Pyrolysis of Plastic Waste: Recycling Hard-to-Recycle Plastics

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CUWP Chemical Upcycling of Waste Plastics

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PYROLYSIS

Plastic Waste Management

The creation of plastics has unquestionably revolutionized various aspects of human life related to food safety, medical technologies, transportation, construction, among others. For example, plastic packaging reduces and prevents food waste, which is a pressing global problem that limits food security, food safety, and has negative effects on the environment and the economy (FAO, 2011). Plastics packaging creates a physical barrier that protects food from environmental conditions such as oxygen and humidity (Plastics Ingenuity, 2021). In addition, plastics are inexpensive and versatile. However, current final disposal practices of single-use and short-life cycle plastics raise environmental concerns (Ragaert et al., 2017). For example, in 2023, only 10% of the global plastic waste is expected to be recycled with the rest of plastics being landfilled (49%), incinerated (19%), and disposed in open dumps (22%) (OECD, 2022). The accumulation of plastics in the environment, due to inappropriate designs or flawed practices across the waste collection chain, raises multiple environmental and health concerns including the entry of micro- and nano-plastics into human and animal food chains (Geyer et al., 2017).

In the U.S., only 5% of the 221 kg (487 lb) of plastics generated per person each year are recycled, with the rest being landfilled (73%), incinerated (19%), or indiscriminately dumped into the environment (3%) (OECD, 2022). Landfilling and incineration keep waste plastics out of the environment, but if poorly implemented, they can have negative health and environmental impacts. Landfilling is a responsible approach to disposing of waste plastics but takes up valuable urban space. Incineration dramatically reduces the volume of waste that must ultimately be landfilled, but is equivalent to burning fossil fuels, releasing carbon dioxide, the most abundant greenhouse gas (GHG) worldwide (Klemeš et al., 2020). Incineration is resource inefficient, requiring the additional extraction of fossil fuels to produce more plastics as it brings an end to the plastic's lifecycle (Klemeš et al., 2020).

Some environmentalists call for a ban on production and utilization of plastics as the only credible way to reduce plastic wastes in the environment. Given the integral role of plastics in modern society, this is an unrealistic expectation. Moreover, plastic waste can be seen as a valuable resource if recovered and remanufactured into new products. There are multiple emerging technologies that can convert plastic waste into new chemicals, fuels, and new plastics (e.g., pyrolysis) and/or break down multilayer films into their original plastic building blocks (e.g., solvent-targeted recovery and precipitation, STRAP) (Xu et al., 2023).

Pyrolysis is a leading an evolving technology for upcycling waste plastics, particularly polyolefins and polystyrene, to produce gas, liquid, and solid products that can be used to produce new plastics that have the same characteristics as the original plastics from which they are derived.

Unlike incineration, pyrolysis aligns with the principles of a circular economy, breathing new life into discarded plastics and reintroducing them into society, thus contributing to resource efficiency and sustainability (Mastral & Callén, 2000). Moreover, pyrolysis complements mechanical recycling as it can upcycle plastics that are currently unfeasible to recover through mechanical recycling.

Greenhouse Gas (GHG): A gas in the atmosphere that absorbs and emits energy within the thermal infrared range. GHGs can be from either natural sources or from man-made activities. Because they reduce the amount of infrared (i.e., heat) radiation Earth loses to space, GHGs increase the average planetary temperature and the rate of global warming. The most man-made abundant GHG is carbon dioxide (CO_2, mostly from fossil fuel combustion), followed by methane (CH_4, mostly from animal agriculture and natural gas extraction), nitrous oxide (N_2O, mostly from agricultural soil management), and chlorofluorocarbons (mostly from refrigerants). The main sources of GHG emissions from industrial processes and produce use in the U.S. are iron/steel and cement production (US EPA), 2023).

What is Pyrolysis?

