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Research Article

Techno-Economic and Life Cycle Analyses of Thermochemical Upcycling Technologies of Low-Density Polyethylene Waste

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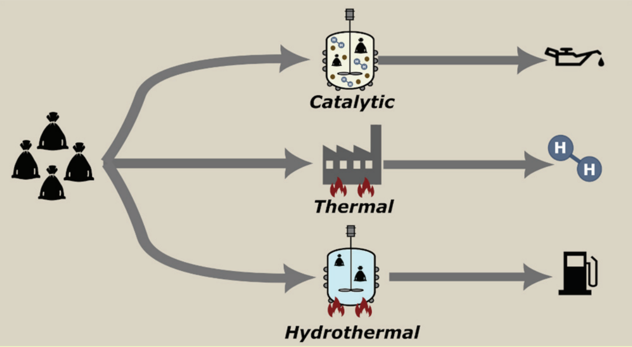
ABSTRACT: In this study we compare techno-economics and life cycle assessment of thermochemical depolymerization technologies, including pyrolysis, gasification, hydrocracking, hydrothermal liquefaction, and hydrogenolysis, to generate various products from low-density polyethylene (LDPE) waste. We elucidate the effects of production scale, collection cost, and concentration of LDPE in plastic waste. Pyrolysis of LDPE to olefins followed by their conversion to lubricant oils is the most profitable technology. Hydrogenolysis, producing a small fraction of lubricant oils, becomes profitable at plant sizes above 25 kt/y and produces the lowest CO_2 emissions. Hydrocracking is the second most environmentally friendly technology but becomes economically competitive at sufficiently large scales, and the supply chain for collecting plastics is optimized. Gasification of LDPE to H_2 produces high emissions, and the price of H_2 of ∼3 $/kg is higher than current markets and recently announced goals. Similarly, hydrothermal liquefaction also gives high emissions, making carbon capture systems imperative for both technologies. Our results demonstrate that lowering the cost of sorting LDPE from plastic waste, collecting waste near big cities, building sufficiently large plants, and achieving high selectivity to value-added products are critical to successful plastic waste management.



KEYWORDS: *plastics waste, upcycling, recycling, pyrolysis, gasification, hydrogenolysis, hydrocracking*

■ INTRODUCTION

Global plastic production is estimated at 350 million tons per year. It is projected to increase to over 1200 million tons by 2050.[1,2] Among them, low-density polyethylene (LDPE) is the highest produced polymer at around 24%.[3] Most plastics are discarded after their first use.[4,5] Only 9% of the United States (US) plastics are recycled, and 16% are incinerated.[6] The remaining 75% is disposed into landfills representing an average estimated annual loss of $7.2 billion of market value, 3.4 EJ as embodied energy[7] (equivalent to 12% of the energy consumption by the industrial sector and 3% of the total energy consumption in the US[8]), and 1.5 EJ as an energy source. Although the amount of plastics consumed is similar to other basic materials (40 million tons/y[6] versus 90 million tons/y of steel[9] or 67 million tons/y of paper[10]), plastics have a higher specific energy (100 MJ/kg versus 26.5 MJ/kg for steel, 10.5 MJ/kg for glass, and 45 MJ/kg for paper).[11] Given the environmental and health threat, recycling plastic waste is essential to ensure energy savings and decarbonization[12] and meeting the 2050 climate goals.[13]

The most widespread technique of post-consumer plastics handling is mechanical recycling. It has a low processing cost (0.38 $/kg for LDPE[14] versus 1 $/kg of virgin LDPE from crude oil)[15] but degrades the polymer properties that can be recycled up to 3 times.[16] Thermochemical recycling has the potential to produce monomers (recycling) and value-added products (upcycling), and such industrial plants exist.[17,18] There are multiple thermochemical recycling technologies, but evaluation and guidance for selecting the best technology are lacking.

Pyrolysis is the most widely used thermochemical technology since it enables handling multiple plastic wastes,[19−21] resulting in naphtha composed of paraffins, olefins, and aromatics. The product can be transformed into multiple final products (e.g., fuel oils,[22] diesel,[23] power, or ethylene and propylene monomers[24]). Gasification to syngas is another popular technology that is more profitable than pyrolysis for producing power.[25] However, several cleaning steps are required. For example, polyvinyl chloride (PVC)[26] and waste tire[27]-generated pollutants are costly to remove.[16] Technoeconomic analysis (TEA) has been performed for

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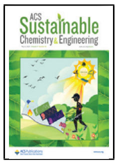

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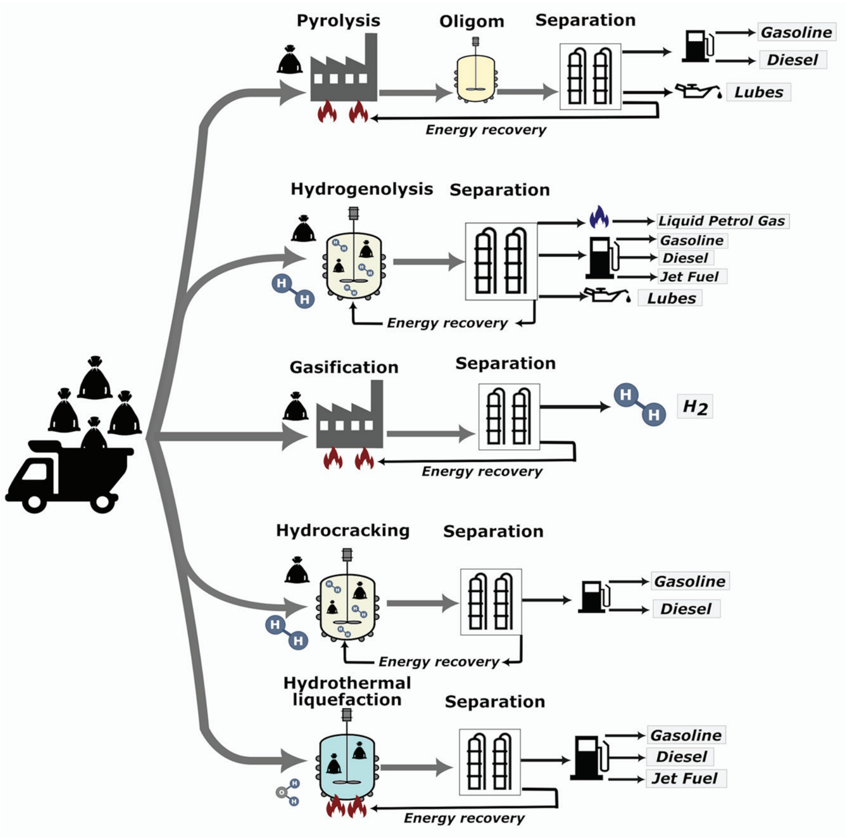

Figure 1. Summary of thermochemical technologies studied and their products.

