Chemical Recycling:

Status, Sustainability, and Environmental Impacts

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GAIA is a global network of more than 800 grassroots groups, NGOs, and individuals. We envision a just, Zero Waste world built on respect for ecological limits and community rights, where people are free from the burden of toxic pollution, and resources are sustainably conserved, not burned or dumped. We work to catalyze a global shift towards environmental justice by strengthening grassroots social movements that advance solutions to waste and pollution.

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TABLE OF CONTENTS

01.

INTRODUCTION

The extremely rapid growth of plastic production, combined with the current shortcomings of mechanical recycling and the recent breakdown of global export markets, have left many local and national governments desperate to contain the problem of post-consumer plastic waste. In response, there has been a rapid rise in proposed technologies which are claimed to effectively and sustainably convert waste plastic into either fuel or petrochemical precursors (Closed Loop Partners, 2019). In mid-November 2019, the Executive Vice President of Shell's global chemical business described the concept (Hydrocarbon Processing, 2019):

'We want to take waste plastics that are tough to recycle by traditional methods and turn them back into chemicals - creating a cycle. This makes sense for the environment and for business'.

Yet, many critics question the environmental benefits and sustainability of chemical recycling. For example, at an international conference in October 2019, Professor Peter Quicker described the motives for promoting this technology as '...independent of its ecological sense and rationality' (Quicker, 2019). He went on to describe practical objections (ibid.):

'...according to many experts, the approach of chemical recycling is not the right way. The special value of plastic, the polymerised structure, is decomposed and transformed into an inferior product, such as a low quality oil that has to be treated with great effort in order to turn it back into plastic'.

As society seeks to transition away from fossil fuel consumption and mitigate the threat posed by plastic pollution, governments, citizens, and NGOs currently struggle to assess the concept with little or no independent data available on the technologies or their capabilities. To address the problem, and drawing predominantly from peer-reviewed, non-industry financed literature, this report considers the following questions with regard to chemical recycling of plastic:

1. What are these technologies and how do they compare with other methods for treating plastic waste?
2. What are the environmental implications?
3. Are they sustainable?
4. Is the technology mature or likely to be so in the next ten years?

02.

UNPACKING THE CHEMICAL RECYCLING CONCEPT

2.1. Terminology

Chemical Recycling

 The term 'chemical recycling' has no formal definition but refers to a diverse set of chemical engineering technologies. In general, these technologies subject plastic waste to a combination of heat, pressure, and/or other chemicals inside some form of reaction vessel. The product of this process can then, theoretically, be made into new plastics or fuel, depending on the technology and post-processing used **(Figure 1)**.

Fossil Fuels
(petroleum, natural gas)

Ethane

Monomers

Polymers

Solvent-based
depolymerization

Solvent-based
purification

gas/oil cleaning
and upgrading

CO_2

HDPE
LDPE
PP
PS
PVC

PET

PU
PLA

Fuel

Pyrolysis oil/
producer gas

Thermal depolymerization
(pyrolysis/gasification)
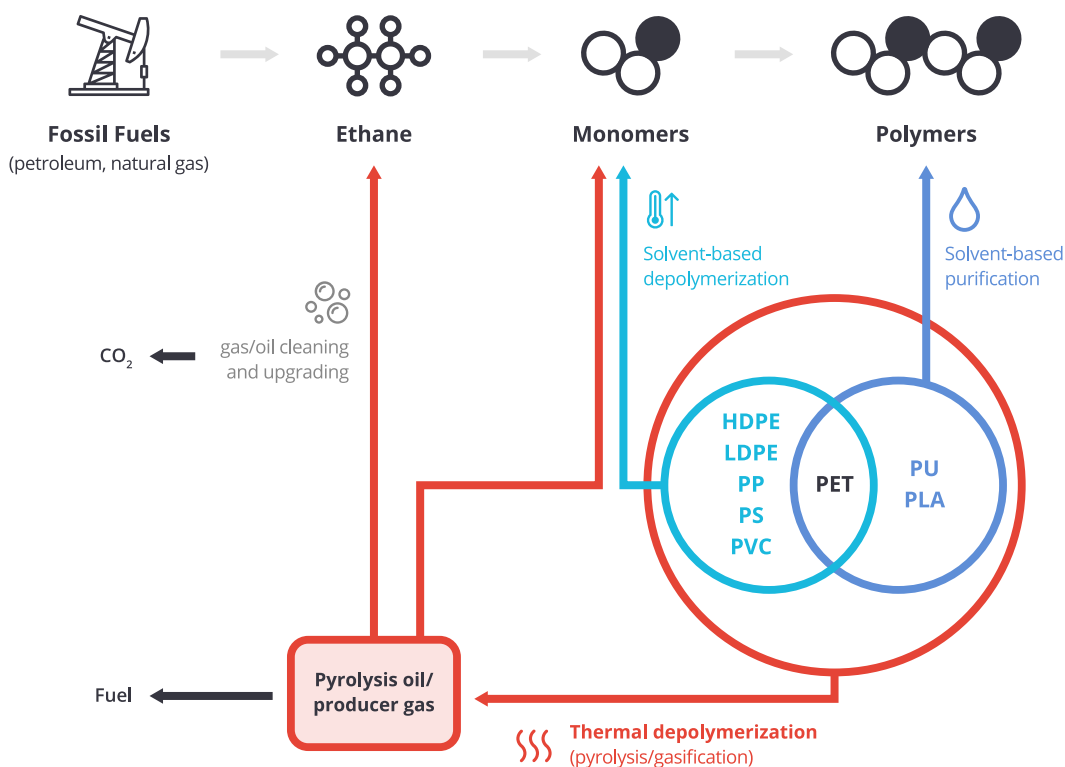
Figure 1. General schematic of chemical recycling processes. For abbreviated plastic types, see Glossary.

Recycling

The European Union defines 'recycling' as:

'Any recovery operation by which waste materials are reprocessed into products, materials or substances whether for the original or other purposes. It includes the reprocessing of organic material but does not include energy recovery and the reprocessing into materials that are to be used as fuels...'.[1]

The Oxford English Dictionary offers a more restrictive definition of recycling:

'to return (material) to a previous stage of a cyclic process'.

In evaluating chemical recycling, there is a critical distinction between turning waste plastic back into plastic of similar quality, and turning it into other products of less utility, such as fuel. The former creates the possibility of a closed material loop in plastic, minimizing both waste disposal and the extraction of natural resources. The latter delivers relatively little environmental benefit (Hopewell et al., 2009).

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[1] Article 3(17), Directive 2008/98/EC on waste

Plastic Feedstock

The word 'plastic' comes from a material's capacity to flow or deform under certain conditions of temperature and pressure. As commonly used, 'plastics' are hydrocarbon polymers – long-chain structures of smaller monomers forming branched and cyclic macro-molecules – which flow or deform at some stage in the manufacturing process. The most common types of waste plastic are: polyolefins, including high density polyethylene (HDPE), low density polyethylene (LDPE), and polypropylene (PP); polystyrene (PS); polyethylene terephthalate (PET); polyvinyl chloride (PVC); ethylene-propylene copolymer (EPC); polyamide (PA); polylactic acid (PLA); and polyurethane (PU).

Plastic polymers were initially made from natural cellulose but the vast majority are now made from petrochemicals, with shale gas in particular driving increased production (American Chemistry Council, 2019). The beneficial properties of petrochemical plastics - durability and resistance to natural enzymatic decomposition - are the same properties which constitute their threat to the biosphere. Though biodegradable and biologically-derived plastics are available, they are not widely utilised (Spierling et al., 2018).

In engineering terminology, 'feedstock' refers to the material input for a process. This report refers to plastic waste as the feedstock for chemical recycling. Some of the chemical recycling technologies described can only handle a single polymer feedstock. Others are capable of processing different plastics but may require extensive reconfiguration between polymers, meaning that effectively a dedicated facility is needed for each.

2.2. Technology Types

⬆ Depolymerization

Solvent-based technologies 🧪

Pyrolysis Gasification
(Plastic-to-fuel)

**Hydrolysis
Methanolysis
Glycolysis
Aminolysis
Ammonolysis**
etc.

Purification
(e.g., Solvolysis)
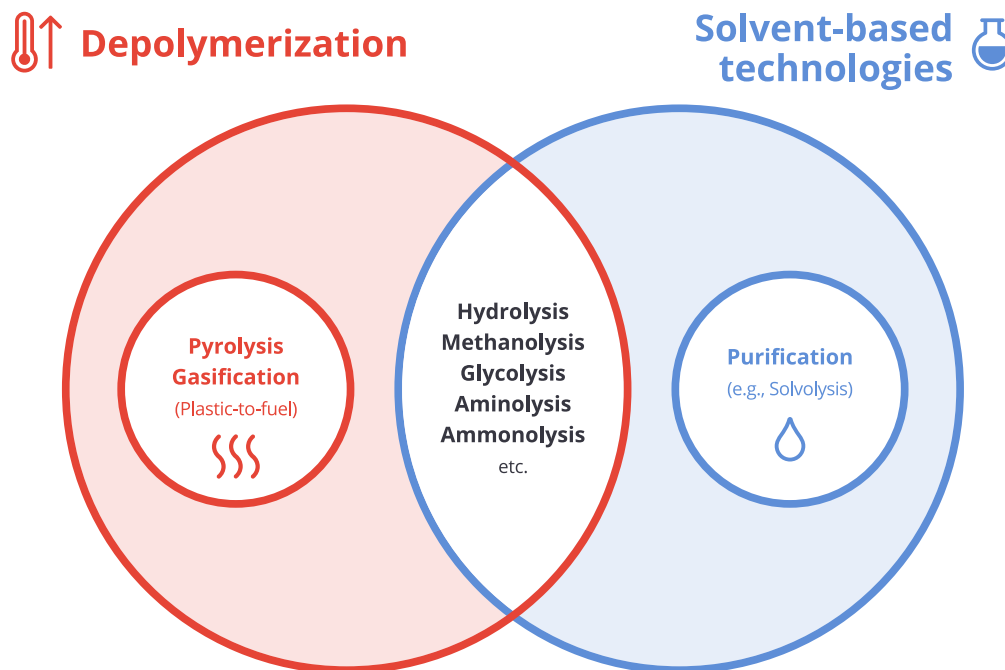
Figure 2. Chemical recycling terminology. Pyrolysis and gasification outputs can be used to produce new plastic after additional upgrading, but are typically burned for energy.

