



Life-cycle analysis of recycling of post-use plastic to plastic via pyrolysis

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ABSTRACT

Advanced recycling enables the application of post-use plastics (PUP) to produce valuable industrial chemicals and develop markets for recycled feedstocks. Pyrolysis is one of the most common advanced recycling technologies undergoing industrial-scale implementation for converting PUP. This paper presents a life cycle analysis (LCA) to assess greenhouse gas (GHG) emissions, fossil energy, water consumption, and solid waste impacts of converting PUP into new plastics such as high-density and low-density polyethylene (HDPE and LDPE, respectively). Data was collected from eight plastic pyrolysis companies. This study addresses the impacts of pyrolysis plant size and maturity; two substitution rate (SR) cases of pyrolysis oil with fossil-derived feedstocks in steam crackers (5% and a 20% of pyrolysis oil SR); and potentially avoided emissions from traditional end-of-life (EOL) management. Because the conventional feedstock slate of steam crackers in the United States is comprised of 94% gases (a mix of ethane, propane, and butane) and 6% naphtha, the 5% SR case looked at polyethylene (PE) derived from 5% pyrolysis oil, 1% naphtha, and 94% gases; while the 20% SR looked at PE derived from 20% pyrolysis oil and 80% gases. Moreover, the results are presented from two perspectives: 1) steam crackers' and 2) plastic recyclers'. In the recyclers' perspective, the results for the 5% SR showed for each kg of PUP used there was a 23% and 18% decrease in GHG emissions for HDPE and LDPE respectively, while the 20% SR showed a 4% and 3% reduction in GHG emissions for HDPE and LDPE respectively compared to virgin plastic. The 20% SR has lower GHG emissions reductions because there is an added step of hydrotreating the pyrolysis oil to remove chlorine concentrations that is not included in the 5% SR scenario. Furthermore, the 5% SR removes most of the naphtha, a more carbon intense feedstock, and replaces it with PUP-based pyrolysis oil, a less carbon intense feedstock. GHG emissions for PUP pyrolysis could be further reduced by 50% and 131% in the United States and European Union respectively if the GHG emissions of current PUP incineration practices were considered as emission reductions credits.

1. Introduction

Plastics are important products in the modern economy reaching a production of 367 and 56 million tonnes (MMT) in the world and North America, respectively in 2020 (ACC, 2022; Plastics Europe, 2021). Currently, the plastic industry relies heavily on fossil resources. The data shows that 6% of the global production of crude oil and natural gas liquids (NGLs) is devoted to the production of plastics, a share expected to increase to 20% in 2050 (Lebreton and Andrady, 2019; Rhodes, 2018). The increasing consumption of plastics results in high waste generation. The United States alone has increased the amount of plastic waste from 28 to 32 MMT (14%) from 2010 to 2018 (U.S. EPA, 2022). Although recycling can reduce the dependence on fossil resources and waste generation in the plastic industry while converting post-use

plastic (PUP) into a resource, only 9% of the total PUP collected in the United States is mechanically recycled due to diverse economic, technical, environmental, and regulatory barriers (OECD, 2018; U.S. EPA, 2022).

One of the major barriers preventing an increase of the recycling rate of PUP is the absence of economically competitive markets for recycled plastics like polypropylene (PP), polyvinyl chloride (PVC), low-density polyethylene (LDPE), and polystyrene (PS). It is challenging to process these recycled plastics as the costs of collection and separation are higher than their market price (Cho, 2020; Milbrandt et al., 2022). Consequently, it is more cost effective for material recovery facilities (MRFs) and municipalities to simply dispose of these plastics into landfills or incineration facilities. They focus the use of their resources (i.e., machinery, energy, time) only on highly recyclable plastics such as

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polyethylene terephthalate (PET) and high-density polyethylene (HDPE), with established markets and collection infrastructure. Additionally, China decided to stop receiving waste plastic from other countries, which resulted in the increase in landfilling of waste plastic by 23% in the U.S. (Vedantam et al., 2022). As a result, there is an expected overload of plastic waste in several nations that will require the creation of alternatives to increase the commercialization of difficult-to-recycle plastics.

The circular economy (CE) is a concept encouraging the continuing flow of materials in the supply chain to reduce finite resource consumption (Ellen MacArthur Foundation, 2020). A common sector that has stimulated the promotion of CE initiatives is plastic packaging because of its contribution to plastic waste accumulation and its inherent short lifetime. Advanced recycling, also known as chemical or molecular recycling, is one of the technologies applicable for recycling plastics. It uses certain temperature and pressure conditions, and may use solvents and catalysts to breakdown the plastic polymers into their monomers and convert them into new chemical products (Luu et al., 2021). Pyrolysis is an advanced recycling technology that transforms complex mixtures of PUP, including nonrecycled plastics, into feedstock materials (e.g., pyrolysis oil) for further upgrading into new plastics or other materials (Sekar et al., 2022). 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 (Kusenberget al., 2022), they can also be drop-in replacements with numerous applications. Therefore, pyrolysis presents an opportunity to (1) enhance the commercialization of non-recycled plastics, (2) promote the circularity of the plastic packaging industry by reducing the dependence on fossil resources, and (3) reduce plastic waste accumulation.

Despite the benefits of plastic waste reduction and lower use of virgin resources (Huang et al., 2022; Vollmer et al., 2020), advanced recycling technology needs to evaluate the potential to reduce the environmental impacts of plastic manufacturing compared to the current fossil-based production. Some studies report LCA results using data from simulations (Gracida-Alvarez et al., 2019; Somoza-Tornos et al., 2020; Zhao and You, 2021) and other reports have presented similar analyses (plastic-to-intermediate products) with data from operations of pyrolysis companies (Broeren and Bergsma, 2020; Environmental Clarity, 2021; Luu et al., 2021). Recently, petrochemical companies implementing pyrolysis-based plastic-to-plastic (P2P) conversion at an industrial scale have released LCA reports showing life-cycle GHG emission reductions ranging from 5 to 126% for advanced recycling compared to traditional polyolefin (PO) manufacture (Honeywell UOP, 2021; Jeswani et al., 2021; Quantis, 2020; Russ et al., 2020; SABIC, 2021; Viveros et al., 2022). Table S1 in the supporting information (SI) shows that these reductions strongly depend on the LCA method and assumptions considered, including the system boundary and the estimations of credits from avoided end-of-life (EOL) management emissions. Note that none of these P2P reports presented an evaluation for the United States or North America, and only the analysis from Viveros et al. (2022) considered the evaluation for more than one facility. Because of the significant differences in the feedstocks used for ethylene production such as naphtha shares in crackers (Franklin Associates, 2020a; Lippe, 2020; Young et al., 2022), and the EOL methods and parameters, none of previous reports reflect the conditions of PUP pyrolysis in the United States.

This study presents an LCA of pyrolysis of PUP focusing on the United States conditions. Key LCA parameters were developed based on the industrial production data of pyrolysis oil, POs, and EOL management of PUP. This study builds on the work previously reported by Benavides et al. (2022, 2017) for the conversion of plastic to ultra-low sulfur diesel and pyrolysis oil. Using operation data from eight pyrolysis facilities (seven located in the United States and one in Europe) that agree to participate and provided detailed information and supplementary

simulation data, the life-cycle impacts on fossil energy use, GHG emissions, water consumption, and solid waste generation of conversion of PUP to pyrolysis oil, and subsequently to new plastics were estimated. The conversion of pyrolysis oil to plastics was compared with plastic production via conventional feedstocks including naphtha and gases (ethane, propane, and butane). The baseline monomer production is based on the U.S. average cracking feedstock slate as reported by Lippe (2020) and polymerization inventory data from U.S. companies for two POs: HDPE and LDPE (Franklin Associates, 2020a, 2021, 2020b). Along with the “base analysis” emissions (cradle-to-gate), the impact of the conventional PUP management practices in the “counterfactual analysis” were considered to account for the emission credits from avoided EOL management as suggested by Tabrizi et al. (2020). In addition, the effects of economies of scale of the pyrolysis plants were evaluated by classifying the pyrolysis facilities into two groups as described previously by Benavides et al. (2022): (1) Pioneer plants, with a processing capacity lower than 50,000 tonnes of PUP per year and (2) N^{th} -plants with a processing capacity higher than or equal to 50,000 tonnes per year. Finally, this work examined the effects of different substitution rates (SRs) of pyrolysis oil in a steam cracker, which refers to the share of pyrolysis oil co-fed in the cracker with feedstocks from refinery. Additional sensitivity cases evaluated two baseline compositions of cracker feedstocks (only naphtha and only gases), sources for electricity generation, and co-produced hydrogen treatment on the GHG emissions for pyrolysis-based plastic pathways.

2. Materials and methods

Fig. 1 describes the system boundary of the two pyrolysis-based plastic pathways: HDPE and LDPE on a cradle-to-gate basis. This process starts with the collection and logistics of waste feedstocks, sorting of post-consumer plastic (PCP) at a MRF, and transportation of PCP and post-industrial plastic (PIP) to pyrolysis facilities (for details refer to section S2 of the SI). 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. At the pyrolysis facilities, PUP (which is the combination of PCP and PIP) goes through additional pretreatment and conversion where the pyrolysis oil and other products (gas phase products and char) are obtained (Benavides et al., 2022). Once pyrolysis oil is produced, it is sent to chemical companies where the pyrolysis oil may go through a purification step. Purified pyrolysis oil is co-fed with conventional feedstocks, which included petroleum naphtha and gases obtained from crude oil and natural gas liquids to a steam cracker to produce monomers (ethylene and propylene) which are polymerized into HDPE and LDPE. Based on discussions with the industry experts, a group of people from the petrochemical industry with expertise in cracking operations, two cases were considered for the co-feeding of pyrolysis oil in this analysis. Case 1 considered a low substitution rate (SR) where no purification step is required due to low concentration of pyrolysis oil in the cracker, that is a 5% SR (on a mass basis). This number was selected because the contaminants in the pyrolysis oil are diluted to concentrations within the specifications of the cracker feed. Case 2 uses a 20% SR (on a mass basis) and therefore it required purification to remove impurities and contaminants such as chloride, silicone, and fluorine (see SI section S3) which can be harmful to the equipment and could affect the operation in the cracker. In this work, it is considered that the 20% SR case is only applicable for N^{th} -plants because they have higher processing capacity than pioneer plants and are more likely to fulfill the demand of U.S. crackers. As observed, the 20% SR case uses a greater amount of pyrolysis oil in the cracker than the 5% SR case and, therefore, requires more PUP to be processed.

