Rebuttal to the Argonne National Laboratory chemical recycling study: (Gracida-Alvarez et al 2023 - *Life-cycle analysis of recycling of post-use plastic to plastic via pyrolysis).*

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Background

Chemical recycling or *advanced recycling* are umbrella terms to describe a group of technologies that claim to be able to process mixed plastic wastes into fuels or feedstocks for producing new plastic. Neither of these terms is a legal definition but are more accurately described as umbrella labels and marketing terminology to differentiate these technologies from conventional, mechanical recycling of plastic. The main technical point of difference being that chemical recycling may use heat, pressure and/or solvents to *split polymer chains* (depolymerisation) in an attempt to produce crude oil, waxes, gases, char or fuels (and in some cases monomers/polymers) while mechanical recycling *maintains the polymer structure* through shredding, granulating and re-melting the polymer into products.

The technology types included in chemical recycling of plastic waste are pyrolysis, gasification, solvolysis and solvent separation[1].

The majority of the currently constructed chemical recycling plants in the US use pyrolysis technology. Pyrolysis plants heat waste plastic in a sealed reactor in the absence of oxygen[2] producing gases, waxes, oils and char. One study describes the outputs as "light oil, medium oil, heavy oil, and sludge." (Kabeyi and Olanrewaju, 2023). The oil, gases and waxes are comprised of mixed hydrocarbons while the char is a carbonaceous solid material.

All of these outputs are contaminated with unwanted chemicals from the waste plastic feedstock or compounds formed in the pyrolysis process. Of these outputs generally only the pyrolysis oil is considered as a potential feedstock for plastic manufacture and must be subject to energy intensive and expensive clean-up and upgrading. The gases are typically used as supplementary fuel for the pyrolysis process which is reliant on fossil fuel energy for heating. Char is typically landfilled and waxes sold as fuel or asphalt additives.

In May 2023 in Geneva, Switzerland, delegates at the Conference of the Parties of The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal, rejected the inclusion of chemical recycling in the global guidance on the management of plastic waste on the basis that there was no evidence to suggest it constituted the environmentally sound management (ESM)of plastic waste.

Introduction

The American Chemistry Council funds a plastic pyrolysis life-cycle assessment (LCA)

In response to widespread scepticism and criticism of chemical recycling and, in particular, pyrolysis of plastic waste, the American Chemistry Council funded researchers from the Argonne National

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[1] There is an increasing consensus that solvent separation may not constitute chemical recycling but is actually physical recycling as it separated contaminants from polymers with solvents rather than breaking down polymers at a molecular level.

[2] While no oxygen is intentionally added or allowed to enter the reactor, the polymer waste contains oxygen in its molecular structure. This leads to the formation of highly toxic compounds in the reactor such as PCDD/DF which can be carried through and contaminate the final hydrocarbon product whether it is fuel or feedstock for plastic production.

Laboratory to produce a so-called ‘cradle to gate’ life cycle analysis (LCA) of plastic waste pyrolysis and compare it to plastic production from virgin petrochemicals.

The study produced by researchers at the Argonne National Laboratory (Gracida-Alvarez et al 2023) (hereafter referred to as ‘the study’) models a life cycle assessment (LCA) comparing virgin plastic production with plastic produced with a blend of various percentages of feedstock content derived from pyrolysis of plastic waste. Pyrolysis oil or ‘pyroil’ derived from mixed, post-consumer plastic waste is a complex mix of hydrocarbons heavily contaminated with chemicals from the plastic waste feedstock to the pyrolysis plant, as well as a range of other contaminants formed in the pyrolysis process under heat and pressure.

The authors conclude that new plastic made with a blend of pyrolysis oil co-fed with conventional feedstock leads to “*reductions of GHG emissions, fossil energy, water consumption, and solid waste*” when compared to virgin plastic produced without adding pyrolysis oil – that is, using 100% virgin petrochemicals. It is notable that the American Chemistry Council (ACC) are heavily promoting chemical recycling as a ‘solution’ to the plastic waste crisis in order to avoid regulated cuts to plastic production and/or plastic product bans.

Our analysis of the study suggests its conclusions about potential greenhouse gas savings, fossil energy and waste, when comparing chemical recycling to virgin polymer production are highly unreliable and heavily overestimated due to range of factors including:

- Non-reproducible data based on ‘discussions’ with industry.
- Reliance on industry funded studies.
- Reliance on modelling and estimation using undisclosed data and not operational data (see para 1 section 3.6 of the study).
- Unrealistic substitution rate scenarios for pyrolysis oil due to technical limitations of cracker plants and high contamination levels in pyrolysis oil.
- Unrealistic assumptions about powering pyrolysis plants using non-condensable gases from the process itself and therefore GHG savings.
- Inadequate data about the energy burden of pyrolysis oil cleanup.
- Lack of definitions of key terms.
- Limitations of the LCA system boundaries.
- Omission of data on toxicity of emissions and toxicity and management of process wastes (including the GHG/energy required to manage them).
- Inclusion of significant volumes of post-industrial plastic (PIP) in the pyrolysis process modelling despite claims that chemical recycling does not compete with mechanical recycling for feedstock.
- Claims of reduced GHG emissions for pyrolysis derived plastic rely heavily on counterfactual arguments about GHG savings from not sending the plastic waste to traditional end of life (EOL) disposal options – i.e. landfill and incineration.
- Carbon emissions from disposal of pyrolysis residues, including via incineration are omitted.
- Use of discredited mass balance allocation schemes to support the findings.