Chemical recycling technologies can be grouped into two categories: thermolysis and solvent-based processes (Figure 2). Thermolysis literally means 'change by heat', and though it broadly encompasses combustion and a wide range of other chemical processes, the only practicable thermolysis methods for chemical recycling are pyrolysis and gasification. They apply high temperatures to the plastic feedstock inside an oxygen-depleted reactor with the aim of breaking the polymers down into smaller fragments, which is why they are also referred to as depolymerisation technologies. These fragments can then, in theory, be repolymerised into new plastic, or simply burnt as fuel with the other outputs. Solvent-based technologies use a variety of media to treat the plastics, often in stages; some depolymerise the plastic while others strip out impurities, leaving the polymer chains relatively intact. Confusingly, many solvent-based technologies also involve high temperatures, but are not considered as thermolysis.

Gasification and Pyrolysis

Gasification and pyrolysis are, at face value, very simple concepts. They were devised over one hundred years ago as technologies for converting woody biomass and coal into gaseous and liquid chemicals along with producing carbon-rich solids. Their names derive from these historical applications.

Pyrolysis

Plastic → Reactor No Oxygen → Clean Up → Gas, Oil, Char → Post Processing

Heat

Complex Product Mixture · Products are burned and/or used as feedstock

Gasification

Plastic → Reactor Low Oxygen → Clean Up → Gas, Oil, Char → Post Processing

Some heat applied; some generated internally

Complex Product Mixture · Products are burned and/or used as feedstock

Incineration

Plastic → Combustion chamber Excess Oxygen → Waste Gases (air emissions)

Figure 3. Simplified comparison of thermolysis processes. Pyrolysis (top) heats the plastic waste without oxygen, producing primarily a liquid output (pyrolysis oil) and, secondarily, a gas that is usually combusted. The pyrolysis oil can be burned or upgraded for repolymerization. Gasification (middle) heats the plastic waste with (typically) a reduced amount of oxygen to produce a gas which requires upgrading before use. Incineration (bottom) burns the plastic waste without requiring additional fuels, but the outputs cannot be re-made into plastic. Many minor variations of these processes exist.

Very generally, the low level of oxygen in gasification and pyrolysis differentiate these technologies from combustion (Figure 3). Both pyrolysis and gasification make use of the fact that in all situations when hydrocarbon polymers are initially heated (i.e., by an applied external heat source), a major fraction of the mass is released as a gas. Without oxygen, the gas will not combust. Crucially therefore, conditions are engineered to prevent combustion by applying heat but limiting oxygenation. Pyrolysis and gasification also operate at relatively low temperatures (ca. 500°C to 850°C) and are incorporated either as stand-alone reactors, or as a stage/processing parameter in more novel chemical recycling proposals (Wong et al., 2015).

All the gases produced by a gasifier originate from pyrolysis, however a reactor designed for gasification (a 'gasifier') encourages other chemical reactions inside it. To be precise, gasification is not defined by temperature, or the amount of oxygen that is allowed to enter the reactor, but is simply, as its name suggests 'the conversion of something into a gas'.

The finer details of how pyrolysis and gasification function is however far from simple, with gasification in particular frequently misunderstood and misrepresented in modern waste treatment proposals. A detailed explanation of gasification and pyrolysis is beyond the scope of this report, but information can be found in the following sources (Kaupp, 1984; Reed and Das, 1988; Rollinson, 2018; Rollinson and Oladejo, 2019).

The resulting products of gasification and pyrolysis are a cocktail of unburned and re-synthesised hydrocarbon molecules in a mixture of gaseous, liquid, and solid states. Product quality and operational stability is governed by complex and highly challenging chemical, physical and thermal inter-relations, making gasification and pyrolysis more akin to chemical processing plants than ordinary incinerators (Rollinson, 2018; and Rollinson and Oladejo, 2019).

Gasification

Gasification was optimised over one hundred years ago and found to be achievable only in highly specific reactor types fed only with woody biomass, charcoal or coal (Rollinson, 2018). In these specific cases, it can produce a gas (historically called 'producer gas') that is relatively rich in carbon monoxide (CO) and hydrogen (H_2). Methane steam reforming (a method of making hydrogen, usually from natural gas) also produces a gas of similar composition (known as 'synthesis gas/syngas'), which is a feedstock for plastic manufacture. This has led to the idea that gasification of plastics could be a method of chemical recycling.

Pyrolysis

The root of the word pyrolysis is 'loosening or changing by heat or fire'. It is however conventionally attributed to heating without oxygen in batch reactors. Known since antiquity for the production of useful chemicals such as methanol, acetone and creosote from wood, pyrolysis is an energy consuming (endothermic) process that is much cruder than gasification. It produces a much poorer quality gas that is overly rich in a complex mixture of hydrocarbons along with a higher and more complex liquid (oil/tar) yield (Rollinson and Oladejo, 2019).

Conversion to Plastic (P2P) by Pyrolysis and Gasification

The ultimate aim of pyrolysis and gasification for P2P (plastic to plastic chemical recycling) would be to use the oil and gas products as building blocks for new plastics. However, the nature of gasification and pyrolysis engineering makes it extremely difficult or even impossible to produce oil and gas outputs of the standard required for plastic manufacture. The subsequent repolymerisation stage also involves additional chemical processing and energy input.

Conversion to Fuel (P2F) by Pyrolysis and Gasification

The difference between P2P and P2F is the end use. In P2F, the products of pyrolysis and gasification are used as a feedstock for petroleum refining. This means that they will ultimately be combusted. This is why P2F cannot contribute to a circular economy for plastic waste: it does not produce new plastic.

It is important to recognize a distinction between close-coupled combustion of gasification and pyrolysis products and their later use as a fuel alternative to petroleum and its derivatives. In the former case, the outputs are quickly combusted within the same facility, with the heat either flared, or designated for electricity generation or to supplement some of the pyrolysis energy demands. To all intents and purposes, these facilities are identical to an incineration plant with energy recovery. When plastic-derived fuel is destined for later use, the re-formed fuel is not burned directly but is stored and often transferred off-site. Such fuels will still require additional treatment to meet much higher quality standards, for example when fed to internal combustion engines (Kalargaris et al., 2017; Wong et al., 2015).

Solvolysis/Liquefaction Technologies

Rather than depolymerisation by heat, various solvents have been used to 'loosen or change' the plastic waste in order to produce purified polymers, oligomers or monomers. Many of these processes also include multiple treatment stages, usually involving high pressures and temperatures in the region of several hundred bar and $100 \leq °C \leq 350$, and with the inclusion of catalysis (Al-Sabagh et al., 2016; Arturi et al., 2018; Sherwood, 2020). No clear consensus exists on how to categorise these alternative technologies; likely evidencing a combination of system complexity, process overlap, and, in some cases, intellectual property restrictions. Here we use a categorisation from Crippa et al. (2019).

Solvent-based Purification

This process seeks to dissolve or liquefy the plastic without damaging the polymeric structure. Often it is chosen for the separation of mixed plastics or the isolation of specific polymers from certain types of plastic composite. It is a multi-stage process involving the removal of dyes, impurities and contaminants followed by filtration, phase extraction, and precipitation of the polymer by an 'anti-solvent' (Sherwood, 2020). The choice of solvent has to be highly specific to a strictly homogeneous feedstock or target compound. Some degradation in product quality follows, meaning that the process is not 'cyclic'; and in this regard, it is more similar to mechanical recycling, since the product cannot cycle infinitely or fully replace virgin polymer (Crippa et al., 2019). Residual toxic contaminants can also remain in the product, and the disposal of spent process chemicals can be problematic (Sherwood, 2020). Practical feasibility remains unclear.

Solvent-based Depolymerisation

A variety of depolymerisation processes dissolve the plastic waste in liquid baths to produce oligomers and monomers. The bath consists of one or more of a variety of liquids, which give their name to the process: water (neutral, acid, or alkaline hydrolysis), methanol (methanolysis), glycol (glycolysis), ammonia (ammonolysis), and various amines (aminolysis), among others. The process is often facilitated by high temperature, pressures and/or catalysis, and adaptations such as hydrogenation and transesterification are used. Of all chemical recycling options, this is the most novel, and information on both product quality and energy expenditure from this category of technologies remains the most under-reported and unresolved.

2.3. Comparisons with Established Treatment Technologies

Apart from landfill and the technologies covered above, the options employed for the management of plastic waste are primarily mechanical recycling and incineration. This section provides brief comparisons of chemical recycling with these options.

