AIChE Paper Number: 41a

Challenges and Opportunities for Plastic Waste Pyrolysis Oils As Steam Cracking Feedstock

Marvin Kusenberg
ir.
Ghent University, Ghent, Belgium

Andreas Eschenbacher
Dr. ir.
Ghent University, Ghent, Belgium

Marko R. Djokic
Dr. ir.
Ghent University, Ghent, Belgium

Azd Zayoud
Dr. ir.
Ghent University, Ghent, Belgium

Kim Ragaert
Prof. Dr. ir.
Ghent University, Ghent, Belgium

Steven De Meester
Prof. Dr. ir.
Ghent University, Ghent, Belgium

Kevin M. Van Geem
Prof. Dr. ir.
Ghent University, Ghent, Belgium

Prepared for presentation at the EPC Technology session: Ethylene Plant Feedstock Contaminants I, at the virtual 2021 Spring National Meeting,
April 18 – April 23, 2021

Challenges and Opportunities for Plastic Waste Pyrolysis Oils As Steam Cracking Feedstock

Marvin Kusenberg
ir.
Ghent University, Ghent, Belgium
Andreas Eschenbacher
Dr. ir.
Ghent University, Ghent, Belgium
Marko R. Djokic
Dr. ir.
Ghent University, Ghent, Belgium
Azd Zayoud
Dr. ir.
Ghent University, Ghent, Belgium
Kim Ragaert
Prof. Dr. ir.
Ghent University, Ghent, Belgium
Steven De Meester
Prof. Dr. ir.
Ghent University, Ghent, Belgium
Kevin M. Van Geem
Prof. Dr. ir.
Ghent University, Ghent, Belgium

Abstract:

Thermochemical recycling of plastic waste to base chemicals via pyrolysis followed by a minimal amount of upgrading and steam cracking is expected to be the dominant chemical recycling technology in the coming decade. However, there are substantial safety and operational risks when using plastic waste pyrolysis oils instead of conventional fossil-based feedstocks. This is due to the fact that plastic waste pyrolysis oils contain a vast amount of contaminants which are the main drivers for corrosion, fouling and downstream catalyst poisoning in industrial steam cracking plants. Contaminants are therefore crucial factors to evaluate the steam cracking feasibility of these alternative feedstocks.

Indeed, current plastic waste pyrolysis oils exceed typical feedstock specifications for numerous known contaminants, e.g. nitrogen (~10000 vs. 100 ppm max.), oxygen (~1000 vs. < 100 ppm max.), chlorine (~2300 vs. 3 ppm max.), iron (~33 vs. 0.001 ppm max.) and calcium (17 vs. 0.5 ppm max.). Pyrolysis oils produced from post-consumer plastic waste can only meet the current specifications set for industrial steam cracker feedstocks if they are upgraded, with hydrogen based technologies being the most effective, in combination with an effective pre-treatment of the plastic waste such as dehalogenation. Moreover, steam crackers are reliant on a stable and predictable feedstock quality and quantity representing a challenge with plastic

waste being largely influenced by consumer behavior, seasonal changes and local sorting efficiencies. Nevertheless, with standardization of sorting plants this is expected to become less problematic in the coming decade.

Introduction

The primary route to recycle the major part of polyolefinic (i.e. polyethylene (PE) and polypropylene (PP)) plastic packaging waste in the coming decade will be chemical recycling [1, 2]. In particular, pyrolysis towards liquid intermediates for producing olefins and aromatics in petrochemical process chains gains momentum with numerous demonstration projects in Europe [3-6]. In this concept, the material loop can be closed since new virgin plastics are produced from the base chemicals ethylene, propylene, 1,3-butadiene and benzene [7]. However, there are still challenges in place such as fluctuating waste compositions, feedstock contaminants and the need for expensive upgrading steps which lower the economic prospect.

The main pyrolysis product is a liquid containing a complex mixture of hydrocarbons with a wide carbon number distribution which may be utilized as petrochemical feedstock [8]. Contaminants present in the original plastic waste distribute over the entire product range and are known to diminish the liquid product quality making further treatment necessary to obtain a high-quality petrochemical feedstock such as fossil naphtha [9]. Steam cracking of plastic waste pyrolysis oils requires a liquid feedstock that is compatible with industrial steam cracking units in terms of physical properties (e.g. viscosity, boiling point), molecular composition (e.g. paraffinic, iso-paraffinic, olefinic, naphthenic and aromatic content: PIONA) and potential contaminant limits [10]. Furthermore, sufficient amounts of high quality feedstock are needed to match the scale of operation of industrial steam crackers. Typically, one naphtha cracking furnace requires feedstock in the order of 100000 tons per year [11]. Therefore, it is likely that plastic waste pyrolysis products will be either blended with fossil feedstocks rather than entirely replacing them [12] or they can be used on a single specific furnace.

Feedstock contaminants play a crucial role for the economics of a steam cracking furnace due to their accelerating effect on coke formation, fouling, corrosion and downstream catalyst poisoning leading to reduced run-length and/or off-spec products [10]. Contaminant levels found in plastic waste pyrolysis oils will therefore be the determining factor for a successful integration of a thermochemical recycling process into a petrochemical complex. The most important contaminants are heteroatomic compounds (nitrogen, sulfur, oxygen and halogens) as well as metals. High amounts of aromatics and olefins are also known to amplify coke formation and fouling [13, 14]. In scientific literature, little systematic information is available on contaminants in plastic waste pyrolysis oil and their potential consequences in the closed loop recycling chain towards steam cracking. In this work, contaminant levels in real post-consumer plastic waste derived feedstocks are compared to the maximum allowable concentrations in industrial steam cracker feedstocks, giving an indication of how challenging it is to use plastic waste pyrolysis oils in a steam cracker and what potential risks are. Thus, a guideline is provided for steam cracker operators when attempting to implement plastic waste pyrolysis oils into their existing petrochemical infrastructure. The presented study is a strong foundation for benchmarking plastic waste pyrolysis oils to conventional fossil feedstocks and for the decision towards potential upgrading technologies.

Hydrocarbon composition of post-consumer plastic waste pyrolysis oils

In the following section an overview is given on the composition of (polyolefinic) post-consumer plastic waste pyrolysis oils reported in open literature. Pure plastic waste streams which predominantly depolymerize into monomers such as polystyrene (PS) or poly(methyl methacrylate) (PMMA) are not included since the pyrolysis products of these polymers can be used for the production of new polymers without the need for steam cracking towards light olefins. Furthermore, a distinction has to be made between catalytic and thermal pyrolysis since the use of catalysts has a substantial influence on the composition of the pyrolysis products [15, 16]. However, contaminants present in post-consumer plastic waste may lead to prompt catalyst deactivation, hence, in the majority of studies involving catalytic decomposition, virgin or pre-treated plastic streams were used. Therefore, it is uncertain if contaminated mixed plastic waste can be tolerated by commercial pyrolysis catalysts. The focus of this review therefore lies on plastic waste pyrolysis oils obtained by thermal pyrolysis.

The composition of liquid plastic waste pyrolysis products largely depends on the type of polymer which was pyrolyzed and can, therefore, be anticipated to a certain extent. Regarding plastic packaging waste which mostly consists of PE and PP, the different branching tendencies of PE and PP are an important aspect. A high PP content shifts the liquid product composition towards higher (branched) olefin concentrations [17]. A high PE content leads to higher paraffin concentrations, while PS favors aromatic products [9, 18]. Other important polymers present in inefficiently sorted polyolefinic plastic waste include polyvinylchloride (PVC) and polyethylene terephthalate (PET). PVC decomposes in a two-step mechanism releasing HCl gas before the polymer backbone is decomposed [19, 20] (see Fig. 1). PET pyrolysis yields oxygenated compounds which may form organic acids.

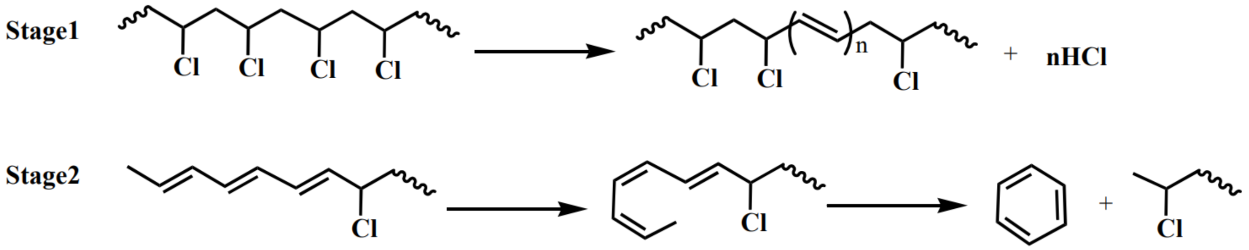

Fig. 1: Thermal decomposition mechanism of PVC [21].

Fig. 2 presents an overview of the respective hydrocarbon families in the pyrolysis products depending on the original plastic waste feedstock material. For the diagram, liquid product compositions for similar post-consumer plastic waste feedstock compositions reported in open literature were averaged [22-30].

