



Leaky loop “recycling”

A technical correction on the quality of
pyrolysis oil made from plastic waste

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Executive Summary

In recent times, the rhetoric around pyrolysis oil made from plastic waste has undergone a shift, not least so because of industry players who stand to gain from its uses. Certain stakeholders have begun using two phrases to epitomise the debate around the supposed quality of pyrolysis oil. One rehashed phrase is that the oil can itself become a constituent, or a 'drop-in', to the industrial plastic production process, and the second is that it can create plastics of 'virgin-like' quality.

As post-consumer waste (PCW) is inherently complex due to its diversity, additives, and contaminant properties, established mechanical recycling techniques alone cannot meet the EU's ambitious recycling targets defined in the Waste Framework Directive (WFD).¹ For this reason, pyrolysis has been pulled into the spotlight. In theory, it offers a win-win scenario: by retaining the existing channels of cheap petrochemical plastic manufacturing and consumption and avoiding disruption to established economies. The problem, however, is that pyrolysis does not really suit the purpose of the task. Another way to achieve the EU's recycling targets is by making reuse and repair the norm, thereby directly reducing the amount of products put on the market, and improving recycling targets in the process.

Pyrolysis of plastic has a long history beset with problems. It is highly sensitive, delicately balanced and incredibly challenging to manage. To make matters worse, it only produces a low oil yield which needs extensive upgrading before a small fraction of the original plastic might be reintroduced into the value chain. Somewhat ironically, the technology was abandoned in Europe a decade ago for its failure to manage the simpler task of transforming waste to energy.

Authorities at Member State and EU level are making efforts to recognise pyrolysis as an approved recycling method within the current framework of legislation for 'contact sensitive applications'. At the same time, ongoing administrative talks revolve around defining end-of-waste (EoW) criteria for plastics, and determining the point at which it is no longer considered waste. In the case of pyrolysis, these criteria would reclassify plastic-derived pyrolysis oil from waste to product status. Such a reclassification could have a significant impact since there is a risk that purification steps might be overlooked if the EoW criteria is set early, leading to a potential underestimation of the true environmental footprint.

This report assesses stakeholder claims regarding plastic-derived pyrolysis oil quality in comparison with information obtained from a literature review of independent empirical research. Framed mainly around

¹ By 2025, member states are required to achieve a minimum recycling and recovery rate of 55% of municipal solid waste (MSW) by weight with additional increases to 60% and 65% by 2030 and 2035 respectively.

polyolefin thermoplastics (common in currently non-recyclable PCW), it also expands to cover other mixed or 'difficult' plastic waste streams. Findings relate to current regulations that would apply to pyrolysis oil being marketed within the EU.

In order to create new plastics, plastic-derived pyrolysis oil has to be fed into a steam cracker to produce polymer precursors. However, it is too contaminated or doesn't meet the specifications to be fed directly into this established industrial system, designed for virgin petroleum naphtha. Purifying it of its contaminants would require multiple stages of energy intensive treatment, so the only other solution is to dilute plastic-derived pyrolysis oil with virgin petroleum naphtha. However:

- To counter nitrogen contamination, the pyrolysis oil must be diluted with petroleum naphtha at a ratio ranging from 12:1 to 17:1.
 - Oxygen makes pyrolysis oil acidic and corrosive, making oxygen-rich plastics undesirable feedstocks for pyrolysis. However, oxygen is also present in many common plastic wastes. One study found that plastic-derived pyrolysis oil would need diluting with petroleum naphtha by a minimum of 7 to 13 times. Many other studies found oxygen concentrations in pyrolysis oil at above the steam cracker limit value by between ten to over a thousand times, even after extensive plastic washing pre-treatment.
 - Chlorine contamination puts plastic-derived pyrolysis oils outside of the acceptable steam cracker limits usually by two, but frequently three, orders of magnitude, even after de-chlorination pre-treatment. One study concluded no feasible level of dilution could bring the oil onto specification for use in steam crackers.
 - Bromine contamination is a new issue for steam crackers to deal with. It forms the same type of toxic products as chlorine and it is found in plastic-derived pyrolysis oil at concentrations of 10,000 times above the chlorine/fluorine limit value.
 - Pyrolysis oil is a sink for the many metals used as plastic additives. Concentrations of sodium, lead, potassium and silicon are much higher than the acceptable limits for the steam cracker, making the pyrolysis oil definitely not a 'drop-in' feedstock. Many other elements coming from plastic waste contaminate pyrolysis oil in high concentrations: lead, iron, arsenic, antimony, zinc, aluminium, vanadium, some over 7,000 times above the steam cracker limit values. Even after washing and other pre-treatment steps, these metals remain chemically bonded to the plastic and cannot be removed to the desired limit value levels through fractional distillation. **Generally, one assumption is that it might be feasible to blend 5 to 20% pyrolysis oil with 80 to 95% petroleum naphtha in order to counter contaminants.**
 - The pyrolysis process, by its nature, produces new, unwanted, and toxic hydrocarbons. All plastics, though notably the polyolefins which are identified as ideal pyrolysis feedstocks, do not simply revert back to the precursor material from which they were formed. Instead, they produce a wide variety of products due to aggressive chemical substances, known as free radicals, splitting from the plastic and re-combining in unwanted forms. These 'pyrosynthetic' hydrocarbons lower the product oil yield and impair its quality. Due to the presence of the wrong type of hydrocarbons, pyrolysis oil from
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polypropylene is off-specification by a factor of 66 to 1,010 times in comparison with petroleum naphtha, while the oil made from polyethylene is similarly substandard by a factor of 44 to 280. To bring the olefin concentration onto specification for steam cracking, pyrolysis oil made from PP, mixed polyolefins, and PE would need diluting with petroleum naphtha in ratios between 1:22 and 1:44.

Toxic polycyclic aromatic hydrocarbon (PAH) compounds that are regulated under REACH are formed during pyrolysis. They are present in pyrolysis oil, usually at two or three orders of magnitude greater than the regulated limit that apply to materials used in toys or oral and skin contact items. Other PAH compounds considered by the European Chemicals Agency (ECHA) to be of very high concern are also present in pyrolysis oils at similar concentrations. When plastic-derived pyrolysis oil is fed into the steam cracking process even more quantities of harmful PAHs are produced. **REACH only covers eight specific PAHs, none of which were tested in the studies of pyrolysis oil steam cracking.** One PAH on the ECHA list was between a thousand and over six thousand times higher than the REACH limit value for products to be used in oral and skin contact materials.

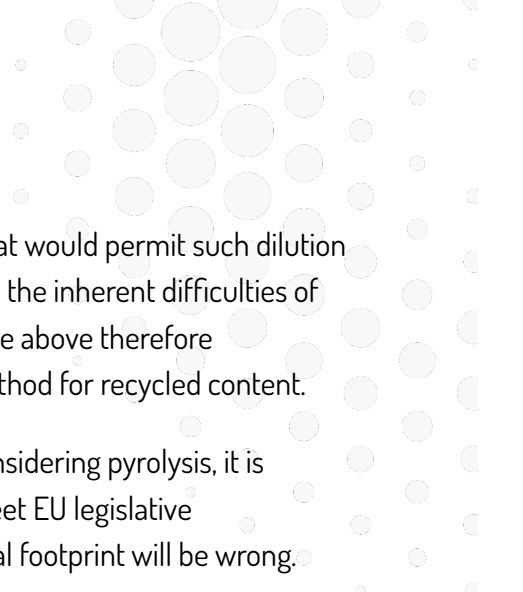
PCDD/PCDFs (dioxins) form during the pyrolysis of plastic waste and transfer into the oil, but the current EU regulatory framework is ill-equipped to address their presence. Another group of persistent organic pollutants, PCBs, are also present in pyrolysis oil made from plastic wastes so that without further treatment products made from the oil shall not be placed on the market.

All studies clearly show that pyrolysis is not a future proof 'chemical recycling' technique capable of managing difficult-to-recycle plastic waste streams, as many industry claims suggest. Only a very narrow range of well-sorted and clean plastics are desirable and even this is proving difficult. Highly mixed, unwashed or difficult-to-recycle plastic waste streams such as automotive shredder residue (ASR) and computer casings result in a pyrolysis oil with substantially increased levels of contamination.

Since the universal laws of physics and chemistry that govern pyrolysis are unlikely to change because of marketing pressure, decision makers would be sensible to accept that pyrolysis is not the wonderful miracle they need merely because no other back end solution exists. Encouragement alone will not be enough to make pyrolysis solve the problem of plastic waste created by linear thinking in plastic production.

A disparity clearly exists between some industry public relations claims about pyrolysis oil quality on the one side, versus multiple corroborating independent empirical research studies and two centuries of engineering evidence on the other. The only way that these can be reconciled is via intermediate stages of pyrolysis oil upgrading and/or blending with petroleum.

This is directly relevant to further discussions ongoing at EU level about mass balance rules for recycled content allocation. Based on the oil yields and contaminant dilution ratios reported in this review, in all cases over 99.9 % of the steam cracker input will need to be virgin fossil-based petroleum naphtha, something that society must desperately avoid using in the future. In other words, **even in the best case scenario only 2% of the plastic waste fed into pyrolysis will actually make the round trip into the steam cracker and then,**



effectively, be recycled. The industry is pushing for permissive free allocation that would permit such dilution to essentially be negated. By doing so, in one single act it superficially covers up all the inherent difficulties of pyrolysis and at the same time enables it to be falsely represented as 'green'. All the above therefore emphasise the importance of adopting a proportional allocation mass balance method for recycled content.

It is also relevant to the current debate on EoW criteria for plastic waste. When considering pyrolysis, it is important to include the necessary steps to upgrade the product oil in order to meet EU legislative requirements for health and safety. Otherwise the calculation of the environmental footprint will be wrong.