Mechanical Recycling vs. Chemical Recycling

Mechanical recycling of plastic waste consists of a number of steps, including pre-sorting, crushing, washing, shredding, and extruding or pelletising of the feedstock. Then melting and physical reshaping can occur, often with the use of additives. These steps, while less energy-intensive than chemical recycling, nevertheless represent a significant energy input relative to the value of the plastic recyclate (Levidow and Raman, 2019). While mechanical recycling aims to replace virgin plastic in similar applications, the variability in quality and transfer of contaminants make closed loop recycling extremely difficult for some plastic waste, particularly packaging. Even with these intensive pre-treatment methods, impurities from both within the plastic structure and from external sources remain. For this reason, industry is currently seeking innovative washing concepts to remove contaminants, odours, labels and water-soluble compounds.

Whereas the objective of depolymerisation technologies is to break down plastic polymers into smaller molecules (monomers or oligomers), mechanical recycling aims to preserve the polymers. In practice, polymer length is generally shortened, resulting in a lower quality plastic than the original (Baytekin et al., 2013). This is known as 'downcycling' or 'open-loop' recycling as it limits the extent to which mechanically recycled polymer can replace virgin polymer; instead, the recycled plastic usually replaces alternative polymers with lower specifications. It is for this reason, and driven by ambitious recycling targets in many countries, that the far less mature chemical recycling concept is being touted (Quicker, 2019). In comparison with mechanical recycling however, chemical recycling suffers from greater novelty and process complexity, while still having the same obstacles of impurities within the feedstock.

Although mechanical recycling has its limitations, a strong argument exists that it is environmentally preferable to chemical recycling. This is because it has lower energy demands, resulting in a smaller carbon footprint, and produces fewer toxic byproducts.

Incineration

The simplest way to depolymerise plastics is to incinerate them (Quicker, 2019). In contrast with pyrolysis, which limits the available oxygen to produce a combustible gas, incineration is intended to achieve complete combustion of the feedstock. This results in ash, carbon dioxide (CO_2) and water vapour (H_2O). With mixed waste incineration, the ash can be highly toxic and despite more than a century of development, processing issues (like acid gas corrosion) remain. Notwithstanding these challenges, incineration is a destructive process, and the product molecules are energetically impractical as either fuels or building blocks for polymers. It does not therefore represent chemical recycling, so will not be discussed further in this assessment.

2.4. Synopsis

All engineering options for chemical recycling described in this report concern only the first (e.g. depolymerisation) stage of a two-stage destruction/restructuring process. This choice is not arbitrary, for the challenge of successfully applying chemical recycling lies in attaining and maintaining a plastic recyclate of sufficient quality and quantity such that it can be used effectively as a feedstock for repolymerisation or as an engine fuel. This is not easy. The product requirements demand highly stringent quality control, and when not attained, the resultant gas or oil is, at best, burnt. Consequently, the distinction between P2P and P2F is often not clear and attempts to conflate the two practices as chemical 'recycling' have been associated with claims of 'greenwash' (GAIA, 2019).

03.

CHALLENGES

:: **Low Viability and Lack of Data**

:: **Adverse Environmental Impacts**

:: **Energy and Carbon Intensity**

Plastic thermolysis has been studied experimentally since at least the 1950's and these lab-scale experimental results can be found in standard texts (Fifield and Haines, 2000). Efforts to chemically recycle plastics commercially can be traced back to at least the 1970s (Matsumoto et al., 1975; Porteous, 1975). Since then, and outside of some current media claims, the concept appears to have stagnated in terms of full-scale practical applications.

In order to address the technical challenges of thermolysis, adaptations have been proposed such as using a hydrogen atmosphere and/or catalysts. These variations create extra cost and problems, such as: 1. Difficulty of recovering spent catalyst. 2. Cost of catalyst and/or hydrogen. 3. Disposal or regeneration of spent catalyst (regeneration is energy intensive and creates additional waste byproducts). 4. Catalyst effectiveness declines as soon as the process starts as it gets clogged with plastic particles and surface sites get blocked by carbon deposition (Miskolczi et al., 2004; Lopez et al., 2017).

Experiments have also shown that chemical recycling is not simply a reversible process. When plastics are made to thermally decompose, hydrocarbon fragmentation produces molecules which are different to their component monomers (the 'building blocks' of plastic). For example, from relatively simple PP a high content of benzene, xylene, toluene, plus polycyclic aromatic hydrocarbons (PAHs) is formed (Williams and Williams, 1999). Similarly, with PVC, as chlorine is progressively removed, new carbon bonds are formed, creating aromatics such as indene, naphthalene, and alkylated naphthalenes (Scheirs and Karminsky, 2006). These components, along with many plastic additives (see Section 3.2), are hazardous to human health, meaning facilities would have to be regulated and managed to avoid potentially high risk situations both on and off site. Any amount of plastic that is profitable to process at a single facility would likely produce these chemicals in significant quantities during processing and storage.

3.1. Low Viability and Lack of Data

Many academic reviews on the chemical recycling concept were studied for this report. In all cases, the focus was on design 'innovation', with little or no emphasis given to critical analysis of operational performance (see for example: Butler et al., 2011; Panda et al., 2010; Rageart et al., 2017). Proof of successful status (and failures) remains largely undisclosed outside of laboratory trials, and for the interested party much will be found in theory but little or no substance given to practice. One logical inference from this is that the concept is entirely or largely a white elephant. There is strong evidence to support such a conjecture with regard to pyrolysis and gasification since these technologies have extreme challenges when fed with mixed or non-standard feedstocks and when attempting scale-up (see references contained in Rollinson, 2018 and Rollinson and Oladejo, 2019). Very briefly, the situation is summarised by Wong et al. (2015):

'While it is possible to produce satisfactory product yield and composition in laboratory scale, it will be a challenge for the industrial developers to maintain the desired result when scaling up polymer pyrolysis'.

The challenge that plastic poses to these technologies is described by Lopez et al. (2017) with respect to P2F:

'Although conventional pyrolysis might seem a convenient method to convert plastic solid waste to fuels, only fuels with low octane values and high residue contents can be obtained at moderate temperatures. For this reason the production of gasoline-range fuels is not efficient...'.

Experimental trials continue to be reported on P2F, such as Kalargaris et al. (2017), who produced oil from plastic pyrolysis and, despite very high processing temperatures of 900°C, the oil still contained a higher density, solid residue, oxygen and PAH concentration than diesel oil. The authors stated that plastic pyrolysis oil requires substantial upgrading before use in transport applications. As evidence of this, when fed to a stationary engine, the oil produced greater quantities of pollutants, with higher nitrogen oxides (NO_x), soot, CO and CO_2 emissions in comparison to diesel.

No evidence was found to support the current claims of technological efficacy of chemical recycling. In fact, independent reviews reported the contrary, extracts from which are as follows in chronological order: In 2011, it was observed that there was not even one successful and widely licenced plastic pyrolysis technology in operation (Butler, et al., 2011). In 2016, the status was described by Miandad et al., 2016:

'Temperature demand may increase up to 700 or 900 °C to achieve high quality products' [but] 'the gaseous products from pyrolysis are also not suitable as a fuel source and they need refining prior to use'.

The authors do not elaborate on why, but this likely refers to low product hydrocarbon quality, despite very high reaction temperatures. They state that the quality of oil is also compromised by the presence of pollutants and they identify how the endothermic nature of pyrolysis makes it a high energy-intensive process.

A year later, Lopez et al. (2017) concluded:

'Although plastic pyrolysis has been widely investigated, most of the studies are of a preliminary nature, with the level of development of pyrolysis units being in general limited'.

The most recent assessment was by Quicker (2019):

'Since there is currently no known pyrolysis plant in (semi)industrial operation that produces relevant amounts [of chemically recycled plastic] for further upgrading, e.g. in the chemical industry, no process examples can be presented here'.

As to the future potential of plastic gasification (Quicker, 2019):

'The fact is that even with essential and sophisticated pretreatment, an economic operation of such a plastic to fuel gasification plant cannot be expected'.