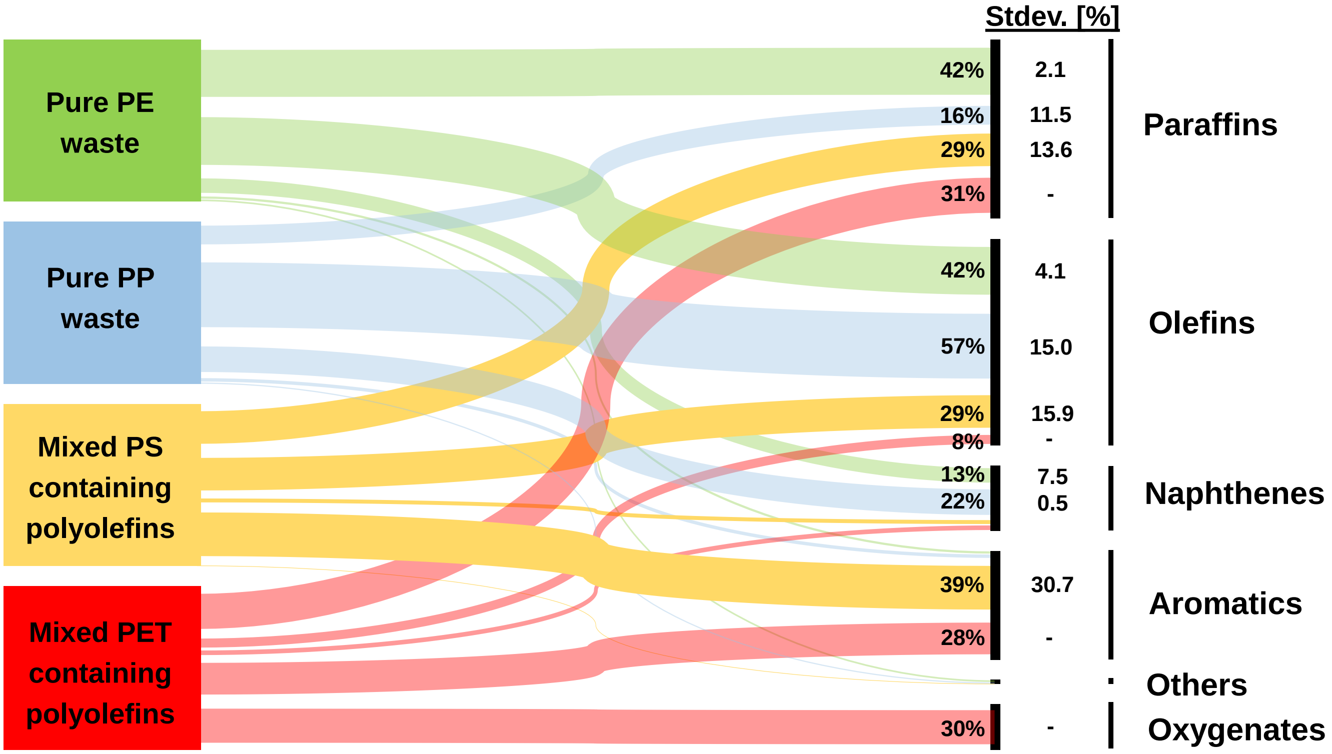

Fig. 2: Sankey chart depicting the influence of the feedstock material on the hydrocarbon composition. Feedstock data is based on averaged values from open literature [22-30] (numbers in wt.%).

Pure PE waste yields equal amounts of paraffins and olefins with only minor amounts of naphthenes and aromatics. Pure PP waste yields mostly olefins and smaller amounts of paraffins, naphthenes and aromatics. Moreover, it can be seen in Fig. 2 that inaccurately sorted waste plastics such as PS and PET may lead to high amounts of aromatics or oxygenates in the pyrolysis oil. However, considering the given standard deviations it becomes clear that there are large discrepancies between the respective reported concentrations. The fact that several authors did not report naphthenes in their products indicates that the paraffinic and olefinic concentrations might be overestimated due to lumping and misidentification. Thus, it is highlighted that standardized high-performance analytical techniques such as comprehensive two-dimensional gas chromatography (GC × GC) coupled to various detectors are needed. In light of trace amounts of highly harmful contaminants present in plastic waste pyrolysis oils this becomes even more obvious to use selective detectors for measuring oxygenates, sulfur and nitrogen such as those based on chemiluminescence [31, 32].

Next to the hydrocarbon composition of the "crude" plastic waste pyrolysis oils, it is interesting how the composition varies according to the boiling point range. Since steam crackers are designed for a certain feedstock boiling point range, it is crucial to assess the individual fractions of the pyrolysis oils in order to compare the composition with conventional feedstocks such as fossil naphtha. Data from the Niigata (Japan) plastic waste liquefaction plant reported by Okuwaki et al. [30] shows that the light fraction (C_5 – C_{12}) of the plastic waste pyrolysis products contained 17 % paraffins, 27 % olefins and 56 % aromatics. The medium fraction (C_8 – C_{20}) contained 41 % paraffins, 28 % olefins and 41 % aromatics. The processed original plastic waste material contained substantial amounts of PS (18 %) and PET (15 %). The values indicate that the formed aromatics predominantly end up in the lighter product fractions. This can be explained by the presence of PS in the waste since its pyrolysis yields mostly (C_8) mono-aromatics as confirmed elsewhere [29].

Steam cracking feasibility of pyrolysis oils in terms of PIONA

To compare the quality of plastic waste pyrolysis oils, fossil naphtha is the logical benchmark. The initial boiling point (IBP) of naphtha lies around 35 °C and the final boiling point (FBP) at around 200 °C. Naphtha can be distilled into a light fraction which has a carbon number range of C_4 to C_7 (FBP 145 °C) and a heavy fraction with a carbon number range of up to C_{12} (FBP 200 °C) [33, 34]. Since naphtha feedstocks are produced from crude oil, there are hundreds of variations depending on the origin of the crude oil source. Naphthas typically consist mostly of paraffins and naphthenes with lower amounts of aromatics and contain, in contrast to plastic waste pyrolysis oils, no olefins [35]. Gas oils are heavier and less favored steam cracker feedstocks due to higher amounts of sulfur compounds and aromatics. Steam cracking of these feedstocks leads to lower ethylene yields and more heavy products (C_{10+}) which reduce the run-length of a steam cracker due to their higher fouling potential. Heavy fossil feedstocks such as petroleum or shale oils can contain significant amounts of heteroatomic compounds which may substantially exceed the specifications set for petrochemical feedstocks [32]. To mitigate the fouling potential, these feedstocks can be upgraded using hydrotreatment to reduce the aromatic and heteroatomic content prior to cracking [36].

In general, olefins inhibit the cracking of paraffins while paraffins accelerate cracking of olefins. This effect was observed already decades ago for paraffin cracking in the presence of propylene and with higher olefins [37]. Furthermore, olefins are subject to polymerization reactions (i.e. "chemical reaction fouling") [38]. Due to the fact that the walls of the heat transfer surfaces are typically at higher temperatures than the bulk flow, chemical reactions might be catalyzed by the wall material yielding insoluble deposits at the inner walls [39, 40]. Consequently, deposits cause a decrease of heat transfer through the externally fired reactor tubes inside the steam cracking furnace. Ultimately, blockages of the tubes might occur [39, 41]. An important fouling reaction is the oxidation of unsaturated hydrocarbons. Olefins are more prone to oxidation reactions than paraffins due to their lower stability [42]. At more severe conditions as found in steam crackers, autoxidation is the major mechanism causing fouling [41, 43]. It has been further reported that high olefin concentrations in liquid feedstocks result in increased radiant coke formation and transfer line exchanger fouling due to secondary reactions [44]. This effect becomes dominant at an olefin concentration of >5 % as found by Kopinke et al. [13, 14] decades ago. According to industrial plant operators, the maximum allowable olefin concentration in naphtha range feedstocks is 2 wt.% [45]. Typically, naphthenes pose a higher coking tendency (by ~50 %) than paraffins due to dehydrogenation reaction towards aromatic products. This has been known for decades [13, 37] and is especially valid for olefinic naphthenes such as cyclopentadiene which are prominent coke precursors [46]. However, it is generally known that the coking potential of a feedstock is essentially dependent on its aromatic content [13, 14, 47]. Aromatics have a higher coking tendency than paraffins due to combination reactions with other aromatics forming heavier species which may condense to highly stable polyaromatic hydrocarbons (PAHs) [48, 49]. PAHs may result in coke deposition in the reactor and the transfer line which ultimately leads to severe blockages [50, 51].

Table 1 lists the concentrations of hydrocarbon families found in plastic waste pyrolysis oil distributed over the light (FBP ~200 °C), medium (FBP ~370 °C) and heavy product fractions (>370 °C). The values are averaged PIONA values from open literature [22-30], thus providing a rough estimate of the average compositions to be expected from mixed plastic waste pyrolysis oils. Potential uncertainties lie, of course, in the accuracy of the literature data regarding lumping of compound groups or unrepresentative plastic waste samples. Hydrocarbon compositions which could not be clearly allocated to a certain carbon number range are not included.

Table 1: Distribution of paraffins, olefins, naphthenes and aromatics over the light, medium and product fractions of post-consumer plastic waste pyrolysis oils (averaged values taken from [22-30]).