Table 1. Summary of Depolymerization Technologies and Critical Operating Conditions

depolymerization technology	catalyst considered	temperature (°C)	pressure (bar)	reactor type
pyrolysis		550	1	fluidized bed
gasification		850	1	spouted bed with H_2O
HTL		400	7	batch, vessel
hydrocracking	HY and $Pt/WO_3/ZrO_2$	250	30	batch, Parr
hydrogenolysis	$Ru/WO_3/ZrO_2$	250	30	batch, Parr

sorted[28] and unsorted[29] plastic to produce power, hydrogen,[30] and methanol.[31] Life cycle assessment (LCA) has also been performed for producing power[32] and syngas.[33] Hydrothermal liquefaction (HTL) is also exploited for treating plastic waste using steam,[19,34] but TEA and LCA for HTL have mainly focused on moist organic residues,[35] such as municipal organic residues,[36] biomass,[37,38] and algae[39,40] rather than plastics.

Recently, attention has shifted from high-temperature noncatalytic to low-temperature catalytic processes. For example, hydrotreating for naphtha obtained from pyrolysis to fuel oil has been evaluated.[41−43] Single-step hydrocracking, which employs metal and acid functionalities, has also been demonstrated by applying H_2 at mild temperatures.[44] Hydrogenolysis, which uses mainly metal functionality, converts plastics into fuels or more valuable chemicals, such as lubricant oils, with potentially improved economics.[45]

A common characteristic of catalytic technologies is their low temperature that can lead to significant energy savings and reduced CO_2 emissions. However, they all use significantly high pressure of H_2, whose production is carbon and energy intensive. Their platinum group metal (PGM) catalysts are costly and sensitive to contamination, unlike high-temperature pyrolysis. Given the disparity in operating conditions and products, comparison of thermochemical technologies with the same methodology is crucial to provide a blueprint for technology selection and advances. This paper closes this gap by performing TEA and LCA of pyrolysis, gasification, HTL, hydrogenolysis, and hydrocracking. Figure 1 depicts the technologies, key steps, and final products. Specifically, we evaluate gasification to produce H_2 since it is a more valuable product than power, and H_2 production from low-carbon feedstocks is envisioned as a critical technology of the green energy future and industrial sustainability.[12] We compare pyrolysis and hydrogenolysis for the production of lubricants as an example of a value-added product (\$1.5−2/kg[46] vs ~\$1/kg[15] for polyethylene). A summary of the technologies and processes evaluated are given in the following section. Finally, we compare the economic indicators and environmental impacts, in particular the CO_2 emissions, of all the technologies. Technologies producing highly valuable products, such as lubricants, like pyrolysis and hydrogenolysis, are the most profitable; meanwhile catalytic technologies like hydrocracking and hydrogenolysis are the most sustainable.

■ METHODOLOGY

Overview of Process Modeling and Technologies. Next, we provide an overview of the technologies, key steps, and main products. The operating conditions of the depolymerization technologies are summarized in Table 1. We employed Aspen Plus with Python using PolyNRTL for thermodynamics.[47] Heat integration was performed following the Synheat method in GAMS.[48] Details are given in the supplementary information (SI).

Pyrolysis. Although the product can be controlled by a catalyst,[49−51] temperature[20,21] and reactor type (e.g., fluidized beds,[52] spouted beds[53] or microwave reactors[54,55]), it is typically composed of alkanes, alkenes, and aromatics with a wide range of molecular weights. Among them, olefins and aromatics are the most valuable; aromatics are rarely higher than 10% and only over specific catalysts the selectivity can reach 60%.[56,57] Olefins are produced in a higher percent and be isomerized to α-olefins to produce eventually final products such as surfactants, lubricants, and aldehydes. In this work, lubricants are selected as the target product following the work of Zhao et al.[52] with a yield of ∼60% to olefins in a non-catalytic fluidized bed at 550 °C and nitrogen as the heating carrier gas. The product is sent to a cyclone to remove the solids' traces and then to a cooler and a flash separator, where the liquid phase is recovered. The remaining gas containing the light olefins (C2−C4) is compressed, and the olefins are isomerized to higher olefins (C5−C10) using HZSM-5 zeolite at 70 bar and 200 °C.[58] The olefins from this light oligomerization reactor are mixed with the α-olefins obtained directly in the liquid fraction from pyrolysis oligomerizing them in a second oligomerization reactor over HZSM-5 at 20 bar and mild temperatures to obtain longer molecules, above C20.[59] The resultant lubricant oil (taken as group I or III), unreacted olefins, and paraffins (assumed as inert) are separated into lubricant oils, diesel, and gasoline, using a fractional tower.

Gasification. Gasification partially oxidizes the plastic waste with oxygen, air, or steam to produce synthesis gas (CO and H_2) with traces of light hydrocarbons (methane, ethane, and ethylene) and ash.[60,61] Syngas can produce power, chemicals (methanol, ethanol, and dimethyl ether), or synthetic fuels. Given the recent emphasis on decarbonization and the use of low-carbon feedstocks, such as plastic waste, hydrogen is desirable. Steam is the best oxidizer for high-selectivity hydrogen and simplifies the separation.[61,62] A spouted bed at 850 °C with olivine as a heat transfer agent was used for modeling the reactor obtaining syngas with an H_2:CO ratio of 2.2.[62] The cleaned syngas was compressed and sent to a high-temperature water-gas-shift (WGS) reactor operating at 400 °C followed by a low-temperature bed working at 200 °C, over chromium iron oxide catalyst.[63,64] Each bed is modeled being in chemical equilibrium using a custom model written in Python integrated through an iterative scheme with the Aspen flowsheet model. The product was cooled down and separated by a pressure swing adsorption (PSA). The PSA system has a recovery of 82.5% for H_2.[65] The hydrogen is not recovered, and the hydrocarbons are burned to produce heat that cover the energy demand in the gasification reactor.

Hydrothermal Liquefaction (HTL). HTL degrades the polymer in subcritical or supercritical water.[16] The process is robust and applicable to mixed waste without sorting. The product contains paraffins, olefins, and aromatics that can produce gasoline with a high octane number.[66] For LDPE, HTL operates at 400 °C and 7 bar in an inert N_2 atmosphere. The reaction takes 2.5 h resulting in naphtha fuel.[66]The process only requires the depolymerization reactors operating in semi-batch, a filter in each reactor, and a fractionation tower for separating the fuels. Jet, diesel, gasoline, and gases are separated. The gases partially provide the energy requirements of the HTL reactor.