The problem is fundamental. Temperature and gas circulation for optimum reaction kinetics must be maintained while also moderating temperature to avoid secondary and tertiary synthesis of unwanted molecules. If the process operates

at a low temperature (and cost), then some lighter monomers will form but incomplete depolymerisation will occur. If the process operates at a higher temperature (and cost) to increase primary depolymerisation, it will increase the formation of heavier aromatic molecules **(Figure 4)**. Gasifiers were designed to manage this trade-off, but only with strictly controlled types of homogeneous feedstock, and not with something 'non-standard' such as plastic waste (Rollinson, 2018). To counter, multiple pre- and post-treatment stages are applied, incurring high costs and energy expenditure, despite which there has been a long history of failed attempts at scale-up with mixed waste or non-standard feedstocks (Quicker, 2019):

'Despite the negative experiences with alternative thermal treatment processes in the past, they are again praised as the solution, this time for plastic recycling'.
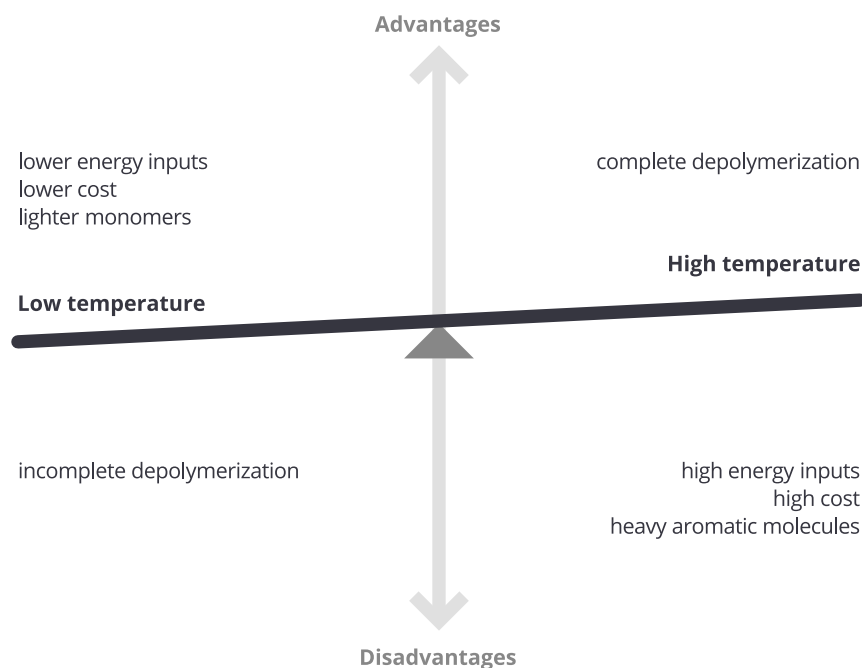

Figure 4. Pyrolysis process trade-offs. Low temperatures (and cost) fail to break down the plastic waste fully, while high temperatures produce unwanted chemical outputs.

With respect to the more novel chemical recycling options, there is also strong evidence that the concept is troublesome and inadequate: Due to the high operating costs, no industrial concepts of hydrogenation are known, while solvolysis is still in development, and catalytic oil bath depolymerisation has been trialled at pilot-scale with high energy expenditure and without satisfactory results (Quicker, 2019). Though there have been systems which have operated for a time at full-scale (such as Vinyloop ®), solvolysis chemical recycling remains currently a lab-scale or pilot-scale technology (Sherwood, 2020). A report by the European Commission recently described the situation (Crippa et al., 2019):

'With one of the few commercial processes (solvent-based PVC purification) recently shut down and most initiatives outlined above at lab scale or pilot level, it is evident that more resources and time investment are needed to improve the technologies'.

Even in the industrial sector, some have estimated that it is 'optimistic to consider that chemical recycling of waste plastics will be viable inside the next decade' (Doherty, 2019). Others suggest a period of 17 years until growth can be achieved (Closed Loop Partners, 2019). This may be too late to address the rapidly growing plastic crisis.

3.2. Adverse Environmental Impacts

Toxicants Inherent in Plastic

Petrochemical plastics are primarily composed of hydrogen and carbon, with significant quantities of oxygen and other chemical elements (known as heteroatoms). Various substances are added to modify the material's properties and production costs, such as antioxidants, flame retardants, plasticizers, lubricants and heat stabilizers. Plastic can also acquire toxic contaminants from its surroundings both during the production process and post-production (Rodrigues et al., 2019). The ultimate fate of these substances, through end of life treatment or unwanted migration, poses a risk of toxicity. Examples of plastic toxicants include: bisphenol-A (BPA), cadmium, benzene, brominated compounds, phthalates, lead, tin, antimony, and volatile organic compounds (VOCs).
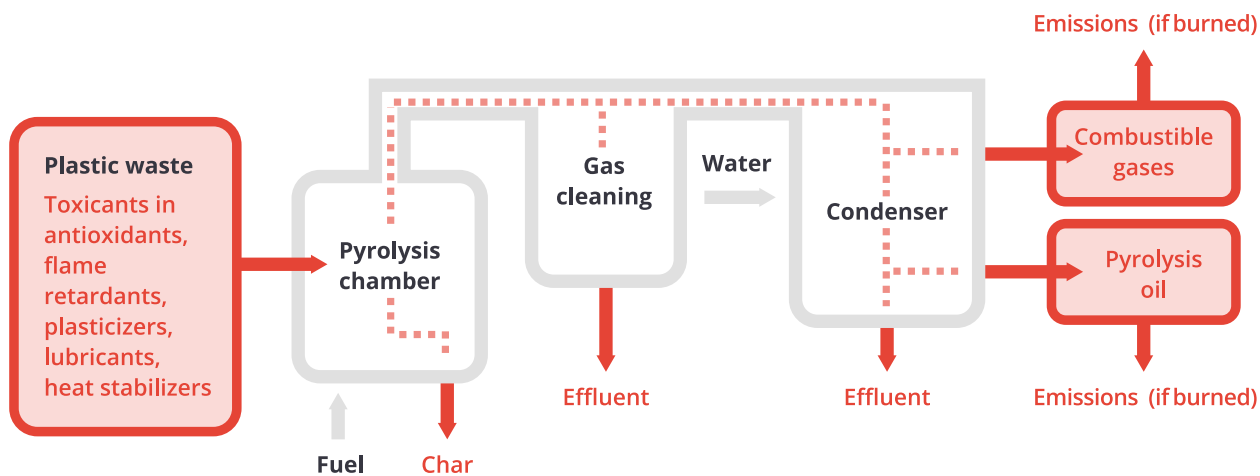
Toxicants include: phthalates, BPA, poly-brominated diphenyl ethers, toxic brominated compounds and poly-cyclic aromatic hydrocarbons (PAH), nitrated PAH (N-PAH), oxygenated PAH (O-PAH), and N/S/O – heterocyclic PAHs, As, Sb, Br, Zn, Cu, Hg, Cd, Dioxin, HCN

Figure 5. The sources and fates of plastic toxicants in pyrolysis. Many toxicants are present in the plastic waste; some, such as dioxins, are generated during the process. All are found in one or more of the outputs: pyrolysis oil, producer gas, air emissions, liquid effluent, and solid char.

Antioxidants, mostly used in plastic packaging, delay the degradation of polymers which may occur when exposed to light or other heat sources. They include: arylamines, phenolics and organophosphates such as BPA, tris-nonyl-phenyl phosphate, octylphenol, nonylphenol, and lead and cadmium compounds which are present in concentrations of 0.05 – 3% by mass (Hahladakis et al., 2018).

Flame retardants include: halogenated hydrocarbons, phosphate esters, antimony and aluminium oxides, halogenated phenols, brominated and phosphorus polyols; compounds like polybrominated diphenyl ethers (PBDEs), chlorinated paraffin (MCCP or SCCP), boric acid, and phosphorus compounds (TCEP or TCPP) which exist in concentrations of 0.7 – 25% by mass (ibid.).

Plasticizers, to improve the durability and elasticity of plastic, are present in concentrations of 10 – 70% by mass, and include hydrocarbon-based phthalates (DBP/BBP/DEHP/DHCP), adipates (DAH/HAD/DOA/HOA) and chlorinated paraffins (LCCP/MCCP/SCCP) (ibid.). Numerous studies have confirmed the migration of these substances from host plastic at ambient temperature, with greater migration levels at higher temperatures. This suggests that the use of recycling techniques, particularly higher-temperature technologies, increases the hazards of exposure. Plastics such as polystyrene and polyesters, nylons and polyurethanes can also decompose into monomers and oligomers at ambient to moderate (ca. 200°C) temperatures. These substances, like styrene, formaldehyde, ethylene, epoxy resins of BPA, and vinyl chloride, have also been identified as toxicants.

Process Emissions and Byproducts

 Sound engineering practice and regulatory requirements necessitate a comprehensive appraisal of both the direct operational hazards and the volume and toxicity of all products, byproducts, and spent process residues. One might therefore expect that studies on chemical recycling would focus on these risks as a matter of course. Surprisingly, this is not the case. This is also despite the fact that the presence of banned substances in the chemical recycling process and the subsequent need to comply with chemical hazard regulations has been identified as a primary cause of commercial plant closure and an important future consideration (Sherwood, 2020). Yet, when researching this report, no single, detailed review of the environmental impacts of plastic chemical recycling could be found in literature, supporting what has elsewhere been stated - that 'such knowledge still does not exist' (Crippa et al., 2019). On the concept of chemical recycling in general, a number of reviews have been published, but they invariably omit coverage of environmental impacts (for example: Butler et al., 2011; Lopez, et al., 2017; Panda et al., 2010; Wong et al., 2015). Only one review was found which made reference to environmental impacts, but here the information provided was old and/or unrelated (Ragaert, 2019). While this no doubt reflects an absence of information accessible to the authors, it does not explain a general lack of consideration given to reporting on emissions and byproduct toxicity in reports which describe both lab and pilot-scale experiments. One reason for this has recently been suggested as being due to a prevailing joint academic/industry competitive funding landscape that encourages a focus only on positive 'selling points' (Rollinson and Oladejo, 2019). Whatever the reason, chemical recycling hazard and toxicity is currently under-reported and inadequately assessed. Here we provide a first attempt at such an assessment.

Being an old technology, literature appraisals have been made on pyrolysis (though not specific to plastic feedstock), and it is well known to create toxic organic products (Idowu, et al., 2019). Gasification also has a wealth of literature that discusses its hazards, environmental impacts and risks (Rollinson, 2018). With these technologies, the formation of smoke, CO, and other hazardous substances are well documented. Specifically, from plastic feedstock, phthalates, BPA, poly-brominated diphenyl ethers, toxic brominated compounds and PAHs are produced, many of which are mutagens, carcinogens, and disruptive to respiratory or neurological systems (Verma et al., 2016).