Pyrolysis is an established technology used mostly to convert biomass into biofuels, biochemicals, and other biobased products (Wang et al., 2020). More recently, pyrolysis has been applied to convert waste plastics into useful products. Pyrolysis is not to be confused with combustion. Unlike combustion or incineration, pyrolysis is the thermal decomposition of organic compounds under oxygen-starved conditions. Temperatures typically range between 350 to 700 °C (662 °F to 1,292 °F) (Li et al., 2022). Pyrolysis breaks polymers into molecules of significantly shorter chain length or even monomers, which are the building blocks of plastics. On the other hand, combustion oxidizes organic molecules and creates carbon dioxide. Thus, pyrolysis can upcycle waste plastics by breaking them down into molecules suitable for producing new plastics and other useful materials (Li et al., 2022)

Depending on reaction conditions, pyrolysis of plastics produces waxes, oils, gases, and char/ash (***Figure 1***) (Zhao et al., 2020). Waxes and oils are the main products of pyrolysis and can be used to produce new products including fuels, chemicals, and the original plastics from which they were derived. Chemicals and new plastics are preferred from the standpoint of encouraging a circular economy as fuels produced from plastics are equivalent to fuels directly produced from fossil fuels, resulting in net GHG emissions to the atmosphere when burned. The fuels generated by pyrolysis can be reused in the production process to reduce the use of purchased fossil fuels. Pyrolysis oil can be used and integrated in the current virgin feedstock stream to produce monomers for plastics production, which will have identical properties to those of virgin plastics made from petroleum. This contrasts to the often-inferior properties of plastics made from mechanically recycled plastic. The quantities of the resulting pyrolysis products depend mainly on the temperature and duration of the pyrolysis reaction. When the conditions are more intense (higher temperature and longer reaction time), oil and gas tend to increase at the expense of wax. Waste plastics that are contaminated with food and dirt tend to produce high levels of char and ash.

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Products from Pyrolysis:

- *Waxes* are longer chain hydrocarbons that are solid at room temperature. They have some value as lubricants, but their value increases if further decomposed into oils. Increasing the temperature and the pyrolysis time are the main factors used to convert waxes into oils.
- *Pyrolysis oils* are shorter chain hydrocarbons that are liquid at room temperature and can be converted into a variety of value-added chemicals, new plastic products that can replace virgin plastics, or liquid fuels that can replace virgin fossil fuels.
- *Pyrolysis gas* has properties similar to natural gas, allowing it to be used in heat and power applications. Most commonly, it is used for heating on site, reducing the need for fossil fuels in the plant.
- *Char/ash* produced from pyrolysis of waste plastic is produced in small amounts compared to the other products, yielding only 1 to 5% of the waste plastic mass. Char has relatively little economic value although, like the gas, the char can be used to heat the pyrolysis reactor.

