

Towards high-quality petrochemical feedstocks from mixed plastic packaging waste via advanced recycling: The past, present and future

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Towards high-quality petrochemical feedstocks from mixed plastic packaging waste via advanced recycling: The past, present and future

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ABSTRACT

Advanced plastic waste recycling via pyrolysis and subsequent steam cracking of pyrolysis oils has the potential to partly close the cycle between the petrochemical production of plastics and current end-of-life waste management (i.e., downcycling, incineration, landfilling). However, the greatest obstacle is the complex composition of real plastic waste and their contamination with numerous additives and residues. Consequently, the lower quality of pyrolysis products compared to fossil feedstocks needs to be drastically improved by universally applicable upgrading and decontamination techniques. Techniques range from waste pre-treatment to reduce the halogen and additive contents, via in-situ techniques applied during pyrolysis to post-treatment techniques to purify the obtained pyrolysis oils using hydrotreatment, filtration or adsorption. Incorporated into a petrochemical cluster, high-quality petrochemical feedstocks can be produced from plastic waste, which, combined with electrification, could lead to a CO₂ emission reduction of >90% compared to incineration as the current mostly used disposal method.

1. Introduction

Plastic waste is gradually becoming a key element in the transition from a linear towards a circular economy. This is due to its abundant use and long lifetime as pollutant as well as its carbon-intensive production processes [1]. Production volumes of plastics increased from a global 1.7 Mt. in 1950 to 367 Mt. in 2020 with an estimated production capacity of 500 Mt. by 2025 [2]. Furthermore, it has been estimated that around 60% of all plastics ever produced ended up in landfills or in the

environment [3]. Recycling is defined in the European Waste Framework Directive as any “recovery operation by which waste materials are reprocessed into products, materials or substances whether for the original or other purposes” [4]. Hence, energy recovery and waste-to-fuel processes are not considered to be recycling. Considering this definition, the recycling rates of plastics across Europe, rarely exceed 50% and differ largely across different countries (see Fig. 1). Furthermore, different pathways of plastic waste processing exist, including unfavorable options such as incineration for energy recovery, which has

Abbreviations: ABS, Acrylonitrile butadiene styrene; BFR, Brominated flame retardant; BTX, Benzene, Toluene, Xylenes; Cat., Catalyst; CCU, Carbon capture and utilization; CO₂-eq, CO₂-equivalent; EVOH, Ethylene vinyl alcohol; FCC, Fluid catalytic cracking; GDP, Gross domestic product; HDCl, Hydrodechlorination; HDM, Hydrodemetallization; HDN, Hydrodenitrogenation; HDO, Hydrodeoxygenation; HDPE, High-density polyethylene; HDS, Hydrodesulfurization; HIPS, High impact polystyrene; HT, Hydrotreatment; HVC, High value chemicals; (L)LDPE, (linear) low-density polyethylene; MOF, Metal organic framework; OECD, Organization for Economic Co-operation and Development; P, Pressure; PA, Polyamide; PE, Polyethylene; PET, Polyethylene terephthalate; PP, Polypropylene; ppb, Parts per billion (weight-based); ppm, Parts per million (weight-based); PS, Polystyrene; PUR, Polyurethane; PV(D)C, Polyvinyl(idene)chloride; REACH, Registration, Evaluation, Authorisation and Restriction of Chemicals; scCO₂, Supercritical CO₂; SCW, Supercritical water; T, Temperature; TAC, Thermal anaerobic conversion; TRL, Technology readiness level; VGO, Vacuum gas oil; WEEE, Waste electrical and electronic equipment.

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a low energy efficiency, while emitting large amounts of greenhouse gases [5]. Generally, possible recycling pathways depend on the quality and quantity of collected waste and the efficiency of sorting and separation processes. The fact that of the plastic waste collected in the EU plus Norway and Switzerland, by 2018, an average of around 43% was still incinerated, only 32% recycled, while still almost a quarter was disposed of in landfills, shows that current plastic waste management is still far from optimal [2]. Especially, waste incineration for energy recovery should be avoided due to the associated greenhouse gas emissions, which need to be drastically reduced in order to keep the global temperature increase below the 1.5 °C goal [6,7].

Importantly, plastic waste is a global problem that cannot be solved by individual countries, but rather requires a global policy change. Currently, plastic waste exports play an important role in industrialized countries and are typically understood as a solution to the plastic waste management problem by governments. This is due to the fact that most of the industrialized countries do not have a sufficient recycling capacity for the plastic waste volumes they produce [9]. Instead, enormous volumes of plastic waste are globally traded. Obviously, this is not a sustainable solution and since environmental policies are more and more being established around the world, such waste management schemes become inhibited. This development culminated in China's total ban on imported plastic waste, which caused a great disturbance in global plastic waste exports leading to increased incineration of waste, stockpiling and more landfill disposal. Waste trade flows have since been largely re-directed to Southeast Asian countries [10,11]. Inevitably, certain amounts of the exported plastic waste leak into natural environments causing the disruption of ecosystems and long-lasting pollution [12]. Hence, exporting plastic waste is not a sustainable solution for the long-term and needs to be decreased aided by policies to reduce the generation of plastic waste. According to a newly published report by

the Organization for Economic Co-operation and Development (OECD), potential policies to reduce the global environmental impact of plastics are taxes on plastic products, specifically plastic packaging, incentives to reuse and repair, target values for recycled products, extended producer responsibility, improved waste management infrastructure and schemes, and increased litter collection rates [13]. On a global scale, it can be distinguished on the one hand between a more regional policy including a mix of fiscal and regulatory policies, which could reduce the plastic waste quantities by almost 20% with no significant impact on the global gross domestic product (GDP). On the other hand, a more global action scenario using more stringent policies could reduce plastic waste generation by a third, while also having a more substantial impact on the global GDP [13]. However, it is still unclear how strategies can be efficiently implemented on a larger scale and it has been recently concluded that even if immediate and vigorous action is taken in reducing plastic waste generation, still enormous amounts of plastic waste will accumulate in the environment [14]. Furthermore, to this day, efficient large-scale plastic waste recycling pathways are scarce [15–19].

High-quality mechanical recycling is mostly limited to high-purity sorted waste fractions such as polyethylene terephthalate (PET), which is the only polymer from post-consumer packaging waste, for which a reasonably efficient recycling scheme is established at global scale at present [19,20]. Other main constituents of plastic waste, which consists of roughly 60% plastic packaging, are polyolefins (i.e., polyethylene (PE), polypropylene (PP)), polystyrene (PS), and heteroatom containing polymers such as polyvinyl(idene)chloride (PV(D)C), polyamide (PA), polyurethane (PUR), or ethylene vinyl alcohol (EVOH) [2,21,22]. Next to the high variety of plastic waste, current legislative regulations for the use of recycled plastics in food-contact applications are a further limiting factor for mechanical recycling [23]. A promising

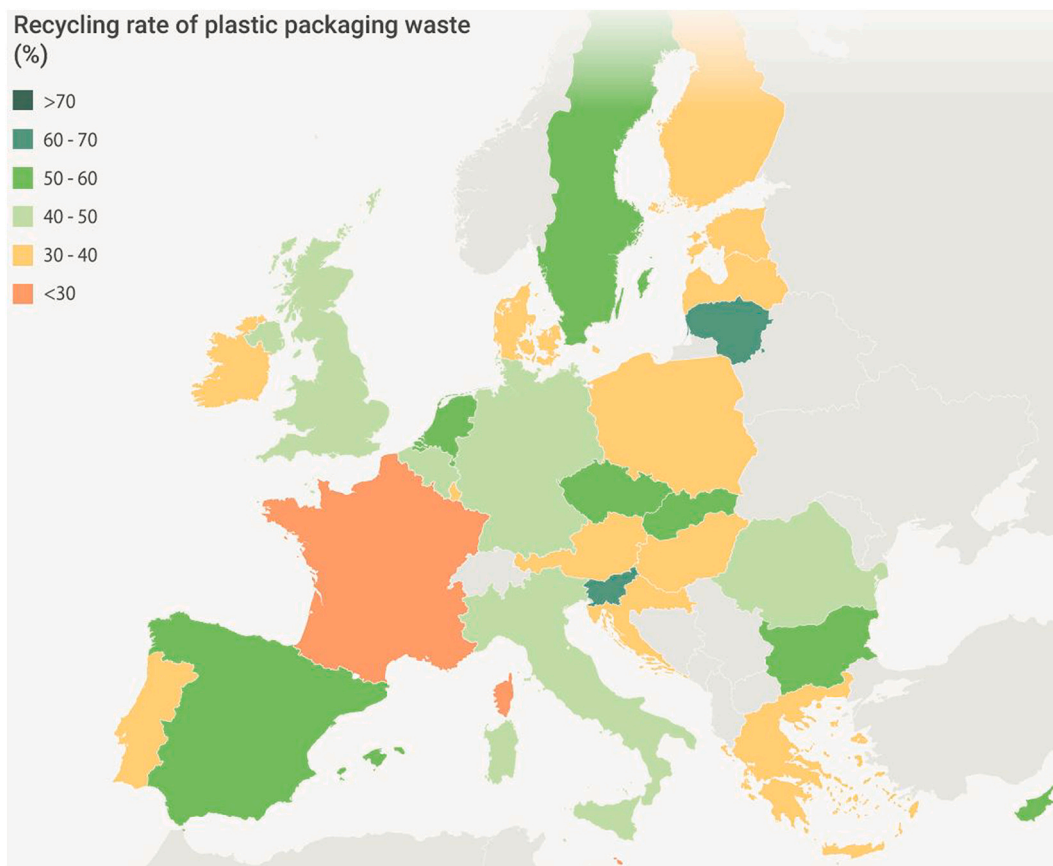


Fig. 1. Recycling rates in Europe (adapted from [8]).

option to recycle more plastic waste is thermochemical recycling as it is expected to be more robust towards mixed waste streams and the associated high degree of contamination compared to mechanical recycling [15,16,24–27]. Within chemical recycling, or alternatively called advanced recycling, pyrolysis is a promising approach in which the plastics are thermally converted into an oil-like liquid product that can be integrated into the petrochemical production schemes of virgin plastics (i.e., steam crackers) and thus closing the material loop [19,28–31].

Chemical recycling of plastic waste still faces challenges such as the presence of so-called contaminants, making (petro-)chemical processing of the obtained pyrolysis oils difficult. Crucial contaminants present in plastic waste pyrolysis oils are nitrogen, oxygen, halogens and metals, originating from heteroatom containing polymers, additives, printed inks and organic and inorganic residues (see Table 1).

These contaminants can severely impact petrochemical processes such as steam cracking and are therefore subject to strict regulations in terms of acceptable feedstock specifications for the petrochemical industry [32]. Especially halogens are among the most dreaded contaminants in steam crackers due to severe corrosion issues [36]. Further problems arising from the mentioned contaminants during steam cracking range from increased coke formation over fouling to downstream catalyst poisoning. In fact, it has been shown that real post-consumer packaging waste pyrolysis oils do not comply with current specifications for industrial steam cracker feedstocks in terms of their hydrocarbon composition and the most crucial contaminants (see Fig. 2) [32,33].

Moreover, unsaturated hydrocarbons in the plastic waste pyrolysis oils (i.e., olefins, aromatics) lead to lower storage stability and are problematic for steam crackers due to high coke formation and fouling tendencies [32,38–40]. Consequently, thorough upgrading is needed before pyrolysis oils can (partly) replace fossil feedstocks such as naphtha. Techniques to remove contaminants and to generally increase the quality of pyrolysis oils can be employed throughout the entire thermochemical recycling chain as shown in Fig. 3.

Upgrading techniques can be distinguished between separate (i.e., stand-alone) treatment steps of waste feedstocks as well as of pyrolysis products, and techniques applied during the pyrolysis process itself (i.e., in-situ). Treatment of the sorted plastic waste involves removal of harmful elements which were introduced via polymers such as PV(D)C,

food residues, or additives (see Table 1) [21,34]. Post-treatment steps of plastic waste pyrolysis oils include catalytic hydrotreatment (HT) for the reduction of unsaturated hydrocarbons and removal of heteroatoms. Adsorbents are another promising material to reduce important heteroatomic components such as nitrogen. Furthermore, filtration processes, distillation or the use of solvents are possible processes to remove particles, inorganics or dissolved organics from the pyrolysis products. In-situ techniques aim to improve the quality of pyrolysis products by adding auxiliary substances such as solvents, sorbents or catalysts to the pyrolysis process itself. In an industrial context, several of the mentioned techniques can be integrated into continuous systems, for instance, combining the use of solvents during pyrolysis with distillation and direct catalytic upgrading of the pyrolysis products.

In short, all mentioned upgrading techniques aim for higher-quality pyrolysis products that can be integrated into existing petrochemical clusters without risking disturbance in running processes. Yet, the individual upgrading requirements depend on many variables such as the plastic waste composition, level of contamination and the availability of a technical environment in which the recycling processes can be integrated. Consequently, it is not straight-forward to select the ideal combination of techniques to, on the one hand, produce a suitable steam cracking feedstock, while, on the other hand, maintaining economic competitiveness. This article therefore comprehensively reviews possible techniques suitable to produce liquid feedstocks from plastic waste that comply with the feedstock specifications of commercial steam crackers. By closing this important knowledge gap, thermochemical recycling of mixed plastic waste can be pushed one step closer to industrial-scale application.

2. Tailored (pre-)treatment techniques for mixed polyolefin-rich plastic waste

In the following section, techniques to upgrade solid plastic waste feedstocks for thermochemical recycling are discussed. Sorting, separation and other pre-treatment methods, which are also performed in mechanical recycling will not be discussed in detail, neither will surface treatment techniques such as de-inking. The interested reader is hereby referred to the respective specialized literature [34,41–48]. The most important waste pre-treatment techniques for thermochemical recycling are dehalogenation and the removal of residues and additives prior to pyrolysis to produce a feedstock more suitable for petrochemical processes.

2.1. Washing

In their recent study Genuino et al. investigated the potential benefits of washing pre-treatment on the pyrolysis products of mixed plastic waste [49]. The authors tested the effect of different washing media such as hot water (85 °C), cold (30 °C) + hot water, or cold + hot water +1 wt % NaOH on the elemental composition of several contaminants compared to an unwashed sample. It was shown that substantial amounts of contaminants could be removed by the respective washing steps, specifically, chlorine and sodium which were related to salt contamination, but also silicon and calcium which were related to inorganic residues could be removed. Furthermore, removal of organic residues was indicated by a substantial reduction of the oxygen content of the washed samples. In terms of the pyrolysis performance, the authors found that the washed samples led to higher amounts of oil/wax product and a reduced gaseous product fraction (see Fig. 4).

The findings show that washing pre-treatment is an effective method to increase the plastic waste quality prior to pyrolysis, hence reducing the downstream processing effort substantially. However, the chlorine concentration in the pyrolysis oil of the washed plastic waste feedstock still exceeded 150 ppm, underlining the need for additional treatment methods such as dehalogenation.

Table 1
Main origins of heteroatoms and metals in plastic packaging waste [32–35].