	Light (C_5-C_{12}) [wt.%]	**Medium (C_{12}-C_{22}) [wt.%]**	**Heavy (C_{23+}) [wt.%]**
Paraffins	17	33	44
Olefins	19	36	46
Naphthenes	0	10	8
Aromatics	65	18	1
Others	0	4	2

Table 1 shows that the lighter fractions are most likely off-spec in terms of their steam cracking feasibility due to the high aromatic concentration. In this case, the aromatic fraction must be separated prior to steam cracking using, for instance, extractive-azeotropic distillation [52]. It is also recommended to remove PS prior to pyrolysis to recover styrene in a separate process instead of removing the aromatics from the pyrolysis oil prior to steam cracking. The olefin concentrations listed in Table 1 exceed the olefin threshold value of 2 wt.% substantially [45] which indicates a high coking and fouling potential when steam cracking these untreated products. Tuning the olefin concentration to reach industrial limits may be performed by hydrotreatment. Another option to reach the proposed olefin limits would be co-feeding with fossil feedstocks thus tuning down the olefin concentration according to the mixing ratio to an acceptable value. For the light product fractions this would mean a blending ratio of ~10 wt.% with olefin-free fossil naphtha. The medium fraction would require a blending ratio of ~5 wt.% in order to reach the specifications.

Steam cracking feasibility of pyrolysis oils in terms of heteroatoms

Heteroatoms in feedstocks can have a severe impact on the steam cracker in terms of fouling potential, coke formation, corrosion and downstream catalyst poisoning. Therefore, strict specifications exist which will be the basis for a feasibility assessment of plastic waste pyrolysis oils as steam cracking feedstocks (see Table 2).

Table 2: Overview of typical heteroatom specifications for fossil-based steam cracker feedstocks.

Contaminant	Industrial limit	Reference
Nitrogen	Naphtha: 100 ppm Gas oils: 2000 ppm	[45]
Sulfur	500 ppm	[45]
Oxygen	100 ppm	[45]
Chlorine	3 ppm	[10, 45, 53]

An overview of the heteroatom concentrations found in the respective light, medium and heavy fractions of plastic waste pyrolysis compared to the corresponding contaminant limits for industrial steam crackers is given in Fig. 3. The heteroatom values are averaged data from [23, 26, 29, 30, 54-59] which are subject to large fluctuations. Therefore, the data should be considered qualitative rather than quantitative. Nevertheless, the data gives an indication of the challenges for plastic waste pyrolysis oils in terms of heteroatoms.

The average nitrogen values found in the light and medium fractions are substantially higher than the allowable nitrogen concentrations in liquid feedstocks for industrial crackers (100 ppm). The average N concentration in the heavy fraction of plastic waste pyrolysis oils lies below the industrial threshold for gas oils of 2000 ppm [45]. However, the data presented by Toraman et al. [29] who detected a nitrogen concentration of 1 wt.% using GC × GC-NCD indicates that the nitrogen concentrations in pyrolysis oils are frequently underestimated by research groups. Nitrogen compounds are responsible for catalyst deactivation in hydrodesulfurization units, hydrocrackers and reforming processes [60]. Furthermore they may cause explosive gum formation in the cold-box sections of a steam cracker plant, which has been known for decades [61, 62]. Thermal decomposition of nitrogen compounds leads to the formation of NO_x species which cause air pollution and acid rain [63]. Amines and other nitrogen containing compounds have a negative impact on the process since they decompose to ammonia and nitriles which are harmful for downstream catalysts causing the steam cracking products to be off-spec [47]. Furthermore, nitrogen gas may contaminate the hydrogen product [45]. Therefore, efficient and accurate nitrogen monitoring techniques for plastic pyrolysis oil are highly important with those based on chemiluminescence being the most effective [31]. An example for a removal technique for nitrogen compounds is hydrodenitrogenation [64]. Considering dilution of plastic waste pyrolysis products with fossil naphtha in order to tune the nitrogen level down to an acceptable concentration, a minimum dilution factor of >30 is required which is likely an underestimation considering the higher measured values reported by Toraman et al. [29].

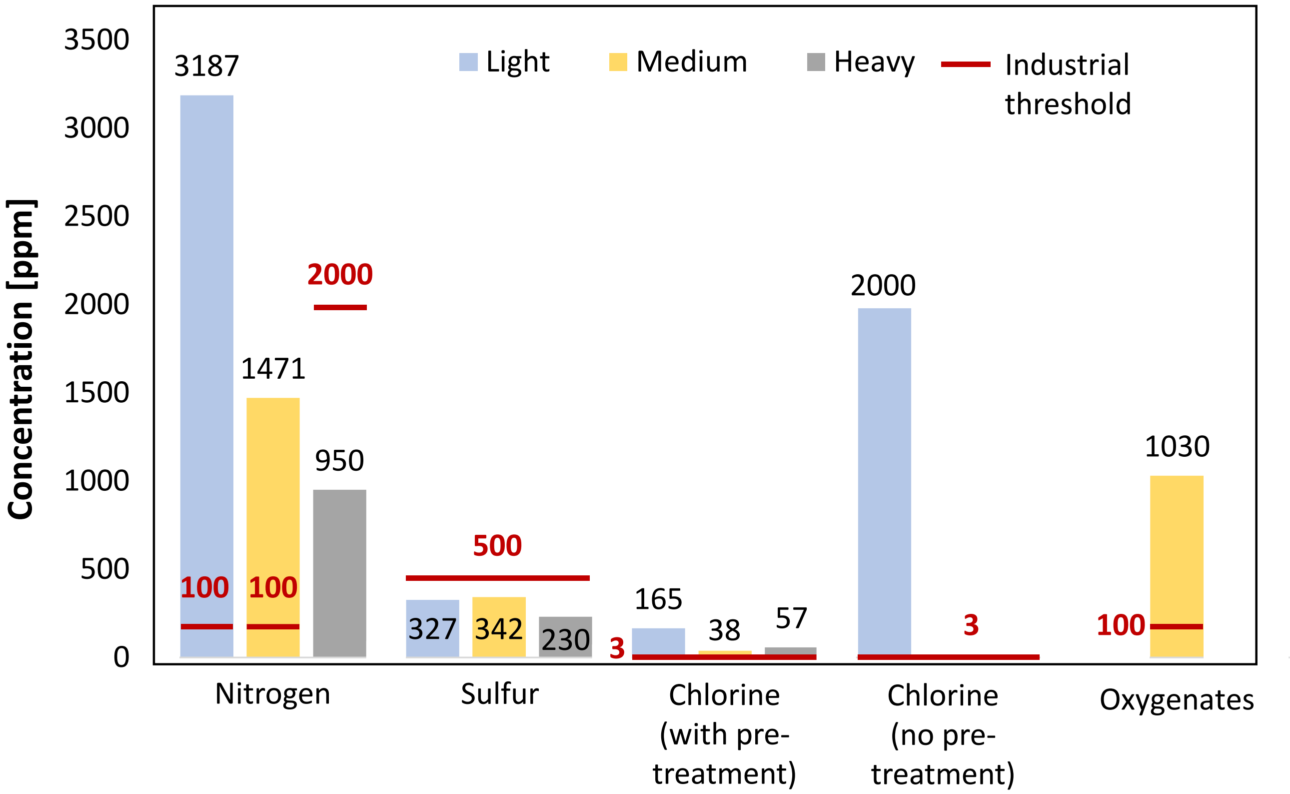

Fig. 3: Overview of the averaged heteroatom content in the light, medium and heavy fractions of plastic waste pyrolysis oils compared with the threshold value for industrial steam crackers. Values taken from [23, 26, 29, 30, 54-59].

The detected sulfur concentrations in the respective light, medium and heavy fractions of plastic waste pyrolysis oil do not exceed the maximum allowable sulfur concentration of 500 ppm [45]. However, due to the fluctuations in the composition of plastic waste, the sulfur contents of the pyrolysis products need to be monitored carefully and sulfur removal processes such as hydrodesulfurization or selective oxidation might need to be applied prior to petrochemical processing [65]. Furthermore, due to inaccurate measurements it is possible that the actual sulfur concentrations present in plastic waste pyrolysis oils are indeed higher. This has been shown by Toraman et al. [29] who measured more than 1000 ppm of sulfur using GC × GC-SCD. Considering a value of 1000 ppm, a dilution with fossil naphtha with a dilution factor of 2 would be required to reach industrial feedstock specifications. The influence of sulfur in steam cracking may be beneficial or harmful depending on the sulfur concentration in the feedstock. On the one hand, sulfur has a beneficial effect in terms of controlling CO and CO_2 formation. The effect is based on the coverage of active nickel sites on the metal surface leading to a reduction of steam reforming reactions [66-68]. However, the role of sulfur in terms of coke formation is controversial [69, 70]. On the other hand, sulfur containing compounds may lead to the formation of hazardous substances, pose threats to the reactor material and have detrimental effects on the final product [71, 72]. Thermal decomposition of sulfur compounds leads to the formation of hydrogen sulfide, carbon disulfide and SO_x which pose a threat to the environment and are therefore subject to strict regulations [73]. Moreover, the Ni-Cr-Fe alloys often used for the steam cracking coil may suffer from corrosive attacks by hydrogen sulfide [66]. Therefore, it is crucial to control and monitor the elemental sulfur content of liquid hydrocarbon feedstocks.