In addition to the inherent toxicants in plastic, toxic gases such as hydrogen cyanide (HCN) and CO are produced, along with new, longer-chain, toxic molecules synthesised during low-oxygen thermolysis, thus increasing product toxicity with respect to the feedstock. Knowledge of these synthesis routes is well established and has been widely studied over the last 100 years (see Kiel et al., 2004; Vreugdenhil and Zwart, 2009). They produce what are collectively called tertiary or high-temperature tars, and these include nitrated PAH (N-PAH), oxygenated PAH (O-PAH), and N/S/O- heterocyclic PAHs, many of which are potent mutagens and carcinogens (Idowu et al., 2019). With plastics, Font et al. (2003) observed that the emission factors of mutagenic PAHs from pyrolysis of polyethylene increased markedly with temperatures above 700ºC. This relates to the trade-off between temperature, depolymerisation, and re-synthesis of unwanted molecules, as discussed in the previous section. The production of these synthesised toxicants is corroborated by other plastic pyrolysis studies (Garrido et al., 2016; Lopez, et al. 2017; Seo and Shin, 2002; Wong, et al., 2015).

There are also known routes for toxicants to accrue in the recyclate following solvolysis. Many of the solvents are themselves highly toxic, flammable or environmentally harmful, such as n-hexane, cyclohexane, and chloroform, and these become trapped in the recyclate (Sherwood, 2020). It is also common for polymer toxicants (such as phthalate esters) to transfer into the solvent, thus imposing additional costs due to the regulatory licenses required for these banned substances (ibid.).

Toxicity of the Resultant Gas, Oil, and Char

Due to systemic contamination of the outputs and industry's ongoing efforts to nevertheless market them as commercial goods, it can often be difficult to make a clear distinction between commodity products and byproducts. toxicants have the potential to be present in all three product phases: gas, liquid, and solid.

Heavy metals in plastic will not be destroyed during depolymerisation but must transfer to one of the outputs or be retained in the spent clean-up materials **(Figure 5)**. This impacts the potential use of these products and byproducts, e.g. subsequent high temperature combustion will release them as airborne particles or vapours, or concentrate them in solid residue. While it is possible for organic toxicants to be depolymerised and hence destroyed, they can equally pass through unaltered, or worse there is a high likelihood that the process will reform them into more toxic molecules. An environmental pathway (and cost) appraisal must include spent scrubbing and capture media from the air and waste-water pollution control equipment. Some examples are provided below:

In a study of mixed plastic pyrolysis, the product oil was found to contain antimony, bromine, zinc, calcium, chlorine, and sulfur, while the gas contained chlorine and bromine, with largest fractions of non-volatiles in the char (Miskolczi et al., 2013). The same research group found appreciable quantities of re-synthesised 'heavy' aromatic polymers in the products, even from substances such as polystyrene which is often claimed to produce monomers under pyrolysis conditions (Miskolczi et al., 2004).

Seo and Shin (2002) analysed the products of mixed plastic pyrolysis and found that the distilled product oil contained significantly more aromatics than engine fuel, amounting to 60-82% of the total hydrocarbons, and that the pyrolysis oils contained few of the branched hydrocarbons desirable by internal combustion engines. They described how many of the aromatics were polynuclear PAHs which were either directly toxic or which were precursors to more toxic substances.

An examination of PAH formation and chlorine distribution in the oil, gas, and char yields from PVC pyrolysis by Cao et al. (2019) found that the PAH content in pyrolysis oil was 'amazingly high' at 95.3%, while chlorine was retained in both oil and char at far greater concentrations than predicted.

Evangelopoulus et al. (2015) studied the pyrolysis of plastics from printed circuit boards and found that low temperature (≤ 700 °C) favours the formation of brominated compounds and BPA, while higher temperature (≥ 700°C) favours PAHs and benzofurans. Similar trends were observed by Iñiguez, et al. (2018), where greater PAHs, chlorobenzenes and chlorophenols were produced from pyrolysis, rather than the combustion of plastic waste.

The presence of inorganic and organo-bromine compounds in chemical recycling products was investigated by Ma et al. (2019) who found that single-step pyrolysis at temperatures of 350-600°C partitioned 25 to 61% of bromine into pyrolysis oil and 34 to 55% into pyrolysis wax, with a maximum of 15.9% bromine retained in solid residues. They described the presence of bromine in pyrolysis products as having 'significant negative impacts on their further application as fuel or chemicals'.

The development of technologies for reducing the formation or emissions of polyhalogenated aromatic hydrocarbons including dioxins and furans is subject to continuing research. There is also a common misperception that pyrolysis conditions negate or inhibit dioxin formation. An insight into the underlying pathways of high dioxin production during low oxygen thermolysis of plastics is evidenced from experiments with automotive shredder residue (ASR). It was clearly shown in a study by Maric et al. (2020) that higher plastic content in the feedstock led to greater production of dioxins, as also did lower reactor temperatures (673°C vs. 831°C) with consequently greater toxicity (TEQ) of the products. This is consistent with previous studies which showed that lower oxygen levels favour the production of both PCDD/Fs and PBDD/Fs and that their retention in the product fractions is also accentuated by the relatively low temperatures required for pyrolysis. Specifically, Rey et al. (2016) studied ASR thermolysis at a range of temperatures and oxygen levels, finding that the maximum TEQ for PBDD/F occurred at oxygen levels in the pyrolysis range and at temperatures of 600°C (rather than 800°C), with similar patterns of maximum TEQ observed for PCDD/Fs at a wider range and maximum PAHs emitted when oxygen levels were at zero. Elsewhere, during the pyrolysis of ASR by Anzano et al. (2017), due to high TEQ from dioxins and PAHs, it was stated that 'Based on these results, the use of solid residue as a fuel can be excluded'.

Chen et al. (2014) reviewed how dioxins form during the pyrolysis of plastics. Routes exist via transfer of trace levels from the feedstock into the outputs, high temperature gas phase formation from chlorinated precursors, and post-reactor de novo synthesis from particulates, inorganic chlorine, and catalytic metals (Mohr et al., 1997). Based on data from the now defunct Burgau plant and lab-scale experimentation with a synthetic plastic waste feedstock, Mohr et al. (1997) also found that 80% of the PCDD/F product was contained in the pyrolysis oil making its toxicity four times higher than that of the feedstock. They concluded that 'Pyrolysis oil should not therefore be used as an energy source'. Weber and Sakurai (2001) also found that PCDD/F's were formed in all experiments of plastic shredder waste pyrolysis. These studies found considerably higher ratios of PCDD/PCDF in comparison with incineration (corroborating other cited studies), and since more than 90% of the total TEQ was found in the pyrolysis oil and gas, they advised that this should not be condensed for further use.

Following a study of mixed and blended plastic pyrolysis, the resultant char was contaminated with heavy metals (cadmium, lead, zinc, copper, mercury, and arsenic) and classified as both hazardous and ecotoxic (Bernado et al., 2010). Solvent extraction was applied to try to clean up the product, but the metals remained in the char and the eluate (resulting liquid waste) had 'significant toxicity' due to the presence of acquired organics. According to the authors, their results 'underline the need for relating ecotoxicological chemical parameters, including inorganic and organic compounds in the hazard assessment of solid residues'.

Cleaning these toxicants from chemical recycling products can be extremely difficult, expensive, and will create additional toxic waste streams. In comparison to other plastic end of life methods, few works have evaluated this subject for chemical recycling technologies. Mølgaard (1995) determined that pyrolysis had the highest global warming and photochemical ozone formation impacts of all options, and the second largest solid waste impact after landfill.

3.3. Energy and Carbon Intensity

Plastic depolymerisation requires large energy inputs, so no chemical recycling technology can offer a net-positive energy balance, even if the products/byproducts are burned for energy (Baytekin et al., 2013). Promotional claims of sustainability cannot be reconciled with this fundamental fact. Part of the reason for these discordant claims may be that technology providers often omit the large amounts of auxiliary energy necessary for pre-treatment (sorting, cleaning, and shredding the plastic), and post-treatment product conditioning and clean-up – these are almost never taken into account in energy and cost audits (Vehlow, 2016). But this is only part of the story.

In theory, the Lower Heating Value (LHV) of plastic is relatively high, and from this superficial viewpoint, some research groups suggest that a plastic-to-fuel system can be sustainable (Joshi and Seay, 2019)[2]. Unfortunately, it is apparent that some authors under-report the high energy cost for pyrolysis and exhibit indifference towards the second law of thermodynamics, thus presenting the concept outside of what is physically possible[3] (see discussion by Rollinson and Oladejo, 2019). Interestingly, some studies also combine convoluted methodologies with literature values and theoretical extrapolations, while avoiding the simpler empirical test which would prove or disprove the matter, i.e. providing an actual demonstration. In a wider literature review, no evidence was found of a self-sustaining chemical recycling plant.

These misrepresentations are attributable in part to a misunderstanding of the true energy costs for pyrolysis (Reed and Gaur, 1997). It is not even widely admitted that continuous heat input is required for pyrolysis, though this is fundamental. For batch processes, heat demands are increased by the need to maintain temperature stability during loading and unloading, which impacts on the extent of 'cracking and vaporizing' during these operational periods. This manifests itself in the quality of depolymerised products, evident by whether the oil is black or clear, which in

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[2] Following personal correspondence with the editor, the original author confirmed that there were errors in the manuscript as published. A corrected paper was to have been published in the journal's March/April 2020 issue.

