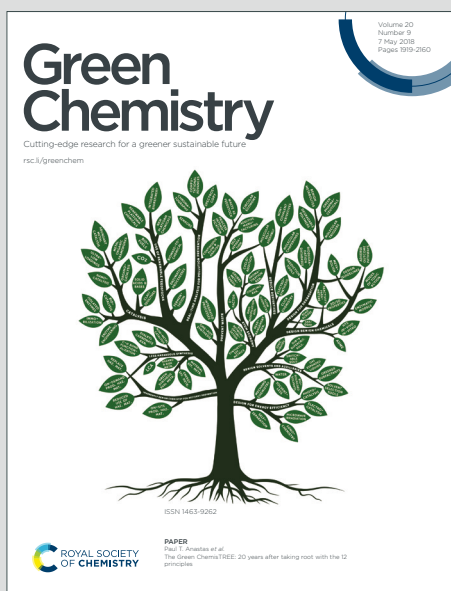


Green Chemistry

Cutting-edge research for a greener sustainable future

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: H. Luo, H. Tyrrell, J. Bai, R. Ibrahim Muazu and X. Long, *Green Chem.*, 2024, DOI: 10.1039/D4GC03127J.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

ARTICLE

Fundamental, Technical and Environmental Overviews of Plastic Chemical Recycling

Hui Luo,^{*a} Helen Tyrrell,^b Jingyang Bai,^b Rukayya Ibrahim Muazu^b and Xiangyi Long^{*b}Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

The accumulation of plastic waste is a severe environmental challenge worldwide. Although mechanical recycling methods are in place for plastics such as polyethylene terephthalate (PET), the physical and chemical properties are significantly compromised after a number of cycles, and eventually reach end-of-life and end up in landfill. Chemical recycling is a collection of emerging innovative technologies that transform plastic waste into base chemicals, monomers and feedstocks. This approach complements mechanical recycling, bridging the gap between waste management and the petrochemical industry. However, regards to the seven types of recyclable plastics, there is currently no clear overview of the suitable techniques. Therefore, we aim to provide a critical perspective of the suitability of different chemical processes towards recycling different types of plastics, by combining fundamental knowledge and research advancements in recent years, with an emphasis on assessing their environmental and economic impacts. Finally, based on the development status, we will highlight the current challenges and future opportunities on implementing chemical recycling technologies to meet the sustainability requirement of a climate neutral circular economy.

Introduction

As of 2021, the global production of plastic amounted to nearly 391 million metric tons, with over 90% derived from virgin fossil-based resources, making the plastic industry heavily reliant on fossil fuels.³ However, a mere 10 % of the total plastic volume collected is recycled, with just 2 % processed through closed-loop recycling, while the majority (79 %) is left to accumulate in landfills or other natural environments.⁵ The rapid growth of plastics production and the accumulated plastic waste exacerbate the triple planetary crisis of habitat loss, plastic pollution and greenhouse gas emissions.⁷ Thus, the effective management of plastic waste and their end-of-life treatment stands as a major challenge. Specifically, there is a growing interest in transitioning to a circular economy in which plastics will be efficiently and sustainably recycled back into the economy. Yet according to the Circularity Gap Report 2023 by the Circle Economy think tank, the current global circularity rate stands at only 7.2%.⁸ It means that we are still primarily operating within a linear economy, resulting in the loss of valuable raw materials. This urges us to work on global solutions, from preventing waste, to extracting more value out of this inevitable waste.

Recent attempts to mitigate plastic waste, such as plastic prohibitions and the Extended Producer Responsibility (EPR) programme, have made substantial progress. Although reducing demand is a valuable strategy to decrease waste, completely

eschewing plastics remains unfeasible due to their ubiquity and essentiality.⁹ On this note, the *Circular Plastics Alliance* aims to boost the EU market for recycled plastics, which covers the full plastics value chains and includes over 330 organisations representing industry, academia and public authorities.

Today, mechanical recycling is the most widely used process to recycle plastics. The mechanical recycling industry has the potential to reach 250 million tonnes by 2060, presenting a revenue opportunity of \$300-400 billion in today's terms.³ Via mechanical recycling, plastics waste is grinded, washed, extruded and pelletised to make recycled plastics. This process allows recycling plastics waste several times, however, with a progressive loss of properties. In addition, mechanical recyclability is restrained by their types and impurities introduced during usage and post-consumer phase. According to a 2015 report from the Environment Protection Authority (EPA), the plastics with the highest recovery rates are polyethylene terephthalate (PET, SPI code 1, 19.5%), high-density polyethylene (HDPE, SPI code 2, 10%) and low-density polyethylene (LDPE, SPI code 4, 5%). All other plastics, including polypropylene (PP, SPI code 5) and polystyrene (PS, SPI code 6), were recovered in less than 1%. The recovery rate for polyvinyl chloride (PVC, SPI code 3) and other plastics (SPI code 7) were effectively zero.¹⁰ However, more recent data shows the recycling rate has grown significantly in the past few years. For example, VinylPlus reported 813,266 tonnes of PVC waste were recycled within their framework in 2022, representing around 27% of the total PVC waste generated in the EU-27, Norway, Switzerland and the UK.¹¹

^a School of Mechanical Engineering Sciences, University of Surrey, Guildford, UK, GU2 7XH Email: hui_luo@surrey.ac.uk

^b Department of Chemical Engineering, Imperial College London, London, UK, SW7 2AZ

Supplementary Information available on life-cycle assessment studies included in this review. See DOI: 10.1039/x0xx00000x



ARTICLE

Table 1 A summary of the main types of recyclable plastics, their Society of the Plastics Industry (SPI) code, applications and recovery rate by mechanical recycling in 2015.^{10, 12, 13}

Plastic type	SPI	Structure	Applications	Recovery rate (by mechanical)
PET	1		Disposable bottles for drinks, medicines and many other consumer products	19.5%
HDPE	2		Durable containers, such as milk jugs or detergent bottles	10%
PVC	3		Piping, cables, garden furniture, carpet, clinical IV bags and tubing	~ 0%
LDPE	4		Manufacturing various containers, computer components, plastic bags or wraps	5%
PP	5		Plastic furniture, vehicle parts, reusable food containers or first-aid products	< 1%
PS	6		Packaging materials, CD/DVD cases or insulation foam	< 1%
Others (e.g. Nylon, PLA)	7		Nylon: fabrics, carpet, fisher net PLA: barriers films, food containers, 3D printing filaments	~ 0%

Chemical recycling, on the other hand, is a process that, through the application of heat, chemicals, or catalytic agents, converts the plastic polymer chains into oligomers, monomers or other basic chemicals (such as carbon monoxide, carbon dioxide, methane, and hydrogen) prior to further reprocessing into monomers/polymers.¹⁴ Unlike mechanical recycling which requires highly segregated feedstocks through intensive sorting and reprocessing, some of the chemical recycling technologies are largely nonselective and have higher tolerance to feedstock contaminants, hereby saving time and additional costs associated with plastic pre-treatment.^{15, 16}

Complementary to mechanical recycling, this process offers the possibility to transform hard-to-recycle or end-of-life plastics waste into petrochemical equivalent feedstocks for virgin plastic production. This prevents this type of waste from being sent to incineration or landfill, which requires extensive downstream gas cleaning due to the production of toxic dioxins during operations,¹⁶ bridging the gap between waste management and the petrochemical industry. It is generally understood that chemical recycling of plastics like PET may be less environmentally favourable than mechanical recycling. However, recent studies suggest that directly comparing



chemical recycling methods to mechanical recycling is now considered obsolete.¹⁷ Hence, the combined utilisation of multiple end-of-life (EoL) management of specific plastic waste stream is currently being employed across various plastic waste management systems.^{18, 19}

However, compared to mechanical recycling, the chemical recycling development is still at early stages. According to Plastics Europe-Circularity, out of 29.5 Mt post-consumer waste collected in the EU27+3, <0.1Mt was chemically recycled, compared to 9.1 Mt sent to mechanical recycling plants.³ This is mainly due to the more complex chemical reaction process and sizable energy input. Despite this, according to a graph from Holland Circular Hotspot, based on data from Nexant/Technip Energies (NexantECA, 2021),²⁰ chemical recycling is projected to grow significantly in the next few decades (Figure 1). Therefore, research and innovation efforts in both academia and industry are looking to develop sustainable and energy-efficient chemical recycling processes.

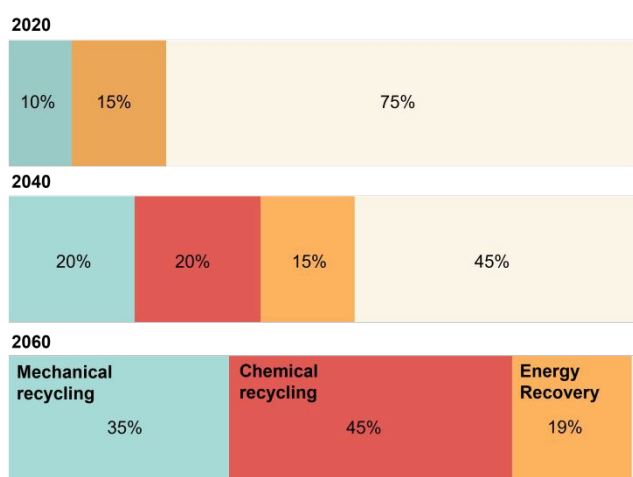


Figure 1 Plastic recycling outlook based on data from Nexant and Technip Energies. The percentage of plastics fall out of mechanical recycling, chemical recycling and energy recovery is sent for landfill (with leakage to nature). Reproduced from ref¹⁴ with permission from Holland Circular Hotspot, copyright 2023.

Chemical recycling can be broadly categorised into three main technologies including depolymerisation (solvolysis), pyrolysis and gasification. Solvolysis turns waste plastic into monomers that can be re-polymerised to produce virgin plastics, while pyrolysis and gasification create recycled intermediate substances such as pyrolysis oil or syngas to be used as precursor feedstock for monomer chemical synthesis. Depending on the chemical structure of the plastic polymer chain and the desired reaction products, different chemical recycling techniques, reaction conditions, catalysts and reagents are being developed to maximize the resource efficiency and minimize energy consumption. Therefore, in this tutorial review, we aim to provide a recommendation of the suitability of chemical processes towards recycling different types of plastics, with an emphasis on assessing their economic and environmental impact. Finally, based on the development status, we will highlight the current challenges and future opportunities in implementing chemical recycling technologies.

Poly(ethylene terephthalate) – SPI code 1

View Article Online
DOI: 10.1039/D4GC03127J

Polyethylene terephthalate (PET) is a low cost, light-weight thermoplastic polyester that displays good durability towards heat and chemicals, high moisture and gas barrier properties and has excellent optical clarity.²¹ It's ubiquitous use in consumer food and drinks packaging, in the form of bottles, trays and films, as well as fibres for textiles results in vast amounts of plastic waste globally. Whilst 60% of PET bottles are currently collected for recycling in Europe, a standardised method for collecting other streams of PET waste has not been established. This contributes to the disposal of 5781 kt of PET waste to landfill and the environment in Europe alone.²² The durable, non-biodegradable nature of PET plastic means that recycling is necessary to tackle the mass accumulation of waste generated.

The production of PET is a multi-step process involving an esterification reaction between terephthalic acid and ethylene glycol to form bis(hydroxyethyl terephthalate) (BHET), followed by polycondensation of BHET in the presence of antimony-base catalysts such as Sb_2O_3 and $Sb(OAc)_3$. Until terephthalic acid became a readily available starting material, dimethyl terephthalate was used in a transesterification reaction with ethylene glycol.²¹ Typically, the starting molecules used to make PET are obtained from petrochemical sources. Companies such as Coca Cola are increasing their efforts to incorporate bio-derived materials into the production of PET drinks bottles. In 2009, Coca Cola released the 30% bio-based PlantBottle™ where petrochemical-derived ethylene glycol was substituted by sugarcane-derived ethylene glycol.^{23, 24} Coca Cola have since produced a 100% bio-based prototype and aims to replace all oil-derived PET with recycled and renewable PET by 2030 in Western Europe and Japan. Whilst the switch to biomass-derived monomers offers a pathway to more sustainable packaging and fibres, it will not solve the problem of tackling the masses of non-biodegradable PET waste accumulated globally. Therefore, it is important that research efforts continue to focus on both sustainable production and recycling of PET.

Mechanical recycling is a common industrial method to convert PET waste into new products due to its simplicity and low-cost. Unfortunately, the desirable properties of virgin-PET are not retained during mechanical recycling. Consequently, only limited amounts of recycled PET can be re-introduced into the plastic bottle production process.²⁵ This results in the majority of PET being downcycled to lower value products, such as carpet fibres, which cannot enter the recycling loop again.²⁶

Alternatively, a chemical recycling approach could address the limitations of current mechanical methods. Using solvolysis, polyester C=O bond can undergo nucleophilic attack to enable the complete breakdown of the polymer chain to reform the initial monomers, oligomers or other useful small molecules. In a closed-loop recycling scenario, the monomers or oligomers would be re-introduced into the production process of virgin-grade PET. Various chemical recycling reactions can be applied depending on the desired products Figure 2. Various solvolysis approaches including hydrolysis, glycolysis and methanolysis will enable the recovery of



feedstock molecules that are suitable for direct addition into the PET production process.

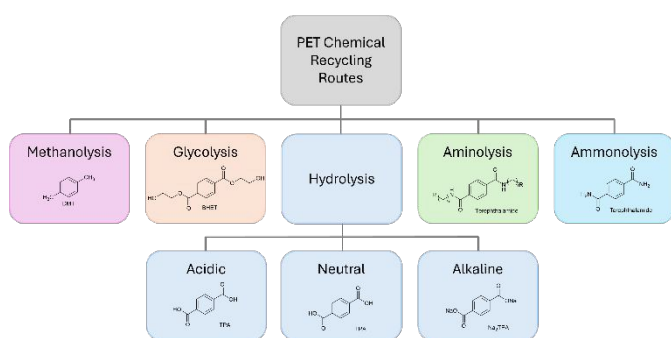


Figure 2 Common PET chemical recycling routes and the associated main products.