2.1. Collection, transportation, pretreatment, and conversion stages

Description of the processes of PCP collection and sorting,

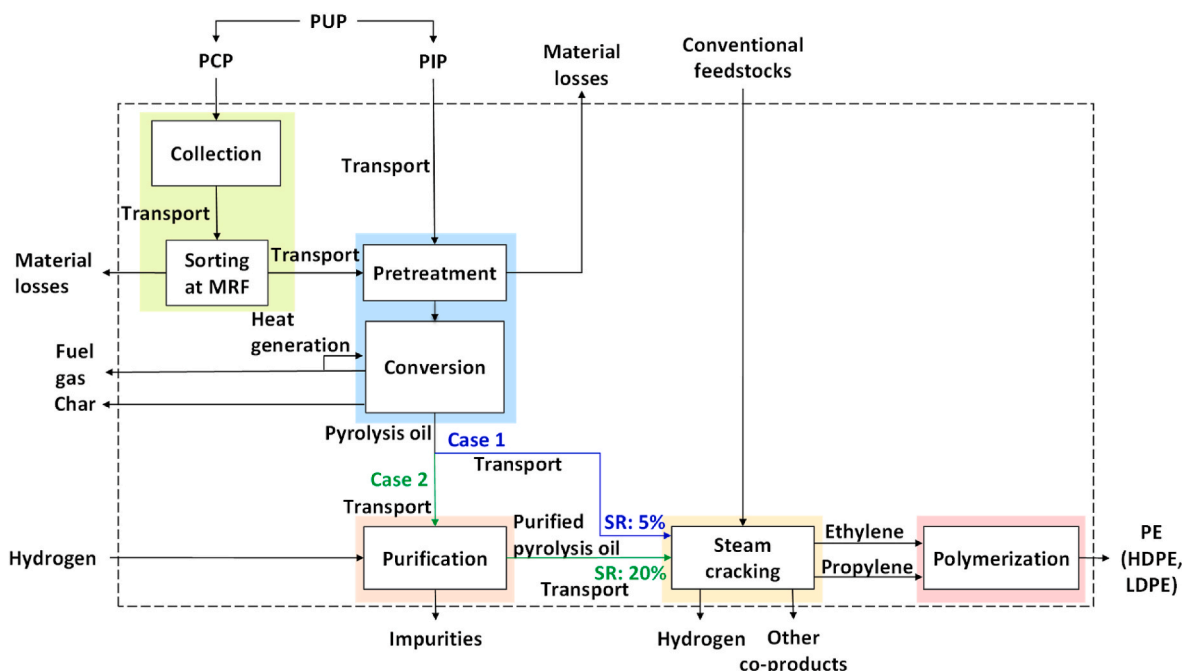


Fig. 1. System boundary of the base analysis of the plastic-to-plastic process. Conventional feedstocks include petroleum naphtha, ethane, propane, and butane derived from crude oil and natural gas liquids. Ethylene is used to produce HDPE and LDPE and propylene is needed only for LDPE manufacturing.

specifications of transportation of PCP and PIP feedstock, and material and energy requirements associated with the pretreatment and conversion processes at pyrolysis facilities have been previously described by Benavides et al. (2022). This information is summarized in Section S2 of the SI.

2.2. Purification stage

After the conversion process, the pyrolysis oil was purified through hydrotreatment, to reduce the chlorine concentration from 600 ppm to 10 ppm (SI section S3). Energy requirements and type of energy sources were modeled from current refinery operations for crude oil, and hydrogen consumption was estimated from the stoichiometric amount required to convert the removed chlorine into hydrochloric acid. Although fluorine, diolefins, and silicon are other contaminants of concern, their removal in the hydrotreatment modeling was not considered due to insufficient information of the fluorine and diolefin concentrations and silicon removal technologies. Therefore, it was considered that focusing only on chlorine removal could provide a close approach to current operations. After purification, the pyrolysis oil is blended with feedstocks from refinery at the SR described before.

2.3. Steam cracking of pyrolysis oil and fossil-derived feedstocks

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), which is available in the Greenhouse Gases, Regulated Emissions and Energy Use in Technologies (GREET®) model (ANL, 2020). A portion of co-produced hydrogen and methane from the cracker is considered to serve as process fuels, reducing the use of external energy inputs. The modeling assumes that 70% of facilities in the United States use the co-produced hydrogen as an internal energy source while the remaining 30% is sold as an external product (Young et al., 2022). A sensitivity analysis of co-produced hydrogen treatment was included in this analysis in Section 3.2.3. The fossil-derived feedstocks were modeled to steam cracking in the United States using information from Lippe (2020); the average feedstock slate consists of 6% naphtha, 76% ethane, 15% propane, and 3% butane. It was assumed that pyrolysis oil

displaces the naphtha portion in the feedstock slate before gases. For the cases where there is not enough naphtha to be displaced, pyrolysis oil also displaces gases. For instance, in the 20% SR scenario, 6% of the pyrolysis oil substitutes naphtha (as it is the amount available based on the U.S. average feedstock slate), and the remaining 14% displaces gases (i.e., ethane, propane, and butane). While the design of a cracker is highly dependent on the feedstock type and composition, its implications were not discussed in this study due to the lack of details on the modeling and operation and proprietary information. However, a sensitivity analysis is conducted in Section 3.1.1. to evaluate the feedstock variability into the cracker.

2.4. Polymerization

For the polymerization stage the inventory data from Franklin Associates (Franklin Associates, 2020a, 2021, 2020b) was used to produce HDPE and LDPE (see section S3 of the SI). The polymerization stage of HDPE consists of a low-pressure catalytic polymerization with a Ziegler-Natta catalyst, however, for LDPE the polymerization reaction is performed at high pressure.

2.5. Life-cycle analysis

This study analyzed two perspectives: 1) steam crackers' perspective and 2) plastic recyclers' perspective. The first perspective analyzed the results when pyrolysis oil is co-fed with conventional feedstocks (gases and naphtha) at 5% and 20% SRs. The second perspective also analyzed the results from co-feeding but allocated the impacts associated with the substitution of conventional feedstocks with pyrolysis oil to a plastic with hypothetical 100% recycled feedstock. The results are reported using a functional unit of one kg of HDPE or LDPE, depending on the plastic under evaluation. A graphical description of these two perspectives is presented in Fig. 2.

2.5.1. Steam crackers' perspective: HDPE and LDPE produced from co-feeding of pyrolysis oil with conventional feedstocks

Co-feeding refers to mixing PUP-based pyrolysis oil and conventional feedstocks in the cracker. The approach discussed in this section is of

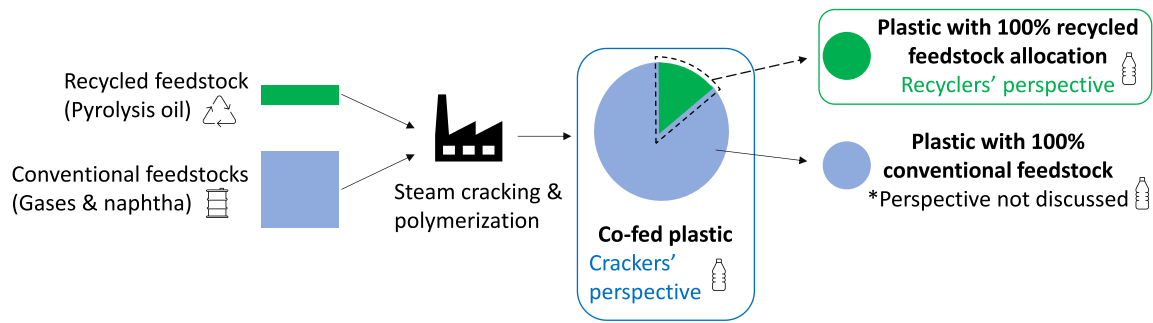


Fig. 2. Perspectives of the analysis of GHG emissions from plastic with recycled feedstock utilized in the analysis.

interest to steam cracking operators as it estimates the environmental impacts of substituting conventional feedstocks in the production of HDPE and LDPE without cracker modifications. The GREET model was employed to estimate the GHG emissions, fossil energy, and water consumption at the process level. Fossil energy accounts for the energy derived from petroleum, natural gas, and coal that is used in the process operation and to produce the required material and energy inputs. Water consumption refers to the amount of water that is lost from evaporation or in the wastewater treatment process and has to be replenished with freshwater. The impacts of the substitution of conventional with recycled feedstock are directly associated with the total impact of the production pathway. In order to present the LCA results per kg of recycled plastics, a mass balance approach was used to be consistent with previous literature (Ellen MacArthur Foundation, 2019; Jeswani et al., 2019). The mass balance approach is a chain of custody model that, in the co-feeding approach, tracks the amount of recycled feedstock through the supply chain to allocate the impacts of recycled feedstocks in the final products (Ellen MacArthur Foundation, 2019). The mass balance approach used in the co-feeding approach is presented in Equation (1).

$$I_{PE_{Cofed}} = I_{PE_{Conv}} + a_1 \cdot \left(CV_{N_{PyOil}} \cdot I_{PyOil} - I_{Naphtha} \right) \cdot AF + b_1 \cdot \left(CV_{G_{PyOil}} \cdot I_{PyOil} - I_{Gases} \right) \cdot AF + (I_{SC_{PyOil}} - I_{SC_{Conv}}) \cdot AF \quad (1)$$

$I_{PE_{Cofed}}$ and $I_{PE_{Conv}}$ represent the environmental impacts (e.g., GHG emissions, fossil energy, or water consumption) per kg of polyethylene (PE; either HDPE or LDPE) from co-fed and conventional production, respectively. a_1 and b_1 are the amount of naphtha and gases, respectively, substituted with pyrolysis oil and AF is the allocation factor. I_{PyOil} , $I_{Naphtha}$, and I_{Gases} indicate the environmental impacts of pyrolysis oil (from Pioneer or N^{th} -plants), naphtha, and gases, respectively. Section S4 in the SI presents the calculation of factors a_1 and b_1 while section S5 explains the estimation of the allocation factors. Table 1 provides a comparison between the cradle-to-gate GHG emissions, fossil energy, and water consumption of the conventional feedstocks (naphtha

Table 1
Cradle-to-gate life-cycle impacts for three different feedstocks used in the steam cracking process (ANL, 2020; Benavides et al., 2022).