It is crucial that any support for alternative technology in the future should be based on sound engineering sense and evidence of proven efficacy. The laws of thermodynamics dictate that the most sensible solution to minimise the disorder of plastic waste lies in upstream intervention. This means putting investment into making plastic products less complex, less contaminated, and more 'recyclable'. Upstream measures will undoubtedly unsettle the economies built on cheap plastic manufacturing and consumption, which is, unfortunately, the only reason that pyrolysis is being proposed by the very same industry.

Acronyms

ASR = Automotive shredder residue

CLP = classification, labelling and packaging of substances and mixtures

EoW = End-of-waste

ECHA = European Chemicals Agency

EU = European Union

EVA = Ethylene vinyl acetate

HDPE = High density polyethylene

I-TEQ = see TEQ

LDPE = Low density polyethylene

LOD = Limit of detection

PA = Polyamide

PAH = Polycyclic aromatic hydrocarbons

PCB = Polychlorinated Biphenyls

PCDD = Polychlorinated dibenzo-p-dioxins

PCDF = Polychlorinated dibenzofurans

PCW = Post consumer waste

PE = Polyethylene

PET = Polyethylene terephthalate

POP = Persistent organic pollutant

PP = Polypropylene

ppmw = parts per million (mass basis)

PS = Polystyrene

PU = Polyurethane

PVA = Polyvinyl alcohol

RDF = refuse derived fuel

REACH = Registration, Evaluation, Authorisation and Restriction of Chemicals

SVHC = Substances of very high concern

TEQ = Toxic equivalent. A weighted measure of the total toxicity of a group of similar compounds (PCDD/PCDFs and PCBs) where each compound has a specific toxic equivalency factor (TEF). I-TEQ refers to one of many systems.

wt% = percent (mass basis)

Concentration Conversions

ppm (mass basis) = mg.kg^{-1} = $\mu\text{g.g}^{-1}$ = 0.0001 weight % = 1000 ng.g^{-1} = $1000000 \text{ pg.g}^{-1}$

1 ppb (mass basis) = 1 ng.g^{-1}

Introduction

The European Union (EU) is increasing its efforts to introduce ambitious recycled content targets in different parts of its legislative framework. The first act was the Single-Use Plastic Directive 2019/904 [1] followed notably by the recently proposed Packaging and Packaging Waste Regulation [2], and adopted last year was the Regulation on Recycled Plastic Materials 2022/1616 [3] introducing rules for recycling technologies and their outputs to ensure the safety of recycled materials. All relate to products for 'contact-sensitive applications'.

Established mechanical recycling techniques cannot meet these ambitious targets due to technical limitations and the complex nature of plastic post consumer waste (PCW). While re-use and repair strategies are preferable they are not widely implemented. And, even though upstream design interventions are more logical there seems to be a political shyness to regulate the petrochemicals industry; all of which might be acceptable if there were some back-end technical option to address the problem of plastic waste, but there is not. So, onto this stage pyrolysis has been brought and placed under the spotlight. The plastics industry sees it as the only tool left available [4]. In theory, it offers a win-win scenario for the plastics industry because it doesn't unsettle the economies built on cheap petrochemical plastic manufacture and the consumption of primarily single-use products.

Some industry stakeholders combined with pyrolysis technology providers are orchestrating a narrative, evident through the collaborative use of two slogans: '**virgin like**' quality and '**drop in**' solution [5, 6, 7, 8]. Both assert that the pyrolysis oil made from PCW plastic can be inserted into conventional plastic production lines without alteration or undue impact and make plastic products of comparable quality.

Pyrolysis of plastic has a long history beset with problems [9]; it functions by burning fossil fuels and this puts it in conflict with wider policy aims for 'net zero' and also the Paris Agreement [10]. Moreover, studies have identified the generation of new toxic substances [11]; the accumulation of plastic contaminants in the products [12]; a low oil yield [13]; and an insignificant contribution to real recycling [14]. Somewhat ironically, the technology was also abandoned in Europe recently for its failure to manage the simpler task of transforming plastic waste into energy [15, 16].

At the same time, there are ongoing administrative discussions about end-of-waste (EoW) criteria for plastics which aim to define the turning point for which a waste ceases to be a waste. In the case of waste-plastic pyrolysis, these criteria would shift consideration of plastic-derived pyrolysis oil from a waste into a product.

Acceleration is happening at the Member State level, notably in France [17]; while the EC's Joint Research Centre (JRC) is currently seeking to define a harmonised set of EoW criteria for Europe [18]. Such change could have an important impact since - if the EoW criterion boundary is drawn early in the process - there is a risk that all purification steps might be discounted thus directly improving the perceived environmental footprint of the process.

A critical review and analysis is needed, comparing independent evidence of pyrolysis oil quality (when made from plastic waste) in parallel with industry claims on the subject. Such is the aim of this report, specifically to provide:

- A critical assessment of plastic-derived pyrolysis oil quality regarding its final use, and
- A description of the relation between input and output material quality.

Written from a pyrolysis and gasification engineer's perspective, this report provides a technical appraisal based on the author's work in research, commercial consultancy, and as expert witness to numerous environmental permit applications over the last ten years. It echoes the feelings expressed by a German technical expert ten years ago amid the heavy marketing of pyrolysis waste-to-energy systems [15]:

"When requests and promises take over facts, an engineering technical correction is in urgent need"

1. Background and Definitions

1.1. The Nature of Pyrolysis Oil

Generally speaking pyrolysis oil is a complicated melt mixture of different hydrocarbon molecules. When made from plastic waste, these hydrocarbon molecules are combined with other elements that originate from the multitude of additives present in plastic.

In appearance, pyrolysis oil is dark brown and viscous; chemically it is acidic and partly soluble in water; physically it condenses over a wide range of temperatures causing blockages and corrosion in downstream equipment. It has a strong smell that persists on clothing and the skin of anyone in contact with it for many days even after repeated washing, the aroma coming from Polycyclic Aromatic Hydrocarbons (PAHs) - a broad group of thousands of compounds, many of which are carcinogenic, teratogenic or mutagenic [19, 20]. So much so that recently the U.S. Environmental Protection Agency (EPA) gave Chevron's plastic pyrolysis oil additive a cancer risk factor of 1.3 in 1, meaning that everyone exposed to pyrolysis oil being burned in engines would be expected to develop cancer during their lifetime [21]. Elsewhere, according to the classification provided by companies to the ECHA in CLP notifications, pyrolysis oil is described as follows [22]:

“This substance may be fatal if swallowed and enters airways, is toxic to aquatic life with long lasting effects, may cause genetic defects, may cause cancer, causes damage to organs through prolonged or repeated exposure, is a flammable liquid and vapour, is harmful if inhaled, is suspected of causing cancer, is suspected of damaging fertility or the unborn child and causes skin irritation”.

1.2. The Physics of Pyrolysis

“Pyrolysis is a chemical recycling process of heating plastic waste without oxygen breaking down the longer chain polymers into shorter chain materials.”[23]

The above quote (from a Shell press release) is not wholly correct. Its omissions concern the technical limitations that cause process instability and devalue the quality of resultant oil.²

A correct definition:

Pyrolysis is a physical phenomenon that happens when all organic material is heated. Molecules break apart across a range of temperatures from around 200°C up to 850°C, though most processing stops at around 550°C [10]. At the same time, and particularly in closed conditions, free radicals³ form and create new double, triple, and cyclic carbon-carbon bonded molecules. These new ‘pyrosynthetic’ products not only significantly lower the usable oil yield and cause downstream process issues of fouling and corrosion, but they also make the oil toxic and create new hazardous waste streams. There is no excuse for omitting this fact since it has been known for over one hundred and fifty years, as stated in 1871 [24]:

“No single pyrogenic reaction goes to the end; if it does not, so to say, check its own progress, other secondary reactions set in and do so, the general result being that ultimately, but in general slowly, a state of dynamic equilibrium is attained in which a set of synthetic reactions on the one hand and a set of analytic reactions on the other compensate one another.”

Also, pyrolysis does not operate ‘without oxygen’. Oxygen is partly excluded, but it is present in small amounts from within the feedstock chemistry. This is important because oxygen leads to the formation of persistent organic pollutants (POPs) and more highly toxic PAHs, once again devaluing the quality of the pyrolysis oils.

1.3. Defining ‘Pyrolysis Oil’

For over one hundred and fifty years, pyrolysis oil has been called ‘tar’ [24]:

“A product of destructive distillation of organic substances – a highly complex material.”

² It’s important to note that ZWE also does not endorse this categorisation of recycling, as we consider these technologies to be a form of chemical recovery.

³ In chemistry, free radicals are extremely reactive atoms or group of atoms.

The word remains widely used today in engineering, but perhaps does not impart the most favourable images for marketing. Other terms are 'wax' and 'pitch', while 'bio-oil' is another but this can only be ascribed to the product of biomass pyrolysis.

All the above define an output that leaves the pyrolysis reactor as a gas but then condenses to a liquid upon cooling (Figure 1). The quantity and quality of this liquid varies depending on the pressure and temperature at which it condenses, and though a tar protocol exists for standardisation, it is not widely applied [25, 26]. This means that there is subjectivity and lack of consistency with how the terms are used, which makes comparisons between studies difficult.

Industry uses some wordplay too, to differentiate between petrochemical plastic and the pyrolysis oil made from the same, by describing the former as 'fossil-based' even though both have one provenance [see 5, 6]. In this report, 'virgin' refers to reagent-grade or 'un-recycled' petrochemicals, while PCW refers to post-consumer waste plastic.