The hydrolysis of PET can be performed under neutral, acidic or alkaline conditions. Generally, neutral hydrolysis occurs in water between temperatures of 200–300 °C and 1–4 MPa to yield TPA and EG with small amounts of the TPA and EG monoester. A large excess of water is required for the hydrolysis; often mass ratios of PET/water up to 1:12 are used. Conducting hydrolysis at temperatures above 245 °C, where PET is in the molten state, has been found to accelerate the depolymerisation.²⁷ This is done in the presence of metal salt catalysts based on Zn, Sb and Mn. Whilst the poor solubility of TPA in water facilitates precipitation and easier separation, impurities from the process also precipitate alongside it. As a result, additional costly purification steps are required to ensure high purities of the monomers.²⁶

Acid hydrolysis is commonly performed in concentrated H₂SO₄ (> 87 %) at lower temperatures compared to neutral hydrolysis (< 150 °C) and yields EG and TPA.²⁸ Whilst this system doesn't require a catalyst, it is highly corrosive and the recovery of high purity EG from the reaction mixture is challenging. Additionally, the use of highly concentrated acid poses safety concerns and a high cost of recovering the acid.²⁹ On the other hand, alkaline hydrolysis requires less-concentrated NaOH or KOH (< 20 %) to give yields of up to 100% EG and disodium or dipotassium terephthalate. This route is often associated with longer reaction times (3–5 hr) and higher reaction temperatures (> 200 °C).²⁹ After the depolymerisation, acidification of the reaction mixture enables precipitation and separation of TPA.²⁶

Alternatively, methanolysis involves the depolymerisation in the presence of methanol to form EG and dimethyl terephthalate (DMT), an alternative to TPA for PET production. Common reaction conditions require 180–280 °C with pressures of 2–4 MPa in the presence of Zn(OAc)₂.²⁶ This method is being used industrially by Eastman, where production began at their first operational plant in Tennessee, US earlier this year and is estimated to reach 110,000 tonnes/year processing capacity. Additionally, Loop Industries recently announced that €35 million of funding will go towards the global rollout of their Infinite Loop™ technology based on methanolysis depolymerisation.^{28, 30, 31}

Glycolysis has gained popularity for chemical PET recycling due to the ease of recovering BHET using milder reaction conditions than hydrolysis processes. Obtaining BHET is advantageous as it can be re-

introduced into the PET production process at the second step, this enables the first esterification reaction between TPA and EG to be bypassed.^{28, 32} The glycolysis process involves combining PET with an excess of a glycol. In ethylene glycol, the depolymerisation proceeds around the boiling point (~200 °C) and atmospheric pressure. Despite the requirement of an additional distillation step to separate the excess glycol, the separation of the glycol-based reaction mixture is much easier compared to the separation of acidic or basic reagents used in hydrolysis.³³ Glycolysis can occur without the presence of a catalyst but at the detriment of longer reaction times (< 5 h) with lower BHET yields.³⁴ Therefore, great research efforts are being made to develop efficient catalysts to increase the efficiency of this process on an industrial scale. Earlier studies identified that metal salt catalysts, such as Zn(OAc)₂^{35, 36} facilitate the glycolysis to BHET, with more recent studies demonstrating BHET yields up to 80% after a reduced time of 1h on a lab scale.³⁷ Concerns over the separation and environmental impacts of metal salt catalysts has led researchers to explore more “green” catalysts consisting of ionic liquids or deep eutectic solvents. These systems offer benefits such as low volatility, high stability, tunable properties and easier separation but are required in larger amounts and are more costly in comparison.³⁸

Whilst most chemical recycling methods focus on the recovery of monomers or oligomers for re-processing into PET, other methods such as ammonolysis or aminolysis have been explored for the production of TPA and EG fine chemical derivatives. Ammonolysis and aminolysis involve depolymerisation of PET using liquid ammonia and primary amines respectively. Ammonolysis results in the formation of terephthalamide and EG, whereas aminolysis forms di-amines of TPA and EG. These reactions occur in milder conditions (< 100 °C) due to the increased nucleophilicity of amines compared to alcohol reagents in alcoholysis. However, ammonolysis and aminolysis methods use expensive, toxic reagents and has only been demonstrated at lab-scale so far.²⁵ Alternatively, high-temperature hydrolysis using steam pyrolysis can also allow the recovery of TPA. EG cannot be recovered via this route as it decomposes into gases such as CO and CH₄. As a result, this process is not commonly used on an industrial scale due to the variety of products formed and the associated separation costs. However, this option could be particularly suitable for chemical recycling of highly contaminated PET waste streams.^{29, 39}

Overall, the costs of the various chemical recycling reactions are estimated to be much higher compared to mechanical recycling. This is because chemical recycling processes require significant energy and/or chemical inputs plus any additional PET waste processing and purification steps to achieve high yields. The knowledge surrounding the tolerance of these processes towards coloured PET and contamination found in waste streams is still fairly limited. Studies by Aguado *et al.* demonstrated that alkaline hydrolysis is more tolerant towards industrial PET waste compared to glycolysis treatment.⁴⁰ Alkaline hydrolysis and glycolysis methods were applied to both virgin-PET samples and PET-rich (>90%) industrial waste samples containing highly coloured PET and small quantities of other plastics, such as polyolefins. Whilst the yields of depolymerisation products decreased when applying real PET waste in both processes, the alkaline hydrolysis enabled the recovery of TPA with > 90 % yields in all cases, compared to > 77 % BHET yields for glycolysis. Similar



studies by Barredo and López-Fonseca on industrial PET waste recycling via alkaline hydrolysis and glycolysis respectively yielded similar findings.^{32, 41} Importantly, Barredo *et al.* demonstrated that TPA recovered from alkaline hydrolysis does not retain the colourants and pigments found in coloured PET waste streams.⁴¹ Despite requirements for highly pure PET waste streams, glycolysis is the preferred commercial route for PET chemical recycling. A number of global chemical companies, such as Dupont and Eastman Kodak, currently operate glycolysis of PET on an industrial scale.⁴² Unfortunately, complex mixed plastic waste streams are not compatible with the processes mentioned in this section as the breakdown occurs at the C=O polyester bonds that are absent in other types of plastics. Therefore, pre-sorting of waste to create PET-rich waste streams with minimal contamination is crucial for widespread application of these chemical recycling approaches.²⁵ Despite these uncertainties, it is estimated that chemical recycling *via* depolymerisation could reach a capacity of 350kt per year by 2025.²²

Polyolefins (HDPE, LDPE, PP and PS) – SPI code 2, 4, 5, 6

Polyolefins are a group of thermoplastic polymers comprised of long, linear heat responsive hydrocarbon chains. They include HDPE, LDPE, PP and PS, which are the most popular and widely used synthetic plastics, representing about two-thirds of all post-consumer plastic waste. The application of PE and PP comprises around 80% of all synthetic plastic.¹³ Due to their moldability, durability and low price, they have been widely used in various applications (**Table 1**). Polyolefins only consist of saturated C-C and C-H bonds, which are highly resistance to chemical functionalisation or degradation due to their strong bond strength. Although the aromatic rings in PS are easily reacted electrophilically, its polymer backbone is identical to that of polyolefins. Therefore, unlike the more reactive carbonyl-containing linkages in polyesters, polyamides, and polyurethanes, they are not easily degraded by chemical methods (such as solvolysis) or enzymatic processes.^{43, 44}

Pyrolysis is one of the main processes for chemically recycling polyolefins, through thermal decomposition of the long polymer chains with less or absence of oxygen at elevated temperatures (300–900 °C) to produce smaller and less complex molecules in an inert atmosphere.^{45, 46} **Figure 3** shows pyrolysis of polyolefins and the main products, which includes alkanes, alkenes, aromatics such as benzene, toluene and xylenes (collectively known as BTX) and styrene. This has been discussed in more detail in the Section of *Liquid products*. The liquid product can be used as fuel but can also be the source of valuable chemicals. Styrene is in demand to make new polystyrene. Alkanes and alkenes can be used to make benzene, which is a key building block in many chemical syntheses.

Pyrolysis has been extensively studied in a variety of reactor geometries and experimental setups, ranging from micro-pyrolyzers⁴⁷ and thermogravimetric analysers (TGA)⁴⁸ for kinetics studies, to laboratory-scale batch reactors,⁴⁹ semi-batch reactors^{50, 51} and fixed bed reactors.^{52, 53} Additionally, medium and large-scale equipment, especially fluidised bed reactor,⁵⁴ have been used primarily for industrial applications. Batch and semi-batch reactors

are often employed in laboratory settings because of their simple design and operation. Moreover, these types of reactors offer flexibility in the amount of plastic and particle sizes making them more comparable to industrial conditions.⁵¹ Semi-batch reactors, with a carrier gas, typically utilise zeolites to study catalytic pyrolysis of PP^{55, 56} and PE,⁵⁶ as well as the thermal cracking of PS.^{57, 58} Batch reactors have been used to investigate the impact of different atmospheres (N₂ vs. H₂) on the pyrolysis of various plastics, including PE and PP,^{59, 60} and the conversion of PS.^{61, 62} Analysing these different studies indicates that the configuration of the reactor greatly affects the pyrolysis of plastics. Depending on whether a catalyst has been involved in the process, pyrolysis can be divided into thermal pyrolysis and catalytic pyrolysis.

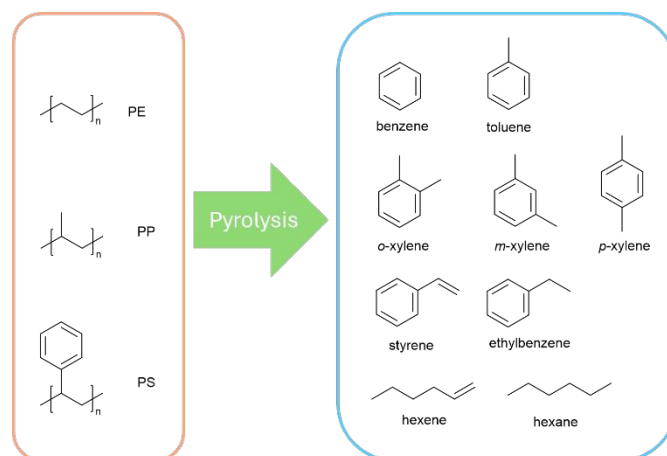


Figure 3 Common products from polyolefin pyrolysis.

Thermal pyrolysis

Thermal pyrolysis is a cost-effective and simple technique for processing polyolefins.^{47, 48} Apart from the reactor configuration which has been discussed above, temperature is one of the most crucial parameters in pyrolysis and is also one of the most extensively studied operational variables.⁴⁹ This parameter has the greatest impact on the thermal cracking of plastics, thus significantly influencing the distribution of pyrolysis products. A common observation in studies on plastic pyrolysis is the advantageous oil yield at lower temperatures.⁵⁰⁻⁵³ Conversely, with rising temperatures, gas production increases, predominantly arising from the further breakdown of liquid products at elevated temperatures. However, it has been noted that at sufficiently low temperatures, the liquid yield increases as the temperature rises (from 250 °C to 300 °C for pyrolysis of PE and PP), thus restraining the cracking liquid products.⁵⁴ This is due to that the decomposition reactions of plastics are not thermodynamically favourable, resulting in lower conversion rates at lower temperatures. Hence, when energy efficiency is a priority, low temperatures with reasonable liquid yields are preferable in order to reduce energy costs.

Catalytic pyrolysis



Table 2 Summary of plastic pyrolysis catalysts in this review.

Catalyst type	Examples	General characteristics
Zeolite	HZSM-5, HY, HUST, SBA-15, and MCM-41	Producing higher aromatics and gasoline-range hydrocarbons
FCC	/	Negligible cost Producing gasoline range hydrocarbons and light olefins
Metal oxides	ZnO, MgO, CaO, and Fe ₂ O ₃	Some are effective, cheap, and sustainable Promoting the cleavage of C-C bonds and suppressing undesirable side reactions
Metal-modified catalysts	Metal loaded Al ₂ O ₃ and ZSM-5	Suitable loading can improve catalytic efficacy in the pyrolysis process
Other novel catalysts	Carbon materials, and clays	Low cost, and special structure Having excellent potentials to get different target products

In the catalytic pyrolysis of plastics, a variety of catalysts have been employed to enhance the target reactions, reduce the reaction temperature and time, improve the product quality, and increase the process efficiency.⁵⁵ **Figure 4** shows the catalytic pyrolysis mechanism over a typical zeolite catalyst, HZSM-5. Apart from the random scission mechanism of C–C bonds in the thermal pyrolysis, the chain scission also initiates on the acidic sites of the zeolite, which involves random and end-chain scission and carbocation reaction. The carbonium ion is created in the long-chain radical because the hydrogen is extracted by the HZSM-5 catalyst. The secondary reactions happen afterwards, including cyclization and aromatization, Diels-Alder reaction, and isomerization, and are promoted because of the HZSM-5 existence. The choice of catalysts is influenced by factors such as the type of plastic feedstock, desired product distribution, and economic feasibility. Some widely used catalysts have been summarised in **Table 2** and discussed further below.

Zeolite and fluid catalytic cracking (FCC) catalysts

Zeolites, particularly those with high surface area and pore volume, have been extensively investigated due to their acidic sites and shape-selective properties, which promote the cracking of large hydrocarbon molecules into smaller, more desirable compounds.^{56–59} Compared to other catalysts for plastic pyrolysis, zeolites have the advantage of producing higher content of aromatics.⁶⁰ There are two groups of zeolites for plastic pyrolysis: microporous zeolites, including HZSM-5, HY, HUST, etc, and mesoporous zeolites, including SBA-15, MCM-41, etc.⁶¹ The acid sites are the key to pyrolysis. There are two types of acid sites in the zeolites, namely Lewis and Brønsted acid sites, as the proton donors. The number of Brønsted acid sites is decided by the ratio of Si/Al in the framework.⁵⁶ The Lewis acid sites

can determine the content of aromatic and alkene chemicals in the pyrolysis product.^{62, 63} DOI: 10.1039/D4GC03127J

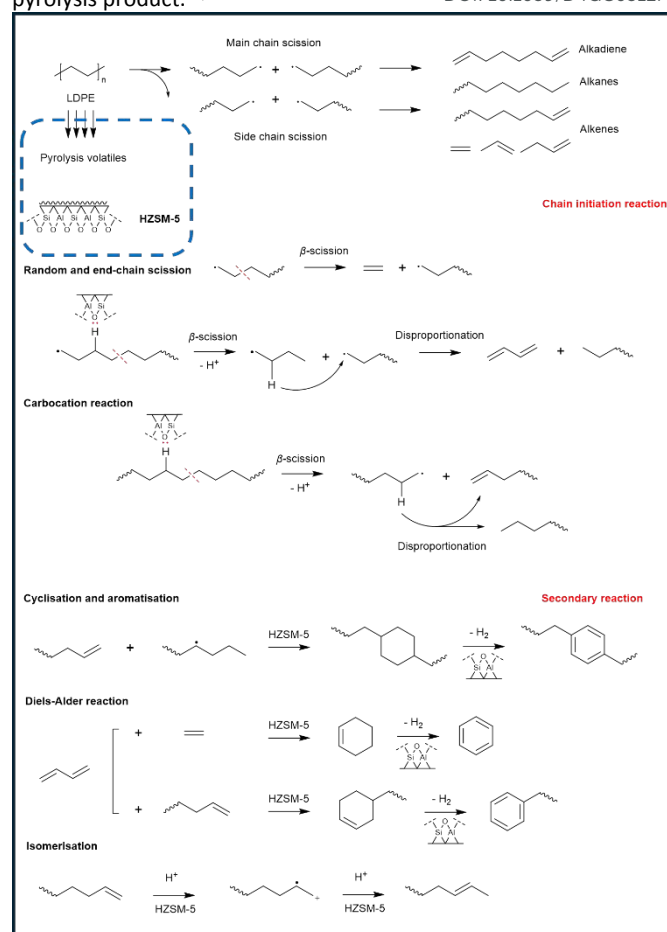


Figure 4 Mechanistic illustration of catalytic pyrolysis process of LDPE over zeolites. Reproduced from ref⁷⁸ with permission from Elsevier, copyright 2022.