[3] The second law of thermodynamics applies to all universal interactions. It can be understood as that whenever there is energy transfer some quantity must always be lost to a system's surroundings (measured as 'entropy').

turn impacts the extent of post-processing that will be needed to create a useful recyclate, which of course would necessitate further energy inputs.

To make matters worse, a common misconception is that a plastic pyrolysis plant could be both self-sustaining and simultaneously produce feedstock for new plastics. This is easily refuted by simple logic: 1. If all of the pyrolysis plant's outputs were burned to make the process as close as possible to self-sustaining, then there is no circularity as no virgin plastic is being displaced. 2. If the pyrolysis oil and/or gas are to be used for reformulating plastic, there is very little energy density left in the waste products to heat the pyrolysis reactor and so it would need to use an external energy source to power the process.

Though it is rare to find reports which include energy balances on thermolysis chemical recycling systems, it is even rarer to find such assessments with respect to solvolysis. Sherwood (2020) stated that 'The electricity demand is too high for chemical recycling to compete with mechanical recycling… [And] start-up and maintenance costs are certainly higher'.

In terms of post-depolymerisation energy demands, two studies have recently illustrated how more processing is needed after what might be considered as 'primary' depolymerisation. Using industry standard components, over 53% of feedstock carbon would be lost in oil upgrading and 48% in gas upgrading (Mamani-Soliz et al., 2020; Seidl et al., 2020). These inefficiencies are on top of energy inputs for pyrolysis (which were excluded from the calculations) and so tend to quash any notion of P2F sustainability **(Figure 6)**. This is even before considering that whenever the products of depolymerisation are burned (as with P2F), equivalent amounts of CO_2 are emitted as if the plastic had been burned directly, thus meaning that the fossil-derived carbon has merely spent a small part of its existence as a plastic product.

When the recyclate is reformed in P2P, the additional and necessary energy demands of repolymerisation are also sizeable, but are again invariably absent from technology appraisals. Baytekin et al., (2013) stated that for each unit of fossil fuel used as plastic feedstock, an equivalent unit is used to provide the manufacturing energy. A more recent report identified the initial plastic resin production stage as being responsible for 61% of all greenhouse gas (GHG) emissions, with a further 30% associated with product manufacture, and with end of life emissions lowest of all (Zheng and Suh, 2019).
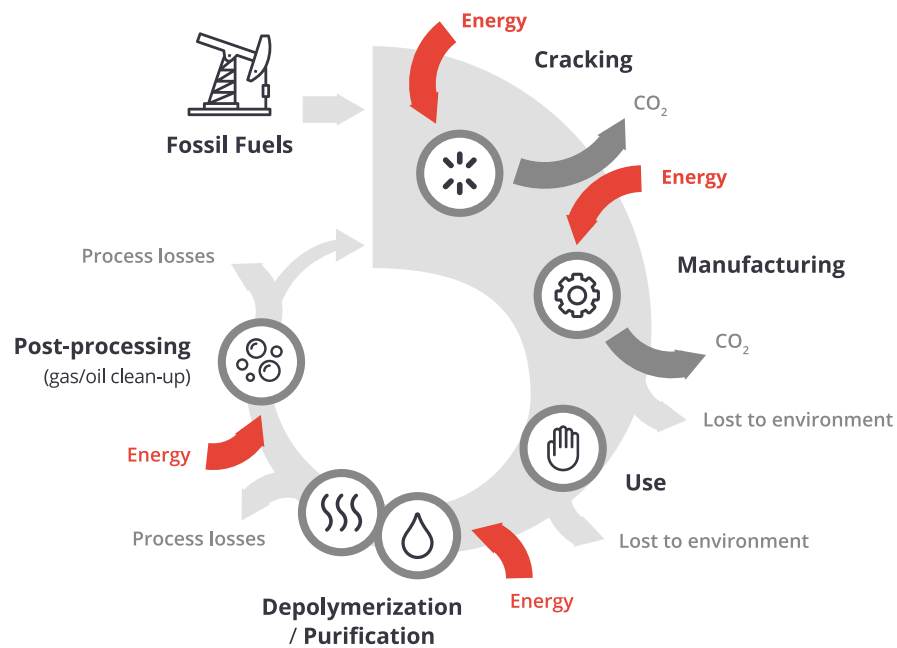
Figure 6. The leaky circular economy in plastic. Chemical recycling is billed as a way to "close the loop" and enable total recovery of plastic waste. In fact, the system is characterized by high energy inputs, process losses, and greenhouse gas emissions; very little of the original material can return to the economy as new plastic.

04.

SYSTEMS

PERSPECTIVE

S herwood (2020) recently provided the following long (and exhaustive) list of factors which are obstacles to the chemical recycling concept: policies and investment for waste collection and separation, product design, consumer choices, business models, resistance by established petrochemical markets, potential increase in complexity of the plastic waste market, greater expense of the recycled polymers, and in terms of technology status: 'The [in]ability to separate combinations of materials...With still much to be done to improve recovery rates of easier to recycle products'. It is interesting that the author identifies 'resistance by established petrochemical markets' as a constraining influence on chemical recycling system uptake. In fact, the technology is heavily promoted by corporate conglomerates including many from the petrochemicals industry. This has led to some criticism of seemingly altruistic associations such as the Alliance to End Plastic Waste, which has pledged to allocate $1.5 billion over five years to mitigate the problem of plastic waste, but include as their members major oil, gas and petrochemical corporations (Laville, 2019). Such scepticism is not helped by the oil and gas industry simultaneously predicting that petrochemicals are to be the fastest growing market over the next twenty years (BP, 2018). So, while industry is planning to greatly increase the use of petroleum for plastic production, the question is: can subsidising research into chemical recycling meet the scale of the problem that the same industry is creating?

 Based on these predictions and industry estimates of chemical recycling technology viability provided in this report, the continued pursuit of chemical recycling does not offer a pathway towards sustainability but rather a high likelihood of enabling at least a decade of more fossil fuel extraction. This is a very dangerous trajectory because it is estimated that fossil fuel combustion must be drastically cut back within the next decade in order to avoid existential threats from anthropogenic climate change (IPCC, 2018). On these timescales, it is highly questionable optimism to even consider the concept as a temporary stop-gap for plastic pollution until some better way can be found. Of course, an alternative option already exists, namely to implement the top tiers of the waste hierarchy: 'reduction' and 'reuse' strategies. These can be stimulated by governments simply legislating against single use and unnecessary plastics.

05.

CONCLUSIONS

This report has shown that chemical recycling is not the answer to society's problem of plastic waste. While such a solution may seem ideal, sound engineering practice and common sense appear to have given way to blind optimism in the pursuit of an impossible dream. In some cases, bold claims are being made about technologies that have been repeatedly found over the last one hundred years to be unfit for purpose. In other cases, even industry admits that more novel technologies have yet to be proven at any useful scale and are a long way from reality. On top of these technology failings are the multiple pathways to environmental and human toxicity, which have so far been under-assessed. Similarly, claims of 'sustainability' are widely put forward without satisfactory disclosure of high energy demands and despite the fact that the technology has a negative energy balance. What chemical recycling does offer, however, is a delusion that society can transition to sustainability without implementing the top tiers of the waste hierarchy. It represents a dangerous distraction from the need for governments to ban single use and unnecessary plastics, while simultaneously locking society into a 'business as usual' future of more oil and gas consumption.

We conclude with four findings:

:: Chemical recycling (both thermolysis and solvent-based) is not at present, and is unlikely to be in the next ten years, an effective form of plastic waste management. With the need to dramatically reduce global fossil fuel consumption, chemical recycling appears, in fact, to represent a dangerous distraction for a society that must transition to a sustainable future.

:: Multiple pathways to adverse environmental impact exist and these are grossly under-assessed. Managing these impacts will impose high costs and operational constraints on technology operators. For this reason, chemical recycling should be treated with extreme caution by investors, decision makers, and regulators.

:: Chemical recycling is energy intensive and has multiple intrinsic and ancillary energy demands which render it unsuitable for consideration as a sustainable technology. No chemical recycling technology can currently offer a net-positive energy balance, and there is no evidence to predict that this can improve in the foreseeable future.

:: Grossly inadequate reporting exists on the status of chemical recycling which, along with a lack of independent evidence on the technology, appears to have led to it being portrayed above and well beyond its capabilities. Much greater transparency on operational performance, energy balances, and environmental impact assessment must be provided as standard.

34

GLOSSARY, ABBREVIATIONS & REFERENCES

Glossary

Aminolysis – A depolymerisation process using amines as the solvent.

Ammonolysis – A depolymerisation process using ammonia as the solvent.

Anti-solvent – Substance that is added to a post solvent-based purification/depolymerisation mixture in order to precipitate the target compound from the solvent.

Depolymerisation – First stage of chemical recycling which breaks down plastic polymers into oligomers and monomers using a combination of heat, pressure, and/or solvents inside some form of reaction vessel.

Gasification – A chemical recycling process based on pyrolysis where oxygen is restricted so that the plastic thermally decomposes but does not combust. Optimised a century ago as a method of producing gas from coal, charcoal and woody biomass. Found to be highly sensitive and intolerant to other feedstock types, resulting in widespread commercial failures when fed with plastic or other mixed waste.

Glycolysis – Solvent-based depolymerisation process using glycols.

Hydrogenation – A chemical reaction process where the feedstock is treated with hydrogen.