Hydrocracking. Hydrocracking provides fuel of a narrower distribution[67] but employs hydrogen.[68] It can be directly applied to plastics[44] or used after pyrolysis to hydrotreat the oil and improve its quality. The two-step process has been deemed less cost-effective and is recommended only when the direct hydrocracking product quality needs improvement.[67] In this work, a single-step hydrocracking process, using a dual HY and $Pt/WO_3/ZrO_2$ catalyst,[44] has been adopted here. The plastic waste is fed into the reactor with H_2 at 250 °C and 30 bar for 2 h. The product obtained is filtered to remove the traces of solids and distilled to recover the fuel fractions. The gas fraction obtained is sent to PSA to recover and recycle H_2. The fraction not recovered in the PSA is sent with all the other gas hydrocarbons to a combined heat and power system to cover the energy of the plant and sell the rest to the network.

Hydrogenolysis. Hydrogenolysis generates more valuable products, such as group III lubricant oils[45] and fuel oils.[69−71] Over a ruthenium/tungstated zirconia catalyst at 250 °C and 30 bar for 2 h, it produces lubricant oil at 15−20 wt %.[71] The product can be separated by distillation into lubricant oils, jet fuel, diesel, gasoline, and gas. A higher amount of gasoline is recovered from the gas fraction using a debutanizer. Since hydrogenolysis is not as energy intensive as the other processes, liquid petrol gas (LPG) is also recovered using a depropanizer and a de-ethanizer. The remaining C2 and C1 fractions and the unreacted H_2 are sent to PSA. In PSA, H_2 is recovered and recycled to the hydrogenolysis reactor. The remaining H_2 with the C_2 and C_1 fractions are converted into heat and power.

Techno-Economic Analysis (TEA) and Life Cycle Assessment (LCA). *Techno-Economic Analysis (TEA).* TEA is performed using the discounted cash flow method to estimate the main product's minimum selling price (MSP), which is compared with the selling price of each product in the market. For comparing different technologies, the return on investment (ROI) and the internal rate of return (IRR) are used as economic metrics. An amortization period of 20 years is considered. In all the economic metrics, the co-products are assumed to be sold. A detailed description of the assumptions and costs is given in the SI. Scenario analysis is also performed to evaluate the effect of plant scale, plastic waste collection price, and sorting cost. Specifically, the plant scale was varied from 5 and 60 kt/y to reflect current and under-construction industrial facilities,[19] with a nominal scale of 25 kt/y of LDPE, reflecting the biggest plant of waste plastic depolymerization in Europe. The price for collecting plastic waste in low and high-density population areas varies between \$0.1/kg and \$0.3/kg in Pennsylvania, Delaware, New Jersey, Maryland, and New York (see SI for further information).[72] The literature values have been adjusted with the gross domestic product per person between Italy and US[73] and the consumer price indices between 2009 and 2021.[74] Finally, the LDPE is sorted from the plastic waste at 0.032 \$/kg of plastic.[28] Its nominal concentration in the plastic waste is 24%,[3] resulting in a nominal sorting price of \$0.13/kg of LDPE. To account for

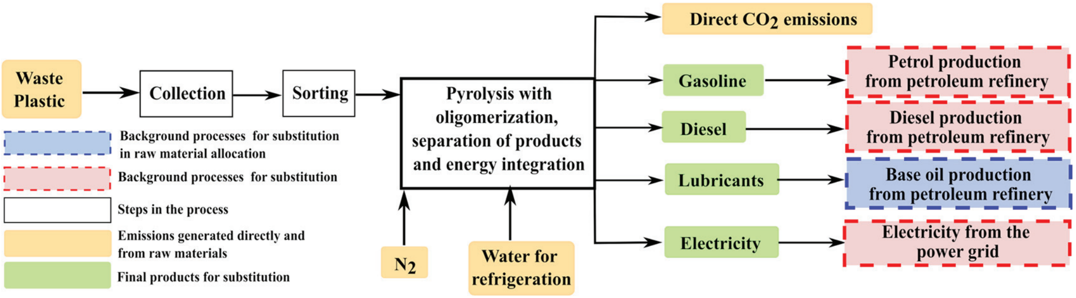

Figure 2. Environmental burdens for the pyrolysis of plastic waste. The product allocation approach only considers the substitution of the background systems for the co-products (red squares). The raw material allocation considers the substitution of the background systems for all the products (red and blue squares).

feedstock variability, the concentration has been varied between 15 and 30%, as higher LDPE concentrations have a lower cost of sorting. Due to the ability to handle mixed waste and plastics,[19] HTL has also been evaluated without sorting.

Life Cycle Assessment (LCA). LCA is performed to evaluate the emissions and the highest contributors to the environmental impacts. Only materials used in continuous operation have been considered. Others related to the construction or infrastructure are not included. The impacts are calculated with Traci[75] and from Ecoinvent v.3.8 database. The analysis is based on bin-to-gate boundary without recycling outlet streams, where plastic waste is considered as a residue. Two approaches have been followed for performing the LCA:

- First, a product allocation is followed with a system expansion method. In this approach, only the co-products are assumed to substitute the same product from a petrol-based process (see red squares in Figure 2), obtaining credits. This allows the emissions to be allocated to the main product of each process and the comparison of the products from the processes studied here with products generated from a fossil-based source. However, this approach does not allow to compare processes since the products are different.
- A second system expansion approach substituting all the products (including the main product) by the emissions of a petrol-based one has been followed, in a similar way to consequential LCA. This allows a common framework for comparison of different processes. In this approach, the main product also substitutes the same product from a petrol-based source, and the emissions are allocated using waste LDPE as a functional unit. A summary of the boundaries is given in Figure 2 using pyrolysis as an example. In this second approach, the co-products (diesel and gasoline) substitute the background systems in red and the main product substitutes its background system in the blue square. The background systems used for substituting all the products are given in Table 2. More details about the boundaries used in each process are given in the SI.

RESULTS

TEA Results. The CAPEX, MSP of the main product vs literature values, ROI, and IRR are listed in Table 3. The MSP is compared to the reported values of the market (MSP market in Table 3).[46,76,77] The IRR is compared with technical reports of market research companies.[78] Pyrolysis and hydrogenolysis making lubricant oils have a positive ROI. The remaining technologies do not generate sufficient profits to recover the investment in 20 years. Gasification, hydrocracking, and HTL have an ROI < −100%; that is, the cost is higher than the profit. This emphasizes the importance of generating high-value-added products. In specialty chemicals, like lubricants, the IRR is between 13 and 17%; in commodity chemicals, like gasoline, a minimum IRR of 8% is required for economic viability. The IRR of pyrolysis above 17% indicates that it could be profitable compared to the current crude oil-based lubricants; meanwhile, hydrogenolysis with an IRR between −1.5 and 1.7% is not competitive for commodity chemicals; see Table 3. This is due to the higher yields achieved for lubricants as shown in Table 4.