HZSM-5 is a typical zeolite for pyrolyzing plastic waste and producing aromatics.⁶⁴ Gasoline-range hydrocarbons and monocyclic aromatic hydrocarbons can be produced with HZSM-5.⁶⁵ HZSM-5 can participate in the cracking reaction at the end of polymers.⁶⁶ HY has a larger micropore and is conducive to producing gasoline-range hydrocarbons.⁶⁷ The selectivity of gasoline-range hydrocarbons in the liquid products can reach 97% in the HDPE pyrolysis reaction.⁶⁸ One disadvantage of HY is the deactivation, which is faster than HZSM-5. The cavities in HY inhibit the diffusion of polycyclic aromatic hydrocarbons, which can finally form the coke blocking the active acid sites.⁶⁹ Similarly, HUSY, which can produce considerable gasoline-range hydrocarbons, also suffers from deactivation. To compare, HZSM-5 has the properties of high connectivity and no cavity, which has a longer lifetime.⁷⁰

SBA-15 and MCM-41 are mesoporous zeolites with uniform channels and high specific surface area.⁷¹ The selectivity of oil is similar to that of microporous catalysts, but these mesoporous zeolites suffer from low stability and acidity.⁷² The metal-loaded mesoporous zeolites can be prepared to get an improved catalysis performance due to the introduction of Brønsted acid sites.^{72, 73}

The FCC catalysts are composited of silica-alumina and the binder, which have the zeolites crystal and non-zeolites matrix.⁷⁴ FCC unit is used in the petroleum industry to convert crude oils to gasoline,



olefinic gases, and base chemicals.⁷⁵ It has an interconnected network containing micro-, meso- and macropores, and the heavy compounds can enter the internal surface and be pre-cracked. The spent FCC catalyst is a promising option for plastic pyrolysis, considering the similar feedstock structure and the negligible cost. The petroleum-based plastic waste can be cracked and pyrolyzed in the meso- and macropores, while the gasoline range hydrocarbons and light olefins can be produced in the micropores.^{76, 77}

Metal oxides and metal-modified catalysts

Metal oxides such as ZnO, MgO, CaO, and Fe₂O₃ have demonstrated promising catalytic activity by promoting the cleavage of C-C bonds and suppressing undesirable side reactions, thus improving the yield of desired products. MgO, which is effective, cheap, and sustainable for plastic upgrading, can achieve the goal of cracking diesel into gasoline and hydrogenating the alkenes to alkanes.⁷⁹ The yield and quality of products can be increased by combining the base and solid acid catalysts.⁸⁰⁻⁸² For example, combining the MgO and HZSM-5 catalysts and making a dual-stage catalytic bed can provide both basic and acidic sites. The quality of products can be improved because of the synergistic effect, and the yield of aromatic hydrocarbons can also be increased.⁸³

Moreover, supported metal catalysts, including noble metals such as Pt, Pd, and Ru, as well as non-noble metals like Ni and Co, have shown catalytic efficacy in enhancing the pyrolysis process. Al₂O₃ is a typical support for different metal. Fe, Ce, Co, Ni, Cu, and Pt have been loaded onto the Al₂O₃ to prepare the plastic pyrolysis catalysts.⁸⁴⁻⁸⁶ Meanwhile, metal modifying the zeolites is a crucial way to prepare more efficient catalysts. With a unique microporous structure and uniform acidic and basic sites, metal nanoparticle-modified zeolites have been used in many reactions, including catalytic isomerisation, cracking, and hydrogenation reactions.⁸⁷⁻⁸⁹ Iliopoulou *et al.* modified ZSM-5 with Ni and Co and found Ni can promote dehydrogenation and facilitate the formation of aromatics.⁹⁰ Nishino *et al.* prepared Ga-ZSM-5 for the PE pyrolysis reaction.⁹¹ The yield of liquid products was more than 50%, and the value-added aromatics accounted for more than 80% of liquid.

Other novel catalysts

Carbon-based catalysts have the advantages of low cost, acidity, numerous pore structures, flexible surface modification, etc., which can convert plastic waste into fuels and value-added chemicals.⁹² González *et al.* tested activated carbon as a catalyst in polyethylene pyrolysis, and the activated carbon had a good selectivity to aromatics.⁹³ Research shows that the pore sizes of activated carbons relate to the molecular weight of the products.^{94, 95} Specifically, Sun *et al.* used H₃PO₄-activated carbon catalysts to convert waste polyethylene into aromatics, alkenes and alkanes, and studied the catalytic effect on the enrichment of the aromatics.⁹⁶ The target products were affected by the phosphorus functional groups. Zhang *et al.* tested the activated carbons in the LDPE plastic pyrolysis and found the yield of aviation fuel could reach up to 100 area.%.⁹⁷ The selectivity of aromatics and alkanes was around 30 area.% and 70 area.%, respectively. Furthermore, Tsang *et al.* used the Pt/C catalyst to upcycle biomass-based polyisoprene rubbers into jet-fuel. Hydrolysis and vapor-phase hydrogenation were conducted in a two-stage fixed-bed reactor. The C₁₀ cycloalkane yield reached

642.7 mg/g with a selectivity of 83.6% at 200 °C.⁹⁸ Therefore, activated carbons have an excellent potential to be applied in plastic pyrolysis. Recently, clays have been chosen for pyrolysis reactions owing to their low cost and high reserves. Their activation could be similar or even superior to zeolites at high temperatures,⁹⁹ and the layer structure they have can form a 2D network with interconnected micropores.¹⁰⁰ Clays tend to produce heavy olefin hydrocarbons, rather than aromatics, because of their mild acidity.⁸⁴

After introducing the different thermal and catalytic pyrolysis processes for polyolefin, the following sections will focus on reviewing the different product compositions.

Liquid products

The liquid products, include alkanes, alkenes, aromatics such as BTEX and styrene, are central components in polyolefin pyrolysis. For thermal pyrolysis, the aromatic structures such as styrene and benzene mostly originate from PS. PP tends to form alkenes and some aromatics while polyethylene produces alkanes and alkenes. Moreover, the liquid and wax-like hydrocarbons from plastic waste have high calorific values. After upgrading and purification, they can be used as petroleum-like diesel for transportation.^{46, 101-103}

In catalytic pyrolysis, the use of catalysts improved the yield of oil with high quality.^{104, 105} Moreover, liquid products with a high concentration of aromatics can also be achieved. Aromatic hydrocarbons such as BTEX are key building blocks in many chemical syntheses. Currently, BTEX are mostly produced from fossil fuels *via* the thermal fractionation of coal and catalytic reforming and aromatising of petroleum. These traditional routes can be altered by using pyrolysis of waste polyolefins to reduce fossil fuels consumption and carbon emissions.

Nishino *et al.* prepared Ga-ZSM-5 and transformed the plastic waste into aromatic liquid products at 520-550 °C.⁹¹ The yield was over 80 %. Valle *et al.* prepared Ni-modified HZSM-5 and converted the heavy oil into total aromatic hydrocarbons, and the yield increased to 65 %.¹⁰⁶ Related research showed that the acid sites of zeolite are significant to the aromatic yield. Metal-modified zeolite can adjust the acid sites.¹⁰⁷ The pyrolysis of plastic waste can be a promising way to produce BTEX.¹⁰³ The liquid products (pyrolysis oil) can be used as fuel without upgrading and can also be the source of valuable chemicals with further separation such as distillation and membrane that are available in the traditional oil refinery industry. It is foreseen that employing the separation infrastructure in oil industry in the waste recycling chain does not require any modification in the production strategy or in the implementation of new units within the refinery complex.¹⁰⁸

Gaseous products

Gaseous products from polyolefin pyrolysis include light alkanes and alkenes from C₁ to C₅ and H₂. The formation of gaseous products is influenced by the type of catalysts in the catalytic pyrolysis.¹⁰⁹ Ratnasari *et al.* found Ethene (C₂), propene (C₃), and butane (C₄) were the major gases in HDPE pyrolysis over MCM-41 and ZSM-5 catalysts.¹¹⁰ Moreover, the amount of gas relates to the amount of zeolite catalysts.¹¹¹ The composition can be tailored by the size of zeolite catalysts. More than 50% of gaseous products were C₁ to C₄ hydrocarbons over the nano-sized HZSM-5 catalyst.¹¹² Many studies also showed the relationship between the yield of gaseous products and the acidity of catalysts.¹¹³ Furthermore, H₂ is a promising energy



carrier due to its efficiency, sustainability, and development potential. It can be produced from plastic waste, which is an efficient way to recycle plastic waste and have high-value products.

Solid products

The solid product from waste polyolefins pyrolysis is a carbon-rich material. The reactor is usually in a two-stage style. The first stage (500-700 °C) is for the waste polyolefins pyrolysis, and the second stage (600-800 °C) is for the synthesis of carbon materials over catalysts.¹¹³ Various high-valued carbon materials including carbon nanotubes (CNTs),¹¹⁴ carbon fibres,¹¹⁵ carbon nanospheres,¹¹⁶ and carbon nanosheets,¹¹⁷ can be produced.

CNTs have potential applications because of their high mechanical resilience, interconnected pore structure, and high electrical conductivity.¹¹⁸ More and more research focus on producing CNTs from plastic waste over specific catalysts.¹¹⁹ Acomb *et al.* produced the CNTs from LDPE over Fe/Al₂O₃ catalyst, and the yield was 26 wt%.¹²⁰ Yao *et al.* used Fe/α-Al₂O₃ and Fe/γ-Al₂O₃ catalysts to produce CNTs from real plastic waste, having a yield of 35 wt.% and 33 wt.%, respectively.¹²¹ Wu *et al.* produced the CNTs from PP plastic and got a carbon yield of 29 wt.% over the Fe/SiO₂ catalyst.¹²² Nahil *et al.* added different metals, including Zn, Mg, Ca, Ce, Mo, and Mn, into Ni-based catalysts and produced CNTs from PP.¹²³ Yao *et al.* used post-consumer mixed waste plastics to prepare CNTs over Ni-Fe bimetallic catalysts.¹²⁴ Different supports, including MCM41, ZSM-5, H-Beta, and NKF5, were used. The highest yield of carbon materials was over 55 wt.%, over the Ni-Fe/MCM41 catalyst. Wang *et al.* used cordierite as the support and prepared the Fe/cordierite, Ni/cordierite, and Ni-Mg/cordierite catalysts.¹²⁵ A high yield of filamentous carbon (93 wt.%) was achieved. The economic viability of this process was verified by Cai *et al.*¹²⁶ The CNTs prepared from plastic pyrolysis have been applied in many fields, such as electrocatalysts,¹²⁷ solid oxide fuel cells,¹²⁸ phase change material,¹²⁹ and pollutant adsorption.¹³⁰

Overall, pyrolysis is a promising chemical recycling method for polyolefins. It has been extensively studied across various reactor types, with temperature being a key parameter influencing product distribution. Lower temperatures favour oil production, while higher temperatures increase gas yields. Catalytic pyrolysis, employing various catalysts, enhances target reactions, reduces reaction times, and improves product quality and process efficiency. Zeolites are extensively studied for their shape-selective properties, promoting the cracking of large hydrocarbon molecules into smaller, desirable compounds. Metal oxides and metal-modified catalysts, such as supported metal catalysts and FCC catalysts, also show promise in enhancing pyrolysis efficiency. Carbon-based catalysts, including activated carbons and clays, offer low-cost alternatives for plastic waste conversion. Pyrolysis yields liquid, gaseous, and solid products. Liquid products, rich in alkanes, alkenes, and aromatics, find applications as fuels and chemical feedstocks. Gaseous products primarily comprise light hydrocarbons and hydrogen, influenced by catalyst type and acidity. Solid products, carbon-rich materials, can be further processed into high-value carbon materials like CNTs and carbon fibres, with various applications including in electrocatalysts and solid oxide fuel cells.

PVC (Polyvinyl chloride) SPI code - 3

View Article Online

DOI: 10.1039/D4GC03127J

PVC is the world's third-largest thermoplastic by volume, after PE and PP. due to its versatile properties such as lightweight, durable, good insulation, high chemical and fire resistance, low cost and easy processability, it finds applications in a verity of fields, such as water pipes, building materials, electronic components and medical devices. PVC is produced from the polymerisation of ethylene dichloride. In the EU-27 + UK, Norway and Switzerland, about 6.5 million tonnes of PVC products are manufactured every year. Annual European consumption of PVC resin totals 5.1 million tonnes - 10% of all plastics used in Europe.¹³¹

Chemical recycling is more suitable for an unsorted PVC waste stream for which mechanical recycling is not achievable or is uneconomical. However, there are also many challenges in chemical recycling, mostly caused by i. plasticiser additives, which are added to PVC at concentrations ranging from 30% to as high as 50% by weight and containing chemicals such as phthalates—which are carcinogenic and mutagenic; ii. Thermal stabiliser that contains heavy metals such as lead, tin and barium. The solution to these problems is discussed in more detail elsewhere.¹³²⁻¹³⁴ In this review, we focus more on the chemical recycling of PVC polymer itself.

The chemical recycling of PVC waste essentially consists of two steps: dechlorination to remove Cl from the PVC macromolecule and the use of the remaining hydrocarbons (**Figure 5a**). The first step is essential as the formed highly corrosive HCl gaseous product can significantly damage the reactor, cause potential environmental hazards, poison metal-based pyrolysis catalyst and contaminate the upcycling products. There are two routines, namely dehydrochlorination and dechlorination, for chlorine removal. Dehydrochlorination, in which chlorine is removed as gaseous HCl when heating up PVC to 400 °C, combined with Cl trapping at the exhaust. Major disadvantages of such treatment include that a certain amount of chlorine is locked in cyclized and crosslinked structure when conjugate polyene is formed even in the presence of steam, and the service life of equipment is short due to the corrosive nature of HCl.^{135, 136} Dechlorination presents a more effective approach, where chlorine is removed by absorbents during the thermal treatment.

Absorbents, usually alkaline compounds such as NaOH,^{137, 138} Na₂CO₃,^{139, 140} etc., or basic metal oxides such as Fe₃O₄,¹⁴¹⁻¹⁴³ ZnO,¹⁴⁴ CaO,^{145, 146} mixed magnesia-alumina oxide² etc., can significantly increase the chlorine removal effectiveness through catalytic acceleration of the process as well as mitigate hazardous gas emissions by forming water-soluble metal chloride. In most of the experiments reported so far, the dichlorination rate, determined by

$$R = \frac{Cl_o - Cl_f}{Cl_o} \times 100\%$$

Where Cl_o is the Cl content in the starting material, and Cl_f is the Cl content in the final product, normally the pyrolysis liquid.

are relatively high (> 80%), leaving the Cl presence in the remaining polymer or pyrolysis liquid to a suitable level (< 10 ppm) for their successful refining processes.¹⁴⁷

A two-stage process is clearly beneficial, as the Cl removal requires lower temperature (usually below 400 °C even without any catalyst) than polymer chain cracking (> 500 °C).^{141, 148, 149} Besides, performing the dechlorination and pyrolysis at the same time, especially when



As detailed in the previous section on polyolefins, pyrolysis yields valuable products including syngas, liquid fuels and carbon-rich solids. On the other hand, gasification at high temperatures in the presence of oxygen or steam transforms PVC into syngas that serves as a valuable chemical feedstock. In this case, Cl is recovered as HCl *via* a scrubbing process. Examples of industrial scale PVC recycling processes are documented by Ait-Touchente *et al.* including two gasification processes operating in Japan - Sumitomo Metals and the Ebara Process.¹³²

The advances in Cl removal methods detailed in this section will ensure that high quality products are formed with minimal Cl content. It is clear that multi-step pyrolysis and gasification approaches are suitable for treating mixed-plastic waste containing PVC. Despite the complexity of the product mixture formed with pyrolysis, it is preferred over gasification due to the high-value and readily applicable liquid oil produced. As both pyrolysis and gasification approaches require high temperatures, further improvements should focus on reducing energy consumption.

