

# Environmental Benefits of Circular Ethylene Production from Polymer Waste

Cecilia Salah, Robert Istrate, Anders Bjørn, Victor Tulus, Javier Pérez-Ramírez, and Gonzalo Guillén-Gosálbez\*



Cite This: *ACS Sustainable Chem. Eng.* 2024, 12, 13897–13906



Read Online

ACCESS |

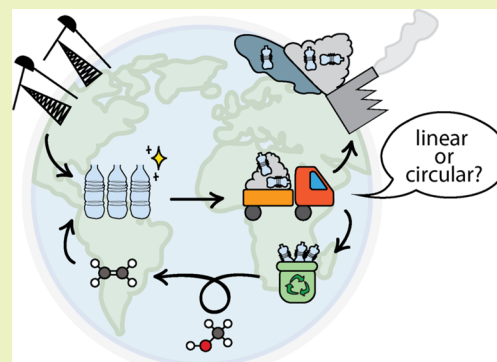
Metrics & More

Article Recommendations

Supporting Information

**ABSTRACT:** The linear nature of the current plastics economy and increasing demand for polymers poses a pressing global problem. In this work, we explore the environmental and economic performance of a circular alternative for polymer production through chemical plastic recycling following the waste-to-methanol-to-olefins (WMO) route. We assess the life-cycle environmental impacts and techno-economic feasibility of this novel circular production route (CPR) in 2020 and 2050, and compare them to the existing linear production route (LPR), deploying naphtha steam cracking for olefin production, and a mix of landfill and incineration as end-of-life treatment. Our results showcase that CPR could enable significant impact reductions, notably in 2050 assuming a low-carbon electricity mix based on renewables. However, the shift from linear to circular comes with burden-shifting, increasing the impacts relative to LPR on five environmental indicators in 2020 (i.e., terrestrial and freshwater eutrophication, particulate matter formation, acidification, and metal/mineral resources use). From the techno-economic viewpoint, we found that ethylene from waste polymers could become competitive with fossil ethylene when deployed at large scale. Moreover, it is significantly cheaper than its green analogs, which deploy methanol-to-olefins with green methanol from captured CO<sub>2</sub> and electrolytic H<sub>2</sub>, showcasing the potential of implementing high-readiness level technologies to close the loop for polymers.

**KEYWORDS:** ethylene, methanol, chemical plastic recycling, circular polymers, life cycle assessment



## INTRODUCTION

The current plastics economy, based on a mostly linear production route (LPR), accounts for 4.5% of the global annual greenhouse gas (GHG) emissions.<sup>1</sup> Additionally, the growing demand for polymers in numerous industrial sectors generates substantial amounts of waste globally.<sup>2</sup> Despite the known threats of plastics to the environment,<sup>3</sup> recycling rates are still small (19.5% in 2015) compared to the share of waste polymers that ends up in landfills (55%) and are incinerated (25.5%).<sup>2</sup> Moreover, most polymers are derived from fossil feedstock, relying on refinery operations for monomer production.<sup>4,5</sup>

The business-as-usual (BAU) process for ethylene production, i.e., naphtha steam cracking, consists of breaking down crude oil components into valuable building blocks for the petrochemical industry, such as olefins, used as monomers.<sup>6,7</sup> The process is energy-intensive, requiring approximately 15 GJ fired heat t<sup>-1</sup> ethylene, in the cracker alone.<sup>6</sup> Electrifying the cracker could decrease GHG emissions from ethylene production assuming large availability of low-carbon electricity in future markets.<sup>8</sup> However, electric crackers still rely on fossil feedstock to operate, and cannot solve the plastic waste problem unless coupled with effective waste management strategies, thus requiring innovations on this front.<sup>4</sup> The

linearity of polymers becomes notably problematic in the packaging sector (42% of the global polymers demand in 2019), in which polymers have a short life span.<sup>4</sup> Polyethylene (PE) is the most used commodity polymer worldwide, representing 24% of the global polymer production in 2019 in the high- and low-density versions (HDPE and LDPE respectively).<sup>9</sup> However, PE recycling rates are very low (5.8% for LDPE in 2014),<sup>10,11</sup> which renders it a cheap, resource-intensive and wasteful polyolefin.

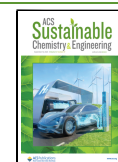
Future projections of global municipal plastic waste showcase a positive outlook on plastics, in a scenario where waste management infrastructures improve with a growing economy.<sup>12</sup> However, improving collection and sorting efficiencies is not sufficient to draw low-carbon circular plastics. Additives incorporated into plastics to enhance their properties prior to commercialization for specific applications pose a challenge to mechanical recycling.<sup>4</sup> Indeed, they might

**Received:** May 23, 2024

**Revised:** August 11, 2024

**Accepted:** August 12, 2024

**Published:** September 3, 2024



cause cross-contamination of chemicals or degrade during the steps of melting and extrusion, thus affecting the final properties of the recycled plastic, which returns to the market with a reduced efficiency compared to virgin polymers.<sup>13</sup> Furthermore, the choice between end-of-life alternatives plays an important role not only in the quality of the recycled polymer but also in its overall carbon footprint.<sup>14</sup> For instance, van der Hulst et al. showed that deploying chemical recycling for mixed waste polymers potentially reduces GHG emissions by 40% compared to incineration.<sup>15</sup>

Growing attention has been given to the development and implementation of chemical recycling technologies to extend polymers' lifetime and decrease the environmental burdens of current end-of-life treatments. Recent studies showcase the environmental benefits of deploying thermo-recycling processes (i.e., pyrolysis and gasification) for producing chemicals and fuels.<sup>16–18</sup> Notably, Schwarz et al. found that gasification for monomer recovery is among the preferred methods for treating HDPE and LDPE waste from an environmental perspective.<sup>14</sup> The main differences between pyrolysis and gasification lay in the operating conditions, which dictate the product distribution.<sup>14</sup> On the one hand, pyrolysis is performed at temperatures between 300 and 600 °C, in the presence of low or no oxidating agent, generating pyrolysis oil, which has to undergo a series of separation steps for product recovery.<sup>18</sup> On the other hand, polymer gasification operates at higher temperatures (>700 °C) to yield syngas, a mixture of H<sub>2</sub>, CO, and CO<sub>2</sub>, widely used in the chemical industry as feedstock to platform chemicals and fuels production.<sup>19,20</sup> For instance, syngas can be converted into methanol, a precursor to the high-technology readiness level (TRL) methanol-to-hydrocarbons processes,<sup>7,19</sup> providing olefins (MTO) and aromatics (MTA) employed in a myriad of synthesis pathways. Moreover, deploying green and renewable methanol in the MTO and MTA processes is conducive to a green chemical industry.<sup>19</sup> Green methanol has gained attention in recent years for that matter, and several studies have arisen to showcase the environmental benefits as well as the techno-economic feasibility of implementing methanol synthesis from captured CO<sub>2</sub> and electrolytic H<sub>2</sub>.<sup>21,22</sup> Furthermore, it was recently shown that plastic waste gasification for methanol production has the potential to decarbonize methanol consumption.<sup>23</sup> Thus, coupling gasification with the high-TRL technologies syngas-to-methanol and MTO allows the production of monomers, which in turn issue virgin polymers with the same properties as their fossil analogs. Namely, closing the loop via waste-to-methanol-to-olefins (WMO) challenges the current LPR both in the production and waste treatment fronts, simultaneously defossilizing and decarbonizing the plastics industry.

To quantify novel technologies' emission-reduction potential and assess their environmental appeal, the field of Process Systems Engineering has increasingly recognized the importance of life cycle assessment (LCA). Ioannou et al. and Negri et al. highlight how LCA allows for the comprehensive evaluation of the environmental and social aspects of a technology.<sup>24,25</sup> It can be used as a powerful tool to guide decision-making and contribute to a sustainable future.<sup>26–28</sup> Prospective LCA (pLCA) is a recent addition to the LCA toolbox, enabling the environmental assessment of activities and technologies at future points in time, by integrating them into an evolving economy.<sup>29</sup> pLCA enables

practitioners to explore different scenario narratives describing alternative plausible futures.<sup>28</sup>