Feedstock type	Carbon intensity (kg CO ₂ e/kg feedstock)	Fossil energy (MJ/kg feedstock)	Water consumption (L/kg feedstock)
Naphtha	0.67	51.7	3.4
Gases	0.41	50.7	0.7
Pyrolysis oil (Pioneer plant)	1.04	15.1	3.3
Pyrolysis oil (N^{th} -plant)	0.40	11.7	0.5

and gases) and the pyrolysis oil from pioneer and N^{th} -plants, which have been normalized to a per kg basis. 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). These impacts are used in equation (1) on a per kg of feedstocks basis. The impacts of pyrolysis oil production were obtained from the analysis by Benavides et al. (2022) with the addition of hydrotreatment impacts for the 20% SR case.

Solid waste is an important metric in analyzing advanced recycling technologies such as pyrolysis because it reflects the impact of circular flows of materials within the system. According to a recent survey of pyrolysis facilities (Benavides et al., 2022) the production of one kg of pyrolysis oil from pioneer and N^{th} -plants avoids the disposal of 1.1 and 0.9 kg of PUP, respectively. In conventional plastic production and use, 0.91 kg of PUP per kg of plastic are disposed through landfill and incineration (U.S. EPA, 2020) while in the co-feeding cases a portion of that PUP is diverted to the production of plastic. The estimations for the avoided PUP from traditional EOL management of pyrolysis oil from pioneer and N^{th} -plants are explained in section S6 of the SI.

The differences of the impacts from the steam cracking are also accounted in Equation (1). The terms, $I_{SC_{PyOil}}$ and $I_{SC_{Conv}}$, refer to the environmental impacts of the steam cracking stage during the co-fed and conventional production of PE, respectively. Because the steam cracking process generated several co-products apart from ethylene and propylene, a hybrid co-product treatment method described by Plastics Europe (2012) was used to allocate the emissions and energy burdens of feedstocks employed and fuels consumed in the cracker. This approach applies mass allocation to the feedstock production (i.e., conversion of PUP to pyrolysis oil and extraction and processing of conventional feedstocks) and high-value chemical (HVC) allocation to the fuels consumed to provide energy to the cracker. The HVC allocation is similar to mass allocation but only considers the products with high market value such as hydrogen, ethylene, propylene, butadiene, benzene, toluene, styrene, xylene, and ethylbenzene. Section S5 in the SI presents the values of the mass and HVC allocation factors for ethylene and propylene in the two SR cases and the two co-produced hydrogen treatment methods.

To compensate for the differences in chemical composition between pyrolysis oil and conventional feedstocks, the impacts of pyrolysis oil are multiplied by a chemical value factor (Ellen MacArthur Foundation, 2019; Jeswani et al., 2019). The chemical value factors employ the ratio between the lower heating values of the substituted conventional feedstock (naphtha or gases) and pyrolysis oil, as shown in Equations (2) and (3):

$$CV_{N_{PyOil}} = \frac{LHV_N}{LHV_{PyOil}} \quad (2)$$

$$CV_{G_{PyOil}} = \frac{LHV_G}{LHV_{PyOil}} \quad (3)$$

$CV_{N_{PyOil}}$ and $CV_{G_{PyOil}}$ are the chemical value factors of naphtha and

gases, respectively, with respect to pyrolysis oil, and LHV_N , LHV_G , and LHV_{PyOil} are the lower heating values of naphtha, gases, and pyrolysis oil, respectively. The chemical value factor of naphtha with respect to pyrolysis oil from both pioneer and N^{th} -plants is assumed as 1, because naphtha and pyrolysis oil can be substituted at the same ratio in the cracker and have very similar LHVs (Russ et al., 2020). The chemical value factor of the gases with respect to pyrolysis oil from pioneer and N^{th} -plants was estimated in 1.09 and 1.1, respectively.

2.5.2. Plastic recyclers' perspective: HDPE and LDPE production LCA results for 100% recycled feedstock allocation

The recyclers' perspective attributes the differences between co-fed and conventional production of PE only to the recycled feedstock (i.e., pyrolysis oil). The chain of custody models track the flow of recycled feedstock through to the final product (Ellen MacArthur Foundation, 2019) and by using the mass balance approach it is assumed that the composition of recycled feedstock in the cracker products (ethylene and propylene) is similar to the SR of pyrolysis oil co-fed with conventional feedstocks. Therefore, it is possible to allocate the life cycle impacts only to the recycled feedstock portion of ethylene and propylene and obtain results for producing a kg of PE with hypothetical 100% recycled feedstock (also abbreviated as kg PE_{recycled}), although in an actual production facility there is no physical separation of the plastic with recycled product. These results for PE with 100% recycled feedstock allocation, whose impacts are attributed solely to pyrolysis oil, are directly relevant for plastic recyclers.

The mass balance approach from Equation (1) has been adapted as shown in Equation (4) by dividing the terms associated with the differences between co-fed and conventional production of PE by the SR.

$$I_{PE_{Recycled}} = I_{PE_{Conv}} + \frac{a_1 \cdot (CV_{N_{PyOil}} \cdot I_{PyOil} - I_{naphtha}) \cdot AF}{SR} + \frac{b_1 \cdot (CV_{G_{PyOil}} \cdot I_{PyOil} - I_{gases}) \cdot AF}{SR} + \frac{(I_{SC_{PyOil}} - I_{SC_{conv}}) \cdot AF}{SR} \quad (4)$$

These results of HDPE and LDPE with the assumption of 100% recycled feedstock with the attribution of the changes from conventional feedstocks to co-feeding feedstocks in crackers and polymerization to pyrolysis oil are for developing results from plastic recyclers' perspective. This approach does not represent the physical adaptation of a cracker to entirely substitute conventional feedstocks with pyrolysis oil and does not project a future operation of steam crackers technology to handle the complete substitution of conventional feedstocks.

2.6. Counterfactual scenarios of PUP EOL management

The counterfactual scenarios account for the GHG emission credits of avoiding traditional EOL management of PUP by advanced recycling. The EOL management strategies assumed for this analysis are landfill and incineration with energy recovery. Mechanical recycling is not considered because advanced recycling is complementing it and does not compete with the feedstock used by mechanical recycling of PUP. The net GHG emissions of traditional EOL management are estimated by adding the emissions from PUP transportation to landfill and incineration and subtracting the emissions from the grid electricity displaced with the electricity generated during the process (ANL, 2020). Because incineration with energy recovery is the major contributor of GHG emissions, the traditional EOL in the United States and the European Union is compared to understand the effect of varying contribution between landfill and incineration in the counterfactual scenarios. In the United States, from the PUP that is not recycled, 17% is incinerated with energy recovery and 83% is landfilled (U.S. EPA, 2020), while in the European Union these percentages are changed to 63% and 37% for incineration with energy recovery and landfill, respectively (European

Parliament, 2021). The amount of PUP diverted from traditional EOL per kg of plastic is derived with the amount of PUP diverted from EOL from producing pyrolysis oil (1.1 and 0.9 kg PUP diverted/kg pyrolysis oil for pioneer and N^{th} -plants, respectively) and the amount of pyrolysis oil fed to the cracker allocated to ethylene and propylene (see sections S5 and S6 in the SI). This amount is multiplied by the corresponding shares of EOL methods depending on the geographical region to obtain the amount of PUP diverted through landfill and incineration. The GHG emissions from landfill storage and incineration with energy recovery, whose estimations are explained in previous publications (Benavides et al., 2022; Gracida-Alvarez et al., 2023), are multiplied by the corresponding amount of PUP diverted in each method and added to obtain the total credits of traditional EOL management. These avoided emissions from traditional EOL management are subtracted from the total cradle-to-gate GHG emissions obtained with equation (4) to calculate the GHG emissions of plastics with 100% recycled feedstock allocation with counterfactual scenarios.

2.7. Sensitivity analyses

This section discussed several sensitivity analyses to understand the effect of key parameters in the LCA results presented here.

2.7.1. Scenarios of naphtha and gas shares in conventional crackers

For this analysis a comparison with two additional conventional scenarios representing an upper and a lower bound of monomer production GHG emissions was included. The upper bound assumes that naphtha is the only feedstock employed in the cracker, similar to the conventional production of PO modeled in European LCA reports (Quantis, 2020; Russ et al., 2020; SABIC, 2021; Viveros et al., 2022). The lower bound case considered only gases as steam cracking feedstock, reflecting the current trend in the United States where gases are displacing the use of naphtha (Kooottungal, 2015; Lippe, 2018, 2020, 2018). In this case, the feedstock slate is 81% ethane, 16% propane, and 3% butane (on a weight basis).

2.7.2. Additional sensitivity analyses

This study also included sensitivity analyses to estimate the effect of treatment of co-produced hydrogen from steam cracking, and sources of electricity on the GHG emissions of pyrolysis oil for HDPE and LDPE. The steam cracker modeled in this study assumed that 70% of cracking facilities combust co-produced hydrogen to provide internal energy need and 30% export the hydrogen to other plants or processes (Young et al., 2022). To understand the impact of each co-produced hydrogen treatment method, the GHG emissions of HDPE and LDPE were evaluated with 100% recycled feedstock allocation when 1) 100% of facilities combust hydrogen as an internal fuel and 2) 100% of facilities exported and sold hydrogen as a product. The electric grid generation mix varies in different regions of the United States. Some regions use more renewable sources while others rely more on fossil sources. The effects on the GHG emissions of pyrolysis-based plastics were evaluated using different electric generation mixes (renewable-vs. fossil-based). The electric generation mix of California represents more renewable power, while the Midwest Reliability Organization (MRO) generation mix represents a high fossil grid (see section S7 of the SI for the share of different energy sources and GHG emissions per kWh of electricity generated of each case).

3. Results and discussion

This section presents the GHG emission results for the base analysis (cradle-to-gate) from two points of view: 1) steam crackers' perspective which refers to the production of HDPE and LDPE from co-feeding recycled and conventional feedstocks (as mentioned in section 2.5.1). The second point of view is the plastic recyclers' perspective, which refers to HDPE and LDPE production with hypothetical 100% recycled

feedstock (as explained in section 2.5.2).

3.1. GHG emissions of co-fed plastic production

The GHG emissions of co-fed production of HDPE and LDPE (net emissions represented with the black bar) are similar to those from conventional production. As seen in Fig. 3, the upstream emissions of pyrolysis oil (light green bars) are added while those of avoided conventional feedstock (pink and dark blue bars for naphtha and gases, respectively) and changes from steam cracking (red bar), associated to variations of product yields observed when gases are substituted with pyrolysis oil, are subtracted from the emissions of conventional production of ethylene. 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. This is a result from the substitution of naphtha with pyrolysis oil from pioneer plants, which have a higher carbon intensity (CI) compared to naphtha as shown in Table 1.