There are many more specific issues of concern in the study detailed below. The following analysis of the assumptions and claims in Gracida-Alvarez et al. 2023 (*the study*) are sufficient to render its findings unreliable for the purpose of proving that a mix of plastic derived pyrolysis oil and virgin petrochemicals result in less GHG emissions, fossil energy, water consumption and solid waste than plastic produced using virgin petrochemicals.

Data sources for the study unavailable

The data and information used in the modelling scenarios for the study is not reproducible as it stated at the end of the study that "*The data that has been used is confidential.*". It is not based on independent studies but is, "*Based on discussions with the industry experts, a group of people from the petrochemical industry...*". It claims to utilise operational data from eight pyrolysis facilities who "*provided detailed information and supplementary simulation data*" to "*estimate*" life cycle impacts.

It is not made transparent to what degree operational data is relied on compared to information and simulation data to produce these estimates. It remains unclear to what extent the estimates derived from the LCA modelling rely on simulation data rather than operational data and which elements of the LCA any operational data is attributed to. It raises the question for instance, whether operational data only form the basis for water use estimates and the rest of the model is constructed upon simulations. In addition certain assumptions are made on the operation of pyrolysis plants that appear to be based on discussions with plant operators that are not supported in the scientific literature.

As an example, it is assumed in the study that pyrolysis can operate perpetually on its own gas, which is impossible (Rollinson and Oladejo 2019) leading to the LCA model underestimating the GHG emissions from pyrolysis by omitting the fossil fuel that would be used to heat the pyrolysis plant. The parameter was, again, based on unsupported claims from two pyrolysis operators (SI, Table S6).

Other key data appears to be omitted resulting in confusion over the definition of key terms. For example, in Table 1 the terms Carbon Intensity and Fossil Energy are not defined. Somehow carbon intensity of pyrolysis is shown as almost twice that of naphtha, but 'fossil energy' is somehow less than a third. This sort of methodological confusion obscures the source data necessary to evaluate the claims in the study.

Reliance on industry funded studies

The study relies heavily on plastic/petrochemical industry funded studies as the basis for many of its LCA assumptions. Primarily the study relies upon data drawn from a previous study (Benavides et al. 2017) conducting an LCA on the conversion of plastic waste to fuel using pyrolysis. This study was also funded by the American Chemistry Council and many of its assumptions with respect to GHG emissions are used as the basis for this study. Notably Benavides et al. 2017, was the subject of a published rebuttal in the Elsevier journal *Fuel*[3]. The rebuttal raised several serious issues including:

- No explanation or source as to the values assigned GHG emissions from petroleum Ultra Low Sulphur Diesel despite it being the main comparator to pyrolysis fuel.
- Claims that pyrolysis plants can run entirely on their own gas production with no external fossil fuel required (this is impossible)[4]

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[3] Rollinson, A. and Tangri, N. (2021) **Update and rebuttal of Benavides et al. (2017) Life-cycle analysis of fuels from post-use nonrecycled plastics** Fuel 285 (2021) 118995

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

- The abstract states that pyrolysis of plastic to fuel has a *"96% lower fossil fuel consumption than conventional ULSD [ultra-low sulphur diesel] in the base case"* despite this claim being contradicted by peer reviewed literature and regulatory filings.
- The LCA included emissions from combustion of conventional fuel but omitted them from the plastic derived fuel. This gave the appearance of better performance to plastic derived fuel.
- The data for the study was again derived from unverifiable, self-reported survey responses from five unidentified plastic to fuel operators. Hence this study was not reproducible and further failed to distinguish between design specification and actual plant performance data.

Mass balance allocation – certified modelling method for recycled content or industry greenwashing?

The plastics and chemical industry have been heavily promoting the use of highly flexible Mass Balance allocation schemes to claim determined recycled content of final plastic products made using a fraction of pyrolysis oil. Critics, including many environmental organisations, argue that it is a form of industry greenwashing to claim false and unrealistic recycled content rates as a way of avoiding regulation and product bans. Such accounting schemes also serve to cover up the fact that very little plastic waste actually gets recycled, being grossly diluted with virgin petroleum". The main criticisms of mass balance allocation credit schemes for recycled plastic content are:

1. Mass balance allocation approaches are a form of virtual credit schemes that allow for sales of artificial "circular" plastics that could contain zero or negligible amounts of recycled plastics.