Element	Main origin
Nitrogen	<ul style="list-style-type: none"> Polymers such as PUR, PA Organic residues (i.e., amino acids) Inorganic residues from detergents and soaps Additives, i.e., antioxidants, flame retardants, foaming agents, adhesives
Oxygen	<ul style="list-style-type: none"> Polymers such as PET, EVOH Organic residues (i.e., amino acids) Additives, i.e., antioxidants, plasticizers, flame retardants, lubricants, antistatics, slip agents, adhesives
Sulfur	<ul style="list-style-type: none"> Organic residues (i.e., amino acids) Additives, i.e., stabilizers, colorants, foaming agents
Chlorine	<ul style="list-style-type: none"> Polymers such as PV(D)C Adsorbed salts from food packaging (as NaCl)
Bromine	<ul style="list-style-type: none"> Flame retardants (occurring mostly in technical polymers and less in packaging waste) Adsorbed salts (as KBr)
Metals	<ul style="list-style-type: none"> Printed inks or masterbatches Aluminum foils, cans and fillers Additives, i.e., calcium (as CaCO₃), silicon (as SiO_x), titanium (as TiO₂) or zinc (as ZnS) Catalysts used in polymer production (i.e., Sb, Ti, Cr, Hg, Mn) Flame retardants (Sb, Al, Mg) Sodium from adsorbed salts Stainless-steel shredding equipment during waste pre-treatment (Cr, Fe)

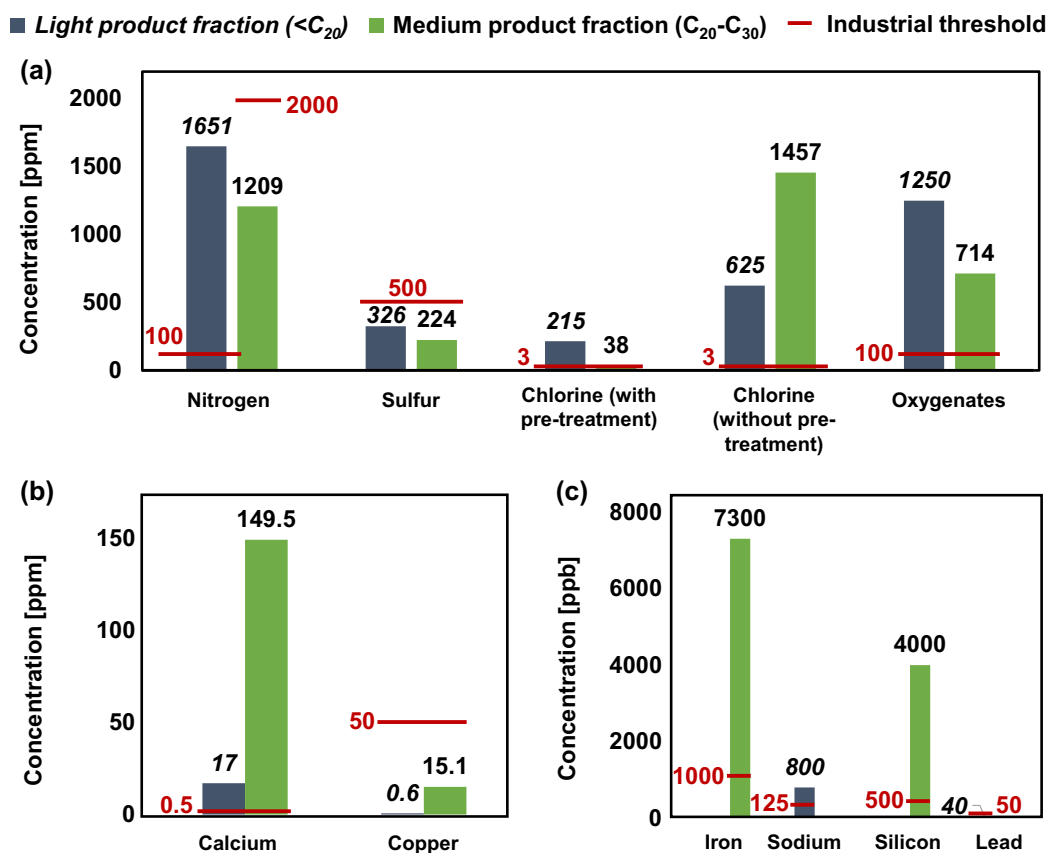


Fig. 2. Average contaminant levels reported in plastic waste pyrolysis oils. (a) Heteroatoms in ppm, (b) metals in ppm, (c) metals in ppb, compared with the threshold values for industrial steam cracker feedstocks [36,37]. Re-drawn from [32].

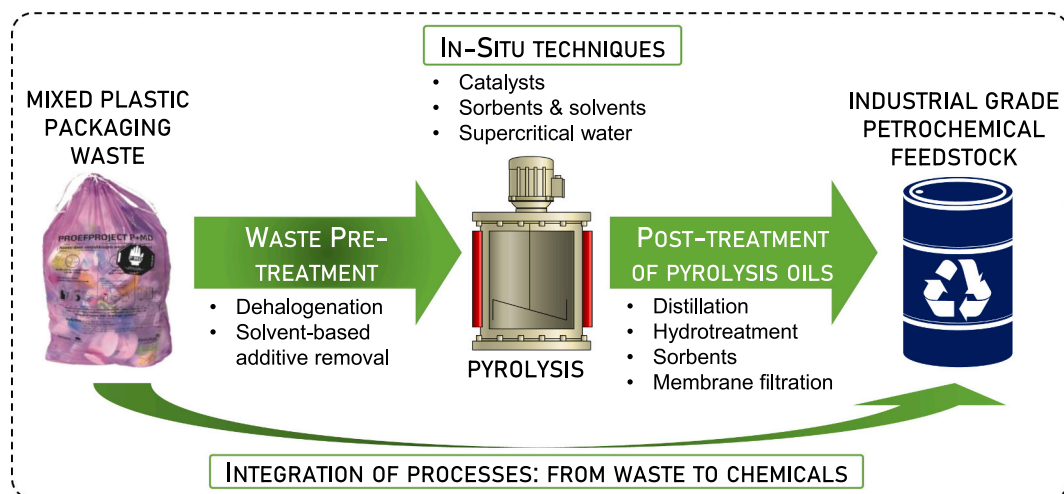


Fig. 3. Overview of upgrading techniques along the process chain from post-consumer plastic waste towards a high-quality petrochemical feedstock.

2.2. Dehalogenation

Removal of chlorine from PV(D)C-containing plastic packaging waste is crucial due to the highly corrosive thermal decomposition products such as HCl which are released during pyrolysis and steam cracking. Halogenic compounds present in additives, such as brominated flame retardants (BFRs), have similar problematic properties [50]. Furthermore, formation of halogen-containing hydrocarbon compounds during pyrolysis, such as bromobenzene or chlorobenzene needs to be

avoided [51,52].

2.2.1. Stand-alone dehalogenation techniques

Table 2 provides an overview of stand-alone dehalogenation techniques for contaminated plastic packaging waste. Thermal chlorine removal techniques (i.e., pyrolysis) make use of the step-wise decomposition mechanism of PVC. The first decomposition step, namely the release of the chlorine in form of HCl occurs between a temperature of approximately 240 °C and 340 °C [53]. The second decomposition step,

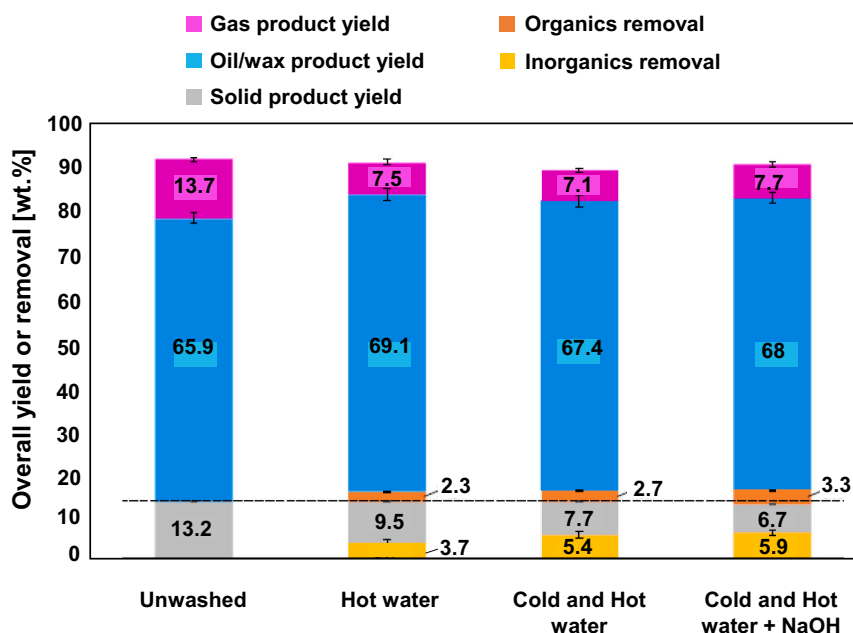


Fig. 4. Pyrolysis product distribution (fixed-bed, 500 °C) and organic and inorganic removal efficiencies for the washed samples. Re-drawn from [49].

Table 2

Overview of halogen removal techniques from plastic waste.

Method	Description	Reference
Thermal	<ul style="list-style-type: none"> Makes use of separate HCl release from PVC at lower temperature as the polymer backbone. Dechlorination occurs between ~240 and 340 °C. 	[55–58]
Microwave irradiation	<ul style="list-style-type: none"> 99.6% chlorine removal possible. Selective agitation of C–Cl bonds due to high polarity. Decomposition temperature lower than for thermal dechlorination (200–210 °C). No decomposition of the polymer structure. Additional engineering and cost effort required. Lower dechlorination efficiency compared to thermal processes (~90%). 	[59–63]
Chemical	<ul style="list-style-type: none"> Addition of solvent which needs to be removed and recovered. Full chlorine removal possible at lower temperatures (150–250 °C) and 1 atm. Solvents might chemically interact with the polymer backbone 	[64–69]

i.e., the decomposition of the polymer backbone takes place between 350 and 450 °C [54]. It was further reported that the dechlorination itself can be distinguished into two distinct regimes occurring at ~280 °C and ~320 °C, respectively. In the first dechlorination step, large amounts of benzene along with HCl are released, while in the second step, predominantly HCl is formed. The third PVC decomposition step, namely the breakdown of the polymer backbone, begins from a temperature of approximately 370 °C, yielding various aromatic hydrocarbons [55,56].

In terms of chemical recycling, it might be interesting to make use of the step-wise decomposition of PVC by directly valorizing the released HCl and benzene prior to pyrolysis of the remaining polymer. For this, the HCl can be washed from the gaseous hydrocarbon stream using an aqueous NaOH solution, or a solvent can be used that captures the HCl from the gas stream [70–72]. This way, the obtained benzene streams as well as the HCl can be directly recovered and a contamination with other (chlorinated) aromatic products from the PVC backbone decomposition at higher temperatures can be avoided. According to Bockhorn et al., a

degree of chlorine removal of 99.6% could be achieved in a batch reactor agitated with metal spheres at a temperature of 330 °C. In the following reactor cascade, the chlorine content may be reduced further down to 22 ppm (see Fig. 5) [73,74]. Similar results were obtained by other authors both with pure PVC and mixed plastics containing PVC [52,75,76].

Next to thermal pre-treatment methods, selective dechlorination of PVC by microwave irradiation was studied by a number of authors [59–62]. While polyolefins have very low dielectric constants and are therefore essentially transparent to microwaves, the C–Cl bond in PVC is highly polar and responsive to microwave irradiation [59,63]. It was reported that microwave irradiation reduced the dechlorination temperature of PVC to 200–210 °C [59]. A disadvantage of dechlorination via microwave irradiation is the specific equipment needed. Compared to thermal dechlorination, the incorporation of microwave heating in a

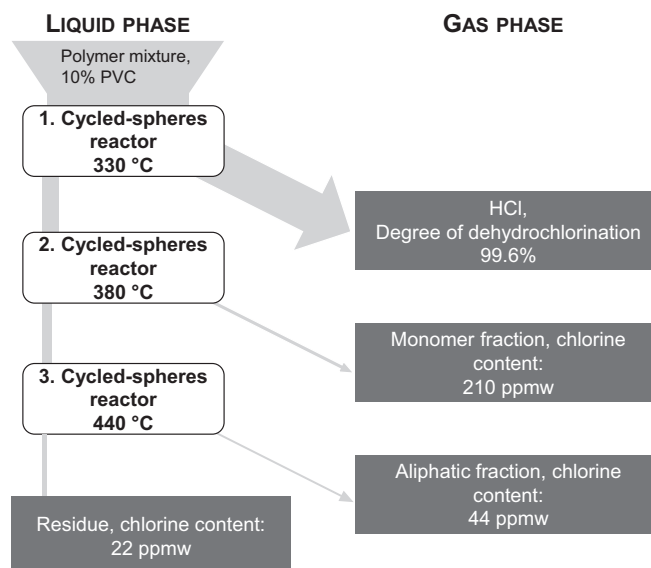


Fig. 5. Chlorine balance over three reactors for the step-wise dechlorination of PVC-containing waste. Redrawn from [74].

continuous pyrolysis process requires additional cost and engineering. Furthermore, a reported dechlorination efficiency of 90% makes additional dechlorination measures necessary in a later step of the thermochemical recycling process [61]. Microwave assisted dechlorination has hence, so far, not been performed at a larger scale.

Another dechlorination technique refers to chemical processes using basic solutions such as NaOH. Shin et al. investigated the dechlorination of PVC pellets using aqueous NaOH solutions in heated stainless steel tubes. The authors reported a strong temperature influence and a chlorine weight-loss of almost 100% at 250 °C after 5 h. The concentration of the NaOH solution showed no more influence after exceeding 3 M NaOH [64]. Yoshioka et al. studied the behavior of flexible PVC in a NaOH/ethylene glycol solution at ambient pressure and different temperatures. The authors found that for PVC with a particle size of 120 µm, a nearly complete dechlorination was achieved at 190 °C after 255 min. At lower temperatures of around 80 °C and a residence time of 1–3 h, a chlorine removal of 98–99% was reached. The only by-product was NaCl. The degree of dechlorination was directly related to the particle size, more specifically, the surface area of the PVC particles [65,66]. However, it is worth noting that in the mentioned studies, PVC powders were used which would be difficult from a process point-of-view using larger amounts of plastic packaging waste in a continuous process on industrial scale.

Another problematic halogen contaminant is bromine which predominantly occurs in legacy flame retardants in waste electrical and electronic equipment (WEEE) as well as in polymers such as high impact polystyrene (HIPS) used for construction applications. Therefore, in terms of thermochemical recycling of polyolefins towards petrochemical feedstocks, it can be assumed that WEEE as well as HIPS for construction applications are typically not present in large amounts. This is due to the fact that these “heavier” polymers can be easily separated from polyolefins in float-sink separation steps [47,77]. Furthermore, separate WEEE recycling systems would help reducing contamination of the plastic waste fractions with WEEE [78,79]. In recent years, recycling of WEEE via pyrolysis has been an active field of research to increase the value of plastics compared to traditional incineration [80–85].

2.2.2. Extrusive dehalogenation and rotary kilns

Dehalogenation of waste feedstocks can be integrated into a continuous process step of thermochemical recycling such as extrusive feeding into the pyrolysis unit (see Fig. 6).

While also possible as stand-alone dehalogenation processes, extrusion as well as rotary kilns have been used in combined dehalogenation and pyrolysis experiments of plastic mixtures. In the study presented by Fukushima et al., a single-screw extruder (heated to 370 °C) with a kneading and discharge section was used for the dehalogenation of a 50/50 mix of virgin pellets of PP and PVC [87]. The authors analyzed the influence of several process parameters such as screw speed and temperature on the residual chlorine content of the samples. It was found that the screw speed had a negligible influence on the residual chlorine content and that the dehalogenation performance of the single-screw extruder including a kneading section was equal to that of a twin-screw extruder. The chlorine content was reduced to less than 0.5 wt% in a time period of 2 min. It was shown that for the same residence time, dehalogenation was accelerated at higher temperatures [87]. It is worth noticing that the used dechlorination temperature also leads to degradation of the polyolefins present in mixed packaging waste which would be problematic for mechanical recycling applications. Hence, extrusive dehalogenation is only suitable for thermochemical recycling. With a heated twin-screw extruder, a chlorine removal of 99.9 wt% was reported which further proves the applicability of heated extrusion as dehalogenation method [88]. This technology has also been transferred to industrial application (see Fig. 6) [86,89].