In the cases co-feeding pyrolysis oil from N^{th} -plants the GHG emissions showed close to 1% reduction compared to the conventional production of plastic. These GHG emissions were slightly lower in the 5% than in the 20% SR case because the latter incorporated the impacts of treating pyrolysis oil via hydrotreatment before being fed into the cracker. The GHG emissions of hydrotreatment accounted for 0.02 kg CO₂ e per kg of plastic. In addition, in the 20% SR case, pyrolysis oil not only substituted naphtha but also a portion of the gases (which have a similar CI compared to the pyrolysis oil from N^{th} -plants). The substitution of gases with pyrolysis oil reduced the yield of ethylene and increased the yield of methane. As a result, more methane is available as an internal energy source which decreases the net energy requirements in comparison to using the conventional feedstock slate. Therefore, increasing the amount of pyrolysis oil and the associated substitution of gases led to slightly lower GHG emissions in the 20% SR case compared to conventional production of plastics.

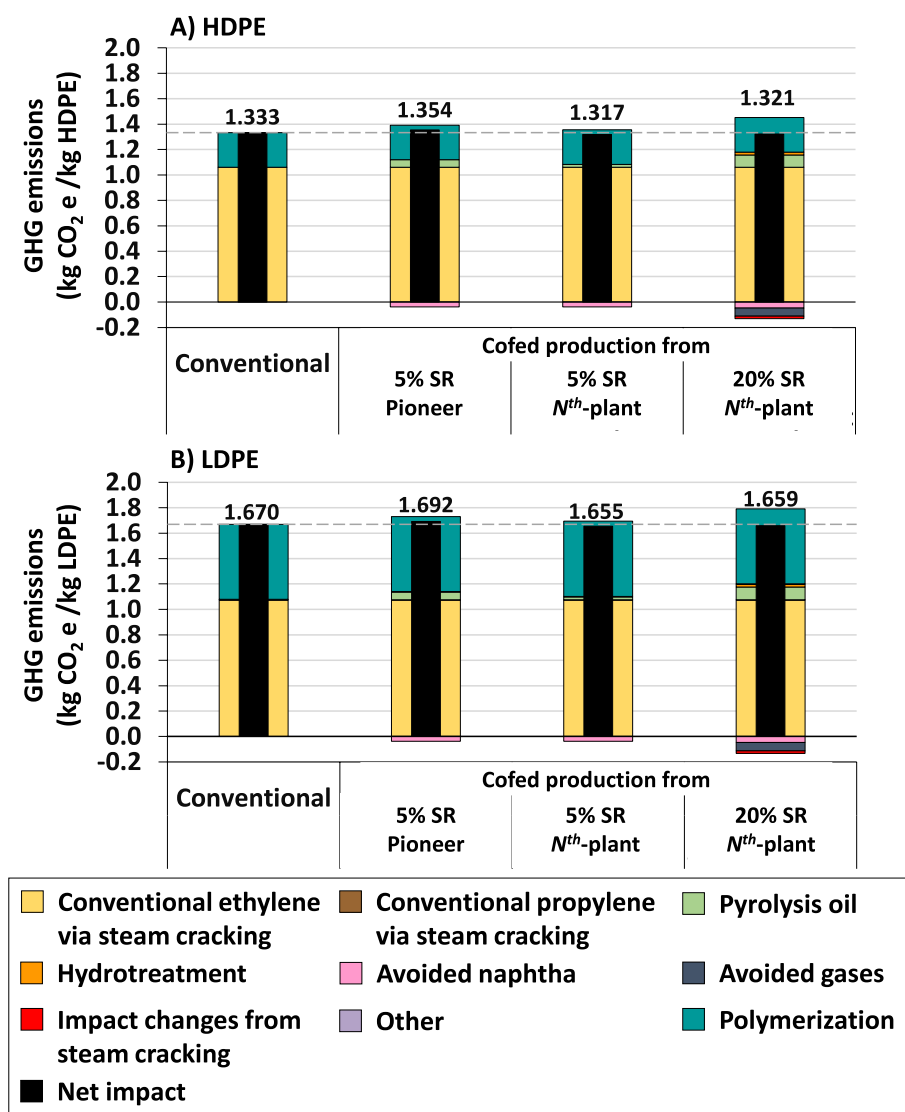


Fig. 3. GHG emissions of plastic produced from co-feeding for A) HDPE and B) LDPE under three scenarios: substituting 5% of cracker feed with pioneer pyrolysis oil, substituting 5% of cracker feed with N^{th} -plant pyrolysis oil, and substituting 20% of cracker feed with N^{th} -plant pyrolysis oil. The conventional case represents production of plastic without recycled feedstocks (0% SR). Here the U.S average feedstock slate was used for the cracking operations (6% naphtha and 94% gases). Purification (via hydrotreatment) is only required in the 20% SR of pyrolysis oil. Other refers to propylene obtained from other refinery processes like fluid catalytic cracking and propane dehydrogenation. Breakdown of the GHG emissions associated with “conventional ethylene via steam cracking” is presented in Fig. S5 of the SI. Tabulated data of this Figure is provided in Table S14 of the SI.

3.2. GHG emissions of PE with 100% recycled feedstock allocation

Fig. 4 shows the estimated GHG emissions for the two plastics with 100% recycled feedstock allocation from the three cases: pioneer 5% SR, N^{th} -plant 5% SR, and N^{th} -plant 20% SR. The net GHG emissions (black bars in Fig. 4) for each case incorporated the avoided emissions associated with the substitution of conventional feedstocks (naphtha and gases) with pyrolysis oil. The net GHG emissions ranged from 1.03 to 1.76 and 1.36–2.10 kg CO₂ e per kg of HDPE and LDPE, respectively. The emissions for LDPE were greater than those of HDPE because of the higher energy intensity required in the high-pressure reactors used in LDPE polymerization compared to the low-pressure process in HDPE (Franklin Associates, 2020b). The results from Fig. 4 also indicated that for the pioneer plant cases, the produced plastic with 100% recycled feedstock allocation increased the GHG emissions in 0.43 kg CO₂ e per kg of HDPE and LDPE compared to the conventional production. In contrast, for the N^{th} -plant 5% SR case, plastic products from an allocation of 100% recycled feedstock demonstrated a reduction of 0.30 and

0.31 kg CO₂e per kg of HDPE and LDPE, respectively. In addition to the differences between the 5% and 20% SR cases mentioned in section 3.1.1, Fig. 4 shows that there are emission changes from steam cracking (red bar) in the 20% SR case compared to the conventional production. As previously discussed, these changes involved a reduction of GHG emissions because substituting gases with pyrolysis oil reduced the fuel consumption of the cracker and increased the quantity of co-products (e. g., hydrogen, methane, etc.) used as internal energy sources.

The emissions during polymerization show minor differences for all the scenarios (for both Figs. 3 and 4) because once the monomer was produced via steam cracking the subsequent stages remain the same for each plastic. Therefore, the major driver of the emissions variation of pyrolysis oil-based plastics vs. conventional plastics comes from the feedstock, cracker operations, and the avoided impacts from displacing naphtha and gases. When the results were compared with the conventional case where no recycled feedstock (i.e., pyrolysis oil) is used, the GHG emissions of plastics produced via pioneer pyrolysis oil are 32% higher for HDPE and 26% higher for LDPE than those of conventional

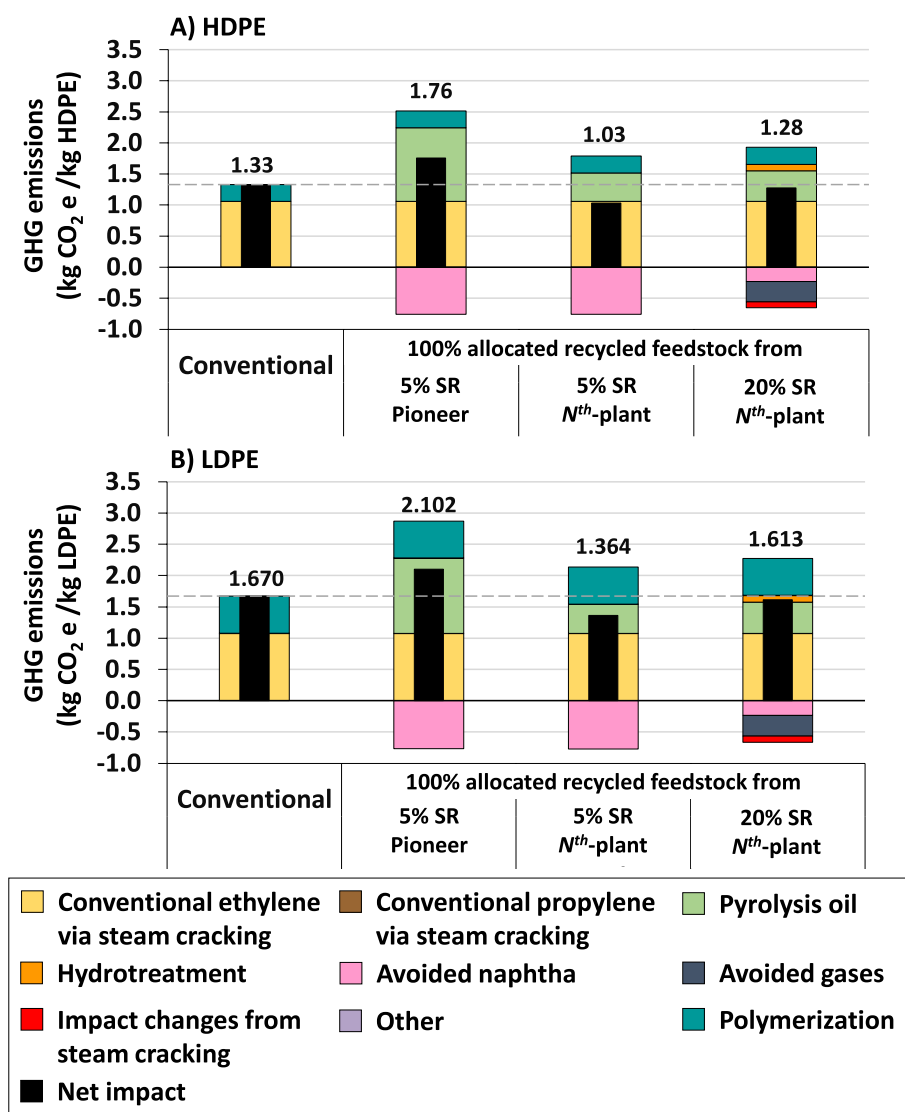


Fig. 4. GHG emissions of plastic with 100% recycled feedstock allocation for A) HDPE and B) LDPE under three scenarios: substituting 5% of cracker feed with pioneer pyrolysis oil, substituting 5% of cracker feed with N^{th} -plant pyrolysis oil, and substituting 20% of cracker feed with N^{th} -plant pyrolysis oil. The conventional case represents conventional production of plastic (0% SR). Here the U.S average feedstock slate was used for the cracking operations (6% naphtha and 94% gases). Purification (via hydrotreatment) is only required in the 20% SR. Other refers to propylene obtained from other refinery processes like fluid catalytic cracking and propane dehydrogenation. Breakdown of the GHG emissions associated with “conventional ethylene via steam cracking” is presented in Fig. S5 of the SI. Tabulated data of this Figure is provided in Table S15 of the SI.

plastics. In these cases, the GHG emissions of producing pyrolysis oil in pioneer plants are higher compared to the credits of substituting the conventional feedstock. Plastics produced via N^{th} -plants pyrolysis oil (at 20% SR) show GHG emission reductions compared to conventional plastic production, ranging from 4% for HDPE and 3% for LDPE. The GHG emissions were even lower (23% for HDPE and 18% for LDPE) compared to those of conventional plastics when the SR lowered to 5%, mainly due to the absence of hydrotreatment of pyrolysis oil and the sole substitution of naphtha. In the recycler's perspective the contribution of GHG emissions from hydrotreatment was estimated in 0.11 kg CO₂e/kg of plastic. Therefore, displacing conventional feedstocks with lower CI feedstocks under improved plant operation conditions shows GHG reduction benefits of pyrolysis oil-based plastics over conventional plastics.