The chlorine content in the pyrolysis oil is directly related to the PVC removal efficiency of the waste sorting plant but also to potential dehalogenation steps during the thermochemical recycling process. Industrial-scale processes typically employ measures to reduce the negative impact of plastic waste impurities such as PVC. This becomes evident when comparing Cl concentrations in liquid products from pyrolysis processes with and without implementation of dehalogenation steps. For instance, industrially produced PVC/PVCD containing plastic waste pyrolysis oil had a reported Cl content of 47 ppm in a carbon number range of $C_8 – C_{20}$ as reported by Okuwaki et al. [30]. Pyrolysis oils of a similar carbon number range from plastic waste with a similar PVC/PVDC content processed without dehalogenation step prior to pyrolysis had a reported Cl concentration of 2000 ppm [59]. The industrial Cl threshold value of 3 ppm [45, 53] is exceeded substantially both by plastic waste pyrolysis oils including dechlorination pre-treatment (165 ppm by average in the light fraction) as well as without pre-treatment (2000 ppm in the light fraction). Therefore, upgrading steps of the pyrolysis products or improved dechlorination steps prior to pyrolysis are of paramount importance. A potential process to remove chlorine from pyrolysis products prior to further petrochemical processing is catalytic hydrotreatment [74]. Organic and inorganic chlorides cause corrosion of equipment such as metal surfaces, heat exchangers and downstream facilities [53, 75]. Inorganic chlorides such as sodium chloride may originate from entrained salt water and in the case of plastic waste from the adsorption of salt which was in the packaged product. Sodium chloride is especially known for corrosion of austenic steel above temperatures of 500 °C [45]. Organic chlorides such as chloroform ($CHCl_3$) and dichloromethane (CH_2Cl_2) are more difficult to detect and separate compared to inorganics due to their higher solubility in liquid hydrocarbons [53, 76]. The main thermal decomposition product of organic chlorides is hydrogen chloride which may lead to severe corrosion in downstream facilities. Moreover, hydrogen chloride can form ammonium chloride with nitrogen which can cause blockages [77]. Finally, chloride contamination in products can lead to environmental concerns [76]. The extremely low threshold for chlorine indicates that essentially no PVC or salts are allowed in the plastic waste fractions. Therefore, both efficient PVC separation and washing techniques must be applied in modern waste sorting plants and dehalogenation techniques need to be integrated in plastic waste pyrolysis units. Furthermore, standardized high-quality analytical techniques such as GC × GC-AED are needed in order to establish pyrolysis oils from a chlorine point-of-view.

The oxygen concentration found in (PET-containing) plastic waste pyrolysis oils exceeds the threshold value for industrial steam crackers (100 ppm [45]) by at least ten times. Considering the inevitable PET content in polyolefinic plastic waste streams, the corresponding pyrolysis oil is most likely not acceptable for industrial crackers regarding the oxygen content. When considering to tune the oxygen levels by diluting the plastic waste pyrolysis products with fossil naphtha, a minimum dilution factor of 10 would be necessary. Oxygenates can diminish the value of steam cracking feedstocks due to the potential formation of methanol, formaldehyde and CO next to the formation of corrosive acids [78]. Furthermore, organic acids formed in quench water systems or elemental oxygen which reacts with butadiene species to promote gum formation are strong drivers for process fouling and corrosion issues [79, 80]. Oxygen and its decomposition products (especially CO) can also be a poison to a number of catalysts downstream of the steam cracker. Furthermore, off-spec propylene can occur due to contamination with formed methanol. In ethylene and propylene product specifications, the elemental oxygen content is typically limited to 5 ppm [78]. Therefore, removal of oxygen through catalytic processes such as hydrodeoxygenation is necessary [81]. Other oxygen removal technologies are presented elsewhere [82].

Steam cracking feasibility of pyrolysis oils in terms of metals

Metal contamination in steam cracking feedstocks may cause issues such as accumulation and blockages in process equipment, corrosion of metal surfaces as well as irreversible poisoning of pre-treatment or downstream catalysts. Furthermore, coke formation and fouling can be increased due to catalytic effects. An overview of contaminant levels found in plastic waste pyrolysis oil as well as the corresponding contaminant limits for industrial steam crackers are shown in Table 3 which is based on values reported in open literature [10, 30, 47, 55, 83]. The listed metal concentrations are the ones found in the liquid fractions of the pyrolysis oils. Metals only found in distillation or pyrolysis residues are not listed. It has to be noted that for some metals which are typically not present in fossil-based feedstocks such as aluminum, chromium or titanium no specifications exist. Since these metals may occur in plastic waste pyrolysis oil stemming from numerous additives and auxiliary materials used in plastic products, there is a knowledge gap still to be filled. Importantly, it is implied that the absence of a maximum specification does not mean that the contaminant is harmless. It indeed indicates that further research is needed targeted at metal contaminants predominantly occurring in plastic waste pyrolysis oils. Furthermore, it is more likely that certain metals remained undetected rather than that they are indeed absent. This is especially valid for metals such as arsenic, nickel and vanadium which are harmful already in ppb levels. Due to the extremely difficult detection of trace metals, it is therefore likely, that the actually occurring metal contamination is substantially higher than reported. Again, the need for highly accurate analytical techniques such as ICP-MS is highlighted.

Table 3: Comparison of metal contamination levels in plastic pyrolysis oil reported in open literature and known contaminant limits for industrial crackers.

Contaminant	Light (C_5-C_{12}) [ppm]	Medium (C_{12}-C_{22}) [ppm]	Heavy (C_{30+}) [ppm]	Industrial limit [ppm]	Reference
Al	<0.2	<LOD	17	n.a.	[30]
As	-	-	-	0.005	[10]
Ca	17	2	368	0.5	[10, 30, 55]
Cr	<0.2	<LOD	8.2	-	[30]
Cu	0.6	0.1	2.3	50	[30, 83]
Fe	<0.2	7.3	33	0.001	[10, 30, 45]
Hg	-	-	-	0.005	[10]
Na	0.8	<LOD	2.8	0.125	[10, 30]
Ni	-	-	-	100	[47]
Pb	<LOD	<LOD	37	0.05 – 0.10	[10, 30, 45]
Si	<100	4	<50	0.5 – 1	[30, 45]
Ti	<LOD	<LOD	456	-	[55]
V	-	-	-	0.05	[10, 45]
Zn	0.6	<LOD	254	-	[30, 55]

Fig. 4 compares the metal contaminants in the light and medium product fractions which are most interesting for steam cracking with the known feedstock specifications for industrial steam crackers. Metals for which no maximum allowable concentration is known are not included.

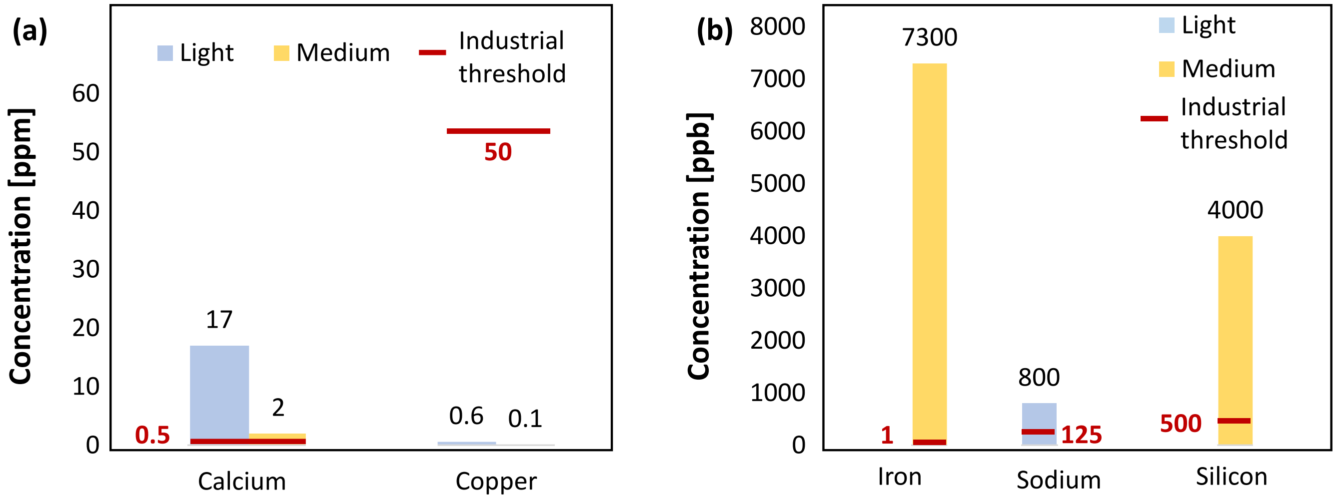

Fig. 4: Concentrations of (a) Ca and Cu (in ppm) and (b) Fe, Na and Si (in ppb) in light and medium fractions of plastic waste pyrolysis oil vs. the threshold for industrial steam crackers.