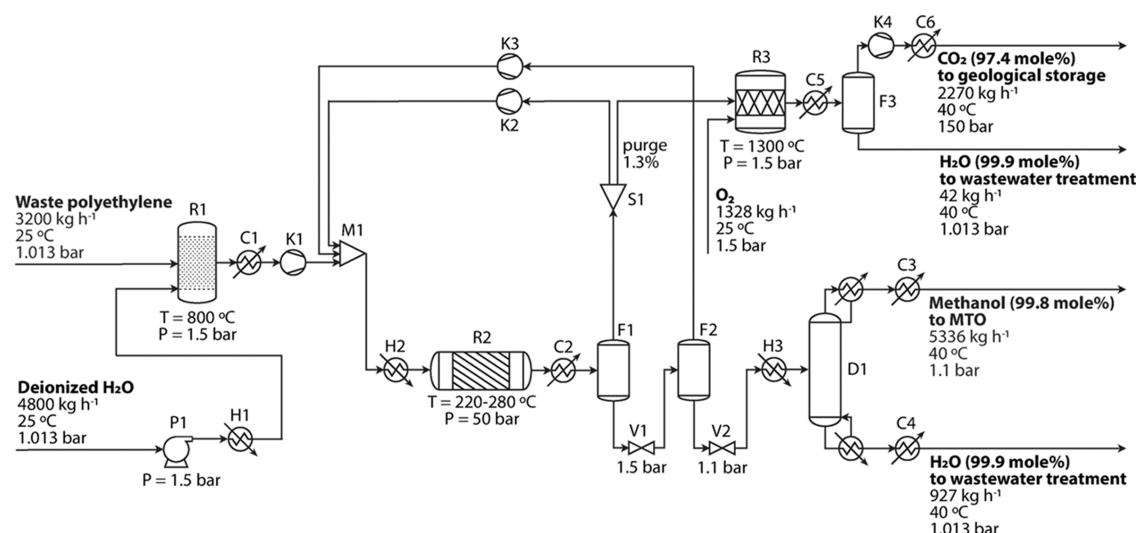
In the context of plastics, Bachmann et al. discuss mitigation strategies to reduce, by 2050, the impacts that current polymers apply on Earth-system processes within the planetary boundaries framework.<sup>30</sup> Their study showcases that increasing recycling rates can reduce planetary footprints related to the current LPR by up to 50%.<sup>30</sup> Analogously, results by Meys et al. indicate that it is possible to realize net-zero GHG emission plastics by 2050 in a cradle-to-grave scope.<sup>31</sup> This can be achieved by switching to biomass- and CO<sub>2</sub>-based plastic production together with increasing waste collection and recycling rates (up to 70%) in a low-carbon economy, which heavily relies on renewable energies and carbon capture and storage.<sup>31</sup> Their study includes emerging technologies for chemical recycling, i.e., pyrolysis to monomers, which have not yet been deployed at scale, and neglects other chemical recycling pathways that deploy high-TRL technologies, such as WMO. Crucially, previous LCAs of chemical recycling technologies assume that the interconnected network of industrial systems with which the chemical processes exchange mass and energy flows, referred to as technosphere, will remain unaltered in the future. However, decarbonization trends in power, transport, cement and steel production, among others, may strongly affect the LCA outcomes, so omitting them could overestimate environmental impacts (EI) from future technologies.<sup>29</sup>

Our study pioneers the assessment of the GHG emission-reduction potential of deploying the high-TRL WMO route for circular polymers. Multiple low-TRL routes are being investigated to recover monomers from polymer waste.<sup>14</sup> However, focusing on a mature pathway, as done here, has the advantage of providing quantitative evidence of environmental benefits from using existing technologies to handle plastic waste while setting a baseline for future comparisons of alternative circular production routes (CPR). Moreover, our study is the first to perform a pLCA to assess how future technological and economic trends might affect the environmental footprint of the plastics economy. Finally, we put our WMO chemical recycling technology into perspective with a techno-economic assessment, comparing it to the BAU ethylene production (naphtha steam cracking), and to other routes based on MTO that have already been studied in the literature. We find that CPR via WMO enables polymers with a significantly lower carbon footprint than the current LPR, notably in a future with low-carbon power mixes.

## METHODS

We quantify the environmental performance and techno-economic feasibility of deploying high-TRL technologies to enable CPR via WMO as an alternative to LPR, based on fossil feedstock. In essence, polymer waste is first gasified to produce syngas, which is converted to methanol, and further transformed into olefins. We focus on developing a detailed waste-to-methanol process model, while the MTO step is modeled based on Ioannou et al.<sup>24</sup> Similarly, the BAU process for fossil ethylene, used for comparison purposes, follows Keller et al.<sup>32</sup>

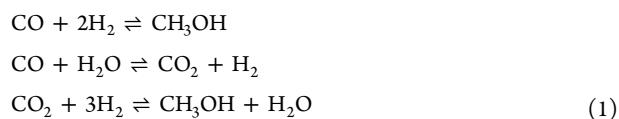
We combine process simulation with pLCA to quantify the global warming impact (GWI) of CPR and LPR at two points in time (2020 and 2050). Moreover, we assess the occurrence of environmental burden-shifting in CPR across 16 impact categories, and include a techno-economic study of the proposed solution for closing the polymers loop, discussing its feasibility.



**Figure 1.** Process flowsheet of the waste-to-methanol process. The produced methanol is sent to MTO to be further transformed into ethylene.

**Waste-to-Methanol Process Modeling.** The waste-to-methanol process is the first step of the CPR scenario. The process was simulated in Aspen Plus v12, using the SRK thermodynamic property method. SRK follows the Soave–Redlich–Kwong cubic equation of state and is suitable for processes involving mixtures of mildly polar gases at high pressures and temperatures.<sup>33</sup> The flowsheet (Figure 1) was designed to produce methanol at 99.8 mol % purity from waste PE (WPE). It was created based on Salah et al.<sup>16</sup> and González-Garay et al.,<sup>20</sup> and consists of three main sections: WPE gasification, methanol synthesis, and carbon capture and storage via oxy-fuel combustion.<sup>24</sup> Two additional property methods were used in R2 (PENG-ROB) and D1 (NRTL) to enable better modeling accuracy for the kinetic model and liquid–liquid separation, respectively.

We feed 3.2 t WPE h<sup>-1</sup> and 4.8 t low-pressure steam h<sup>-1</sup> to the gasifier (R1), to generate syngas, which is then compressed to 50 bar in three steps with intercooling (K1). CO and CO<sub>2</sub> react with H<sub>2</sub> in the syngas to produce methanol in the presence of a commercial Cu–ZnO–Al<sub>2</sub>O<sub>3</sub> catalyst (R2), following the Langmuir–Hinshelwood type kinetic model by Vanden Bussche and Froment (eq 1).<sup>34</sup> R2, modeled as an RPLUG, operates at 50 bar with a temperature gradient going from 220 to 280 °C.<sup>20</sup>



The outlet of R2 is a mixture of methanol, water, and unreacted syngas, that is cooled down to 40 °C (C2) before entering a flash drum (F1), which separates syngas (vapor phase) from the liquid content at high pressure (48.9 bar). The vapor stream leaving F1 is split into a recycle stream, recompressed to 50 bar (K2) before re-entering R2, and a purge (1.3%), used for energy generation via oxy-fuel combustion (R3). R3 is modeled as an RGIBBS reactor and operates at 1.5 bar and 1300 °C.<sup>35</sup> The resulting stream has a high CO<sub>2</sub> content. It is cooled down to 40 °C (C5) and the remaining water is flashed (F3). The pure CO<sub>2</sub> vapor stream (97.4 mol %) is compressed to storage conditions (40 °C, 150 bar) in four steps with intercooling (K4 and C6).

The liquid stream leaving F1 contains traces of syngas and undergoes a second flash (F2) at 1.1 bar. The recovered syngas is recompressed to 50 bar (K3) and recirculated to R2. Analogously, the water/methanol liquid mixture is heated to 80 °C (H3), and fed to the distillation column (D1), modeled with the RadFrac model, which separates methanol with a 99.8 mol % purity.

**Methanol-to-Olefins (MTO) and BAU Processes.** Methanol leaving the afore-described process is fed to MTO, where ethylene is generated. Mass and energy flows for MTO were obtained from

Ioannou et al.,<sup>24</sup> and used to perform the techno-economic and environmental assessment of the WMO section of CPR. The high-TRL process deploys SAPO-34 to dehydrate methanol into light olefins, producing ethylene and propylene in a 1.52 ratio. To date, MTO has been successfully scaled and implemented industrially, enabling large-scale production of olefins from synthetic methanol.<sup>36</sup> It is currently implemented in China with methanol from coal as its primary feedstock, and four main technologies are available for commercial implementation.<sup>37</sup> The variety of technologies available for MTO provides a greater flexibility to the process to meet future olefins demand, as the catalyst of choice determines the ratio of ethylene/propylene.<sup>38</sup> Additionally, MTO offers the possibility of producing environmentally appealing building blocks for the chemical industry, when coupled to low-carbon methanol sources.<sup>39</sup> We here aim at closing the polymer loop via WMO, in contrast with BAU ethylene.

