regarding the yields were given for the waxes or other formed products.[59] Another successful reactor technology is the auger reactor, which, in the work of Al-Salem, yielded a substantial yield of waxes (65%).[60] Lastly, a rotary kiln reactor resulted in a low wax yield (13%), the addition of sand in the reactor as a heat carrier further reduced wax yields.[61] Thermal co-pyrolysis of plastic waste with biomass can also be carried out. Low amounts of heavy fractions were obtained, however, explained by synergetic cracking effect, increasing the oil yields.[62,63]

Thermal pyrolysis is also applicable to more complex feeds, such as metallized food packaging plastic waste.[64] In a study, 250 g of this waste was converted in a small cylindrical pyrolysis reactor, resulting in a maximum wax yield of 20% at 700 °C. Further processing steps on the char/Al mixture resulted in isolated Al chloride and pure carbon particles. A TEA study resulted in an economic return of 610 $/ton plastic waste, showcasing promising potential for this technology.[64]

As evident in the mentioned studies, thermal pyrolysis is effective for producing high MW products such as waxes. Generally, higher reaction temperatures were used compared to the catalytic polyolefin conversion. Fluidized systems, while yielding high wax yields, may consume high nitrogen amounts. Reducing this consumption would make this technology more attractive for industrial adaptations. On the other side, the technology is straightforward, devoid of deactivation issues. Thermal pyrolysis has demonstrated scalability to work on larger scales without expensive catalysts and without the extended reaction times, as observed in the catalytic conversion strategies.

3. Chemical upgrading of pyrolysis products

Given the broad product distribution of (waste) plastic pyrolysis products, product upgrading or transformation is often needed to tailor products properties and compositions for specific applications. Various physical and chemical upgrading techniques can be employed for the high MW products. The following sections overview the secondary chemical upgrading and transformation strategies toward refined waxes, surfactants, base oils, lighter molecules, and impurity removal.

3.1 Toward refined waxes

Refined petroleum waxes consist of *n*-paraffins, iso-alkanes, and/or cycloalkanes. When analogue waxes want to be produced from polyolefin plastics *via* pyrolysis, (catalytic) upgrading steps should be implemented. Crude petroleum waxes are upgraded by removing oils, asphaltenes, resins, olefins, and sulfur and nitrogen compounds, with the degree of removal depending on their application. This can be done through different techniques such as de-oiling, using adsorbents, and through hydro-finishing, as is done for treating (unrefined) slack waxes. These are mature and widely applied techniques.[7]

Another feature of petroleum waxes is the average MW and the degree and site of branching. The average MW and branching increase as follows: paraffin waxes < intermediate waxes < microwaxes.[7] Generally, pyrolysis waxes do not have the precise average MW and appropriate branching nature. Branching occurs due to the radical recombination mechanisms during pyrolysis, or branches are already present in the plastic feed, *viz.,* PP and LDPE. However, this branching (regarding amount, length, and site on the wax chain) is unsuitable for certain wax types. No isomerization studies of pyrolysis waxes have been found surprisingly. One related patent described the use of a mild hydroisomerization of Fischer-Tropsch (FT) waxes, not crude plastic waste waxes, for the creation of softer waxes.[65]

3.2 Toward surfactants

Waxes obtained from pyrolysis can also be upcycled into surfactants. Xu *et al.* pyrolyzed 500 mg PE, PP, and mixes hereof in a quartz reactor at 360 °C for 8 to 16 h.[66] The waxes were then oxidized using air and manganese (Mn) stearate for 6 to 10 h. The Mn stearate catalyzed the oxidation of the plastic-derived wax, after which a saponification step using aqueous KOH was performed. Using these steps, *ca*. 80% conversion towards fatty acids could be obtained. By producing these fatty acids, value-added products are created, as the market price per metric ton of common surfactants is almost double that of virgin plastics. Although the experiments were carried out on a small scale with long reaction times, increasing the scale of the experiment and decreasing the reaction time could make this technology a more interesting conversion way for industrial applications.[66]

3.3 Toward base oils

Only a limited number of studies have been conducted on the conversion of polyolefin pyrolysis products toward base oils for lubricant production. Base oils typically consist of a blend of highly isomeric molecules.[8] Enhancing this presence of isomers can be accomplished by hydroisomerization. While this technology has been extensively researched for the production of lube oils using FT waxes, its application to plastic pyrolysis oils remains underexplored.[67]

Miller *et al.* explored the co-processing of waste plastics and FT wax to produce lube range molecules.[68] The tested feedstocks included PE (100%), PE (96%) with polyethylene terephthalate (4%); and PE (50%) with FT wax (50%). After initial thermal pyrolysis, the products underwent hydroisomerization using an unnamed catalyst. The major byproduct was a diesel fraction with minimal gas production. Product quality and distribution exhibited little variation among the tested feedstocks. The reported yield ranged from 37-57 wt% for products with a boiling point exceeding 385 °C (>C23). Given the highly olefinic nature of the lighter fractions, a potential theoretical yield of 60-70 wt% could be achieved through oligomerization, when all olefins are assumed to be able to convert to the lube fraction.[68–70] However, this oligomerization of this smaller olefinic fraction remains unstudied for polyolefin-derived products.

In another study, lubricants were produced from actual plastic waste (mainly LDPE) and compared with those derived from FT wax.[71] The pyrolysis waxes were created with a screw reactor using quartz sand to facilitate heat transfer. Subsequently, the products underwent hydrogenation and hydroprocessing in a three-phase fixed-bed reactor. Isomerization of the produced waxes was achieved using a Pt/H-SAPO-11 catalyst, known for its high isomer selectivity and minimal hydrocracking ability due to its narrow pore size. Prior to isomerization, sulfur removal was conducted through hydrogenation using a commercial Co-Mo/Al_2O_3 catalyst, a crucial step to eliminate sulfur first as it is detrimental to noble metal catalysis. In contrast to lubricants made from FT waxes, those made from plastic waste had lower cloud points and improved temperature stability at the same cloud points. The authors do note, however, that additional research is necessary to evaluate this discrepancy, particularly analytical research on lubricant composition.[71]

3.4 Toward lighter products from waxy primary feeds

Several investigations implemented an initial mild pyrolytic stage, followed by cracking of the resultant wax fraction to lighter products. This approach aims to generate fuels, monomers, or other chemical compounds, like those from fossil oil cracking. In line with the focus of this perspective, only studies mentioning substantial wax fractions after the first pyrolysis step were considered in the following discussion.