Calcium will be increasingly relevant in terms of plastic waste pyrolysis, since $CaCO_3$ is a popular performance-enhancing additive [84]. Another possible source for Ca is the addition of Ca salts during the pyrolysis process in order to bind organic acids forming when PET is thermally decomposed [30]. Calcium has been found to cause fouling and corrosion leading to a reported concentration limit in liquid steam cracker feedstocks of 0.5 ppm [10]. As can be seen in Fig. 4 the Ca concentration in the light and medium fraction of plastic waste exceeds the maximum allowable concentration substantially. In order to reach an acceptable concentration, the light fraction of plastic waste pyrolysis oil needs to be diluted with naphtha by a factor of ~34. Considering the strong possibility that the reported Ca concentration is underestimated, steam cracking of these feedstocks is not feasible regarding the Ca concentration. Potential Ca removal techniques include liquid phase extraction using aqueous solution and a calcium removal agent [85].

Iron is a crucial feedstock contaminant. The catalytic effect of iron attached to the reactor wall surface may induce rapid coke formation causing a reduction of the furnace run-length. It has been reported that the run-length of an industrial liquid feedstock cracker was halved within days when exposed to iron contamination [86]. Iron further causes corrosion and (pre-treatment) catalyst poisoning issues. Especially iron oxide has been listed as a high concern contaminant due to plugging issues [45]. The maximum tolerable concentration in steam cracking feedstocks has been reported as <1 ppb, underlining the importance of highly accurate measurements [10]. It can be seen from Fig. 4 that while no iron was reported in the light fraction of the pyrolysis oil, the concentration in the medium fractions exceeds the industrial threshold by orders of magnitude. To comply with the industrial threshold value the most accurate metal detection technique ICP-MS is needed. This can be seen by means of the detection limits of other techniques which are already substantially higher than 1 ppb. Based on these values it is possible that the actual iron concentration in plastic waste pyrolysis oils is always higher than the threshold value. Considering the large iron concentration in the medium fraction, blending of the pyrolysis oils with iron-free naphtha will not be feasible due to the extremely high dilution factor necessary to reach the given specification. Instead, metal removal techniques are needed such as hydrodemetallization, solvent extraction [87] or membrane filtration [88].

Sodium contamination may occur in liquid feeds of fossil origin following desalting of crudes or from certain storage modes for instance in salt caverns. In plastic waste it occurs due to absorption of salts present in the packaged goods. In steam cracking, Na may cause severe corrosion issues which is called sodium attack [86]. Na reacts with Cr in the steam cracking coil forming compounds such as sodium chromite (NaCrO2) which has a melting point of 762 °C. By this mechanism, the chromium layer of the coil will gradually be depleted, permanently damaging the radiant coil [10]. Sodium is a strong catalyst poison [47]. This can pose severe problems to potential pre-treatment catalysts. Furthermore, Na is a strong coke promoter [89]. Due to the listed issues, Na is among the top five problematic contaminants for liquid crackers with a maximum tolerable concentration of 1 ppm. Even lower maximum concentrations of 125 ppb have been reported by other authors [10]. A Na concentration of 800 ppb was reported in the light fraction of plastic waste pyrolysis oil. This implies that a minimum dilution factor with fossil naphtha of ~8 can be sufficient to reach the specifications. However, due to the very low threshold, data must be treated with care and additional analyses are advised.

Lead containing compounds in steam cracker feedstocks are not desirable due to their thermally induced decomposition into elemental Pb which deposits irreversibly on surfaces of potential pre-treatment catalysts [90, 91]. Additionally, Pb induced corrosion problems have been reported [10]. Several operators of liquid feedstock crackers named values below 100 ppb as maximum tolerable Pb level in the feedstock [45]. Other authors reported values <50 ppb [10]. No Pb was reported in the light and medium fractions of the plastic waste pyrolysis oils. However, Okuwaki et al. [30] reported a Pb concentration of 37 ppm in the heavy fraction and concentrations below the limit of detection in the medium and light fraction of the plastic waste pyrolysis oil. However, due to the fact that the maximum Pb level in industrial steam cracker feedstocks is in the low ppb range, it can be assumed that traces of Pb in the lighter fractions were not detected due to limited detector capacities but were still higher than the threshold.

Silicon is another relevant contaminant in terms of plastic waste due its use in additives and coatings for plastic products [84]. Silicon has been known to poison catalysts irreversibly [92]. Furthermore, silicon dioxide is known to cause fouling [78]. The maximum tolerable concentration in liquid feedstocks has been reported to be between 0.5 and 1 ppm [10, 45]. Okuwaki et al. [30] reported a Si concentration of 4 ppm in the medium fraction. Furthermore, the reported value for the light fraction is <100 ppm which indicates that the accuracy of the used analytical method is insufficient and that the analytical procedure might have led to operational errors. However, based on the found concentration, dilution with fossil naphtha with a dilution factor of 4-8 would be sufficient.

Next to the metals found in plastic waste pyrolysis oils, other metals are known to have severe impacts on steam crackers. These are arsenic, mercury, nickel and vanadium. Given the extremely low threshold values for these metals (see Table 3) detection techniques such as ICP-MS are needed to fully clarify the steam cracking feasibility of plastic waste pyrolysis oils. Furthermore, for aluminum, chromium, titanium and zinc, no threshold exist which underlines the need for further investigation of the impact of these metals during steam cracking.

Implications for plastic waste pyrolysis oils as steam cracker feedstocks

The discussion in the previous sections shows that (untreated) plastic waste pyrolysis oils are indeed not suitable to be steam cracked due to several contaminants. However, it needs to be noted that the largest steam crackers require roughly 100000 tons per year of feedstock per furnace with multiple furnaces in parallel operation. On the contrary, the largest waste sorting plants in Europe process 100000 tons of collected waste per year of which only a fraction will be available for thermochemical recycling [93]. Therefore, using plastic waste pyrolysis oils as a drop-in feedstock in the range of 5-20 % is the most likely scenario. Table 4 depicts an overview of the feasibility of plastic waste concerning the respective contaminant groups including the most accurate analytical characterization techniques. Furthermore, it includes the minimum dilution factors needed in a blend with contaminant-free fossil naphtha in order to reach industrial specifications.

Table 4: Feasibility matrix of plastic waste pyrolysis oils as steam cracking feedstocks.

Category	Recommended analytical method	Critical contaminant	Minimum dilution factor	Further treatment necessary?
Hydrocarbon composition	GC × GC-FID/ToF-MS	Olefins	10-20	☑
		Aromatics	10-20	☑
Heteroatoms	GC × GC-NCD	Nitrogen	>30	☑
	GC × GC-SCD	Sulfur	~2	×
	GC × GC-AED	Oxygen	>10	☑
		Chlorine	>55-766	☑
Metals	ICP-MS	Calcium	>34	☑
		Iron	>7000	☑
		Sodium	>7	×
		Lead	>350	☑
		Silicon	>4	×

The only contaminants which most likely do not require additional treatment are sulfur, sodium and silicon. All other contaminants such as nitrogen, chlorine, calcium, iron and lead are exceeding the feedstock specifications for steam crackers to such an extent that additional upgrading technologies such as hydrotreatment are needed which, of course, challenge the economic potential of plastic waste pyrolysis oil as steam cracking feedstock. Table 9 is a rough estimation due to the fact that it is based on partly inaccurate measurements with detection limits above the maximal allowable concentration. Therefore, the actual upgrading effort will likely be higher. However, it clearly shows which contaminants should have the highest priority regarding upgrading.

In a future integrated chemical recycling scheme (see Fig. 5), alternative technologies such as solvent treatment of contaminated plastic waste streams may be employed. Subsequent catalytic cracking and depolymerization steps may be used to produce a broad range of important chemicals. This way, energy intensive conversion to platform chemicals via conventional petrochemical routes can be avoided. Furthermore, pyrolysis of the waste residue can be used for the production of carbon nanotubes. Finally, downcycling and disposal in landfills can be avoided entirely while energy recovery via incineration can be reduced to a minimum.

