

# Industrial Perspective of Electrified Ethylene Production via Membrane-Assisted Nonoxidative Dehydrogenation of Ethane

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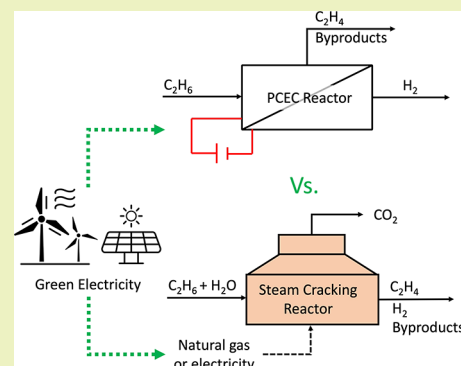
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**ABSTRACT:** The potential of applying ceramic proton-conducting electrolysis cell (PCEC) membranes in ethylene production processes was explored in this work. To this end, the techno-economics of a PCEC-assisted ethane dehydrogenation process were compared against the conventional ethane steam cracking (SC) process. The PCEC process required four to five times more electricity than the SC process. Consequently, fully renewable electricity needed to be utilized in the PCEC process to outcompete conventional SC in terms of carbon dioxide emissions. Notably, the PCEC process was financially and environmentally competitive with conventional SC only when achieving similar ethylene yields (ca. 50%). For an ethylene yield of ca. 25%, which is currently achievable using PCEC technologies, the capital investment and carbon emissions of the PCEC process were too excessive to outcompete electrified SC. The total energy usage, utility demand, and capital investment were substantially higher for the 25% ethylene yield PCEC case as compared to the 50% PCEC one, due to larger process streams and process units as a result of the lower single-pass yield. The results further highlighted that carbon emissions could be reduced from ca. 1.5  $t_{CO_2}/t_{ethylene}$  when employing green electrified SC or PCEC processes instead of conventional fossil fuel-based SC, but only if fully renewable electricity was utilized. Moreover, a carbon tax of more than 100 USD/ $t_{CO_2}$  would need to be imposed to make the green electrified SC and PCEC process more viable than their fossil-based counterparts. Lastly, technological challenges related to attainable ethylene yield, PCEC stability, large-scale sustainable production of PCECs, and the continuous availability of green electricity were identified as the main hurdles for the industrial implementation of PCECs for green ethylene production.

**KEYWORDS:** process intensification, process electrification, membrane reactors, sustainable design, techno-economic study, carbon footprint, proton-conducting electrolysis cell



## 1. INTRODUCTION

Ethylene is a crucial building block for the chemical industry, as it functions as monomer to produce various plastics (e.g., polyethylene, polyvinyl chloride, polyethylene terephthalate).<sup>1</sup> Due to an ever-increasing demand for commodity chemicals, the ethylene market size is anticipated to grow from ca. 196 billion USD in 2023 to ca. 287 billion USD in 2030.<sup>2</sup> Most of the commercial ethylene is produced via steam cracking of hydrocarbon reactants ranging from ethane to naphtha.<sup>3</sup> Despite its dominating industrial appearance, steam cracking is a highly energy intensive process, due to the high temperature required ( $T: >800\text{ }^\circ\text{C}$ ). This results in significant carbon dioxide emissions ( $1.0\text{--}2.0\ t_{CO_2}/t_{olefin}$ ), related to the combustion of the natural gas fuel.<sup>4</sup> To reduce global greenhouse gas emissions while expanding the ethylene market, it is therefore crucial to develop more energy efficient ethylene production routes.

An emerging alternative pathway to produce ethylene is the direct dehydrogenation of ethane.<sup>5,6</sup> This reaction can be conducted either in an oxidative or nonoxidative manner.