Several studies focused on cracking of HDPE waxes produced in the CSBR in a fixed-bed reactor. When using different H-ZSM-5 zeolite catalysts, high yields (up to 58 wt%) of light olefins (C2-C4) could be obtained at 500 °C. When comparing this to *in-situ* catalytic pyrolysis in the CSBR, slightly lower olefin yields in the single step were obtained, despite the use of a higher catalyst space-time in the single step (8 *vs.* 15-30 $g_{cat}.min^{-1}.g_{HDPE}^{-1}$).[46,72–74] The fixed-bed reactor, unlike the CSBR, was not limited by hydrodynamics, providing operational and scale-up advantages. Moreover, the separation of thermal and catalytic cracking into two reactors prevented competition for acidic sites and allowed independent optimization. This two-step strategy facilitated controlled conditions, reduced secondary reactions, and could be advantageous for processing municipal waste with potential additives. Additives in the waste can easily poison the catalytic sites, making single-step catalytic cracking challenging. The two-step reaction could allow for the separation of the inorganic additives in the first thermal pyrolysis step. In addition, after the first thermal pyrolysis reactor, a set of parallel catalytic cracking reactors may be used. These reactors can then operate in reaction-regeneration cycles, allowing for fewer issues due to catalyst deactivation.[44,75] Tuning the catalyst bed effectively to prevent deactivation involves finding the right balance of acidic sites in terms of strength and nature, along with a pore network favoring fast coke precursor removal. The latter can be foreseen by using highly connected pore networks.[76] This can be achieved by selecting a proper binding material or by using mesoporous (hierarchical) zeolites.[77] Kinetic data of this secondary cracking of waxes with H-ZSM-5 can be found elsewhere.[78] Another study used a spent FCC catalyst instead in the fixed-bed reactor, producing fewer light olefins compared to the use of the H-ZSM-5 (24 and 49%, respectively), which can be attributed to the different zeolite's pore sizes.[79]

HDPE and PP waxes have additionally been co-cracked in several studies with fossil fuels. Vacuum gas oil (VGO), atmospheric gas oil, and hydrotreated VGO were blended with the PE or PP waxes in a riser reactor with the FCC equilibrium catalyst. Synergetic effects were noticed when co-cracking the different feeds, altering product compositions. The results highlight the possibility of cofeeding the plastic-derived waxes with the other fossil fuels in FCC units. However, care should be taken in selecting the feedstock, catalyst quantity, and cracking conditions, as they influence the product compositions and coke formation.[80–87]

Besides waxes obtained from virgin plastics, waxes derived from post-consumer plastics have been subjected to secondary cracking using acid catalysts. Waxes derived from municipal waste were cracked in a fixed-bed system using three catalysts: H-ZSM-5 (pure and with 20% clay); H-

Y (with 20% clay); and H-Mordenite (with 20% clay).[88] H-ZSM-5 exhibited the highest conversion rate towards gases and gasoline-range hydrocarbons, favoring naphthenes and aromatics (mainly benzene, toluene and xylene). H-Y showed medium activity in the conversion towards the lighter components, producing a high fraction of branched light hydrocarbons. The product has a high octane number and a high fraction of aromatics in the gasoline-range components. H-Mordenite showed the lowest conversion, this one-dimensional catalyst mainly produced non-gaseous paraffinic products with similar product characteristics as the raw pyrolysis product.[88]

Thermal pyrolysis followed by a two-step catalytic cracking was also studied for the formation of a low aromatic naphtha fraction.[89] Virgin HDPE, LDPE, PP, their mixtures, and real-world post-consumer waste were tested. Different metals on H-SBA-15 catalysts were tested in the first reforming reactor. Zn/H-SBA-15 performed best in converting the HDPE wax toward shorter hydrocarbon olefins. The incorporation of ZnO did not influence the mesoporosity of the H-SBA-15 while increasing its acidity, resulting in increased cracking activity with a high conversion toward C5-C12 olefins. These fractions were then further reformed toward C5-C12 paraffins due to hydrogen transfer and hydrogenation reactions that were performed in a secondary reforming reactor using an Al_2O_3-pillared montmorillonite clay catalyst. This reaction scheme is presented in Figure 10.[89]

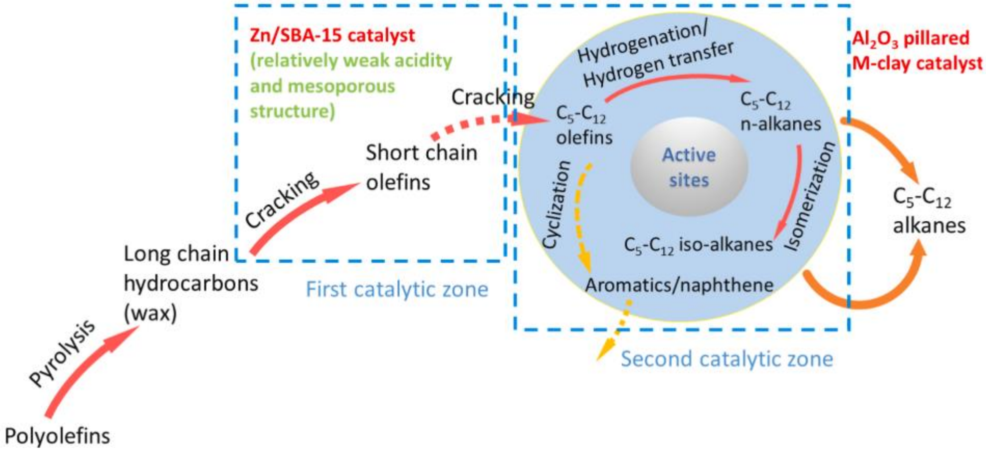

Figure 10. The proposed reaction mechanism that uses thermal pyrolysis, followed by catalytic reforming using a Zn/SBA-15 and Al_2O_3 montmorillonite clay (M-clay) catalyst. Reprinted with permission from ref 89. Copyright 2021 Elsevier.