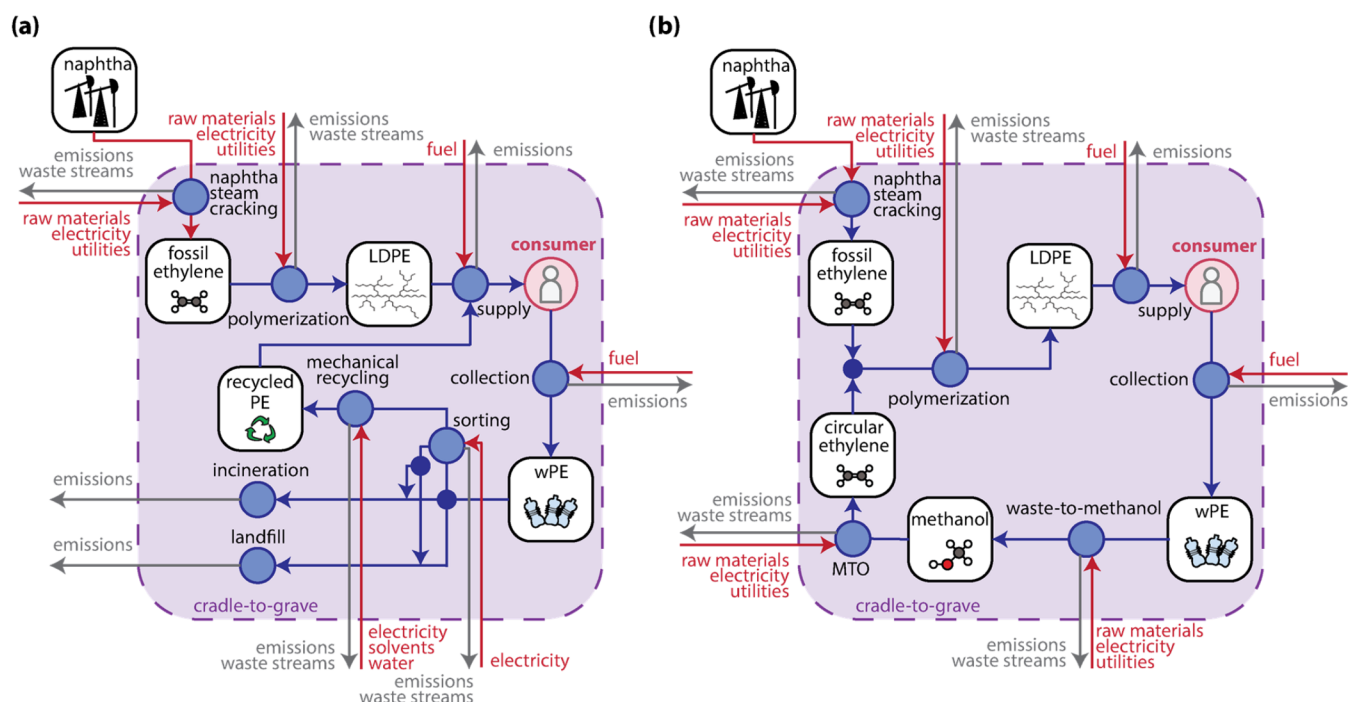
The latter is a fossil route, deploying prominent refinery products as feedstock, i.e., naphtha, LPG, and ethane, typically obtained from coal tar or crude oil.<sup>32,40</sup> In the steam cracking process, fossil feedstock and steam are fed to a furnace and heated to around 850 °C, thus requiring high heat inputs (6 MJ kg<sup>-1</sup> ethylene).<sup>41</sup> Operating the cracker with lighter hydrocarbons (i.e., naphtha, LPG, or ethane) results in light alkenes (i.e., ethylene, propylene, and butadiene), whereas heavier hydrocarbons generate aromatics and longer carbon chains, generally used for liquid fuel production.<sup>41</sup> Here we deploy naphtha steam cracking as BAU technology for ethylene production.

**Techno-Economic and Feasibility Assessment.** A techno-economic assessment was carried out to determine the production cost of the proposed ethylene technology. For this purpose, we first computed the total annual cost (TAC) of our waste-to-methanol process, and coupled it to MTO, to compare the cost of circular ethylene to that of fossil and green ethylene. The TAC was calculated following the approach described by Sinnott and Towler eq 2, considering the annual capital cost (ACC), and the fixed and variable operating costs (FOC and VOC respectively).<sup>42</sup>

$$\text{TAC} = \text{ACC} + \text{FOC} + \text{VOC} \quad (2)$$

The capital expenditures (CAPEX) were calculated using cost correlations from Martelli et al.<sup>43</sup> for the gasifier and Sinnott and Towler for the other equipment.<sup>42</sup> ACC was derived from the CAPEX considering a plant lifetime of 25 years and an interest rate of 10%. The operational expenditures (OPEX) correspond to the sum of FOC and VOC. The FOC consists of costs related to labor, taxes, insurance, maintenance, land, and plant overheads, thus being a function of the CAPEX. It is calculated following the approach described by Sinnott and Towler.<sup>42</sup> All remaining operation costs, i.e., the purchase of raw materials, electricity, and utilities are included in





**Figure 2.** Scenarios for the LCA of (a) LPR and (b) CPR deploying solely the WMO recycling route (waste-to-methanol + MTO) as an end-of-life alternative. The dashed line corresponds to the system boundaries, enabling exchanges with the global market (background system) for mass and energy flows.

the VOC. Tables S13 and S14 contain the data used in the OPEX and CAPEX calculations. All costs of the economic assessment are expressed in USD 2022 and were adjusted with the Chemical Engineering process cost index (CEPCI) whenever needed.

**Life Cycle Assessment (LCA).** An attributional LCA was carried out following the ISO14040/14044 framework.<sup>44,45</sup> First, we define the scope of the LCA whose main objective is to assess CPR's GWI-reduction potential compared to the current LPR scenario in 2020 and 2050. Additionally, we aim to investigate potential burden-shifting across 15 additional impact categories. The analysis follows a cradle-to-grave approach, taking into account all life-cycle stages needed to produce and treat the subsequent waste of one kilogram of LDPE for consumption.

In the second phase of the LCA, the life cycle inventories (LCI) of the foreground system (i.e., all the inputs and outputs of energy, natural resources, and emissions associated with the relevant processes) were generated in Brightway2 v2.4.3 as global averages using background data from ecoinvent v3.8.<sup>46,47</sup> The LCIs were defined by combining simulation data with literature and background data. Assumptions made for LCI modeling are described in section 2 of the Supporting Information. As shown in Figure 2, LPR deploys BAU ethylene and the global average end-of-life strategies for polymers (i.e., 19.5% is recycled, 25.5% incinerated, and 55% landfilled).<sup>2</sup> In contrast, CPR deploys WMO, hence avoiding the treatment of WPE through other means while producing ethylene that partly substitutes fossil virgin feedstock. A detailed description of the scenarios in Figure 2 is provided in the Supporting Information, with the LCI data sets (Tables S1–S10).

As a third LCA step, we calculate the life-cycle GHG emissions of LPR and CPR according to the IPCC 2021 GWP100 method, which accounts for the global warming potential of GHGs, short-lived climate forces, H<sub>2</sub>, and biogenic CO<sub>2</sub> during the 100 years after their release to the atmosphere. We apply this method for both scenarios in 2020 and 2050, to further assess their emission-reduction potential. For 2020, the data sets were linked to ecoinvent v3.8, whereas for 2050, a prospective database was used as the background system. We used the premise v1.6.7 framework<sup>59</sup> to align the LCIs in the ecoinvent database with the output data of the REMIND v2.1.0 integrated assessment model (IAM) for the year 2050 following the

“middle of the road” shared socio-economic pathway (SSP) and the SSP2-PkBudg500 scenario, which estimates a remaining carbon budget from 2020 to 2100 of 500 Gt CO<sub>2</sub> with a 50% likelihood of limiting global warming to 1.5 °C.<sup>48,49</sup> This scenario estimates that the net global CO<sub>2</sub> emissions will go from 40.9 Gt y<sup>-1</sup> in 2020 to 1.1 Gt y<sup>-1</sup> in 2050.

The interpretation of results is the last phase of the LCA and is carried out iteratively with the three previous steps. Here, we interpret the results, concluding on the emission-reduction potential of the proposed CPR scenario. Moreover, to identify potential burden-shifting, we assess the EIs of LPR and CPR on the remaining 15 categories (additionally to global warming) of the environmental footprint (EF) 3.1 method recommended by the European Commission for product LCA i.e., acidification, freshwater ecotoxicity, fossil resources use, eutrophication (freshwater, marine, and terrestrial), human toxicity (carcinogenic and noncarcinogenic), ionizing radiation, land use, metal/mineral resources use, ozone depletion, particulate matter formation, photochemical oxidant formation, and water use.<sup>50</sup>

An uncertainty assessment of the 2020 scenarios was made with a Monte Carlo sampling for 500 different backgrounds, stochastically generated from the ecoinvent Pedigree matrix, which contains information on the uncertainty level of LCI parameters, estimated based on temporal and spatial approximations.<sup>51–53</sup> An analogous assessment could not be performed for the year 2050, due to the lack of uncertainty data for this year and the absence of an analogous Pedigree matrix in the premise database. Assumptions and limitations of this approach are described in section 2 of the Supporting Information.