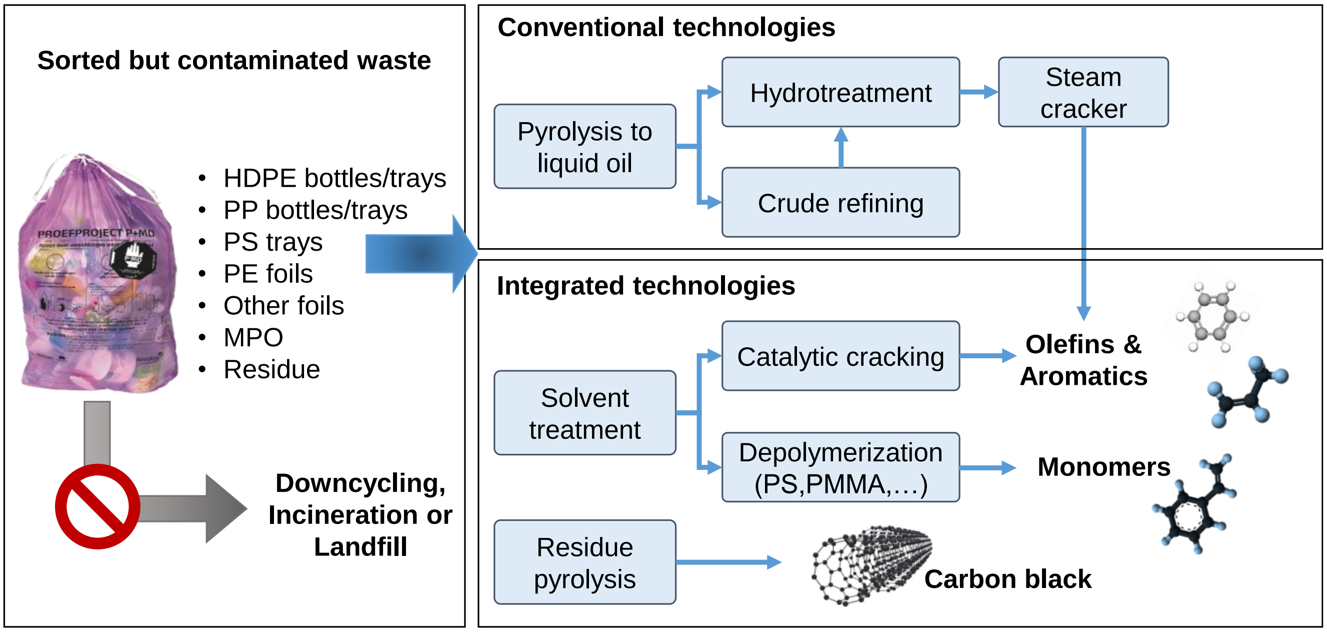

Fig. 5: Plastic waste recycling scheme of the future.

Conclusions and Outlook

Plastic waste pyrolysis and subsequent steam cracking of the pyrolysis oil has the potential to be an economically attractive and sustainable technique for the recycling of plastic waste. However, the composition of plastic waste pyrolysis oil significantly differs from liquid fossil-based steam cracking feedstocks. Contaminant levels exceed established feedstock quality specifications by one or more orders of magnitude such as for nitrogen, chlorine and iron. All these contaminants are known to cause corrosion issues, increase coke formation, destroy expensive reactor tubes or deactivate catalysts in the separation sections of a steam cracker. Even the typical amounts of olefins, oxygenates and aromatics found in plastic waste pyrolysis oils are substantially off-spec. In a nutshell, today the quality of crude plastic waste pyrolysis oils is unacceptable as feedstocks for industrial steam crackers. In order to close the quality gap between conventional fossil feedstocks and plastic waste pyrolysis oils, thorough upgrading is needed using, for instance, hydrotreatment.

However, due to the enormous scale of operation of industrial steam crackers which exceeds the availability of sorted plastic waste, a steam cracker will unlikely run on 100 % plastic waste feedstock but rather use blends with fossil feedstocks, thereby reducing the contaminant levels. Furthermore, improved automation and standardization in waste sorting plants will help to systematically purify the polyolefinic waste from other polymers thereby reducing one of the main sources of contaminants.

A key aspect in establishing plastic waste pyrolysis oils as steam cracking feedstocks is detailed characterization together with a better understanding of the impact of contaminants on process fouling and coke formation. Quality standards which are based on standardized methods to assess important feedstock properties such as chlorine or nitrogen concentrations and the most important metals are needed. Removing the uncertainty for plant operators and thus the associated risk of using these alternative synthetic feedstocks instead of conventional fossil-based ones is needed in order to overcome the hurdles of thermochemical plastic waste recycling.

Acknowledgment

The authors acknowledge financial support by the Catalisti ICON project MATTER (Mechanical and Thermochemical Recycling of mixed plastic waste), the Catalisti SBO project WATCH (Plastic Waste to Chemicals) and the Catalisti Moonshot project PREFER (The Plastics Refinery: No More Waste). Furthermore, Kevin M. Van Geem is holder of the ERC Grant OPTIMA (Process Intensification and Innovation in Olefin Production by Multiscale Analysis and Design) with the grant agreement ID 818607.

References

[1] Solis, M. and Silveira, S., "Technologies for chemical recycling of household plastics – A technical review and TRL assessment," *Waste Manage.,* vol. 105, pp. 128-138, 2020, 10.1016/j.wasman.2020.01.038.

[2] Dogu, O. et al., "The chemistry of chemical recycling of solid plastic waste via pyrolysis and gasification: State-of-the-art, challenges, and future directions," *Prog. Energy Combust. Sci.,* vol. 84, p. 100901, 2021, 10.1016/j.pecs.2020.100901.

[3] Fitzsimons, S. (2020, 13/10/2021). *Total And Plastic Energy Announce A Strategic Partnership And The Construction Of The First Chemical Recycling Plant In France* Accessed on 04/01/2021. Available: https://plasticenergy.com/total-and-plastic-energy-announce-a-strategic-partnership-and-the-construction-of-the-first-chemical-recycling-plant-in-france/

[4] Bailey, M. P. (2020, 29/12/2021). *Neste successfully processes liquefied plastic waste at industrial scale* Accessed on 04/01/2021. Available: https://www.chemengonline.com/neste-successfully-processes-liquefied-plastic-waste-at-industrial-scale/

[5] Pilkington, B. (2020, 23/12/2021). *The Future of Chemical Recycling to Turn Plastic into Virgin-Quality Materials* Accessed on 04/01/2021. Available: https://www.azom.com/article.aspx?ArticleID=19986

[6] Young, I. (2021, 21/01/2021). *Sabic, Plastic Energy to start building plant in Netherlands for chemical recycling of plastics* Accessed on 24/01/2021. Available:

https://chemweek.com/CW/Document/116768/Sabic-Plastic-Energy-to-start-building-plant-in-Netherlands-for-chemical-recycling-of-plastics

[7] Ragaert, K. et al., "Mechanical and chemical recycling of solid plastic waste," *Waste Manage.,* vol. 69, no. 1, pp. 24-58, 2017, 10.1016/j.wasman.2017.07.044.

[8] Al-Salem, S. M. et al., "The valorization of plastic solid waste (PSW) by primary to quaternary routes: From re-use to energy and chemicals," *Prog. Energy Combust. Sci.,* vol. 36, no. 1, pp. 103-129, 2010, 10.1016/j.pecs.2009.09.001.

[9] Al-Salem, S. M. et al., "A review on thermal and catalytic pyrolysis of plastic solid waste (PSW)," *J Environ Manage,* vol. 197, pp. 177-198, 2017, 10.1016/j.jenvman.2017.03.084.

[10] Sundaram, K. M. and Stancato, B., "How much is too much? Feed contaminants and their consequences," in *AIChE Spring National Meeting, Ethylene Producers Conference*, Orlando, Florida, 2018, p. 24.

[11] Van Geem, K. M. et al., "Energy efficiency of the cold train of an ethylene cracker," *Oil Gas-Eur. Mag.,* vol. 34, no. 2, pp. 95-99, 2008,

[12] Amghizar, I. et al., "New Trends in Olefin Production," *Engineering,* vol. 3, no. 2, pp. 171-178, 2017, 10.1016/J.ENG.2017.02.006.

[13] Kopinke, F. D. et al., "Relative rates of coke formation from hydrocarbons in steam cracking of naphtha. 2. Paraffins, naphthenes, mono-, di-, and cycloolefins, and acetylenes," *Ind Eng Chem Res,* vol. 32, no. 1, pp. 56-61, 1993, 10.1021/ie00013a009.

[14] Kopinke, F. D. et al., "Relative rates of coke formation from hydrocarbons in steam cracking of naphtha. 3. Aromatic hydrocarbons," *Ind Eng Chem Res,* vol. 32, no. 11, pp. 2620-2625, 1993, 10.1021/ie00023a027.

[15] Murata, K. et al., "The effect of PVC on thermal and catalytic degradation of polyethylene, polypropylene and polystyrene by a continuous flow reactor," (in English), *J. Anal. Appl. Pyrolysis,* vol. 86, no. 1, pp. 33-38, 2009, 10.1016/j.jaap.2009.04.003.

[16] Anene, A. F. et al., "Experimental Study of Thermal and Catalytic Pyrolysis of Plastic Waste Components," *Sustainability,* vol. 10, no. 11, p. 3979, 2018, 10.3390/su10113979.

[17] Tsuge, S. et al., *Pyrolysis-gc/ms data book of synthetic polymers pyrograms, thermograms and ms of pyrolyzates*. Elsevier B.V., 2011.

[18] Pinto, F. et al., "Pyrolysis of plastic wastes. 1. Effect of plastic waste composition on product yield," *J. Anal. Appl. Pyrolysis,* vol. 51, no. 1, pp. 39-55, 1999, 10.1016/S0165-2370(99)00007-8.

[19] Miranda, R. et al., "Vacuum pyrolysis of commingled plastics containing PVC I. Kinetic study," *Polym. Degrad. Stab.,* vol. 72, no. 3, pp. 469-491, 2001, 10.1016/s0141-3910(01)00048-9.

[20] López, A. et al., "Dechlorination of fuels in pyrolysis of PVC containing plastic wastes," *Fuel Process. Technol.,* vol. 92, no. 2, pp. 253-260, 2011, 10.1016/j.fuproc.2010.05.008.

[21] Ye, Q. et al., "Development and Investigation of Lanthanum Sulfadiazine with Calcium Stearate and Epoxidised Soyabean Oil as Complex Thermal Stabilizers for Stabilizing Poly(vinyl chloride)," *Polymers,* vol. 11, no. 3, 2019, 10.3390/polym11030531.