A drawback of thermal dechlorination using single- or twin-screw extruders is the possible loss of hydrocarbons along with the released chlorine. Therefore, a separation step to remove the formed HCl from the released hydrocarbon vapors for direct utilization of, for instance, benzene is needed. It must be noted that highly corrosion resistant materials are obligatory for process equipment used for the dechlorination of PVC. The chromium alloy steel types 1.2083, 1.2085 or 1.2315 would be suitable for processing corrosive materials, however, at roughly 2 times higher cost compared to average steel [90]. It is worth noting, that dechlorination using extruders is possible at shorter residence times compared to the step-wise pyrolysis which is an important

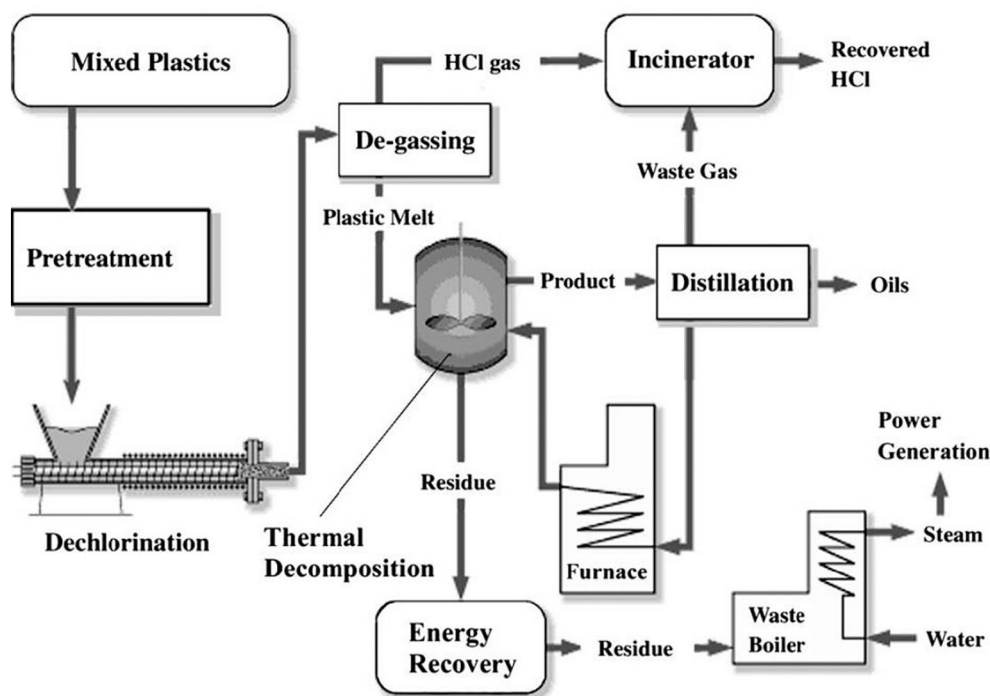


Fig. 6. Process flow sheet of the Niigata waste plastics liquefaction plant in Japan. Re-used with permission [86].

aspect for continuous processes. The application of rotary kilns for the dehalogenation of plastic waste has been investigated in the past. However, with a reported maximum chlorine removal of 95%, rotary kilns are not suitable for completely removing chlorine from waste fractions [91]. Although, in rotary kilns, dechlorination and pyrolysis can be directly combined and several examples of this have been elaborated at industrial scale in the past [92,93].

2.3. Melt filtration

Next to pre-treatment techniques for the removal of halogens, melt filtration as an effective way to remove contaminants from waste fractions has been an active field of research [94–96]. It has been reported that melt filtration of polyolefins is effective in the removal of higher-melting plastics such as PET along with solid contaminants. The key properties of contaminant removal are herewith the particle size and melting temperature [96,97]. However, the heat and shear forces which are applied during melt filtration contribute to the degradation processes of the polymers which is problematic for mechanical recycling, although, does not affect the thermochemical recyclability of the treated plastics [96].

Metals in plastic waste pyrolysis oils can occur due to entrainment of metal-containing ash residue that formed during pyrolysis [32,33]. Removal of organic and inorganic residues from the waste fractions prior to pyrolysis using melt filtration might lead to a reduction of metal contaminants thus making the pyrolysis products easier to implement in further processing steps [47]. Filtration-based removal of contaminants from pyrolysis oils will be discussed in a later section of this review article. Various kinds of melt filtration systems exist [95]. In terms of mechanical recycling, melt filtration is typically well-suited for the removal of remaining impurities in the percent range, but not as a separation technique to remove significant contaminant fractions from the waste streams. It has, however, been shown that the removal of contaminants via melt filtration of PP waste leads to improved mechanical properties of the recyclates [96]. In terms of chemical recycling of real plastic waste, however, additional research is clearly needed to shed more light on the potential of melt filtration for the efficient removal of feedstock contaminants.

2.4. Solvent-based purification of waste fractions

Removal of additives such as pigments, fillers and others is typically not possible with mechanical processes. Solvent-based purification methods include dissolving the waste in a solvent to remove additives and dyes to produce waste streams with a higher recycling potential [47,98]. It is worth noting that these techniques are not specifically intended to be followed by pyrolysis, however, removal of additives would also largely benefit the chemical recycling process via pyrolysis and steam cracking. A prominent example of an established solvent-

based cleaning technology is the CreaSolv® process developed by Fraunhofer IVV (see Fig. 7) [99,100]. In this process, plastic waste is treated with a solvent and subsequently cleaned from contaminants and additives. The precipitated and dried plastics can be converted to a higher quality recyclate. The process is suitable for mechanical recycling applications but also as a treatment step prior to chemical recycling. Currently, the CreaSolv® process is part of a PS recycling system developed by The PolystyreneLoop Cooperative [101].

Another solvent-based method developed for PVC waste on pilot-scale was the Vinyloop® process which, however, was stopped in 2018 due to problems with the REACH classification of products. It became obvious that the process was not capable of removing additives and impurities to a sufficient extent [102]. Another patented and commercialized solvent-based technology was developed by Procter & Gamble and is currently used by PureCycle Technologies [103]. The technology aims for the purification of PP waste and has shown promising results which led to a long-term strategic partnership with TotalEnergies [104]. The Newcycling® technology developed by APK AG is another promising process which can be used to produce pure polymer streams from complex packaging waste such as multilayer foils by dissolution and precipitation steps [105]. Currently, a pilot-scale plant processing 8000 tons/year is in operation in Germany [106]. It is worth noting that thorough solvent removal steps are required to purify the products prior to further processing. Consequently, processes become more costly due to energy-intensive steps such as drying.

Another attractive technique for the removal of organic contaminants from waste fractions is supercritical CO₂ (scCO₂) extraction. CO₂ can be considered a “green solvent” with low toxicity, which does not require sophisticated solvent removal steps [107]. Anouar et al. reported that a 100% extraction of the organic antioxidant Irganox 101 from PE film fractions was reached after 12 h using scCO₂ at 50 °C and 300 bar. According to the authors, conventional solvent extraction at the same conditions led to an extraction of 83% [108]. For more detailed information about applications of scCO₂ in polymer processing, the interested reader is referred to the textbook of Kemmere and Mayer [109].

3. Techniques applied during pyrolysis (in-situ)

Next to the described waste treatment techniques which can be used to purify waste feedstocks prior to further recycling steps, there are techniques which can be applied during pyrolysis (i.e., in-situ). These techniques refer to steps taken to capture harmful substances in the reaction mixture or to influence the composition of the pyrolysis products.

3.1. Sorbents and auxiliary materials

Sorbents can be added to the pyrolysis reactor in order to bind corrosive thermal decomposition products such as HCl (from PVC), HBr

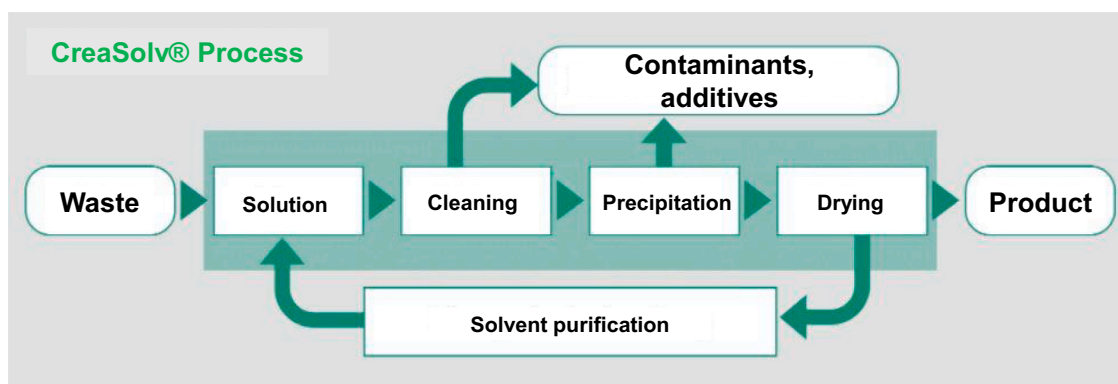


Fig. 7. Schematic overview of the CreaSolv® process developed by Fraunhofer IVV. Redrawn from [99].

(from brominated compounds), and organic acids (e.g., benzoic acid from PET impurities). These efforts are typically related to the protection of process equipment from corrosion, rather than aiming for a purified pyrolysis product. For this purpose, calcium-based sorbents such as CaO have been used widely to adsorb HCl and other organic acids such as terephthalic acid, benzoic acid and phthalic acid, forming chemically stable Ca salts which are stable up to ~ 600 °C [89,110]. However, it has been reported that CaO may also influence the chemistry of the thermal decomposition of aromatic polymers such as PET, leading to increased formation of styrene [111–113]. The in-situ dechlorination of mixed plastic waste containing 10% PVC by using a calcium carbonate – carbon composite sorbent has been investigated by different researchers [51,114]. Without sorbent, a chlorine content of 360 ppm in the liquid product was measured. Using the sorbent, a complete dechlorination was achieved for 4 consecutive experimental runs at 350 °C without necessary reactivation of the sorbent in between the runs. After the 4th run, the sorbent needed regeneration.

Sorbents have also been used in combination with catalysts as shown by Sakata et al., who utilized a combination of an iron oxide catalyst and calcium carbonate as a sorbent in a composite catalyst/sorbent system [51]. The authors optimized the process conditions for the complete removal of both chlorine and bromine from the pyrolysis products. The developed catalyst/sorbent system was tested for model waste plastics and for real post-consumer waste, both containing chlorine from PVC and bromine from BFR containing HIPS. In the single-step process, the plastic samples were decomposed at a temperature of 430 °C and, simultaneously, the bromine and chlorine was removed completely. It was further reported that iron-oxide acts as a catalyst and as chlorine sorbent at the same time [115,116]. To avoid catalyst deactivation, a calcium sorbent can be added in a separate bed before the actual catalyst bed (see Fig. 8) [51].

The halogen removal efficiency depends strongly on the used sorbent/catalyst system and protection of expensive catalysts from deactivation by waste contaminants is highly important. For the application of the proposed process for real waste, it is questionable if catalysts will not be poisoned in the long run by real waste contaminants such as metals [32].

It can be concluded that, from a process point-of-view, sorbents are effective to reduce corrosion issues during pyrolysis by binding corrosive reaction products immediately. However, it is questionable if sorbents alone can reduce the chlorine concentration in the pyrolysis products to a sufficiently low value [117–119]. Therefore, additional treatment methods (i.e., waste dehalogenation, or post-treatment of pyrolysis oils) are needed to ensure that the product contaminant levels fall within acceptable limits. Furthermore, a negative aspect is the limited capacity of sorbents which requires frequent exchange and regeneration. It was even reported by Hubáček et al. that adsorbed chlorine was released again at higher temperatures leading to a recontamination of pyrolysis products. This issue could be circumvented by using step-wise pyrolysis [120]. In this regard it needs to be noted that chemically bound elements cannot be removed easily from the sorbent materials. This is, for instance, the case for spent CaO/CaCl₂ which needs to be landfilled and replaced [121]. Therefore, additional research is still needed to shed more light on the technical and economic feasibility of regenerating sorbents.

3.2. Catalytic pyrolysis

Catalytic pyrolysis of plastic waste as a means to steer the composition of the produced pyrolysis oils is a promising technique to further improve the quality of the products as extensively described by Miandad et al. [122–124]. Often used catalysts are zeolites and acidic solids [125–130]. A disadvantage of catalysts for the pyrolysis of end-of-life plastics is the high content of feedstock contaminants which may lead to a rapid deactivation of the used catalysts [32,33,128,131]. Especially sulfur, nitrogen chlorine and metal contaminants, but also coke formation on the catalyst surface may lower the catalyst activity rapidly [132–134].

Benefits of catalysts are lower activation energies of the decomposition reactions and hence the lower required operating temperature and energy consumption [135]. Furthermore, shape selectivity of the catalysts leads to a narrower product distribution and reaction rates may increase significantly. From a product point-of-view it has been shown that the products from catalytic pyrolysis of polyolefins contain a narrower boiling point range. However, the high amounts of isoparaffins and aromatics make the products more suitable for fuel applications rather than as petrochemical feedstock. This has been shown by several authors [136–142]. Thus, the overall benefit of the currently tested catalysts to produce petrochemical feedstocks via catalytic pyrolysis of plastic waste is questionable. However, BTX aromatics are valuable products which may be removed from the pyrolysis products prior to further thermal cracking. In terms of potential deactivation issues it has to be noted that the sensitivity towards contaminants is substantially higher compared to thermal pyrolysis. Hence, in order to study the catalyst behavior on polymer decomposition, most research in that field was carried out using virgin polymers rather than contaminated mixed plastic waste streams [143]. An exception is the recently published article by Eschenbacher et al. who directly produced high concentrations of C₂-C₄ olefins ($\sim 75\%$) from real mixed polyolefin waste using mesoporous HZSM-5 zeolite catalysts. The authors reported that unmodified HZSM-5 was rapidly deactivated but that phosphorous-modification and steam treatment was effective in substantially increasing the deactivation resistance of the used catalyst against real-waste contaminants [144]. It has been reported extensively in the past that the addition of phosphorous can enhance the hydrothermal stability of HZSM-5 [145–147]. In combination with steam treatment, the stability of the aluminum framework can be further increased as reported previously [148,149]. Next to the increased catalyst stability, which is highly relevant for the use in plastic waste pyrolysis, it was also found that the mentioned modification techniques increase the selectivity towards light olefins in the C₄-range [145]. It is important to note that the phosphorous loading is highly influential for the catalyst performance, as the reduced accessibility of active sites can lead to a reduced conversion [145,148,150]. Moreover, steam treatment has been reported effective in lowering the coking tendency on the catalyst surface due to the lower acidity [147]. In a continuous process it is however recommended to combine guard beds to first remove harmful contaminants with effectively treated, more contaminant resistant catalysts.

A different and more integrated approach using catalysts can consist of a thermal pyrolysis step (with or without in-situ added materials) in combination with an in-line catalytic upgrading step of the gaseous pyrolysis products. In this concept, product vapors can be passed over an active material, e.g., a catalyst, for the direct upgrading of the pyrolysis products towards the desired properties. Such more integrated solutions

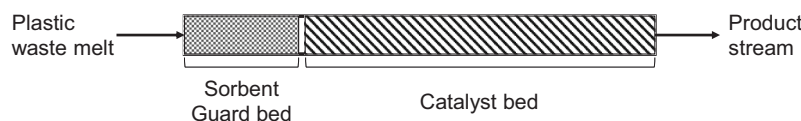


Fig. 8. Schematic of a catalyst bed preceded by a sorbent guard bed to protect the catalyst from deactivation.

including technical concepts that are currently being developed are discussed in a later section of this article.