3.3. Fossil energy, water consumption, and solid waste of PE with 100% recycled feedstock allocation

Fossil energy consumption results are shown in Fig. 5A and B. The results followed a similar trend as the GHG emissions. The major driver of the reduction of fossil energy consumption of plastics with 100% recycled feedstock allocation approach is the avoided fossil energy use from the substitution of conventional feedstocks. The scenarios with 5% SR show fossil energy reductions of between 64% (pioneer) and 70% (N^{th} -plant) for HDPE and 60% (pioneer) and 65% (N^{th} -plant) for LDPE compared to the conventional plastic production. The fossil energy consumption is further reduced to 71% and 66% for HDPE and LDPE, respectively, when the SR is increased to 20%. Pyrolysis oil, especially from N^{th} -plants, has lower fossil energy consumption compared to gases and naphtha (see Table 1) because the energy requirements (for collection, sorting, and conversion) and embodied fossil energy in PUP

employed per unit of pyrolysis oil are lower compared to the energy use of refinery operations and embodied fossil energy per unit of naphtha and gases, which is consistent with a previous study (Benavides et al., 2022). Therefore, there is a clear benefit in terms of fossil energy reduction when pyrolysis oil substitutes conventional feedstocks to produce HDPE and LDPE plastics.

Fig. 5C and D show the comparison of water consumption of pyrolysis-based HDPE and LDPE. For pioneer plants, water consumption is slightly reduced by 2% and 1% for HDPE and LDPE, respectively, compared to conventional plastics. Both N^{th} -plant cases show reduction in water consumption compared to the conventional plastics. At 5% SR, the reductions are 55% and 48% for HDPE and LDPE, respectively, while for 20% SR the water consumption decreases by 7% and 6% for HDPE and LDPE, respectively. The higher reduction in the 5% SR case is because naphtha is the only conventional feedstock substituted with pyrolysis oil and naphtha has approximately three times higher water consumption compared to that of N^{th} -plants' pyrolysis oil. In the 20% SR case, pyrolysis oil substitutes a portion of the gases along with naphtha (both with similar water consumption per kg as presented in Table 1); in addition, the steam cracking process involves higher water consumption. Substituting gases with pyrolysis oil reduces the yield of ethylene and propylene produced. Therefore, more pyrolysis oil is consumed in the cracker to compensate for the yield losses. A higher use of pyrolysis oil increases the steam requirements and water consumption in the cracker correspondingly. The results for fossil energy and water consumption of co-fed plastic production are discussed in section S8.2 of the SI. Regarding the impacts of the hydrotreatment in fossil energy and water consumption, it is observed that they are small as shown in Fig. 5.

The results for solid waste for plastics with 100% recycled feedstock allocation are presented in Fig. 6. These results subtracted the amount of PUP diverted to produce the pyrolysis oil required per kg of plastic with

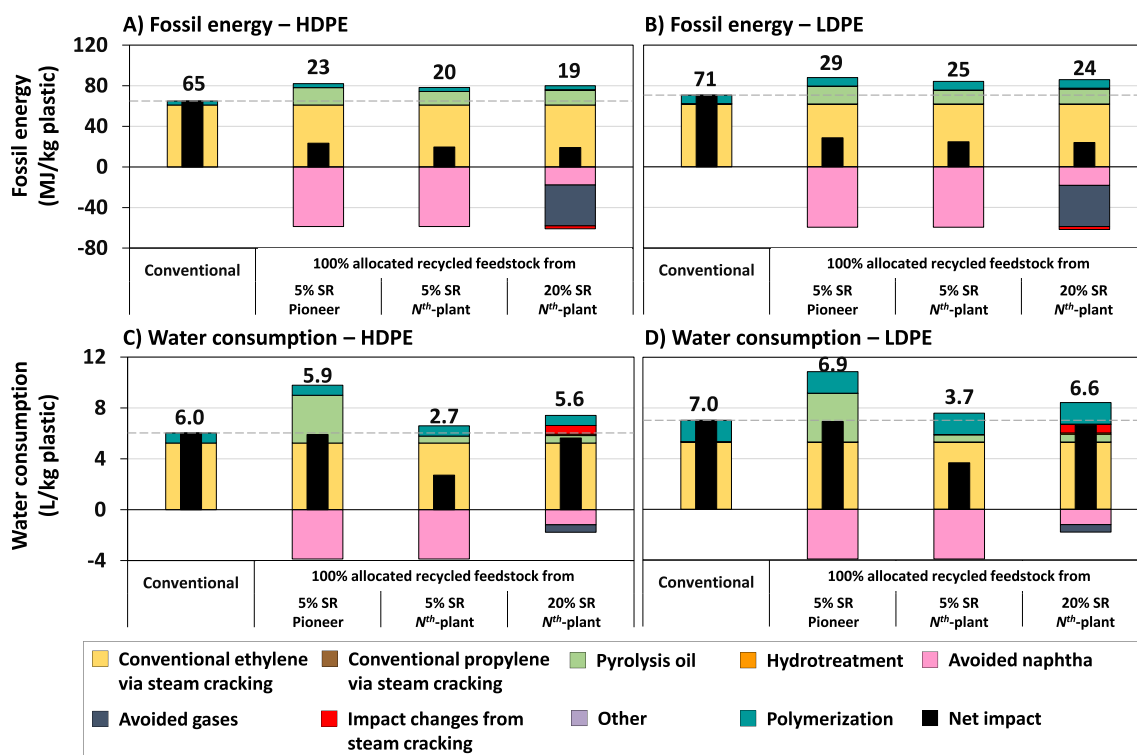


Fig. 5. Fossil energy (A and B) and water consumption (C and D) of plastic with 100% recycled feedstock allocation for HDPE (A and C) and LDPE (B and D). The conventional case represents production of plastic without recycled feedstocks (0% SR). Other refers to propylene obtained from other refinery processes like fluid catalytic cracking and propane dehydrogenation. Breakdown of the fossil energy and water consumption associated with “conventional ethylene via steam cracking” is presented in Fig. S5 of the SI, respectively. Tabulated data of fossil energy and water consumption in this Figure is provided in the SI in Table S16 and Table S17, respectively.

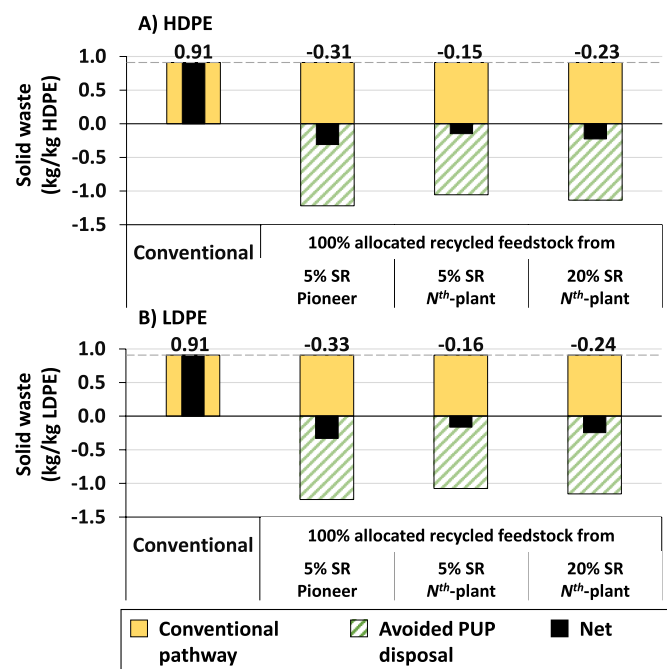


Fig. 6. Solid waste of plastic with 100% recycled feedstock allocation for A) HDPE and B) LDPE based on U.S. EOL management. The conventional case represents production of plastic without recycled feedstocks (0% SR). The avoided PUP waste disposal bar indicates the amount of PUP diverted from landfill to pyrolysis oil production. Tabulated data of this Figure is provided in Table S18 of the SI.

100% recycled feedstock allocation from the solid waste generation of conventional plastic. Fig. 6 confirms that using PUP-derived pyrolysis oil as feedstock reduces solid waste due to the avoided PUP disposal from traditional EOL management. For the N^{th} -plant scenarios the solid waste is reduced by 116–125% for the HDPE cases and 118–127% for the LDPE cases compared to the conventional HDPE and LDPE, respectively. The high reductions observed are due to increased amount of PUP diverted from landfill to produce the pyrolysis oil needed in plastics with 100% recycled feedstock allocation. The solid waste reduction is slightly improved with the use of pyrolysis oil from pioneer plants, which resulted in 134% and 136% lower solid waste for HDPE and LDPE, respectively, compared to conventional plastics. The avoided PUP disposal from traditional EOL per kg of pyrolysis oil is higher in pioneer plants compared to N^{th} -plants, as more PCP is needed to compensate for the material losses of the sorting process. Therefore, the avoided PUP disposal is higher in pioneer plants because they rely more on PCP than N^{th} -plants (83% vs 22% of total PUP, respectively) (Benavides et al., 2022). For the LDPE case, the solid waste reduction is slightly higher than those of HDPE due to the use of propylene as a comonomer in the production of LDPE.