Ethane oxidative dehydrogenation (ODH) is usually operated autothermally, due to the exothermic nature of the reaction, but suffers from a poor olefin selectivity (ca. 70%), due to unwanted consecutive oxidation reactions.<sup>5,7</sup> On the contrary, the endothermic nonoxidative dehydrogenation (NODH) of ethane allows for much more selective ethylene formation (>93%).<sup>5,6</sup> Moreover, ethane NODH allows for the generation of a valuable hydrogen byproduct. Therefore, alkane NODH is generally industrially preferred to alkane ODH.<sup>8–10</sup>

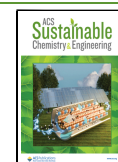
Alkane NODH processes have been successfully commercialized to produce propylene and butylenes from propane and butanes, respectively.<sup>10,11</sup> These processes are commonly operated in the temperature range from 550 to 700  $^\circ\text{C}$ .<sup>11</sup> In

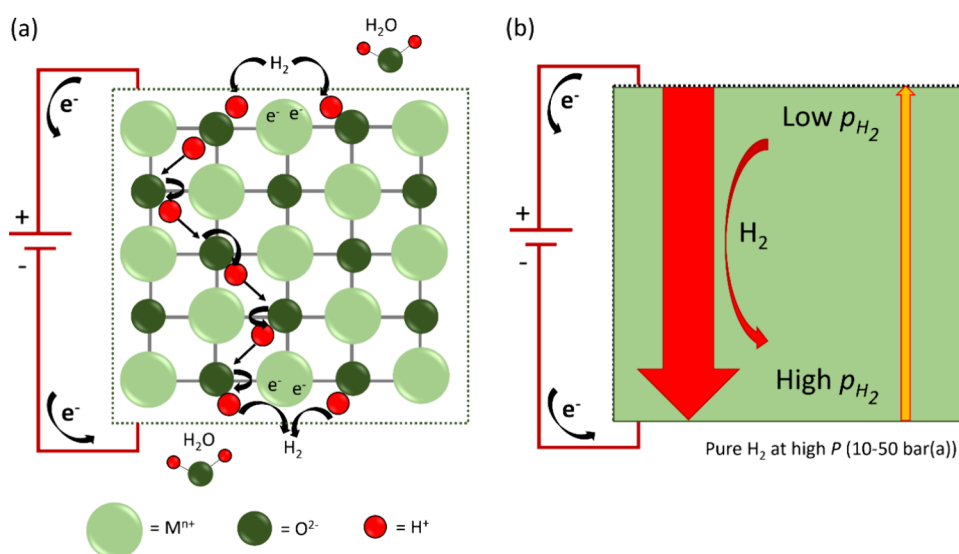
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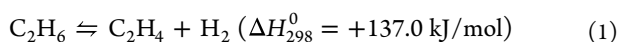
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**Figure 1.** (a) Transport mechanism of protons and electrons in proton-conducting electrolysis cell (PCEC) membranes, (b) driving force for hydrogen transport through PCEC membranes. The yellow and red arrows represent the driving forces for  $H_2$  permeation induced by the  $H_2$  partial pressure gradient and electrostatic potential gradient, respectively.

sharp contrast, the more stringent thermodynamic equilibrium of ethane NODH (eq 1) limited the application of this approach at commercial scales. Here, exceedingly high reaction temperatures ( $>700$  °C) are needed to attain significant ethylene yields (ca. 40%) via ethane NODH (see Supporting Information B).



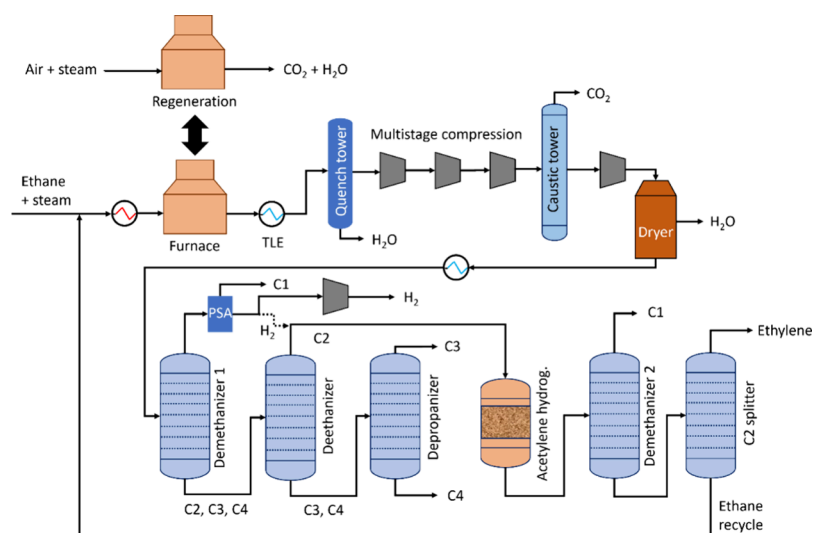
Ethylene formation is thermodynamically favored at elevated temperatures and reduced pressures. By using hydrogen permeable dense membranes, the ethane NODH equilibrium (eq 1) can be shifted toward ethylene, thereby allowing higher ethylene yields at milder reaction temperatures (550–700 °C). Despite the higher  $H_2$  permeation fluxes through metallic membranes,<sup>12</sup> dense ceramic membranes are preferred for integration with high-temperature reactions ( $T = 550$ –700 °C), due to their considerably greater stability.<sup>13</sup> The strategy of using hydrogen permeable membranes further offers an opportunity to realize process electrification, and integration of reaction, *in situ*  $H_2$  separation, and  $H_2$  compression.