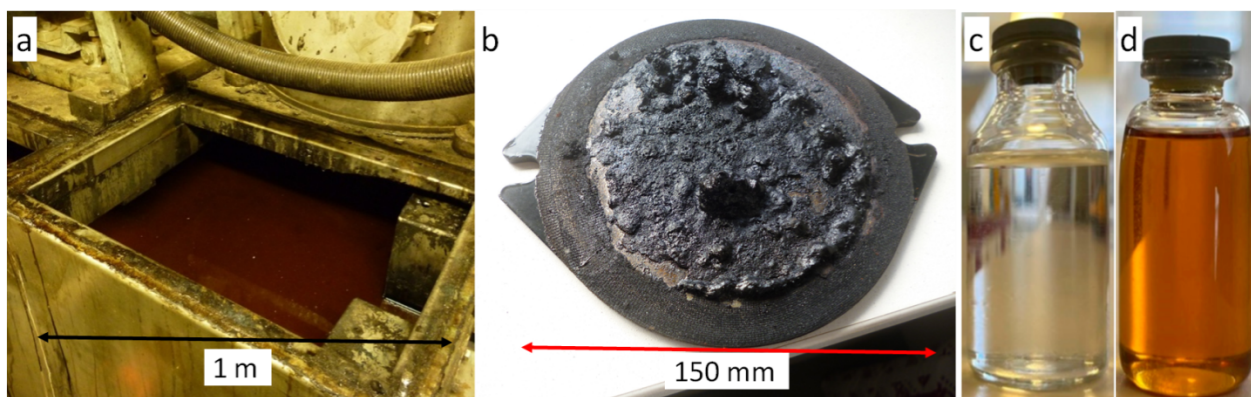


Figure 1. (a) Pyrolysis tar in scrubber water, (b) Pyrolysis tar condensed on downstream component after six hours run time, (c) petroleum naphtha, (d) pyrolysis oil made from PP waste distilled between 370 to 400 °C. Images (c) and (d) adapted from [27].

1.4. Pyrolysis Engineering

1.4.1. L'histoire se répète

"Honeywell today announced the commercialization of a revolutionary process that expands the types of plastics that can be recycled and can produce feedstock used to make recycled plastics with a lower carbon footprint." [28]

*Pyrolysis is not new (Figure 2). It has been trialled commercially for half a century and found wanting; though it can work with coal for which the technique goes back over two centuries, and also with wood from ancient times. Much information exists to document its technical capabilities and limitations. **In the 1930s it was***

concluded that pyrolysis and gasification could not operate successfully on mixed wastes and this has never been revoked⁴ [29].

From the 1980s to the 2010s, in mainland Europe and North America, pyrolysis was deployed at large-scale for municipal solid waste destruction. But this resulted in failure, lost investments and abandonment, sometimes with catastrophic accidents and environmental pollution [15, 30, 31, 32]. Technology purveyors sought markets elsewhere and the same failures and abandonment occurred [16].

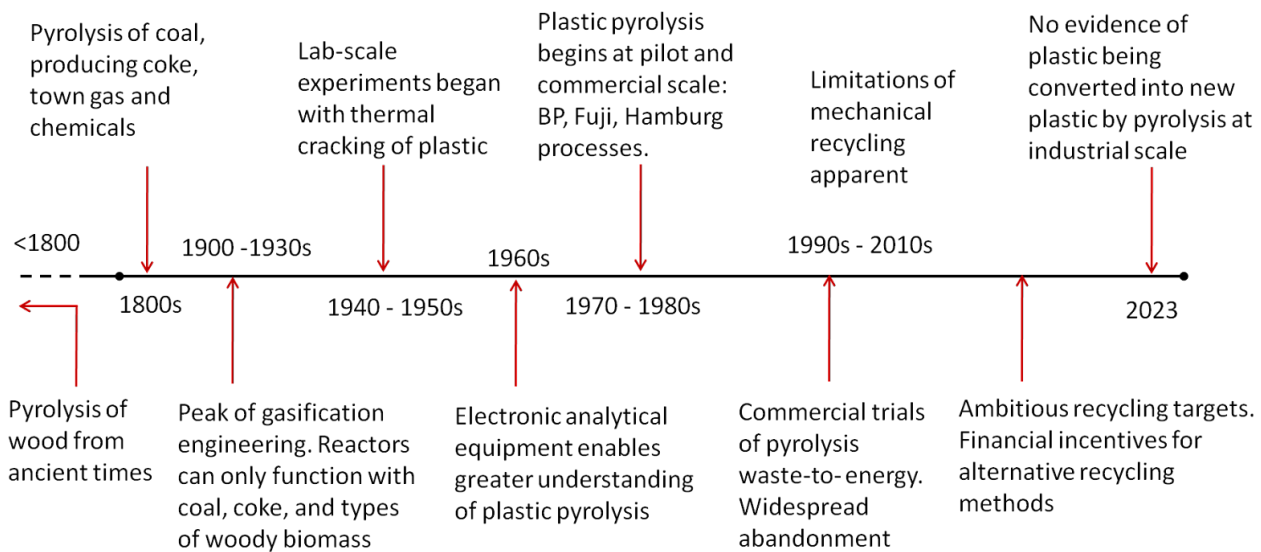


Figure 2. Pyrolysis engineering timeline. See text for references.

In the early 1970s there was considerable commercial application of what was then called 'thermal cracking' and later 'feedstock recycling'. Large corporations (such as BP and Fuji) rolled out pyrolysis at large-scale, along with others based on academic enterprise (such as the Hamburg process); all were intent on recovering oil, and all of them soon closed [9 33, 34, 35]. This commercialisation was based on experimentation in the 1950s and 1960s [9].

Seemingly in the hope that this history can be just ignored, marketing of pyrolysis has continued apace with the technique being re-branded by technology purveyors as 'chemical recycling', or also unsuitably (considering its long history) 'advanced recycling'. Rather than on technical merit, this is due to an increase in plastic waste and the announcement of ambitious recycling targets, putting those who profit from plastic under pressure. It also creates a lucrative business opportunity for entrepreneurs, who devise and patent proprietary processes aiming to upcycle plastic into feedstocks [36].

⁴ Some high temperature waste disposal gasifiers have operated (particularly in Japan) close coupled to an incinerator and bolstered by fossil fuels. No plastic-to-plastic industrial gasification plant currently exists.

1.5. Why Pyrolysis Engineering Remains Challenging

Despite seventy years of endeavour, the correct method to make standardised quality pyrolysis oil from plastic waste is still a long way from being understood, less so from being practically managed. Consequently there is no consensus on the best reactor set-up nor reactor designs [37]. A description of the reactor types trialled for the pyrolysis of plastic wastes can be found in [9, 33, 34, 35].

Pyrosynthetic reactions occur in both gas and liquid phase along with heterogeneous reactions on the surface of solids [25]. For even homogeneous feedstocks, engineered pyrolysis is a precariously unstable and highly sensitive melting pot where even a slight variation in localised temperature can significantly alter the types of molecules produced [38].

Although outwardly simple, pyrolysis is tremendously difficult to implement. Managing heat transfer is key, but this becomes increasingly difficult with the larger scale of reactor necessary at industrial level – heat losses through reactor walls, through apertures during feeding and emptying, and particularly with internal temperature variations. All the above-mentioned aspects thwart industrial attempts at what in the laboratory may seem potentially feasible, while this is all greatly accentuated by heterogeneity [29, 35, 39, 40].

Plastic makes these very difficult and inherent problems even worse. Its low thermal conductivity leads to the formation of localised temperature variations, a problem further complicated by the presence of contaminants always present in plastic waste, particularly flame retardants, heat stabilisers, and fluxing agents [9, and see §6.2]. The other problem is physical: plastic is amorphous and lacks a 'fixed carbon framework' which allows the pyrolysis and gasification of wood and coal to be possible. With this framework, wood and coal are robust during feeding, and inside the reactor they create void spaces between which the pyrosynthetic molecules are cracked and the pyrolysis gas cleaned [41]. Without it, plastic melts during feeding and inside the reactor where it blocks heat and gas transfer meaning that the tars are not 'cleaned' [35, 41]. This is why studies which compared the pyrolysis of plastic and from biomass find that plastic pyrolysis oil contains far more heavy PAHs [42, 43].

1.6. Plastic Types – the Stated Pyrolysis Feedstock

Certain types of plastic commonly used for packaging (called thermoplastics) are, according to industry, the preferred feedstock for pyrolysis. These are the polyolefins (PO), namely polypropylene (PP) and polyethylene

(PE), the latter subdivided into low-density (LDPE) and high-density (HDPE), and also polystyrene (PS) [44]. Others are polyvinyl chloride (PVC) and polyethylene terephthalate (PET) but these are not suitable for pyrolysis as they generate unwanted products (see §4.2.2).

1.7. Methodology and Scope

This study was based on literature review of peer-reviewed empirical research, with data supplemented to a lesser extent by other independent publications. Both were compared against pyrolysis purveyor claims. Life cycle analyses were excluded.

The main focus was the plastic wastes (and their mixtures) asserted to be the target input material for pyrolysis. This frame was broadened to other plastic wastes that are considered 'difficult' to recycle, not least because some industry claims are that pyrolysis can accept them. Studies of tyre pyrolysis were set outside the scope.

There are two different pyrolysis routes for plastic to plastic chemical recovery⁵: Gasification is pyrolysis with adaptations which can improve the quantity and quality of the (non-condensable) gas fraction, the gas would then need to be converted by Fischer-Tropsch synthesis. Though having relevance, this gas route is not part of the current review; rather the scope is limited to liquid processing which subjects pyrolysis oil to secondary high temperature steam treatment known as steam (or naphtha) cracking. Naphtha is a distillation cut from petroleum/crude oil.

Claims of "drop-in" are taken to mean that the quality of pyrolysis oil produced from plastic waste is such that it can be fed into industrial steam/naphtha crackers without any adaptation of, or adverse impact on, the steam cracking process.