3.4. LCA with expanded system boundary

Fig. 7 compares the GHG emissions of plastics with 100% recycled feedstock allocation when emission credits from counterfactual scenarios in the United States and European Union are included. With the U.S. counterfactual scenario, the GHG emissions of pyrolysis-based HDPE at a 5% SR are 2% higher for pioneer and 50% lower for N^{th} -plants than those of conventional HDPE (black dash line in Fig. 7). Similarly, the pyrolysis-based LDPE presents that pioneer plants have 2% higher and N^{th} -plants show 40% lower GHG emissions compared to conventional LDPE production. The GHG emissions are also reduced when the SR is increased to 20%, which represents a reduction of 32% and 26% for HDPE and LDPE, respectively, compared to conventional

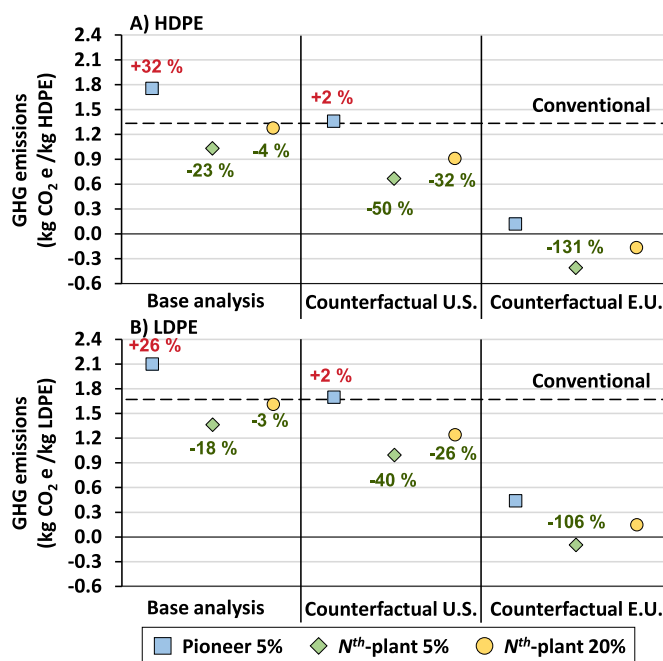


Fig. 7. Comparison of GHG emissions of PUP-based plastic with 100% recycled feedstock allocation for A) HDPE and B) LDPE under three cases: base case analysis, system expansion with counterfactual scenario of U.S. EOL treatment of PUP, and system expansion with counterfactual scenario of E.U. EOL treatment of PUP. The relative change results are compared to the conventional plastic production scenario with a feedstock slate of 6% naphtha and 94% gases (Lippe, 2020).

HDPE and LDPE. As observed in Fig. 7, the highest reduction in GHG emissions is observed in the case of co-feeding pyrolysis oil from N^{th} -plants at 5% SR because this case shows the lowest GHG emissions in the base case analysis among all the scenarios. The values in the 5% SR with pyrolysis oil from N^{th} -plants drop from 1.33 (conventional HDPE production) to 0.67 kg CO₂ e per kg of PUP-based HDPE and from 1.67 (conventional LDPE) to 0.99 kg CO₂ e per kg PUP-based LDPE.

Due to the higher amount of avoided PUP incineration in the European scenario, more GHG emissions credits are accounted for, up to 131% and 106% for HDPE and LDPE, respectively, when pyrolysis-based plastics is compared to conventional plastics (black dash line in Fig. 7). Although more reductions are observed in the E.U. counterfactual scenario compared to the U.S. counterfactual scenario, it is not expected that the U.S. PUP EOL management would move towards the incineration rate of PUP in the E.U. (EPA, 2020).

3.5. Sensitivity analyses

The following subsection describes the effects of varying the shares of the conventional feedstock, the co-produced hydrogen in steam cracking, and the electricity grid source.

3.5.1. Variations of feedstock slates to crackers

The GHG emissions of conventional plastic production for cases with feeding “naphtha only” and “gases only” to a steam cracker were estimated and compared with the pyrolysis oil co-feeding into the cracker under these tested feedstock slates. The results for the base analysis of the “naphtha only” scenarios (Fig. 8A and Fig. S10A for HDPE and LDPE, respectively) show an overall increase of the GHG emissions with pyrolysis oil co-feeding compared to those from the conventional feedstock slate in Fig. 7. It is because of the higher GHG emissions associated with having 100% naphtha as the feedstock source compared to a mix of feedstocks, in which gases (at 94 % wt.) has lower GHG emissions as described in Table 1. The comparison of the plastic with 100% recycled

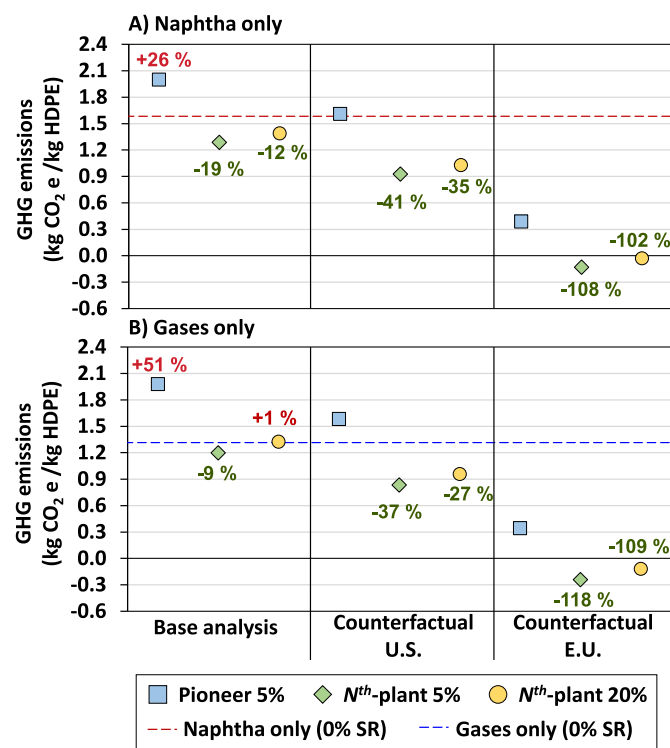


Fig. 8. Comparison of GHG emissions between plastic with 100% recycled feedstock allocation and that with a feedstock slate comprised of (A) naphtha only and (B) gases only for HDPE.

feedstock allocation with baseline production (red dash line) shows a higher decrease of GHG emissions by substituting PUP-based pyrolysis oil when naphtha is the only cracker feedstock compared to the conventional feedstock slate (Fig. 7) for the 20% SR of Nth-plant pyrolysis oil case. Including the U.S. EOL counterfactual emissions further reduces the GHG emissions of the 20% SR case to 35% (HDPE) and 29% (see Fig. S10 for LDPE) compared to the baseline (red dashed line). This is due to the higher avoided emissions associated with feedstock substitution because naphtha is the only feedstock that is replaced with pyrolysis oil at the 20% SR. The GHG emissions of the plastic with 100% recycled feedstock allocation can be reduced to 108% (for HDPE) in the 5% SR Nth-plant case compared to the baseline when the E.U. counterfactual emissions are considered because of the higher share of incineration of PUP under the E.U. counterfactual scenario. Similar trend was followed by LDPE; however, the emission reductions are lower than those of HDPE, as LDPE is more energy intensive to produce.

In the “gases only” scenario, the GHG emission reductions of plastics with 100% recycled feedstock allocation in comparison to the baseline (blue dashed line in Fig. 8B and Fig. S10B) are lower than the reductions observed under “naphtha only” scenarios in the base analysis and the U.S. counterfactual scenario. In the “gases only” base analysis the 5% SR pioneer and the 20% SR Nth-plants cases do not show a benefit in comparison with the conventional plastic production. Moreover, with the U.S. counterfactual EOL scenario, there are less emission reduction benefits compared to the other two scenarios. This is the result of substituting the baseline with lower GHG feedstocks (i.e., gases in Table 1) and improved conversion yields (Young et al., 2022) with pyrolysis oil, which reduces the yield of ethylene per kg of feedstock and the pyrolysis oil has GHGs similar to gases when produced by the Nth-plant case. The comparison of the results between Figs. 7 and 8 indicates that substituting a cracker feed slate that contains higher shares of naphtha leads to more GHG emission reductions when pyrolysis oil is used at SRs closer to the current technical capability (20% SR).

The results presented in sections 3.2 and 3.5.1 indicate the effect of

the composition of the feedstocks of steam crackers in the estimation of the GHG emission reductions of plastics with 100% recycled feedstock allocation. As noted, feed slates with more naphtha share generated more GHG emission reductions by PUP-based plastics compared to the average feedstock slate. However, for economic reasons, the recent trend, at least in the United States, has shown an increase of the share of gases for the operation of the steam crackers (Kootungal, 2015; Lippe, 2018, 2020, 2018). This is a challenging situation for cracker operators aiming to adopt the use of PUP-based pyrolysis oil in their cracker operations. However, a reduction in the price of naphtha could expand its use as a cracker feed and provide more opportunities for the co-feeding of PUP-derived pyrolysis oil in the production of new plastics.

3.5.2. Treatment of co-produced hydrogen in steam cracking

Fig. 9 shows the effects of assuming 100% of refineries either combust or export co-produced hydrogen from the cracker. For plastics with 100% recycled feedstock allocation (calculated from 20% SR of pyrolysis oil from Nth-plants), using hydrogen as an internal energy source reduces the GHG emissions by 9% and 7% for HDPE and LDPE, respectively, compared to the base case (substitution of the U.S average feedstock slate with 20% SR of pyrolysis oil) obtained from Fig. 4. On the other hand, if all hydrogen was exported, the GHG emissions increase by 20% and 16%, for HDPE and LDPE, respectively, compared to the base case because the steam cracking relies more on external energy sources like natural gas. It is important to mention that the percent change due to shifting the treatment of co-produced hydrogen vary among the different cases (pioneer 5% SR, Nth-plant 5% SR, and Nth-plant 20%). For instance, in the 5% pioneer and Nth-plant cases the reductions from assuming 100% co-produced hydrogen combustion are estimated to be 7% and 13%, respectively, for HDPE and 6% and 10%, respectively, for LDPE.