The conversion of more contaminated pyrolysis wax has additionally been studied. Chlorinated wax (0.14 wt% Cl) from municipal plastic waste was cracked in a fixed bed reactor using H-Y and Fe/H-Y zeolites using a time on stream of 2 h.[90] It was observed that the chlorine was adsorbed on the iron oxide on the zeolite surface, resulting in a form of iron chloride, thus reducing the free chlorine content. The use of Fe/H-Y zeolite with the lowest tested iron content (3 wt% Fe) yielded the highest fraction of liquids (67 wt% gasoline and kerosene/diesel), while the use of high Fe loadings (20 wt% Fe), exhibited the least cracking activity due to the reduction of free acid sites, albeit with the least amount of chlorine (60 ppm). No information related to catalyst deactivation was given. However, a regeneration of the catalyst was shown by calcination, showing a complete removal of the adsorbed chlorine and almost full removal of the cokes. The regenerated catalyst showed similar trends in the product composition when compared with the fresh catalyst.[90]

In addition to acid catalysts, base catalysts can also be used in the cracking of waste polyethylene wax. Kasetsupsin *et al.*, investigated activated carbon, spent FCC, and magnesium oxide as catalysts.[91] The use of these catalysts, alone or in combination, increased the yield of diesel-like oil, with the highest yield achieved by the combination of the activated carbon with MgO. Positive synergetic effect were observed when combining FCC on activated carbon with MgO, attributed to the presence strong Lewis acid and base sites, effectively cracking the long-chain hydrocarbons.[91]

Hydrocracking can also be used to form lighter products. This requires a metal-impregnated catalyst for the cracking in the presence of hydrogen gas. Hydrocracking in a stirred batch reactor was done using: Ni/H-Beta + H-ZSM-5; Ni/H-SAPO-11 + H-ZSM-5; and Ni/H-MCM-41 + H-ZSM-5. It was noted that the Ni/H-Beta + H-ZSM-5 mixture resulted in a high fraction of gases, diesel, and higher viscosity index base oils. The Ni/H-SAPO-11 + HZSM-5 resulted in the highest fraction of gasoline and lube base oil. The Ni/H-MCM-41 + H-ZSM-5 resulted in lower hydrocracking activity, resulting in a lower pour point of lube base oil and a lower olefinic gasoline and diesel fraction.[92] Another study cracked wax derived from post-consumer waste, containing mainly PE, using H-Beta, H-Y, H-ZSM-5, and silica-alumina. The highest conversion toward liquids (naphtha) was found using H-ZSM-5, yielding 83% aromatics, which is undesired for the naphtha quality. On the other hand, H-Beta, produced mainly linear unsaturated hydrocarbons. Pd addition to H-Beta enhanced activity, achieving complete conversion at lower temperatures (360 °C), reducing olefinic content, and increasing iso-paraffin contents.[93]

Thermal cracking was also investigated. Compared to catalytic cracking, non-catalytic thermal cracking eliminates the problems associated with catalyst deactivation due to the presence of impurities in the waxes. A purely thermal process may thus be easier for scale-up processes in industry compared to using a single catalytic step. One disadvantage is the higher temperatures that need to be used in the thermal cracker, as catalytic cracking can operate at substantially lower process temperatures. This is illustrated in a study of Artetxe *et al.*, who used a CSBR for producing a waxy feed from HDPE.[94] The authors performed an in-line secondary thermal cracking using a quartz tube reactor at 800-950 °C with short residence times (0.016-0.032 s). The highest light olefin yield (C_2-C_4) was obtained at 900 °C (77 wt%), this was surprisingly higher than the H-ZSM-5 zeolite cracking in the fixed-bed reactor at 550 °C (62 wt%). However, the thermal cracking produced significantly more methane than the catalytic cracking (5.2 wt% *vs.* <0.4 wt%, respectively).[44,75,94]

Other researchers tried to use the waxes obtained from the pyrolysis step as a viscosity-reducing agent in the thermal cracking of PE and PP plastics. A schematic representation of the reactor can be seen in Figure 11. Waxes were mixed here with the PE and PP plastics in a dissolution tank that operated in a semi-batch mode. The pyrolysis was subsequently performed in a tubular reactor at 600 °C, obtaining complete conversion after 2 s. The addition of the wax prior to pyrolysis reduced the viscosity in the used temperature range (220-240 °C) and improved the flow and thermal efficiency during the pyrolysis process.[95–97]

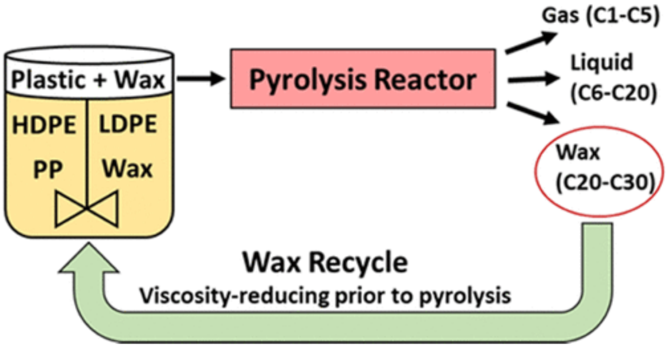

Figure 11. Schematic representation of the polyolefin thermal pyrolysis system where the obtained wax products are used as a viscosity-reducing agent. Reprinted with permission from ref 96. Copyright 2022 American Chemical Society.

The above studies prove that the formation of secondary products out of pyrolysis waxes is feasible. When making refined products, these steps are especially necessary. Studies show that the cracking of pyrolysis waxes might be beneficial compared to the one-step plastic cracking towards lighter components. Synergetic effects can be found when coprocessing the pyrolysis waxes with different petroleum feeds. Also here, catalytic cracking is subject to catalyst poisoning due to impurities. Cleaning of the pyrolysis wax prior to secondary upgrading can be achieved using different techniques, as will be discussed in the following section.

3.5 Impurity removal

Impurities that are found in (post-consumer) plastics are often detrimental for the further use of the pyrolysis products, as strict product requirements are often in place. In addition, impurities can poison catalysis, hampering further catalytic process steps. Therefore, impurity levels generally must be reduced, as can be done using different techniques. Analogies can be found in the petrochemical industry, where impurity removal is a mature technology. However, impurities found in plastic waste diverge in various aspects as different impurity sources can be present. Impurities can originate from internal (*e.g.,* additives, catalysts, and metal and tie layers) or external (*e.g.,* paper or food scraps) sources.[98,99]

When plastics are used for specific chemical recycling, a sorting step will most likely be required for polymer type isolation. However, after remelting, re-extrusion and washing, most plastic product streams will still contain certain levels of impurities. Different strategies might be implemented to remove these impurities. One strategy is the removal of these impurities before further chemical recycling of the plastics. This might be needed when direct catalytic conversions are envisaged on the plastics, thus preventing possible poisoning of the catalysts. Information of plastic cleaning can be found elsewhere.[100–108] In contrast, thermal pyrolysis can convert contaminated plastics. It is thus possible to remove the impurities from the pyrolysis oil before further catalytical processes are applied. This strategy might be more feasible than the direct removal of the impurities from plastics, as the pyrolysis products are more easily manipulated. In addition, a thermal pyrolysis step might already isolate a significant portion of the impurities, as might be the case for the CSBR. Data is, however, lacking for the comparison of different reactor types. The impurity levels are largely influenced by the effectiveness of the sorting steps. Determining if a pyrolysis stream is sufficiently clean will depend on the requirements of the further chemical processes. An example for usage in a steam cracker is given in the following.

