ROYAL SOCIETY OF CHEMISTRY

SUSTAINABILITY

Chemical recycling

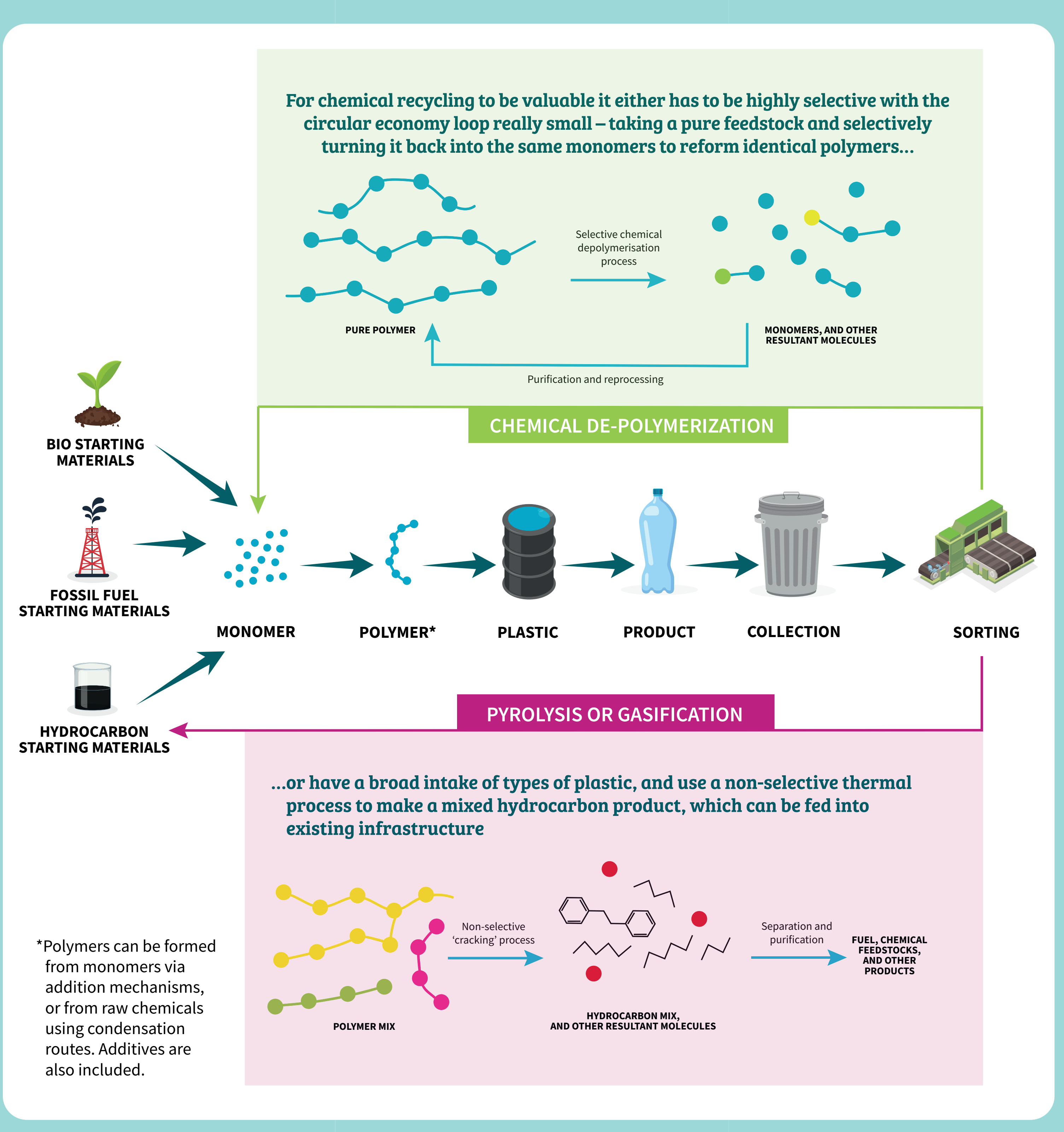
Following the resource hierarchy, it is first important to reduce plastic usage, and then to reuse what we have. Then mechanical recycling should be optimised to efficiently recycle used plastics and reform them into new products.