[22] Miskolczi, N. and Ateş, F., "Thermo-catalytic co-pyrolysis of recovered heavy oil and municipal plastic wastes," *J. Anal. Appl. Pyrolysis,* vol. 117, pp. 273-281, 2016, 10.1016/j.jaap.2015.11.005.

[23] Anuar Sharuddin, S. D. et al., "Energy recovery from pyrolysis of plastic waste: Study on non-recycled plastics (NRP) data as the real measure of plastic waste," *Energy Convers. Manage.,* vol. 148, pp. 925-934, 2017, 10.1016/j.enconman.2017.06.046.

[24] Lee, K.-H. et al., "Thermal and catalytic degradation of waste high-density polyethylene (HDPE) using spent FCC catalyst," *Korean J. Chem. Eng.,* vol. 20, no. 4, pp. 693-697, 2003, 10.1007/BF02706909.

[25] Seo, Y.-H. et al., "Investigation of catalytic degradation of high-density polyethylene by hydrocarbon group type analysis," *J. Anal. Appl. Pyrolysis,* vol. 70, no. 2, pp. 383-398, 2003, 10.1016/S0165-2370(02)00186-9.

[26] Miskolczi, N., "Co-pyrolysis of petroleum based waste HDPE, poly-lactic-acid biopolymer and organic waste," *J Ind Eng Chem,* vol. 19, no. 5, pp. 1549-1559, 2013, 10.1016/j.jiec.2013.01.022.

[27] Demirbas, A., "Pyrolysis of municipal plastic wastes for recovery of gasoline-range hydrocarbons," *J. Anal. Appl. Pyrolysis,* vol. 72, no. 1, pp. 97-102, 2004, 10.1016/j.jaap.2004.03.001.

[28] Lee, K.-H., "Pyrolysis of municipal plastic wastes separated by difference of specific gravity," *J. Anal. Appl. Pyrolysis,* vol. 79, no. 1, pp. 362-367, 2007, 10.1016/j.jaap.2006.12.020.

[29] Toraman, H. E. et al., "Detailed compositional characterization of plastic waste pyrolysis oil by comprehensive two-dimensional gas-chromatography coupled to multiple detectors," *J. Chromatogr. A,* vol. 1359, no. 1, pp. 237-246, 2014, 10.1016/j.chroma.2014.07.017.

[30] Okuwaki, A. et al., "The Liquefaction of Plastic Containers and Packaging in Japan," in *Feedstock Recycling and Pyrolysis of Waste Plastics*, J. Scheirs and W. Kaminsky, Eds., 2006, pp. 663-708.

[31] Ristic, N. et al., "On-line analysis of nitrogen containing compounds in complex hydrocarbon matrixes," *J Vis Exp,* vol. 114, no. 1, pp. 1-12, 2016, 10.3791/54236.

[32] Djokic, M. R. et al., "Quantitative on-line analysis of sulfur compounds in complex hydrocarbon matrices," *J. Chromatogr. A,* vol. 1509, no. 1, pp. 102-113, 2017, 10.1016/j.chroma.2017.06.006.

[33] Robinson, P. R., "10 - Hydroconversion processes and technology for clean fuel and chemical production," in *Advances in Clean Hydrocarbon Fuel Processing*, M. R. Khan, Ed.: Woodhead Publishing, 2011, pp. 287-325.

[34] Speight, J. G., *Handbook of Petroleum Product Analysis*, 2 ed. Wiley, 2015.

[35] Pandey, S. et al., "Physicochemical characterization and applications of naphtha," *J Sci Ind Res (India),* vol. 63, pp. 276-282, 2004, 0975-1084.

[36] Matar, S. and Hatch, L. F., *Chemistry of Petrochemical Processes*. Elsevier Science, 2001.

[37] Albright, L. F. et al., *Pyrolysis: Theory and Industrial Practice*. New York: Academic Press Inc, 1983.

[38] Ibrahim, H. A.-h. et al., "Investigation of the Fouling Mechanisms in the Heat Exchangers of a Hydrotreater," *Engineering Journal of the University of Qatar,* vol. 18, pp. 9-14, 2005, 10.13140/RG.2.1.2168.2648.

[39] Müller-Steinhagen, H. et al., "Heat Exchanger Fouling: Mitigation and Cleaning Strategies," *Heat Transf. Eng.,* vol. 32, no. 3-4, pp. 189-196, 2011, 10.1080/01457632.2010.503108.

[40] Müller-Steinhagen, H., "C4 Fouling of Heat Exchanger Surfaces," in *VDI Heat Atlas*, VDI, Ed.: SpringerMaterials, 2010.

[41] Asomaning, S., "The Role of Olefins in Fouling of Heat Exchangers," Master of Applied Sciences, Faculty of Graduate Studies Chemical Engineering, The University of British Columbia, 1990.

[42] Ibrahim, H. A.-H., "Fouling in Heat Exchangers," in *MATLAB - A Fundamental Tool for Scientific Computing and Engineering Applications - Volume 3*, V. N. Katsikis, Ed.: BoD – Books on Demand, 2012.

[43] Epstein, N., "Thinking about Heat Transfer Fouling: A 5 × 5 Matrix," *Heat Transf. Eng.,* vol. 4, no. 1, pp. 43-56, 1983, 10.1080/01457638108939594.

[44] Van Geem, K. M. et al., "Coke Formation in the Transfer Line Exchanger during Steam Cracking of Hydrocarbons," *Ind Eng Chem Res,* vol. 48, no. 23, pp. 10343-10358, 2009, 10.1021/ie900124z.

[45] Baumgartner, A. J. et al., "Feedstock Contaminants in Ethylene Plants - an Update," in *AIChE Spring National Meeting, Ethylene Producers Conference*, New Orleans, Louisiana, 2004.

[46] Guisnet, M. and Magnoux, P., "Organic chemistry of coke formation," *Appl. Catal. A. Gen.,* vol. 212, no. 1, pp. 83-96, 2001, 10.1016/S0926-860X(00)00845-0.

[47] Letzsch, W. S. and Ashton, A. G., "Chapter 12 The Effect of Feedstock on Yields and Product Quality," in *Stud. Surf. Sci. Catal.*, vol. 76, J. S. Magee and M. M. Mitchell, Eds.: Elsevier, 1993, pp. 441-498.

[48] Richter, H. and Howard, J. B., "Formation of polycyclic aromatic hydrocarbons and their growth to soot—a review of chemical reaction pathways," *Prog. Energy Combust. Sci.,* vol. 26, no. 4, pp. 565-608, 2000, 10.1016/S0360-1285(00)00009-5.

[49] Wauters, S. and Marin, G. B., "Kinetic Modeling of Coke Formation during Steam Cracking," *Ind Eng Chem Res,* vol. 41, no. 10, pp. 2379-2391, 2002, 10.1021/ie010822k.

[50] Towfighi, J. et al., "Coke Formation Mechanisms and Coke Inhibiting Methods in Pyrolysis Furnaces," *J. Chem. Eng. Jpn.,* vol. 35, no. 10, pp. 923-937, 2002, 10.1252/jcej.35.923.

[51] Ristic, N. D. et al., "Compositional Characterization of Pyrolysis Fuel Oil from Naphtha and Vacuum Gas Oil," *Energy Fuels,* vol. 32, no. 2, pp. 1276-1286, 2018, 10.1021/acs.energyfuels.7b03242.

[52] Gaile, A. A. et al., "Removal of Aromatic Hydrocarbons from Reforming Naphtha. Combined Extraction — Extractive–Azeotropic Distillation Process," *Chem. Technol. Fuels Oils,* vol. 40, no. 4, pp. 215-221, 2004, 10.1023/B:CAFO.0000041217.96743.22.

[53] Alanazi, N. et al., "Organochloride Contamination in a Refinery Naphtha Hydrotreater Unit," *Mater Perform,* vol. 56, no. 10, pp. 1-5, 2017,

[54] Angyal, A. et al., "Petrochemical feedstock by thermal cracking of plastic waste," *J. Anal. Appl. Pyrolysis,* vol. 79, no. 1, pp. 409-414, 2007, 10.1016/j.jaap.2006.12.031.

[55] Miskolczi, N. et al., "Thermal degradation of municipal plastic waste for production of fuel-like hydrocarbons," *Polym. Degrad. Stab.,* vol. 86, no. 2, pp. 357-366, 2004, 10.1016/j.polymdegradstab.2004.04.025.

[56] Miranda, R. et al., "Vacuum pyrolysis of commingled plastics containing PVC II. Product analysis," *Polym. Degrad. Stab.,* vol. 73, no. 1, pp. 47-67, 2001, 10.1016/s0141-3910(01)00066-0.

[57] Lee, K.-H., "Thermal and catalytic degradation of pyrolytic oil from pyrolysis of municipal plastic wastes," *J. Anal. Appl. Pyrolysis,* vol. 85, no. 1, pp. 372-379, 2009, 10.1016/j.jaap.2008.11.032.