The cost breakdown of all technologies is shown in Figure 3A (details in the SI). In most cases, the main cost is the collection and sorting of plastics. Interestingly, due to the smaller scale of a recycling facility than typical industrial plant sizes, the amortization and other costs (labor, administration, and overhead) contribute significantly. Utility costs have a minor contribution since the gases generated in the conversion produce heat and power for the plant. Only in HTL, this contribution is slightly higher due to its high energy consumption. The cost of other raw materials is relatively low (<10%), except for hydrogenolysis and hydrocracking, since H_2 is more expensive than water or N_2 of other technologies. Overall, reducing collection costs and automating and streamlining plastics sorting, possibly by changing customer habits and setting up the necessary infrastructure, are crucial to plastics recycling. For example, more specialized recycling bins for various waste streams exist in some of the EU country airports and cities than in the US.

Table 2. Products and Background Processes Used for Substitution[a]

product	background process from ecoinvent
lubes	base oil production, petroleum refinery operation. Location: rest of the world
diesel and jet fuel	diesel production, low sulfur, petroleum refinery operation. Location: rest of the world
gasoline	petrol production, low-sulfur, location: rest of the world
H_2	hydrogen production, gaseous, petroleum refinery operation. Location: rest of the world
electricity	market for electricity, medium voltage, location: US-RFC
LPG (butane fraction)	market for butane, location: global
LPG (propane fraction)	market for propane, location: global

[a] All the emission factors are taken from Ecoinvent.

Table 3. Summary of TEA for Various Technologies for a Nominal Plant Size of 25 kt/y

technology	CAPEX (MM$)	MSP[a] ($/kg)	MSP market[b] ($/kg)	ROI (%)	IRR (%)	target product
pyrolysis	39.3	0.66	1.5−1.8	413−559	25.4−32.8	lubes GI-GIII
gasification	35.7	2.97	2.1	−175	Na[c]	H_2
hydrocracking	44.8	0.74	0.57	−107	Na[c]	Gasoline
HTL	15.9	0.88	0.57	−237	Na[c]	Gasoline
hydrogenolysis	50.8	1.67	1.5−1.8	(−14)−19	(−1.5)−1.7	lubes GI-GIII

[a] MSP is computed with IRR = 0% (minimum selling price without any benefit). [b] The MSP of pyrolysis and hydrogenolysis is compared to lubricants (groups I and III for pyrolysis and group III for hydrogenolysis); gasification MSP to hydrogen; and HTL and hydrocracking MSP to gasoline. Values are defined in Section 2.3. [c] IRR < −100% cannot be computed.

Table 4. Summary of Yields to the Main Products and Co-Products for Each of the Technologies Studied

technology	product	yield (kg/kg_{LDPE})
pyrolysis	lubes	0.4896
	jet oil	0.0704
	diesel	0.1296
	gasoline	0.1360
gasification	H_2	0.1795
hydrocracking	diesel	0.0297
	gasoline	0.7260
	electricity (kWh/kg_{LDPE})	0.1435
HTL	jet oil	0.2208
	diesel	0.3296
	gasoline	0.2988
hydrogenolysis	lubes	0.1935
	jet oil	0.0667
	diesel	0.1168
	gasoline	0.1866
	LPG	0.0752

Figure 3B shows the CAPEX breakdown for the various technologies. Unsurprisingly, separations are the main contributor, especially for gasification, due to using PSA to separate H_2. The energy recovery unit constitutes the second highest contributor, with turbines representing almost 20% of the CAPEX. Gasification is an exception due to having no energy recovery cost, as leftover gases are burnt directly in the gasification furnace. The reactor cost is low except for hydrogenolysis and to an extent hydrocracking due to operating at a higher pressure and using a relatively expensive (ruthenium-tungstated zirconia) catalyst. Operating at lower pressures and introducing non-platinum group metal (PGM) catalysts are opportunities for lowering the cost. This is further manifested in pyrolysis, which operates at 1 atm and exhibits a lower reactor cost. Narrowing the pyrolysis product distribution will reduce separation costs and make the technology even more competitive.

Different scenarios regarding the effect of plant size, LDPE concentration, and collection cost on ROI are considered. The results in Figure 4 illustrate the profound impact of these facets on ROI. The dominant factor is technology-dependent. The ROI of technologies making higher value products, such as pyrolysis, gasification, and hydrogenolysis, varies the most among scenarios. The second most relevant factor is the plastic waste price. In cities with concentrated plastic waste (e.g., Manhattan or Philadelphia), transportation and collection costs are lower, improving the ROI by up to 250% in HTL. Higher concentrations of LDPE in plastic waste reduce the sorting cost and give a higher ROI (Figure 4). Since HTL can treat heterogeneous waste without sorting (an LDPE concentration of 100% is used), sorting is more relevant than the plant scale for sizes between 5 and 60 kt/y.

Figure 5 compares the MSP vs plant scale. At 5 kt/y, which corresponds to an existing operating plant in Spain,[17] the technologies are not profitable and subsidies are needed. Pyrolysis is more profitable than hydrogenolysis, even in the case where hydrogenolysis generates better (grade III) lubricants. Hydrogenolysis has a higher amortization cost and nearly twice the MSP of pyrolysis. Gasification to H_2 is not profitable but can be at sufficient large scales with an optimized plastic waste collection. The price of H_2 is higher than steam reforming of methane, $2.1/kg, but lower than electrolysis, $4/kg.[77] This suggests that gasification combined with CO_2 capture could be valuable for transitioning to sustainable (brown) hydrogen production from low carbon feedstocks. Finally, production of fuels, such as gasoline, is not profitable. Hydrocracking shows a better economic performance at small scales but similar prices to HTL at large scales. Since HTL can manage waste mixtures at the industrial scale,[19] it has an advantage.

LCA Results Following an Allocation to the Products. A summary of the GWP is provided in Table 5, when the emissions are allocated to the product. The comparison versus petrol-based products downgrades these plastic-based processes studied here. All the processes have slightly higher emissions than petrol. The conversion of LDPE, as a solid component with long chains, to lighter fractions requires higher energy and produces more CO_2 emissions than petrol (some of them also available in petrol). A more detailed breakdown of the emissions for each process is given in Figure 6. Pyrolysis shows lower emissions than hydrogenolysis, see Figure 6,A, to produce lubricants since the yield achieved in the process is higher; see Table 4. Hydrogenolysis has been studied with H_2 from different sources: H_2 produced in a refinery with the carbon captured in other chemicals, H_2 from electrolysis based on renewable electricity, and H_2 produced by steam reforming of natural gas (see approaches in the supplementary); but in all cases, the emissions are higher than the ones from pyrolysis. The second analysis is performed for gasification where the high energy requirements result in high quantity of CO_2; see Figure 6B. The CO_2 emissions produced in generating H_2 by gasification to syngas are similar to the ones produced by means of natural gas reforming and by far higher than green and blue H_2. However, carbon capture systems can be also used to lower the emissions to values similar to H_2 produced within a refinery (carbon is captured in the production of the other chemicals of the refinery). The last product considered is gasoline. Contrary to lubricants, the catalytic technology based on hydrogen is more sustainable than the thermal technology, HTL. HTL requires high energy consumption for heating the water; see breakdown of Figure