For plastics that can't be easily or effectively mechanically recycled – for instance mixed polymers or composite plastics – chemical recycling provides an opportunity to 'close the loop', retaining some value and avoiding materials going to landfill or incineration. Chemical recycling also provides the opportunity to 'upcycle' low value plastic waste into higher value products, such as feedstock chemicals for broader industry applications.

In chemical recycling the basic chemical structure of the material is changed, with the polymer broken apart into smaller molecules, which can be monomers or raw chemicals.

What is chemical recycling?

Chemical recycling is an umbrella term for several technologies that use heat or chemical processes, or both, to break apart the polymer chain within the plastic.

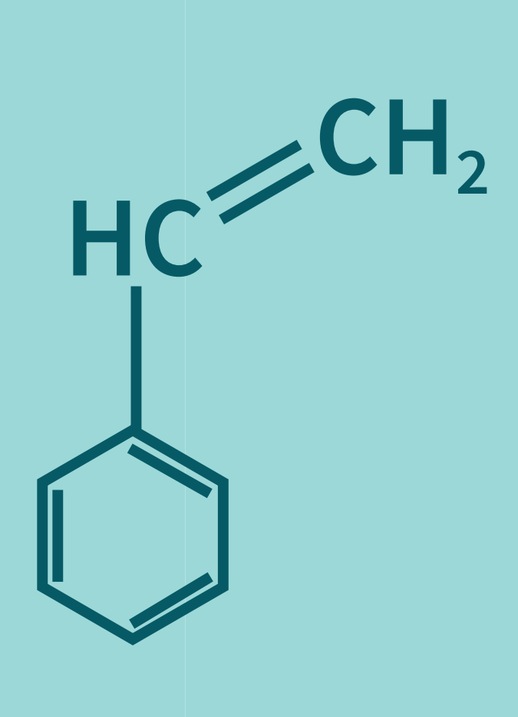

For chemical recycling to be valuable it either has to be highly selective with the circular economy loop really small – taking a pure feedstock and selectively turning it back into the same monomers to reform identical polymers…

…or have a broad intake of types of plastic, and use a non-selective thermal process to make a mixed hydrocarbon product, which can be fed into existing infrastructure

*Polymers can be formed from monomers via addition mechanisms, or from raw chemicals using condensation routes. Additives are also included.

What is a monomer?

A monomer is the molecular building block of a particular type of polymer. For instance, polystyrene is made by polymerising (chemically linking together) the monomer styrene. Polymers can also be formed by condensation mechanisms where one or more type of molecule react together creating the polymer along with by-products, for example PET formation. In the chemical representation the brackets and 'n' denote the chain continuing 'n' number of times, potentially in both directions.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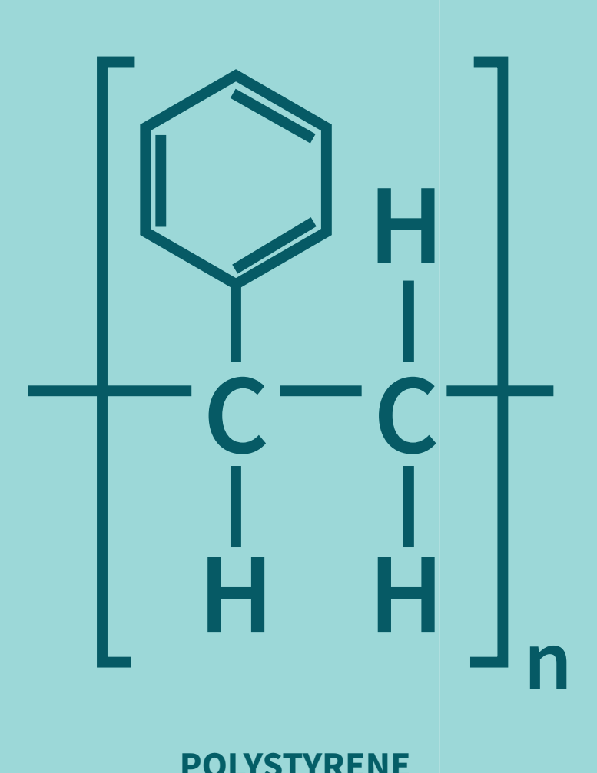
POLYSTYRENE

Chemical recycling processes[1]