Other Plastics – SPI code - 7

The SPI code #7 category was designed as a catch-all for “other” plastics, such as bio-based polylactic acid (PLA, polyester), nylon (polyamide), polymethyl methacrylate (PMMA), polycarbonate (PC), acrylonitrile butadiene styrene (ABS), etc. Therefore, the reuse and recycling protocols are not standardised within this category. However, based on their polymer chain structures, similar chemical recycling methods introduced above can still be applied on them.

PLA

As a flagship bio-based plastic, PLA is used in many applications such as food packaging materials. The main constituent, lactic acid, is produced through fermentation from biomass feedstocks such as food crops (corns) and waste sugars (cellulose, glucose). Industrially, the polymerisation to PLA is preferentially achieved by ring opening polymerisation of lactide (a cyclic diester of lactic acid), rather than the polycondensation of lactic acid, which is limited by the need to remove water and difficulty in achieving high molecular weight.¹⁵⁴

Compared to petroleum-based plastics, PLA is currently more expensive due to increased production costs associated with the fermentation and purification of LA, which accounts for approximately 50% of the total cost. Besides, despite the dynamic growth of biopolymers, their waste streams are still small and scattered, and no separate recycling stream yet exists for PLA. A study has shown that it is more energetically favourable to attain lactic acid from chemical depolymerisation of PLA rather than to produce virgin feedstock from the costly fermentation route.¹⁵⁶ Besides, as the formation of lactide from lactic acid can contribute up to 30% of the total cost of the polymerisation of PLA,¹⁵⁷ there's also a tendency in research to obtain the dimer directly when chemically recycling PLA. This process is typically done *via* thermal depolymerisation in the presence of suitable catalysts (such as organic compounds of Zn, Sn, Al, Ti, Zr), at high temperature (200 – 250 °C) and under vacuum conditions.^{156, 158-161} This process is also rather complex and expensive, both for the severe operating conditions and for the need of several purification steps of the final product.¹⁶¹ Therefore, recent research efforts have been leaning towards advancing base catalysed hydrolysis which can also lead to

lactide formation. Another high-value product can be recovered from PLA is alkyl lactates, which are green solvents with good biodegradability and low toxicity. They can also be used to produce lactide with a similar transformation process as lactic acid, thus “closing the loop” on the PLA life-cycle. **Figure 6** presents the main chemical recycling methods for PLA.¹⁵⁵

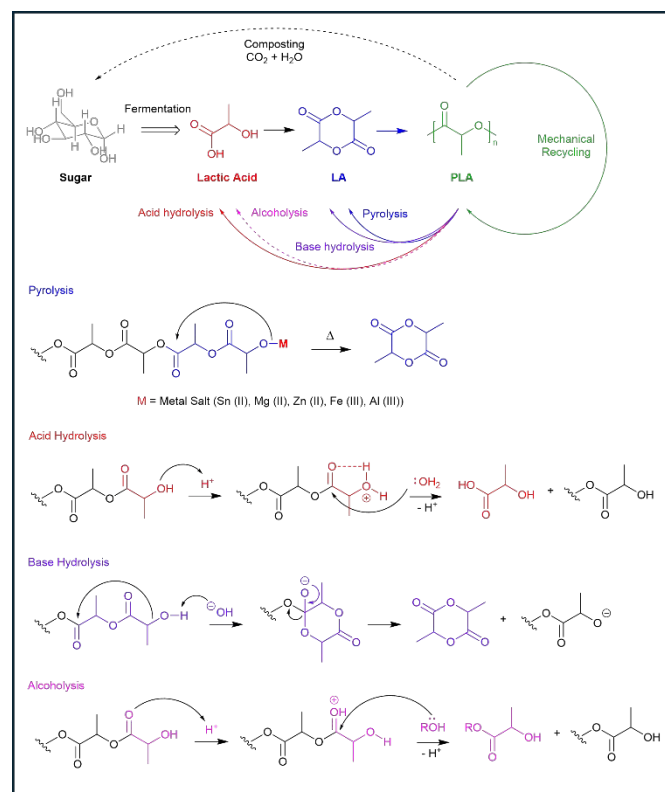


Figure 6 Illustration of different chemical recycling reactions for PLA and the corresponding products: Pyrolysis (lactide); Acid hydrolysis (lactic acid); Base hydrolysis (lactide) and Alcoholysis (alkyl lactate). Reproduced from ref¹⁵⁵ with permission from MDPI, copyright 2020.

pH plays an important role on PLA hydrolysis. The use of acid and base provides alternative mechanisms for the depolymerisation. Under acidic condition, the dominating process is a chain-end scission, whereby the terminal hydroxyl group is activated by protonation and is hydrolysed directly to lactic acid. The rate of degradation is independent of chain length due to the hydrophobicity of the polymer chain compared to the increased hydrophilicity of the chain end.^{162, 163} In contrast, the use of basic conditions leads to random chain scission *via* back biting reaction to generate lactide, which is subsequently hydrolysed. Accordingly, the process kinetics is dictated by the nature of the hydroxyl terminal groups. When the terminating OH was blocked, no significant PLA degradation was observed by de Jong *et al.*¹⁶⁴ By analysing the fraction of total initial lactide present as one of the chain-ends, random scission and chain-end scission can be determined.¹⁶⁵ Due to the insolubility of PLA in aqueous media, hydrolysis can require high temperatures in the range of 180 – 350 °C.¹⁵⁵ Various methods have been proposed to reduce the temperature requirement, including microwave heating (170 °C), high pressure steam (100 – 130 °C) and combine with other solvents, such as 50% ethanol (90 °C) and ionic liquid (130 °C). Recently, Friscic and Auclair's



research group demonstrated the use of a mechano-enzymatic depolymerisation method with moist-solid reaction mixtures with *Humicola insolens* cutinase (HiC) enzyme, to avoid the need of dissolving PLA in aqueous solution. After 5 days of milling + aging conditions, the percentage yield of depolymerisation reached over 90 %, marking the effectiveness of this process.¹⁶⁶

Alcoholysis of PLA to alkyl lactates follows a simple reaction pathway as illustrated in **Figure 7**. A range of commercial reagents including alkali/alkaline metals (Li–K/Mg–Ba) and selected alkoxides Na(OEt), K(OEt), Ca(OMe)₂, as well as organometallic/chlorido Zn, Sn, and Al reagents are commonly used to catalyse the reaction.¹⁵⁵ These catalysts effect as Lewis acid sites arise via binding to the carboxyl of the ester to facilitate the attack of the chemical bonds, thus driving the transesterification process.¹⁶⁷

In addition to research advancements, an overview of the chemical recycling of PLA technologies disclosed in the patent literature is provided by Niaounakis, where the pros and cons at an industrial relevant context is discussed.¹⁶⁸

Nylon (Polyamide)

Another commonly used plastics falls in this category are engineering plastics such as polyamides, which is designed to withstand harsh mechanical and environmental conditions, the same property that dictates the challenge in recycling. For example, Nylon-6 is a thermoplastic polyamide produced industrially by water-assisted ring-opening polymerization of ϵ -caprolactam on a 6.21 million tons annual scale in 2021,¹⁶⁹ with the market size estimated at USD 34.39 billion in 2023.¹⁷⁰ According to the World Wildlife Federation, up to 1 million tons of Nylon based fishing gear is abandoned in the ocean each year, with fishing nets composed of Nylon-6 making up at least 46% of the Great Pacific Garbage Patch.

Currently, less than 1% Nylon is recycled worldwide due to the various technical challenges. Mechanical recycling is rarely used since the high manufacturing temperature leads to partial degradation of the polyamide chain, leaving recycled Nylon products with inferior properties.¹⁷¹ The idea of burning plastics for energy recovery does not apply to Nylon either, as a limitation for Nylons is that toxic HCN, CO, CO₂, and NH₃ are produced in combustion,¹⁷² and the economic value of fossil fuel derived ϵ -caprolactam will be lost.

The current chemical recycling strategies for polyamides are focus on pyrolysis, hydrolysis/solvolytic, hydrogenolysis, ammonolysis or aminolysis, as well as depolymerisation in ionic liquids. **Figure 7** presents the reaction temperature range among different methods. It can be seen that with the aid of metal complex catalyst, hydrogenation of polyamide can take place under relatively low temperature (150 – 200 °C), yet the high H₂ pressure, usage of solvent as well as the low product yield still posts safety and efficiency concerns. The reaction is typically catalysed by ruthenium pincer complexes using DMSO as a solvent, which plays a critical role in the process by disrupting the hydrogen bonding of the polyamide and at the same time remaining uncoordinated to the metal center, thus allowing the catalysis to occur.¹⁷³ Improvements are yet to be made to increase the product yield and find alternative proton sources than H₂ for the hydrogenation of amide bonds. In comparison, hydrolysis with sub- and supercritical water and acid catalyst (e.g. HCl) can effectively decrease the reaction temperature requirement, while achieving a high product yield. Bockhorn and co-

workers compared the apparent activation energy E_a of the thermal degradation of Nylon-6 by means of TG/MS. The E_a is calculated to be 211.3 kJ/mol without any catalyst. The value decreases to 163.9 kJ/mol in the presence of H₃PO₄, and further to 113 kJ/mol with the eutectic mixture of NaOH/KOH as catalyst. However, a disadvantage of this process is the high yield of salts and traces of acids in the recovered ϵ -caprolactam, which is a drawback for the production of virgin Nylon materials. Without the aid of acid catalyst, hydrolysis takes place in the temperature range of 300 – 370 °C, with varied product yield depending on the solvent type (water, toluene, methanol, etc) and reaction time.

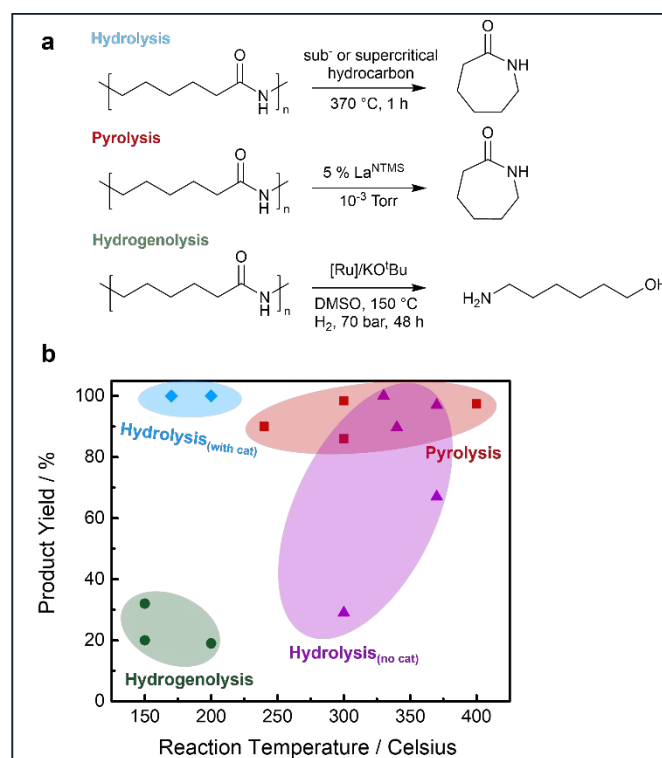


Figure 7 a. Examples of hydrolysis, pyrolysis and hydrogenolysis reactions of Nylon polymers. b. A summary of Nylon depolymerisation product yield as a function of reaction temperature.

Pyrolysis approach with reduced pressure, oxygen free conditions normally deliver high product yield. The temperature ranges from 240 °C to 400 °C, varies depending on the catalyst being used. For example, Wursthorn *et al.* reported the use of Ln(N(TMS)₂)₃ (Ln = lanthanide), a commercially available lanthanide trisamide catalyst to treat post-consumer Nylon-6.¹⁷⁵ Under solvent-free, 10⁻³ Torr and 240 °C, ϵ -caprolactam yield can reach 93%. As shown in **Figure 8**, experimental and theoretical mechanistic analysis argue that the reaction proceeds *via* a novel mechanism involving an initial deprotonation step of the Nylon amide N-H bond which binds the catalyst covalently to the polymer. This step is followed by predominant chain-end backbiting steps in which ϵ -caprolactam units are sequentially excised from the chain ends. There are rare reports on ammonolysis of Nylon in the literature, with a handful of examples documented in the patent domain.¹⁷⁶⁻¹⁸⁰ Therefore, we will not review this technique here in great detail.



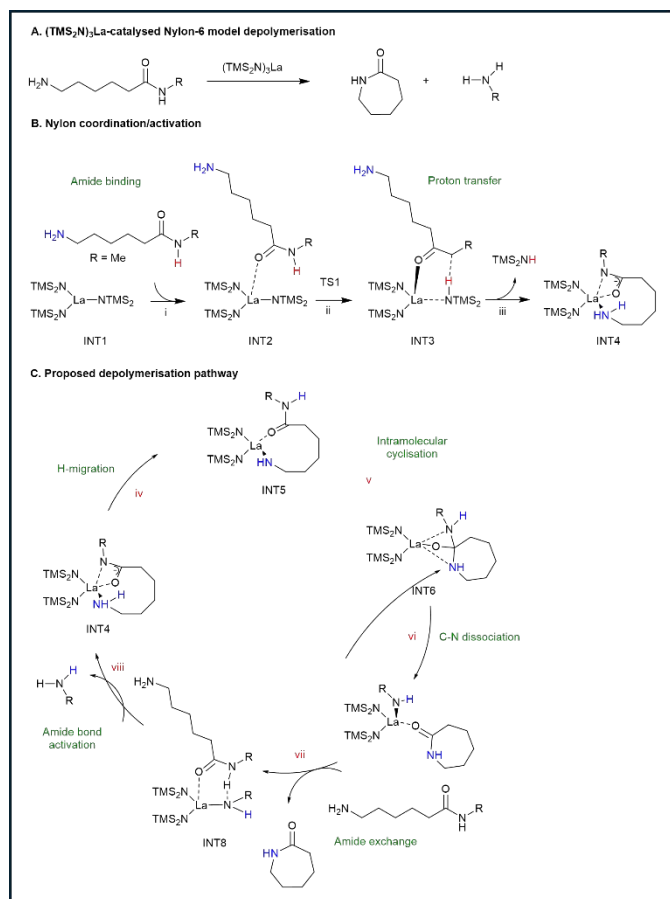


Figure 8 Mechanistic illustration of Nylon-6 depolymerisation with commercially available lanthanide tris(amido) catalysts $\text{Ln}(\text{N}(\text{TMS})_2)_3$ (Ln =lanthanide): A) Computed Nylon-6 model reaction. B) Nylon coordination. C) Proposed depolymerisation mechanism. Reproduced from ref¹⁷⁵ with permission from Wiley, copyright 2023.