3.3. Supercritical water (SCW)

Recently, the use of supercritical water for the pyrolysis of plastic waste has been an active field of research due to several beneficial aspects [151–160]. These are, for instance, a suppression of secondary reactions due to dilution, favoring of unimolecular reactions and thus the reduction of heavy products and coke formation, and the removal of contaminants via the supercritical fluid phase [161,162]. Supercritical fluid technologies make use of the combined liquid and gas-phase properties of fluids in the supercritical state. The critical point of water is reached at a temperature of 374 °C and a pressure of 221 bar. After passing the critical point, SCW has properties of both a gas and a liquid such as high diffusivity and low viscosity like a gas, while still being able to dissolve solids like a liquid. Furthermore, the low dielectric constant of SCW leads to favorable solvent properties [163,164]. During SCW pyrolysis, the non-polar environment leads to an increase in temperature-driven reactions such as radical reaction pathways [165]. Furthermore, higher concentrations of shorter chain hydrocarbons in the products of SCW pyrolysis compared to classical pyrolysis were reported, which was explained by the more pronounced β -scission reactions in the diluted reaction mixture [166]. In SCW pyrolysis, aromatic species (i.e., coke precursors) that are formed during pyrolysis are extracted into the SCW phase, leading to a reduction in coke formation [167]. It has to be noted that using supercritical fluids in a continuous pyrolysis process requires a separation step to remove the water from the pyrolysis products including a purification and clean-up step to recycle the water which may add substantially to the total operational cost [168]. Furthermore, considering the harsh conditions needed and the presence of corrosive substances (i.e., HCl and organic acids, among others), highly corrosion resistant and therefore expensive steel alloys are required. The higher associated capital and operational costs need to be taken into account when designing a commercial process. Furthermore, the presence of hydrogen in the reaction mixture at the mentioned conditions may lead to so-called hydrogen embrittlement which might lead to depletion of the inner reactor surface [169,170]. Hydrogen embrittlement can be prevented by using steel types such as chromium- or molybdenum-alloys or cadmium- or titanium-plated nickel, which are adding substantially to the capital costs of a prospective plant [170].

Next to the mentioned coke suppression properties of SCW treatment, the mentioned properties of SCW can also be utilized to remove contaminants during pyrolysis of plastic waste (see Table 3). The chlorine and nitrogen removal potential from mixed plastic waste using SCW treatment has been investigated by Akimoto et al. The authors reported a full removal of chlorine from an initial concentration of 62 ppm after 15 min of processing at 425 °C. At the same conditions, the nitrogen concentration could be reduced from initially 1150 ppm to 49 ppm [171].

Similar observations have been reported by Takeshita et al., who observed full chlorine removal from the organic product phase when processing PVC-containing waste using SCW treatment for 1 h [175]. SCW treatment has also been used for the desulfurization of heavy oils

Table 3
Contaminant removal efficiencies using SCW treatment.

Contaminant	Reaction time [min]	Temperature [°C]	Removal efficiency [%]	Reference
N	30	425	89%	[171]
Cl	15	425	100%	[171]
O	–	380	78%	[172]
S	31	400	<5–60%	[173]
Br	35	450	>90%	[174]
Sb	35	450	99%	[174]

[165,173]. It has been reported that more than 90% of aromatic sulfides were converted into H₂S and R₂H using SCW treatment at 400 °C and 235 bar for 31 min [173]. However, the conversion was highly dependent on the molecular structure of the respective sulfur compounds: with benzyl disulfide, a sulfur removal of 60% was achieved, while with thiophene, only <5% of sulfur could be removed. Since sulfur compounds in plastic waste pyrolysis oils are often found in the thiophene family, as reported in recent works, SCW treatment might not be ideal for the removal of sulfur from plastic waste [33,176]. However, sulfur does not occur to a large extent in plastic waste pyrolysis oils and is therefore a contaminant of lesser concern [21,32,33].

The use of SCW has also been extensively researched for the hydrothermal liquefaction of biomass [177–182]. It has been claimed that during SCW treatment of biomass, hydrogen is transferred to oxygenates present in the biomass [182]. In the context of plastic waste decomposition using SCW it can, therefore, be assumed that next to the achieved oxygen removal, lower amounts of hydrogen are needed for a later catalytic hydrotreatment step of the produced pyrolysis oils. An oxygen removal of 78% from waste biomass using SCW treatment was reported [172]. Since oxygen concentrations in plastic waste are expected to be considerably lower compared to biomass, SCW can be a viable technique to lower the oxygen concentrations in the final product [32]. SCW technology has further been used to decompose BFR containing waste fractions such as acrylonitrile butadiene styrene (ABS) or HIPS. It was reported that more than 90 wt% of the initial bromine and almost the entire initial antimony, which is a common synergist of BFRs, was removed in the SCW phase [174].

Technical solutions using the SCW technology have been recently reported in several patents. The recently filed patents by the company Mura Technology Ltd. describe a large-scale process of converting contaminated plastic waste into light hydrocarbon products suitable as steam cracker feedstocks by using SCW treatment [183,184]. Recently, Dow announced a long-term partnership with Mura Technology Ltd. with plans to reach an annual capacity of 1 million metric tons of plastic waste by 2025 [185].

4. Post-treatment of plastic waste pyrolysis oils

It has been shown recently that plastic waste pyrolysis oils typically exceed known petrochemical feedstock specifications by orders of magnitude in terms of heteroatoms, metals as well as olefins and aromatics [32,33]. Therefore, upgrading of pyrolysis oils towards industrial-quality petrochemical feedstocks is inevitable. In the following sections, upgrading techniques for plastic waste pyrolysis oils are reviewed such as fractionation, hydrotreatment and adsorption techniques.

4.1. Fractionation via distillation

Plastic waste pyrolysis oils typically contain hydrocarbons distributed throughout a wide boiling point range which can be up to a final boiling point of >600 °C, depending on the pyrolysis conditions [33]. First and foremost, if pyrolysis oils are intended to be used as steam cracker feedstocks, it is highly relevant that the boiling point range of the used pyrolysis oils are complying with the maximum acceptable evaporation temperatures of the evaporation sections of the steam crackers. Typical fossil feedstocks such as (heavy) naphtha have a maximum boiling point of around 200 °C, hence, commercial naphtha steam crackers have evaporation sections designed according to this boiling range [186,187]. Therefore, crude pyrolysis oils need either to be fractionated, analogue to crude oil refining, into lighter fractions that are compatible with the evaporation sections of naphtha crackers, or costly modifications of the steam cracker units are needed. Considering the ongoing transition in the petrochemical industry towards heavier steam cracker feedstocks, wider boiling point ranges might become acceptable for newly designed steam crackers in the future [188,189].

However, it has been shown that distilled pyrolysis oil perform better in steam cracking in terms of process-related issues such as fouling and coke formation compared to undistilled samples [190].

Fractionation may have several benefits as a first upgrading step of crude plastic waste pyrolysis oils. It was shown that most metal contaminants end up in the heavy fractions of the pyrolysis oils or in the solid residue fractions of the pyrolysis process [32,33]. Furthermore, it was reported that via fractionation of crude plastic waste pyrolysis oil, transparent products with a significantly reduced viscosity and density compared to the crude pyrolysis oils could be obtained [191–193]. In terms of the mass-balance, it was reported by Lee et al. that out of 1000 kg of plastic waste, a combined 390 kg of light and middle distilled fraction could be obtained which indicates that other valorization pathways must be found for the gaseous pyrolysis fraction, the solid char residue as well as the waxy distilled fraction [194]. Potential applications for the heavy distillation residue that is unsuitable for steam cracking could be co-feeding with vacuum gas oil (VGO) derived from a refinery stream to a fluid catalytic cracker (FCC) unit which was recently described by Rodriguez et al. [195]. Moreover, hydroisomerization of pyrolysis waxes for the production of lubricating oils is another potential valorization pathway [196,197]. A possible application for the char residue of pyrolysis could be the production of carbon nanomaterials [198]. Gaseous pyrolysis products can be utilized as fuel gas to fire the process, however, producing CO₂ emissions. Since the pyrolysis gases of polyolefins contain large amount of valuable chemicals such as ethane, ethylene, propane, propylene and others, direct utilization might also be an option [199–201]. Fig. 9 depicts an example of distilled product fractions compared to the crude pyrolysis oil (produced at the Laboratory for Chemical Technology, Ghent University and part of a follow-up study, unpublished).

It can clearly be seen that the crude pyrolysis oil contains particulate matter that was removed in the distilled fractions. Moreover, the light distillation cut has the lightest color which also indicates that it is the “cleanest” fraction and that more contaminants are removed the lighter the fractions get. However, it was also shown in our recent review article that the light fractions may still contain considerable amounts of contaminants exceeding known feedstock specifications substantially, i.e., for chlorine, nitrogen, oxygen and metals such as calcium and sodium [32].

Numerous authors have investigated the possible application of plastic waste pyrolysis oils as diesel fuel [202–206]. The research often involves fractionation since physical parameters such as boiling points, viscosities and densities are crucial for fuel applications. Faussonne et al. investigated the usability of plastic waste pyrolysis oil for fuel applications by producing three fractions according to the boiling point ranges

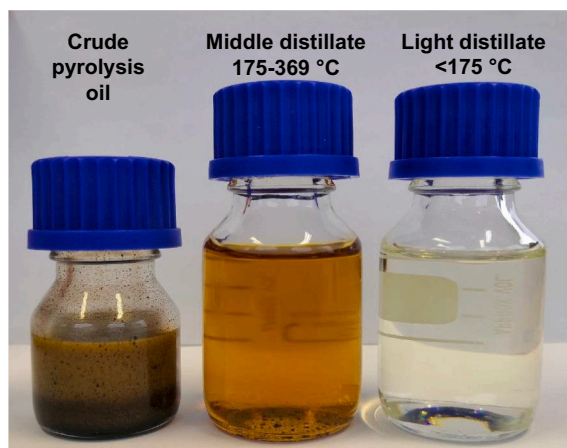


Fig. 9. Distilled cuts of a crude pyrolysis oil (produced at the Laboratory for Chemical Technology, Ghent University and part of a follow-up study, unpublished).

0–170 °C, 170–370 °C and > 370 °C and found that some parameters of the medium and the heavy fraction already lie within the EN590 standard specifications for transportation fuels without further upgrading. The lightest distillation cut, on the other hand, resembled a naphtha range feedstock rather than an (automotive) fuel [207].

In terms of the chemical compositions, it was found that the respective hydrocarbon families (i.e., paraffins, olefins, aromatics, naphthenes) are not spread evenly throughout the respective light and medium fractions of pyrolysis oils. Typically, olefins and aromatics are more prominent in the lighter distilled fractions, while the heavier fractions are more paraffinic [32,176,208]. It can hence be concluded that, on the one hand, fractionation of pyrolysis oils is needed in order to comply with boiling point range requirements of commercial steam cracking units. Furthermore, the removal of large parts of metal contaminants present in the heavier fractions is a convenient side effect. On the other hand, it does not solve problems related to crucial feedstock constituents such as aromatics, olefins or heteroatoms (i.e., nitrogen, oxygen, sulfur or halogens). Hence, additional post-treatment is needed, such as catalytic hydrotreatment which is discussed in the following.

4.2. Catalytic hydrotreatment

Catalytic hydrotreatment of liquid hydrocarbon feedstocks for the production of more valuable products such as fuels or petrochemical feedstocks has been performed for many years [209–212]. In Table 4, an overview of the different aspects of catalytic hydrotreatment is given.

With hydrotreatment it is possible to reduce the concentration of heteroatoms i.e., nitrogen (hydrodenitrogenation, HDN), sulfur (hydrodesulfurization, HDS), oxygen (hydrodeoxygenation HDO), chlorine (hydrodechlorination, HDCl) and even metals (hydrodemetallization, HDM) as well as to saturate olefinic and aromatic compounds [212].

4.2.1. Removal of heteroatoms

Considering its wide range of applications, hydrotreatment is a promising upgrading technology for pyrolysis oils [223,228–231].

Table 4

Overview of individual catalytic hydrotreatment processes for the removal of heteroatoms and metals from hydrocarbon feedstocks.

Process	Example conditions	Description and example reactions	Reference
HDS	T: 300–425 °C P: 10–200 bar Cat.: Co–Mo or Ni–Mo	$C_{12}H_{26}S + 2H_2 \rightarrow C_{12}H_{26} + H_2S$ Sulfur is released in form of H ₂ S. ExxonMobil's SCANfining® process allows reduction below 10 ppm.	[37,213–216]
HDO	T: 400 °C P: 135 bar Cat.: Co–Mo or Ni–Mo	$R-OH + H_2 \rightarrow R-H + H_2O$ Oxygen is released in form of H ₂ O. Complete removal can be achieved.	[36,217–219]
HDN	T: 450 °C P: 150 bar Cat.: Ni–Mo	$C_5H_5N + 5H_2 \rightarrow C_5H_{12} + NH_3$ Nitrogen is released in form of NH ₃ . Complete conversion of nitrogen compounds can be reached.	[220,221]
HDCl	T: 300–450 °C P: 5–50 bar Cat.: Ni–Mo or HZSM-5	$C_6H_5Cl + H_2 \rightarrow C_6H_6 + HCl$ Cl is released in form of HCl. Cl reduction to 2–8 ppm.	[36,37,222–224]
HDM	T: 400 °C P: 50 bar Cat.: Ni, Mo or Co oxides	$M-P \rightarrow M-PH_2 \rightarrow \text{deposit} + \text{hydrocarbon}$ M – P: metalloporphyrin Metals released from metalloorganic complexes immediately deposit on catalyst surfaces permanently deactivating it. Vi, Ni, and Fe content could be reduced from 80 ppm to 8 ppm.	[225–227]

However, not many studies exist that elaborate on upgrading of actual plastic waste pyrolysis oils. In a recent study, the pyrolysis, distillation and subsequent Pd-catalyzed hydrotreatment of waste PE, PP and PS was investigated. The authors reported that pyrolysis oils could be obtained that are applicable for fuel applications. However, no catalyst deactivation issues by potentially present contaminants were discussed [232]. In theory, individual and selective hydrotreatment steps exist to reach acceptable feedstock limits for every heteroatom as shown in Table 4 such as ExxonMobil's SCANfining® process, which is capable of reducing the sulfur amount of hydrocarbon feedstocks below 10 ppm [213,214]. In terms of halogen removal, it was recently shown that using a nickel-based catalyst on a titanium support, full conversion of tetrachlorobenzene was achieved at mild conditions (140 °C, 45 bar H₂) [233]. Yet, it has been reported that the removal efficiencies for individual heteroatoms can be significantly lower when nitrogen components are present in the fuel samples due to inhibiting effects of the nitrogen compounds [221,234]. Investigations in the simultaneous hydrogenation of chlorobenzene, quinoline and benzothiophene diluted in hexadecane as reaction medium have shown that the presence of quinoline had a strong inhibiting effect on both HDS and HDCl [235]. For reference, all compounds have been hydrotreated separately and in admixture at 320 °C and at a hydrogen pressure of 40 bar using a Ni—Mo on Al₂O₃ catalyst. It was reported that decahydroquinoline, an important intermediate in the HDN of quinoline showed high affinity towards the active surface of the acidic catalyst, thus strongly inhibiting the adsorption of benzothiophene and chlorobenzene. Furthermore, both organic nitrogen and ammonia can have strong inhibiting effects on all hydrotreating reactions [221]. Therefore, alternative techniques for the removal of nitrogen compounds are needed, which will be elaborated in a later section of this article. Typical nitrogen compounds found in plastic waste pyrolysis oils are anilines, porphyrines, quinolines and their derivatives which are mostly aromatic structures that require more severe conditions than linear nitrogen compounds such as amines [33,176,222,236–238]. Consequently, higher temperatures and pressures are needed for HDN compared to other hydrotreatment processes [239].

In conclusion, it can be stated that the biggest obstacle when hydrotreating plastic waste pyrolysis oils is the co-existence of a large range of heteroatomic compounds which all influence the individual hydrotreatment steps and hence make the application of hydrotreatment processes for the selective removal of certain contaminants difficult [32,33,176,237]. In practice, this issue could be circumvented by operating at higher hydrogen pressures and using larger catalyst volumes. However, this would increase the cost of processes due to higher hydrogen requirements and pressures. Additionally, highly stable steel alloys capable to withstand the harsher process conditions are needed. Hence, hydrotreatment processes designed specifically for plastic waste pyrolysis oils are needed considering their unique composition and high concentrations of problematic contaminants. On a commercial level, Dow and Haldor Topsoe recently joined forces to combine plastic waste pyrolysis with the PureStep™ process that utilizes a patented hydro-processing technology to remove impurities and contaminants from pyrolysis oils [240]. Furthermore, Clariant has developed a de-waxing catalyst to improve the cold flow properties of plastic waste-derived diesel fuels [241].