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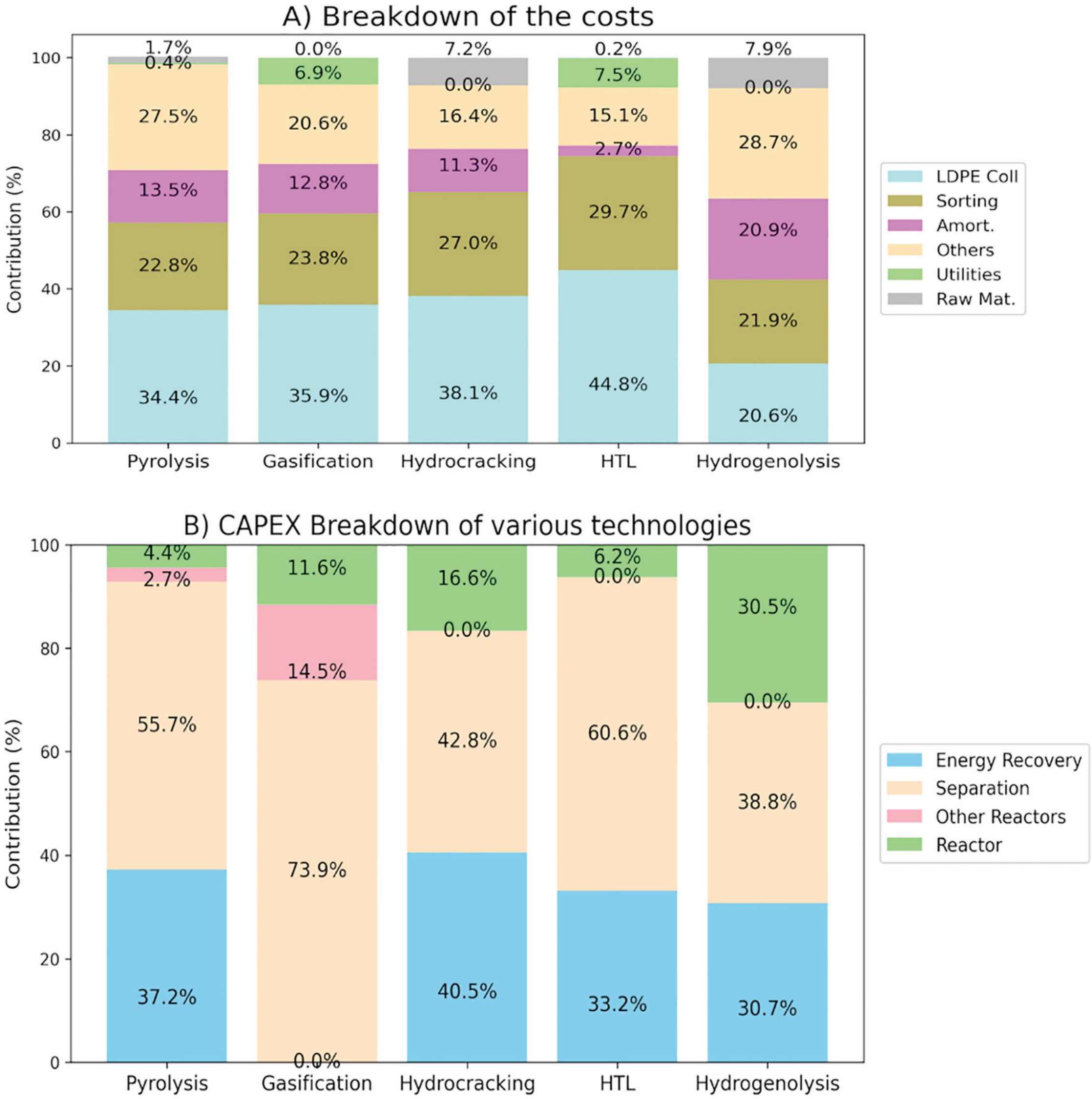

Figure 3. (A) Cost breakdown of various technologies. In the legend: "LDPE Coll" refers to the collection of LDPE, "Sorting" refers to sorting, "Amort." refers to amortization costs of the depolymerization plant, "Others" include other costs like labor, overhead, and maintenance; "Utilities" involve the cost of utilities and "Raw Mat." include the costs of all raw materials except LDPE. (B) CAPEX breakdown of various technologies. In the legend of (B) "Energy Recovery" refers to the energy recovery composed of a burner and/or a CHP with a turbine, "Separation" involves all the units required in the separation (e.g., distillation towers, PSA systems, and compressors), and "Reactor" refers to the depolymerization reactor and "Other Reactors" involve the WGS reactor after the gasification and the oligomerization reactors after the pyrolysis.

6C. Furthermore, hydrocracking also results in high yield of gasoline, resulting in lower emissions. Although hydrocracking has less credits from the co-products than HTL (other fuels in Figure 6C), it has a higher yield to gasoline and the emissions per kg gasoline are lower. In order to avoid this effect of the allocation, the result of a consequential approach substituting only the main product by its petrol-based equivalent is considered in the next section.

LCA Results Allocating the Emissions to the Raw Material. A summary of the environmental impact categories per kg of LDPE is provided in Table 6. This approach allows us to compare all the technologies and decide the best path for upcycling since all are referred to the same functional unit. More details about the breakdown and the categories considered are given in the SI. The results show that hydrogenolysis is the most environmentally friendly technology in all categories. On the contrary, gasification shows the worst environmental performance, having positive indicators in all categories except ozone depletion, where more chlorofluorine emissions are reported from a petrol-based H_2. On the other hand, eutrophication has a positive contribution mainly due to plastic sorting that requires cleaning stages to remove the organic wastes using detergents and chemicals. Figure 7 shows the positive contributors that generate CO_2 emissions and the credits. Hydrogenolysis has the lowest CO_2 emissions mainly due to the high credits generated by selling the lubes and fuels (negative values of the bar plot). Together with hydrocracking, they operate at mild temperatures reducing the energy consumption and use gases to generate power and substitute fossil-based power of negative value in emissions. Pyrolysis also has significant credits due to producing lubricant oils and fuels instead of using fossil fuels. Although pyrolysis reduces the direct emissions by eliminating a very energy intensive raw material like H_2, it requires higher temperatures