To summarise, depending on the polymer structure, the reactions for chemical recycling of different plastics need to be carefully chosen.

Table 3 provides a list of reaction types mentioned in this review, along with the operation temperatures. When energy efficiency is a priority, low temperatures may help reduce energy costs. Yet this need to be reviewed alongside other parameters, such as catalyst type, product yield, post separation, etc, in order to find the suitable process.

Table 3 Summary of the different reaction types and the operation temperature for different plastics in this review.

Plastic type	Reaction	Temperature / °C
PET	Acid hydrolysis	< 150
	Neutral hydrolysis	200 – 300
	Alkaline hydrolysis	> 200
	Methanolysis	180 – 280
	Glycolysis	~ 200

	Ammonolysis	View Article Online DOI: 10.1039/D4GC03127J
Polyolefins	Thermal pyrolysis	300 – 900
	Catalytic pyrolysis	< 500
PVC	Dichlorination + pyrolysis	400 – 500
PLA	Hydrolysis	180 – 350
	Hydrogenolysis	150 – 200
Nylon (polyamide)	Hydrolysis	300 – 370
	Pyrolysis	240 – 400
	Ammonolysis	300 – 400

Mixed plastics

Although upcycling single-component plastic waste is feasible, upcycling real-life plastic waste, that is, plastic mixtures comprising diverse plastic types (including polyolefins, polyesters, polyurethane, polyvinyl chloride and so on), is more challenging. It is claimed that PLA bottles can contaminate the PET waste stream making its recycling process less efficient and increasing its cost by necessitating investment in new sorting equipment. It is noteworthy that these plastics cannot be easily or cheaply sorted by sight and the separation methods based on density are not efficient enough due to their similar densities. Only near infrared sensors can ensure good separation, but this technology requires an expensive initial investment, and it is not common place in the current recycling facilities.

Yet, we should aim to transform these mixed plastics. There are two strategies that warrant special consideration: 1) transformation of mixed plastics into a product with a simple composition, and 2) stepwise transformation of the mixed plastics. In both cases, the rational design of the underlying carbon cycle is very crucial.⁹ In for former case, pyrolysis method has been widely adapted by industry (e.g. ChemCycling® from BASF), to recycle low quality mixed waste streams, such as the municipal solid waste. Such method has high tolerance to contaminants and impurities, and is more suitable for streams consisting of mostly polyolefins that have high carbon contents. However, polyolefins are difficult to selectively depolymerise due to the uniformity of chemical structure across the polymer chain, which lacks differentially cleavable bonds. Therefore, under reaction conditions, the C-C and C-H bonds break in a statistical fashion, resulting in a mixture of short, medium and long-chain alkanes (C_1 - C_{35}), alkenes and aromatics. This phenomenon posts additional challenges in post-reaction product separation.¹⁵ The latter case is more adaptable to mixed streams containing other elements, such as PVC (Cl), polyester (O) and polyamides (N). For example, Sanchez and Collinson reported the use of $\text{Zn}(\text{Ac})_2$ in PLA/PET mixer solvolysis can effectively depolymerise PLA, while PET remains as unconverted solid.¹⁶⁷ Similarly, Yang *et al.* discovered by adjusting the reaction conditions, a zinc bis[bis(trimethylsilyl)amide] ($\text{Zn}(\text{HMDS})_2$) catalyst is capable of sequentially depolymerising mixed BPA-PC/PET, PLA/PBS and PLA/PBAT.¹⁸¹ These solvolysis based



studies have attempted to capture the impacts of some of the plastics waste chemical recycling techniques¹⁸ including gasification, pyrolysis, feedstock recycling, solvolysis, and hydrocracking. **Figure 9** and **Table S1** show the results of environmental and economic assessments from a review of 14 existing studies and 27 case studies. These studies show pyrolysis as the main route for chemical recycling being modelled using LCA.^{16, 18, 195-197} Over 90% of the 27 case studies focused on only LCA,^{18, 197-200} while only two studies reported the economic potential of the assessed systems.^{195, 201} Most of the studies employed a mass basis with a system function as 1t of treated plastic waste. A cradle-to-gate system boundary is common among the reviewed studies mainly due to limited or absence of EoL data of the products derived from the plastics, which is not uncommon among LCAs of emerging technologies.²⁰² For comparative purpose, some of the studies omitted the cradle stage *i.e.* the pre-conversion stages listed above, thus, only the gate-to-gate impact was reported.^{197, 201} Some of the plastics evaluated as mixed or individual plastics among the reviewed studies include PET, HDPE, low LDPE, PP, PVC, PS and others that were not specified in the reported studies.

Since greenhouse gas (GHG) emissions are viewed as the most important environmental aspect for plastic waste management or recycling, the most reported environmental impact indicator is the global warming potential (GWP). Thus, all the reported GWP impact values from the 27 case studies were normalised to a reference function of 1 kg treated plastic waste, to allow fairer comparison of assessment outcomes. Apart from the climate change impacts, a range of environmental impact particularly Acidification potential (AP-kgSO₂-eq), Photochemical ozone creation potential (POCP-kg C₂H₄-eq), Abiotic depletion potential (ADP-(kgSb-eq.)) was also reported by some of the studies.^{16, 197, 199, 203}

The GWP impact of chemically recycling various plastic waste is in the range of 0.37 to 12 kgCO₂-eq per kg of plastic waste across all the 27 case studies, employing different chemical recycling methods (**Figure 9**). As with many LCA studies of other products, variations exist in the LCA outcomes of the reviewed studies due to differences in the technologies used for recycling, type of polymer and LCA methodological choices, nevertheless, some level of consistency across most of the studies can be observed.^{202, 204}

Rickert *et al.* proposed a new approach of evaluating the performance of pyrolysing mixed plastic wastes by using the environmental budget, which was defined as the margin of environmental impact by two systems supplying the same function, with one system supplying energy and the other focused on monomer recovery from the processed plastic waste (PET trays).¹⁶ Four scenarios as a function of monomer recovery and energy generation were analysed, of which the percentage monomer recovery and efficiency of the recovery influence the total environmental budget. In terms of GWP, 100% monomer recovery offered the highest environmental budget across all scenarios assessed in the study. Meanwhile, recovery without ethylene glycol, offered higher environmental budget than 50% recovery but lower environmental budget than 100% and 80% monomer recovery scenarios. Out of all the impact categories reported, acidification potential performed worst for the specific chemical recycling technology, which was also influenced by the recovery efficiency. A specific monomer recovery efficiency may be required for a given

recycling system to operate within an environmental budget, consequently providing environmental benefits. A breakeven recovery efficiency was estimated at 40.95% for the modelled system.¹⁶ This is useful particularly with the complexity of the various chemical recycling options. For the recovery of pyrolysis fractions such as ethylene, propylene, -n-butane, 1-butene, isobutene, light naphtha, and aromatics, a GWP impact values of 3.66 kgCO₂-eq and 4.22 kgCO₂-eq was associated with the pyrolysis route adopting a consequential and attributional LCAs respectively.¹⁹⁵

Low temperature pyrolysis had higher GWP impact compared to hydrocracking in the case of PET/PE treatment.¹⁹⁸ Likewise, chemical recycling of PLA into dilactide *via* cyclic depolymerization followed by melt crystallization and ring-opening, was 1.5 times greater than solvent based treatment of PLA using selective dissolution to remove impurities such as adhesives, paints, and paper.¹⁹⁶ Technical difficulties were reported in the case of chemical route, even so, a 100% lactic acid replacement was assumed. While solvent was recycled within the system, the loss of it, contributed mainly to ozone formation, acidification and eutrophication potential.¹⁹⁶ In terms of benefits to the system, the two main sources come from credit allocation and product substitution in the market. Selective dissolution and precipitation which uses a solvent and anti-solvent to recover polymers of interest was also reported to have relatively low GWP of 1.9 kgCO₂-eq compared with other assessed technologies including one solvolysis, one pyrolysis, four mechanical recycling technologies and ten different incineration scenarios.⁴⁴ The main setback for this system in terms of environmental consideration is the use of hazardous organic solvents, which can be reduced via high-rate recycling.

Comparing with mechanical recycling, Vollmer *et al.* reported CO₂-eq values of ~ 5.5, 4.3, 2.9, and 3.1 kg CO₂-eq/kg of plastic waste for mechanical recycling of four types of polymers including acrylonitrile butadiene styrene, high-impact polystyrene, PET and PET-PE respectively.⁴⁴ Khoo *et al.* obtained GWP of 0.37 and 0.65 kgCO₂-eq for gasification and pyrolysis of mixed plastic respectively (**Table S1**), the same study obtained a GWP of 0.40 kgCO₂-eq per kg of plastic waste via mechanical recycling, showing a slightly higher impact of mechanical recycling compared with the pyrolysis and gasification for this specific case study.¹⁸ While mechanical recycling is known to have lower EoL processing impact, the lower product quality reduces its overall benefit against chemical technologies (**Figure 9**). Their study combined gasification and pyrolysis routes alongside mechanical recycling and waste to energy across 8 different scenarios.

Most of the reviewed studies showed significant reduction in GWP impact associated with the recovered products by credit allocation for avoided virgin material production, which contributed up to 59% GWP savings.¹⁹⁹ This emphasises the need to maximise product quality and focus on high value commodities. In terms of other environmental impact indicators, acidification potential, photochemical ozone creation and particular matter formation were also reported by some of the reviewed studies, with acidification potential as the most widely reported next to GWP. For 1 kg of plastic waste, a range of acidification potential values of chemical recycling by gasification was 0.00018 kgSO₂-eq¹⁸ and 0.0007 kgSO₂-eq,¹⁹⁷ while the value for pyrolysis was obtained as 0.00014 kgSO₂-eq.¹⁸ Other chemical recycling had values of 0.0015 kgSO₂-eq while solvent



based extraction was 0.00083 kgSO₂-eq.¹⁹⁶ For all the reviewed recycling pathways, recycling back to monomer (dimethyl terephthalate (DMT)) showed higher value of 0.021 kgSO₂-eq/kg PET fibre compared with values reported in this study, and for mechanical recycling with values in the range of 0.00064 kgSO₂-eq¹⁹⁶ and 0.003 kgSO₂-eq.²⁰⁰ The remaining indicators were sparsely reported which presents a limitation for comparative analysis.

Considering the economics of plastic chemical recycling, a baseline scenario for the consequential LCA approach, had a net present value (NPV) of \$220.3/t of HDPE plastic waste.¹⁹⁵ Products with high yields such as propylene and butene had strong control of the market dynamics. These market dynamics pose significant environmental consequences with specific influence on GWP (kgCO₂-eq). It is worth noting that literature on economic analysis of plastic chemical recycling is relatively limited, however, emerging interest in low-cost sustainable pathways for plastic waste valorisation, has stimulated increased research in this domain.²⁰⁵ For example, a study by Singh et al. reported a base-case minimum selling price (MSP) of \$1.93/kg of TPA recovered from waste PET via enzymatic recycling.²⁰⁶ Likewise, MSP values of \$ 0.87/kg, \$ 0.96/kg and \$1.05 /kg was achieved for PET dissolution, glycolysis and methanolysis respectively.²⁰⁷ The same study reported an MSP in the range of \$0.73/kg to \$1.10/kg for dissolution of polyolefins. The cost of feedstock (plastic waste) and its pre-treatment had significant influence on the overall cost of recycling the plastic waste across all the reported studies with up to 58% contribution to the total MSP.²⁰⁸ As with environmental impact, the cost of the treatment pathways and product of interest are also key players in achieving viability of plastic chemical recycling processes. An MSP of \$0.70 was achieved for 1 kg of methanol via gasification of mixed plastics. For both economic and environmental perspectives, plastic waste pre-processing including collection, transportation, sorting, cleaning, flake production indicate significance on the overall performance of the recycling pathway. 30% burden resulted from primary treatment preceding collection and sorting of PLA waste for solvent based treatment.¹⁹⁶ A large contribution of transportation on the total environmental impact of chemical recycling is further highlighted. In such case, optimum location of the pre- processing and main recycling should be prioritised. More so, reducing the mass of plastic feedstock by pre-processing at source, will lower the transportation burden.^{193, 197} To maximise the benefits of plastic waste chemical recycling, the cost and environmental impact of feed and pre-treatment must be lowered through adoption of improved logistics and advanced sorting techniques, reduction in the consumption of reagents and energy in pre-treatment stages. More so, optimisation of other parameters such as main processing conditions, reagents and/or catalysts, feed quality and reference products should also be prioritised. Future sustainability assessments should also capture the influence of these parameters to provide more holistic comparative analysis of emerging chemical recycling pathways.

Implementation of chemical recycling technologies

Today, most plastics are still produced from fossil-based feedstock. A lack of appropriate waste management infrastructure, policy

incentives and business models are currently preventing the full value of plastics waste being captured. Transitioning to a circular, climate neutral economy demands special investment and innovation to develop new feedstocks from recycled plastics to reduce dependence on fossil-based oil and gas, contributing to the goals of the Paris and Glasgow Agreements. Despite the technology development reviewed above, chemical recycling processes are more complex and thus more expensive, especially in the implementation phase, and therefore need more financial incentives and value chain considerations.

- Over the last decade, the chemical recycling industry has grown significantly. As of 2022, the global chemical recycling input capacity has reached close to 1.2 million tonnes, with Europe at the forefront of technological developments.¹⁴ A significant number of demo and commercial plants are planned to launch in the upcoming years, as shown in **Figure 9**. The size of installations matters and is expected to grow with TRL (Technology Readiness Level) and market maturity. For pyrolysis plants, it is expected that the size will grow from 30-50 kilotonnes/year in 2021 to 100 kilotonnes/year in 2030. In parallel, development of improved and more efficient technologies needs to take place. These include technologies that are more tolerant for feedstock quality, higher efficiency, lower environmental impact, and are better scalable with much larger unit operations via improved process and reactor design. In recent years, emerging research focuses on combining mechanical processing and biological treatment with chemical methods have gain momentum. For example, mechanochemical process utilises mechanical energy and stoichiometry to drive plastic depolymerisation with minimal solvent usage;²⁰⁹⁻²¹¹ enzymolysis, such as the technique used by Carbios, utilises enzymes to effectively breakdown plastics such as PET.^{212, 213}
- In addition to the technical aspects reviewed above about catalyst and reaction conditions, there are two other key factors that influence the efficiency and output quality of these chemical recycling processes, namely the feedstock purity and size reduction. Among different recycling technologies, solvolysis depolymerisation typically requires high feedstock purity with minimum contaminants such as other plastic types, dyes, adhesives. Smaller size particles (e.g. 5-20 mm) are preferred to improve surface area and reaction efficiency. Pyrolysis is more tolerable on this aspect as it can handle mixed plastic waste, but excessive contamination by non-plastic materials (metal, glass, paper) can negatively affect the process and damage equipment. A moderate size reduction can ensure consistent and uniform heating. Gasification has the lowest purity requirement amongst all three technologies. Not only it can handle mixed plastic waste, some non-plastic wastes like biomass and municipal solid wastes are also tolerable. Taken these factors into account, one opportunity lies in having chemical recycling as an added step to the mechanical recycling process, to treat the stream that has been rejected for mechanical re-processing that otherwise goes to incineration or landfill.²¹⁴



Planned investments in chemical recycling

View Article Online
DOI: 10.1039/D4GC03127J

Figure 10 Planned investments in chemical recycling in Europe. Data is based on the announcement made by members and non-members of Plastic Europe by May 2023. Adapted from ref¹ with permission from Plastic Europe, copyright 2023.