For each generated background (i) and foreground system (s), and each impact category (c) of EF 3.1 (C), the environmental impact (EI<sub>c,s,i</sub>) was calculated. The paired comparison (P<sub>ci</sub>) was computed as the relative difference between the impact of CPR and LPR eq 3.

$$P_{ci} = \frac{EI_{c,CPR,i} - EI_{c,LPR,i}}{EI_{c,LPR,i}} \quad \forall (i \in I \text{ and } c \in C) \quad (3)$$

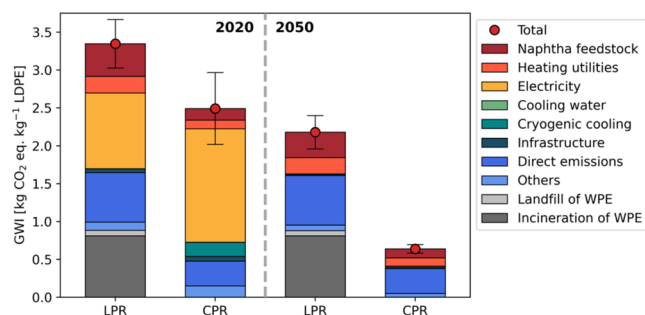
As an example, a score of P<sub>ci</sub> = 75% corresponds to a 75% likelihood of CPR having a higher impact than LPR on category (c).<sup>54</sup>

Here, we consider that  $P_{ci} > 75\%$  indicates a high likelihood of burden-shifting, and  $P_{ci} \leq 25\%$  a high likelihood of impact reduction.

## RESULTS AND DISCUSSION

The results are presented and discussed in three subsections. First, we assess the GWI of LPR and CPR in 2020 and 2050, providing insights into the benefits of deploying CPR. Then, we compare both routes in 2020 based on the 16 impact categories of the EF 3.1 method, to identify eventual burden-shifting. Finally, we assess the economic feasibility of deploying WMO as an alternative to BAU ethylene to produce LDPE.

**Global Warming Impacts (GWI).** Figure 3 depicts the breakdown of the main life-cycle GHG emissions contributors



**Figure 3.** Global warming impact of the LPR and CPR scenarios in 2020 and 2050. Breakdown of main contributors to the total life-cycle GHG emissions. Acronyms used: LPR: linear production route; CPR: circular production route; GWI: global warming impact; WPE: waste polyethylene.

of both scenarios in 2020 and 2050. In 2020, closing the loop with CPR resulted in a 25.5% GWI reduction from LPR, going from 3.35 to 2.49 kg CO<sub>2</sub> eq kg<sup>-1</sup> LDPE. Different by design, CPR deploys technologies that make use of both the carbon and hydrogen content of WPE to generate new LDPE, which is reinserted into the economy, instead of generating incineration emissions.

The breakdown of impacts showcases that electricity is the main GWI contributor to both LPR (29.8%) and CPR (60.1%) in 2020, as all processes considered in LDPE's life cycle deploy electricity (Figure S1b), namely the ones requiring high-pressure conditions. For instance, olefins separation is carried out at 30 bar in naphtha steam cracking and MTO,<sup>24,32</sup> the conventional high-pressure polymerization process takes place at 15 to 35 bar,<sup>55</sup> waste-to-methanol requires 50 bar and mechanical recycling deploys electricity in the shredding and extruding steps.<sup>56</sup> Moreover, the global 2020 electricity grid relies mainly on fossil feedstock (i.e., 36% coal and 23% natural gas),<sup>57</sup> and has a high carbon intensity (0.68 kg CO<sub>2</sub> eq kWh<sup>-1</sup>).<sup>58</sup> However, to meet the 1.5 °C climate target of the IPCC, the REMIND IAM estimates that the global electricity mix in 2050 will mainly consist of renewables i.e., solar photovoltaic cells (52.7%), onshore wind (25.2%), hydropower (9.1%), offshore wind (6.2%), and nuclear power (4.8%), with fossil fuels accounting for only 0.1%.<sup>48,59</sup> Consequently, GHG emissions from electricity generation are expected to decline to  $5.1 \times 10^{-3}$  kg CO<sub>2</sub> eq kWh<sup>-1</sup>, leading to a significant drop in both scenarios' GWI by 2050: LPR's drops to 2.18 kg CO<sub>2</sub> eq kg<sup>-1</sup> LDPE (35% reduction from 2020), and CPR's to 0.64 kg CO<sub>2</sub> eq kg<sup>-1</sup> LDPE (74% reduction from 2020). Hence, deploying low-carbon power mixes enables a significant

decarbonization of the polymers sector. Life-cycle processes that contribute to LPR and CPR's GWI in both years are shown in Figures S2–S5.

Another key contributor to LPR's GWI in 2020 is end-of-life emissions of WPE incineration (24.3%). These are inexistent in the CPR scenario, which deploys WMO as the sole end-of-life alternative. It is worth noting that LPR assumes the same landfilling, incineration, and recycling rates in 2020 and 2050.

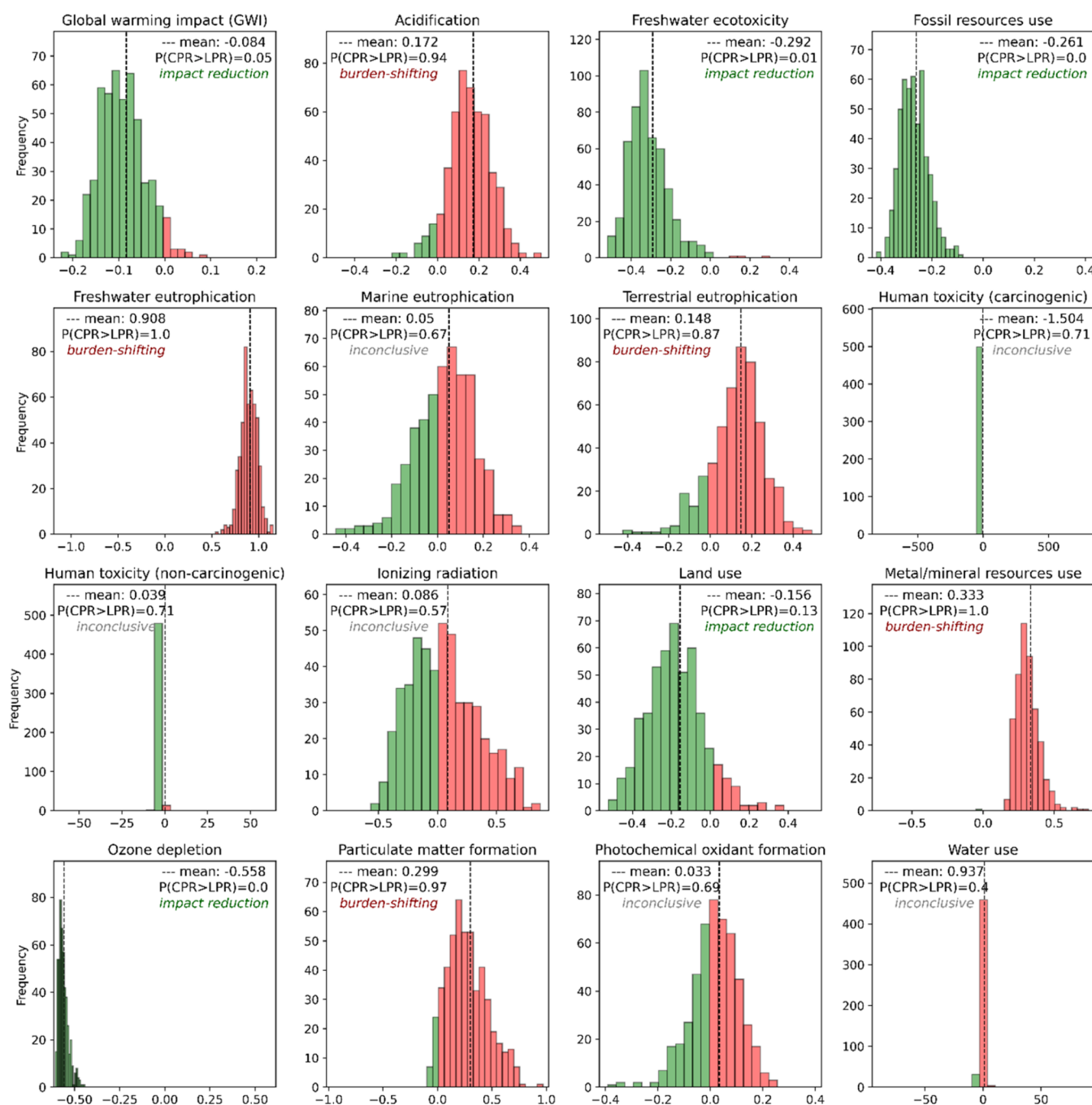
Analogously, direct emissions of LPR and CPR show no reduction potential by 2050. In both cases, the emissions come mainly from naphtha steam cracking (Figure S1a), which is used to produce 100% of LPR's ethylene, and the 30.3% fossil ethylene makeup in CPR (Figure 2b). Deploying a fossil ethylene makeup in CPR also implies that emissions linked to the naphtha feedstock are present in the life cycle of circular polymers (Figure 3), though 64.3% less than in LPR. The GWI of the remaining life-cycle processes sees little to no change in both scenarios when transitioning from 2020 to 2050.