Hydrolysis – Solvent-based depolymerisation process using water at high temperature and pressure, often with chemical additives to make the solvent acidic or alkaline.

Lower Heating Value (LHV) – Measure of the energy density of feedstock/fuel (in this case plastic), usually expressed as $MJ.kg^{-1}$. It represents the maximum amount of energy released per unit mass of plastic when completely combusted. Formerly known as 'net calorific value', it excludes energy recovery from the latent heat of vaporisation of product water.

Methanolysis – Solvent-based depolymerisation process using methanol.

Monomer – A basic single unit molecule that constitutes the building block of plastics. Examples include: ethylene, propylene, styrene, phenol, formaldehyde, ethylene glycol, vinyl chloride.

Oligomer – Small group of monomers. Smaller than a polymer.

Polymer – A large hydrocarbon molecule consisting of many parts. Often described as a 'macromolecule'. Plastics are polymers composed of smaller units called 'monomers'.

Polyolefin – A type of polymer formed from olefin (alkene) monomers. [An alkene is a hydrocarbon molecule with a double carbon bond].

Pyrolysis – A chemical recycling process in which heat is applied but oxygen is restricted so that the plastic thermally decomposes but does not combust. A complex cocktail of molecules can be produced in three product phases - oil, gas, and char. Product quality, depolymerisation and re-synthesis is dependent on many inter-connected physical, chemical and thermal factors.

Repolymerisation – The second stage of chemical recycling in which the products are re-manufactured into new plastic.

Solvolysis – A form of chemical recycling which utilises a range of feedstock specific solvents, often in multiple stages and with other process conditions such as catalysis, high temperature and high pressure. Sub-categorised into:

1. Purification – where the polymer is isolated from contaminants/composite material then collected by further processing and with the use of anti-solvents;

2. Depolymerisation – where the polymer is decomposed into monomers and oligomers.

Thermolysis – Decomposition ('loosening or change') by heat. Used for the first 'depolymerisation' stage of chemical recycling. Technologies include pyrolysis and gasification.

Transesterification – A chemical reaction that converts a type of hydrocarbon molecule called an ester into a different type of ester. The process is made to occur in the presence of alcohol and catalyst.

Abbreviations

ASR – Automotive Shredder Residue

BPA – Bisphenol-A

EPC – Ethylene-propylene copolymer

HDPE – High density polyethylene

LDPE – Low density polyethylene

PA – Polyamide

PAH – Polycyclic aromatic hydrocarbon

PBDD/F – Polybrominated dibenzo-p-dioxins and dibenzofurans

PCDD/F – Polychlorinated dibenzo-p-dioxins and dibenzofurans

PLA – Polylactic acid

PP – Polypropylene

PS – Polystyrene

PET – Polyethylene tetraphthalate

PU – Polyurethane

PVC – Polyvinyl chloride

TEQ – Toxic Equivalency Factor

VOC – Volatile Organic Compounds

References

Al-Sabagh, A.M., Yehia, F.Z., Eshaq, Gh., Rabie, A.M., ElMetwally, A.E. 2016. Egyptian Journal of Petroleum, 25, pp. 53-64.

American Chemistry Council. 2019. U.S. Chemical Investment linked to Shale Gas: $204 Billion and Counting (online). Accessed 7th January 2020. Available from: https://www.americanchemistry.com/Shale_Gas_Fact_Sheet.aspx

Anzano, M., Collina, E., Piccinelli, E., Lasagni, M. 2017. Lab-scale pyrolysis of the Automotive Shredder Residue light fraction and characterisation of tar and solid products. Waste Management, 64, pp.263-271.

Arturi, K.R., Sokoli, H.U., Søgaard, E.G., Vogel, F., Bjelic. 2018. Recovery of value-added chemicals by solvolysis of unsaturated polyester resin. Journal of Cleaner Production, 170, pp. 131-136.

Baytekin, B., Baytekin, H.T., Grzybowski, B.A. 2013. Retrieving and converting energy from polymers: deployable technologies and emerging concepts. Energy and Environmental Science, 6, pp. 3467- 3482.

Bernardo, M., Lapa, N., Gonçalves, M., Bardosa, R., Mendes, B., Pinto, F., Gulyurtlu, L. 2010. Toxicity of char residues produced in the co-pyrolysis of different wastes. Waste Management, 30, pp. 628-635.

BP. 2019. Energy Outlook 2018 edition (online). Accessed 8th January 2019. Available from: https://www.bp.com/content/dam/bp/business-sites/en/global/corporate/pdfs/energy-economics/energy-outlook/bp-energy-outlook-2018.pdf

Butler, E., Devlin, G., McDonnell, K. 2011. Waste polyolefins to liquid fuels via pyrolysis: review of commercial state-of-the-art and recent laboratory research. Waste Biomass and Valorisation, 2, pp.227-255.

Cao, B., Sun, Y., Guo, J., Wang, S., Yuan, J., Esakkimuthu, S., Uzoejinwa, B.B., Yuan, C., Abomohra, A.E., Qian, L., Liu, L., He, Z., Wang, Q. 2019. Synergistic effects of co-pyrolysis of macroaalgae and polyvinyl chloride on bio-oil/bio-char properties and transferring regularity of chlorine, Fuel, 246, pp. 319-329.

Chen, D., Yin, L., Wang, H., He, P. 2014. Pyrolysis technologies for municipal solid waste: A review. Waste Management, 34, 2466-2486.

Closed Loop Partners. 2019. Accelerating Circular Supply Chains for Plastics (online). Accessed 7th January 2020. Available from: https://www.closedlooppartners.com/wp-content/uploads/2020/01/CLP_Circular_Supply_Chains_for_Plastics.pdf

Crippa, M., De Wilde, B., Koopmans, R., Leyssens, J., Muncke, J., Ritschkoff A-C., Van Doorsselaer, K., Velis, C., Wagner, M. 2019. A circular economy for plastics – Insights from research and innovation to inform policy and funding decisions, (M. De Smet & M. Linder, Eds.). European Commission, Brussels, Belgium.

Doherty, J. 2019. Chemical recycling of plastics '10 years away' (online). Accessed 7th January 2019. Available from: https://www.letsrecycle.com/news/latest-news/chemical-recycling-of-plastics-10-years-away/

Evangelopoulos, P., Kantarelis, E., Yang, W. 2015. Investigation of the thermal decomposition of printed circuit boards (PCBs) via thermogravimetric analysis (TGA) and analytical pyrolysis (Py-GC/MS), Journal of Analytical and Applied Pyrolysis, 115, pp. 337-343.

Fifield, F.W., Haines, P.J. 2000. Environmental Analytical Chemistry (2nd Ed.). Blackwell Science: Oxford, p.261-262.

Font, R., Aracil, I., Fullana, A., Martin-Gullón, I., Conesa, J.A. 2003. Semivolatile compounds in pyrolysis of polyethylene. Journal of the Analytical and Applied Pyrolysis, 68-69. pp.599-611.

GAIA, 2019. Questions and Answers: Chemical Recycling (online). Accessed 7th January 2020. Available from: https://www.no-burn.org/chemical-recycling-fact-sheet/

Garrido, M.A., Font, R., Conesa, J.A. 2016. Pollutant emissions during the pyrolysis of flexible polyurethane foam. Waste Management, 52, pp.138-146.

Hahladakis, J.N., Velis, C.A., Weber, R., Iacovidou, E., Purnell, P. 2018. An overview of chemical additives present in plastics: Migration, release, fate and environmental impact during their use, disposal and recycling, Journal of Hazardous Materials, 344, pp. 179-199.

Hopewell, J., Dvorak, R., Kosior, E. 2009. Plastics recycling: challenges and opportunities, Philosophical Transactions of the Royal Society B, 364, 2115-2126. doi:10.1098/rstb.2008.0311

Hydrocarbon Processing 2019. Shell uses plastic waste to produce chemicals (online). Accessed 23rd December 2019. Available from: https://www.hydrocarbonprocessing.com/news/2019/11/shell-uses-plastic-waste-to-produce-chemicals

Idowu, O., Semple, K.T., Ramadass, K., O'Connor, W., Hansbro, P., Thavamani, P. 2019. Beyond the obvious: Environmental health implications of polar polycyclic aromatic hydrocarbons. Environment International, 123, pp.543-557.

Iñiguez, M.E., Conesa, J.A., Soler, A. 2018. Effect of marine ambient in the production of pollutants from the pyrolysis and combustion of a mixture of plastic materials. Marine Pollution Bulletin, 130, pp. 249-257.

IPCC, 2018: Summary for Policymakers. In: Global Warming of 1.5°C. An IPCC Special Report on the impacts of global warming of 1.5°C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change, sustainable development, and efforts to eradicate poverty (online). Accessed 8th January 2019. Available from: https://www.ipcc.ch/site/assets/uploads/sites/2/2019/05/SR15_SPM_version_report_LR.pdf

Joshi, C.A., Seay, J.R. 2019. Total generation and combustion emissions of plastic derived fuels: a trash to tank approach. Environmental Progress and Sustainable Energy. DOI: 10.1002/ep.13151

Kalargaris, I., Tian, G., Gu, S. 2017. Combustion, performance and emission analysis of a DI diesel engine using plastic pyrolysis oil. Fuel Processing Technology, 157, pp. 108-115.

Kaupp, A., 1984. State of the art for small-scale gas producer-engine systems, First published by the German Appropriate Technology Exchange (GATE), Reissued by the Biomass Energy Foundation Press: Golden.