- Optimising waste management processes is essential to increase the level of resource efficiency, and thus the level of recycling. Encouraging separate waste collection is key as it leads to a much higher level of recycling rates. According to EU report,³ plastics waste recycling rates are 13 times higher when collected separately compared to mixed collection schemes. In a recent social science study led by Walzberg *et al.*, modelling results have also illustrated the importance of changing the habits of disposal behaviours. It is shown that in the US context, while behavioural interventions would require about 300–900 GJ of additional energy at end-of-life due to improved collection rates, they would avoid about 500–700 thousand metric tons of GHG emissions related to sorting and reprocessing.²¹⁵
- Combining high recycling rates with renewable feedstocks improves the absolute sustainability of plastics. A recent study shows that if the plastics industry achieves a 75% recycling rate with advanced recycling technologies in 2030, plastics can comply with their assigned share of the safe operating space and be considered absolute environmentally sustainable regarding the considered eight planetary boundaries.⁷ The remaining virgin plastic production would predominantly rely on CO₂ and renewable electricity from wind, hydro or nuclear power. A smaller portion of plastics would come from biomass.²¹⁶
- Any attempt to upcycle plastics should be accompanied by a comprehensive LCA - from raw material extraction to recycling and transformation - to evaluate the overall process environmental impact. An aggressive implementation of multilayered strategies is required to curb the GHG emissions from plastics. Currently GHG mitigation strategies are often implemented within energy, materials, waste-reduction and management policies in isolation, yet the absolute reduction in GHG emissions of plastics' life cycle requires a combination of energy infrastructure decarbonisation, recycling capability improvement, bio-based plastics adaption and demand management.²¹⁷
- Although being the key to sustainability, recycling alone cannot cope with the growth in plastics demand predicted until 2050. Therefore, achieving absolute sustainability of plastics requires a fundamental change in both producing and using plastics.⁷ By now, many stakeholders have put focus on either upstream solution (so called pre-consumer) such as material design, substitution and plastic reduction, or downstream solution (so called post-consumer) such as mechanical and chemical recycling. However, Systemiq's analysis pointed out the solutions need to be balanced out.²¹⁸ Overall, reducing plastic consumption while treating plastic waste as a valuable resource will be essential for reducing the planetary footprint of plastics. Accordingly, society needs to decide whether or not to stop considering plastics as cheap and disposable and to start placing a higher value on this versatile and durable product.

Conclusion

This tutorial review highlights the considerations in developing, implementing and assessing chemical recycling technologies for different plastic wastes. The major conclusions are as follows:

- Chemical recycling converts the plastic polymer chains into oligomers, monomers or other basic chemicals (such as carbon monoxide, carbon dioxide, methane, and hydrogen) prior to further reprocessing into monomers/polymers. Complementary to mechanical recycling, this process offers the possibility to transform hard-to-recycle or end-of-life plastics waste into petrochemical equivalent feedstocks for virgin plastic production.



- PET - Solvolysis processes, in particular glycolysis and alkaline hydrolysis, are recommended for chemical recycling of PET back into the starting monomers or intermediates. As solvolysis targets the degradation of polyester bonds, mixed-plastic waste streams are not suitable for these processes. Future research in this area should focus on process optimisation using real-industrial waste and investigating tolerances towards coloured PET streams and contamination.
- PP, PE, PS - Pyrolysis is a promising chemical recycling method for polyolefins. It thermally decomposes the long polymer chains to produce smaller and less complex molecules in an inert atmosphere. Liquid products, rich in alkanes, alkenes, and aromatics, can be utilised as fuels and chemical feedstocks. Gaseous products primarily comprise light hydrocarbons and hydrogen. Solid products, carbon-rich materials, can be further processed into high-value carbon materials with various applications including electrocatalysts and solid oxide fuel cells.
- PVC - Two-step process: dechlorination (remove Cl from the PVC macromolecule) + pyrolysis/gasification (use of the remaining hydrocarbons) has been developed in recent years to recover the Cl element and improve the quality of the final hydrocarbon products. However, due to the high additive content in PVC compared to other plastic types, novel methods are still required to maximise the recycling rate.
- Others and mixed plastics – SPI-7 category was designed as a catch-all for “other” plastics, with the reuse and recycling protocols currently not standardised. These “others” waste is often mixed with the main plastic streams, adding complexity for mechanical and chemical recycling. However, based on their polymer chain structures, similar chemical recycling methods introduced above can still be applied on them, via “one-pot” transformation into products with simple composition, or sequential treatment processes.
- Existing literature indicates the importance of recovering high value products via chemical recycling technologies as it underpins the sustainability of recycling technologies since up to ~60% of the total burden could be avoided compared with 25% presented by some mechanical recycling technologies. Furthermore, the utilisation of renewables or alternative low impact energy sources could further reduce the environmental intensity of processing plastic waste via chemical recycling. Economic benefits could also be obtained from sale of high value products as well as avoided CO₂ costs.
- The sustainability profile of a recycling system is a function of several factors including the combination of polymer and recycling process, as well as the assessment methodology. The suitability of polymers for a recycling technology should be assessed and prioritise as combination that yields highest product of interest, to maximise the environmental and economic benefits of the recycling system.
- The implementation of chemical recycling technologies requires support from waste management infrastructure, policy and financial incentives as well as tailored business models. Alongside the deployment of higher TRL pyrolysis plants, the development of other technologies with better feedback quality tolerance and scalability is key. Stakeholders need to look at both the upstream of plastic production and downstream plastic recycling as a whole to achieve overall sustainability, where coupling with other renewable carbons (CO₂, biomass) may come into play.

Author contributions

HL conceived the idea for the review. The manuscript was written and reviewed through contributions of all authors.

Conflicts of interest

There are no conflicts to declare.

Data Availability Statement

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Acknowledgements

HL thanks the support from the Surrey Future Fellowship Scheme funded by University of Surrey. HT would like to acknowledge the EPSRC Centre for Doctoral training in Next Generation Synthesis and Reaction Technology (Imperial College London, EP/S023232/1). RIM would like to acknowledge support from the VALUED project funded by Engineering and Physical Sciences Research Council (EPSRC) UK, project grant: EP/W031019/1. XL gratefully acknowledge funding from the European Union Horizon 2020 programme (iCAREPLAST Project, Grant agreement No. 820770).

Reference

1. Plastics Europe Chemical Recycling, <https://plasticseurope.org/sustainability/circularity/recycling/chemical-recycling/>, (accessed 10/08, 2024).
2. P. A. Kots, B. C. Vance, C. M. Quinn, C. Wang and D. G. Vlachos, *Nature Sustainability*, 2023, **6**, 1258-1267.
3. P. Europe, *THE CIRCULAR ECONOMY FOR PLASTICS*, 2023.
4. D. E. Fagnani, D. Kim, S. I. Camarero, J. F. Alfaro and A. J. McNeil, *Nature Chemistry*, 2023, **15**, 222-229.
5. E. Anglou, A. Ganesan, Y. Chang, K. M. Gołębek, Q. Fu, W. Bradley, C. W. Jones, C. Sievers, S. Nair and F. Boukouvala, *Chemical Engineering Journal*, 2024, **481**, 148278.
6. R. Cao, M. Q. Zhang, Y. Jiao, Y. Li, B. Sun, D. Xiao, M. Wang and D. Ma, *Nature Sustainability*, 2023, **6**, 1685-1692.
7. M. Bachmann, C. Zibunas, J. Hartmann, V. Tulus, S. Suh, G. Guillén-Gosálbez and A. Bardow, *Nature Sustainability*, 2023, **6**, 599-610.
8. *The Circularity Gap Report - 2023*.
9. D. Ma, *Nature Sustainability*, 2023, **6**, 1142-1143.



10. A. Rahimi and J. M. García, *Nature Reviews Chemistry*, 2017, **1**, 1-11.
11. VinylPlus, Progress Report, <https://www.vinylplus.eu/our-achievements/progress-report-2023/>).
12. U. E. Programme, *Single-use plastics: a roadmap for sustainability*, International Environmental Technology Centre, 2018.
13. A. Lee and M. S. Liew, *Journal of Material Cycles and Waste Management*, 2021, **23**, 32-43.
14. H. Holland Circular, *Chemical Recycling in circular perspective*, 2023.
15. R. A. Clark and M. P. Shaver, *Chemical Reviews*, 2024, **124**, 2617-2650.
16. J. Rickert, F. Cerdas and C. Herrmann, *Procedia CIRP*, 2020, **90**, 426-431.
17. R. D. Allen and M. I. James, in *Circular Economy of Polymers: Topics in Recycling Technologies*, American Chemical Society, 2021, vol. 1391, ch. 4, pp. 61-80.
18. H. H. Khoo, *Resources, Conservation and Recycling*, 2019, **145**, 67-77.
19. M. G. Davidson, R. A. Furlong and M. C. McManus, *Journal of Cleaner Production*, 2021, **293**, 126163.
20. NexantECA, Advances in depolymerization technologies for recycling. Retrieved from, <https://www.nexanteca.com/news-and-media/advances-depolymerization-technologies-recycling>).
21. R. Nisticò, *Polymer Testing*, 2020, **90**, 106707.
22. *How circular is PET?*, Zero Waste Europe, 2022.
23. Coca - Cola Collaborates with Tech Partners to Create Bottle Prototype Made from 100% Plant-Based Sources, <https://www.coca-colacompany.com/media-center/100-percent-plant-based-plastic-bottle>, (accessed 09/08, 2024).
24. R. Mori, *RSC Sustainability*, 2023, **1**, 179-212.
25. E. Barnard, J. J. Rubio Arias and W. Thielemans, *Green Chem.*, 2021, **23**, 3765-3765.
26. J. Payne and M. D. Jones, *Journal*, 2021, **14**, 4041-4070.
27. P. Pereira, P. E. Savage and C. W. Pester, *ACS Sustainable Chemistry & Engineering*, 2023, **11**, 7203-7209.
28. V. Sinha, M. R. Patel and J. V. Patel, *Journal of Polymers and the Environment*, 2010, **18**, 8-25.
29. T. Thiounn and R. C. Smith, *J. Polym. Sci.*, 2020, **58**, 1347-1347.
30. LOOP INDUSTRIES AND REED MANAGEMENT SIGN AGREEMENT FOR €35 MILLION FINANCING FOR GLOBAL COMMERCIALIZATION OF THE INFINITE LOOP™ TECHNOLOGY AND TO FORM FRENCH JOINT VENTURE, <https://www.loopindustries.com/cms/loop-industries-and-reed-management-sign-agreement-for-e35-million-financing-for-global-commercialization-of-the-infinite-loop-technology-and-to-form-french-joint-venture/>, (accessed 09/08, 2024).
31. Eastman's depolymerisation plant starts production, generates revenue, <https://www.sustainableplastics.com/news/eastmans-depolymerisation-plant-starts-production-generates-revenue>, (accessed 09/08, 2024).
32. R. López-Fonseca, I. Duque-Ingunza, B. de Rivas, S. Arnaiz and J. I. Gutiérrez-Ortiz, *Polymer Degradation and Stability*, 2010, **95**, 1022-1028.
33. A. Bohre, P. R. Jadhao, K. Tripathi, K. K. Pant, B. Likozar and B. Saha, *Journal*, 2023, **16**.
34. *US Pat.*, US6410607B1, 2002.
35. U. R. Vaidya and V. M. Nadkarni, *Industrial & Engineering Chemistry Research*, 1987, **26**, 194-198.
36. S. Baliga and W. T. Wong, *Journal of Polymer Science Part A: Polymer Chemistry*, 1989, **27**, 2071-2082.
37. R. López-Fonseca, I. Duque-Ingunza, B. de Rivas, L. Flores-Giraldo and J. I. Gutiérrez-Ortiz, *Chemical Engineering Journal*, 2011, **168**, 312-320.
38. J. Xin, Q. Zhang, J. Huang, R. Huang, Q. Z. Jaffery, D. Yan, Q. Zhou, J. Xu and X. Lu, *Journal of Environmental Management*, 2021, **296**, 113267.
39. W. Kaminsky, *Fuel Communications*, 2021, **8**, 100023.
40. A. Aguado, L. Martínez, L. Becerra, M. Arieta-araunabeña, S. Arnaiz, A. Asueta and I. Robertson, *Journal of Material Cycles and Waste Management*, 2014, **16**, 201-210.
41. A. Barredo, A. Asueta, I. Amundarain, J. Leivar, R. Miguel-Fernández, S. Arnaiz, E. Epelde, R. López-Fonseca and J. I. Gutiérrez-Ortiz, *Journal of Environmental Chemical Engineering*, 2023, **11**, 109823.
42. N. George and T. Kurian, *Industrial & Engineering Chemistry Research*, 2014, **53**, 14185-14198.
43. C. W. S. Yeung, J. Y. Q. Teo, X. J. Loh and J. Y. C. Lim, *ACS Materials Letters*, 2021, **3**, 1660-1676.
44. I. Vollmer, M. J. F. Jenks, M. C. P. Roelands, R. J. White, T. van Harmelen, P. de Wild, G. P. van der Laan, F. Meirer, J. T. F. Keurentjes and B. M. Weckhuysen, *Angewandte Chemie International Edition*, 2020, **59**, 15402-15423.
45. S. D. Anuar Sharuddin, F. Abnisa, W. M. A. Wan Daud and M. K. Aroua, *Energy Conversion and Management*, 2016, **115**, 308-326.
46. R. Miandad, M. A. Barakat, A. S. Aburiazzaiza, M. Rehan and A. S. Nizami, *Process Saf. Environ. Prot.*, 2016, **102**, 822-822.
47. Y. Zhang, G. Ji, D. Ma, C. Chen, Y. Wang, W. Wang and A. Li, *Process Safety and Environmental Protection*, 2020, **142**, 203-211.
48. J. Jiang, K. Shi, X. Zhang, K. Yu, H. Zhang, J. He, Y. Ju and J. Liu, *Journal of Environmental Chemical Engineering*, 2022, **10**, 106867-106867.
49. O. Dogu, M. Pelucchi, R. Van de Vijver, P. H. M. Van Steenberge, D. R. D'Hooge, A. Cuoci, M. Mehl, A. Frassoldati, T. Faravelli and K. M. Van Geem, *Progress in Energy and Combustion Science*, 2021, **84**, 100901-100901.
50. A. López, I. de Marco, B. M. Caballero, M. F. Laresgoiti and A. Adrados, *Chemical Engineering Journal*, 2011, **173**, 62-71.
51. E. A. Williams and P. T. Williams, *Journal of Analytical and Applied Pyrolysis*, 1997, **40-41**, 347-363.
52. Y. Liu, J. Qian and J. Wang, *Fuel Processing Technology*, 2000, **63**, 45-55.
53. R. Bagri and P. T. Williams, *Journal of Analytical and Applied Pyrolysis*, 2002, **63**, 29-41.
54. I. Ahmad, M. I. Khan, H. Khan, M. Ishaq, R. Tariq, K. Gul and W. Ahmad, *International journal of green energy*, 2015, **12**, 663-671.
55. D. P. Serrano, J. Aguado and J. M. Escola, *Acs Catalysis*, 2012, **2**, 1924-1941.
56. R. Thahir, M. Irwan, A. Alwathan and R. Ramli, *Results in Engineering*, 2021, **11**, 100231-100231.
57. K. Sivagami, K. V. Kumar, P. Tamizhdurai, D. Govindarajan, M. Kumar and I. Nambi, *RSC advances*, 2022, **12**, 7612-7620.