A membrane configuration that is particularly interesting for improving the energy efficiency of endothermic reactions, while allowing for facile process electrification, is the proton-conducting electrolysis cell (PCEC) configuration.<sup>14–16</sup> In PCECs, only protons are transported through the membrane, while electrons are directed via an external circuit by applying a voltage (see Figure 1a). PCECs thereby offer the possibility to tailor the thermodynamics and kinetics of the targeted reaction and to electrify ethylene production processes. Optimal PCEC hydrogen permeation fluxes are claimed to be attained when wetting both sides of the membrane with ca. 3 wt % of steam to generate sufficient surface hydroxyl groups that facilitate hydrogen incorporation and recombination.<sup>17</sup> Hydrogen transport through PCEC membranes is driven by a gradient in hydrogen electrochemical potential, i.e., a combination of a gradient in hydrogen partial pressure and a gradient in electrostatic potential under ideal conditions.<sup>18</sup> A PCEC is commonly operated at high voltages, such that the gradient in electrostatic potential dominates the driving force and

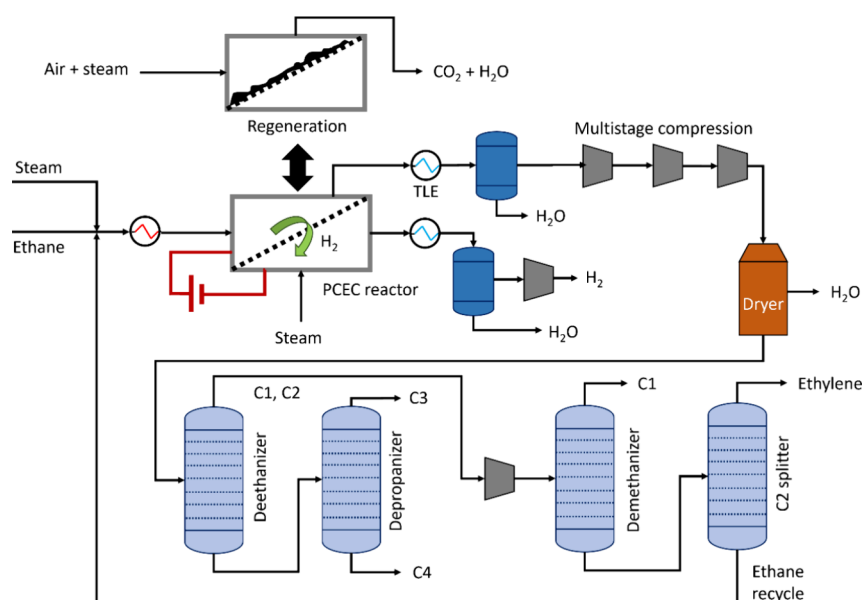
hydrogen can be transported in a direction opposing the  $H_2$  partial pressure gradient (see Figure 1b). In other words, a pure hydrogen product stream can be generated in PCECs. Malerød-Fjeld et al.<sup>15</sup> showed that  $H_2$  can be pressurized to 50 bar(a) using this concept.