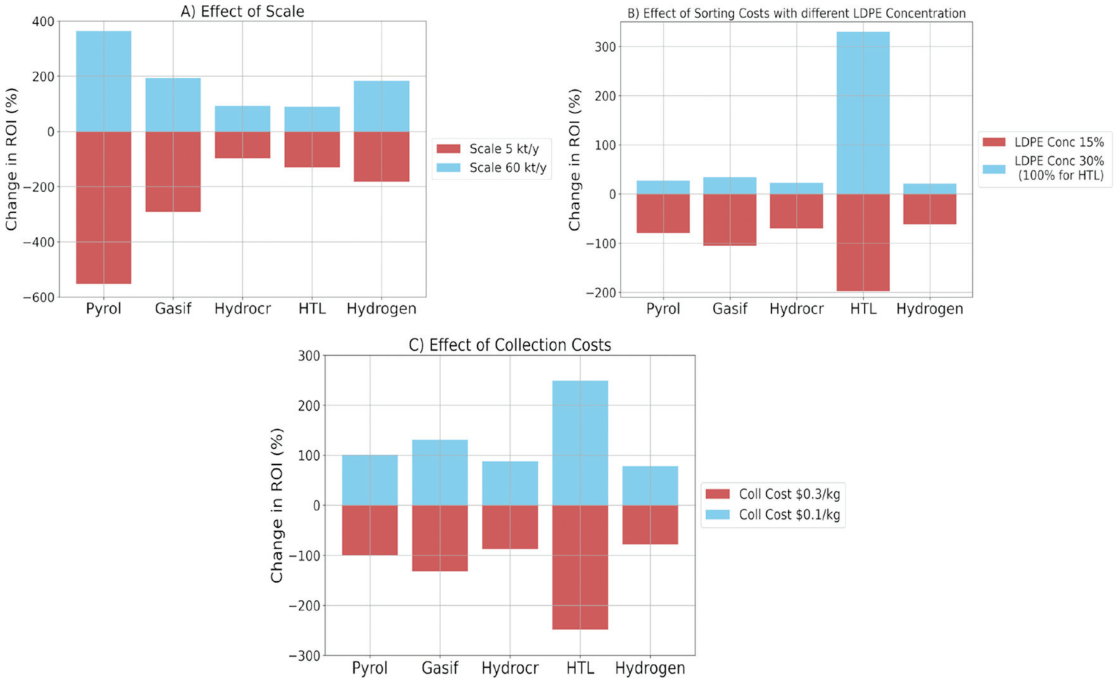

Figure 4. Scenario analysis for the ROI of various technologies. Effects of (A) plant scale, (B) concentration of LDPE in the waste, and (C) collection cost of plastic waste. Pyrol. refers to pyrolysis, Gasif. refers to gasification, Hydrocr. refers to hydrocracking, HTL refers to hydrothermal liquefaction, and Hydrogen refers to hydrogenolysis.

Table 5. Comparison of GWP by Allocating the Emissions to the Main Products versus the GWP of the Products from Fossil-Based Sources Reported by Ecoinvent

technology	main product	emissions of this work ($kg_{CO2}/kg_{product}$)	emissions petrol-based products ($kg_{CO2}/kg_{product}$)
pyrolysis	lubes	1.582	1.170
gasification	hydrogen	11.12	1.568
hydrocracking	gasoline	0.906	0.611
HTL	gasoline	3.372	0.611
hydrogenolysis	lubes	1.825	1.170

and N_2, whose production needs an energy intensive O_2/N_2 separation. As a result, the emissions of pyrolysis overcome the other two technologies. Reducing N_2 in fluidized bed reactors while maintaining fluidization is a challenge. One way for reducing the N_2 requirements is by separating the N_2 with PSA in the gas hydrocarbon outlet stream and recycling it to the pyrolysis reactor. This recycle reduces the emissions to 0.23 kg_{CO2}/kg_{LDPE}, but it increases the MSP of lubricant base oils from \$0.66/kg_{lubes} to \$0.68/kg_{lubes} (see the Supplementary Material). The process with internal N_2 recovery has lower emissions than hydrogenolysis. Thus, pyrolysis apart from being more robust than hydrogenolysis, it could also lower the net emissions. HTL and gasification have the highest emissions due to their increased energy requirements. Gasification to H_2 with CO_2 released to the atmosphere gives the highest emissions, even higher than incineration; see Figure 8. It presents the net values of every technology compared with the emissions reported by Ecoinvent for incineration and landfilling (Landfill UB refers to the highest value reported for plastics in Ecoinvent and Landfill LB to the lowest value). The comparison shows that gasification and HTL also overcome the emissions generated by plastic landfilling. Thus, CO_2 capture and utilization or storage are imperative for gasification and HTL to be environmentally relevant. More details about other environmental impacts are available in the SI.

CONCLUSIONS

We have compared TEA and LCA metrics of five thermochemical technologies for the depolymerization of LDPE waste to valuable products: three medium to high temperature, non-catalytic ones (gasification, HTL, pyrolysis), and two low temperature, high H_2 pressure, catalytic ones (hydrogenolysis and hydrocracking). We examined various products to assess the effect of product value: H_2 from gasification, lubricant oils from pyrolysis and hydrogenolysis, and fuels (gasoline as focus) from HTL and hydrocracking. We also assessed the impact of plant size, plastic waste collection, and sorting of plastic waste, as there is large uncertainty in these quantities at these early stages of technology development.

Pyrolysis to light olefins and their isomerization and oligomerization to lubricant oils is the most profitable technology. Additional final products made from olefins can also be explored given that they are platform molecules. Hydrogenolysis to lubricant oils is also potentially profitable. Gasification for the production of H_2 gives an estimated cost of ~3 \$/kg, which is higher than the Department of Energy (DOE)'s goal of \$1/kg.[12] HTL and hydrocracking are not viable for small plant scales due to producing low value products (fuels).

Aside from the specifics of technologies, the work revealed overarching recommendations. First, generating value-added products, as part of a product portfolio, is crucial for plastic management. Olefins are key in this regard as they are platform chemicals of the industry. Direct production of other valuable products, such as lubricants, is also desirable. Strategic decisions on product selection are necessary. Second, product selectivity is essential. In this work, the considered yield to