There is no independent information on any plastic actually having been made from recycled plastic pyrolysis oil commercially. So, the 'virgin-quality' claims were assessed in relation to three EU regulations, namely: Regulation EC 1272/2008 on the classification, labelling and packaging of substances and mixtures (CLP) [45]; Regulation EC 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) [46]; and Regulation EC 2019/1021 on persistent organic pollutants (POPs) [47]. The rationale was that this metric is chosen in the latest draft technical proposals for determining EoW criteria for plastic waste to address major stakeholder concerns about the presence of hazardous substances in pyrolysis oils [18].

All concentrations and limit values presented in this report are expressed on a mass basis. The empirical research dataset can be found in the Appendix.

⁵ DUH, ECOS, ZWE, Chemical Recycling and Recovery, Recommendation to Categorise Thermal Decomposition of Plastic Waste to Molecular Level Feedstock as Chemical Recovery, 2021

2. “Drop-in” Quality of Plastic-derived Pyrolysis Oil

2.1. Claims – What Industry Says

“A drop-in solution, the feedstock can be used to produce virgin-quality polymers, eligible for just the same applications as conventional, fossil-based polymers.” [5]

“SABIC’s certified circular materials...are an easy drop-in solution to current production processes.” [6]

“a high-quality drop-in feedstock for the production of new polymers. Borealis is feeding this raw material into their steam cracker and consequently polymerizing it into polyethylene.” [8]

2.2. Results

Raw pyrolysis oil made from plastic waste cannot be used as a 'drop-in' feedstock for naphtha steam crackers due to the carry-over of multiple contaminants and also the synthesis of unsuitable hydrocarbon chemistry. This finding comes from a recent review of many empirical research studies [48]:

*“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.**”*

The following sections explain in greater detail the above citation. They also present results of studies which are newer than or which were absent from above review, tabulated and discussed within the text.

2.2.1. Nitrogen

Nitrogen enters pyrolysis oil in the form of both straight-chain and hetero-aromatic compounds [49]. It has steam cracker limit values to protect against the formation of nitrogen oxides (air pollutants), avoid explosive gum deposits, and to minimise hydrogen contaminants in the steam cracking product [48].

From twelve empirical studies, using various common plastic wastes, the presence of nitrogen caused the pyrolysis oil to be unsuitable as a 'drop-in' feedstock for steam crackers by an order of magnitude (powers of 10) or more for light and medium naphtha fractions (limit value = 0.01 %) but slightly below the threshold for heavy fraction naphtha (limit value = 0.2 %) [48]. It has been suggested that to bring plastic pyrolysis oil on-spec' to counter nitrogen contamination, pyrolysis oil would need diluting with petrochemical naphtha by a factor of 12 to 17 [Ibid.]. Various types of washing techniques, applied to mixed plastic from a sorting facility (German standard DKR-350), were ineffective at bringing the nitrogen content in pyrolysis oil below the heavy fraction naphtha steam cracking limit value [50].

More results are shown in Table 1 from experiments with a range of plastic waste types. Only one study found nitrogen concentrations below the light naphtha steam cracking threshold, this coming after the plastic had been subjected to washing, float-sink separation, shredding and drying prior to pyrolysis [51]. The same research group however, in another study using the same methodology, reported values which over the limit value by between 6 and 45 times, thus suggesting that either the waste plastic was widely variable and/or that there was significant error associated with the method [52].

Table 1. Concentration of some elements in oil from the pyrolysis of various plastics. Steam cracker limit values are shown in square brackets [taken from 48 and 53], RDF = refuse derived fuel.

Sample	Nitrogen (wt%)	Oxygen	Chlorine (ppmw)	Fluorine	Ref.
[Threshold Value]	[0.01 light; 0.2 heavy]	[0.01]	[3]	[2]	
RDF	0.5 to 1.2	0.9 to 9.2	100 to 300		[54]
Mixed Plastic	0.8 to 1.5	0.5 to 4.3	10 to 500		
Mixed Plastic			400		[55]
Mixed Plastic	0.2 to 0.3	7.7 to 15	151 to 275	30 to 60	[50]
Mixed Plastic	0.08	0.52	119	12	[53]
Marine	0.12	0.25	297	10	
PE	0.18	0.43	223		[52]
Mixed plastic	0.67	0.32	349		
Mixed PO	0.11	0.1	474		[51]
PP	0.003	0.1	137		
PE	0.004	0.2	143		

2.2.2. Oxygen

Oxygen creates thermal instability in pyrolysis plus it makes the product oil acidic and corrosive [56]. This is why oxygen-containing polymers such as PET and polyamide (PA) are to be kept below 5 % in the pyrolysis feedstock [44]. For similar reasons, oxygen must be limited in steam cracking, with threshold values reported to be 0.01 % [48].

But, oxygen is in many other common polymers: at 23 % in polyurethane (PU) [57]; and 2 % in virgin PE and PS [42], though this is not always identified due to the low limits of analytical detection. It can be seen, for example, by the amounts of carbon dioxide in the gaseous product of virgin PE pyrolysis [58]. Therefore all plastic wastes are likely to create oxygen contamination issues, and as mentioned, pyrolysis is not an 'oxygen free' process.

This is confirmed by research: The earlier cited review found oxygen levels in pyrolysis oil to be well over the steam cracker threshold such that dilution with petroleum naphtha would be required by a minimum of 7 to 13 times [48]. Results from other studies are shown in Table 1, where oxygen concentrations were above the steam cracker limit in pyrolysis oil made from all plastic waste types, by between ten to over a thousand times, even after extensive plastic washing pre-treatment, and also after fractional distillation of the oil.

2.2.3. Sulphur

Sulphur concentrations in plastic pyrolysis oil were below the steam cracker limit value in most studies [48, 51, 53, 59, 60]. This was corroborated by the additional data sources consulted during review (not shown in Table 1). Sulphur content is therefore unlikely to impair pyrolysis oil from being a steam cracker 'drop-in'.

2.2.4. Halogens

Table 1 shows that chlorine contamination makes plastic-derived pyrolysis oils off-specification for industrial steam crackers with concentration values at usually two, but frequently three, orders of magnitude greater than the threshold of 3 ppm. This is even when de-chlorination pre-treatment had been applied to the plastic waste prior to pyrolysis [48].

Chlorine levels in pyrolysis oil made from plastic were so high that one study concluded no feasible level of dilution (with petroleum naphtha) could bring the oil onto specification [51]. Another study found the chlorine content to be fifty times the steam cracker limit value, even after washing the plastic waste using multiple different methods [50]. Yet another study added calcium oxides to the pyrolysis reactor but this did not prevent the formation and carry-over of halogenated compounds into distilled fractions of pyrolysis oil derived from mixed plastic [53].

Being of the same chemical group, bromine and fluorine form similar products to chlorine during thermal treatment; but they are uncommon in petroleum naphtha and so their impact on industrial steam cracking is under reported [48]. Two studies assessed fluorine in pyrolysis oil made from mixed plastic, finding that the element was 5 to 30 times above the steam cracker threshold (of 2 ppm) [50, 53]. No limit value is reported for bromine but its widespread use as a flame retardant in plastic materials means that it is a major contaminant of pyrolysis oil often in concentrations similar to chlorine: between $161 \leq \text{ppm} \leq 1900$ from the pyrolysis of mixed plastics [49, 60], and $4 \leq \text{ppm} \leq 32$ for PE [51, 52].

Further discussion on halogen contamination in pyrolysis oil can be found in §5.2. The impact of PVC and other high-halogen plastics is discussed in §6.2.

2.2.5. Metals

Pyrolysis oil is a sink for the metals used as additives in plastic [51]. Most of them are considered to pose a high risk to human health and the environment [61, 62]. Some metals have steam cracker limit values, but many do not as they are absent in petroleum naphtha, which does not mean that they are acceptable, rather that more research is needed to determine their impact [48]. Others (such as arsenic, and vanadium) have limit values in the parts per billion range which is well below the detection level of common analytical equipment used by research studies, thus limiting a comprehensive assessment of pyrolysis oil quality [51].

Aluminium transfers to pyrolysis oil to a great extent along with potassium, magnesium, sodium and silicon [51]. There are no reported limit values for aluminium but it is known to cause furnace problems, while no information was found on steam cracker limit values for magnesium [48]. Potassium, sodium, and silicon, along with lead and calcium, all have established limit values due to adverse effects of catalyst poisoning, corrosion and fouling. A study showed that even when the pyrolysis oil was distilled, the calcium concentration in pyrolysis oil distillate (originating from mixed plastic) was over the steam cracker threshold by a factor of between 550 and 1300 times [63]. From the same study, two other elements (titanium and zinc) were both detected in similar concentrations but no steam cracker thresholds are available for comparison. In a study of mixed plastic waste pyrolysis by the same research group, relatively high (mean) concentrations of calcium (305 ppm), zinc (133 ppm), and antimony (109 ppm) were detected, along with 207 ppm bromine, while the use of pyrolysis catalysts had no clear overall effect and in many cases actually increased the metal concentrations in pyrolysis oil [60].

Very generally, the high concentrations of contaminants with limit values indicate that pyrolysis oil dilution factors above 7000 times would be required for some of them, while overall it is suggested that it might be feasible to attempt blending ratios of 5 to 20 % pyrolysis oil with 80 to 95% petroleum naphtha [48]. Blending with petroleum naphtha in such large ratios of course undermines any possible 'circularity' or 'green tech' claims about the process.

Table 2 contains the findings of additional studies, wherein polyolefin plastics produced pyrolysis oil with concentrations of sodium, lead, potassium and silicon many times higher than the steam cracker 'drop-in' thresholds, though calcium levels were below the limit of detection in two samples [51]. There, the plastic wastes were pre-treated by washing, sorting and float separation using typical commercial methods, indicating that metals were chemically bound. This was proven by fractional distillation being unable to bring the oil towards required specification due to concentrations of sodium, potassium, silicon, and also calcium with a note for careful monitoring of iron [53].