In a previous study,<sup>19</sup> we compared the techno-economics and carbon footprint of an existing Honeywell UOP Oleflex process for propane NODH to that of a PCEC-assisted process and a process integrated with nonelectrically driven mixed proton–electron conducting (MPEC) membranes. There, we showed that the MPEC process is not a financially and environmentally attractive alternative to conventional Oleflex. The MPEC reactor costs were substantial, since an exceedingly large MPEC membrane area was required, due to the extremely low  $H_2$  permeation rates. Additionally, heating of the sweep gas in the MPEC reactor required a large energy input. We also demonstrated that, in contrast to the MPEC process, the PCEC-assisted propane NODH process could be an attractive alternative to conventional Oleflex. The shift in thermodynamic equilibrium toward propylene induced by the PCEC membranes caused a reduction in the size of process streams and process units, resulting in a lower capital investment and a smaller energy input. However, the latter resulted in a lower carbon footprint only when fully renewable electricity was used.

Since our previous study on the commercialized propane NODH technology indicated that the usage of PCEC membranes could lead to substantial financial and environmental benefits, we decided to investigate in this work if PCEC membranes could improve the industrial perspective of the noncommercialized ethane NODH technology. We further aim to identify hurdles that could prevent industrial implementation of the PCEC systems. To this end, we benchmarked a PCEC-assisted ethane NODH process against a conventional ethane steam cracking process for ethylene production. We conducted a comprehensive assessment of the process economics, energy usage, and carbon dioxide emissions, including the impact of both fossil and electrical heating.



**Figure 2.** Schematic process flow diagram of the ethane steam cracking process. Adapted from Seifzadeh Haghighi et al.<sup>22</sup> with permission from Elsevier.



**Figure 3.** Schematic process flow diagram of the PCEC membrane-assisted ethane dehydrogenation process.

## 2. CASE STUDY

The process flow diagram of the ethane steam cracking (SC) process (Figure 2) was constructed using information available in literature,<sup>3</sup> while the methodology proposed by Douglas<sup>20</sup> for conceptual process design was employed for developing the process flow diagram of the PCEC-assisted process (Figure 3). For more detailed process flow diagrams as implemented in the process simulations, including the corresponding stream tables, see Supporting Information C. Besides, for more details on the process simulations, we refer the reader to Supporting Information D.

**2.1. Ethane Steam Cracking Process.** Ethane steam cracking is conventionally operated in fired tubular furnaces.<sup>3</sup> The residence time of the gas in these furnaces is commonly very short (0.1–0.5 s) to optimize the yield toward light olefins, as secondary oligomerization reactions are enhanced for longer residence times. The cracking furnace here was operated at 850 °C and 2 bar(a) and with a steam/

hydrocarbon ratio of 0.3 kg/kg.<sup>3</sup> Besides, the ethane steam cracking reaction was simulated with an ethane conversion of 65% in combination with an ethylene selectivity of 80%, resulting in an ethylene yield of ca. 52%.<sup>3</sup> The side products comprised hydrogen, carbon monoxide, carbon dioxide, and C1, C2, C3, C4, and C4+ hydrocarbons. The carbon oxides were formed upon steam reforming of coke deposits. For a complete list of side products, see Supporting Information D1. The cracking furnace had to be regenerated periodically in a stream of air to remove coke deposits that were formed inside the furnace coils during the cracking reaction. Steam was cosupplied with the air for heat dilution in an optimized steam/air ratio of 4.67 kg/kg.<sup>21</sup> The design of the ethane steam cracking furnace is further explained in Supporting Information E.

Downstream the cracking furnace, the hydrocarbon stream was quickly cooled to ca. 300 °C in a transfer line exchanger (TLE) to avoid olefin oligomerization (Figure 2).<sup>3,23</sup> In the

quench tower, the majority of the water was removed before compression to 17 bar(a) in a multistage compressor system with interstage cooling.<sup>3,26,27</sup> After compression, a caustic tower was used to remove carbon dioxide impurities.<sup>3</sup> Succeeding the caustic tower, the hydrocarbon product stream was further pressurized to 32 bar(a). Then, a dryer pressure swing adsorption (PSA) column was applied with pressure swings between 32 and 2 bar(a) to remove the remaining moisture.