Steam crackers require a certain level of purity for proper functioning. Plastic pyrolysis oils can contain a vast quantity of contaminants that can cause corrosion, fouling, and downstream catalyst poisoning in industrial steam cracking plants. Figure 12 depicts the concentration of different heteroatoms in different waste plastic pyrolysis streams together with the industrial thresholds for steam crackers. These contaminants clearly exceed the thresholds by one or more orders of magnitude. Besides this, the amounts of olefins and aromatics are unacceptable for industrial steam crackers. Impurity removal is clearly needed for improving the quality of the products.[109,110]

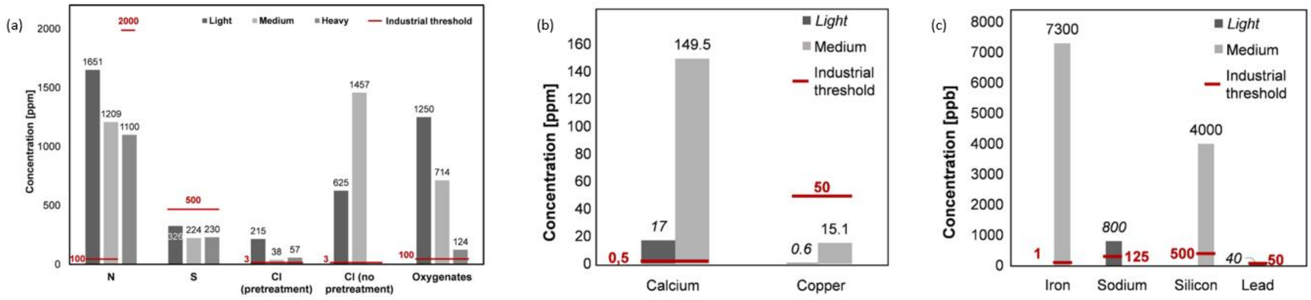

Figure 12. The level of heteroatoms in different plastic pyrolyzates, together with the industrial threshold for industrial steam crackers for light, medium, and heavy fractions. (a) Overview of N, S, Cl (with or without pretreatment), and oxygenates concentrations (in ppm). (b) Concentrations of Ca and Cu (in ppm). (c) Concentration of Fe, Na, Si, and Pb (in ppb). Adapted with permission from ref 110. Copyright 2022 Elsevier.

Clearly, different impurities are present in pyrolysis oils. Integrating the pyrolysis units into conventional refineries is, however, only possible when plastic pre-treatment methods are applied, which include sorting, washing, and dehalogenation.[111] Removal of impurities from pyrolysis oils can be done using catalysis or by using physical processes. Catalytic cleaning often involves hydrotreating processes, which are highly useful in removing heteroatoms. With this method, olefins and aromatics may be removed by double bond hydrogenation, as well as the N, S, Cl, and O heteroatoms. Detailed information can be found in another review paper.[111]

In addition to catalytic methods for impurity removal, physical approaches can also be utilized for the purpose of cleaning impurities. This is a favorable strategy when, for example, (valuable) (alpha-)olefins need to be preserved as hydrotreating will convert them into saturated hydrocarbons. Fractional distillation is a frequently used method in the petroleum industry. This method enables to largely concentrate the metallic and oxidic constituents in the distillation residues.[112] Nevertheless, rather few studies have been reported that use distillation of the pyrolysis products.[113–116] However, detailed elemental analysis studies before and after distillation of waste plastic pyrolyzates are missing.

The use of (membrane) filtration for pyrolysis oils might be another technique for removing impurities.[112] Kusenberg *et al.* used depth-filtration for the removal of particulate contamination from pyrolysis oils of post-consumer mixed polyolefins.[117] A reduction of *ca*. 20% to 81% could be achieved, depending on the filter medium used, this could be achieved without affecting the hydrocarbon composition of the pyrolysis oil. Interestingly, the study found that that the particle composition depended on the particle sizes, with calcium being the dominant element in the smallest particles (< 5 µm), whereas oxygen and silicon were the dominant elements in the bigger particles (50-100 µm).[117]

Sorbents can be used to remove impurities from the pyrolysis products as well. In one approach, Park *et al.*, utilized hydrated lime ($Ca(OH)_2$) as a sorbent to remove HCl from pyrolysis gases.[118] Pyrolysis of LDPE contaminated with PVC (4 wt%) in a two-stage auger-fluidized bed reactor, the gases passed through a hydrated lime filter, resulting in a pyrolysis product with a chlorine content of 9.25 ppm.[118] De Meester's group demonstrated the efficacy of activated carbon as an adsorbent in purifying pyrolysis oils.[119] The group tested activated carbon for the removal of nine of the most important heteroatom model components in pyrolysis oil: pyridine, benzonitrile, chlorobenzene, 1-chloropentane, cyclopentane, cyclopentanone, phenol, methacrylic acid, benzoic acid, and hexamethylcyclotrisiloxane. In the used model mixture benzoic acid was most easily removed; less polar components, such as cyclopentanone, hexamethylcyclotrisiloxane and

1-chloropentane (no detectable removal), were harder to remove without excessive dosing of the activated carbon.[119]

Yao *et al*. reported the use of supercritical fluid extraction with CO_2 for the removal of organic and inorganic impurities from PE and PP pyrolysis oil and wax.[98] The method, which is depicted in Figure 13, showed a high organic impurity removal efficiency (81% for PE, 97% for PP), along with color and small improvements. The researchers proposed a solvating sphere phenomenon, where multiple CO_2 molecules surround the organic impurity molecules. Despite high pressure challenges (241 and 310 bar used) for scale-up, advantages over traditional methods include fast reaction rates (15 min), minimal liquid waste, and straightforward solute separation that requires only a few separation stages.[98]

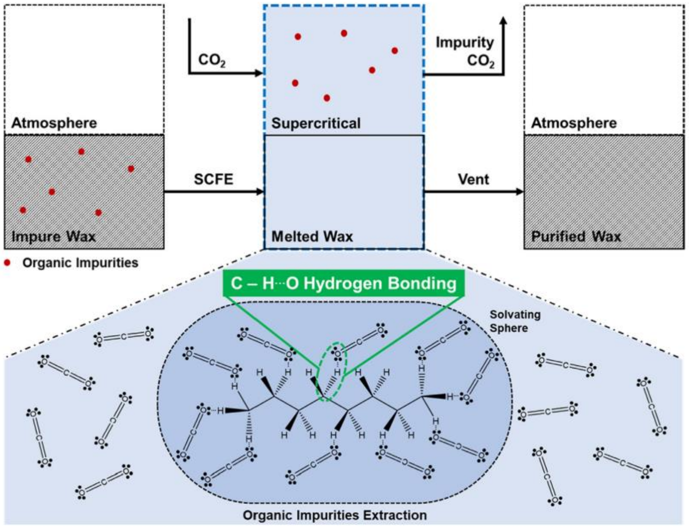

Figure 13. Schematic representation of the pyrolysis purification using supercritical CO_2. Reprinted with permission from ref 98. Copyright 2019 Elsevier.