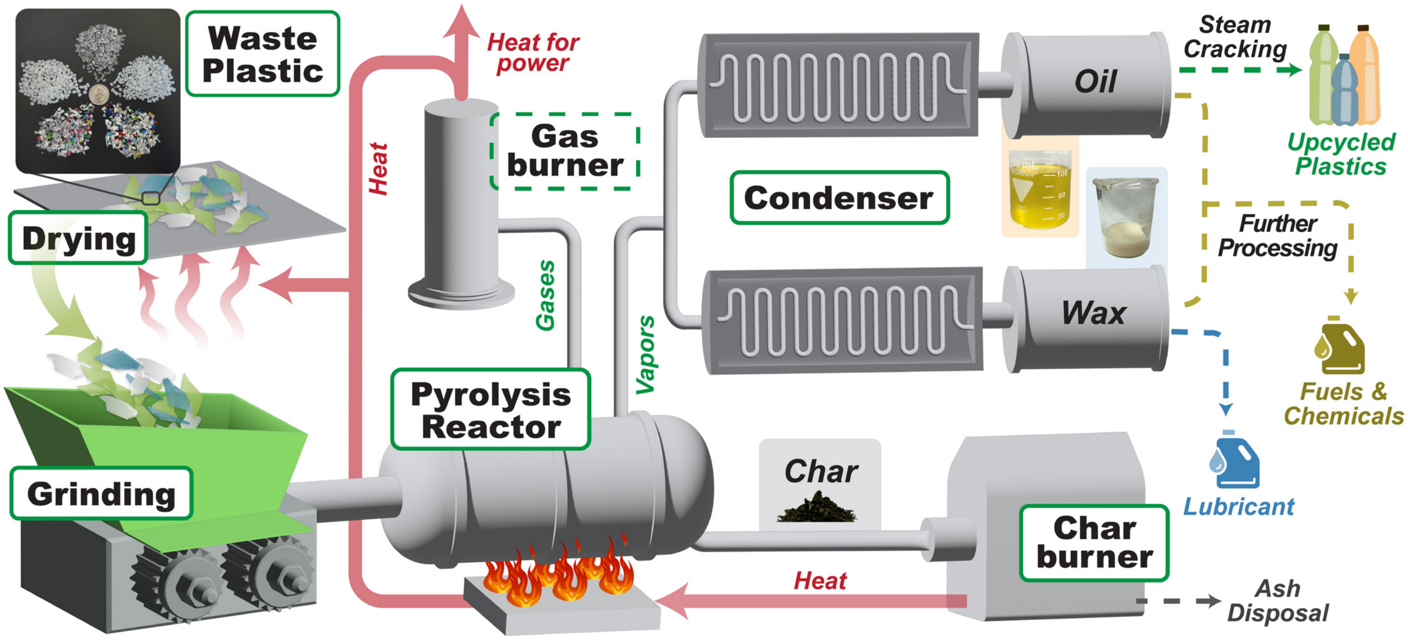

Figure 1. Generalization of the pyrolysis process. Dashed lines represent alternative pathways for products. Red lines represent energy flows.

• Understanding Pyrolysis

Pyrolysis of waste plastics, as shown in ***Figure 1***, involves several steps, starting with drying and grinding to produce a uniform material to feed to the reactor. Plastic enters the reactor, which is ideally operated at temperatures around 600 °C (1,112 °F), where it rapidly melts and decomposes to produce vapors, gases, and char. The vapors and gases exit the reactor where they pass through a cooler that condenses the vapors to wax, oil, and water while the gases pass to a burner that oxidizes the gases to carbon dioxide and water. This process also generates thermal energy that can be used to help heat the pyrolysis reactor or in other processes such as drying and pre-treatment requiring heat inputs. Char is separately removed from the product stream, which can be burned to produce additional heat for the pyrolysis reactor. The cooled wax and oil can be upgraded to molecules suitable for production of new plastics and other chemicals.

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There are multiple types of reactors that can be used for pyrolysis including fluidized bed, stirred tank, screw/auger, rotary kiln, and conical spouted bed, among the most reviewed (Li et al., 2022). One of the main targets of the reactor is to achieve high and constant heat transfer for the production of pyrolysis oil. As a result, reactors that achieve good mixing and continuous flow (***Figure 2***) are preferred to batch reactors that have low heat transfer and can experience clogging (Ragaert et al., 2017). New pyrolysis reactors designs can also improve the operability of the production avoiding shutdowns for cleaning and maintenance. Moreover, companies and startups have been continuously improving the pyrolysis technology as they build know how on processing plastic waste. For example, effectively processing different types of plastic (including plastics containing halogen molecules), contaminants, and organic streams will allow to convert more plastic waste into usable products and reduce the operation costs in feedstock pre-treatment.