The dried and cooled hydrocarbon stream was sent through a sequence of cryogenic distillation columns (Figure 2).<sup>3</sup> Light impurities were removed from the process in a demethanizer column. The light impurities were separated into a fuel gas and a hydrogen stream in a pressure swing adsorption (PSA) unit. The fuel gas contained primarily methane and was combusted to generate part of the energy needed for the steam cracking furnace. A major part of the hydrogen stream was sold as a valuable byproduct. The deethanizer column isolated the C2's from the heavy impurities (C3+). The C3 and C4 impurities were separated in a depropanizer column to be sold as byproducts. The C2 stream was sent to an acetylene hydrogenation reactor to selectively hydrogenate the acetylene content to maximize the ethylene yield and to avoid possible detrimental effects to the process induced by the acetylene.<sup>23</sup> The hydrogen needed for this hydrogenation step originated from the PSA (Figure 2) and was supplied in a hydrogen/acetylene ratio of 1.8.<sup>3</sup> A second demethanizer was then required to remove the last methane and hydrogen impurities. Lastly, the ethylene product was separated from the unconverted ethane in a C2 splitter. The vapor ethylene product ( $\geq 99.9$  wt %) was obtained at 18 bar(a) and 10 °C, while the unconverted liquid ethane was recycled to the cracking furnace. The operating conditions and dimensions of the distillation columns applied in the SC process are summarized in Supporting Information G3.

**2.2. PCEC Membrane-Assisted Process.** Since ceramic membranes are known to function optimally in the presence of steam,<sup>17</sup> 3 wt % of steam was cosupplied with the ethane feed stream to the PCEC reactor (Figure 3).<sup>24,25</sup> For the same reason, steam was cofed to the PCEC permeate side, in such an amount that the permeate side outlet stream contained 3 wt % of steam. The PCEC membrane was assumed to be fully permselective, implying that the permeate side effluent stream only contained hydrogen and steam. The steam cosupply on the membrane feed side also helps in suppressing coke formation, thereby improving catalyst stability.<sup>26</sup>

The PCEC membrane reactor consisted of parallel-configured tubular membrane cells (see Supporting Information F). Continuous operation was achieved by running some of these reactors in dehydrogenation mode ( $T = 550$  °C,  $P = 5$  bar(a)) and other ones in regeneration mode ( $T = 620$  to 830 °C,  $P = 5$  bar(a)) with intermediate flushing runs.<sup>3,21</sup> The PCEC membrane reactor was simulated with 98% hydrogen removal, in which the hydrogen removal fraction was defined as the ratio between the amount of hydrogen extracted and the amount of hydrogen present. This extremely high fraction of hydrogen removal was selected, since more than 95% of the hydrogen needs to be removed to substantially shift the ethane NODH equilibrium yield (Supporting Information B). The single-pass ethylene yield in the base case PCEC process was ca. 25%, based on an ethane conversion of 39.5% and an ethylene selectivity of 63.3%, as obtained by Wu et al.<sup>27</sup> in their experimental study on PCEC-assisted ethane NODH. An

additional PCEC case was included in which the single-pass ethylene yield was 50%, similar to the SC process. This second PCEC case, referred to as the PCEC target case, aimed at evaluating the impact of using PCEC membranes on process economics and sustainability aspects if technological advancements in the field of PCEC research would allow for attaining ethylene yields competitive to conventional SC.

Possible reforming reactions caused by the steam were disregarded in both PCEC process cases. Similar to the ethane steam cracking furnace, the PCEC membrane reactor had to be regenerated periodically because of the anticipated carbon deposition inside the PCEC reactor. This regeneration step was conducted using air at 5 bar(a) and with an inlet temperature of 620 °C.<sup>3,21</sup> Moreover, steam was again cosupplied in a steam/air ratio of 4.67 kg/kg in the regeneration step for heat dilution.<sup>21</sup>

The PCEC composition considered in this work equaled the PCEC composition applied by Wu et al.<sup>27</sup> in their experimental work on PCEC-assisted ethane NODH. This concerned a cathode-supported cell in which the cathode consisted of nickel-functionalized barium zirconium cerium yttrium ytterbium oxide ( $\text{Ni/BZCYb}$ ,  $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ ) with a thickness of 450  $\mu\text{m}$ . The electrolyte was a BZCYb layer with a thickness of 15  $\mu\text{m}$ . The anode ( $t = 80$   $\mu\text{m}$ ) was composed of a praseodymium barium iron molybdenum oxide (PBFM,  $\text{PrBa}_{0.95}(\text{Fe}_{0.9}\text{Mo}_{0.1})_2\text{O}_{5+\delta}$ ) impregnated with catalyst phases consisting of platinum and gallium supported on ZSM-5 zeolite (PtGa/ZSM-5). The respective platinum and gallium loadings of this catalyst were 0.175 and 1.02 wt %. BZCY-based PCEC systems are known for their outstanding proton conductivity properties in combination with good stability in hydrocarbon atmospheres.<sup>14,15</sup>