3.5.3. Electric grid generation mix

Fig. 9 also shows the variation of GHG emissions compared to the use

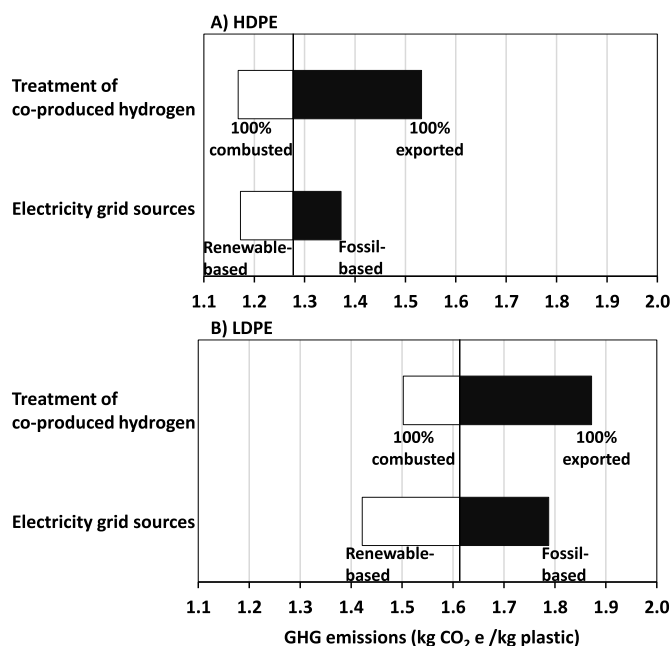


Fig. 9. GHG emission variation for pyrolysis-based A) HDPE and B) LDPE with 100% recycled feedstock allocation under different electricity generation mixes and methods to treat co-produced hydrogen from steam cracking. The results are based on the 20% SR pyrolysis oil from Nth-plants case. The base case uses electricity with the U.S. average electricity generation mix according to GREET (ANL, 2020) and 70% and 30% combusted and exported hydrogen shares, respectively.

of the U.S. average generation mix. Supplying an electricity grid mix with more renewable sources (i.e., wind, solar, etc.) reduces the GHG emissions of pyrolysis-based plastics by 8% (HDPE) and 12% (LDPE), compared to the base case, while the use of electricity with more fossil sources (i.e., coal, oil, etc.) in the grid mix led to 7% (HDPE) and 11% (LDPE) higher GHG emissions compared to the base case. Higher emission reductions in the LDPE case are because more electricity is used in the manufacturing compared to HDPE, especially in the polymerization stage (see section S3.2 in the SI). The reductions in GHG emissions by using high renewable grid in HDPE production are 17% and 6% for the 5% SR pioneer and the 5% SR N^{th} -plant cases, respectively. Therefore, the feedstock substitution due to the SR and capacity of the pyrolysis facility influence the impact of the changes in electricity generation mix.

3.6. Impacts, limitations, and potential challenges

The results discussed in this study are based on the best available life-cycle inventory data of the involved process stages. Although the data of pyrolysis oil production comes from industry operations, it is acknowledged that the energy requirements and product yields of the steam cracking process were based on standard operations available in the literature (Young et al., 2022) and discussions with the industry partners because this information is considered sensitive and proprietary. Therefore, the steam cracking inventory data does not consider the effects of feedstock residence times and cracking operation conditions (i.e., temperature, pressure, and elemental composition). Similarly, the information of hydrotreatment is limited and confidential which required the reliance of assumptions and inventory development from different literature sources (see section S3 in the SI). For similar reasons, the inventory data of hydrotreatment only focused on the removal of chlorine, while conditions for the removals of other contaminants were not considered. Although the assumptions utilized were considered reasonable when reviewed by industry experts, it is suggested to develop life-cycle inventory data with as much operational data as possible and observe the variations on the results for the two proposed perspectives.

As discussed in the results, advanced recycling has the benefit of diverting PUP from traditional EOL management, reducing solid waste generation. However, its widespread implementation will require a constant and secured supply of PUP and development from current infrastructure and logistics to meet the current U.S. ethylene demand. According to Lippe (2020), the annual feedstock demand of ethylene steam crackers in the United States is of 80 MMT, which for the 5% and 20% SR cases would require the supply of 4.4 and 17.8 MMT of pyrolysis oil, respectively, and the corresponding pyrolysis conversion of 6.6 and 22.9 MMT of PUP. Because of the current limited scale of plastic recycling infrastructure, handling such an amount of PUP will require larger infrastructure for collection, transportation, sorting, and pyrolysis conversion, improvements in sortation yields, and agreements between different stakeholders in the plastic recycling and manufacturing supply chain.

4. Conclusions

This study presents an LCA on plastics produced from PUP-based pyrolysis oil co-fed with conventional feedstock of naphtha and gases (ethane, propane, and butane). The results showed that pyrolysis-based plastic can benefit from economies of scale and maturity of pyrolysis plants resulting in reductions of GHG emissions, fossil energy, water consumption, and solid waste.

Two perspectives were studied in this LCA, the steam crackers' perspective which analyzed the results of co-feeding pyrolysis oil with conventional feedstocks (gases and naphtha) in the overall process volume, and the recyclers' perspective that also analyzed co-feeding but allocated the impacts of feedstock substitution entirely to the recycled feedstock. The recyclers' perspective showed for a unit of PUP

processed, there was a reduction in GHG emissions of up to 23% and 18% for HDPE and LDPE respectively compared to conventional plastics. The steam crackers' perspective showed the co-feeding of pyrolysis oil of 5 and 20% with naphtha and gases and saw a more modest reduction in GHG emissions compared to the recyclers' perspective. Additionally, the purification of pyrolysis oil required for the 20% SR resulted in increases in GHG emissions that reduce the net benefit for PUP-based plastics. The 5% SR scenario is more reflective of the current landscape of available PUP feedstocks and advanced recycling technologies, but the 20% SR rate is included to show the complete range of results.

Expansion of the LCA system boundary to include avoided emissions from current PUP incineration in EOL management resulted in significant environmental benefits of PUP-based plastic. Accounting for the so-called counterfactual emission reduction credits resulted in 40 and 50% lower GHG emissions of PUP-based plastic (for LDPE and HDPE, respectively) in the United States, compared to conventional plastic, while the reductions are much higher in the E.U. because in this region more PUP is incinerated.

5. Future work

To conduct this analysis, several assumptions were made with regards of the purification technology, steam cracker operation, co-product treatment methods in pyrolysis facilities, and allocation methods. For future work, it is suggested expanding some of these topics to have a better understanding of the effect of newer purification technologies and the integration with the steam crackers to adapt to a higher SR compared to what was discussed here. Because of the current decarbonization efforts in the chemical industry to electrify pyrolysis it is also suggested to explore its impact of new pyrolysis technology. The analysis can also be expanded to evaluate circularity metrics (e.g., reduction of virgin material use) associated with the plastic-to-plastic process presented.

CRedit authorship contribution statement

Ulises R. Gracida-Alvarez: Formal analysis, Methodology, Data curation, Validation, Visualization, Writing – review & editing, Writing – original draft. **Pahola Thathiana Benavides:** Formal analysis, Conceptualization, Methodology, Data curation, Validation, Writing – review & editing, Writing – original draft, Supervision, Project administration. **Uisung Lee:** Methodology, Validation, Writing – review & editing. **Michael Wang:** Conceptualization, Funding acquisition, Methodology, Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

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Acronyms

ANL	Argonne National Laboratory
a_1	Amount of pyrolysis oil substituting naphtha
AF	Allocation factor
b_1	Amount of pyrolysis oil substituting gases
CE	Circular economy
CI	Carbon intensity
CV	Chemical value
E.U.	European Union
EOL	End-of-life
GHG	Greenhouse gas
GREET	Greenhouse Gases, Regulated Emissions and Energy Use in Technologies
HDPE	High-density polyethylene
HVC	High-value chemical
I_{PE}^{Cofed}	Impact of HDPE or LDPE from cofeeding production
I_{PE}^{Conv}	Impact of HDPE or LDPE from conventional production
I_{PyOil}	Impact of pyrolysis oil
$I_{naphtha}$	Environmental impact of naphtha
I_{gases}	Environmental impact of gases
$I_{SCPyOil}$	Environmental impacts of the steam cracking stage during the co-fed production of PE
I_{SCconv}	Environmental impacts of the steam cracking stage during conventional production of PE
LCA	Life cycle analysis
LDPE	Low-density polyethylene
LHV	Low heating value
NGLs	Natural gas liquids
MFRs	Material recovery facilities
MMT	Million tonnes
MRO	Midwest Reliability Organization
PE	Polyethylene
PET	Polyethylene terephthalate
PCP	Post-consumer plastic
PIP	Post-industrial plastic
PO	Polyolefin
PS	Polystyrene
PP	Polypropylene
PVC	Polyvinyl chloride
PUP	Post-use plastics
P2P	Plastic-to-plastic
US	United States
SI	Supporting information
SR	Substitution rate

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jclepro.2023.138867>.

References

- 2021 Resin situation and trends, 2022. <https://www.americanchemistry.com/content/download/10907/file/ACC-2021-Resin-Situation-and-Trends.pdf> (Accessed 27 July 2022).
- ANL, 2020. Greenhouse gases, regulated emissions, and energy use in technologies model (GREET)® (2020 excel). <https://doi.org/10.11578/GREET-Excel-2021/dc.20210902.1>.
- Benavides, P.T., Gracida-Alvarez, U.R., Lee, U., Wang, M., 2022. Life-cycle Analysis of Conversion of Post-Use Plastic via Pyrolysis with the GREET Model (No. ANL-22/37). Argonne National Laboratory (ANL), Lemont, IL (United States).
- Benavides, P.T., Sun, P., Han, J., Dunn, J.B., Wang, M., 2017. Life-cycle analysis of fuels from post-use non-recycled plastics. *Fuel* 203, 11–22. <https://doi.org/10.1016/j.fuel.2017.04.070>.
- Broeren, M., Bergsma, G., 2020. Exploration chemical recycling – extended summary. What is the potential contribution of chemical recycling to Dutch climate policy? https://cedelft.eu/wp-content/uploads/sites/2/2021/03/CE_Delft_2P22_Explorati_on_chemical_recycling_Extended_summary.pdf (Accessed 10 August 2022).
- Burnham, A., 2022. Updated natural gas pathways in GREET 2022. https://greet.es.anl.gov/publication-update_ng_2022. (Accessed 15 October 2022).
- Cho, R., 2020. Recycling in the U.S. Is broken. How do we fix it? <https://news.climate.columbia.edu/2020/03/13/fix-recycling-america/> (Accessed 28 July 2022).
- Upstream innovation. A guide to packaging solutions, 2020. <https://emf.thirdlight.com/link/aiqpsmx3517n-bl186j/@/download/1> (Accessed 30 July 2022).
- Ellen MacArthur Foundation, 2019. Enabling a circular economy for chemicals with the mass balance approach. A white paper from co-project mass balance. https://www.basf.com/global/documents/en/sustainability/we-source-responsibly/EllenMacArthur_White%20Paper_2019.pdf. (Accessed 15 August 2022).
- Environmental assessment of full brightmark products, 2021. <https://77f90741.flowpaper.com/LCALayoutFlowpaper/docs/LCA-Layout-Flowpaper.pdf?refresh=1634734701530> (Accessed 10 August 2022).
- EPA, 2020. U.S. National recycling goal. <https://www.epa.gov/recyclingstrategy/us-national-recycling-goal>. (Accessed 16 August 2022).
- European Parliament, 2021. Plastic waste and recycling in the EU: facts and figures. <https://www.europarl.europa.eu/news/en/headlines/society/20181212STO21610/plastic-waste-and-recycling-in-the-eu-facts-and-figures>. (Accessed 2 August 2022).