[58] Kaminsky, W. and Kim, J.-S., "Pyrolysis of mixed plastics into aromatics," *J. Anal. Appl. Pyrolysis,* vol. 51, no. 1, pp. 127-134, 1999, 10.1016/S0165-2370(99)00012-1.

[59] López, A. et al., "Catalytic pyrolysis of plastic wastes with two different types of catalysts: ZSM-5 zeolite and Red Mud," *Appl. Catal. B,* vol. 104, no. 3, pp. 211-219, 2011, 10.1016/j.apcatb.2011.03.030.

[60] Adam, F. et al., "Comprehensive two-dimensional gas chromatography for basic and neutral nitrogen speciation in middle distillates," *Fuel,* vol. 88, no. 5, pp. 938-946, 2009, 10.1016/j.fuel.2008.11.032.

[61] Charlesworth, J. M., "Monitoring the products and kinetics of oil shale pyrolysis using simultaneous nitrogen specific and flame ionization detection," *Fuel,* vol. 65, no. 7, pp. 979-986, 1986, 10.1016/0016-2361(86)90208-5.

[62] Dinneen, G. U. and Bickel, W. D., "Gum Formation in Shale-Oil Naphtha," *Ind. Eng. Chem.,* vol. 43, no. 7, pp. 1604-1607, 1951, 10.1021/ie50499a039.

[63] Dijkmans, T. et al., "Comprehensive compositional analysis of sulfur and nitrogen containing compounds in shale oil using GC×GC – FID/SCD/NCD/TOF-MS," *Fuel,* vol. 140, no. 1, pp. 398-406, 2015, 10.1016/j.fuel.2014.09.055.

[64] Prado, G. H. C. et al., "Nitrogen Removal from Oil: A Review," *Energy Fuels,* vol. 31, no. 1, pp. 14-36, 2017, 10.1021/acs.energyfuels.6b02779.

[65] Khan, M. R. and Al-Sayed, E., "Hydrocarbon Desulfurization to Clean Fuels by Selective Oxidation Versus Conventional Hydrotreating," *Energ Source Part A,* vol. 30, no. 3, pp. 200-217, 2007, 10.1080/02713680701638788.

[66] Reyniers, M.-F. S. G. and Froment, G. F., "Influence of Metal Surface and Sulfur Addition on Coke Deposition in the Thermal Cracking of Hydrocarbons," *Ind Eng Chem Res,* vol. 34, no. 3, pp. 773-785, 1995, 10.1021/ie00042a009.

[67] Jakobi, D. and Karduck, P., "Behavior of High-Temperature Tube Materials in Sulfur-Containing Steam-Cracking Conditions," presented at the Corrosion, Phoenix, Arizona, 2018.

[68] Sarris, S. A. et al., "Optimization of the in Situ Pretreatment of High Temperature Ni–Cr Alloys for Ethane Steam Cracking," *Ind Eng Chem Res,* vol. 56, no. 6, pp. 1424-1438, 2017, 10.1021/acs.iecr.6b04537.

[69] Symoens, S. H. et al., "State-of-the-art of Coke Formation during Steam Cracking: Anti-Coking Surface Technologies," *Ind Eng Chem Res,* vol. 57, no. 48, pp. 16117-16136, 2018, 10.1021/acs.iecr.8b03221.

[70] Patil, M. et al., "Catalytic Effect of Dimethyl Disulfide on Coke Formation on High-Temperature Alloys: Myth or Reality?," *Ind Eng Chem Res,* vol. 59, no. 34, pp. 15165-15178, 2020, 10.1021/acs.iecr.0c01693.

[71] Dhuyvetter, I. et al., "The Influence of Dimethyl Disulfide on Naphtha Steam Cracking," *Ind Eng Chem Res,* vol. 40, no. 20, pp. 4353-4362, 2001, 10.1021/ie001131b.

[72] Depeyre, D. et al., "Pure n-nonane steam cracking and the influence of sulfur compounds," *Ind. Eng. Chem. Process. Des. Dev.,* vol. 24, no. 4, pp. 920-924, 1985, 10.1021/i200031a005.
[73] Jafarinejad, S., "Control and treatment of sulfur compounds specially sulfur oxides (SOx) emissions from the petroleum industry: a review," *Int. J. Chem.,* vol. 2, no. 4, pp. 242-253, 2016, 10.31221/osf.io/bxmsr.
[74] Lingaiah, N. et al., "Removal of organic chlorine compounds by catalytic dehydrochlorination for the refinement of municipal waste plastic derived oil," *Fuel,* vol. 80, no. 13, pp. 1901-1905, 2001, 10.1016/S0016-2361(01)00046-1.
[75] Gutzeit, J., "Effect of Organic Chloride Contamination of Crude Oil on Refinery Corrosion," presented at the Corrosion 2000, Orlando, Florida, 01/01/2000, 2000.
[76] Arjang, S. et al., "Experimental and Modeling Study of Organic Chloride Compounds Removal from Naphtha Fraction of Contaminated Crude Oil Using Sintered γ-Al2O3 Nanoparticles: Equilibrium, Kinetic, and Thermodynamic Analysis," *Energy Fuels,* vol. 32, no. 3, pp. 4025-4039, 2018, 10.1021/acs.energyfuels.7b03845.
[77] Li, X. et al., "Hazards of Organic Chloride to Petroleum Processing in Chinese Refineries and Industrial Countermeasures," *PPS,* vol. 2, no. 3, 2018, 10.31031/PPS.2018.02.000539.
[78] Reid, J. and Nowowiejski, G., "Overview of oxygenates in olefin units in relation to corrosion, fouling, product specifications, and safety," in *AIChE Spring National Meeting, Ethylene Producers Conference*, New Orleans, Louisiana, 2003: American Institute of Chemical Engineers New York.
[79] Ristic, N. D. et al., "Quantitative compositional analysis of Estonian shale oil using comprehensive two dimensional gas chromatography," *Fuel Process. Technol.,* vol. 167, pp. 241-249, 2017, 10.1016/j.fuproc.2017.07.008.
[80] Li, Y. et al., "Formation of Gum and Deposits in an Oxygenated Naphtha Stream," in *ECI Symposium Series, Volume RP5: Proceedings of 7th International Conference on Heat Exchanger Fouling and Cleaning - Challenges and Opportunities*, Tomar, Portugal, 2007: Engineering Conferences International.
[81] Zacher, A. H. et al., "A review and perspective of recent bio-oil hydrotreating research," *Green Chem.,* 10.1039/C3GC41382A vol. 16, no. 2, pp. 491-515, 2014, 10.1039/C3GC41382A.
[82] Chuang, S.-Y. et al., "Contaminants key to refinery offgas treatment unit design," *Oil Gas J.,* vol. 106, no. 35, pp. 68-72, 2008,
[83] Tatterson, D. F. and Vasalos, I. A., "Fluid catalytic cracking of heavy petroleum fractions," US Patent US4280898A, 1981.
[84] Ügdüler, S. et al., "Challenges and opportunities of solvent-based additive extraction methods for plastic recycling," *Waste Manage.,* vol. 104, pp. 148-182, 2020, 10.1016/j.wasman.2020.01.003.
[85] Yoon, H. C. and Jung, S. J., "Calcium Removal from Heavy Crude Oil Using Aqueous Solution Containing a Calcium Removal Agent," in *AIChE Spring National Meeting and Global Congress on Process Safety*, Houston, Texas, 2016.
[86] Orriss, R., "Effects of Contaminants in Ethylene Plants: Sodium and Iron," in *AIChE Spring National Meeting, Ethylene Producers Conference*, New Orleans, Louisiana, 1996.

[87] Ali, M. F. and Abbas, S., "A review of methods for the demetallization of residual fuel oils," *Fuel Process. Technol.,* vol. 87, no. 7, pp. 573-584, 2006, 10.1016/j.fuproc.2006.03.001.

[88] Ates, N. and Uzal, N., "Removal of heavy metals from aluminum anodic oxidation wastewaters by membrane filtration," *Environ Sci Pollut Res,* vol. 25, no. 22, pp. 22259-22272, 2018, 10.1007/s11356-018-2345-z.

[89] Brayden, M. et al., "Improve Steam Cracking Furnace Productivity and Emissions Control through Filtration and Coalescence," in *AIChE Spring National Meeting, Ethylene Producers Conference*, Orlando, Florida, 2006.

[90] Audeh, C. A., "Removal of lead alkyl contaminants from naphtha reformer feed," *Ind. Eng. Chem. Prod. Res. Dev.,* vol. 24, no. 4, pp. 666-668, 1985, 10.1021/i300020a031.

[91] Griffing, M. E. et al., "Determination of Trace Amounts of Lead in Gasolines and Naphthas," *Anal. Chem.,* vol. 29, no. 2, pp. 190-195, 1957, 10.1021/ac60122a005.

[92] Gazulla, M. F. et al., "High precision measurement of silicon in naphthas by ICP-OES using isooctane as diluent," *Talanta,* vol. 164, pp. 563-569, 2017, 10.1016/j.talanta.2016.12.023.

[93] PlasticsEurope. (2021). *Waste Collection, Pre-treatment and Sorting* Accessed on 15/02/2021. Available: https://www.plasticseurope.org/en/focus-areas/circular-economy/zero-plastics-landfill/waste-collection-pre-treatment-and-sorting