An external voltage was applied to drive hydrogen (proton) permeation through the PCEC membrane (Figure 3). It was demonstrated by Malerød-Fjeld et al.<sup>15</sup> for BZCY-based electrochemical cells that hydrogen could be electrochemically compressed to 50 bar(a) using this concept.<sup>20</sup> However, electrochemical compression is most efficient for light compressions.<sup>28</sup> Hydrogen was therefore compressed electrochemically to 20 bar(a) in the PCEC reactor in this work, followed by mechanical compression to 50 bar(a). This 50 bar(a) hydrogen pressure is a typical pressure for hydrogen storage in spherical vessels.<sup>29</sup> The hydrocarbon retentate stream of the PCEC reactor was quickly cooled in a transfer line exchanger (TLE), before separating the water in a flash drum. Afterward, the hydrocarbon stream was compressed to 27 bar(a) in a multistage compression section. The last traces of water were again removed in a dryer PSA column, operated in this case with pressure swings between 27 and 2 bar(a).

The hydrocarbon product stream was further purified in a sequence of cryogenic distillation columns (Figure 3). A front-end deethanizer configuration was selected for the PCEC process, because this configuration had lower operational costs than the possible alternative configurations, as it had the lowest overall heating and cooling duties (see Supporting Information C). In the deethanizer column the heavy impurities were removed from the fraction containing C2's and lighter compounds. Subsequently, the depropanizer column further purified the heavy impurities to C3 and C4 fractions, respectively, which were sold as valuable byproducts. Besides, the stream containing C2's and lights was pressurized to 32 bar(a) and then fed to a demethanizer column, in which the



light impurities were isolated from the C2's. The remaining lights fraction contained mainly methane and was combusted to generate a fraction of the energy needed to operate the endothermic dehydrogenation reactors. Lastly, the ethylene product ( $\geq 99.9$  wt %) was separated from the unconverted ethane in a C2 splitter. The unconverted ethane was recycled to the feed of the PCEC process, similar to the ethane SC process. The operating conditions and dimensions of the distillation columns applied in both PCEC processes are summarized in [Supporting Information G3](#).

### 3. METHODOLOGY

The ethane steam cracking process and the two PCEC-assisted ethane NODH processes were all simulated in Aspen Plus V12.1 using the Soave–Redlich–Kwong equation of state as the property method and using equal design bases.

**3.1. Process Feed and Product Specifications.** The targeted product was polymer grade ethylene ( $\geq 99.9$  wt %, see [Supporting Information A1](#)) at 18 bar(a), which was within the typical operating range of C2 splitter columns (17–28 bar(a)).<sup>3</sup> Commercial steam cracking plants generally operate with an ethylene production capacity of more than 1000 ktpa ([Supporting Information A3](#)).<sup>30,31</sup> However, since immediate industrial implementation of the emerging PCEC technology on such a large scale is unrealistic, an ethylene production capacity of 100 ktpa was selected in this work. By doing so, the competitiveness of the PCEC technology on this relatively small scale will provide key insights for the potential scale up approaches in the future. In addition to the ethylene product, high purity fuel grade hydrogen ( $\geq 99.95\%$ , [Supporting Information A2](#))<sup>32</sup> was targeted as byproduct and was pressurized to 50 bar(a) for transportation and storage.<sup>29</sup> The ethane feed stream was obtained from a natural gas processing plant and contained 96.16 wt % of ethane, 1.83 wt % of methane, and 2.01 wt % of propane.<sup>33</sup> Possible H<sub>2</sub>S impurities were assumed to be removed in desulfurization pretreatment steps, which were outside the scope of this study. The ethane feed stream was at 31 bar(a) and 11 °C, which was equivalent to the conditions of the ethane stream from the deethanizer column of a natural gas processing plant.<sup>34,35</sup> The number of operating hours per year was set to 8766.