NAME	PROCESS	PRODUCT	BENEFITS	LIMITATIONS
Dissolution/ solvent-based purification	Doesn't fall under either mechanical or chemical recycling. Polymers are selectively dissolved in a solvent, with any additives or impurities being non-soluble and filtered out. Polymers are then precipitated out of the solvent and reformulated.	Pure recycled polymers	+ Useful when there is a known additive to be removed before reformulation + Produces a high purity recycled polymer + Theoretically a step-by-step solvent process could deal with a mixed polymer stream	− Potentially high environmental impact depending on type of solvents used − Polymer can be degraded during process as with mechanical recycling
Pyrolysis	High temperatures of 250–700°C, under an inert atmosphere, break apart the polymer. Also called 'thermal cracking'.	Mixed oil	+ Can be useful for mixed streams, or where different polymers cannot be separated, eg for multilayer film	− Poor selectivity in product, requiring further purification (distillation) and processing before use as feedstock − Uses high temperatures, and therefore a lot of energy
Catalytic cracking/ catalytic pyrolysis	Pyrolysis process with the introduction of a catalyst to reduce processing temperatures and increase yields of high value products.	Mixed products, but can be tuned for higher value products	+ Reduced energy usage in comparison to pyrolysis	− Still needs research to find a catalyst that ticks all the boxes for industrial implementation − Requires further purification (distillation) of products
Controlled thermal depolymerisation	For very pure waste streams, a critical temperature for specific polymers can be found to convert directly to their monomer.	Monomers and by-products	+ Creates high value monomers that can easily be fed back into polymer production	− Some further separation still needed to remove by-products, and the yield is unknown − Only works for specific polymers with bonds that are easier to break catalyst and steam
Gasification	Very high temperatures up to 1500°C in a limited amount of oxygen, which breaks the polymers down to their simplest components – including carbon monoxide and hydrogen.	Synthesis gas ('syngas') made up of CO and H_2 mainly	+ Can take mixed waste, but can require pre-treatment	− Requires further processing from syngas to hydrocarbons and then to monomers or polymers − Need large infrastructures to be profitable, generally on larger scale than pyrolysis plants − Very high energy due to temperatures needed
Hydro-pyrolysis/ hydro-cracking	Pyrolysis type process using a catalyst and steam (which introduces hydrogen instead of inert atmosphere) temperature is lower than pyrolysis at 350–550°C.	Mixed products, but hydrogen can create higher value products	+ The addition of hydrogen can improve the quality of products + Lower temperature than regular pyrolysis	− Creates a mixture of products, only a proportion of which can be recycled into plastics − Still requires a lot of energy − Handling hydrogen can be challenging (as with other flammable gases), along with the cost of the catalyst
Solvolysis	Dissolving polymers in solvents at high temperature and pressure to break down to monomers. Includes 'hydrolysis' with water as the solvent, 'alcoholysis' with an alcohol, 'aminolysis' with amines.	Monomers or longer chain oligomers, and by-products	+ Produces monomers, which can then be reformed into polymers	− Cannot be used to break carbon–carbon bonds, so only works on polymers with specific groups in their chain − Often requires a very pure waste stream
Hydrothermal treatment[2]	A solvolysis process where supercritical or near-critical water is used as the solvent. At a certain temperature and pressure water takes on special properties, which make it an excellent solvent for this process.	Mixed oil/synthetic crude oil	+ Can be used for products with plastics mixed with other materials (composites or multi-layered)	− Product requires further processing, but this can be handled by existing refinery infrastructure − Supercritical conditions require high temperature and pressure, which could mean expensive facilities and significant energy use

Further questions

- **Some say that processes can only be considered to be recycling if the product can be used as a secondary raw material, in this case if new polymers or plastics can easily be made. Through pyrolysis type methods for example, there are often low yields of secondary raw materials, with the remaining product used for fuel.[3]**
- In a truly circular economy model, plastic that could have been recycled further up the value stream should not be turned into fuel. It is therefore important that every opportunity should be taken to redesign plastics to be easily mechanically recycled, rather than relying on downstream chemical recycling.
- **It is reported that the environmental impacts and commercial scale viability of chemical recycling technologies are not well known at this time, which limits the ability to understand how these technologies might be used in reality. Environmental concerns centre around the energy usage, yield and creation of by-products or waste from these processes.[4] The use of Life Cycle Analysis (LCA) could help to standardise comparisons.**
- Many chemical recycling technologies rely on efficient sorting techniques in the same way mechanical recycling does. Any improvements in the quality of sorted polymer will benefit recycling as a whole. Further research is needed on how chemical recycling technologies cope with more contaminated and mixed waste streams, closer to real-life material inputs.