A great deal of studies dealing with the (catalytic) upgrading of plastics or pyrolysis oils solely focus on virgin plastics or non-representative (clean or unused) post-consumer plastics. Although comprehensible for first tests, it omits one of the great challenges of real post-consumer plastic waste. Post-consumer pyrolysis products are complex mixtures with a great number of heteroatom components, which likely hamper further (catalytic) upgrading steps. Although different catalytic and non-catalytic purification techniques are being explored, continued research is essential. Besides, TEA and LCA studies should be conducted that compare pyrolysis product purifications for specific applications.

4 Techno-economic assessment and life cycle analysis

For the practical implementation of converting post-consumer polyolefins into heavy products, it is essential to achieve favorable outcomes from both the techno-economic assessment (TEA) and life cycle analysis (LCA). Different recycling strategies need to be considered when comparing different product outcomes. Figure 14 categorizes plastic recycling strategies into three distinct groups: (I) Plastics can undergo a recycling process where their transformation returns monomers. These can subsequently be used for repolymerization into polymers. (II) Plastics can be downcycled, transforming them into lower-value products, *e.g.,* electricity or recycled plastics for carpets. Lastly, (III) plastics can be transformed toward value-added products *via* an upcycling process. Waxes and lubricants are considered such products due to their market value, rendering them interesting and viable product streams.[120]

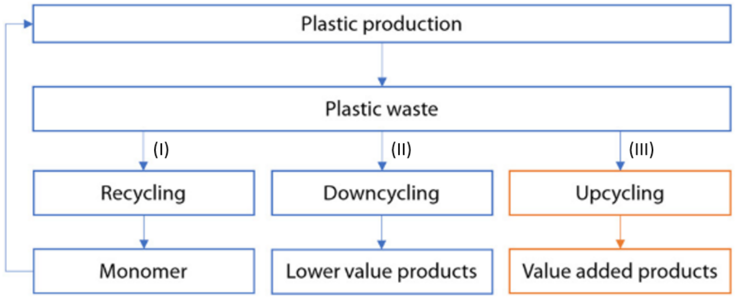

Figure 24. Different plastic waste management pathways. (I) Recycling pathway by transforming the polymers into monomers. (II) Downcycling of polymers by transforming them into lower-value products. (III) Upcycling of polymers by transforming them into value-added products. Reprinted with permission from ref 120. Copyright 2022 Royal Society of Chemistry.

Another categorization for different chemical recycling strategies can be seen in Figure 15, in which three scenarios are depicted: (I) the linear economy, which is the conventional scenario where polymers are produced from fossil fuels and thereafter burned or dumped; (II) closed-loop chemical recycling, where polymers are produced from fossil fuels and then converted toward intermediate chemicals, which are then transformed back into polymers; and (III) open-loop chemical recycling, polymers are produced from fossil fuels, after which they are transformed into other valuable chemicals. The addition of other monomers and chemicals, preferably from renewable resources, might be needed in this process for obtaining these valuable products.[121] The production of waxes and base oils from polyolefin plastics is an example of open-loop recycling. Conversion strategies should, however, only be considered if favorable TEA and LCA outcomes are obtained.

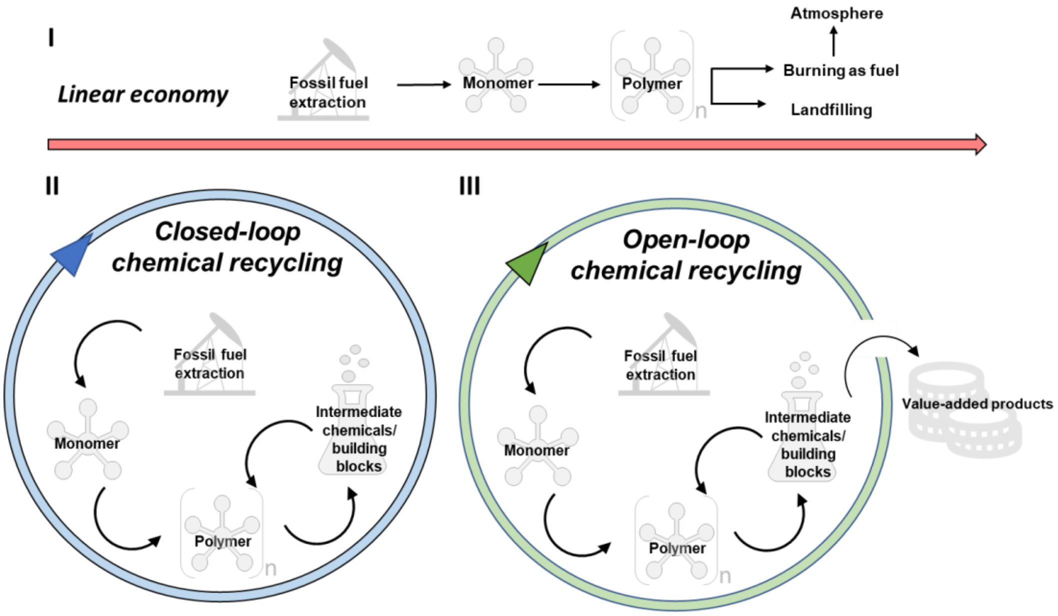

Figure 15. Three different recycling pathways for polymers: (I) linear economy, (II) closed-loop chemical recycling, and (III) open-loop chemical recycling.