2. In addition to artificial content claims, allocation credit schemes are inherently non-transparent and allow for credit of production of non-plastic products, including lubricants, waxes, and even transportation fuels destined for combustion to CO_2.

3. Companies' claims on the need for and credibility of artificial allocation of credits are proven false by scientific and economic evidence:

   a. On economic evidence - Companies claim that they must be allowed to artificially allocate recycled content to a limited amount of plastic production in order to fund expansion of plastic recycling through sales of circular credit certificates.[5] The 223 companies that belong to and fund the American Chemistry Council and the Recycling Partnership include 60 publicly held companies with a combined annual revenue of $2.7 trillion and net profit of $210 billion.[6] Plastics and products companies can fund recycling operations from their own profits that are generated from the production and sales of plastics themselves.[7]

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[5] National Institute of Standards and Technology, An Assessment of Mass Balance Accounting Methods for Polymers Workshop Report, NIST Special Publication 1500-206, February 2022

[6] The Intercept, Big Plastics Asks for $1 Billion Coronavirus Bailout, April 27, 2020

[7] The Last Beach Clean-up. Submission to **EPA's Safer Choice and Design for the Environment (DfE) – Proposed 2023 Updates (Docket identification (ID) number EPA–HQ–OPPT–2023–0520)** Regulations.gov

b. On scientific evidence: Companies claim that it is impossible to follow the molecules in pyrolysis and steam cracker operations. Hence the need for flexible mass balance allocation schemes[8]. The reality is that the conversion yield of plastic waste to pyrolysis oil and then the yield of pyrolysis oil to polyolefin products are scientifically known and can be used to credibly estimate the physical recycled content in new plastic production that employs pyrolysis oil with new hydrocarbons on an annual basis.[9,10 11]

The study relies on mass balance accounting assumptions for LCA drawn from Jeswani et al. 2021 which was funded by BASF who are heavily promoting chemical recycling. Further mass balance accounting assumptions are drawn from the Ellen MacArthur Foundation, 2019 who has partnered[12] with BASF to promote the concept which has been criticised by environment groups as unscientific greenwashing (IPEN/ Beyond Plastics 2023).

Currently there is no standard to calculate the carbon footprint for mass balanced product. The International Sustainability and Carbon Certification organisation accrediting the ISCC plus certification scheme (commonly claimed by chemical recycling proponents) are aware that there is currently no standard for calculating carbon footprint for mass balanced product and have not yet formed a working group to come up with the standard proposal. The certification scheme openly acknowledged this lack of standard in public forums.

Other LCA studies referenced in the study using mass balance allocation include those produced and paid for by Saudi Basic industries Corporation (SABIC), Plastic Energy (study by Quantis) and even cited data from a promotional pamphlet from Honeywell UOP[13] with claims based on LCA studies by BASF and Plastic Energy.

The use of mass balance allocation in this study is unreliable, and is not supported by the scientific literature which have determined the maximum possible physical content of recycled pyrolysis oil in finished product can be no more than 2% (Zero Waste Europe 2023).

Contamination and yield of plastic pyrolysis product

Pyrolysis of plastic waste produces gas, oil and waxes (and tars) that are a complex mix of hydrocarbons and char.

Char is a carbonaceous solid waste from the process, often contaminated with highly toxic polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/DF), polycyclic aromatic hydrocarbons (PAH) and other toxic compounds and is typically disposed to landfill or incinerated. The waxes can

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[8] National Institute of Standards and Technology, An Assessment of Mass Balance Accounting Methods for Polymers Workshop Report, NIST Special Publication 1500-206, February 2022

[9] Kusenberg, et al, "Assessing the feasibility of chemical recycling via steam cracking of untreated plastic waste pyrolysis oils: Feedstock impurities, product yields and coke formation," March 15, 2022

[10] Kusenberg, et al, "Maximizing olefin production via steam cracking of distilled pyrolysis oils from difficult-to-recycle municipal plastic waste and marine litter," April 29, 2022

[11] The Last Beach Clean-up. Submission to **EPA's Safer Choice and Design for the Environment (DfE) – Proposed 2023 Updates (Docket identification (ID) number EPA–HQ–OPPT–2023–0520)** Regulations.gov

[12] https://www.basf.com/au/en/who-we-are/sustainability/whats-new/sustainability-news/2019/EllenMacArthurfoundation-White-Paper-Mass-balance.html

[13] https://uop.honeywell.com/content/dam/uop/en-us/documents/product-services/honeywell-uop-upcycle-plastics-recycling.pdf

create equipment fouling and reduced process efficiency due to their high viscosity and are typically separated from the oils and may be sold as fuel. The only current identified uses of pyrolysis wax from plastic waste are asphalt additives for pavement construction and potential feedstock to manufacture chemicals (Ong et al. 2023).