4.2.2. Hydrodemetallization

Metals in crude oil typically occur in two chemical forms depending on the respective elements. Zinc, titanium, calcium and magnesium, which are all present in plastic waste pyrolysis oil [32,33], are usually present in combination with naphthenic acid as soaps. Other metals such as vanadium, copper, nickel, and iron are bound within metalloporphyrins (see Fig. 10) [89,225,226].

Total metal concentrations of between 560 and 790 ppm in post-consumer plastic packaging waste pyrolysis oils have been recently reported [33]. Some of the detected metals such as iron or lead are harmful

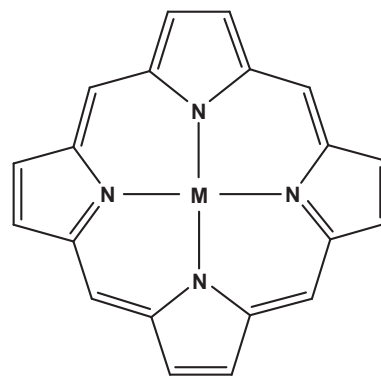


Fig. 10. Structural formula of a metalloporphyrin. Re-used with permission [32].

to petrochemical operations already in ultra-trace amounts.

Another important motivation for the quick removal of residual metals from pyrolysis oils is to protect hydrotreatment catalysts from swift deactivation due to metal deposition [226,227,242,243]. In catalytic HDM of metalloporphyrins, metals are released from the complexes and immediately bind on the catalyst surface, permanently poisoning the catalyst. For this reason, mostly cheap aluminum oxide catalysts as so-called guard beds are used for the removal of metals. These guard beds are installed upstream of the units which utilize more expensive (e.g., precious metal) catalysts to reduce the risk of poisoning of the latter (comparable to the sorbent guard bed shown in Fig. 8) [226,243]. HDM catalysts are for instance nickel, molybdenum or cobalt oxides on Al₂O₃. It has been reported that a heavy petroleum distillate feed containing vanadium, nickel and iron of 80 ppm in total was treated with hydrogen at 397 °C leading to a reduced total amount of 8 ppm [226]. Although a significant reduction, other methods of metal removal are still needed to meet the threshold values for industrial steam crackers. Similarly, in the study of Kang et al., who investigated the effect of the catalyst composition on the HDS and HDM of atmospheric residual oil, a demetallization of almost 70% was achieved using a Ti/Co/Mo catalyst [244]. However, it can be anticipated that the fractions which are interesting for steam cracking, i.e., the naphtha and middle distillate fractions are relatively lean in metalloorganic compounds since metalloporphyrins are mostly found in higher carbon number ranges [32,226,245].

4.2.3. Reduction of unsaturated compounds

Hydrotreatment is a well-established process to lower the concentrations of unsaturated compounds via catalytic hydrogenation [223,228,229]. The main motivation for this process is either to meet fuel specifications regarding the aromatic content or to upgrade heavy petroleum fractions for further use in the petrochemical process chain. Furthermore, plastic waste-derived products are rich in unsaturated hydrocarbons which leads to a reduced storage stability [40]. Addition of antioxidants might be needed for plastic waste-derived fuels if no hydrotreatment is performed.

Studies investigating the catalytic hydroreforming of plastic waste pyrolysis oil using Ni-supported hierarchical zeolites and mesostructured aluminosilicates were conducted by Escola and co-workers [246–250]. It was found that at 310 °C and 20 bar hydrogen pressure, complete hydrogenation of an LDPE pyrolysis oil containing 27% of olefins was achieved. After hydrotreatment, the products contained less than 1 wt% of olefins [246,248]. Furthermore, hydroreforming of LDPE pyrolysis oil was studied using bifunctional hierarchical beta zeolite catalysts with high accessibility of the active sites. It was found that the presence of nickel in the catalyst favored the olefins conversion substantially. It was further found that higher temperatures (up to 350 °C) led to increased hydrocracking. Above 300 °C, aromatization reactions began to occur. Increased hydrogen pressure up to 40 bar led to a swift

increase in hydrogenation of olefins and further inhibited the formation of aromatics [249].

Hydrogenation of aromatics is typically more difficult using HDN/HDS catalysts at operating conditions normally applied for HDS or HDN [251]. This is due to thermodynamic restrictions regarding equilibrium conversion which means that at HDS and HDN conditions, complete conversion of aromatics cannot be achieved. Higher hydrogen pressure might be used to increase the conversion. However, this often requires new and expensive equipment. Noble metal catalysts might be used to reduce the aromatic content significantly, however, at much higher costs. It has also been reported that heavier aromatic species may inhibit the HDS effectivity which underlines the need for reduction of the aromatic content of plastic waste pyrolysis oils prior to catalytic hydro-treatment [252]. Another possible technique is homogeneous catalysis under lower hydrogen pressure which has been proposed in an early patent [253]. The invention makes use of hydrocarbon-aluminum compounds reacting with a transition metal compound to produce a complex which is soluble in liquid hydrocarbons and active in catalyzing hydrogenation reactions in a homogeneous system. This technique is selective for the hydrogenation of aliphatic unsaturation over aromatic unsaturation therefore mainly hydrogenating olefins instead of aromatics [253]. However, a major drawback of homogeneous catalysis is the required separation of catalyst and products after the reaction, necessitating additional separation technologies and often extraction agents which in turn need to be separated from the catalyst.

4.3. Purification via adsorption

Considering the high degree of contamination in plastic waste pyrolysis oils, it is likely that catalytic hydrotreatment without prior removal of critical components such as nitrogenates, aromatics, and metals will be far less effective. Adsorbents are promising in selectively removing contaminants from hydrocarbon samples prior to hydro-treatment and are explained in the following [252,254,255].

4.3.1. Activated carbon

Kim et al. conducted purification experiments at ambient temperature and pressure of a model diesel fuel containing sulfur and nitrogen compounds as well as two-ring aromatics using activated carbon with a surface area of 1843 m²/g [256]. As model compounds, dibenzothiophene, 4,6-dimethyl-dibenzothiophene, indole, and quinoline were used, well representing sulfur and nitrogen compounds present in plastic waste pyrolysis oils [33,176]. The authors reported that activated carbon showed better properties (both breakthrough capacity and saturation capacity) for the removal of total nitrogen and total sulfur compared to an activated alumina and a Ni/SiO₂-Al₂O₃ sorbent, respectively [256]. The breakthrough capacity of the activated carbon for sulfur was 3.3× higher than that of Ni/SiO₂-Al₂O₃ and 4.6× higher than that of activated alumina. For nitrogen, the difference was also substantial (4.4× higher than Ni/SiO₂-Al₂O₃ and 2.5× higher than activated alumina). However, it has also been shown that nickel-based adsorbents have a higher sulfur removal capacity at higher temperatures. It is worth pointing out that based on the surface area, both the activated alumina and the Ni/SiO₂-Al₂O₃ sorbents have a much higher adsorption capacity per m² for both nitrogen and sulfur components. The higher weight-based adsorption capacity of the activated carbon is hence related to the 12× higher surface area per gram of activated carbon compared to the other two materials [256]. In terms of the adsorbed species, the nitrogen compounds quinoline and indole were removed with a higher efficiency by all sorbent classes. This finding is promising in a scenario where a sorbent-based nitrogen removal step is performed before a catalytic hydrotreatment unit. Further research was performed by Sano et al., who investigated the adsorption kinetics of sulfur and nitrogen compounds on different activated carbon types. The authors concluded that efficient nitrogen removal is mainly dependent on the surface properties of the activated carbon material. In particular,

the authors identified the oxygen functional groups on the activated carbon which liberate CO as the main driver for the adsorption capacity. The deactivation of such groups hence leads to a strong reduction of the adsorption capacity [254].

In a recent publication, removal of 49.56% of colorants and full removal of particle matter from waste PP pyrolysis oil using activated carbon was reported [257]. The obtained pyrolysis oil had similar physico-chemical properties as conventional diesel fuel. It has been shown that adsorption using activated carbon could be a viable technique to remove nitrogen and other contaminants from pyrolysis oils. However, additional research is needed that elaborates the effect of impurities in plastic waste pyrolysis oils on the adsorption capacity of different materials. Considering the importance of oxygen functional groups on the sorbent surfaces to efficiently capture nitrogen compounds, it is at least questionable, if highly contaminated plastic waste pyrolysis can be used without prior removal of the most severe contaminants.

4.3.2. Metal organic frameworks (MOFs)

MOFs are a promising class of porous polymeric materials in which metal ions are linked by organic ligands forming a framework (see Fig. 11). By using different organic bridging ligands, the properties of MOFs such as the sorption capacity can be rationally tuned [258]. The various possibilities of application have been reviewed extensively in the past [259–262]. Furthermore, several studies exist that investigate the selective adsorptive separation of sulfur [263–265] and nitrogen compounds [266–268] from fuel samples. In the study of Wang et al., MOFs were used to remove nitrogen model compounds such as pyridine, pyrrole, quinoline and indole from fuels at atmospheric temperature and pressure [269]. It was found that Lewis acid sites present in the MOF structure combined with the high specific surface area (typically ranging from 1000 to 10,000 m²/g [270]) led to a high selective adsorption capacity of the basic nitrogen compounds [269]. The adsorption capacity was stronger for nitrogen compounds with a higher basicity. The MOFs could be regenerated by a simple washing step using ethanol.

Maes et al. investigated different MOFs for the selective removal of nitrogen and sulfur compounds from fuel samples containing ~1000 ppm sulfur and ~700 ppm nitrogen [266]. The tested concentrations are herewith roughly in the same range as found in plastic waste pyrolysis oils [32,33]. After adsorption, <2 ppm of sulfur and <0.5 ppm of nitrogen were reported, which is well below the maximum allowable concentrations for steam cracker feedstocks [37]. Next to the removal of nitrogen and sulfur compounds, MOFs can also be used for the selective removal of heavy metals as described in recent review articles

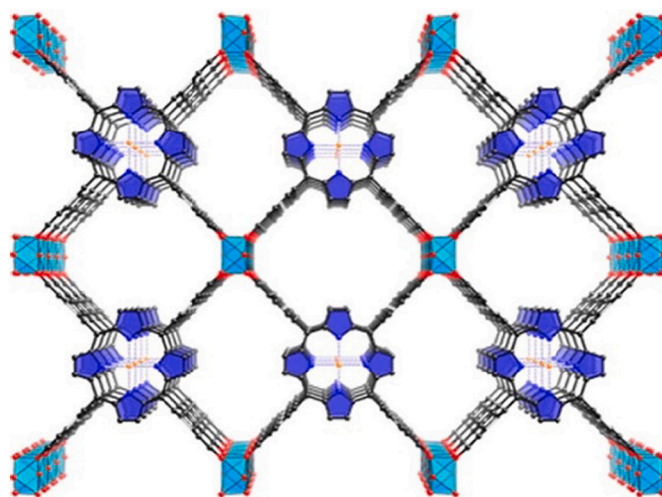


Fig. 11. Example of a MOF structure. Shown framework is [Al₂(OH)₂(Co(tcpp))]. Re-used with permission [271].

[272,273]. Rouhani and Morsali investigated the removal of mercury and lead from contaminated water samples at atmospheric conditions and reported a reduction of the mercury concentration from initially 40 ppm down to 2 ppb after treatment [274]. The authors did not report the final lead concentration, however, the high reduction of mercury in the sample is highly promising considering the hazard of mercury in a petrochemical context [275,276]. In terms of steam cracking, a residual mercury concentration of 2 ppb would comply with feedstock specifications of ~10 ppb [37].

A possible drawback of MOFs could be the need for compound-specific MOF systems for multiple contaminants which would make a continuous process less flexible and more expensive. To this day, MOFs have not been used for the purification of plastic waste pyrolysis oils. Hence, additional research is needed and no definite conclusion can be made in terms of the applicability on a larger scale in continuous processes.

4.4. Solvent-based contaminant extraction

Next to solvent-based techniques applied prior to or during pyrolysis such as CreaSolv®, solvent extraction methods can also be used as a post-treatment step to upgrade pyrolysis oil. The removal of metals from residual fuel oils has been subject to the review article of Ali and Abbas [226]. Furthermore, in their patent, Yamada et al. report demetallization using solvent extraction by heating of the crude metal-containing oil (159 ppm of vanadium) to ~240 °C in presence of an organic solvent such as hexane and subsequent centrifugation. According to the authors, full removal of vanadium, which can also occur in plastic waste pyrolysis oils, could be achieved [277]. Furthermore, extraction methods for the deasphalting of crudes using hydrocarbons such as propane, butane or isobutene proved effective for the removal of metals from vacuum residues, leading to a reduction of the vanadium content by 95% using n-pentane as solvent [278]. In another patent, a process was shown to remove nickel- and vanadium-containing metalloporphyrins from a heavy petroleum feedstock using extraction with 1-butylolactone, leading to a vanadium removal of 97% [279].

Furthermore, supercritical fluid extraction as a method to purify contaminated waxes derived from PE and PP pyrolysis was investigated. High removal efficiencies of up to 93% for calcium, 67% for aluminum and 72% for sodium were reported. Furthermore, up to 80% of organic contaminants were reduced leading to a lighter color and removal of odor compounds [280]. Although a significant removal, supercritical fluid extraction might not be sufficient to reach the strict feedstock specifications in terms of metal contaminants.

4.5. Filtration

Filtration techniques using membranes have been researched in recent years [226]. In the patent of Kutowy et al., high molecular weight contaminants were removed by a membrane system using a microporous membrane made from a swellable polysulfone compound [281]. Viscosity limitations were overcome by heating of the hydrocarbon liquid. The authors reported the removal of aluminum, chromium, copper, nickel, and vanadium as well as asphaltenes and heteroatoms such as nitrogen and sulfur. Of these compounds, especially aluminum, chromium, and copper can also be found in plastic waste pyrolysis oil [32,33]. Membrane filtration processes have been described in a few further patents [282–284]. Membrane processes have the disadvantage that they are mostly employed in smaller scales and that effective membranes often incorporate expensive or sensitive materials. Furthermore, fouling of the membrane surfaces makes frequent regeneration or replacement of membranes necessary. However, next to membrane filtration, depth filtration is a viable method to purify pyrolysis oils from contaminants that gain increasing attention in processing of bio-based fluids [285,286]. Particularly interesting is the removal of contaminants by in-line filtration of hot pyrolysis gases

which would be a more integrated solution for continuous larger scale operations [287]. It is important to note that these processes have not yet been applied for plastic waste pyrolysis products on a larger scale to this day. Hence, further research is needed to assess the impact of plastic waste-specific contaminants and potentially harmful compounds that could decrease the filtration efficiency. However, in-line filtration downstream of the pyrolysis reactor would be highly promising as it protects subsequent equipment as well as prevents entrainment of particles with the pyrolysis vapors.

4.6. Acidic demetallization

Chemical methods of demetallization aim for selectively removing metals without altering the remaining hydrocarbon matrix. Demetallization of metalloporphyrins might be performed using acids according to the following reversible reaction [226].