In a study by Larrain *et al.*, the economic performance of open-loop and closed-loop recycling for mixed polyolefin (MPO) pyrolysis was compared.[122] The proposed recycling scheme is illustrated in Figure 16. In open-loop recycling, waxes were the main product, while closed-loop recycling was aimed at producing naphtha. This naphtha is usable for steam cracking to produce ethylene and propylene, besides butadiene and benzene, for PE and PP production. Clear advantages were found in favor of the open-loop (wax) pathway, which could be explained by the higher wax market prices. This was found despite the required extra wax-naphtha separation, as the value of the waxes justified this step. The results, however, varied considerably due to crude oil price volatility. With increasing oil price projections towards 2035 (714 and 1195 €/ton median price naphtha and slack wax, respectively), the likelihood of positive outcomes was about 98% for open-loop and 57% for closed-loop recycling. In a future scenario where decarbonized electricity decreases oil prices towards 2035 (462 and 776 €/ton median price naphtha and slack wax, respectively), the chances drop to 57% and under 8%, respectively. To attract investors, plant capacity should be ≥70 kt/y for the open-loop and ≥115 kt/y for the closed-loop pathway. At 120 kt/y capacity, open-loop needs ≥80% utilization, while closed-loop should approach full capacity. Securing a feedstock supply is, however, vital for both pathways.[122]

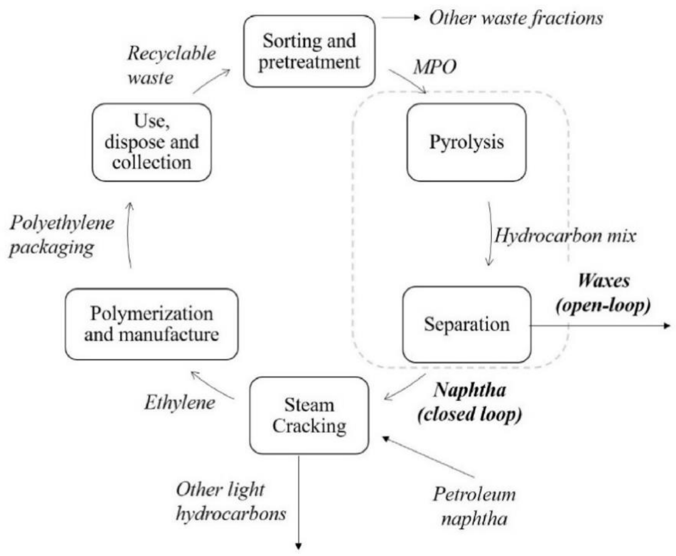

Figure 16. The polyolefin value chain for mixed polyolefin (MPO) packaging material for open and closed-loop recycling. Reprinted with permission from ref 122. Copyright 2020 Elsevier.

Besides pyrolysis, catalytic hydrogenolysis was subjected to TEA and LCA, also resulting in favorable outcomes.[120] The study focused on high-quality liquid (HQL) production, akin to PAO lubricants, as seen above in Section 1.[16,17] Two scenarios, a high yield (HY) and a low yield (LY), were evaluated. In Figure 17a, greenhouse gas (GHG) emissions are shown, emphasizing the influence of the produced lubricant yield. The resulted LCA showed emissions ranging from 0.48 to 1.2 $kg_{CO2e}.kg_{LUBRICANT}^{-1}$. The optimal case reduces emissions by 52% compared to petroleum lubes and 74% relative to PAO lubes. Emissions are notably impacted by hydrogen sourced from steam methane reforming, with greener methods using hydrogen produced by water electrolysis using renewable or nuclear generated electricity significantly reducing the GHG impact.[120]

The TEA resulted in a production cost range of 0.6-1.98 \$/kg of lubricant, varying with operating conditions, as can be seen in Figure 17b. The estimated minimum selling point (MSP) of 0.6 \$/kg (or 1.8 \$/gal) is notably lower than petroleum-based Group III and PAO lubes, priced at 6-10 \$/gal. Hydrogen has a very low impact on the lubricant production cost as a relatively low amount of hydrogen is needed, especially in the high yield scenario. Thus, process profitability showed itself to be robust even with nuclear or renewable hydrogen sources. Other production cost influencers include plastics cost and catalyst volume, while leasing the catalyst can further enhance profitability.[120]

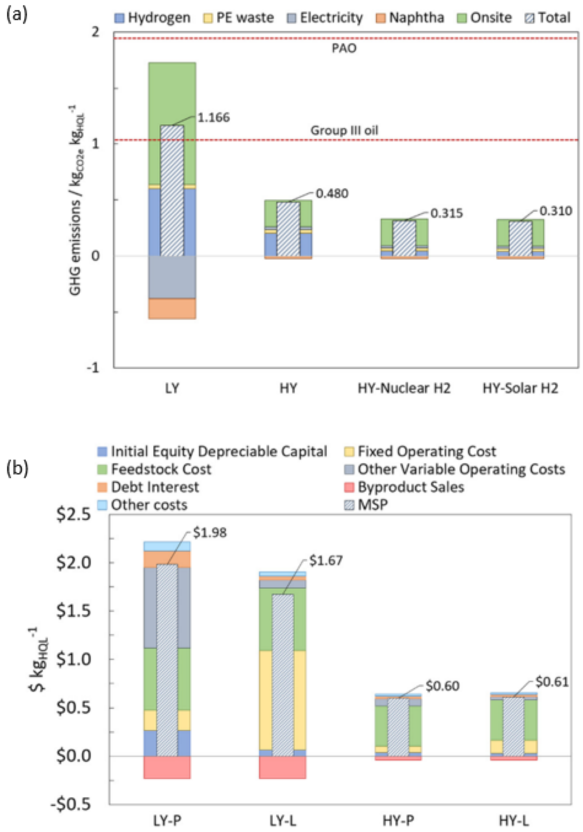

Figure 17. (a) The breakdown of the greenhouse gas (GHG) emissions of the obtained high-quality liquid (HQL) for low-yield (LY) and high-yield (HY) scenarios. The HY scenario is

complemented by hydrogen obtained from nuclear or solar sources. (b) The cost breakdown for producing the HQL in the different scenarios. LY and HY are divided into scenarios where the catalyst is purchased (-P) or leased (-L). Adapted with permission from ref 120. Copyright 2022 Royal Society of Chemistry.