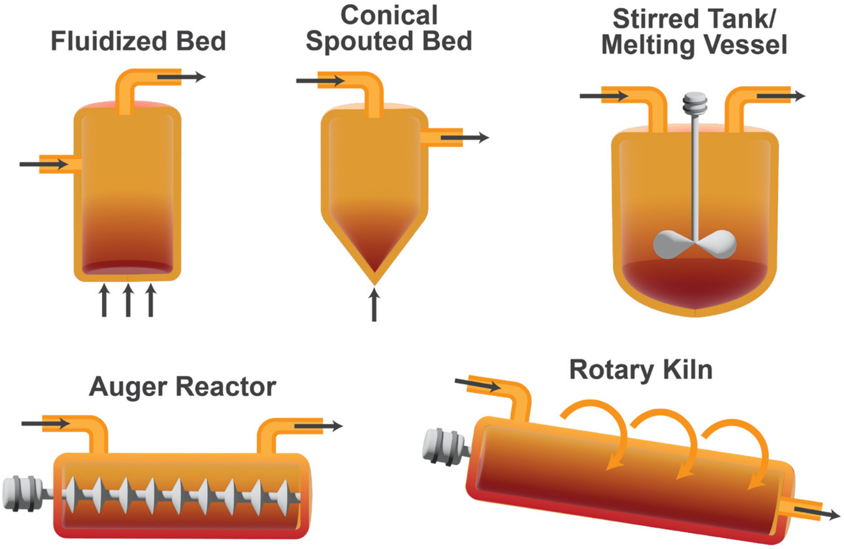

Figure 2. Reactors used for pyrolysis of waste plastics (from (Li et al., 2022)).

- **How Does Pyrolysis Integrate into Current Plastics Production?**

There are different applications for pyrolysis oil including chemical and polymer synthesis and energy production. Using plastics for energy production (electricity, heat, or liquid fuels) is sometimes criticized as not contributing to a circular economy and emitting carbon dioxide into the atmosphere (Dai et al., 2022). Ideally, plastics upcycling would mitigate plastics pollution, reduce GHG emissions, and produce material and energy products that are cost-effective compared to similar products from fossil resources (Zheng & Suh, 2019). However, more often it is a matter of balancing these beneficial outcomes against one another. One of the best ways to achieve an optimal outcome is to employ the wax and oil from pyrolysis in the production of new plastics or other chemical products rather than producing energy.

Many plastics are produced from hydrocarbons derived from natural gas and crude oil (Li et al., 2022). As shown in ***Figure 3***, the conversion of natural gas and crude oil into plastics follow different reaction pathways. Steam cracking is the first step in the pathway for plastic production, in which large hydrocarbon molecules are broken down into smaller hydrocarbon molecules. This is where pyrolysis integrates with the current production of plastics as pyrolysis oil can undergo steam cracking to produce upcycled plastics. Moreover, steam cracking guarantees the polymer grade of the monomers. Alternative approaches to upgrading the plastic pyrolysis oils, such as hydroformylation and catalytic cracking, are also being studied (Dong et al., 2023; Li et al., 2023).

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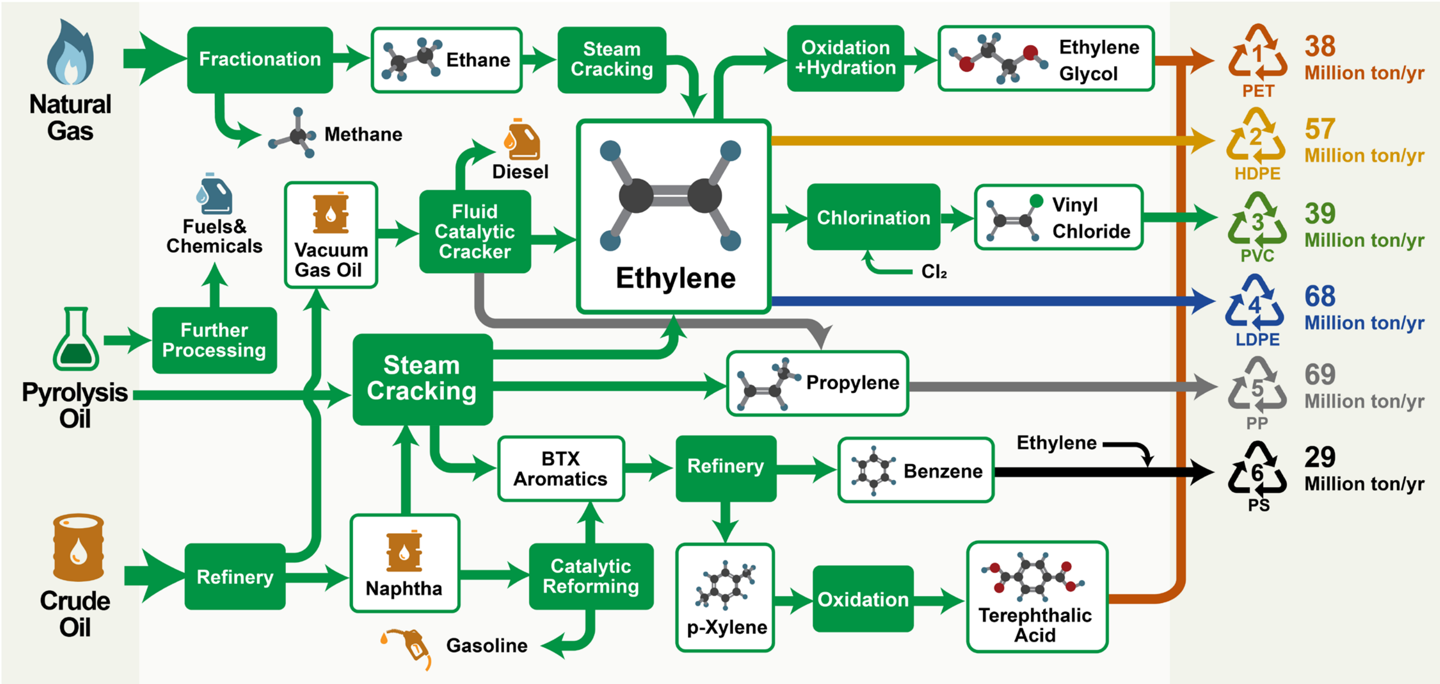