Depending on operating parameters of the pyrolysis plant including temperature, residence time of the waste, and catalysts, the ratio of outputs (oil, waxes, gas and char) can vary considerably. One study using plastic waste recovered from landfill, pretreated and the subject to pyrolysis found the relative percentage output of “pyro-oil, light wax, heavy wax and gases were 5.5, 23.8, 69.4 and 1.3 wt%, respectively” (Al-Salem et al. 2020). This amounts to a potentially useful pyrolysis oil yield for potential plastic recycling of only 5.5%. The ratios of gas, wax and oil can be manipulated by changing operating conditions.

When plastic waste is processed through a pyrolysis unit there are material losses. Some of the plastic waste is converted to non-condensable gases and a significant amount of this gas may be used as fuel to heat the process, though this is not sufficient to completely displace the need for fossil fuels for heating. Char is also produced as a residual and may account for 10% of the initial input. Waxes and tars are also contaminated may not be commercially viable as a product and become wastes requiring incineration for which GHG emissions should be assessed.

Some industry estimates suggest the useful yield of pyrolysis oil may only be around 20% of the initial waste input by weight. A case described in a recent report (IPEN/Beyond Plastics 2023), noted a US plastic waste pyrolysis company reported that 20% of its material output consisted of a gasoline-diesel fuel blend that was “sent off-site for further refinement” and therefore subject to further material losses. Ten percent was char that was landfilled, and 70% was gas. Of the gas, 80% was used internally to power the pyrolysis unit (i.e., it was burned as fuel), and 20% was flared (burned as waste gas). This equates to around 20% oil yield with unknown material losses in the further refinement stage.

One of the largest waste management companies in the world, Veolia, claimed similar yields and has rejected the use of plastic pyrolysis. Its German representative (Markus Binding’, Veolia’s Managing Director for EVA Verwaltungs GmbH – Veolia) was quoted as saying *"From the sequence of process steps in chemical recycling, the result is a material pellet yield of only about 22 percent,"* [14].

He went further to criticise chemical recycling Life Cycle Assessments based on undisclosed industry data, raising concerns that promotion was being put ahead of sound science stating, *"And this is precisely the risk for our industry: without proof of safe, reliable and sustainable mode of operation on an industrial scale, without a transparent database for life cycle analyses from sources that are as neutral sources as possible, without critical consideration of the proven and the new,* ***we run the risk of being used as a stirrup holder for a vision of the petrochemical industry****."*[15]

The pyrolysis oils are contaminated and are not simply ‘drop-in’ replacements for virgin naphtha used in plastic production (Zero Waste Europe 2023). They must be heavily diluted to protect the operation and equipment of the steam cracker. The cost and energy required to clean pyrolysis oil for this purpose can be uneconomic, often resulting in the oil being sold as a fuel and combusted.

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[14] Euwid 15/2022, page 3. Euwid Recycling und Entsorgung weekly https://www.euwid.de/en/euwid-recycling-und-entsorgung/

[15] Ibid

Conversion of plastic waste to fuel by pyrolysis is not regarded as any form of recycling Basel Convention on Hazardous waste that produces global guidance[16] on plastic waste management.

Dilution rates for pyrolysis oil unrealistic and over-estimated

The study models two LCAs for GHG, water use, solid waste and fossil energy- blending either 5% or 20% pyrolysis oil with traditional virgin feedstocks naphtha and gases (ethane, propane, and butane) at a dilution rate of 95% and 80% respectively to be fed to steam crackers that produce monomers for production of polyolefins.

The study models two scenarios. The first (Fig 3 of the study) is relevant as it shows GHG emissions from plastic made with pyrolysis oil blended with petroleum naphtha and the GHG emissions are similar to virgin plastic production. However, in a second modelled scenario 100% pyrolysis oil (Fig 4 of the study) is used to make plastic, which is impossible, and most of the remainder of the study is devoted to this. As explained below, contamination in pyrolysis oil limits it use in steam crackers to around 2% with 98% dilution by virgin petrochemicals. The allocated benefits in terms of GHG emissions from 100% pyrolysis oil in plastic production are not possible to achieve given the limits on pyrolysis oil use for steam crackers.

The study claims that, *"The pyrolysis oil produced from PUP can substitute fossil feedstocks (e.g., naphtha) in the manufacturing of ethylene and propylene, two important monomers in the polymerization of polyolefins (HDPE, LDPE, and PP) while meeting the specifications of products from current steam crackers (Kusenberg et al., 2022), they can also be drop-in replacements with numerous applications*." This is not however the true findings of the study (Kusenberg et al., 2022) cited by ANL, in fact the cited authors find the opposite.