In a study by Hernández *et al.*, LCA and TEA were examined in relation to various LDPE conversion technologies.[123] This included pyrolysis (with olefin oligomerization), gasification, hydrocracking, hydrothermal liquefaction (HTL) and hydrogenolysis, as illustrated in Figure 18. The used yields for these reactions were obtained from data from other experimental studies. The yields for the gasification reaction were modeled, with data obtained from other studies. The catalytic oligomerization process, however, was based on existing literature that explored the oligomerization of olefin model compounds and not of polyolefin pyrolysis products.[124,125] Among these technologies, pyrolysis with oligomerization reactions for producing lubricants were found to be the most profitable. The calculated yield of lubricants from this technology was higher compared to hydrogenolysis, making it a more economically viable option. It proved crucial to target value-added products, such as lubricants, to enhance economic considerations.[123]

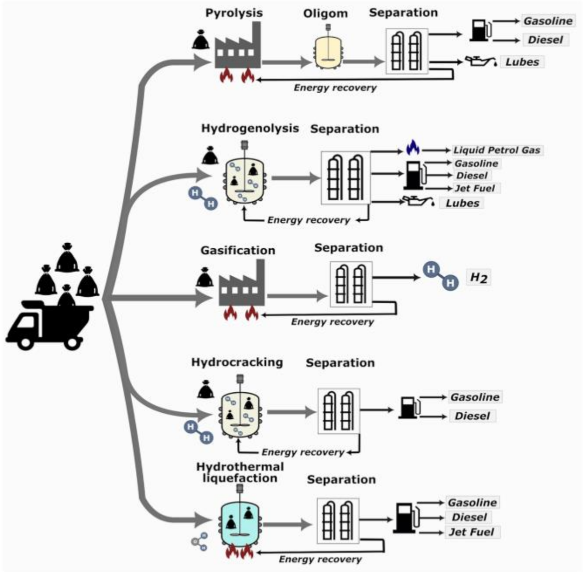

Figure 18. A schematic representation of the compared thermochemical technologies and their products. Reprinted with permission from ref 123. Copyright 2023 American Chemical Society.

The study revealed that separation costs significantly impact capital expenditures (CAPEX). In this study, a fluidized bed reactor was selected for thermal pyrolysis. This reactor can achieve higher selectivity toward the desired value-added products, thus reducing the associated separation costs. In this comparative study, the thermal pyrolysis process could yield 49 wt% lubes, contrasting with hydrogenolysis, where 19 wt% lubes were calculated. It is also important to note that the utilization of catalytic polymer breakdown necessitates an extra initial sorting process for the plastics to avoid catalyst deactivation, increasing its costs. Another significant factor to consider is plant size. Since lubricants are considered as added-value products, even modest-scale plants (25 kt/y) can already generate profitability. Larger plants are desirable but may pose higher risks.[123]

In terms of environmental impact, hydrogenolysis and hydrocracking exhibited the lowest CO_2 emissions, followed by pyrolysis, as shown in Figure 19. Pyrolysis reduces emissions by eliminating the need for hydrogen but often employs nitrogen, which has an energy consumption 40 times higher than that of hydrogen used in hydrocracking and hydrogenolysis. Therefore, reducing the use of nitrogen is highly advantageous. One approach to achieving this is through the implementation of a pressure swing adsorption system, which allows for the recycling of nitrogen.[123]

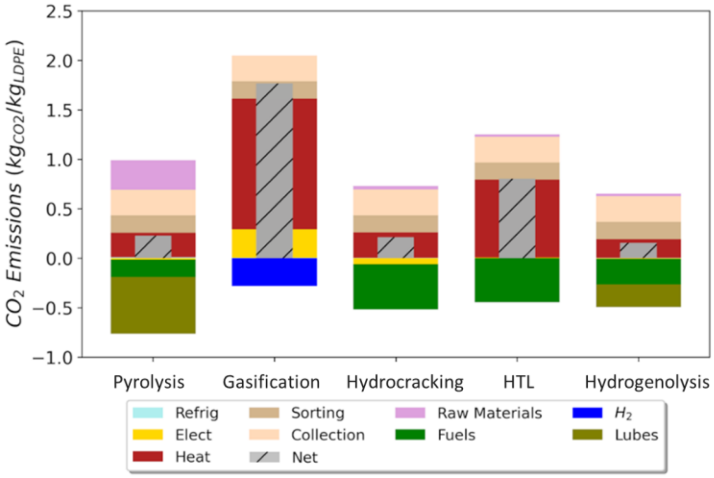

Figure 19. Breakdown of the CO_2 emissions for the different compared technologies. Reprinted with permission from ref 123. Copyright 2023 American Chemical Society.

The above studies suggest positive TEA and LCA outcomes for the production of waxes or lubricants from polyolefins. However, some key factors need to be considered, including: the future price of fossil feedstocks; the costs and source of raw materials, such as preferably clean H_2 produced with a low or zero carbon footprint; the availability of a steady plastic waste supply;

the selectivity or product formation; and the effectiveness of presorting and cleaning of the plastic feeds.

Conclusion and perspectives

The conversion of polyolefin plastics toward heavy products, such as waxes and lubricants, was reviewed in this perspective. Favorable results were found in the techno-economic analysis and life cycle assessments, making this strategy a viable chemical recycling pathway. It was found that different catalytic and thermal conversion techniques can be used to obtain these heavy fractions. Currently, thermal pyrolysis is the most promising as it is relatively simple and catalyst deactivation problems are less of an issue. It is seen that different reactor types can be used, where reactors with a short contact time that operate at lower temperatures are especially promising to produce high yields of heavy fractions. Of these, a conical spouted bed reactor (CSBR) produced the highest wax yields. Lowering nitrogen consumption in these types of reactors will be beneficial both economically and environmentally. Catalytic conversions could operate at very mild temperatures. However, the conversion studies were usually conducted on a very small scale, with costly metal catalysts, and often needed very long reaction times. Future improvements to these conditions and scaling might further validate these conversion strategies.

Secondary upgrading or transformation of the produced pyrolysis waxes seems beneficial in most cases. Little research is, however, conducted for obtaining refined high molecular weight products, despite its substantial added value, and therefore lots of innovative research can be done. This is opposed to the extensive literature on the cracking of heavy pyrolysis products toward light products. It was proven that pyrolysis waxes, either pure or together with other hydrocarbon streams, can be cracked toward light olefins, naphtha, or other streams.

Presence of various impurities in real post-consumer waste is likely one of the greatest challenges to deal with. Different techniques are in use for impurity reduction in pyrolysis fractions. Of these, hydroprocessing, despite being expensive, has been studied more extensively. Other non-catalytic impurity removal strategies remain underexplored. More elaborate studies on the effect of certain pyrolysis reactors on impurities in pyrolysis oils will be beneficial for future implementations.

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Author Contributions

J.V.W.: Writing of the original draft. B.S., Z.Z., T.V.V., M.A., K.V., S.S., H.V.L. & X.W.: Revision and correction of the original draft. B.S: Supervision, projects administration, funding acquisition, revision, and correction of the original draft. All authors have read and agreed to the published version of the manuscript.

Biographies

Jonathan Van Waeyenberg obtained his Msc Bioscience Engineering (Catalytic Technology) at KU Leuven in 2018. He is currently doing a PhD at the Center of Sustainable Catalysis and Engineering (CSCE) under the guidance of Prof. Bert F. Sels. Here he studies the thermal pyrolysis of polyolefin plastics using a conical spouted bed reactor. He additionally investigates secondary catalytic steps for producing refined lubricants and waxes out of pyrolysis products.