Kiel, J.H.A., van Paasen, S.V.B., Neeft, J.P.A., Devi, L., Ptasinski, K.J., Janssen, F.J.J.G, Meijer, R., Berends, R.H., Temmink, H.M.G., Brem, G., Padban, N., Bramer, E.A. 2004. Primary measures to reduce tar formation in fluidised-bed biomass gasifiers. Final report SDE project P1999-012, ECN-C—04-014. Energy Research Centre of the Netherlands.

Laville, S. 2019. Founders of plastic waste alliance 'investing billions in new plants' (online). Accessed 14th February 2020. Available from: https://www.theguardian.com/environment/2019/jan/21/founders-of-plastic-waste-alliance-investing-billions-in-new-plants

Levidow, L., Raman, S. 2019. Metamorphosing waste as a resource: Scaling waste management by ecomodernist terms. Geoforum, 98, pp. 108-122.

Lopez, G., Artetxe, M., Amutio, M., Bilbao, J.,

Olazar, M. 2017. Thermochemical routes for the valorization of waste polyolefinic plastics to produce fuels and chemicals. A review. Renewable and Sustainable Energy Reviews, 73, pp. 346-368.

Ma, C., Yan, Q., Yu, J., Chen, T., Wang, D., Liu, S., Bikane, K., Sun, L. 2019. The behavior of heteroatom compounds during the pyrolysis of waste computer casing plastic under various heating conditions, Journal of Cleaner Production, 219, pp.461-470.

Mamani-Soliz, P., Seidl, L, G., Keller, F., Lee, R.P., Meyer, B. 2020. Chemisches Recycling – Aktueller Stand und neue Entwicklungen. In Holm O., Thomé-Kozmiensky, E., Goldmann, D., & Friedrich, B. (Eds.) Recycling und Sekundärrohstoffe, Band 13, Thomé-Kozmiensky Verlag GmbH, pp. 268 – 284.ntal Sciences, 35, pp. 701-708.

Maric, J., Vilches, T.B., Pissot, S., Vela, I.C., Gyllenhammer, M., Seemann, M. 2020. Emissions of dioxins and furans during steam gasification of Automotive Shredder Residue; experiences from Chalmers 2-4 MW indirect gasifier.

Waste Management, 102, pp.114-121.

Matsumoto, K., Kurisu, S., Oyamoto, T. 1975. Development of process of fuel recovery by thermal decomposition of waste plastics. International Conference on Conversion of Refuse to Energy, 1st Proc, Montreux, Switzerland, 3rd to 5th November.

Miandad, R., Barakat, M.A., Aburiazaiza, A.S., Rehan, M., Nizami, A.S. 2016. Catalytic pyrolysis of plastic waste: A review. Process Safety and Environmental Protection. 102, pp. 822-838.

Miskolczi, N., Bartha, B., Deák, G., Jóver, B. 2004. Thermal degradation of municipal solid waste for production of fuel-like hydrocarbons. Polymer Degradation and Stability, 86, pp.357-366.

Miskolczi, N., Ateş, F., Borosodi, N. 2013. Comparison of real waste (MSW and MPW) pyrolysis in batch reactor over different catalysts. Part II: Contaminants, char, and pyrolysis oil properties. Bioresource Technology, 144, 370-379.

Mohr, K., Nonn, Ch., Jager, J. 1997. Behaviour of PCDD/F under pyrolysis conditions. Chemosphere, 34 (5-7), pp. 1053-1064.

Mølgaard, C. 1995. Environmental impacts by disposal of plastic from municipal solid waste. Resources, Conservation and Recycling, 15, pp. 51-63.

Panda, A.K., Singh, R.K., Mishra, D.K. 2010. Thermolysis of waste plastic to liquid fuel: A suitable method for plastic waste management and manufacture of value added products - A world perspective. Renewable and Sustainable Energy Reviews, 14, pp. 223-248.

Porteous, A. 1975. An assessment of energy recovery methods applicable to domestic refuse disposal. Resources Policy, 284-294.

Quicker, P. 2019. Evaluation of recent developments regarding alternative thermal waste treatment with a focus on depolymerisation processes. In: Thomé-Kozmiensky and Thiel, S. (Eds): Waste Management, 9, Waste-to-Energy. Neuruppin: TK Verlag Karl Thomé-Kozmiensky, pp. 361-370.

Ragaert, K., Delva, L., Van Geem, K. 2017. Mechanical and chemical recycling of solid plastic waste. Waste Management, 69, pp.24-58.

Reed, T., Das, A., 1988. Handbook of Biomass Downdraft Gasifier Engine Systems, Solar Energy Research Institute: Colorado.

Reed, T.B., Gaur, S. 1997. The high heat of fast pyrolysis for large particles. In: Bridgwater, A.V., Boocock, J.D.G.B. (Eds.), Developments in Thermochemical Biomass Conversion Vol. 1, Blackie Academic and Professional: London, pp. 97-103.

Rey, L., Conesa, J.A., Aracil, I., Garrido, M.A., Ortuño, N. 2016. Pollutant formation in the pyrolysis and combustion of Automotive Shredder Residue. Waste Management, 56, pp.376-383.

Rodrigues, M.O., Abrantes, N., Gonçalves, F.J.M., Nogueira, H., Marques, J.C., Gonçalves, F.J.M. 2019. Impacts of plastic products used in daily life on the environment and human health: What is known? Environmental Toxicology and Pharmacology, 72, 103239.

Rollinson, A.N. 2018. Fire, explosion and chemical toxicity hazards of gasification energy from waste. Journal of Loss Prevention in the Process Industries, 54, pp.273-280.

Rollinson, A.N., Oladejo, J.M. 2019. 'Patented blunderings', efficiency awareness, and self-sustainability claims in the pyrolysis energy from waste sector. Resources, Conservation and Recycling, 141, pp. 233-242.

Scheirs, J., Kaminsky, W. 2006. Feedstock recycling and pyrolysis of waste plastics: converting waste plastics into diesel and other fuels, J. Wiley & Sons: London.

Seidl., L.G., Lee, R.P., Keller, R.P., Meyer, B. 2020. Beitrag des chemischen Recyclings zur Defossilierung von Rohstoffketten – Konzeptstudie für die nachhaltige Olefinerzeugung in Deutschland. In Thiel, S., Thomé-Kozmiensky, E., Quicker, P., Gosten, A. (Hrsg.): Energie aus Abfall, Band 17, Thomé-Kozmiensky Verlag GmbH, pp. 115-137.

Seo, Y-H., Shin, D-H. 2002. Determination of paraffin and aromatic hydrocarbon type chemicals in liquid distillates produced from the pyrolysis process of waste plastics by isotope-dilution mass spectrometry. Fuel, 81, pp. 2103-2112.

Sherwood, J. 2020. Closed-loop recycling of polymers using solvents. Johnson Matthey Technology Review, 64, pp. 4-15.

Spierling, S., Knüpffer, E., Behnsen, H., Mudersbach, M., Krieg, H., Springer, S., Albrecht, S., Herrmann, C., Endres, H-J. 2018. Bio-based plastics – A review of environmental, social and economic impact assessments. Journal of Cleaner Production, 185, pp.476-491.

Verma, R., Vinoda, K.S., Papireddy, M., Gowda, A.N.S. 2016. Toxic pollutants from plastic waste - a review. Procedia Environmental Sciences, 35, pp. 701-708.

Vahk, J. 2019. Joint briefing: Recycled carbon fuels in the renewable energy directive (online). Accessed 10th December 2019. Available from: https://zerowasteeurope.eu/wp-content/uploads/2019/04/NGO-joint-briefing-RCF.pdf

Vehlow, J. 2016. Overview of the Pyrolysis and Gasification Processes for Thermal Disposal of Waste In: Löschau, M. (ed), Air Pollutant Emissions from Combustion Processes and their Control, Vivis, TK Verlag. pp. 431-444.

Vreugdenhil, B.J., Zwart, R.W.R., 2009. Tar formation in pyrolysis and gasification, ECN-E—08-087. Energy Research Centre of the Netherlands.

Weber, R., Sakurai, T. 2001. Formation characteristics of PCDD and PCDF during pyrolysis processes. Chemosphere, 45, pp.1111-1117.

Williams, P.T., Williams, E.A. 1999. Fluidised bed pyrolysis of low density polyethylene to produce petrochemical feedstock. Journal of Analytical and Applied Pyrolysis, 51, pp. 107-126.

Wong, S.L., Ngadi, N., Abdullah, T.A.T., Inuwa, I.M. 2015. Current state and future prospects of plastic waste as source of fuel: A review. Renewable and Sustainable Energy Reviews, 50, 1167-1180.

Xu, Q., Yin, X., Wang, M, Wang, H., Zhang, N., Shen, Y., Xu, S., Zhang, L., Gu, Z. 2010. Analysis of phthalate migration from plastic containers to packaged cooking oil and mineral water, Journal of Agricultural and Food Chemistry, 58 (21), pp.11311-11317.

Zero Waste Europe. 2018. Hidden emissions: A story from the Netherlands – Case study (online). Accessed 23rd March 2020. Available from: https://zerowasteeurope.eu/wp-content/uploads/2018/11/NetherlandsCS-FNL.pdf

Zheng, J., Suh, S. 2019. Strategies to reduce the global footprint of plastics. Nature Climate Change, 9. pp.374-378.