In essence, CPR has a higher decarbonization potential than LPR considering future footprints adjusted based on low-carbon power mixes. Shifting from LPR to CPR deploying WMO increases LDPE's reliance on electricity and reduces direct emissions linked to LDPE production and end-of-life, thus enabling a 25.5% GWI decrease in 2020, and 70.6% in 2050, with decarbonized power mixes. This result is consistent with the work by Bachmann et al., who estimate a 50% GHG reduction in the plastics' life cycle by 2050, considering a 70% polymers recycling rate via mechanical recycling and pyrolysis-to-monomers.<sup>30</sup>

**Burden-Shifting to Other Environmental Impact (EI) Categories.** The EIs of both scenarios were calculated for the 16 indicators of the EF 3.1 method and the 500 sampled backgrounds in 2020. The distribution of the relative difference between the EI of CPR and LPR for each impact category is shown in Figure 4.

The first subplot of Figure 4 reiterates the previous observations on GWI (Figure 3): switching from LPR to CPR in 2020 shows a 95% likelihood of lowering LDPE's life-cycle emissions. Four other indicators, i.e., freshwater ecotoxicity (99%), fossil resources use (100%), land use (87%), and ozone depletion (100%), also show a high likelihood of impact reduction when deploying CPR instead of LPR. Indeed, these four categories are heavily affected by naphtha production, notably by the onshore extraction of fossil fuels, which uses land to create wells<sup>60</sup> (Figure S7), and involves refinery operations that generate a significant amount of water discharge,<sup>60</sup> affecting freshwater toxicity (Figure S6). Moreover, petroleum extraction by definition depletes fossil resources, and the process emits ozone-depleting substances<sup>60</sup> (Figures S8 and S9).

Furthermore, although CPR showcases environmental benefits compared to LPR, burden-shifting is observed in five categories, for which the probability of  $EI_{CPR} > EI_{LPR}$  is high in the sampled backgrounds; i.e., acidification (94%), freshwater eutrophication (100%), terrestrial eutrophication (87%), metal/mineral resources use (100%), and particulate matter formation (97%). For four out of five categories (i.e., excluding metal/mineral resources use), electricity is the main impact driver (Figures S10–S13). Indeed, the current global electricity mix strongly relies on coal (36%),<sup>57</sup> which when combusted for power generation releases pollutants such as NO<sub>x</sub>, SO<sub>x</sub>, and particulate matter, creating a toll on ecosystems.<sup>61,62</sup> For instance, acidification is measured as the



**Figure 4.** Probability of burden-shifting ( $\text{CPR} > \text{LPR}$ ) in 2020 across the 16 impact categories of the EF 3.1 methods recommended by the European Commission for product LCA. Acronyms used: CPR: circular production route; LPR: linear production route. Green bars correspond to cases where the environmental footprint of CPR is lower than the LPR; red bars correspond to cases where the environmental footprint of CPR is higher than the LPR. Burden-shifting is observed when  $P(\text{CPR} > \text{LPR}) \geq 0.75$ ; impact reduction is observed when  $P(\text{CPR} > \text{LPR}) < 0.25$ .

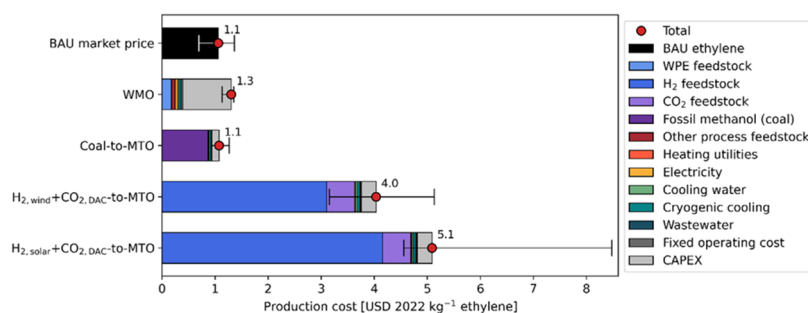
concentration of  $\text{H}^+$  ions in soil and lakes as a result of  $\text{NO}_x$ ,  $\text{SO}_x$ , and  $\text{NH}_3$  emissions, while eutrophication is measured as  $\text{O}_2$  depletion caused by nitrogen and phosphorus nutrients.<sup>50</sup> Therefore, the significant electricity dependency of CPR compared to LPR translates into higher impacts on the four categories in 2020. These observations are subject to change in a future with a defossilized electricity grid, relying on renewables. Moreover, uncertainties of the foreground systems were not quantified in this study, and are therefore not taken into account in the burden-shifting assessment. This represents a limitation of the current work since parameters of BAU

technologies are likely to have lower uncertainty compared to new technologies.

For the six remaining categories (i.e., marine eutrophication, human toxicity (carcinogenic and noncarcinogenic), ionizing radiation, photochemical oxidant formation, and water use), no conclusion could be drawn on burden-shifting nor impact reduction according to our criterion since the probability of  $\text{EI}_{\text{CPR}} > \text{EI}_{\text{LPR}}$  was found to be between 25 and 75%.

Lastly, to complement the analysis on the best-performing route from an environmental viewpoint, we calculated the single overall score of LPR and CPR in both years, following





**Figure 5.** Total annual cost (TAC) breakdown of different ethylene production routes. All costs were calculated to 2022 prices, or adjusted using the CEPCL. The BAU market price was taken from the literature,<sup>64</sup> based on naphtha steam cracking; WMO corresponds to the production cost of the chemical recycling route here proposed; Coal-to-MTO corresponds to methanol obtained via coal gasification, here estimated assuming the methanol market price in China; H<sub>2,wind</sub> + CO<sub>2,DAC</sub>-to-MTO corresponds to green methanol obtained from electrolytic H<sub>2</sub> powered by wind and CO<sub>2</sub> from DAC, following González-Garay et al.,<sup>20</sup> coupled to MTO; H<sub>2,solar</sub> + CO<sub>2,DAC</sub>-to-MTO is an analogous route to the latter, deploying H<sub>2</sub> from electrolysis powered by photovoltaic panels. Acronyms used: BAU: business-as-usual; WMO: waste-to-methanol-to-olefins; MTO: methanol-to-olefins; WPE: waste polyethylene, CAPEX: capital expenditures; DAC: direct air capture. The error bars correspond to the TAC calculated respectively with the minimum and maximum prices of raw materials (WPE, H<sub>2</sub>, CO<sub>2</sub>, and fossil methanol) indicated in Table S13.

the European Commission recommendations for the EF 3.1 method.<sup>50,63</sup> The characterized EIs on the 16 impact categories of EF 3.1 (Table S11) were normalized and weighted with the factors listed by Bassi et al.<sup>63</sup> (Table S12). The weighted sum of EIs issued an overall score of  $2.91 \times 10^{-4}$  person eq kg<sup>-1</sup> LDPE for LPR, and  $2.42 \times 10^{-4}$  person eq kg<sup>-1</sup> LDPE for CPR in 2020. In 2050, the scores were respectively  $2.17 \times 10^{-4}$  person eq kg<sup>-1</sup> LDPE for LPR, and  $1.19 \times 10^{-4}$  person eq kg<sup>-1</sup> LDPE for CPR. These results indicate that CPR has a better overall environmental potential than LPR both in 2020 (16.8%) and 2050 (45.1%), also showing a bigger potential for improvement in a future with decarbonized energy mixes. CPR's overall score sees a 50.7% decrease from 2020 to 2050 whereas LPR's score decreases by 25.4% in the same time horizon. Further details on the single score calculations are found in Section 3 of the Supporting Information.