Future research could focus on:[5]

- More efficient processes to recover valuable oligomers, monomers and/or small molecules
- Technologies that function effectively using polymer composites and mixtures of plastics
- New and better catalysts, which lower operating temperatures and can selectively produce higher value chemicals. It is also important that the catalysts themselves are as sustainable as possible – for example these need to move away from reliance on precious metals
- Investigation of reactions for polymerisation and depolymerisation that are closer to equilibrium, and therefore require less energy to move in either direction
- The development and use of comprehensive Life Cycle Analysis (LCA) tools

The carbon economy

Carbon is an element found in all known life, and is the main element in plastics. In order to keep carbon in circulation and avoid it being lost to the atmosphere as harmful greenhouse gases, there needs to be value in its reuse. For example, the value of reusing and recycling plastic must be higher than that of sending it to landfill or incineration.

Chemical recycling technologies may not always provide products that are directly formed into recycled plastic, but as long as the products are reused in some form they are retaining value in the carbon. It is thought that global demand for carbon may increase, and in order to avoid using fossil fuel resources, plastic waste could be a source of carbon for a variety of chemical applications, for instance in pharmaceutical production.

Energy recovery and landfill

Unfortunately, across the world, waste is still predominantly disposed of via landfill and incineration.[6]

Landfill means loss of land for other developments, and, if badly managed, gas emissions and environmental contamination.[4]

Energy recovery from waste – where waste is burned, and the energy created is recovered as electricity - is an increasingly commonly used waste management technique. If the process is contained, and the pollution and CO_2 created is appropriately captured, it could be acceptable as a last resort for specific highly contaminated materials. However, open burning of plastics, which may occur in countries without the infrastructure to deal with waste, creates polluting emissions, particulate matter and other environmental and health concerns.

It has been calculated that the CO_2 footprint of plastic incineration is approximately 50% larger than that of burning crude oil due to the energy intensiveness of plastic manufacturing.[7]

More independent research is needed to understand the utility and environmental suitability of commercial scale chemical recycling infrastructure. This should go alongside collaboration across the sector, including academia, industry, government, and wider society to ensure the best collective outcomes.

Long term investment in the most appropriate infrastructure is needed, in order to develop a domestic recycling infrastructure which allows us to meet our targets on reducing waste, and truly move towards a circular economy for plastics and other materials.

CASE STUDY

Chemical recycling can help create value from plastics that are too contaminated to be processed by any other means, for instance the plastic historically left to degrade in landfill sites.

Dr Stuart Wagland at Cranfield University works with the UK Enhanced Landfill Mining (ELFM) Network to remediate closed landfill sites by finding suitable avenues for the materials, allowing them to return to the circular economy loop. Most landfill sites contain large amounts of plastic, potentially providing a sustainable source of polymers for recycling. Plastics extracted from landfill are notably contaminated and degraded, so conventional recycling is not a viable route.

Pyrolysis treatment, which can take in a mixed and contaminated waste stream, allows the plastic to be utilised rather than wasted or incinerated.

The ELFM project covers other materials, with precious metals and Critical Raw Materials (CRMs) trapped in landfill sites which could be reintroduced to the economy.

> **Remediation of closed landfills, applying the enhanced landfill mining principles, will reclaim land for development, recover valuable resources and remove a long-term burden on the environment. Extraction of wastes from such sites yield plastic materials which need to be managed responsibly. Chemical recycling through pyrolysis produces liquid fuels and chemicals which would be valuable for our chemical industries.**
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> DR STUART WAGLAND, CRANFIELD UNIVERSITY

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[1] https://onlinelibrary.wiley.com/doi/full/10.1002/anie.201915651
[2] https://www.bpf.co.uk/plastipedia/chemical-recycling-101.aspx
[3] https://wrap.org.uk/sites/default/files/2020-08/WRAP-Non-Mechanical-Recycling-of-Plastics-WRAP-v.3_0.pdf
[4] https://chemtrust.org/wp-content/uploads/Chemical-Recycling-Eunomia.pdf
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[7] https://onlinelibrary.wiley.com/doi/full/10.1002/anie.201915651