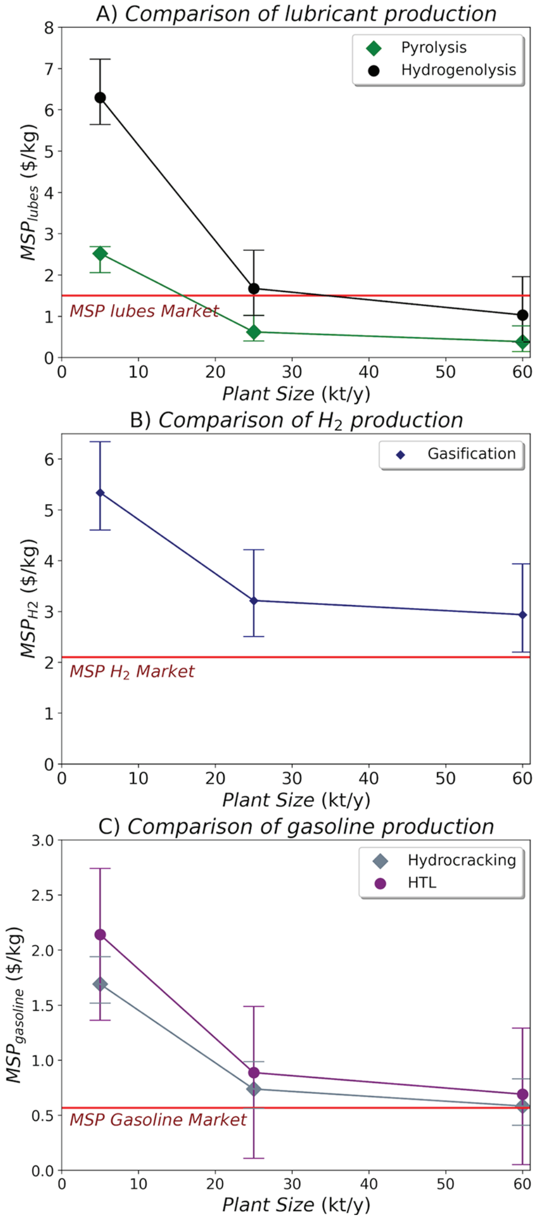

Figure 5. MSP vs the benchmark current prices. (A) Pyrolysis and hydrogenolysis are compared to grade I lubricants. (B) Gasification is compared to H_2 from steam reforming of methane. (C) Hydrocracking and HTL are compared to gasoline. Blue is below the current price of the product and red is above. The lowest bounds correspond to high density of plastic waste collection cost of \$0.1/kg and 30 wt % of LDPE in the plastic waste. Conversely, the highest bounds correspond to low density of plastic waste collection cost of \$0.3/kg and 10 wt % of LDPE in the plastic waste.

olefins and thus to lubricant oil was modest (pyrolysis) and low (hydrogenolysis). Clearly, more selective catalytic processes will profoundly improve the economics by making more value-added product and significantly reducing the separation costs that dominate the CAPEX. Catalysts undergo some deactivation, such as coking, but limited information is available regarding the mechanism and long-term stability. Furthermore, the best catalyst varies with plastic waste. For example, hydrogenolysis employs Ru over titania for polypropylene to make lubricants[79] and Ru on tungstated zirconia for polyethylene to make fuels.[80] The use of different

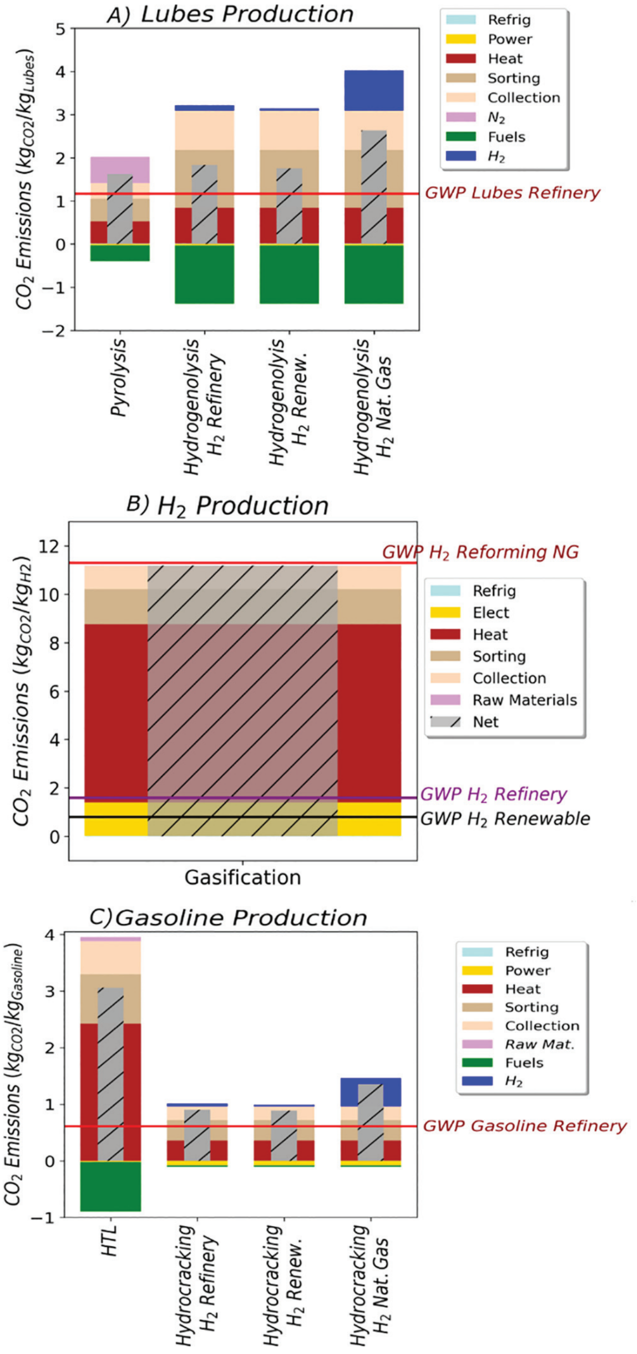

Figure 6. Results of the environmental impacts allocating the emissions to the products. (A) Breakdown of the GWP of pyrolysis and hydrogenolysis compared to petrol-based production of lubes. Hydrog. Ref assumes that the H_2 for hydrogenolysis is produced in the refinery as a byproduct where the carbon is captured. Hydrog. Renew. H_2 for hydrogenolysis produced from electrolysis supplied by wind power. Hydrog. No-CC assumes H_2 produced by steam reforming without carbon capture. (B) Breakdown of the GWP of gasification compared to H_2 by several methods (in a refinery with carbon capture (CC), by electrolysis and by steam reforming of natural gas without CC). (C) Breakdown of the GWP of HTL and hydrocracking compared to petrol-based production of gasoline. Hydrocr. Ref assumes that the H_2 for hydrocracking is produced in the refinery as a byproduct where the carbon is captured. Hydrocr. Renew. assumes the H_2 for hydrocracking produced from electrolysis supplied by wind power. Hydrocr. No-CC assumes the H_2 produced by steam reforming without carbon capture.