With PM representing the metalloporphyrin complex and HX an acid such as sulfuric acid (H₂SO₄). PH represents the hydrogenated porphyrin complex and MX the bound metal. A drawback of sulfuric acid is the formation of SO₂ which might react with the remaining unsaturated hydrocarbons. According to Ali and Abbas, hydrofluoric acid (HF) is the most effective demetallization reagent with an achievable 90% removal of metals [226]. In the patent filed by Kukes and Battiste, phosphorous acid (H₃PO₃) was used as a demetallization agent which reacts with the metals forming insoluble compounds that can be removed via filtration or centrifugation. The acid proved highly effective for the removal of nickel and vanadium from heavy oil [288]. In the patent filed by Blytas, activated carbon treated with a highly acidic oxidizing fluid was used to demetallize heavy hydrocarbon feedstocks at 375–450 °C. The oils originally contained 33 ppm of nickel and 99 ppm of vanadium. With the process, the nickel and vanadium levels could be reduced to ~5 ppm and ~4–5 ppm, respectively [289]. Although significant, the achieved removal efficiency is still not sufficient to comply with petrochemical feedstock specifications. Another disadvantage of using acids is the re-introduction of hetero elements into the pyrolysis oils.

5. Integration of processes: from waste to chemicals

In the previous sections techniques were discussed that refer to stand-alone applications either prior, during or after pyrolysis. However, in an industrial context, processes are typically highly interconnected which is especially evident in petrochemical clusters where the product of one process is often the feedstock of another. This way, resources and utilities can be more efficiently used and storage times and transport distances are reduced. It is therefore highly interesting to explore solutions, how the discussed techniques can be combined into a more integrated process scheme and to assess if advantages can be found compared to the sequential process of waste pre-treatment followed by pyrolysis and subsequent post-treatment of pyrolysis oils.

Integrated solutions refer to processes where crude plastic waste pyrolysis oil or plastic waste as a solid feedstock are used to directly produce high value chemicals. These systems can refer to innovative reactor concepts or to petrochemical units such as fluid catalytic crackers (FCC) or delayed cokers. In the latter, existing clusters and petrochemical production complexes may be utilized instead of designing new plants specifically for the advanced recycling of plastic waste. There are only few academic publications on this topic in open literature since the idea of an integrated solution refers more to larger industrial enterprises and is therefore more frequently found in patent literature.

5.1. Academic research on integrated chemical plastic waste recycling

The recent review paper by Palos et al. describes the integration of

plastic waste in refinery units [230]. In their study, the authors state that FCC and hydroprocessing units are the best suited for valorizing mixed plastic waste at a large scale. Furthermore, it is concluded that blending waste feedstocks with current refinery streams such as vacuum gas oils is highly feasible from a technical standpoint. In their review paper, Thunman et al. addressed the transition of existing petrochemical clusters into thermochemical recycling plants with an envisaged 100% recovery of the plastics based on theoretical concepts (see Fig. 12) [290]. Different hypothetical cases were investigated: A) 45% replacement of fossil feedstocks with plastic waste-derived feedstocks and B) total replacement of fossil feedstocks. Based on these cases, carbon and energy balances were set up and an economic assessment for a step-wise transformation of an existing petrochemical cluster into a thermochemical plastic waste recycling plant was performed.

According to the authors, a full transition to plastic waste as feedstock for the petrochemical cluster is highly feasible from an economic point-of-view. In their scenario, waste PE from marine litter would be used with an (unspecified) pre-washing step before entering the crackers. Regarding possible operational issues due to heteroatoms in the waste streams, the authors suggest the use of lime-based sorbents for the removal of HCl. Regarding contaminants from fillers incorporated in the plastics, filter systems are proposed to recover the filler materials. It is important to note that the “cracker” depicted in Fig. 12 does not refer to a conventional steam cracker but to a so-called dual fluidized bed reactor system for the direct steam cracking of solid plastic waste towards gaseous chemical building blocks [291–293]. The used fluidized bed material is olivine activated with biomass ash. Four steady-state cases with two plastic feedstocks (pure PE and automotive shredder residue from car recycling) have been investigated. Using PE, the authors reported a combined ethylene and propylene yield of 48 wt% at a temperature of 655 °C which is on par with product compositions from conventional fossil naphtha cracking [292,294].

High temperature pyrolysis of solid plastic waste in a fluidized bed reactor in the presence of steam to directly yield light olefins has been investigated by Simon et al. [295]. Process temperatures between 600 and 700 °C were studied and the residence time was varied between 1.8 and 3.2 s. At temperatures of 700 °C, ~30 wt% ethylene and ~15 wt% propylene were obtained using municipal plastic waste. For virgin PE,

36 wt% ethylene and 15 wt% propylene were obtained. As a reference, the authors mention steam cracking yields for fossil naphtha of 29 wt% ethylene and 16 wt% propylene. The used temperature range has been confirmed as the best for achieving light olefin products [296,297]. The presented product yields of high-temperature steam pyrolysis are in a similar range as the reported light olefin yields from conventional steam cracking of fossil naphtha and crude pyrolysis oil/naphtha mixtures as reported in our previous works [190,294].

In recent studies, a catalytic reactive distillation approach in HDPE pyrolysis was reported [298,299]. The authors developed an integrated reactor/separator system which promotes the production of light hydrocarbons by recycling the heavier boiling compounds back to the pyrolysis reactor. In their concept, HDPE was pyrolyzed thermally and catalytically (HZSM-5 catalyst) using process temperatures between 400 °C and 500 °C. With the proposed system, it was possible to steer the reaction towards lighter hydrocarbon products.

5.2. Patent literature on integrated chemical plastic waste recycling

Several patents have been published in the past decades on the use of plastic waste in steam crackers or in petrochemical processes. In fact, the use of plastic waste as a petrochemical feedstock is not new and has been pursued by industrial companies extensively during the 1990s, although severe operational issues made processes technically unfeasible and economically unattractive [300]. However, in light of new waste purification techniques, technical concepts developed in the past are noteworthy and interesting for the development of new integrated recycling plants. Interestingly, most inventions have in common that plastic waste streams are “pre-cracked” in order to produce a pumpable oil that is subsequently thermally cracked in a more conventional way aided by the addition of steam. Hence, the plastic feedstocks are typically not directly converted into olefins, however, due to the interconnection of the cracking units, costly storage and transportation of pyrolysis products prior to steam cracking can be avoided leading to a more efficient process.

The patent filed by Hover and Hammer, describes a process for the production of ethylene and propylene from solid plastic waste [301]. The authors claim in their invention to produce approximately 30 wt%

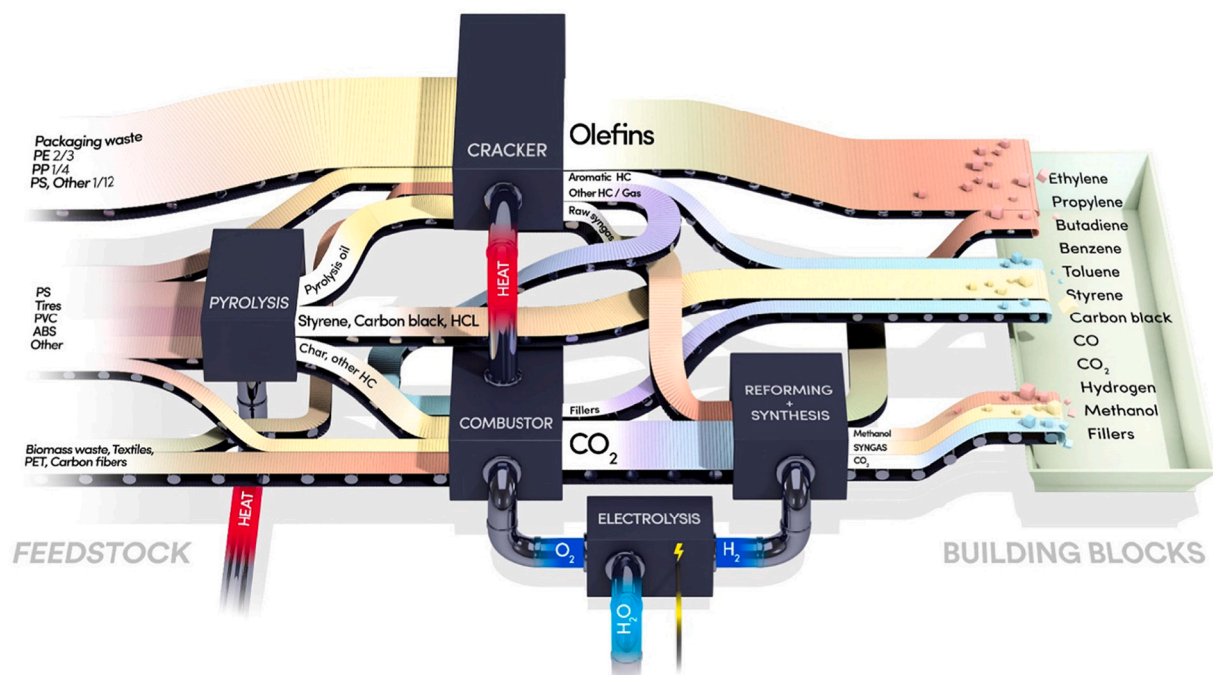


Fig. 12. Overview of a technical solution to integrate plastic waste recycling into a petrochemical cluster. Re-used with permission [290].

of ethylene from solid plastic waste by first heating the waste to 400–500 °C, adjusting its viscosity and consequently cracking the liquid feedstock at 700–1100 °C. The residence time in the pre-treatment stage may be 2–1500 min. The residence time of the second step is reported to be 0.02–10 s. Steam will be introduced already in the pre-treatment stage. Chlorine might be eliminated entirely in form of HCl. The process might be facilitated using inert gas streams such as nitrogen or steam. Addition of basic materials might further facilitate HCl removal.

The invention of Stabel et al. specifically addresses industrial-scale use of plastic waste as steam cracking feedstocks without the addition of a fossil feedstock [302]. For this, the authors propose a two-step process, first producing a pyrolysis oil at 400–550 °C from the plastic waste which is melted at 280–380 °C in a pre-heating step. The produced plastic pyrolysis oil is directly fractionated in a continuous distillation step and the boiling point fraction <280 °C will be subsequently fed to a steam cracker. The remaining distilled fractions (boiling point >280 °C) will be recycled to the first reactor except residues and inorganic compounds. Chlorine containing compounds will be removed in the first pyrolysis step. The authors report that product yields can be obtained that are equal or higher compared to conventional steam cracking feedstocks such as naphtha. The invention of Stabel et al. is therefore a direct improvement of the invention by Hover and Hammer since it includes a distillation step prior to steam cracking, thus reducing process-related issues caused by heavy boilers and residues.

The patent filed by Hardman et al. describes the cracking of polyolefin waste in a fluidized bed reactor for the production of light hydrocarbons [303]. According to the authors, it is crucial that the final boiling point of the primary plastic pyrolysis oil matches the top specification of an industrial feedstock such as naphtha (~300 °C). The invention, therefore, aims at the production of a feedstock free of a high molecular weight tail. The fluidized bed consists of a solid particulate material such as quartz sand or silica and is operated at temperatures between 450 °C and 550 °C. Primary products might be integrated into typical petrochemical process units such as steam crackers, catalytic crackers, cokers, etc.

In a similar patent filed by Kirkwood et al. (see Fig. 13), the plastic waste feedstock is mixed with a fossil feedstock such as naphtha or gas oil prior to pyrolysis in the fluidized bed reactor [304]. There are several further patents addressing the thermal and catalytic conversion of plastic waste to valuable chemicals combining a pre-pyrolysis with a thermal or catalytic cracking step. The interested reader is referred to, for instance, the patent of Hashimoto et al., who invented a process for producing light-weight oil from waste plastics containing phthalic polyester and/or PVC [305].

5.3. Recent commercial developments in integrated chemical plastic waste recycling

Next to the mentioned inventions, several different thermochemical recycling technologies have already been commercially implemented as recently summarized [26,306]. Furthermore, an overview of commercial pyrolysis processes that have been in operation in the past can be found in the book section “Overview of Commercial Pyrolysis Processes for Waste Plastics” by Scheirs [229]. Recently, integrated thermochemical recycling technologies have been installed in pilot-scale such as the thermal anaerobic conversion technology (TAC) patented by PlasticEnergy or the ReOil® technology by OMV. In the TAC process, which is already applied at larger scale in two demonstration plants in Spain, up to 20 tons of plastics per day are mechanically pre-treated to remove contaminants before they are thermally degraded in a stirred-tank-reactor at moderate temperatures (320–425 °C). Via a continuous vapor-phase catalytic upgrading step using catalysts designed by Haldor Topsoe, high-quality products in the naphtha- and diesel-range can be produced which are subsequently fed to a steam cracker [26,306,307]. PlasticEnergy claims that 90 to 95% of the plastic material are converted to naphtha- and diesel-range products [308]. Recently, PlasticEnergy has engaged in a collaboration with Sabic [309].

The ReOil® process developed by OMV is already in operation at pilot-scale in Austria and is currently scheduled to be operational with a capacity of up to 16,000 tons of plastic waste per year by 2023 [310]. The process (see Fig. 14) makes use of a solvent which is added after the extrusive feeding step.

As solvent, an intermediate, high-boiling product from a refinery process is used. The solvent reduces the viscosity of the plastic melt for the subsequent tubular pyrolysis reactor in which the low-viscosity polymer melt is thermally decomposed at around 400 °C. In the following flashing step, lighter pyrolysis products are separated from heavy boilers and subsequently separated into light and medium products which can be fed into the petrochemical infrastructure for the production of virgin plastics. Heavier products are recycled and cracked again [311–314]. Since there is no solvent-removal step involved, it can be assumed that the used solvent is an aromatic side-stream produced in the refinery process. It is known that BTX aromatics, which are a byproduct of steam cracking, are capable of dissolving polymers [315,316].

The Norwegian company Quantafuel has developed a process where the plastic waste is pyrolyzed and the pyrolysis oil is subsequently fed to a continuous upgrading train. In this train, ashes and other impurities such as chlorine are removed before the purified pyrolysis oil is

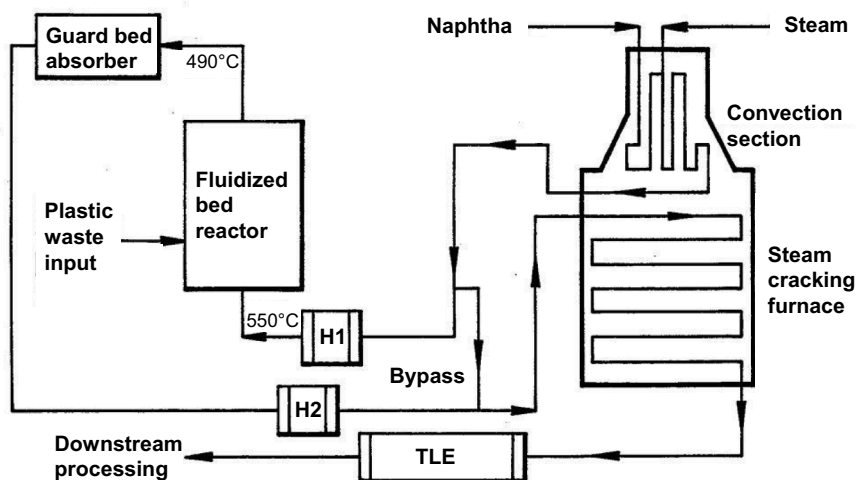


Fig. 13. Integrated process of pyrolysis and steam cracking. Re-drawn from [304]. H1, H2: heat exchangers; TLE: Transfer line exchanger.