A recent report by Zero Waste Europe, authored by an independent expert combustion engineer and pyrolysis expert, Dr Andrew N Rollinson, elaborates on the Kusenberg et al., 2022 paper, noting that pyrolysis oil is not a 'drop-in replacement' for virgin petrochemicals due to the high contamination levels of the oil and the sensitivity of steam crackers to contaminated feedstock. The report *Leaky Loop 'Recycling': A technical correction on the quality of pyrolysis oil made from plastic waste.* concludes that **no more than 2% pyrolysis oil** from plastic waste feedstock can be fed into steam crackers for production of monomers.

The conclusions of the Zero Waste Europe Report are supported by independently analysed operational data from publicly available sources showing that the ExxonMobil's Baytown petrochemical plant only operates at 1.7% plastic waste feed to its pyrolysis plant (flexicoker unit) and 0.4% pyrolysis oil feed to steam crackers. Based on ExxonMobil's global plastic production and commitment to process 500,000 tons of plastic waste annually, the feed to their global steam crackers would be about 1% pyrolysis oil[17].

Not only does this totally debunk the assumptions made by the ACC-funded ANL study, but it draws a line under the fact that plastic derived pyrolysis oil cannot be regarded as circular, sustainable or a

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[16] https://www.basel.int/Implementation/Plasticwaste/Technicalguidelines/Overview/tabid/7992/Default.aspx

[17] The Last Beach Clean-up. Submission to **EPA's Safer Choice and Design for the Environment (DfE) – Proposed 2023 Updates (Docket identification (ID) number EPA–HQ–OPPT–2023–0520)** Regulations.gov

replacement for traditional fossil based plastic production feedstock: use of the oil relies on massive levels of dilution with virgin petrochemical feedstock to be able to produce new plastic. Even if it could be demonstrated to have better GHG, fossil consumption, water use and waste impacts (which it cannot) then the 1-2% substitution rate limit would suggest that such impact reductions would be negligible in the overall global production of plastic.

Further, in the ACC-funded ANL study, for both HDPE and LDPE, the 5% blend Pioneer plant shows greater GHG emissions than virgin polymer production. But there is no presentation of data on the 20% blend. It should be expected to have even greater GHG emissions, as per the trends for other plants, but this trend is omitted from the study. Why has this part of the study been selectively removed from presentation?

The scenarios in the study claim higher LCA impact reduction for the 5% substitution scenario than the 20% substitution scenario on the basis that steam cracker plants can tolerate the pyrolysis oil contaminants at a 95% dilution rate with virgin petrochemicals. The GHG savings are significantly reduced for the 20% substitution scenario because of the need to treat the oil to reduce some of the contaminant levels to steam cracker specifications. However, the GHG emissions to remove all of the necessary contaminants are not included in the analysis.

Substitution rates limited by heavy contamination of pyrolysis oil.

"There are substantial safety and operational risks when using plastic waste pyrolysis oils instead of conventional fossil-based feedstocks. This is due to the fact that plastic waste pyrolysis oils contain a vast amount of contaminants which are the main drivers for corrosion, fouling and downstream catalyst poisoning in industrial steam cracking plants."[18]

The 5% substitution rate quoted in the study using uncleaned, contaminated pyroil appears to be hypothetical based on the available literature where a maximum of only 2% is tolerated by steam crackers. The 5% pyroil/95% virgin petrochemical dilution rate, gave the highest GHG savings as it was assumed no energy was expended on the clean-up of pyroil before it was used as input to steam crackers. This does not appear to be technically possible.

The study models the removal of chloride alone to make their assumptions on energy consumption of pyroil clean up processes. This is not enough, but the authors suggest this is sufficient and that the chloride removal energy consumption is a proxy for all contaminant removal in terms energy consumption. Bizarrely, they then go on to concede that the energy consumption values used did not include data for the energy required to remove fluorine and diolefins. Such befuddlement is commonplace through, as was identified in an earlier study by the same research group[19].

Diolefins require separate reactors to the main hydrotreating reactor (fluorine and bromine can be reduced in the main hydrotreating reactor). Silicon removal is also critical but its energy consumption

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[18] Kusenberg, et al, "Opportunities and challenges for the application of post-consumer plastic waste pyrolysis oils as steam cracker feedstocks: To decontaminate or not to decontaminate?", February 1, 2022

[19] Rollinson, A. and Tangri, N. (2021) **Update and rebuttal of Benavides et al. (2017) Life-cycle analysis of fuels from post-use nonrecycled plastics** Fuel 285 (2021) 118995

in a separate silicon trap reactor is omitted due to *"insufficient information*" on this technology. Thus the study just discounts the issue. Therefore, the study's claim that "*chlorine removal could provide a close approach to current operations"* is inadequate for estimating pyrolysis oil cleanup energy requirements and therefore GHG impacts. Notably, under section 2.2 of the study, it concedes energy requirements for hydrotreatment are modelled and not based on operational data. Similarly in section 2.3 of the study it is stated that "*The estimations of the upstream life-cycle impacts and emissions of the steam cracking operation were based on the model by Young et al. (2022)*,". Given that this study is supposedly based on information and data from direct interviews with steam cracker experts, it seems unusual that modelling is preferred over operational data.