View Article Online

Industrial & Engineering

Chemistry Research

1987, 26, 194-198.

Journal of Polymer Science Part

A: Polymer Chemistry, 1989, 27, 2071-2082.

Chemical Engineering

Journal, 2011, 168, 312-320.

Journal of Environmental

Management, 2021, 296, 113267.

Fuel Communications, 2021, 8, 100023.

Journal of Material

Cycles and Waste Management, 2014, 16, 201-210.

Journal of Environmental Chemical

Engineering, 2023, 11, 109823.

Industrial & Engineering

Chemistry Research, 2014, 53, 14185-14198.

ACS

Materials Letters, 2021, 3, 1660-1676.

Journal of Environmental Chemical

Engineering, 2023, 11, 109823.

Angewandte

Chemie International Edition, 2020, 59, 15402-15423.

Energy Conversion and Management, 2016, 115, 308-326.

Process Saf. Environ. Prot., 2016, 102, 822-822.

Process Safety and Environmental Protection, 2020, 142, 203-211.

Journal of Environmental Chemical Engineering, 2022, 10, 106867-106867.

Progress in Energy and Combustion Science, 2021, 84, 100901-100901.

Chemical Engineering Journal, 2011, 173, 62-71.

Journal of Analytical and Applied Pyrolysis, 1997, 40-41, 347-363.

Fuel Processing Technology, 2000, 63, 45-55.

Journal of Analytical and Applied Pyrolysis, 2002, 63, 29-41.

International journal of green energy, 2015, 12, 663-671.

Acs Catalysis, 2012, 2, 1924-1941.

Results in Engineering, 2021, 11, 100231-100231.

RSC advances, 2022, 12, 7612-7620.



58. S. L. Wong, S. Armenise, B. B. Nyakuma, A. Bogush, S. Towers, C. H. Lee, K. Y. Wong, T. H. Lee, E. Rebrov and M. Muñoz, *Journal of Analytical and Applied Pyrolysis*, 2023, **169**, 105793-105793.
59. Y. Chai, W. Dai, G. Wu, N. Guan and L. Li, *Accounts of Chemical Research*, 2021, **54**, 2894-2904.
60. L. Dai, N. Zhou, Y. Lv, Y. Cheng, Y. Wang, Y. Liu, K. Cobb, P. Chen, H. Lei and R. Ruan, *Progress in Energy and Combustion Science*, 2022, **93**, 101021.
61. W. Vermeiren and J. P. Gilson, *Topics in Catalysis*, 2009, **52**, 1131-1161.
62. R. K. Singh, B. Ruj, A. K. Sadhukhan and P. Gupta, *Journal of environmental management*, 2019, **239**, 395-406.
63. R. K. Singh, B. Ruj, A. K. Sadhukhan and P. Gupta, *Journal of environmental management*, 2020, **261**, 110112-110112.
64. J. Jae, G. A. Tompsett, A. J. Foster, K. D. Hammond, S. M. Auerbach, R. F. Lobo and G. W. Huber, *Journal of Catalysis*, 2011, **279**, 257-268.
65. X. Zhang, H. Lei, G. Yadavalli, L. Zhu, Y. Wei and Y. Liu, *Fuel*, 2015, **144**, 33-42.
66. M. Artetxe, G. Lopez, M. Amutio, G. Elordi, J. Bilbao and M. Olazar, *Industrial & engineering chemistry research*, 2013, **52**, 10637-10645.
67. P. Castano, G. Elordi, M. Olazar, A. T. Aguayo, B. Pawelec and J. Bilbao, *Applied Catalysis B: Environmental*, 2011, **104**, 91-100.
68. Y.-H. Seo, K.-H. Lee and D.-H. Shin, *Journal of Analytical and Applied Pyrolysis*, 2003, **70**, 383-398.
69. A. Marcilla, M. I. Beltrán and R. Navarro, *Applied Catalysis B: Environmental*, 2009, **86**, 78-86.
70. E. Epelde, M. Ibañez, A. T. Aguayo, A. G. Gayubo, J. Bilbao and P. Castaño, *Microporous and mesoporous materials*, 2014, **195**, 284-293.
71. G. A. Eimer, L. B. Pierella, G. A. Monti and O. A. Anunziata, *Catalysis Communications*, 2003, **4**, 118-123.
72. S. J. Choi, Y.-K. Park, K.-E. Jeong, T.-W. Kim, H.-J. Chae, S. H. Park, J.-K. Jeon and S.-S. Kim, *Korean Journal of Chemical Engineering*, 2010, **27**, 1446-1451.
73. A. Marcilla, A. Gómez-Siurana and D. Berenguer, *Applied Catalysis A: General*, 2006, **301**, 222-231.
74. T. F. Degnan Jr, *Topics in Catalysis*, 2000, **13**, 349-356.
75. E. Rodríguez, A. Gutiérrez, R. Palos, F. J. Vela, M. J. Azkoiti, J. M. Arandes and J. Bilbao, *Chemical Engineering Journal*, 2020, **382**, 122602-122602.
76. E. Rodríguez, A. Gutiérrez, R. Palos, F. J. Vela, J. M. Arandes and J. Bilbao, *Waste Management*, 2019, **93**, 162-172.
77. G. Elordi, M. Olazar, P. Castaño, M. Artetxe and J. Bilbao, *Industrial & Engineering Chemistry Research*, 2012, **51**, 14008-14017.
78. Y. Wu, K. Wang, B. Wei, H. Yang, L. Jin and H. Hu, *Science of The Total Environment*, 2022, **806**, 151287.
79. L. Fan, Y. Zhang, S. Liu, N. Zhou, P. Chen, Y. Liu, Y. Wang, P. Peng, Y. Cheng and M. Addy, *Energy Conversion and Management*, 2017, **149**, 432-441.
80. H. Zhang, J. Zheng, R. Xiao, Y. Jia, D. Shen, B. Jin and G. Xiao, *Energy & Fuels*, 2014, **28**, 4294-4299.
81. J. Wang, B. Zhang, Z. Zhong, K. Ding, A. Deng, M. Min, P. Chen and R. Ruan, *Energy Conversion and Management*, 2017, **139**, 222-231.
82. H. Iftikhar, M. Zeeshan, S. Iqbal, B. Muneer and M. Razzaq, *Bioresource technology*, 2019, **289**, 121647-121647.
83. G. Kabir and B. H. Hameed, *Renewable and Sustainable Energy Reviews*, 2017, **70**, 945-967. DOI: 10.1039/D4GC03127J
84. J. Wang, J. Jiang, X. Meng, M. Li, X. Wang, S. Pang, K. Wang, Y. Sun, Z. Zhong, R. Ruan and A. J. Ragauskas, *Environmental Science & Technology*, 2020, **54**, 8390-8400.
85. F. Zhang, M. Zeng, R. D. Yappert, J. Sun, Y. H. Lee, A. M. LaPointe, B. Peters, M. M. Abu-Omar and S. L. Scott, *Science*, 2020, **370**, 437-437.
86. Ç. Çelikgöğüs and A. Karaduman, *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 2015, **37**, 2507-2513.
87. J. Kang, K. Cheng, L. Zhang, Q. Zhang, J. Ding, W. Hua, Y. Lou, Q. Zhai and Y. Wang, *Angewandte Chemie International Edition*, 2011, **50**, 5200-5203.
88. X. Peng, K. Cheng, J. Kang, B. Gu, X. Yu, Q. Zhang and Y. Wang, *Angewandte Chemie International Edition*, 2015, **54**, 4553-4556.
89. C. Zhao and J. A. Lercher, *Angewandte Chemie International Edition*, 2012, **51**, 5935-5940.
90. E. F. Iliopoulou, S. D. Stefanidis, K. G. Kalogiannis, A. Delimitis, A. A. Lappas and K. S. Triantafyllidis, *Applied Catalysis B: Environmental*, 2012, **127**, 281-290.
91. J. Nishino, M. Itoh, H. Fujiyoshi and Y. Uemichi, *Fuel*, 2008, **87**, 3681-3686.
92. Y. Chen, Y. Zhu, Z. Wang, Y. Li, L. Wang, L. Ding, X. Gao, Y. Ma and Y. Guo, *Advances in colloid and interface science*, 2011, **163**, 39-52.
93. Y. S. González, C. Costa, M. C. Márquez and P. Ramos, *Journal of Hazardous Materials*, 2011, **187**, 101-112.
94. A. do Couto Fraga, C. P. B. Quitete, V. L. Ximenes, E. F. Sousa-Aguiar, I. M. Fonseca and A. M. B. Rego, *Journal of Molecular Catalysis A: Chemical*, 2016, **422**, 248-257.
95. Z. Yang, H. Lei, Y. Zhang, K. Qian, E. Villota, M. Qian, G. Yadavalli and H. Sun, *Applied Energy*, 2018, **220**, 426-436.
96. K. Sun, Q. Huang, X. Meng, Y. Chi and J. Yan, *Energy & Fuels*, 2018, **32**, 9772-9781.
97. Y. Zhang, D. Duan, H. Lei, E. Villota and R. Ruan, *Applied Energy*, 2019, **251**, 113337.
98. J. Wang, J. Jiang, Z. Zhang, X. Meng, Y. Sun, A. J. Ragauskas, Q. Zhang and D. C. W. Tsang, *Energy Conversion and Management*, 2022, **270**, 116250.
99. K. M. Rajendran, V. Chintala, A. Sharma, S. Pal, J. K. Pandey and P. Ghodke, *Materials Today Communications*, 2020, **24**, 100982.
100. K. Li, J. Lei, G. Yuan, P. Weerachanchai, J.-Y. Wang, J. Zhao and Y. Yang, *Chemical Engineering Journal*, 2017, **317**, 800-809.
101. S. Lee, K. Yoshida and K. Yoshikawa, *Energy and Environment Research*, 2015, **5**, 18-18.
102. S. Frigo, M. Seggiani, M. Puccini and S. Vitolo, *Fuel*, 2014, **116**, 399-408.
103. M. B. Al Rayaan, *Cleaner Engineering and Technology*, 2021, **2**, 100062.
104. J. Chattopadhyay, T. S. Pathak, R. Srivastava and A. C. Singh, *Energy*, 2016, **103**, 513-521.
105. C. Li, C. Zhang, M. Gholizadeh and X. Hu, *Journal of Hazardous Materials*, 2020, **399**, 123075.
106. B. Valle, A. G. Gayubo, A. Alonso, A. T. Aguayo and J. Bilbao, *Applied Catalysis B: Environmental*, 2010, **100**, 318-327.
107. E.-M. El-Malki, R. A. Van Santen and W. M. H. Sachtler, *The Journal of Physical Chemistry B*, 1999, **103**, 4611-4622.