Figure 3. Processing steps for the production of #1–#6 plastics and their volume of production in 2019 globally (adapted from (Li et al., 2022)).

- **Advantages and Disadvantages of Pyrolysis**

One of the main advantages of pyrolysis is that it can process different kinds of plastic wastes, including mixed plastics and multi-layer films, unlike mechanical recycling that needs highly separated plastics by type (e.g., only PET waste) (Li et al., 2022). In this sense, chemical recycling complements mechanical recycling. In addition, pyrolysis can process contaminated plastics with fats, oils, grease, and dirt as well as other chemical components that give plastics their properties. This flexibility to process mixed and contaminated plastic waste also reduces the logistic effort, costs, and energy consumption associated with segregating and classifying plastic waste by households and material recovery facilities (MRFs). More importantly, it provides an alternative to sending waste plastics to landfills, dumps, and the environment.

Like every technology, pyrolysis has shortcomings. In general, pyrolysis demands more energy than mechanical recycling to produce the same amount of product (see ***Table 1***). However, pyrolysis can recycle plastics that are currently hard to recycle using current mechanical technologies, so rather than competing with, chemical recycling complements mechanical recycling. The impacts of high energy demand can be addressed by implementing renewable energy systems with pyrolysis projects. Another disadvantage is that hydrochloric acid formed during the pyrolysis of polyvinyl chloride (PVC) and polyvinylidene chloride (PVDC), usually present in small amounts (~1% wt) in waste plastics, can corrode the pyrolysis reactor (Gendell & Lahme, 2022; Xu et al., 2020). This can be prevented by adding an acid scavenger like calcium oxide to remove the chlorine content as a pretreatment process (Li et al., 2022; Matsuzawa et al., 2004). Inclusion of oxygen-containing plastics like PET may reduce the yield of desirable liquid fractions and generate more char, carbon dioxide, and carbon monoxide (Genuino et al., 2023; Holland & Hay, 2002). Including sorting to remove PVC and PET could also improve the quality of the final product. In addition, the wax and oil from pyrolysis need to be further processed before they can be used to produce new plastics, adding complexity and processing steps (Li et al., 2022). Additives in plastics can also cause issues during pyrolysis. The additives can end up in both the char and the oil. These additives must be dealt with in any real pyrolysis process (Li et al., 2022).

How is Pyrolysis Different from Incineration?