Kseniia received her PhD degree in 2020 in Zelinsky Institute of Organic Chemistry of Russian academy of sciences on the topic of selective hydrogenation of aldehydes, ketones and nitro compounds on platinum catalysts based on cerium-contained supports. She joined the group of Prof. Bert F. Sels in 2022 at KU Leuven as a postdoctoral researcher and currently she is working on catalytic cracking of polyolefins.

Brent Smeyers obtained his MSc Bioscience Engineering (Catalytic Technology) at KU Leuven in 2019. He performed his master thesis at the Center of Sustainable Catalysis and Engineering (CSCE) under the guidance of Prof. Bert F. Sels, where he studied the role of heterogeneous catalysis in the synthesis of safer BPA alternatives. He is currently doing a PhD in the same research group, where he investigates in-situ catalytic pyrolysis of polyolefins as a chemical recycling strategy towards high-value chemicals (light olefins, naphtha). More specifically, he focuses on the role of heterogeneous catalysis in these conversion processes.

Toon Van Vaerenbergh obtained his MSc in Bioscience Engineering at KU Leuven in 2021. He did his master thesis at the Centre for Surface Chemistry and Catalysis under the guidance of Prof. Bert F. Sels, where he investigated the catalytic activation of N_2O and O_2 by iron zeolites.

He is currently doing a PhD in the same research group. His research focuses on the conversion of polyolefins towards carbon nanotubes and H_2.

Michiel Aerts obtained his MSc in Bioscience Engineering (Catalytic Technology) at KU Leuven in 2020. He did his master’s thesis at the Center for Sustainable Catalysis and Engineering (CSCE) under the guidance of Prof. Bert F. Sels, where he investigated the role of basic catalysis on the valorization of glycerol towards novel branched polyols. He is currently doing a PhD in the same research group, focusing on the catalytic conversion of plastic waste to chemicals.

Zhenlei Zhang holds a bachelor's and master's degree in chemical engineering from Qufu Normal University and the Institute of Process Engineering, Chinese Academy of Sciences, respectively. In 2022, he obtained his Ph.D. at University of Groningen under the supervision of Prof. Peter Deuss and Prof. Hero Heeres. His Ph.D. research was the catalytic valorization of lignin, with a specific focus on lignin structural simplification, structure-activity relationship, acidolysis and hydrogen borrowing reductive depolymerization methodologies. Following the completion of his Ph.D., he pursued postdoctoral research at the University of Groningen, where his work centered on the ex-situ catalytic pyrolysis of paper sludge, aiming at the production of bio-based fuels and chemicals. In 2022, he joined Prof. Sels' group in KU Leuven as post-doctoral fellow. In this role, he focused on developing robust catalytic systems designed for the upcycling of post-consumer multilayer plastics. From Jan 2024, he works as an assistant professor in China University of Petroleum-Beijing.

Sajan Sivanandan obtained his master’s in Biopolymer Science from CIPET (Central Institute of Petrochemicals Engineering & Technology)-IPT, Kochi which is affiliated with CUSAT (Cochin University of Science and Technology) in 2022. He did his master thesis work at IICT (Indian Institute of Science and Technology) under the supervision of Dr. Pratyay Basak and the co-supervision of Dr. Kesavarao Sykam. For the thesis work, he focused on the synthesis and characterization of non-halogenated, phosphorus, and triazole-containing castor oil- based flame-retardant polyurethanes. He joined the group of Prof. Bert F. Sels in 2023 at KU Leuven as a PhD fellow and his work will be devoted to catalytic recycling of polystyrene.

Hendrik Van Leuven graduated with a MSc degree in Bioscience Engineering (Catalytic Technology) at KU Leuven in 2023. He performed his master thesis at the Center for Sustainable Catalysis and Engineering (CSCE) under the guidance of Prof. Bert F. Sels. In his PhD, his focus includes the catalytic pyrolysis to valorize low value post-consumer plastic waste into feedstocks suitable for integration in the chemical industry.

Xuejiao Wu received her B.S. degree (2015) from Xiamen University and obtained her Ph.D. degree (2020) from Xiamen University under the supervision of Prof. Ye Wang. She then carried out postdoctoral research at Prof. Bert F. Sels group at KU Leuven. Her research interest focuses on the valorization of lignocellulose and other renewable feedstocks, in particular by photocatalytic approaches.

Bert F. Sels is currently a full professor at KU Leuven. His research focuses on the conversion of renewable feedstock to chemicals, materials and fuels, and the role of heterogeneous catalysis, with strong eye at the molecular level. The research covers organic chemistry, fundamental kinetics, reaction network and intermediate product studies, catalytic site identification, reactor and process designs including TEA and life cycle assessments. Main topics are biorefineries, biobased chemicals, green chemistry, and catalytic strategies for plastic waste and CO_2 conversion.

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ABBREVIATIONS

API, American Petroleum Institute; CAM, catalytic cross alkane methathesis; CAPEX, capital expenditures; CSBR, conical spouted bed reactor; GHG, greenhouse gas; HDPE, high-density polyethylene; HQL, high-quality liquid; HTL, hydrothermal liquefaction; HY, high yield; i-PP, isotactic PP; -L, leased; LCA, life cycle assessment; LCO, light cycle oil; LDPE, low-density polyethylene; LLDPE, linear low-density polyethylene; low yield, LY; MPO, mixed polyolefin; MSP, minimum selling point; MW, molecular weight; -P, purchased; PAO, poly-alpha-olefin; PE, polyethylene; PDI, polydispersity index; PP, polypropylene, PSW, plastic solid waste; PVC, polyvinyl chloride; TEA, techno-economic analysis. VGO, vacuum gas oil.

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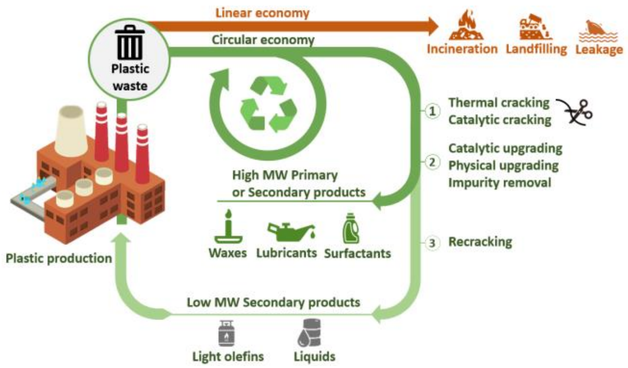

The circular economy of plastics includes the potential for creating high-molecular weight products such as waxes, lubricants, and surfactants.