Table 6. Summary of Environmental Footprint of Various Technologies Allocating the Emissions to the Raw Material[a]

technology	GWP	Acid.	Ecotox.	Eutroph.	O_3 Dep.	Photo.
pyrolysis	0.225	−0.154	0.821	5.04×10^{-3}	-5.44×10^{-7}	5.99×10^{-5}
gasification	1.726	2.53×10^{-2}	0.862	5.55×10^{-3}	-1.66×10^{-7}	1.27×10^{-3}
hydrocracking	0.214	−0.114	−0.697	5.26×10^{-3}	-4.12×10^{-7}	-1.7×10^{-4}
HTL	0.743	-8.58×10^{-2}	0.769	5.14×10^{-3}	-4.71×10^{-7}	1.81×10^{-4}
hydrogenolysis	0.127	−0.102	0.719	5.39×10^{-3}	-3.35×10^{-7}	-1.91×10^{-5}

[a] All the cases include the emissions due to collection and sorting. GWP = Global Warming Potential in kg_{CO2}/kg_{LDPE}. Acid. = acidification potential in mols of H^+ Eq./$kg_{lubricant}$. Ecotox. = ecotoxicity in kg 2,4-D,e/$kg_{lubricant}$. Eutroph. = eutrophication potential in kgN/$kg_{lubricant}$. O_3 Dep = ozone depletion in kg CFC-11-e/ $kg_{lubricant}$. Photo. = photochemical oxidation potential in kg NO_x-e/$kg_{lubricant}$.

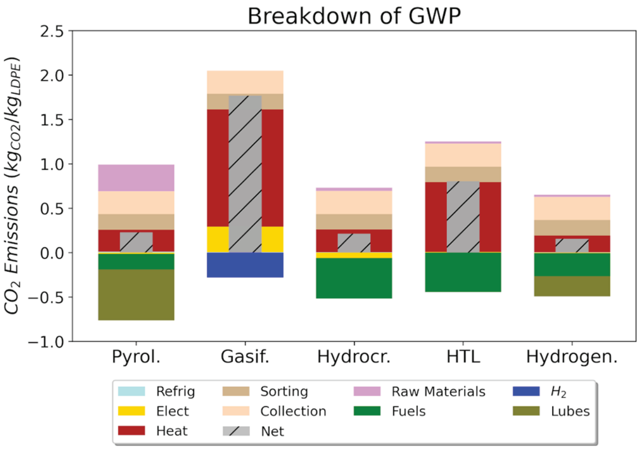

Figure 7. Breakdown of CO_2 emissions of (A) pyrolysis, (B) hydrogenolysis, (C) HTL, (D) hydrocracking, and (E) gasification. Legend: Refrig represents the emissions generated by refrigerating water, Heat represents the emissions for generating heat and the emissions in the energy recovery for heat and power production, Sorting represents the emissions associated with the sorting of LDPE and its transport to the plant, Raw Mat corresponds to the other raw materials used (N_2, H_2, and water), Power corresponds to the emissions due to electricity from an external source, Collection represents the emissions generated in collecting the plastic waste, Fuels represent the credits obtained by substituting petrol-based Fuels, Lubes represent the credits obtained by substituting petrol-based lubes, and H_2 represent the credits by substituting H_2 generated with steam reforming of natural gas.

catalysts implies that the plastics need to be separated, increasing the cost; meanwhile, non-catalytic processes, such as gasification, HTL, and non-catalytic pyrolysis can deal with these mixtures. Further development of catalysts and catalytic processes is therefore needed focusing on catalyst stability and product selectivity. Third, the plant scale plays a significant role. In the case of value-added products, even modest scales can give profitable plants. Larger plants are desired but bring higher risk. It is important to build demonstration plants and de-risk the technologies. Fourth, and rather unexpected, collection and sorting of plastic waste are the most influential factors in terms of economics. Waste treatment near large cities, which produce most of it, can significantly reduce the collection and transportation cost. Highly concentrated polyethylene streams, aided by the industry, commercial users, and consumers with the right infrastructure, can have a significant impact on the economics of plastic recycling. Improving these technologies to treat mixed waste will reduce the sorting cost and is an essential direction of future catalysis and separation research. Along these lines, integrating waste collection with supply chain optimization can provide significant insights into determining the location, technology, and geographical area for profitable plants. The hydrogenolysis and hydrocracking reactor cost is a significant fraction of CAPEX. Eliminating PGMs and reducing the H_2 pressure are obvious catalysis challenges and opportunities.

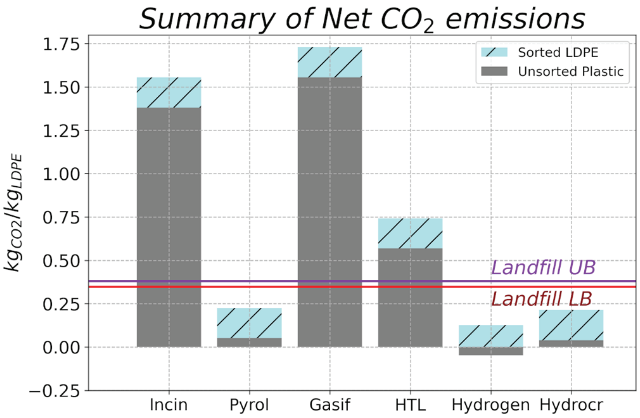

Figure 8. Comparison of CO_2 emissions against landfill and incineration. The technologies are compared with and without the emissions due to sorting. Landfill LB (low bound) represents the lowest emissions in a Landfill, according to Ecoinvent (0.27 kg_{CO2}/kg_{LDPE}), Landfill UB (upper bound) represents the highest emissions for landfilling the plastic based on Ecoinvent (0.45 kg_{CO2}/kg_{LDPE}). Incin refers to incineration, Pyrol. refers to pyrolysis, Gasif. refers to gasification, Hydrocr. refers to hydrocracking, HTL refers to hydrothermal liquefaction, and Hydrogen. refers to hydrogenolysis.

In terms of CO_2 emissions, hydrogenolysis and hydrocracking are the most environmentally friendly, followed by pyrolysis. Although pyrolysis reduces emissions from using H_2, it often employs N_2 with an energy consumption 40 times higher than the H_2 required in hydrocracking and hydrogenolysis. Reducing the nitrogen in the pyrolysis is therefore very desirable. Another alternative is to reduce emissions in heat production. Carbon capture technologies can be used by maintaining conventional heating, but the substitution of heat by electricity-based heating (e.g., electric boilers or furnaces) or reactors supplied with electricity such as microwaves[55] is crucial to exploit. Electrification can be powerful in all depolymerization technologies reducing emissions from 0.2 $kgCO_2/kg_{LDPE}$ up to 1.2 $kgCO_2/kg_{LDPE}$ in more emission intensive processes like HTL and gasification.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.3c00636.

Detailed description of the processes modeled, description of the assumptions in the technoeconomic analysis, estimation of the capital costs of reactors, estimation of the capital costs in the pressure swing adsorption units, detailed description of the assumptions in the LCA, boundaries of the LCA and estimation of the direct emissions by burning, and detailed results for economic and environmental assessment (PDF)

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Notes

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