However, there are many more contaminants that must be significantly reduced or removed to allow the pyroil to be used as steam cracker feedstock, all requiring direct energy use and catalysts with embedded energy costs.

The pyroil contaminants that restrict use in steam crackers and/or contaminate final product include but are not limited to:

- Nitrogen
- Sulphur
- Chlorine
- Bromine
- Fluorine
- Polycyclic aromatic hydrocarbons (PAHs)
- Silicon
- Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/DF)
- Diolefins (causes unwanted gum formation in crackers)
- Metals (e.g. lead, iron, arsenic, antimony, zinc, aluminium, vanadium)
- Chemical plastic additives in the waste plastic feedstock to pyrolysis
- oxygen

Many of these contaminants are found in pyrolysis oil at levels magnitudes of order above acceptable specifications for steam crackers and must be removed in expensive and energy intensive clean up steps before the pyroil can be used (Zero Waste Europe 2023).

Of all these contaminants the study only analysed the GHG impacts of hydrotreating processes to lower chlorine from 600 ppm to 10 ppm. This was used as a proxy value for the removal of other named contaminants such as fluorine, diolefins and silicon. However, the first assumption as to threshold values for chlorine in steam crackers appears significantly overestimated as other publications assess the steam cracker limit as 3ppm based on extensive literature review of pyrolysis oil contamination levels and steam cracker limits for feedstock contamination (Zero Waste Europe 2023). The extra GHG impacts and catalyst requirements to meet the 3 ppm chlorine limits are not specified in the study. The GHG impact of hydrotreating of chlorine may not be readily used as a substitute value for the removal of silicon and diolefins which cause gum formation in steam crackers blocking process equipment and shortening the process cycle.

Silicon may be found in plastic waste feedstock and poisons catalysts in the steam cracker refining process. Diolefins polymerise at steam cracker feed temperatures fouling process equipment. Best practice removal and treatment of these contaminants requires the addition of a diolefin saturation reactor and a separate silicon trap reactor in addition to the main hydrotreating reactor. These additional reactors consume additional energy and catalysts which have not been factored into the

GHG impacts in the study. They also generate hazardous wastes which requires EOL management (I.e. incineration) for which the emissions have been omitted in the study.

Limitations on mixed plastic feedstock to pyrolysis: PCP, PUP and PIP

The study claims that pyrolysis plants will be able to accept mixed waste plastics and recycle them into useful output that can go on to produce new plastic. They even allocate GHG savings in their counterfactual assessment for mixed plastic waste GHG emissions avoided by sending the waste to pyrolysis plants and not to traditional EOL management such as landfills and incinerators. However, pyrolysis plants have technical limitations on the types of plastic they can accept, and this common claim is now totally refuted, by both independent authors and pyrolysis operators themselves:

Chemical industry experts, Independent Commodity intelligence Service (ICIS) stated: *"It is a common misconception that chemical recycling can take any and all types of plastic waste, and there are still a number of technical requirements for waste input depending on which chemical recycling process is used. Pyrolysis for example, typically requires the minimisation of chlorine content (typically to 0.1% or less) due to its corrosive effect, the removal of PET because it oxygenates the process and does not depolymerise using pyrolysis, and the avoidance of nylon and flame retardants."* [20]

Yet, the ACC-funded ANL study still uses several definitions of the type of plastic waste used in the modelling. Post-consumer plastic waste (PCP) generally assumed to be household mixed plastic waste, post-industrial plastic waste (PIP) and post-use plastic (PUP) which is claimed to be a mix of PCP and PIP. Proponents of chemical recycling claim that it is a complementary recycling technology to conventional, mechanical recycling *and not a competitor*. However, PIP is highly sought after by mechanical recyclers as it is much cleaner than PCP, has less pre-treatment requirements (washing/cleaning, sorting etc) and associated energy and water use. It also tends to be polymer specific, reducing or eliminating sorting steps required for mixed plastics which requires significant energy use. The study specifically acknowledges this by stating, *"Because PIP is not mixed with other municipal solid wastes and is cleaner than PCP, it is supplied directly to the pyrolysis facilities without requiring sorting at MRFs."*

By including PIP in the LCA modelling the study not only boosts hypothetical pyrolysis GHG savings by avoiding pretreatment such as cleaning and sorting, but makes these savings contingent on competing with mechanical recycling – a system that has been demonstrated to be 9 times more energy efficient than chemical recycling (Oeko-Institut. 2022). No account is made for GHG emission increases created by taking PIP from the far more energy efficient mechanical recycling sector and processes them in far less efficient pyrolysis operations.