Table 2. Metal concentrations (in ppmw) in pyrolysis oil derived from various plastic wastes along with steam cracker limit values in square brackets [all limit values from 48].

Sample	Sodium	Calcium	Lead	Potassium	Silicon	Ref.
[Threshold Value]	[0.125]	[0.5]	[0.05]	[0.5]	[0.5]	
Mixed	0.126	1.3	0.0006	0.19	12.5	[53]
Marine	0.19	3.0	0.004	0.5	1.9	
PE	2.5	12.2	<LOD		17.2	[52]
Mixed Plastic	19.3	17.4	<LOD		<LOD	
Mixed PO	82	17	4.6	36	28	[51]
PP	114	LOD	5.9	37	43	
PE	82	LOD	3.8	171	47	
Mixed PO	19	17	0.1		2	[64]

2.2.6. Hydrocarbon Chemistry

An ideal petroleum naphtha is rich in higher alkanes (paraffins) with 5 to 12 carbon atoms (C5 – C12), and with aromatics and olefins present in much lower concentrations [27]. The olefin group of compounds inhibit steam cracking of paraffins, while both olefins and particularly aromatics form PAHs that contaminate the output [see §4] and lead to coke deposition downstream in the installations [48].

In contrast, pyrolysis of plastic PCW sometimes yields oils where there are no paraffins at all, with 72% to 74% aromatics from pyrolysis at 460°C to 500°C, and 99% aromatics via pyrolysis at 600°C [55]. The same pyrolysis oil was described as highly viscous, caused blockages, and was deemed unsuitable from an environmental perspective due to the high content of PAHs.

Though some properties, such as density and initial boiling point, are similar to petroleum naphtha, the pyrolysis oil made from single PP (the supposed ideal pyrolysis feedstock) is not drop-in quality for steam crackers, as stated [27]:

*“The evaluation of pyrolysis oil compositions [from PP] in terms of tendency for coke formation shows that significant operational issues would arise if these fractionated pyrolysis oils were to be fed to the steam crackers directly without any upgrading. Thus **as a stand-alone technology, pyrolysis oil can neither replace nor be blended with naphtha and is not a viable option for closing the circularity of waste plastics**...The results demonstrate that although there is a very small fraction of pyrolysis oil consisting of saturated alkanes and cycloalkanes, pyrolysis oil obtained from PP exhibits distinct compositional differences than naphtha and cannot be used as a substitute for it.”*

2.2.6.1 Carbon Number Distribution

Pyrolysis of plastic produces an oil with hydrocarbons in a wide carbon number distribution up to C44 [27, 33, 42, 65, 66]. This means a heavier oil in comparison to petroleum naphtha and that greater energy will be needed to create the required distillate.

2.2.6.2 Bromine Number

Bromine number measures the unsaturated non-aromatic hydrocarbon content and is one way to quantify whether the oil is 'on-' or 'off-' specification. From the pyrolysis of PP, distilled oil fractions were above the petroleum naphtha bromine number (0.3 to 1.2 g/100g) by a factor of between 70 and 1010 [27]. As shown by another study, also from the pyrolysis of PP, the oil bromine number of different fractions was between 79 and 104 g/100g (66 to 347 times 'off-spec'), while oil derived from PE exceeded the limit of specification by 44 to 280 times [67].

2.2.6.3 Olefins content

Ten different empirical studies found that pyrolysis oils made from a variety of plastic samples were all well above the steam cracker olefin threshold (2 %) with concentrations in the range $9 \leq \% \leq 72$ [48]. In a separate study, the pyrolysis oil from mixed and marine plastic was distilled and the olefin content was still above the olefin threshold by a factor of nineteen (39 % and 38 % olefins in the pyrolysis oil) [53]. More pyrolysis experiments with pre-washed mixed polyolefins and PE film produced pyrolysis oil which contained 50 % olefins, while the olefin content of virgin naphtha was zero [52]. And, in separate pyrolysis experiments with PP, mixed polyolefins, and PE, the olefin content in oil was between 44 % and 88 %, meaning that dilution factors of between 1:22 and 1:44 would be required with petroleum naphtha to bring it onto specification [51].

2.2.6.4 Aromatics Content

Under the right conditions, aromatic compounds progressively condense into heavier and more recalcitrant PAHs and so increase in tendency to foul process lines and catalyst surfaces [48]. A threshold value of ~4 % has been suggested by one research group against which the pyrolysis oil from their mixed plastic waste experiments was compared: the oil was off specification by a factor of 3 to 7 [53]. However, making estimates based purely on 'aromatics' is highly imprecise because the rate for coke formation varies across molecules. For instance, benzene has a coke forming rate coefficient of $k = 0.3$ while larger PAHs such as acenaphthylene, anthracene, and chrysene have $k = 4.5$ to 6 [68]. Consequently, estimates of a dilution factor of 2 to meet steam cracker requirements based purely on 'aromatics' (as per [48]) should be treated with caution. The important factor is the content of heavier PAHs, and multiple studies show that these are synthesised during pyrolysis of all plastic types, not just PS, but also virgin-grade PE and PP in particular with (though not restricted to) higher temperatures [35, 42, 63, 65, 66, 69]. To avoid duplication, the main discussion on aromatics and their impact on pyrolysis oil quality is in §5.2 and §5.3.

3. “Virgin Quality” Products

3.1. Claims – What Industry Says

“The company’s patented, innovative technology transforms plastic waste into raw materials that can be used to create virgin-quality polymers.” [7]

“This plant will convert plastic wastes into pyrolysis oil which will then be used as feedstock for the production of polymers with identical properties to virgin polymers. In particular, they will be suitable for use in food-grade applications, enabling full circularity for plastics.” [70]

“Because chemical recycling breaks down polymers into their building blocks, it also allows the production of recycled plastic (recyclate) with virgin plastic properties that can be used in demanding applications, such as food contact.”⁶ [71]

3.2. Results

3.2.1. Polycyclic Aromatic Hydrocarbons (PAHs)

Entry 50 (paragraphs 5 and 6) of Annex XVII to the REACH Regulation [46], also called a restriction list, restricts the placing on the market of articles containing specified PAHs where individual concentrations are greater than 1 mg.kg⁻¹ for oral and skin contact materials and 0.5 mg.kg⁻¹ for toys. Table 3 shows that these PAHs are in plastic-derived pyrolysis oils at mostly two or three orders of magnitude greater than the REACH limit values. Without further purification steps, the presence of these substances makes pyrolysis oil non-compliant with this EU regulation.

PAHs are a large group of compounds containing several thousand molecules, and REACH specifies just eight. Missing from the REACH list are many PAHs that are carcinogens, teratogens and mutagens, with some of the most potent being oxygenated or nitrated PAHs [19, 20]. The ECHA has recently added more PAH molecules onto its candidate list of Substances of Very High Concern (SVHC) [72]. The pyrolysis oil concentrations of these PAHs are shown in Table 4. Though of course no REACH limit values apply, concentrations found in oil from the pyrolysis are in the same range as those of the REACH regulated PAHs, therefore well above the associated thresholds.

However, a small range of specified compounds should also not be taken as a proxy for the overall / total toxicity of pyrolysis oil [20]. Dibenzofuran – an oxygenated heterocyclic and endocrine disruptor – has been found in the pyrolysis oils of polyester, polyvinyl alcohol (PVA) and mixed PCW in concentrations above the REACH limit value for other PAH compounds [58, 73, 74]. The production of benzofuran – another heterocyclic endocrine disruptor and dioxin precursor – is identified as the main drawback to the pyrolysis of printed circuit boards [75]. There are also a range of toxicity equivalent factors for PAHs registered under the REACH list: Dibenzo[a,h]anthracene for example is ten times more toxic than benzo[a]pyrene [20].

The most abundant PAH produced by pyrolysis is naphthalene, but it is not covered by entry 50 to Annex XVII to REACH. However, according to Annex IV of CLP, any mixture in which it is present above 10,000 mg.kg⁻¹ is classified as a carcinogen; while lower concentrations (1000 mg.kg⁻¹) classify a mixture as having acute and chronic aquatic toxicity. Table 5 indicates that regardless of the specific plastic types and the various pyrolysis conditions employed, the pyrolysis oil consistently exceeded thresholds for acute and chronic aquatic toxicity, while three samples would have been classified as carcinogenic.

⁶ Though 'chemical recycling' includes other techniques, the cited article refers to pyrolysis and gasification as representing 80% of the planned capacities.

In context: **though restricted to a narrow range of PAH compounds, these results show that raw pyrolysis oil made from plastic is unsuitable for making into plastic for contact-sensitive applications, i.e. for toys and/or for oral and skin applications, as such materials would breach the REACH regulatory limits. The same pyrolysis oils would also likely be classified as having acute and chronic aquatic toxicity according to the CLP Regulation, while some would also be classified as carcinogenic.** Such shortcomings of EU regulations concerning other types of chemicals associated with food contact materials have previously been identified, with the call for a more generic or "hazard-based" approach to risk management, which means removing hazardous substances from products [76]. § 5.3 shows the PAH concentrations in effluent from the steam cracking of pyrolysis oils.

Table 3. PAH concentrations in oil from the pyrolysis of various plastic types (see Appendix). Values are in mg.kg⁻¹. All compounds are regulated under REACH [limit values in square brackets]. * = polyester, † = Pyrolysis at 850°C only, ‡ = combined benzo[a]anthracene and chrysene.