108. R. Palos, A. Gutiérrez, F. J. Vela, M. Olazar, J. M. Arandes and J. Bilbao, *Energy & Fuels*, 2021, **35**, 3529-3557.
109. F. J. Christopher, P. S. Kumar, L. Jayaraman and G. Rangasamy, *Fuel*, 2023, **332**, 126168.
110. D. K. Ratnasari, M. A. Nahil and P. T. Williams, *Journal of Analytical and Applied Pyrolysis*, 2017, **124**, 631-637.
111. B. Kunwar, B. R. Moser, S. R. Chandrasekaran, N. Rajagopalan and B. K. Sharma, *Energy*, 2016, **111**, 884-892.
112. A. L. Figueiredo, A. S. Araujo, M. Linares, Á. Peral, R. A. García, D. P. Serrano and V. J. Fernandes, *Journal of Analytical and Applied Pyrolysis*, 2016, **117**, 132-140.
113. H. Qiao, X. Hou, H. Zhou, C. Song, L. Yin, J. Huang, E. Yuan and T. Cui, *Fuel*, 2023, **351**, 128821.
114. D. Yao and C.-H. Wang, *Applied Energy*, 2020, **265**, 114819.
115. J. M. Younker, T. Saito, M. A. Hunt, A. K. Naskar and A. Beste, *J. Am. Chem. Soc.*, 2013, **135**, 6130-6141.
116. H. Zhang, X.-L. Zhou, L.-M. Shao, F. Lü and P.-J. He, *ACS Sustainable Chemistry & Engineering*, 2019, **7**, 3801-3810.
117. Y. Wen, K. Kierzek, X. Chen, J. Gong, J. Liu, R. Niu, E. Mijowska and T. Tang, *Waste Management*, 2019, **87**, 691-700.
118. R. Vicentini, W. Nunes, B. G. A. Freitas, L. M. Da Silva, D. M. Soares, R. Cesar, C. B. Rodella and H. Zanin, *Energy Storage Mater*, 2019, **22**, 311-322.
119. S. He, Y. Xu, Y. Zhang, S. Bell and C. Wu, *Journal of Hazardous Materials*, 2021, **402**, 123726.
120. J. C. Acomb, C. Wu and P. T. Williams, *Applied Catalysis B: Environmental*, 2016, **180**, 497-510.
121. D. Yao, Y. Zhang, P. T. Williams, H. Yang and H. Chen, *Applied Catalysis B: Environmental*, 2018, **221**, 584-597.
122. X. Liu, Y. Zhang, M. A. Nahil, P. T. Williams and C. Wu, *Journal of Analytical and Applied Pyrolysis*, 2017, **125**, 32-39.
123. M. A. Nahil, C. Wu and P. T. Williams, *Fuel Processing Technology*, 2015, **130**, 46-53.
124. D. Yao, H. Yang, Q. Hu, Y. Chen, H. Chen and P. T. Williams, *Applied Catalysis B: Environmental*, 2021, **280**, 119413.
125. J. Wang, B. Shen, M. Lan, D. Kang and C. Wu, *Catalysis Today*, 2020, **351**, 50-57.
126. N. Cai, S. Xia, X. Li, L. Sun, P. Bartocci, F. Fantozzi, H. Zhang, H. Chen, P. T. Williams and H. Yang, *Journal of Cleaner Production*, 2021, **315**, 128240.
127. N. Cai, S. Xia, X. Zhang, Z. Meng, P. Bartocci, F. Fantozzi, Y. Chen, H. Chen, P. T. Williams and H. Yang, *ChemSusChem*, 2020, **13**, 938-944.
128. Q. Liu, F. Wang, E. Hu, R. Hong, T. Li, X. Yuan, X. B. Cheng, N. Cai, R. Xiao and H. Zhang, *iScience*, 2022, **25**, 104855.
129. Y. Wang, J. Bailey, Y. Zhu, Y. Zhang, S. K. S. Boetcher, Y. Li and C. Wu, *Waste Management*, 2022, **154**, 96-104.
130. D. Yao, H. Li, B. C. Mohan, A. K. Prabhakar, Y. Dai and C.-H. Wang, *ACS Sustainable Chemistry & Engineering*, 2022, **10**, 1125-1136.
131. M. The European Council of Vinyl, PVC applications, <https://pvc.org/pvc-applications/>, (accessed 10/08, 2024).
132. Z. Ait-Touchente, M. Khellaf, G. Raffin, N. Lebaz and A. Elaissari, *Journal*, 2024, **35**.
133. K. Lewandowski and K. Skórczewska, *Polymers*, 2022, **14**, 3035.
134. S. Xu, Z. Han, K. Yuan, P. Qin, W. Zhao, T. Lin, T. Zhou and F. Huang, *Nature Reviews Methods Primers*, 2023, **3**, 44-44.
135. G. Wang, S. Liu, H. Zhang, J. Wang and Q. Xue, *Polymers*, 2022, **14**, 1689.
136. Z. Yuan, J. Zhang, P. Zhao, Z. Wang, X. Cui, L. Gao, Q. Guo and H. Tian, *ACS Omega*, 2020, **5**, 11291-11298.
137. J. Lu, S. Borjigin, S. Kumagai, T. Kameda, Y. Saito and T. Yoshioka, *Waste Management*, 2019, **99**, 31-41.
138. T. Kameda, M. Ono, G. Grause, T. Mizoguchi and T. Yoshioka, *Industrial and Engineering Chemistry Research*, 2008, **47**, 8619-8624.
139. D. Torres, Y. Jiang, D. A. Sanchez-Monsalve and G. A. Leeke, *Journal of Analytical and Applied Pyrolysis*, 2020, **149**, 104831.
140. G. Jiang, D. A. Sanchez Monsalve, P. Clough, Y. Jiang and G. A. Leeke, *ACS Sustainable Chemistry and Engineering*, 2021, **9**, 1576-1589.
141. J. Hubáček, J. Lederer, P. Kuráň, P. Koutník, Z. Gholami, M. Zbuzek and M. Bačiak, *Fuel Processing Technology*, 2022, **231**, 107226.
142. L. Ye, T. Li and L. Hong, *Waste Management*, 2021, **126**, 832-842.
143. L. Hong, L.-H. Ye and T.-L. Li, De-chlorination effectiveness and efficiency of poly(vinyl) chloride (PVC) co-pyrolyzing with iron oxide, <https://ssrn.com/abstract=4402944>.
144. A. M. Hapipi, H. Suda, M. A. Uddin and Y. Kato, *Energy and Fuels*, 2018, **32**, 7792-7799.
145. H. Nishibata, M. A. Uddin and Y. Kato, *Polymer Degradation and Stability*, 2020, **179**, 109225.
146. H. Mio, S. Saeki, J. Kano and F. Saito, *Environmental Science and Technology*, 2002, **36**, 1344-1348.
147. M. H. Cho, S. H. Jung and J. S. Kim, *Energy and Fuels*, 2010, **24**, 1389-1395.
148. K. B. Park, S. J. Oh, G. Begum and J. S. Kim, *Energy*, 2018, **157**, 402-411.
149. T. Bhaskar, R. Negoro, A. Muto and Y. Sakata, *Green Chemistry*, 2006, **8**, 697-700.
150. L. Chen, Y. Zhu, L. C. Meyer, L. V. Hale, T. T. Le, A. Karkamkar, J. A. Lercher, O. Y. Gutiérrez and J. Szanyi, *Reaction Chemistry and Engineering*, 2022, **7**, 844-854.
151. S. Kumagai, J. Lu, Y. Fukushima, H. Ohno, T. Kameda and T. Yoshioka, *Resources, Conservation and Recycling*, 2018, **133**, 354-361.
152. M. Sadat-Shojai and G. R. Bakhshandeh, *Journal*, 2011, **96**, 404-415.
153. J. Huang, A. Veksha, W. P. Chan, A. Giannis and G. Lisak, *Renewable and Sustainable Energy Reviews*, 2022, **154**, 111866.
154. *Synthesis, Structure and Properties of Poly(lactic acid)*, Springer, 2018.
155. P. McKeown and M. D. Jones, *Sustainable Chemistry*, 2020, **1**, 1-22.
156. V. Piemonte, S. Sabatini and F. Gironi, *Journal of Polymers and the Environment*, 2013, **21**, 640-647.
157. L. Shen, J. Haufe and M. K. Patel, *Product overview and market projection of emerging bio-based plastics*, Copernic Institute for Sustainable Development and Innovation - Utrecht University, 2009.
158. F. d. Kopinke, M. Remmler, K. Mackenzie and M. Milder, *Polymer Degradation and Stability*, 1996, **53**, 329-342.
159. D. Cam and M. Marucci, *Polymer*, 1997, **38**, 1879-1884.
160. H. Nishida, T. Mori, S. Hoshihara, Y. Fan, Y. Shirai and T. Endo, *Polymer Degradation and Stability*, 2003, **81**, 515-523.
161. H. Abe, N. Takahashi, K. J. Kim, M. Mochizuki and Y. Doi, *Biomacromolecules*, 2004, **5**, 1606-1614.



162. S. Lazzari, F. Codari, G. Storti, M. Morbidelli and D. Moscatelli, *Polymer Degradation and Stability*, 2014, **110**, 80-90.
163. C. F. Van Nostrum, T. F. J. Veldhuis, G. W. Bos and W. E. Hennink, *Polymer*, 2004, **45**, 6779-6787.
164. S. J. De Jong, E. R. Arias, D. T. S. Rijkers, C. F. Van Nostrum, J. J. Kettenes-Van Den Bosch and W. E. Hennink, *Polymer*, 2001, **42**, 2795-2802.
165. C. Shih, *Journal of Controlled Release*, 1995, **34**, 9-15.
166. M. Pérez-Venegas, T. Friščić and K. Auclair, *ACS Sustainable Chemistry and Engineering*, 2023, **11**, 9924-9931.
167. A. Carné Sánchez and S. R. Collinson, *European Polymer Journal*, 2011, **47**, 1970-1976.
168. M. Niaounakis, *European Polymer Journal*, 2019, **114**, 464-475.
169. Statista, Production of polyamide fibers worldwide from 1975 to 2022, <https://www.statista.com/statistics/649908/polyamide-fiber-production-worldwide/#:~:text=In%202022%2C%20global%20polyamide%20production,of%20polyamide%20fibers%20produce d%20worldwide.,> (accessed 12/08, 2024).
170. Nylon Market Size, Share & Trends Analysis Report, <https://www.grandviewresearch.com/industry-analysis/nylon-6-6-market>, (accessed 12/08, 2024).
171. M. J. Lozano-González, M. T. Rodríguez-Hernandez, E. A. Gonzalez-De Los Santos and J. Villalpando-Olmos, *Journal of Applied Polymer Science*, 2000, **76**, 851-858.
172. M. Nielsen, P. Jurasek, J. Hayashi and E. Furimsky, *Journal of Analytical and Applied Pyrolysis*, 1995, **35**, 43-51.
173. A. Kumar, N. Von Wolff, M. Rauch, Y. Q. Zou, G. Shmul, Y. Ben-David, G. Leitun, L. Avram and D. Milstein, *J. Am. Chem. Soc.*, 2020, **142**, 14267-14275.
174. H. Bockhorn, A. Hornung, U. Hornung and J. Weichmann, *Thermochimica Acta*, 1999, **337**, 97-110.
175. L. Wursthorn, K. Beckett, J. O. Rothbaum, R. M. Cywar, C. Lincoln, Y. Kratish and T. J. Marks, *Angewandte Chemie - International Edition*, 2023, **62**, e202212543.
176. US005302756A, 1994.
177. WO1997003040A1, 1996.
178. US005302756A, 1994.
179. UA005395974A, 1995.
180. US005668277A, 1997.
181. R. Yang, G. Xu, B. Dong, X. Guo and Q. Wang, *ACS Sustainable Chemistry and Engineering*, 2022, **10**, 9860-9871.
182. T. W. Walker, N. Frelka, Z. Shen, A. K. Chew, J. Banick, S. Grey, M. S. Kim, J. A. Dumesic, R. C. Van Lehn and G. W. Huber, *Science Advances*, 2020, **6**, eaba7599.
183. J. Yu, A. d. C. Munguía-López, V. S. Cecon, K. L. Sánchez-Rivera, K. Nelson, J. Wu, S. Kolapkar, V. M. Zavala, G. W. Curtzwiler, K. L. Vorst, E. Bar-Ziv and G. W. Huber, *Green Chemistry*, 2023, **25**, 4723-4734.
184. K. L. Sánchez-Rivera, C. Granger, H. Appiah, K. Nelson, S. Grey, D. J. Sun, J. E. Estela-García, E. Chen, Z. Xu, T. A. Osswald, L.-S. Turng, A. G. McDonald, R. C. Van Lehn, E. Bar-Ziv and G. W. Huber, *ACS Materials Letters*, 2024, DOI: 10.1021/acsmaterialslett.4c01048, 4042-4050.
185. Y. B. Zhao, X. D. Lv and H. G. Ni, *Chemosphere*, 2018, **209**, 707-720.
186. S. C. Aparício, P. M. Castro, B. D. Ribeiro and I. M. Marrucho, *Green Chemistry*, 2024, **26**, 6799-6811.
187. M. Ramírez-Martínez, S. L. Aristizábal, G. Szekely and S. P. Nunes, *Green Chemistry*, 2022, **25**, 966-977.
188. M. Mohan, J. D. Keasling, B. A. Simmons and S. Singh, *Green Chemistry*, 2022, **24**, 4140-4152.
189. A. Lindfors, *Environmental and Sustainability Indicators*, 2021, **12**, 100149.
190. *ISO 14044:2006 Environmental management — Life cycle assessment — Requirements and guidelines*, 2006.
191. R. I. Muazu, R. Rothman and L. Maltby, *Journal of Cleaner Production*, 2021, **293**, 126120.
192. I. G. Hakeem, A. Sharma, T. Sharma, A. Sharma, J. B. Joshi, K. Shah, A. S. Ball and A. Surapaneni, *Biofuels, Bioproducts and Biorefining*, 2023, **17**, 718-750.
193. *Guidelines for Social Life Cycle Assessment of Products and Organisations - UN Environment Programme*, 2020.
194. K. Ragaert, L. Delva and K. Van Geem, *Waste Management*, 2017, **69**, 24-24.
195. X. Zhao and F. You, *ACS Sustainable Chemistry & Engineering*, 2021, **9**, 12167-12184.
196. D. Maga, M. Hiebel and N. Thonemann, *Resources, Conservation and Recycling*, 2019, **149**, 86-96.
197. A. Demetrious and E. Crossin, *Journal of Material Cycles and Waste Management*, 2019, **21**, 850-860.
198. F. Perugini, M. L. Mastellone and U. Arena, *Environmental Progress*, 2005, **24**, 137-154.
199. S. M. Al-Salem, S. Evangelisti and P. Lettieri, *Chemical Engineering Journal*, 2014, **244**, 391-402.
200. L. Shen, E. Worrell and M. K. Patel, *Resources, Conservation and Recycling*, 2010, **55**, 34-52.
201. G. Faraca, V. Martinez-Sanchez and T. F. Astrup, *Resources, Conservation and Recycling*, 2019, **143**, 299-309.
202. R. I. Muazu, P. Yaseneva, N. Shah and M.-M. Titirici, unpublished work.
203. *LCA of Management Options for Polymer Waste from Bank Notes - Final Study Report (Bank of England)*, 2015.
204. N. Ryan and P. Yaseneva, *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 2021, **379**, 20200335.
205. BOTTLE™ research analysis, <https://www.bottle.org/research/analysis>, (accessed 13/08, 2024).
206. A. Singh, N. A. Rorrer, S. R. Nicholson, E. Erickson, J. S. DesVeaux, A. F. T. Avelino, P. Lamers, A. Bhatt, Y. Zhang, G. Avery, L. Tao, A. R. Pickford, A. C. Carpenter, J. E. McGeehan and G. T. Beckham, *Joule*, 2021, **5**, 2479-2503.
207. T. Uekert, A. Singh, J. S. DesVeaux, T. Ghosh, A. Bhatt, G. Yadav, S. Afzal, J. Walzberg, K. M. Knauer, S. R. Nicholson, G. T. Beckham and A. C. Carpenter, *ACS Sustainable Chemistry and Engineering*, 2023, **11**, 965-978.
208. G. Yadav, A. Singh, A. Dutta, T. Uekert, J. S. DesVeaux, S. R. Nicholson, E. C. D. Tan, C. Mukarakate, J. A. Schaidle, C. J. Wrasman, A. C. Carpenter, R. M. Baldwin, Y. Román-Leshkov and G. T. Beckham, *Energy & Environmental Science*, 2023, **16**, 3638-3653.
209. A. H. Hergesell, R. J. Baarslag, C. L. Seitzinger, R. Meena, P. Schara, Ž. Tomović, G. Li, B. M. Weckhuysen and I. Vollmer, *J. Am. Chem. Soc.*, 2024, DOI: 10.1021/jacs.4c07157.
210. V. Štrukil, *ChemSusChem*, 2021, **14**, 330-338.
211. S. Kaabel, J. Arciszewski, T. H. Borchers, J. P. D. Therien, T. Friščić and K. Auclair, *ChemSusChem*, 2023, **16**, e202201613.



ARTICLE

Journal Name

212. V. Tournier, C. M. Topham, A. Gilles, B. David, C. Folgoas, E. Moya-Leclair, E. Kamionka, M. L. Desrousseaux, H. Texier, S. Gavalda, M. Cot, E. Guémard, M. Dalibey, J. Nomme, G. Cioci, S. Barbe, M. Chateau, I. André, S. Duquesne and A. Marty, *Nature*, 2020, **580**, 216-219.
213. C.-C. Chen, L. Dai, L. Ma and R.-T. Guo, *Nature Reviews Chemistry*, 2020, **4**, 114-126.
214. P. U. Vasileios Rizos, Edoardo Righetti, Amin Kassab, *Chemical Recycling of Plastics: Technologies, trends and policy implications*, CEPS, 2023.
215. J. Walzberg, S. Sethuraman, T. Ghosh, T. Uekert and A. Carpenter, *Energy Research & Social Science*, 2023, **100**, 103116.
216. E. T. C. Vogt and B. M. Weckhuysen, *Nature*, 2024, **629**, 295-306.
217. J. Zheng and S. Suh, *Nat Clim Change*, 2019, **9**, 374-378.
218. Systemiq, *ReShaping Plastics Report*, 2022.

View Article Online
DOI: 10.1039/D4GC03127J

Open Access Article. Published on 05 outubro 2024. Downloaded on 11/10/2024 20:24:43.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.



Green Chemistry Accepted Manuscript

Fundamental, Technical and Environmental Overviews of Plastic Chemical Recycling

View Article Online

DOI: 10.1039/D4GC03127J

Hui Luo,^{*a} Helen Tyrrell,^b Jingyang Bai,^b Rukayya Ibrahim Muazu^b and Xiangyi Long^{*b}

The authors confirm that no primary research results, software or code have been included and no new data were generated or analysed as part of this review.