Some people mistakenly equate pyrolysis with incineration, which has an unfavorable reputation for pollution. Incinerators were introduced into communities many years ago to simplify waste management by burning garbage, often with lower emissions than burning trash in one's backyard. Incinerators have been largely shutdown or replaced with modern energy recovery boilers, burning wastes in streams of air at high temperatures in conjunction with pollution control devices to reduce the various emissions produced to predominantly carbon dioxide and water vapor. Incineration follows a linear life cycle; that is, plastics are produced and used only once before being destroyed (see ***Figure 4***).

Pyrolysis, on the other hand, operates at more modest temperatures and in the near absence of air to produce mostly waxes and oils instead of gas, depending on the reactor conditions. The relatively small amount of gas produced passes through a thermal oxidizer to convert any organic compounds that are not collected as oil into carbon dioxide and water (Li et al., 2022). The recovered oil can be used in a steam cracker to be converted to monomers and new plastics. Pyrolysis can potentially reintroduce most of the plastic waste into the economy, where resources are conserved and continuously utilized, minimizing the depletion of fossil resources, and also preventing plastic waste from contributing to air, water, or soil pollution from manufacturing and final disposal (***Table 1***).

Table 1. Key differences between incineration and pyrolysis (from (Hermanns et al., 2023)

Description	Incineration	Pyrolysis
Process	High oxygen (≥ 20%)[1]	Low oxygen (≤3% in the gas carrier)[2]
Products	Electricity: 4.4 MJ/kg (430 Btu/lb) plastic waste[3] Thermal energy: 11.1 MJ/kg (4,772 Btu/lb) plastic waste[3]	Oils and waxes: 50-85 %wt[3] Gases: 5-28 %wt[3] Solid residue: 3-18 %wt[3]
Energy Input	Thermal energy: 0.49 MJ/kg (211 Btu/lb) plastic waste[3] Electricity: 0.46 MJ/kg (198 Btu/lb) plastic waste[3] Total: 0.95 MJ/kg (408 Btu/lb) plastic waste[3]	Thermal energy: 2.6-3.1 MJ/kg (1,118-1,333 Btu/lb) plastic waste[3] Electricity: 1.9 MJ/kg (817 Btu/lb) plastic waste[3] Total: 4.5-5.0 MJ/kg (1,935-2,150 Btu/lb) plastic waste[3]
Greenhouse Gas (GHG) Emissions	3.05 kg CO_2-eq/kg (3.05 lb CO_2-eq/lb) plastic waste, not considering credits of replaced energy[3]	0.8 kg CO_2-eq/kg (0.8 lb CO_2-eq/lb) plastic waste, not considering credits of replaced products[3]
Circularity	**No** – adopts a linear carbon economy as waste plastics are converted to air emissions	**Yes** – achieves a circular carbon economy as waste plastics are reconverted to useful products

[1]*(Ma et al., 2019)*
[2]*(Fu et al., 2023)*
[3]*(Hermanns et al., 2023)*

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Safety of Pyrolysis

Pyrolysis is a moderately high temperature process, operating at temperatures comparable to a commercial pizza oven (500 to 600 °C or 932 to 1,112 °F) and well below the temperature achieved in a gasoline engine (2,500 °C or 4,532 °F) (Zhao et al., 2020). The process converts plastic wastes into waxes, oils, and gases, all of which are flammable materials. Accordingly, it carries potential risk of fire and exposure to toxic vapors if appropriate environmental, health, and safety measures are not practiced, which would be similar to those implemented at a petroleum refinery or power plant. In addition, pyrolysis generates byproducts and residual waste which must follow the appropriate procedures for disposal in accordance with the local regulations. This is critical for the success of the operation of pyrolysis plants and to avoid issues with local communities.

With combustion characteristics similar to diesel fuel, it is important to realize that neither waste plastics nor the wax and oil derived from their pyrolysis represent inordinate ignition or explosion hazards during storage or transport. Like other potentially flammable materials, problems arise when vapors and gases are exposed to some combination of high temperature, oxygen, and ignition source, especially if under high pressure. Most pyrolysis reactors are operated at atmospheric pressure, which reduces the hazard of uncontrolled release of gases and vapors to the atmosphere. Pyrolysis plants should maintain safety standards and procedures like any other plant handling flammable products.