PLASTIC SAMPLE TYPE								
PAH	PE	EVA	PET	PS	PVC	PVA	PUR	Ref.
<i>[limit value = 0.5 for toys, 0.1 for oral and skin contact materials]</i>								
Benzo[a]pyrene	180	20	120					[58]
			2 to 200					[73]
	≤ 760							[65]
							44 to 76	†[57]
						7 to 329		[74]
Benzo[a]anthracene	150	220	7					[58]
							137 to 155	†[57]
	0		700	1300	1500			‡[42]
			1 to 60					*[73]

PLASTIC SAMPLE TYPE

PAH	PE	EVA	PET	PS	PVC	PVA	PUR	Ref.
<i>[limit value = 0.5 for toys, 0.1 for oral and skin contact materials]</i>								
						9 to 198		[74]
Benzo[k]-fluoranthene	60	7	150					[58]
							22 to 48	†[57]
			5 to 470					*[73]
	≤ 720							[65]
							6 to 129	[74]
Benzo[j]-fluoranthene			≤ 560					*[73]
Dibenzo[a,h]-anthracene						2 to 27		[74]
							6 to 9	†[57]

Table 4. PAH substances of very high concern but not regulated by REACH and their concentration in oil from the pyrolysis of various plastic types (see Appendix). Values are in mg.kg⁻¹.

PLASTIC SAMPLE TYPE								
PAH	PE	EVA	PET	PS	Sam ple PVC	PVA	PUR	Ref.
<i>Phenanthrene</i>	970	3500	820					[58]
							8 to 478	[57]
	20		920	0	1550			[42]
			120 to 3390					[73]
	≤ 2200						7 to 329	[65]
							65 to 1496	[74]
	520	770	240					[58]
							0 to 106	[57]

PLASTIC SAMPLE TYPE

PAH	PE	EVA	PET	PS	Sam ple PVC	PVA	PUR	Ref.
Fluoranthene	0		40	380	160			[42]
			10 to 1350					*[73]
	≤ 1500							[65]
						18 to 926		[74]
Pyrene	570	1400	90					[58]
	0		30	350	150			[42]
							1 to 317	[57]
			5 to 630					*[73]
	≤ 1450							[65]
						19 to 960		[74]

3.2.2. Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF)

The first identification of a dioxin originated from pyrolysis experiments in the 1950s, subsequently named the Servaso dioxin after the infamous industrial accident, this in-turn led to the report by Olie et al. [77] on PCDD emissions from three Dutch incinerators, culminating in Europe with the Industrial Emissions Directive (IED) [78]. A brief history of the subject is provided by [79].

Since then, there has been unequal emphasis placed on minimising incinerator and other combustion-derived airborne emissions of PCDD/PCDFs to the detriment of recognising the pyrolysis pathway to dioxin formation. This has perhaps been acceptable until now, but the new push toward pyrolysis of plastic on the large scale requires a significant re-balance to mitigate the adverse impact of PCDD/PCDFs on human health and the environment. This is well reflected by the weakness of the EU legislation to cater for dioxin toxicity linked to plastic-derived pyrolysis oils.

Pyrolysis (a.k.a. 'primary', or 'slow') dioxin formation happens in the gas phase in oxygen depleted/fuel rich conditions [80, 81]. It is a different mechanism to de-novo synthesis during incineration which occurs on the surface of fly ash catalysed by copper during post combustion gas cooling (Table 6). But, pyrolysis also provides the carbon backbone (incomplete combustion products) which leads to the de novo synthesis of PCDD/PCDFs. This backbone combines with halogens, and some amount of oxygen is essential [79, 82].

Therefore, pyrolysis conditions - low oxygen with significant amounts of organic compounds present - are where peak concentrations of PCDD/PCDFs are formed, with only low concentrations of chlorine required [79]. Conditions are made more favourable to pyrolysis formation of PCDD/PCDFs due to the low thermal conductivity of plastics, localised high temperatures creating oxygen depletion, presence of catalyst and fluxing agent contaminants, and the many flame retardants present in plastic waste. This is seen with studies of incinerator bottom ash where, despite the regulatory requirements of the IED, large concentrations of PCDD/PCDFs are present [83].

Table 6. Comparison between incinerator and pyrolysis operational conditions.

Incineration	Pyrolysis
A process designed to 'burn to cinders'.	A process designed to form incomplete combustion products
Post combustion gas phase burnout to minimise PCDD/PCDFs (Above 850°C for at least 2 seconds)	No second-stage combustion. Incomplete combustion products are needed.
Excess oxygen (>100 %) to ensure complete and avoiding dioxin precursors being produced	Low oxygen (< 5 %) encourages the formation of dioxin precursors
High temperature (> 1000°C) in combustion zone	Pyrolysis temperature usually 400°C to 600°C (though can go to 850°C).

Annex III to Regulation 2019/1021 (POPs) defines the list of substances being subject to release reduction provisions and directs Member States to give priority considerations to alternative processes which avoid the formation and release of PCDD/PCDFs, so this applies to pyrolysis. However, PCDD/PCDFs are not included in Annex I which regulates the control of manufacturing and placing on the market of materials, so their presence in pyrolysis oil is not covered. Annex IV, which sets concentration limits for certain POPs in waste, classifies PCDD/PCDFs as subject to waste management provisions with concentration limit values of 15 ng TEQ.g⁻¹ for disposal or recovery. Three studies reported PCDD/PCDF concentrations in pyrolysis oil, and all values were between 1 to 9.1 ng. l-TEQ.g⁻¹) [84, 85, 86]. But of course, the limit value for waste should not be used as a reference for plastics used for example in food contact materials, further evidencing that the EU rules are ill equipped to cover for recylates from plastic-derived pyrolysis oil.

No empirical research report was found that analysed the pyrolysis oil made from PE, PP, and PS for PCDD/PCDFs. Nevertheless, due to the known pathways for formation and the ubiquitous presence of halogens in waste plastics, this is a significant gap in knowledge which needs more research attention. A number of studies analysed the oil from pyrolysis and fuel-rich combustion of more 'difficult' plastic waste streams (such as industrial and automotive shredder residues), which all show that a higher ratio of PCDFs to PCDDs are produced during pyrolysis along with a tendency to form lower, more toxic, chlorinated homologues [84, 87]. In one study, at oxygen levels between 0.5 % to 2 % and pyrolysis temperatures of 430°C and 470°C, up to 400 times more PCDFs formed than PCDDs [86].

Following industrial municipal solid waste (MSW) pyrolysis, 80 % of the PCDD/PCDF product went into the pyrolysis oil making its toxicity four times higher than that of the feedstock, while these were again mostly lesser chlorinated homologues [80]. The same study used trace labelled carbon to show that 85 % of the input PCDD went through the pyrolysis process undergoing some de-chlorination but not thermally decomposing.

3.2.3. Polychlorinated Biphenyls (PCBs)

PCBs are listed in Annex I of POPs regulations [47] to prohibit any placing on the market of articles which contain these substances. PCBs are produced during pyrolysis of PU and also ASR, with reported concentrations up to 2000 pg TEQ.g⁻¹ [57, 87]. Conditions that favour their formation are the same as the high molecular weight PAHs – low oxygen environment, high levels of organic carbon and temperatures in the range of 550°C to 850°C.

3.2.4. Other POPs

Information is sparse on other POPs in plastic-derived pyrolysis oils, both EU regulated and otherwise. This is also an area that needs more research focus. It has been observed that other POPs – polyfluoroalkyl substances (PFASs), brominated diphenylethers (PBDEs) and brominated dioxins and furans (PBDD/PBDFs) – are present in incinerator bottom ash along with the high concentrations of PCDD/PCDFs and PCBs [83]. Concerns have also been raised about plastic waste pyrolysis as a mechanism for the formation and release of fluorinated POPs [11].

3.3. Results from Steam Cracking Experiments

Bench-top steam cracking experiments with pyrolysis oil produced reasonable quantities of monomer, but there were several operational difficulties, issues with optimising the steam cracker temperature, large amounts of PAH present in the steam cracker effluent and, as expected, relatively higher coke formation. In one study the pyrolysis oil had to be blended in a 1:3 ratio with petroleum naphtha due to its “waxy state and high boiling point” which made direct feeding into the steam cracker impractical [52]. Another study used distilled pyrolysis oil, but again the output was rich in heavy aromatic compounds relative to petroleum naphtha and coke formation was still 1.5 to 3.1 times higher than during petroleum naphtha runs [53]. In a third study, 1:3 blended pyrolysis oil/naphtha was sequentially filtered in three stages, but many metal contaminants were still left in the oil above the industrial steam cracker thresholds. Also, though the technique did bring radiant coil coke formation within levels comparable to petroleum naphtha cracking (this was in only one

section of the steam cracker), fouling effects were observed but not investigated, and the authors express caution that this was not a long-term study [64]. All experiments were over a six hour duration, and so a relevant appraisal of long-term efficacy at industrial scale is weakened, while effects on process catalysts were also un-reported.

Probably the most striking result of these experiments is the large amount of PAHs created by steam cracking itself. Only four PAH compounds were reported in both studies (indene, naphthalene, anthracene and phenanthrene), but it can be inferred that many more were present as “other” compounds which comprised between 14 to 31 % of the total steam cracker product, excluding lower weight hydrocarbons (benzene, toluene and xylene, etc. Though none of the above reported PAHs currently have limit values set by REACH, phenanthrene is on the ECHA list of SVHC, and it is relevant to compare the concentrations of PAHs in steam cracker effluent with the REACH limit values of 1 mg.kg⁻¹ for oral and skin contact materials and 0.5 mg.kg⁻¹ for toys (§5.2). From the steam cracking of marine litter and mixed PCW plastic pyrolysis oil, the reported limit of detection was 100 mg.kg⁻¹ (a hundred times above the highest threshold) and one sample recorded a value of zero, but the rest had minima of 1000 mg.kg⁻¹ so a thousand times greater than the REACH limit value for oral and skin contact materials [53]. From the steam cracking of mixed polyolefins and PE-derived pyrolysis oils, even greater concentrations of phenanthracene and anthracene were recorded (2800 ≤ mg.kg⁻¹ ≤ 6200 mg.kg⁻¹) [64].