**Techno-Economic Assessment and Feasibility of WMO.** The TAC of ethylene obtained via WMO was estimated at 1.3 USD 2022 kg<sup>-1</sup> ethylene, only 23% higher than the average market price of ethylene in 2022 (1.1 USD kg<sup>-1</sup> ethylene).<sup>64</sup> The focus of this work is to assess the feasibility of chemical recycling via WMO, which seems appealing from both an environmental and economic perspective. However, to put the technology's cost into perspective, additional scenarios were added to the economic assessment, to enable a comparison of the circular route with its fossil and green analogs (Figure 5). Thus, the costs of MTO from coal-based and green ethylene were also calculated. Methanol from coal was assumed to be the market technology in China,<sup>36</sup> for which the corresponding average market price in 2022 was 0.36 USD kg<sup>-1</sup> methanol.<sup>65</sup> In counterpart, green methanol was obtained from electrolytic H<sub>2</sub> powered by wind and solar energy, as well as CO<sub>2</sub> from direct air capture (DAC), as described by González-Garay et al.<sup>20</sup> Cost parameters used to estimate the respective TACs are summarized in Tables S13 and S14. Although more expensive than the BAU and coal-based technologies (1.1 USD kg<sup>-1</sup> ethylene), ethylene from plastics is much cheaper than the green analogs H<sub>2,wind</sub> + CO<sub>2,DAC</sub>-to-MTO (4.0 USD kg<sup>-1</sup> ethylene) and H<sub>2,solar</sub> + CO<sub>2,DAC</sub>-to-MTO (5.1 USD kg<sup>-1</sup> ethylene). Moreover, it can become competitive with the BAU technology in periods of high market variability, linked to

social-economic contexts<sup>66</sup> (e.g., April 2022, when the ethylene price peaked at 1.34 USD kg<sup>-1</sup>).<sup>67</sup>

The main contributor to the WMO cost is the annualized CAPEX (70%), specifically the cost of compressors used in the waste-to-methanol process (53.5% of the total CAPEX; Figure S15). Indeed, the process requires large compressors to bring syngas from 1.5 to 50 bar (K1 in Figure 2), and to set CO<sub>2</sub> to geological storage conditions (i.e., 150 bar; K4 in Figure 2).<sup>68</sup> These compression steps are not as prominent in the green olefins routes, where CO<sub>2</sub> storage is not deployed and H<sub>2</sub> is supplied at 30 bar, thus requiring smaller compressors and less electricity to bring H<sub>2</sub> and CO<sub>2</sub> to reaction conditions (50 bar). Moreover, the plant sizes considered for the different methanol routes deployed in MTO are not comparable to the waste-to-methanol plant, which is designed to withhold a plastic flow rate that corresponds to the average hourly plastic waste generation in big cities (i.e., London),<sup>16</sup> thus having a low capacity of 49.4 kt methanol year<sup>-1</sup>. Therefore, following an economy of scale with a centralized methanol production from plastics, and increased plant capacities, the overall CAPEX of the WMO process would need a 27% reduction to become competitive with the global ethylene average market price (Figure S16).

Unlike the green MTO scenarios, i.e., H<sub>2,wind</sub> + CO<sub>2,DAC</sub>-to-MTO, and H<sub>2,solar</sub> + CO<sub>2,DAC</sub>-to-MTO, the cost of waste-based ethylene is CAPEX-driven. Indeed, WPE feedstock only accounts for 13.5% of the WMO TAC, whereas H<sub>2</sub> and CO<sub>2</sub> combined account for 89.9% and 92.0% of the green routes' TAC, respectively for H<sub>2,wind</sub> and H<sub>2,solar</sub>. Therefore, deciding to place the WMO plant in locations with low to null waste cost, could further decrease ethylene's TAC to 1.1 USD kg<sup>-1</sup> ethylene if WPE is free, thus becoming competitive with the ethylene market price. Hence, the WMO route could become a viable option for polymer production in a circular economy. Moreover, since ethylene is the biggest contributor to the LDPE cost (70.5 to 77.5% of the total cost),<sup>55</sup> deploying more expensive monomers could drastically increase polymers' costs.

## CONCLUSIONS

In this work, we modeled a waste-to-methanol process, which we coupled to the well-implemented methanol-to-olefins (MTO) to close the loop on plastics. We compared the circular approach for LDPE, CPR, to the linear model, LPR,

which deploys fossil feedstock to produce olefins (via naphtha steam cracking), and a mostly linear end-of-life for waste polymers, mainly consisting of landfilling and incineration.

We found that implementing the proposed CPR in the following years can reduce GHG emissions from the plastics sector even without any changes in the electricity mix. By deploying WMO, we shift from a high-emitting plastics economy with direct emissions from polymer production and incineration, to a low-emissions chemical recycling option, which heavily depends on electricity. This shift enables a high decarbonization potential, specifically in a future with low-carbon power grids, based on renewables. Moreover, reducing life-cycle emissions via WMO leads to a high likelihood (>90%) of decreasing impacts on four other environmental indicators, i.e., freshwater ecotoxicity, ozone depletion, and land and fossil resources use, as CPR has a lower dependency on naphtha and thus requires less fossil feedstock and refinery operations. Nevertheless, burden-shifting is observed for terrestrial and freshwater eutrophication, particulate matter formation, acidification, and metal/mineral resources, where impacts could increase compared to LPR.

Additionally, adopting CPR issues an ethylene cost of 1.3 USD 2022 kg<sup>-1</sup> ethylene, only 23% higher than the global 2022 ethylene market price and significantly cheaper than green ethylene from solar- and wind-based H<sub>2</sub>. Moreover, the cost of chemical recycling via WMO is dominated by CAPEX (70%), which could be reduced by deploying bigger plants in a centralized economy with large-scale chemical recycling. Indeed, a 27% CAPEX reduction is enough to be competitive with the 2022 ethylene market price. Furthermore, implementing WMO in regions with cheaper or free WPE could further contribute to achieving competitive costs, thus highlighting CPR's economic appeal.

In summary, this work demonstrates the economic and global warming benefits of deploying WMO to close the loop on polymers. The herein assessed process comprises a short-term solution to impact plastic circularity until other chemical recycling approaches reach maturity. It enables a faster decarbonization of the polymers sector in a future with low-carbon power mixes at economically appealing costs. Here, increasing circularity goes hand-in-hand with decarbonizing plastics. Thus, adopting low-carbon policies that limit the use and exploitation of fossil resources, apply stricter emission targets, and incentivize recycling can drastically change the current plastics scene. Moreover, thoroughly regulating waste management and virgin material production routes is critical to building a low-carbon plastics economy.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.4c04241>.

List of acronyms employed in the text, information on the main data used in the LCA and economic assessments, a brief description of the assumptions and limitations of the current work (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

Gonzalo Guillén-Gosalbez – Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zürich, 8093 Zürich, Switzerland;

[orcid.org/0000-0001-6074-8473](https://orcid.org/0000-0001-6074-8473);

Email: [gonzalo.guillen.gosalbez@chem.ethz.ch](mailto:gonzalo.guillen.gosalbez@chem.ethz.ch)

### Authors

Cecilia Salah – Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zürich, 8093 Zürich, Switzerland; [orcid.org/0000-0002-3376-706X](https://orcid.org/0000-0002-3376-706X)

Robert Istrate – Institute of Environmental Sciences (CML), Leiden University, 2333 CC Leiden, The Netherlands

Anders Bjørn – Center for Absolute Sustainability, Department of Environmental and Resource Engineering, Technical University of Denmark, 2800 Kongens Lyngby, Denmark; [orcid.org/0000-0001-9332-5346](https://orcid.org/0000-0001-9332-5346)

Victor Tulus – Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zürich, 8093 Zürich, Switzerland

Javier Pérez-Ramírez – Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zürich, 8093 Zürich, Switzerland; [orcid.org/0000-0002-5805-7355](https://orcid.org/0000-0002-5805-7355)

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acssuschemeng.4c04241>

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This publication was created as part of NCCR Catalysis (grant 180544), a National Centre of Competence in Research funded by the Swiss National Science Foundation.

## ■ REFERENCES

- (1) Stegmann, P.; Daioglou, V.; Londo, M.; van Vuuren, D. P.; Junginger, M. Plastic Futures and Their CO<sub>2</sub> Emissions. *Nature* **2022**, *612* (7939), 272–276.
- (2) Geyer, R.; Jambeck, J. R.; Law, K. L. Production, Use, and Fate of All Plastics Ever Made. *Sci. Adv.* **2017**, *3* (7), No. e1700782.
- (3) Jambeck, J. R.; Geyer, R.; Wilcox, C.; Siegler, T. R.; Perryman, M.; Andrady, A.; Narayan, R.; Law, K. L. Plastic Waste Inputs from Land into the Ocean. *Science* **2015**, *347* (6223), 768–771.
- (4) Ellen MacArthur Foundation; McKinsey & Company New Plastics Economy—Rethinking the Future of Plastics, 2016. <https://ellenmacarthurfoundation.org/the-new-plastics-economy-rethinking-the-future-of-plastics>. (accessed August 09, 2024).
- (5) Falcke, H.; Holbrook, S.; Clenahan, I.; Carretero, A. L.; Sanalan, T.; Brinkmann, T.; Roth, J.; Zenger, B.; Roudier, S.; Sancho, L. D. Best Available Techniques (BAT) Reference Document for the Production of Large Volume Organic Chemicals Abstract, 2017.
- (6) Ren, T.; Patel, M.; Blok, K. Olefins from Conventional and Heavy Feedstocks: Energy Use in Steam Cracking and Alternative Processes. *Energy* **2006**, *31* (4), 425–451.
- (7) Amghizar, I.; Vandewalle, L. A.; Van Geem, K. M.; Marin, G. B. New Trends in Olefin Production. *Engineering* **2017**, *3* (2), 171–178.
- (8) Tiggeloven, J. L.; Faaij, A. P. C.; Kramer, G. J.; Gazzani, M. Optimization of Electric Ethylene Production: Exploring the Role of Cracker Flexibility, Batteries, and Renewable Energy Integration. *Ind. Eng. Chem. Res.* **2023**, *62*, 16360–16382.
- (9) OECD Global Plastics Outlook—Plastics Waste by Region and End-of-Life Fate, 2023 <https://ourworldindata.org/grapher/plastic-fate>. (accessed August 09, 2024).
- (10) Klotz, M.; Haupt, M.; Hellweg, S. Limited Utilization Options for Secondary Plastics May Restrict Their Circularity. *Waste Manage.* **2022**, *141*, 251–270.
- (11) OECD Improving Markets for Recycled Plastics - Trends, Prospects, and Policy Responses; OECD Library, 2018.