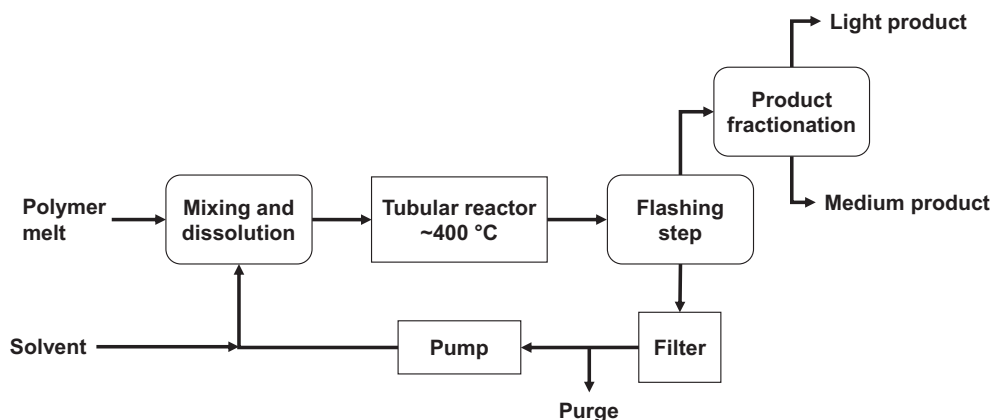


Fig. 14. Basic flowsheet of the OMW ReOil® process. Re-drawn from [311].

converted to a high-quality fuel using a two-stage catalytic process [317,318]. Quantafuel has entered a strategic partnership within BASF's ChemCycling project in 2019 [319]. The company Agilyx (USA) uses a screw reactor without a catalyst to produce around 50 tons per day of light synthetic crude oil that can be sold to refineries [26,306].

It can be concluded that the integrated direct valorization of plastic waste towards chemicals recently receives more and more attention with commercial projects being launched or already in operation. Of course, compared to the rather simple classical pyrolysis, integrated processes often involve auxiliary materials or innovative reactor concepts which are costly in development, construction and maintenance. However, this development indicates that there is a large interest from the petrochemical industry to circumvent the classical pyrolysis pathway by producing higher-quality pyrolysis products that can directly be utilized in existing petrochemical infrastructures with less or no required upgrading.

5.4. Plastic waste pyrolysis oils as drop-in feedstocks for industrial crackers

Different scales of operation will pose challenges to the proposed transition from fossil steam cracking feedstocks towards plastic waste pyrolysis oils. This is mainly because industrial steam crackers are located at strategic points such as harbors or close to petroleum refinery sites which guarantees a continuous supply of high-quality feedstock in high amounts. In contrast to this more centrally designed supply system, plastic waste is typically collected at curb side and is processed, sorted and washed in a more decentralized way close to municipalities spread throughout countries at a much smaller scale. Moreover, the enormous feedstock demand of a petrochemical plant (in the range of Mt./year) exceeds the amount of plastic waste that is available for thermochemical recycling via steam cracking (i.e., polyolefin-rich plastic packaging waste, in the range of 100,000 t/year) by orders or magnitude. Therefore, plastic waste pyrolysis oils will most likely not be available in sufficient amounts for entirely replacing the feedstock demand of industrial steam crackers. This becomes even more obvious when considering additional waste purification steps in advanced waste separation and sorting plants which produce purer streams, however, at lower quantities. On the other hand, allowing a higher degree of mixing and thus a higher degree of contamination in thermochemical recycling schemes would drastically increase the upgrading requirements before steam cracking. This leads to the most likely scenario of plastic waste pyrolysis oils being used as drop-in feedstocks complementing fossil feedstocks instead of entirely replacing them.

Plastic waste pyrolysis oils as drop-in feedstock have been investigated by few researchers. In our recent study we investigated the steam cracking feasibility of untreated plastic waste pyrolysis oils blended in a

1:3 mixture with fossil naphtha [294]. It was found that, although the pyrolysis oil/naphtha blends achieved slightly higher light olefin yields than an industrial light naphtha feedstock, coke formation and fouling tendencies were substantially higher. Therefore, it is still uncertain if industrial steam crackers can be fed with, for instance, 10% of plastic waste pyrolysis oil without disturbing running processes due to issues such as increased fouling, or extensive coking. Nevertheless, some theoretical indications can be drawn from the hydrocarbon composition (i.e., aromatics, olefins, etc.) as well as from the contaminant concentrations found in plastic waste pyrolysis oils. Regarding the hydrocarbon composition, 10% mixing with fossil naphtha already absorbs the strongest impacts from high aromatic or olefinic concentrations by simple mixing rules [32]. However, for more hazardous contaminants, which are unwanted even in trace amounts, simple mixing will not suffice to comply with the set specifications, highlighting the importance of efficient upgrading techniques. Another important aspect which will determine the success of the proposed thermochemical recycling route is the cost of the produced (and upgraded) pyrolysis oils. Hence, a trade-off needs to be found between costly additional upgrading steps and necessary mixing ratios to comply with the strict feedstock specifications.

Furthermore, simulation tools such as COILSIM1D will further be able to help evaluate the influence of plastic waste pyrolysis oils blended in fossil feedstocks on product yields and coke formation [320]. Moreover, important insights can be obtained by fundamental kinetic modeling. Due to its unique composition originating from synthetic materials rather than natural sources, heteroatom compounds are present in pyrolysis oils that are not present in feedstocks from fossil origin. The thermal decomposition behavior of these compounds under steam cracking conditions is, to this day, largely unknown. With new insights on the chemical impact of certain components specific for plastic waste pyrolysis oils, feedstock specifications for steam crackers might be updated in the future allowing for an easier implementation of these alternative feedstocks into industrial-scale petrochemical units.

5.5. Smart combinations of processes

It has been shown in this article that several technical solutions exist to produce a liquid hydrocarbon product from plastic waste that complies with the known feedstock specifications for petrochemical processes such as steam cracking. However, when considering a large-scale enterprise producing high-quality petrochemical feedstocks from mixed post-consumer plastic waste, it is clear that the greatest technical challenge lies in the co-existence of numerous contaminants [32]. On the contrary, the presented decontamination techniques are mostly directed at certain contaminant groups and are hence prone to disturbances by other contaminant groups (i.e., catalytic hydrotreatment). Thus, no

universal technique exists that can cope with all present contaminants at once and in a robust way. Consequently, a smart combination of techniques is required to meet both product specifications as well as economic requirements to establish a valuable process that is still capable of reducing the carbon footprint of the current plastic waste management systems. Clearly, compared to the current production pathways of base chemicals, i.e., refining of crude oil and steam cracking, every mean of thermochemical recycling of plastics, i.e., pyrolysis, purification of pyrolysis oils and steam cracking imposes additional economic burdens on the overall process. This is especially obvious when considering the different scales, which are huge in terms of crude oil refining and logistics, compared to waste management schemes which are often smaller and decentralized, mainly because of the more challenging logistics when transporting solid waste compared to liquid or gaseous fuels. Furthermore, the production of the “starting material” is more challenging for thermochemical recycling, as plastic waste streams

require thorough sorting which can be complicated due to fluctuating waste streams and compositions. According to the recent study by Larain et al. [30], the economic attractiveness of plastic pyrolysis largely depends on the scales, which should be at least 70 kt/year to be profitable. However, this implies a stable supply of plastic waste feedstocks. On the other hand, crude oil extraction is an established process, being performed at large scales in an efficient and standardized manner. Hence, there is an intrinsic difference in the economic frameworks of conventional petrochemical processes and chemical plastic waste recycling. Therefore, it is important that governmental policies and incentives are established that bridge the economic gap between the two processes by, for instance, implementing a carbon tax for the use of fossil-based resources such as naphtha, or subsidies for plastic products (or base chemicals) that were produced from waste. Obviously, the potential impact of a carbon tax on the economics of thermochemical recycling is closely related with emission savings compared to the

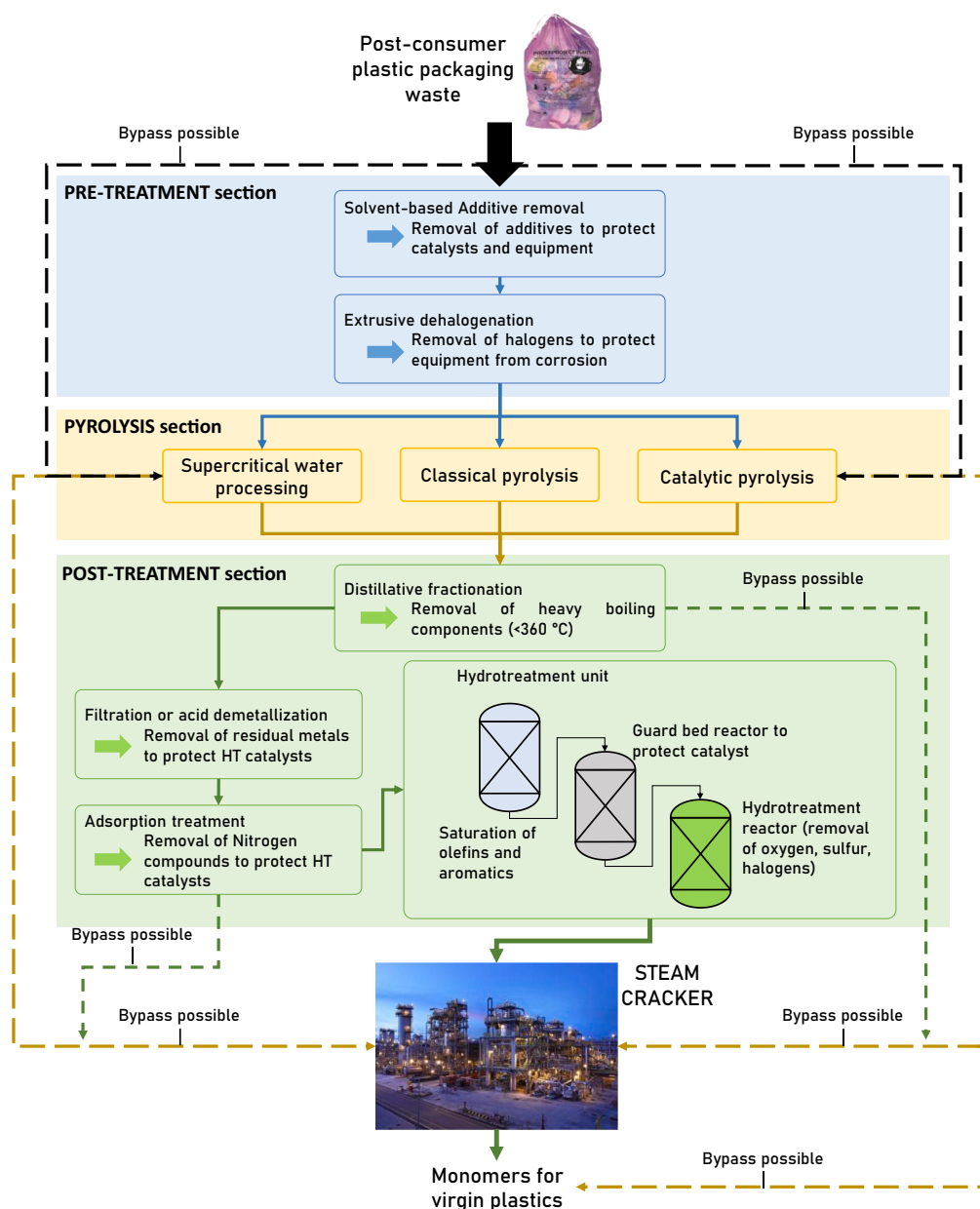


Fig. 15. Overview of potential pathways to produce industrial-grade steam cracker feedstocks from polyolefin-rich plastic waste. Side streams, i.e., filter retentate, distillation residues, etc., are not shown. When combined, potentially not all of the mentioned techniques are needed and bypasses are possible (marked with dashed lines).

conventional petrochemical pathway [321]. In the EU, since 2018 there are laws implemented to prevent waste generation and to boost recycling. According to this law, member countries are required to recycle at least 55% of the municipal waste by 2025 and at least 65% by 2035 [322]. Furthermore, a new, directive for packaging waste including circular packaging concepts to meet recycling targets will come into effect in 2022 [323]. Thus, it can be expected that in the near future, as more and more policies towards sustainable processes are implemented, the economic attractiveness of thermochemical recycling via the pathways reviewed in this article will substantially increase.

The following overview shows a theoretical scenario describing the pathway from mixed polyolefin-rich plastic packaging waste towards an industrial-grade steam cracker feedstock using techniques presented in this review article (see Fig. 15). In the first part of the figure, waste pre-treatment steps are shown in a blue section. The second part of the figure (marked in orange) shows the thermal decomposition steps (i.e., classical pyrolysis, SCW processing or catalytic pyrolysis). In the third part of the figure (marked in blue), applicable post-treatment steps to thoroughly upgrade pyrolysis oils are shown. The techniques can be used to remove important contaminants in subsequent steps using filtration or acid demetallization, followed by the adsorptive removal of nitrogen. Subsequently, the pyrolysis oils can be fed to a hydrotreatment unit to both saturate the hydrocarbon matrix and remove the remaining heteroatoms oxygen, sulfur and halogens. Note that side streams, such as heavy distilled fractions or filter retentates are not explicitly shown. It is worth noting, that it is possible that not all methods depicted in Fig. 15 are needed, depending on the respective contaminant removal efficiencies of the abovementioned steps. Furthermore, when comparing SCW processing or catalytic pyrolysis with classical pyrolysis, it becomes obvious that certain upgrading steps can be bypassed (marked with dashed arrows). For instance, it can be expected that in SCW, large amounts of metals and heteroatoms are removed via the SCW phase.

However, when using pyrolysis products as steam cracker feedstocks, further decontamination steps might still be needed in order to guarantee the steam cracking feasibility in terms of trace contaminants. Therefore, careful monitoring of product compositions throughout the entire process chain is indispensable. Furthermore, auxiliary materials and solvents need to be separated from the pyrolysis products adding an additional step which is not needed in classical pyrolysis (and not shown in Fig. 15). This has to be considered in economic evaluations to find an ideal trade-off between the required number of individual processing steps from waste to high-quality products and the additional cost of integrated systems and innovative reactor concepts. However, it was also shown that catalytic pyrolysis can be used to directly produce monomers from plastic waste which would even allow to bypass the steam cracker [144].

6. Emission reduction potential of advanced recycling

It was shown that, from a technical point-of-view, it is possible to close the gap between mixed plastic waste and the petrochemical production of polymers. However, given the increasing relevance of emission control, it is important to evaluate advanced recycling from an emission point-of-view. In the current linear economy, polymers are produced from base chemicals derived from steam cracking of fossil feedstocks. At the same time, the end-of-life of most plastics is incineration to recover energy, however, at low efficiencies and huge emissions. Even when mechanically recycled, the limited amount of life-cycles of mechanically recycled products eventually leads to incineration, and hence to emissions of CO₂. Obviously, linking the end-of-life management of plastics to the production of chemicals towards full circularity is necessary to reduce CO₂ emissions. In the following, we elaborate on emission savings when using advanced recycling, also including innovations in electrification of processes that, if using renewable energy, will reduce emissions even further.

In the recently published study by Eschenbacher et al., the authors

compared the emission saving potential of plastic waste pyrolysis processes with a conventional waste incineration and naphtha steam cracking case [144]. The carbon footprint of the benchmark cases was given as 3.1 kg CO₂ equivalent (kg_{CO₂-eq}) per kg of plastic waste in the case of conventional incineration, using PE as reference plastic waste stream and 1.1 kg_{CO₂-eq} per kg of high value chemicals (HVC: ethylene, propylene, hydrogen, benzene, butadiene) in conventional steam cracking. On the contrary, using plastic waste pyrolysis oil in conventional gas fired steam crackers led to a carbon footprint of 0.95 kg_{CO₂-eq}/kg_{HCV} which already is a substantial reduction of emissions considering both the lower footprint during petrochemical processing as well as the avoided incineration. Taking into account only the steam cracking process, similar carbon footprints can be achieved when using plastic waste-derived feedstocks compared to, for instance, fossil naphtha. The slight reduction (~14%) can be explained by the fact that plastic waste-derived feedstocks are considered a burden-free carbon source, while the production of fossil-based feedstocks accounts for ~30% of the total carbon footprint of conventional steam cracking [324]. Hence, although the production of pyrolysis oils is more energy intensive due to the required cracking of polymer chains compared to crude oil fractionation, from an environmental point-of-view, pyrolysis and subsequent steam cracking is still beneficial. This is also highlighted by BASF in their 2021 life cycle assessment report, where it is stated that via pyrolysis, 50% of CO₂ can be saved compared to incineration [325]. Consequently, in the case of conventional gas-fired steam cracking, the majority of the emission savings by using plastic waste pyrolysis oil stems from the avoided incineration.

