

Leaky loop "recycling"

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

Publication Type: Report October 2023 zerowasteeurope.eu

Executive Summary

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

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

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

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

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

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

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

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

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

polypropylene is off-specification by a factor of 66 to 1,010 times in comparison with petroleum naphtha, while the oil made from polyethylene is similarly substandard by a factor of 44 to 280. To bring the olefin concentration onto specification for steam cracking, pyrolysis oil made from PP, mixed polyolefins, and PE would need diluting with petroleum naphtha in ratios between 1:22 and 1:44.

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

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

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

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

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

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

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

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

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



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



Zero Waste Europe gratefully acknowledges financial assistance from the European Union. The sole responsibility for the content of this material lies with Zero Waste Europe. It does not necessarily reflect the opinion of the funder mentioned above. The funder cannot be held responsible for any use that may be made of the information contained therein.



Author: Dr. Andrew Rollinson Editors: Lauriane Veillard, Seán Flynn Date: October 2023

General information: hello@zerowasteeurope.eu Media: news@zerowasteeurope.eu

zerowasteeurope.eu