The ratio of PIP to PCP used in the modelling is somewhat obscured by the relabelling of the waste mix of PIP and PCP as 'PUP'. However, the supplementary information provides two different versions of the ratio of PIP to PCP in input feedstock. In section S6 figure S2 describes the material balance of the pioneer pyrolysis process. Accounting for losses in the MRF for PCP, the 'blend' of PUP input to pyrolysis comprises 17% PIP waste. For S6 figure S3 the material balance for Nth plants comprises PUP inputs of 0.34 kg PCP to 1.25 kg PIP. In other words, the input feed for Nth plants is 21.3% post-consumer plastic and *79.7 % post industrial plastics*. This suggests that both plant types have to use

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[20] https://www.icis.com/explore/commodities/chemicals/mixed-plastic-waste-and-pyrolysis-oil/

significant quantities of PIP to claim GHG savings while the Nth plants appear to be largely reliant on PIP.

In discussing the data sourced from 8 constructed pyrolysis facilities that form the basis of the study, it is noted in the supplementary data that the facilities operated at different scales *“(ranging from 300 to 291,800 tonnes of PCP and PIP per year)”* (SI S2.2) This confirms that plants in the US are currently using PIP in direct competition with mechanical recyclers.

Claimed GHG impact savings rely heavily on counterfactual EOL estimates

The study relies heavily on the use of EOL waste management energy consumption values in a ‘counterfactual assessment’ to claim that pyrolysis of plastic waste should be credited with ‘avoided’ EOL management emissions from incinerating or landfilling plastic waste. It does not take into account that, under US EPA classifications, plastic waste pyrolysis is categorised as waste combustion/incineration and therefore should not be allocated such credits.

Even if this were not the case other factors have been omitted that would reduce the GHG savings. The study does not consider that the US exports large quantities of plastic waste for mechanical recycling as an EOL management option in addition to domestic mechanical recycling (which is accounted for). Chemical recycling using pyrolysis has been found to have a GHG impact 9 times higher than mechanical recycling (Oeko-Institut. 2022). Therefore, GHG savings from waste plastic exported from the US for mechanical recycling overseas has no been factored into any ‘counterfactual assessment’ which would significantly reduce the GHG savings attributed to pyrolysis in the study. Current estimates of US plastic waste export are 392,400 tonnes per annum. Data on the fraction of exports destined for recycling is not available though all exports are counted in the US plastic recycling figures.

The weighting on EOL counterfactual assessment between plastic waste incinerated (very high GHG emissions) and plastic waste landfilled (lower GHG emissions -mainly transport) are not accurate and inflate GHG savings by giving a higher share to incineration. According to a 2022 report by Beyond Plastics and The Last Beach Clean Up, 85 percent of US plastic waste went to landfills, and 10 percent was incinerated. The assumption in the study is for 17% incineration and 83% landfill. Overestimating the incineration rate by 70% overestimates the GHG impact savings.

The heavy reliance on avoided GHG emissions credits of incineration and landfill is exposed in Table 1 of the study which shows conventional naphtha has a much lower carbon intensity of 0.67 kg CO_2 e/kg feedstock compared to pioneer plant pyroil which has much higher carbon intensity of 1.04 kg CO_2 e/kg feedstock. The EOL credits are used to close this gap.

This can be seen in Figure 3 of the study where the bar furthest to the right for each chart (20% SR N*th* plant for HDPE and LDPE respectively) show much higher GHG emissions than the base case – unless avoided emissions from EOL are included. The study even states *“Co-feeding with pyrolysis oil from pioneer plants resulted in 1.6% (HDPE) and 1.3% (LDPE) higher GHG emissions compared to conventional production of plastics.”*

Use of controversial data on fugitive methane leakage to boost GHG savings

The study includes controversial data on methane leakage in the form of fugitive emissions, and venting based on satellite data. The study states, "*The impacts associated with the extraction and production of conventional feedstocks were obtained from GREET (ANL, 2020) with updated methane leakage rates of the natural gas supply chain as described by Burnham (2022)*." Currently there is no stakeholder agreement about the scale and reliability of the satellite-based data of fugitive methane leakage from the oil and gas sector. The International Association of Oil and Gas Producers have disputed the findings[21] and Plastics Europe has indicated that LCA's are potentially misrepresenting methane impacts by using this data[22]. While those facts may be in dispute among stakeholders it can be said that by using an LCA, as this study does, with significantly increased methane emissions attributed to virgin production of plastic, it significantly improves the modelled GHG profile of pyrolysis derived plastic compared to the use of virgin feedstock alone.

Toxic emissions and toxic waste left outside of LCA system boundaries.