- Franklin Associates, 2021. Cradle-to-gate life cycle analysis of high-density polyethylene (HDPE) resin. <https://www.americanchemistry.com/content/download/8059/file/Cradle-to-Gate-Life-Cycle-Analysis-of-High-Density-Polyethylene-HDPE-Resin.pdf> (Accessed 2 August 2022).
- Franklin Associates, 2020a. Cradle-to-gate life cycle analysis of olefins. <https://www.americanchemistry.com/content/download/8062/file/Cradle-to-Gate-Life-Cycle-Analysis-of-Olefins.pdf>. (Accessed 1 August 2022).
- Franklin Associates, 2020b. Cradle-to-gate life cycle analysis of low-density polyethylene (LDPE) resin. <https://www.americanchemistry.com/content/download/8060/file/Cradle-to-Gate-Life-Cycle-Analysis-of-Low-Density-Polyethylene-LDPE-Resin.pdf>. (Accessed 2 August 2022).
- Gracida-Alvarez, U.R., Winjobi, O., Sacramento-Rivero, J.C., Shonnard, D.R., 2019. System analyses of high-value chemicals and fuels from a waste high-density polyethylene refinery. Part 2: carbon footprint analysis and regional electricity effects. *ACS Sustainable Chem. Eng.* 7, 18267–18278. <https://doi.org/10.1021/acssuschemeng.9b04764>.
- Gracida-Alvarez, U.R., Xu, H., Benavides, P.T., Wang, M., Hawkins, T.R., 2023. Circular economy sustainability analysis framework for plastics: application for poly (ethylene terephthalate) (PET). *ACS Sustainable Chem. Eng.* 11, 514–524. <https://doi.org/10.1021/acssuschemeng.2c04626>.
- Honeywell, U.O.P., 2021. Honeywell UOP upcycle plastics recycling. <https://uop.honeywell.com/content/dam/uop/en-us/documents/product-services/honeywell-uop-upcycle-plastics-recycling.pdf> (Accessed 1 August 2022).
- Huang, J., Veksha, A., Chan, W.P., Giannis, A., Lisak, G., 2022. Chemical recycling of plastic waste for sustainable material management: a prospective review on catalysts and processes. *Renew. Sustain. Energy Rev.* 154, 111866 <https://doi.org/10.1016/j.rser.2021.111866>.
- Jeswani, H., Krüger, C., Russ, M., Horlacher, M., Antony, F., Hann, S., Azapagic, A., 2021. Life cycle environmental impacts of chemical recycling via pyrolysis of mixed plastic waste in comparison with mechanical recycling and energy recovery. *Sci. Total Environ.* 769, 144483 <https://doi.org/10.1016/j.scitotenv.2020.144483>.
- Jeswani, H.K., Krüger, C., Kicherer, A., Antony, F., Azapagic, A., 2019. A methodology for integrating the biomass balance approach into life cycle assessment with an application in the chemicals sector. *Sci. Total Environ.* 687, 380–391. <https://doi.org/10.1016/j.scitotenv.2019.06.088>.
- Koottungal, L., 2015. International survey of ethylene from steam crackers - 2015. *Oil Gas J.* 85–91.
- Kusenberger, M., Eschenbacher, A., Djokic, M.R., Zayoud, A., Ragaert, K., De Meester, S., Van Geem, K.M., 2022. Opportunities and challenges for the application of post-consumer plastic waste pyrolysis oils as steam cracker feedstocks: to decontaminate or not to decontaminate? *Waste Manage. (Tucson, Ariz.)* 138, 83–115. <https://doi.org/10.1016/j.wasman.2021.11.009>.
- Lebreton, L., Andrady, A., 2019. Future scenarios of global plastic waste generation and disposal. *Palgrave Commun* 5, 1–11. <https://doi.org/10.1057/s41599-018-0212-7>.
- Lippe, D., 2020. US ethylene producers evaluate post-pandemic capacity additions. *Oil Gas J.* 118, 56–64.
- Lippe, D., 2018. US olefins industry enters new era. *Oil Gas J.* 116.
- Luu, P., Daly, K., Croke, B., Sherwin, G., Miñana, B., 2021. Transitioning to a circular system for plastics. Assessing molecular recycling technologies in the United States and Canada. https://www.closedlooppartners.com/wp-content/uploads/2021/11/AR-report-V23_final7.pdf (Accessed 30 July 2022).
- Milbrandt, A., Coney, K., Badgett, A., Beckham, G.T., 2022. Quantification and evaluation of plastic waste in the United States. *Resour. Conserv. Recycl.* 183, 106363 <https://doi.org/10.1016/j.resconrec.2022.106363>.
- Improving markets for recycled plastics. Trends, prospects, and policy responses, 2018. <https://doi.org/10.1787/9789264301016-en>.
- Plastics Europe, 2021. Plastics - the Facts 2021. An analysis of European plastics production, demand, and waste data. <https://plasticseurope.org/wp-content/uploads/2021/12/Plastics-the-Facts-2021-web-final.pdf> (Accessed 27 July 2022).
- Plastics Europe, 2012. Eco profiles and environmental product declarations of the European plastics manufacturers. Ethylene, propylene, butadiene, pyrolysis gasoline, ethylene oxide (EO), ethylene glycols (MEG, DEG, TEG). https://legacy.plasticseurope.org/application/files/8315/1783/7824/20130114101708-plasticseurope_co-profile_ethylene_others_2012-11.zip (Accessed 10 August 2022).
- Quantis, 2020. Life cycle assessment of Plastic Energy technology for the chemical recycling of mixed plastic waste. <https://plasticenergy.com/wp-content/uploads/2020/10/Plastic-Energy-LCA-Executive-Summary.pdf> (Accessed 1 August 2022).
- Rhodes, C.J., 2018. Plastic pollution and potential solutions. *Sci. Prog.* 101, 207–260. <https://doi.org/10.3184/003685018X15294876706211>.
- Russ, M., Gonzalez, M., Horlacher, M., 2020. Evaluation of pyrolysis with LCA – 3 case studies. https://www.basf.com/global/documents/en/sustainability/we-drive-sustainable-solutions/circular-economy/selected-down_load/BASF_ChemCycling_LCA_Study.pdf (Accessed 1 August 2022).
- Certified circular polymers via advanced recycling of mixed plastic waste, 2021. https://www.sabic.com/en/Images/certified-circular-polymers-life-cycle-assessment-lca-study-summary_tcm1010-29345.pdf (Accessed 1 August 2022).
- Sekar, M., Ponnusamy, V.K., Pugazhendhi, A., Nizetic, S., Praveenkumar, T.R., 2022. Production and utilization of pyrolysis oil from solidplastic wastes: a review on pyrolysis process and influence of reactors design. *J. Environ. Manag.* 302, 114046 <https://doi.org/10.1016/j.jenvman.2021.114046>.
- Somoza-Tornos, A., Gonzalez-Garay, A., Pozo, C., Graells, M., Espuña, A., Guillén-Gosálbez, G., 2020. Realizing the potential high benefits of circular economy in the chemical industry: ethylene monomer recovery via polyethylene pyrolysis. *ACS Sustainable Chem. Eng.* 8, 3561–3572. <https://doi.org/10.1021/acssuschemeng.9b04835>.
- Tabrizi, S., Rollinson, A.N., Hoffmann, M., Favoino, E., 2020. Understanding the Environmental Impacts of Chemical Recycling. Ten concerns with existing life cycle assessments. https://zerowasteurope.eu/wp-content/uploads/2020/12/zwe_jointpaper_UnderstandingEnvironmentalImpactsofCR_en.pdf (Accessed 5 August 2022).
- National overview: facts and figures on materials, wastes and recycling, 2022. <https://www.epa.gov/facts-and-figures-about-materials-waste-and-recycling/national-overview-facts-and-figures-materials> (Accessed 27 July 2022).
- U.S. EPA, 2020. Advancing Sustainable Materials Management: 2018 Tables and Figures. Assessing Trends in Materials Generation and Management in the United States. https://www.epa.gov/sites/default/files/2021-01/documents/2018_tables_and_figures_dec_2020_fnl_508.pdf. (Accessed 20 July 2021).
- Vedantam, A., Suresh, N.C., Ajmal, K., Shelly, M., 2022. Impact of China's national sword policy on the U.S. Landfill and plastics recycling industry. *Sustainability* 14, 2456. <https://doi.org/10.3390/su14042456>.
- Viveros, A., Imren, C., Loske, F., 2022. Life cycle assessment of chemical recycling for food grade film. <https://www.theconsumergoodsforum.com/wp-content/uploads/2022/04/Life-Cycle-Assessment-of-Chemical-Recycling-for-Food-Grade-Film.pdf> (Accessed 1 August 2022).
- Vollmer, L., Jenks, M.J.F., Roelands, M.C.P., White, R.J., van Harmelen, T., de Wild, P., van der Laan, G.P., Meirer, F., Keurentjes, J.T.F., Weckhuysen, B.M., 2020. Beyond mechanical recycling: giving new life to plastic waste. *Angew. Chem. Int. Ed.* 59, 15402–15423. <https://doi.org/10.1002/anie.201915651>.
- Young, B., Hawkins, T.R., Chiquelin, C., Sun, P., Gracida-Alvarez, U.R., Elgowainy, A., 2022. Environmental life cycle assessment of olefins and by-product hydrogen from steam cracking of natural gas liquids, naphtha, and gas oil. *J. Clean. Prod.* 359, 131884 <https://doi.org/10.1016/j.jclepro.2022.131884>.
- Zhao, X., You, F., 2021. Consequential life cycle assessment and optimization of high-density polyethylene plastic waste chemical recycling. *ACS Sustainable Chem. Eng.* 9, 12167–12184. <https://doi.org/10.1021/acssuschemeng.1c03587>.