Environmental Benefits and Economics of Pyrolysis

Plastic products made through pyrolysis-based upcycling can help address many of the environmental challenges of producing the same plastic products from fossil sources (Gracida-Alvarez et al., 2019). Moreover, pyrolysis of waste plastics results in lower GHG emissions than incineration (***Figure 4***), which is a significant benefit on top of the fact that pyrolysis reinserts plastics into the economy rather than disposing them. As with many other processing plants, small-scale pyrolysis plants are typically not economically competitive when compared to chemical plants producing virgin products from fossil fuels (Fivga & Dimitriou, 2018).

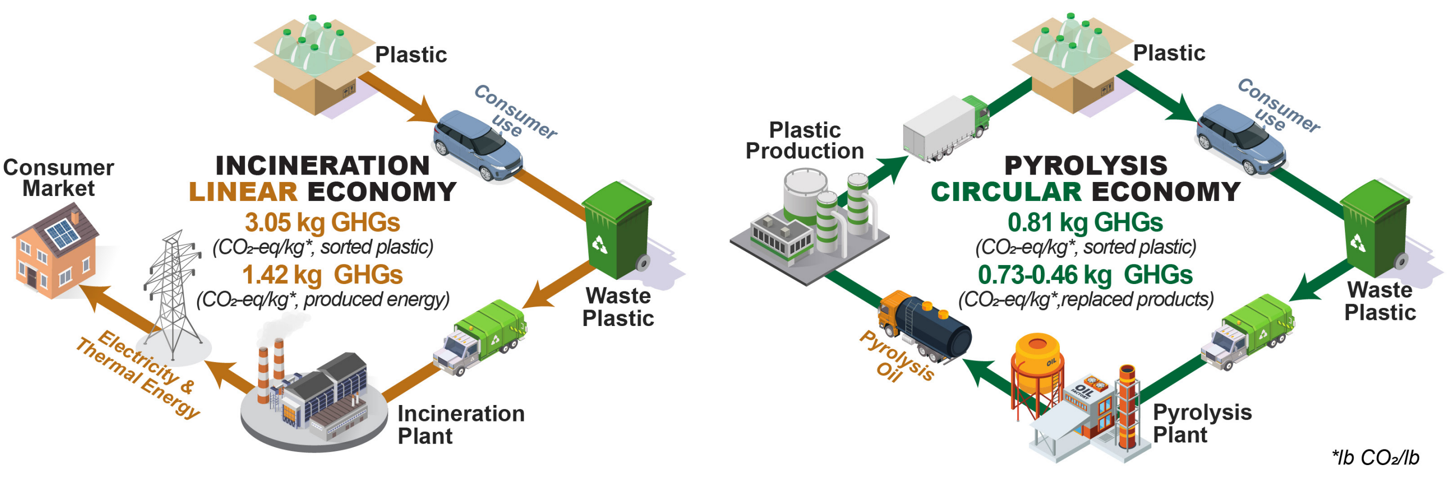

Figure 4. Processing steps and related greenhouse gas (GHG) emissions needed to a) burn waste plastics through incineration or b) recycle waste plastics through pyrolysis. GHG emission values are from (Hermanns et al., 2023).

The clear advantage of upcycling over landfilling is elimination of an enormous waste management problem and providing economic motivation to keep plastic waste out of the environment. Moreover, a pyrolysis life cycle leads to nearly four times lower carbon dioxide emissions than incineration and avoids the production of virgin plastics from petroleum (Hermanns et al., 2023). On the other hand, like so many sustainability solutions, it may be more expensive than simply producing new plastics from fossil fuels. These cost barriers could be minimized when the benefits of reducing plastic waste and promoting circularity are realized. Upcycling of plastics offers a way to address the waste management issue of plastics while retaining their societal benefits with relatively minor impact on consumer costs and GHG emissions.

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