The naphthalene concentrations in all steam cracker products made from mixed plastic waste and marine litter were also over and above the CLP regulation limit values which classify mixtures as carcinogenic, with the greatest concentration being three times the threshold value [53]. From mixed polyolefin and PE-derived pyrolysis oils, the naphthalene concentration in the steam cracker product was above the same threshold in one sample only [52].

Results substantiate that pyrolysis oils are not 'drop-in' feedstocks for steam crackers. They show that the steam cracking process does not diminish PAHs but rather creates more than were already in the feedstock oil making the output even further off-specification. Altogether, the results emphasise the absolute need for upstream interventions, such as the removal of contaminants by plastic manufacturers, and designing plastics for recyclability.

4. Mixed/Difficult-to-Recycle Plastics

4.1. Claims – What Industry Says

“The plant will convert difficult-to-recycle mixed plastic waste into raw materials that can be transformed into certified circular polymers and other high-value products at ExxonMobil’s petrochemical complex.”[7]

“We can create virgin quality polymers from pyrolysis oil produced from low quality mixed plastic using a chemical recycling technology.”[6]

“Today’s advanced recycling technologies can handle unsorted mixed plastics, which includes all sorts of packaging (think: chip bags, snack wrappers, food pouches – even toys). This makes it much easier and more efficient to re-process large volumes of discarded plastics that traditional recyclers can’t use.”[88].

4.2. Results

Those who make claims about pyrolysis being able to handle highly mixed, difficult-to-recycle plastic wastes are doing their industry no favours because the veracity of such common claims is challenged by lack of supporting evidence, is disputed by independent authors, conflicts with well established science, and perhaps most tellingly – is refuted by pyrolysis operators [4, 44, 89]. The evidence provided by pyrolysis operators is illuminating [44]:

Feedstock should account for a minimum of 85% polyolefins (PO), i.e. polyethylene (PE) or polypropylene (PP), which are clean and well rinsed. The feed must have a maximum moisture content of 7 %, and all contaminants should not exceed 15% - with maximum concentrations of the PVC (1 %), PET/PA 5%, PS (7 %), metal/glass/dirt/fines (7 %), paper/organics (10 %).

Even single plastic articles are complex and heterogeneous, being a mixture of polymers [56, 90]. For example, commercial impact PS has elastomers (polybutadiene), while expanded PS has blowing agent (3 to 7 % pentane), while there are colourants which contain heavy metals, and halogens in the flame retardants and accompanying ‘synergist’ antimony trioxide [62, 91]. The effects are shown for example when PS with and without fire retardants is heated: only 1.5% styrene monomers were produced by the pyrolysis of fire-retarded PS, in comparison with 37% from non-fire retarded samples, with approximately five times greater [heavy] ‘tar’ produced from fire retarded PS [91].

PVC has a two-stage thermal decomposition during which steel-corroding hydrochloric acid is formed, and also a series of chemical reactions which create largely PAH compounds [55, 66]. The oil yield from PVC is also very low, mainly aromatic and many of these are chlorinated-PAHs, while a large amount of soot is produced [42]. Hydrochloric acid is so corrosive that pyrolysis reactors burst during single experiments [66]. Unfortunately, excluding PVC is not enough because chlorine and other halogens are widely dispersed in many types of plastic wastes since they are used as additives in a variety of applications (e.g. plasticiser, heat stabiliser, filler colourant, antioxidant) [62]. Worryingly, although under-reported, the same chemical pathways during pyrolysis are identified for bromine [62].

The pyrolysis of computer casings yielded an oil with 11 to 16 wt% bromine, which put it over 10,000 times above the chlorine and fluorine steam cracker thresholds, while 61 wt% of the feedstock bromine went into the pyrolysis oil leading authors to advise against using the oil for further applications such as fuel or chemicals [92]. Various washing techniques have been applied to mixed plastics prior to pyrolysis, but were found ineffective at removing bromine and fluorine, with removal efficiency of approximately 50 % [50].

At low to moderate pyrolysis temperatures (350°C to 600°C), the pyrolysis oil made from computer-casings was rich in mostly aromatic nitrogen-containing compounds [92]. This was supported at higher temperatures (700°C to 900°C) where nitrogen in the pyrolysis oil from PE and other plastic types was in heavier N-PAH compounds [69]. Oxygen (present in all types of plastic waste) also selectively forms heterocyclic PAHs during higher temperature pyrolysis [ibid.]. Both O- and N-PAHs are among the most toxic of the PAH compound group [19, 20]. From the pyrolysis of PU, large quantities of ammonia and nitrogen oxides are produced [57].

The obstacle is not simply due to chemical composition but is also due to physical properties of the plastic as it melts creating unequal heat transfer issues along with the catalytic influence of metals. Sodium, magnesium, potassium, and calcium are particularly interesting as these are fluxing agents which lower the melting temperature of inorganic elements and thereby increase the localised heat transfer problems, which in-turn leads to the formation of unwanted 'pyrosynthetic' molecules [93].

All this is seen in studies of mixed plastic pyrolysed at relatively low temperatures (400°C to 500°C), where distillate contained significantly more aromatics (60 % to 82 % of the total hydrocarbons) than oil distilled from petroleum, while the distilled oils also contained undesirable PAHs which were either directly toxic or which were precursors to more toxic substances when combusted [94]. This was corroborated where the plastic waste had been washed using various methods, pyrolysed at 450°C and distilled, with approx. 40 % aromatics in the light fraction [50].

5. Leaky Loop Recycling – Bringing the Pyrolysis Oil ‘On Specification’

5.1. Purification – What Industry Says

“The purification of plastic pyroils is an absolute must...”[95]

5.2. What Industry also Says

Though not always apparent in the headline of 'virgin-like' quality press releases, deeper scrutiny reveals that there is a step 'behind the scenes', namely the essential purification or 'upgrading' of pyrolysis oil. SABIC, for example refer to a “newly to be built hydrogenation unit” for upgrading its plastic waste pyrolysis oil [6], while both Neste and DOW advertise the building of pyrolysis oil upgrading and purification plants [5, 96]. The necessary purification/'upgrading' is an unresolved issue, and evidence that it is still at the nascent stage is provided in an interview with numerous pyrolysis technology providers [4].

5.3. Blending and its Impact on Fossil Resources – What Industry Says

“The new technology can reduce the need for fossil fuels in the creation of virgin plastics while enabling hundreds of cycles of recycling, with the goal of enabling a circular economy for plastics.”[28]

“The use of pyrolysis oil as feedstock can avoid the need for fossil resources, potentially reducing the depletion of fossil resources by up to 80%.”[6]

5.4. Results

Pyrolysis is a high energy consuming process that requires the burning of fossil fuels to keep it functioning [10]. While extra energy will be needed for upgrading the oil, blending will mean lock-in to a future of more

fossil carbon consumption. The question is therefore, how much blending would be required to bring plastic pyrolysis oil 'on specification' or in other words, how much plastic can actually make the round trip from plastic to plastic via pyrolysis. This question has so far only been assessable by LCAs which are widely criticised as untrustworthy for their incorrect energy costs and simplistic assumption that all the raw pyrolysis oil is useable [37, 54, 97]. While making bold claims of 'green' capabilities, industry does not provide data on operational performance [98]. The findings of this study permit such a quantified assessment.

One industry estimate of the oil yield from pyrolysis of plastic waste is 22 % [13]. This corroborates with a permit application in the US, where 70% of the plastic feedstock is burned onsite (supplemented by the burning of natural gas), 10 % is landfilled, meaning only 20 % of the input material would be reclaimed as pyrolysis oil, though the company (Brightmark) allegedly says that the figures were submitted in error [4].

Multiplying the range of oil yields taken from empirical studies of (largely polyolefins) plastic waste pyrolysis (as shown in Appendix A) by the amount of petroleum naphtha recommended as necessary diluents to bring pyrolysis oil on specification for steam cracking (in terms of olefin limit value of 2 %), data in Table 7 show that over **99.9 % of the steam cracker input will need to be petroleum naphtha. In other words, even in the best case scenario, only 2% of the plastic waste fed into pyrolysis will actually make the round trip into the steam cracker, and at worst less than 1% of plastic will be recycled.**

Table 7. Estimates of plastic mass losses during the pyrolysis to steam cracking process line and final blending ratios of pyrolysis oil to petroleum naphtha using data provided by independent studies. Oil yield maxima and minima taken from the Appendix Table 8. Dilution factor from [51].

Oil yield	Dilution Factor	Plastic Oil Fraction	Petroleum Fraction
Minimum	0.045	< 0.01	>99.99
0.05	0.033	< 0.01	>99.99
	0.023	< 0.01	>99.99
Maximum	0.045	0.04	99.96
0.89	0.033	0.03	99.97
	0.023	0.02	99.98

It is of note that these results exclude novel methods such as filtration and other purification which are currently subject to experimentation and which may lead to improved figures. But these methods will incur *extra* mass losses and also the use of more energy and resources. It is also notable that this only represents the input to the steam cracker and therefore excludes further downstream mass losses. It is also likely that the oil yield is skewed to the higher end and overestimates relative to real world pyrolysis due to the more comprehensive oil capture techniques used in laboratory settings.

5.5. Recommendations

The results of this study are important for two reasons: firstly, they bring much needed quantification to the ongoing discussions at EU-level with regard to the allocation of recycled content for plastics. Industry is pushing for permissive flexible allocation which would permit a product put on the market to be claimed as 100% recycled, even if for example only 1% of its composition is a recycle and the other 99% comes from virgin petroleum. **As this study has shown such accounting methods, in one simple measure bypass all the inherent difficulties of pyrolysis, while at the same time enabling it to be falsely represented as 'green'.** The analyses and results presented here support calls for proportional allocation which offers the least

freedom and greatest environmental benefit, also reflecting the inherent and substantial imperfections of pyrolysis and on what this technology will actually be able to deliver [99].