In order to reduce the carbon footprint of steam cracking, electrification will play a key role to reduce up to 90% of the CO₂ emissions as reported by BASF [326]. It can be estimated that the global emission of steam cracking accounts for more than 300 million tons of CO₂ per year [327]. Furthermore, around 30% of the direct CO₂ emissions of the chemical industry stem from olefin production [328]. Around 90% of these emissions can be directly related to the heating of steam cracking furnaces which relies on combustion of a natural gas/hydrogen mixture [329]. It is hence clear that electrification of petrochemical processes will lead to huge emission savings compared to the current state-of-the-art, if renewable energy sources are used. Next to electrification of existing crackers, new disruptive technologies are being developed such as rotor dynamic reactors using a turbomechanical approach as proposed by Coolbrook [330]. It was calculated by Eschenbacher et al. that wind-derived electricity utilization results in the highest emission saving potential if used to heat the steam cracking process. In this case the carbon footprint of electrified steam cracking could be reduced drastically to 0.07 kg_{CO₂-eq}/kg_{HCV} [144]. Combining this saving with avoided incineration of plastic waste, huge potential emission reductions are possible, compared to the state-of-the-art. It has to be noted that carbon capture and utilization (CCU) techniques in combination with incineration would also be a possible solution to massively reduce the carbon footprint of the current waste disposal schemes. The same is valid when considering CCU for steam cracking of fossil feedstocks using conventional combustion-based heating [331]. Furthermore, a potential alternative to electrification of steam cracking furnaces would be the use of hydrogen firing in conventional steam cracking furnaces [327].

An overview of a potential (electrified) advanced recycling process is shown in Fig. 16. In the presented theoretical cases it was assumed that fossil-based feedstocks can be completely substituted with plastic waste pyrolysis oils without disturbing the processes. However, it was shown in this article that a substantial technical effort is needed to remove the vast amount of contaminants. Obviously, every step needed in the process chain from mixed waste towards industrial steam crackers increases the carbon footprint and hence lowers the emission saving potential. This is an important limitation that requires further research, investigating the carbon footprints of the respective required upgrading steps and potential electrification of the respective steps. Considering the large range of potential upgrading techniques it is difficult to estimate

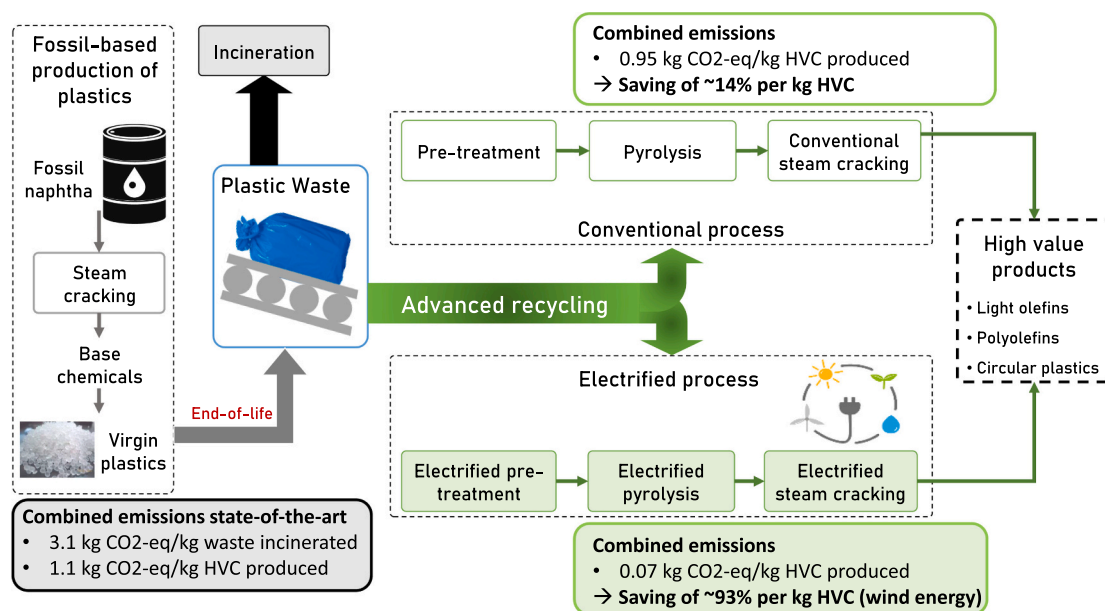


Fig. 16. Emission saving potential of advanced recycling (conventional and electrified) in comparison with the state of the art (fossil-based production of plastics and incineration of waste). Numbers taken from [144].

the carbon footprint contribution of individual steps, however, given that most upgrading techniques are already existing at larger scale in petrochemical plants (such as hydrotreatment), or require only mild conditions (such as adsorption), a limited additional CO₂ emission can be expected. In the case of hydrotreatment, the use of green hydrogen, produced via electrolysis using green electricity would be indeed carbon neutral. Together with electrified heating, a very low additional carbon footprint can be expected.

Evidently, smart integrations of processes as shown in Fig. 15 are beneficial since transport and storage of intermediate products can be avoided. This was also shown by Eschenbacher et al., who concluded that a one-step catalytic pyrolysis process from plastic waste to high value chemicals has a lower carbon footprint than the conventional two-step process comprising of pyrolysis and subsequent steam cracking [144]. The trend towards integrated processes in industry as elaborated earlier in this article underlines this conclusion. It has been reported that using supercritical water processing for plastic waste, compared to incineration, 1.5 tons of CO₂ emissions can be saved per ton of plastic waste processed. At the same time, emission savings of 20–50% compared to fossil naphtha steam cracking could be achieved [332]. Combining this with existing synergies in petrochemical plants will be a key aspect in the large-scale implementation of advanced recycling. Furthermore, the upgrading effort can always be balanced against blending with fossil feedstocks, however, at a higher environmental burden due to the increased dependency on fossil-based resources.

It is evident that all upgrading efforts could be reduced substantially, if the initial level of contaminants present in collected plastic waste could be reduced. Therefore, it is of paramount importance that progress is made in terms of waste collection and sorting and the removal of additives before the waste enters (advanced) recycling schemes. In this context, design-for-recycling becomes increasingly important, also for chemical recycling. However, to this day, initiatives to design plastic products that are easier to recycle are mostly targeted at mechanical recycling [16,19,333]. Such products could, for instance, use washable inks or avoid certain multilayers and the most problematic additives in order to reduce the complexity of waste fractions that is the current main hurdle for plastic waste recycling.

7. Conclusion and outlook

Thermochemical recycling of plastic packaging waste including pyrolysis and subsequent petrochemical processing (i.e., steam cracking) is a highly promising pathway towards a circular economy and to tackle global issues such as climate change and the ever growing pollution of ecosystems. However, to this day, several uncertainties such as contaminants and the high variety of plastics are hampering the use of plastic waste in (petro-)chemical process systems. Therefore, processes and techniques are needed to provide a stable supply of high-quality pyrolysis products for subsequent petrochemical processing steps.

Producing high-quality liquid hydrocarbon products from contaminated mixed plastic waste is not straight-forward and requires several dedicated treatment steps. These steps can be applied prior to, during or after pyrolysis or a combination thereof. It has been shown in this review article that techniques are available to reach feedstock specifications in terms of heteroatoms and metals. The most promising waste pre-treatment is a combination of waste dehalogenation combined with solvent-based additive removal. During pyrolysis, auxiliary materials can be used such as solvents, sorbents or catalysts, all leading to an improvement of the pyrolysis product quality in terms of contaminants. However, it was found that upgrading steps of the pyrolysis oils are unavoidable in order to reach the required purities for subsequent petrochemical processes such as steam cracking. First upgrading steps should be distillation and metal removal via membrane filtration to avoid contaminant-induced catalyst deactivation in later upgrading steps. Regarding heteroatom removal, catalytic hydrotreatment is the most established treatment method, however, it was reported that especially nitrogen compounds in the samples can severely decrease the removal effectivity for other heteroatoms. Therefore, adsorptive separation using activated carbon or metal organic frameworks is a promising alternative to remove nitrogen and metals prior to catalytic hydrotreatment. In an integrated process, using solvent-assisted pyrolysis or supercritical water, higher quality products can be obtained. Thus, certain treatment steps can be avoided, increasing the economic competitiveness of integrated processes. However, it is likely that, next to the increased engineering effort of integrated processes, additional solvent removal and purification steps are required before further processing.

In terms of emissions it was found that advanced recycling has the

potential to reduce up to 90% of the CO₂ emissions due to avoided incineration on the one hand and substitution of fossil-based feedstocks on the other hand. Combined with electrified processes using green energy (i.e., wind or solar), even higher emission savings can be achieved. Today those processes are at low technology readiness levels (TRL) so they need to be scaled-up supported by fundamental understanding. Furthermore, a key aspect in plastic waste recycling is the waste collection, separation and sorting. Improvement of the feedstock quality at the earliest stage will largely facilitate thermochemical recycling leading to higher quality feedstocks for pyrolysis as well as lower upgrading requirements prior to steam cracking. This way, competitive synthetic petrochemical feedstocks can be provided, which, in the long term, can (at least partly) replace fossil feedstocks leading us further towards a circular economy.

As outlined in this review article, decontamination of plastic waste-derived feedstocks for the petrochemical industry is fairly cumbersome. Therefore, any improvements by further technological developments in reducing the level of contaminants in the collected waste before it enters the pyrolysis process, either by improved sorting or better design of plastic products, have the potential to considerably facilitate and accelerate a wider adoption of chemical recycling. The most important aspects in terms of plastic pre-treatment are de-inking, additive removal and de-lamination of multilayer film fractions. Dehalogenation steps implemented as early as possible in the recycling process will also have a substantial impact on every (chemical) recycling pathway.

A highly relevant aspect that affects the entire discussion how and to what extent pyrolysis oils need to be decontaminated is the resistance of steam crackers towards contaminants. As the strict specifications are built on longstanding experience with fossil-based feedstocks, it is possible that certain requirements need to be re-evaluated. Next to the technical feasibility of processes and the technical specifications of produced waste-derived petrochemical feedstocks, another important challenge is the availability of sufficient amounts of sorted plastic waste, to meet the production scales necessary to be profitable. Furthermore, it is highly important that governmental policies are being implemented to incentivize thermochemical plastic waste recycling by subsidizing chemicals production such as ethylene and propylene derived from plastic waste. Moreover, the implementation of economic penalties such as a carbon tax on conventionally produced feedstocks will further improve the economic attractiveness of thermochemical recycling.

CRedit authorship contribution statement

Marvin Kusenberg: Conceptualization, Methodology, Investigation, Writing – original draft, Writing – review & editing. **Andreas Eschenbacher:** Conceptualization, Writing – review & editing. **Laurens Delva:** Writing – review & editing. **Steven De Meester:** Conceptualization, Writing – review & editing. **Evangelos Delikonstantis:** Data curation. **Georgios D. Stefanidis:** Conceptualization, Writing – review & editing. **Kim Ragaert:** Writing – review & editing. **Kevin M. Van Geem:** Conceptualization, Project administration, Funding acquisition, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare no conflict of interest.

Data availability

Data will be made available on request.

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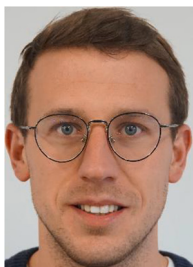
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Andreas Eschenbacher completed his master's degree at the Technical University of Munich and went on to earn a Ph.D. in Chemical Engineering from the Technical University of Denmark, working in the field of applied catalysis and biomass fast pyrolysis. Subsequently, he built up expertise as a post-doctoral researcher in the field of thermo-chemical recycling of polyolefins at the LCT at Ghent University before joining bp in the UK working as a research chemist.



Laurens Delva is a Research Scientist at Centexbel-VKC in Belgium. In 2015, he obtained his PhD in Polymer Engineering from Ghent University on a topic related to the processing and characterization of nanoclay filled polypropylene. Between 2015 and 2022, he was active as postdoc in the circular plastics research group of prof. Kim Ragaert at Ghent University focusing on the mechanical recycling of solid plastic waste. His areas of expertise include recycling of challenging waste streams, design for circularity, design from recycling, polymer degradation, and polymer characterization with a focus on the relationship between processing, structure and properties.



Steven De Meester is associate professor since 2016 at the Faculty of Bioscience Engineering of Ghent University. Prof. De Meester leads the Laboratory for Circular Process Engineering, which focuses on better chemical engineering in the circular economy. The group brings fundamental science to the processes used in waste management companies, as well as bringing in more innovative approaches, including topics such as sorting, separation and washing, delamination, deinking or dissolution of waste plastics. Furthermore, the team is active on purification of mixtures from depolymerisation or pyrolysis of plastics.



Evangelos Delikonstantis earned his Diploma in Chemical Engineering from Aristotle University, Greece, in 2012. In 2015, he completed the Professional Doctorate in Engineering from TU Delft, the Netherlands. For his thesis, he worked on the conceptual process design of novel plastic chemical recycling processes. Then, he worked as a consultant engineer. In 2016, he joined KU Leuven, Belgium as a Ph.D. candidate to deal with the development of plasma reactors for rich-in-methane gas streams valorisation. Since 2020, he has been working as a senior researcher on plasma reactor systems up-scaling and plasma-assisted processes evaluation at Ghent University, Belgium.



Georgios D. Stefanidis holds an MSc degree in Chemical Engineering from the National Technical University of Athens (Greece) and a PhD degree in the same field from the University of Gent (Belgium). He has co-authored over 100 peer-review papers in the broad field of Process Intensification, mostly focusing on alternative energy forms and transfer mechanisms (mainly microwaves and plasma), and the first book on the "Fundamentals of Process Intensification" (Wiley VCH, 2019). His research activity includes modeling of simultaneously occurring flow, chemistry and multiscale transport phenomena in electromagnetic and plasma fields as well as design and development of tailored equipment for microwave- and plasma-assisted reaction and separation processes including, among others, CO₂, CH₄ and waste valorization processes. He is currently one of the Editors of the *Chemical Engineering and Processing: Process Intensification Journal* (Elsevier), Chair of the EFCE Working Party on Process Intensification and serves on the management board of the Association of Microwave Power in Europe for Research and Education (AMPERE).



Kim Ragaert is full professor at Maastricht University, holding the Chair of Circular Plastics. She obtained her PhD in polymer processing at Ghent University in 2011 and began to develop her research in mechanical recycling of plastics soon after. Her lab and research group are on the Chemelot industrial site in Geleen, NL. The Circular Plastics team focuses on structure-property-processing relationships in thermoplastics and translates these fundamentals to methods for increased quality and quantity in recycling. Research topics include concepts of quality for recycling, the macromolecular interactions in complex mixes, the effects of contaminations and degradation, design for & from recycling and the balance between different recycling pathways. Interdisciplinary topics include systems thinking for plastics, cost calculation in recycling and how to connect technical quality to LCA. Kim is a strong believer in value-chain cooperation and interdisciplinary research. She was the 2020 European Plastics Recycling Ambassador.



Kevin M. Van Geem (full professor) is member of the Laboratory for Chemical Technology of Ghent University. Thermochemical reaction engineering in general and in particular the transition from fossil to renewable resources are his main research interests. He is a former Fulbright Research Scholar of MIT and directs the Pilot plant for steam cracking and pyrolysis. He is the author of more than two hundred scientific publications and has recently started his own spin-off company. He is involved in on-line and off-line analysis of complex petrochemical and biochemical samples using comprehensive two-dimensional gas chromatography. Pyrolysis, detailed kinetic modeling, process, scale-up, modeling, and anti-fouling technology belong to his main expertise. He is currently the coordinator of 3 different large-scale projects: ELECTRO (HORIZON Europe, Scientific coordinator 2022–2026), OPTIMA (ERC consolidator, Scientific coordinator, 2019–2024), C-Planet (H2020, Scientific coordinator 2019–2023).