- (12) Lebreton, L.; Andrady, A. Future Scenarios of Global Plastic Waste Generation and Disposal. *Palgrave Commun.* **2019**, *5* (1), No. 6.
- (13) Istrate, I. R.; Galvez-Martos, J. L.; Vázquez, D.; Guillén-Gosálbez, G.; Dufour, J. Prospective Analysis of the Optimal Capacity, Economics and Carbon Footprint of Energy Recovery from Municipal Solid Waste Incineration. *Resour. Conserv. Recycl.* **2023**, *193*, No. 106943.
- (14) Schwarz, A. E.; Lighthart, T. N.; Bizarro, D. G.; De Wild, P.; Vreugdenhil, B.; van Harmelen, T. Plastic Recycling in a Circular Economy; Determining Environmental Performance through an LCA Matrix Model Approach. *Waste Manage.* **2021**, *121*, 331–342.
- (15) van der Hulst, M. K.; Ottenbros, A. B.; van der Drift, B.; Ferjan, S.; van Harmelen, T.; Schwarz, A. E.; Worrell, E.; van Zelm, R.; Huijbregts, M. A. J.; Hauck, M. Greenhouse Gas Benefits from Direct Chemical Recycling of Mixed Plastic Waste. *Resour. Conserv. Recycl.* **2022**, *186*, No. 106582.
- (16) Salah, C.; Cobo, S.; Pérez-Ramírez, J.; Guillén-Gosálbez, G. Environmental Sustainability Assessment of Hydrogen from Waste Polymers. *ACS Sustainable Chem. Eng.* **2023**, *11* (8), 3238–3247.
- (17) Klotz, M.; Oberschelp, C.; Salah, C.; Subal, L.; Hellweg, S. The Role of Chemical and Solvent-Based Recycling within a Sustainable Circular Economy for Plastics. *Sci. Total Environ.* **2024**, *906*, No. 167586.
- (18) Somoza-Tornos, A.; Gonzalez-Garay, A.; Pozo, C.; Graells, M.; Espuña, A.; Guillén-Gosálbez, G. Realizing the Potential High Benefits of Circular Economy in the Chemical Industry: Ethylene Monomer Recovery via Polyethylene Pyrolysis. *ACS Sustainable Chem. Eng.* **2020**, *8* (9), 3561–3572.
- (19) Galán-Martín, A.; Tulus, V.; Díaz, I.; Pozo, C.; Pérez-Ramírez, J.; Guillén-Gosálbez, G. Sustainability Footprints of a Renewable Carbon Transition for the Petrochemical Sector within Planetary Boundaries. *One Earth* **2021**, *4* (4), 565–583.
- (20) González-Garay, A.; Frei, M. S.; Al-Qahtani, A.; Mondelli, C.; Guillén-Gosálbez, G.; Pérez-Ramírez, J. Plant-to-Planet Analysis of CO<sub>2</sub>-Based Methanol Processes. *Energy Environ. Sci.* **2019**, *12* (12), 3425–3436.
- (21) Pérez-Fortes, M.; Schöneberger, J. C.; Boulamanti, A.; Tzimas, E. Methanol Synthesis Using Captured CO<sub>2</sub> as Raw Material: Techno-Economic and Environmental Assessment. *Appl. Energy* **2016**, *161*, 718–732.
- (22) Kaiser, S.; Siems, F.; Mostert, C.; Bringezu, S. Environmental and Economic Performance of CO<sub>2</sub>-Based Methanol Production Using Long-Distance Transport for H<sub>2</sub> in Combination with CO<sub>2</sub> Point Sources: A Case Study for Germany. *Energies* **2022**, *15* (7), No. 2507.
- (23) Prifti, K.; Lechtenberg, F.; Manenti, F.; Espuña, A.; Graells, M. Comparing the Climate Impact of Methanol Production in Europe: Steam Methane Reforming vs. Plastic Waste Gasification Processes. *Resour. Conserv. Recycl.* **2024**, *208*, No. 107653.
- (24) Ioannou, I.; Javaloyes-Antón, J.; Caballero, J. A.; Guillén-Gosálbez, G. Economic and Environmental Performance of an Integrated CO<sub>2</sub> Refinery. *ACS Sustainable Chem. Eng.* **2023**, *11*, 1949–1961.
- (25) Negri, V.; Charalambous, M. A.; Medrano-García, J. D.; Guillén-Gosálbez, G. Navigating within the Safe Operating Space with Carbon Capture On-Board. *ACS Sustainable Chem. Eng.* **2022**, *10* (51), 17134–17142.
- (26) Adrianto, L. R.; van der Hulst, M. K.; Tokaya, J. P.; Arvidsson, R.; Blanco, C. F.; Caldeira, C.; Guillén-Gosálbez, G.; Sala, S.; Steubing, B.; Buyle, M.; Kaddoura, M.; Navarre, N. H.; Pedneault, J.; Pizzol, M.; Salieri, B.; van Harmelen, T.; Hauck, M. How Can LCA Include Prospective Elements to Assess Emerging Technologies and System Transitions? The 76th LCA Discussion Forum on Life Cycle Assessment, 19 November 2020. *Int. J. Life Cycle Assess.* **2021**, *26* (8), 1541–1544.
- (27) Bruhn, S.; Sacchi, R.; Cimpan, C.; Birkved, M. Ten Questions Concerning Prospective LCA for Decision Support for the Built Environment. *Build. Environ.* **2023**, *242*, No. 110535.
- (28) Nabera, A.; Martín, A. J.; Istrate, R.; Pérez-Ramírez, J.; Guillén-Gosálbez, G. Integrating Climate Policies in the Sustainability Analysis of Green Chemicals. *Green Chem.* **2024**, *26*, 6461–6469.
- (29) Beltran, A. M.; Cox, B.; Mutel, C.; van Vuuren, D. P.; Vivanco, D. F.; Deetman, S.; Edelenbosch, O. Y.; Guinée, J.; Tukker, A. When the Background Matters: Using Scenarios from Integrated Assessment Models in Prospective Life Cycle Assessment. *J. Ind. Ecol.* **2020**, *24* (1), 64–79.
- (30) Bachmann, M.; Zibunas, C.; Hartmann, J.; Tulus, V.; Suh, S.; Guillén-Gosálbez, G.; Bardow, A. Towards Circular Plastics within Planetary Boundaries. *Nat. Sustainability* **2023**, *6* (5), 599–610.
- (31) Meys, R.; Kästelhorn, A.; Bachmann, M.; Winter, B.; Zibunas, C.; Suh, S.; Bardow, A. Achieving Net-Zero Greenhouse Gas Emission Plastics by a Circular Carbon Economy. *Science* **2021**, *374*, 71–76.
- (32) Keller, F.; Soliz, P. M.; Seidl, L. G.; Lee, R. P.; Meyer, B. Life Cycle Inventory Data Generation by Process Simulation for Conventional, Feedstock Recycling and Power-to-X Technologies for Base Chemical Production. *Data Brief* **2022**, *41*, No. 107848.
- (33) Aspen Technology Inc. Physical Property Methods and Models 11. 1, 2001 <https://www.aspentech.com/en/products/engineering/aspen-plus>. (accessed August 09, 2024).
- (34) Bussche, K.; Froment, G. F. A Steady-State Kinetic Model for Methanol Synthesis and the Water Gas Shift Reaction on a Commercial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> Catalyst. *J. Catal.* **1996**, *161* (1), 1–10.
- (35) Susmozas, A. I.; BURJC-Digital Database. Analysis of Energy Systems Based on Biomass Gasification (Doctoral thesis Universidad Rey Juan Carlos) 2015 <https://burjcdigital.urjc.es/handle/10115/13599>. (accessed August 09, 2024).
- (36) Tian, P.; Wei, Y.; Ye, M.; Liu, Z. Methanol to Olefins (MTO): From Fundamentals to Commercialization. *ACS Catal.* **2015**, *5* (3), 1922–1938.
- (37) Gogate, M. R. Methanol-to-Olefins Process Technology: Current Status and Future Prospects. *Pet. Sci. Technol.* **2019**, *37* (5), 559–565.
- (38) Yang, M.; Fan, D.; Wei, Y.; Tian, P.; Liu, Z. Recent Progress in Methanol-to-Olefins (MTO) Catalysts. *Adv. Mater.* **2019**, *31* (50), No. 1902181.
- (39) Ioannou, I.; D'Angelo, S. C.; Martín, A. J.; Pérez-Ramírez, J.; Guillén-Gosálbez, G. Hybridization of Fossil- and CO<sub>2</sub>-Based Routes for Ethylene Production Using Renewable Energy. *ChemSusChem* **2020**, *13* (23), 6370–6380.
- (40) Collin, G.; Höke, H.; Greim, H. Naphthalene and Hydro-naphthalenes. In *Ullmann's Encyclopedia of Industrial Chemistry*; John Wiley & Sons, 2003.
- (41) Zimmermann, H.; Walzl, R. Ethylene. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA, 2012.
- (42) Sinnott, R.; Towler, G. Costing and Project Evaluation. In *Chemical Engineering Design*; Butterworth-Heinemann, 2020; pp 275–369.
- (43) Martelli, E.; Kreutz, T.; Consonni, S. Comparison of Coal IGCC with and without CO<sub>2</sub> Capture and Storage: Shell Gasification with Standard vs. Partial Water Quench. *Energy Procedia* **2009**, *1* (1), 607–614.
- (44) International Standards Organization (ISO) ISO 14044: Environmental Management—Life Cycle Assessment—Principles and Framework, 2006. <https://www.iso.org/standard/37456.html>. (accessed August 09, 2024).
- (45) International Standards Organization (ISO) ISO 14044: Environmental Management—Life Cycle Assessment—Requirements and Guidelines, 2006. <https://www.iso.org/standard/38498.html>. (accessed August 09, 2024).
- (46) Mutel, C. Brightway: An Open Source Framework for Life Cycle Assessment. *J. Open Source Software* **2017**, *2* (12), No. 236.
- (47) Wernet, G.; Bauer, C.; Steubing, B.; Reinhard, J.; Moreno-Ruiz, E.; Weidema, B. The Ecoinvent Database Version 3 (Part I): Overview and Methodology. *Int. J. Life Cycle Assess.* **2016**, *21* (9), 1218–1230.