There is no mention in the study of environmental metrics other than GHG emissions. No account is given to human health and ecosystem impacts of toxic emissions and waste from pyrolysis.

Pyrolysis units generally have a flare to burn dirty gaseous emissions during startup and shutdown, as well as gas released to keep pressure within safety specifications for the unit during emergencies (Elsdon and Pal 2011). Flaring of contaminated gases from these units will produce and release some entrained pollutants, such as VOCs and particulate matter (including PAHs), into the local atmosphere (Kindzierski, 1999) and may create new combinations of pollutants, such as dioxins, which are carried on fine particulates from the flares.

Many unknown products of incomplete combustion may also be released from flares, including benzene and naphthalene, carbon black particles (Fawole et al. 2016) CO, and partially burned and altered hydrocarbons and BTEX (Mirrezaei and Orkomi 2020). Also emitted are nitrogen oxides (NOx) and — if sulfur-containing material, such as hydrogen sulfide or mercaptans, is flared — sulfur dioxide (SO2) (US EPA Emission Factors – Industrial Flares[23]).

However, the exact composition of emissions from any chemical recycling facility will depend on the input plastic waste types and operational controls. For example, if high levels of PVC and brominated WEEE plastics are used, brominated and chlorinated dioxin levels can be expected to be much higher, due to the precursor levels of chlorine and bromine in the system. Contaminants identified in flue gas from plastic pyrolysis plants include alkanes, alkenes, polycyclic aromatic hydrocarbons, dioxins, PCBs, and large quantities of VOCs, including mono-aromatics, oxygenated VOCs (O-VOCs), chlorinated VOCs (Cl-VOCs), and acrylonitrile (He et al. 2015, An et al. 2014; Paladino and Moranda, 2021). The primary sources of pollution identified in pyrolysis air toxics emissions are contained into the un-condensable gas and flue gas exiting by the flare.

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[21] https://www.iogp.org/blog/europe/iogp-response-to-iea-global-methane-tracker-report-2/

[22] https://plasticseurope.org/sustainability/circularity/life-cycle-thinking/eco-profiles-set/ "Oil and Gas emission intensity: Need for a collective approach"

[23] https://www.epa.gov/air-emissions-factors-and-quantification/new-and-revised-emissions-factors-flares-and-new-emissions

Pyrolysis of plastic generates large quantities of hazardous waste with GHG implications.

The system boundaries described in the study include an LCA of solid waste – but only in the sense of accounting for plastic solid waste avoided by sending it to pyrolysis instead of incineration or landfill as EOL management options. The GHG emissions claimed to be avoided by using pyrolysis for mixed plastic waste instead of landfilling or incinerating that waste is the greatest contributor to the so-called GHG reductions attributed to pyrolysis in the study.

However, and a perfect example of the imbalance within the study, no consideration or assessment is given to practical EOL management for the residues from the pyrolysis process. These solid wastes are mainly hazardous waste (IPEN/Beyond Plastic 2023). They include contaminated char, sludges and off-spec oil and waxes that cannot be sold; wastes which are generated in large volumes and must be transported and treated (often by incineration) before final disposal in landfill. If they are incinerated, then the GHG emissions from the incineration process should be included in the LCA system boundary as should the transport costs of the residual ash from the incinerator to landfill. In the case of residues sent directly to landfill, the transport GHG factors should be assessed. Ironically, the study even credits GHG savings to the landfill disposal of char, a hazardous waste, for "*carbon sequestration*" (SI S2.2). However, the amount of waste generated by pyrolysis is not deducted or otherwise offset against the so-called solid waste 'savings' claimed in the study.

There is also no consideration of microplastic pollution that is generated through the handling, storage and pretreatment, especially washing, of plastic waste before it is pyrolyzed. These are known sources of significant microplastic pollution (Brown et al. 2023).

Conclusion

In our view, the combination of undisclosed data, extensive use of modelling, reliance on industry studies and industry funding, omission of key emission sources, general and widespread befuddlement, unrealistic assumptions about pyroil substitution rates and contamination, all make this study unreliable for the purposes of claiming that pyrolysis oil sourced plastic has a better emission, waste, water and fossil energy than plastic made from virgin feedstock. The omission of discussion on hazardous residues from pyrolysis, their EOL management and consequent emissions compounds our concerns as does the use of dubious mass balance allocation schemes that have no basis in physical reality. The highly relevant generation of toxic emissions and hazardous waste from chemical recycling is not discussed at all. It is also of great concern that the conclusion of the study are almost entirely reliant on avoided emissions from EOL management while claiming carbon reductions from extensive use of post industrial plastic waste in the pyrolysis unit in direct competition with mechanical recyclers who are far more energy efficient. The combination of these factors means that the study is largely hypothetical, lacking in key considerations and should not be regarded as a useful policy reference regarding the future of chemical recycling.

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