Secondly, the results further substantiate the concerns already expressed about the 'green' credentials of pyrolysis as a plastic waste recycling method as they run counter to the wider aims of the EU to be carbon neutral by 2050.

And finally, these results have relevance to ongoing EU discussion with regard to defining EoW criteria for plastics. They emphasise that such criteria, where pyrolysis oil is concerned, must include upgrading/purification steps within the boundary, else they will not capture the full environmental footprint of the process.

6. Future prospects

Regulation EU 2022/1616 appears to be attempting to reconcile the technical limitations and historical antecedents of pyrolysis with stakeholder claims. It allows novel recycling technologies to be placed on the market then revoked later if collected safety data shows critical consumer exposure [100]. **Such permission to operate is essentially a licence to experiment. However, pyrolysis is only covered by Regulation (EU) No 10/2011 and has been excluded from the scope of the Regulation 2022/1616, which leaves the sector without many reporting obligations therein, including on safety requirements** such as extensive reasoning, scientific evidence and studies, compiled by the developer, demonstrating that the technology can manufacture recycled plastic materials and articles that comply with Article 3 of Regulation (EC) No 1935/2004. Therefore, without any monitoring requirements it is impossible to ensure traceability along the value chain.

This is concerning because a similar situation occurred just over a decade ago with the pursuit of pyrolysis as a waste-to-energy method, based on reasons other than technical merit. The end result was failure, abandonment and lost investments. Its recurrence has been the rationale for this report, since, if society does not learn from history it is forever doomed to make the same mistakes as in the past.

The laws of physics, specifically the laws of thermodynamics, dictate that the nature of pyrolysis is to synthesise new molecules rather than simply to decompose plastic polymers, a phenomenon that is aggravated by the unsuitable properties of plastic and its many additives. Since these universal laws are unlikely to yield in response to legislated policy goals or alter as a consequence of marketing pressure, it would be sensible for decision makers to accept that pyrolysis of plastic waste will not somehow miraculously step up to the task required merely because no other back-end solution exists.

Encouragement alone will not be enough to make pyrolysis solve the problem of linear thinking that currently exists with plastic products design and production.

Support for any future alternative technology should be based on sound engineering sense and evidence of proven efficacy. The same laws of thermodynamics guide that the sensible solution lies in upstream intervention which keeps the entropy of plastic waste low. This means putting investment in re-use systems to meet recycling targets, but also making plastic less complex, less contaminated, and more 'recyclable'.

There can be no 'circular economy' without the input of energy and resources, as per the same laws of thermodynamics. The greater extent to which plastic is decomposed, the greater will be the amount of energy and resources needed to re-construct it again. Therefore, accepting its limitations, mechanical recycling will always be a more efficient recycling option as it deconstructs plastic at a shallower level.

Only two options exist for pyrolysis as a plastic recovery method: **Either apply multiple and energy intensive purification steps to bring the oil 'on specification', or highly dilute the oil with virgin petroleum naphtha. Both undermine the concept's 'green' or 'circular' credentials and lock-in society to a future dependent on fossil carbon.** Both are also currently very relevant to other discussions ongoing about plastic recycling.

Those tasked with improving pyrolysis oil cannot do better than study the history of gasification. Gasifiers were designed to improve the quality of the pyrolysis output (though they also increase the amount of gaseous product so reduce the oil yield even further). More costly to build and more complex to operate than pyrolysis - the gain is a better product, if gasification can be made to work. So, while pyrolysis is simpler, it produces a product which is more difficult to upgrade and thereby it shifts the necessary upgrading to an external domain. This is the place where pyrolysis technology providers are now at. Worryingly however, **the history of gasification shows that if the reactor is not right and the feedstock is not right, no amount of upgrading can make the process viable** [101].

7. Limitations

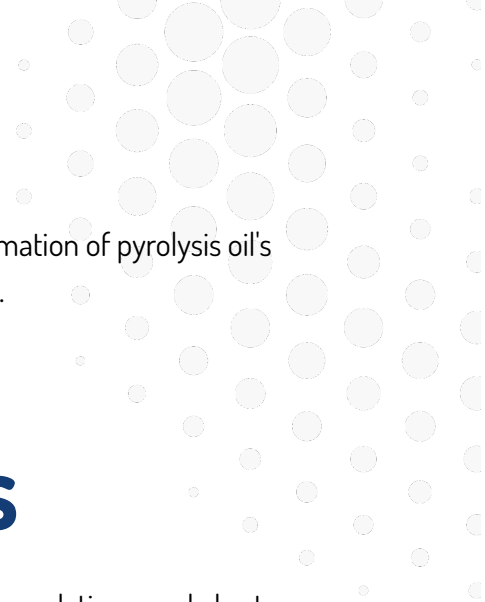
Some empirical research papers may have been missed during this review. Some others were excluded due to not presenting pyrolysis oil hydrocarbon concentrations on a calibrated mass basis.

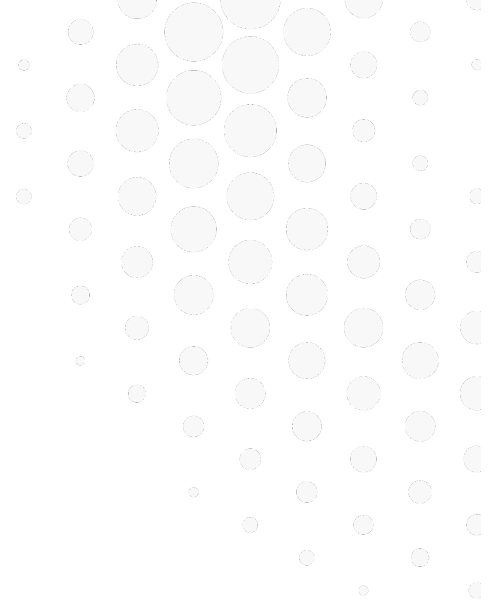
Almost all empirical studies cited in this report used gas chromatography (GC) as the analytical technique to identify specific hydrocarbon chemistry, but this has known limitations in that it cannot detect a significant fraction of heavy tar molecules [26, 69, 102]. Since this group contains the most toxic and recalcitrant

compounds for fouling industrial processes, there is undoubtedly some underestimation of pyrolysis oil's toxicity and capacity for being a steam cracker 'drop-in' feedstock in these studies.

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Appendix

Table 8. Data sources – empirical studies on the pyrolysis of common plastic wastes

Sample	Pyrolysis Temp'	Notes	Oil Yield (wt%)	Ref.
PCW polyester	650°C to 1050°C			[73]
Single virgin plastic (PE, PS, PET, PVC)	800°C			[42]
Mixed virgin plastic (PE, PP, PET, PS, PVC) and mixed PCW plastic	500°C		33 – 48	[66]
Virgin PE	600°C to 900°C			[65]
Mixed virgin plastic (PE, PP, PET, PS, PVC)	500°C to 700°C		18-39	[103]
Single virgin plastic (PE, PS, PET, PVC)	850°C			[58]

Sample	Pyrolysis Temp'	Notes	Oil Yield (wt%)	Ref.
PU	550°C to 850°C			[57]
Mixed PCW plastic (PE, PP, PA, PS, PU)	500°C to 550°C	Distilled	5-24	[63]
Mixed PCW plastic (PE and PP). Washed	520°C			[59]
Mixed PCW plastic	500°C to 600°C			[60]
Mixed PCW plastic (PE, PP, PS, PVC)	400°C to 500°C			[93]
Virgin PE	500°C to 700°C	Distilled	25-51	[33]
Virgin PVA	650°C to 950°C			[74]
RDF and PCW (multi-layer film)	u/k		65-75	[54]
PCW (PP)	270°C to 400°C	Distilled		[27]
Virgin plastic (PP and LDPE)	450°C		79- 85	[67]

Sample	Pyrolysis Temp'	Notes	Oil Yield (wt%)	Ref.
Mixed virgin and PCW plastic (PE, PP, PS, PET, PVC)	460°C to 600°C	Washing pre-treatment	43 - 72	[55]
Mixed virgin plastic (PE, PP, PS, ABS, PVC)	450°C		59-67	[49]
Mixed PCW plastic (DKR-350). Washed	450°C		66	[50]
Mixed PCW plastic and marine litter	400°C	Distilled		[53]
Two PCW sample (PE and mixed). Washed	450°C			[52]
PCW plastic (PE and PP, with ≤ 2% other material). Washed.	450°C		85 - 89	[51]

Table 9. Data sources – empirical studies on the pyrolysis of ‘difficult’ plastic wastes

Sample	Pyrolysis Temp'	Notes	Ref.
ASR	600°C and 850°C		[87]
ASR (light fraction)	500°C to 800°C		[83]
Rural municipal solid waste	Approx 400°C to 500°C in pyrolysis zone	Updraft gasifier	[85]
Mostly ASR and refrigerator shredder residue (both light fractions).	430°C to 470°C		[86]
Printed circuit boards	400°C to 900°C		[75]
Municipal solid waste	500°C to 600°C		[80]



Zero Waste Europe (ZWE) is the European network of communities, local leaders, experts, and change agents working towards the prevention and elimination of waste in our society. We advocate for sustainable systems; for the redesign of our relationship with resources; and for a global shift towards environmental justice, accelerating a just transition towards zero waste for the benefit of people and the planet. www.zerowasteurope.eu



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Author: Dr. Andrew Rollinson
Editors: Lauriane Veillard, Seán Flynn
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General information: hello@zerowasteurope.eu
Media: news@zerowasteurope.eu

zerowasteurope.eu