- (48) Aboumahboub, T.; Auer, C.; Bauer, N.; Baumstark, L.; Bertram, C.; Bi, S.; Dietrich, J.; Dirnaichner, A.; Giannousakis, A.; Haller, M.; Hilaire, J.; Klein, D.; Koch, J.; Körner, A.; Kriegler, E.; Leimbach, M.; Levesque, A.; Lorenz, A.; Luderer, G.; Ludig, S.; Lüken, M.; Malik, A.; Manger, S.; Merfort, L.; Mouratiadou, I.; Pehl, M.; Pietzker, R.; Piontek, F.; Popin, L.; Rauner, S.; Rodrigues, R.; Roming, N.; Rottoli, M.; Schmidt, E.; Schreyer, F.; Schultes, A.; Sörgel, B.; Streifer, J.; Ueckerdt, F. REMIND—REgional Model of INvestments and Development, 2024 <https://rse.pik-potsdam.de/doc/remind/2.1.0/>. (accessed August 09, 2024).
- (49) Intergovernmental Panel on Climate Change *Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*; Masson-Delmotte, V.; Zhai, P.; Pirani, A.; Connors, S. L.; Péan, C.; Berger, S.; Caud, N.; Chen, Y.; Goldfarb, L.; Gomis, M. I.; Huang, M.; Leitzell, K.; Lonnoy, E.; Matthews, J. B. R.; Maycock, T. K.; Waterfield, T.; Yelekçi, O.; Yu, R.; Zhou, B., Eds.; Cambridge University Press: Cambridge, United Kingdom and New York, NY, USA, 2021.
- (50) European Commission Commission Recommendation on the Use of the Environmental Footprint Methods to Measure and Communicate the Life Cycle Environmental Performance of Products and Organisations; Brussels, 2021. [https://environment.ec.europa.eu/publications/recommendation-use-environmental-footprint-methods\\_en](https://environment.ec.europa.eu/publications/recommendation-use-environmental-footprint-methods_en). (accessed August 09, 2024).
- (51) Müller, S.; Lesage, P.; Ciroth, A.; Mutel, C.; Weidema, B. P.; Samson, R. The Application of the Pedigree Approach to the Distributions Foreseen in Ecoinvent V3. *Int. J. Life Cycle Assess.* **2016**, *21* (9), 1327–1337.
- (52) Groen, E. A.; Heijungs, R.; Bokkers, E. A. M.; de Boer, I. J. M. Methods for Uncertainty Propagation in Life Cycle Assessment. *Environ. Modell. Software* **2014**, *62*, 316–325.
- (53) Michiels, F.; Geeraerd, A. Two-Dimensional Monte Carlo Simulations in LCA: An Innovative Approach to Guide the Choice for the Environmentally Preferable Option. *Int. J. Life Cycle Assess.* **2022**, *27* (3), 505–523.
- (54) Rosenbaum, R. K.; Georgiadis, S.; Fantke, P. Uncertainty Management and Sensitivity Analysis. In *Life Cycle Assessment: Theory and Practice*; Hauschild, M. Z.; Rosenbaum, R. K.; Olsen, S. I., Eds.; Springer: Cham, 2018; pp 271–321.
- (55) Whiteley, K. S. Polyethylene. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA, 2012.
- (56) PlasticsEurope Circular Economy for Plastics—A European Overview, 2019. <https://plasticseurope.org/knowledge-hub/the-circular-economy-for-plastics-a-european-overview/>. (accessed August 09, 2024).
- (57) International Energy Agency (IEA) Global Electricity Generation Mix, 2010–2020. Licence: CC BY 4.0 2024. <https://www.iea.org/data-and-statistics/charts/global-electricity-generation-mix-2010-2020>. (accessed August 09, 2024).
- (58) Ecoinvent Association Electricity Analysis v3.8, Allocation, Cut-Off, 2021. <https://ecoinvent.org/database/>. (accessed August 09, 2024).
- (59) Sacchi, R.; Terlouw, T.; Siala, K.; Dirnaichner, A.; Bauer, C.; Cox, B.; Mutel, C.; Daioglou, V.; Luderer, G. PRospective EnvironMental Impact AsSEment (Premise): A Streamlined Approach to Producing Databases for Prospective Life Cycle Assessment Using Integrated Assessment Models. *Renewable Sustainable Energy Rev.* **2022**, *160*, No. 112311.
- (60) Alfke, G.; Irion, W. W.; Neuwirth, O. S. Oil Refining. In *Ullmann's Encyclopedia of Industrial Chemistry*; John Wiley & Sons, 2012.
- (61) Munawar, M. E. Human Health and Environmental Impacts of Coal Combustion and Post-Combustion Wastes. *J. Sustainable Min.* **2018**, *17* (2), 87–96.
- (62) Turconi, R.; Boldrin, A.; Astrup, T. Life Cycle Assessment (LCA) of Electricity Generation Technologies: Overview, Comparability and Limitations. *Renewable Sustainable Energy Rev.* **2013**, *28*, 555–565.
- (63) Bassi, S. A.; Biganzoli, F.; Ferrara, N.; Amadei, A.; Valente, A.; Sala, S.; Ardente, F. *Updated Characterisation and Normalisation Factors for the Environmental Footprint 3.1 Method 2023*.
- (64) Statista Price of Ethylene Worldwide from 2017 to 2022, 2023. <https://www.statista.com/statistics/1170573/price-ethylene-forecast-globally/>. (accessed August 09, 2024).
- (65) Methanol Institute MMSA-Monthly-Price-Forecast-for-Methanol-Institute, 2024 <https://www.methanol.org/methanol-price-supply-demand/>. (accessed August 09, 2024).
- (66) Nabera, A.; Istrate, I. R.; Martín, A. J.; Pérez-Ramírez, J.; Guillén-Gosálbez, G. Energy Crisis in Europe Enhances the Sustainability of Green Chemicals. *Green Chem.* **2023**, *25* (17), 6603–6611.
- (67) Krungrsri Research Monthly Price of Ethylene Worldwide from January 2020 to March 2024, 2024. <https://www.statista.com/statistics/1318102/monthly-price-ethylene-worldwide/>. (accessed August 09, 2024).
- (68) Qiu, Y.; Lamers, P.; Daioglou, V.; McQueen, N.; de Boer, H. S.; Harmsen, M.; Wilcox, J.; Bardow, A.; Suh, S. Environmental Trade-Offs of Direct Air Capture Technologies in Climate Change Mitigation toward 2100. *Nat. Commun.* **2022**, *13* (1), No. 3635.