The two ethylene production processes were considered to be constructed in the Asia-Pacific region, as the financial margin between the ethane and ethylene prices was substantial (see [Table 1](#)), and since the share of renewable resources to the generation of grid electricity is yet significant (ca. 30%) in this region.<sup>36</sup>

**3.2. Utility Specifications.** The different types of utilities needed, including the corresponding specifications and costs, are available as [Supporting Information A4](#). In the utility assessment, the reactors were either heated using fossil fuels via natural gas incineration or using electricity. All heating steps

above 285 °C were conducted using fired heaters, while the heating steps at lower temperatures were carried out using either high pressure (80 bar(a)), medium pressure (11 bar(a)), or low pressure (2.3 bar(a)) steam. On the contrary, the cooling steps were executed using cooling water or refrigerants. The cooling water was supplied at 25 °C and discharged at 45 °C,<sup>41</sup> while the refrigerants were based on methane, ethylene, and propylene cycles. Lastly, pumps and compressors in the process required electricity. Two different types of electricity were considered, namely Asia-Pacific grid electricity and fully renewable electricity. In the base case analysis, green electricity was assumed to be equally expensive as the grid electricity, even though solar and wind-based electricity can already be generated at lower costs than grid electricity.<sup>42</sup>

**3.3. Reactor Simulations.** The ethane steam cracking furnace was simulated in Aspen Plus as a stoichiometric reactor. The single-pass ethane conversion was 65% with an ethylene selectivity of 80% (i.e., an ethylene yield of ca. 52%), with mainly light hydrocarbon byproducts (see [Supporting Information D1](#) for the full product distribution). The PCEC membrane reactor was simulated in Aspen Plus by a combination of a stoichiometric reactor and a component splitter. The stoichiometric reactor defined the fractional conversion of all reactions taking place inside the PCEC reactor. In the base case PCEC process, dealing with a single-pass ethylene yield of ca. 25% the fractional conversions were retrieved from the work by Wu et al.<sup>27</sup> (see [Supporting Information D2.1](#)). By contrast, the product distribution of the PCEC target case in which the single-pass ethylene yield was adjusted to 50% is provided in [Supporting Information D2.2](#). The component splitter compartment of the PCEC reactor in Aspen Plus specified the fraction of hydrogen that was effectively removed by the PCEC membrane. In this work, a fraction of 98% hydrogen removal was used, theoretically allowing for an ethane dehydrogenation yield increase to ca. 60% at 550 °C (see [Supporting Information B](#)).

We utilized the polycyclic aromatic hydrocarbon coronene, with chemical formula C<sub>24</sub>H<sub>12</sub>, as coke model compound in both process simulations. Coronene was in the gas phase under reaction conditions and therefore transportable to a regeneration unit in the Aspen Plus simulations. This regenerator was simulated as a stoichiometric reactor with complete combustion of the coronene content and was used to quantify the amount of energy generated upon regeneration. Based on Wu et al.<sup>27</sup> the amount of coronene formed was set to 2.06 g per kg of ethane converted for the SC as well as the PCEC processes. For more information on the simulations of the (membrane) reactors in both processes, see [Supporting Information D](#).

**3.4. Equipment Design.** The tubular ceramic membrane reactor design developed by CoorsTek<sup>14,43</sup> was used for dimensioning the PCEC membrane reactor. This tubular design was preferred to a planar design for systems dealing with considerable pressure gradients that arise e.g., upon electrochemical hydrogen compression. The CoorsTek design represents a modular approach in which tubular ceramic PCEC units are stacked together in membrane modules. The total active membrane area per module is about 44 m<sup>2</sup>. For more details on the membrane reactor design and the applied membrane multilayer composition, the reader is referred to [Supporting Information F](#). The design of other process equipment, e.g., compressors, and distillation columns, is available in [Supporting Information G](#).

**Table 1. Feedstock and Product Prices**

compound	price (USD/t)	reference year	location	reference
ethane	270	Q1, 2023	Asia-Pacific	estimated based on ref 37
ethylene	950	Q1, 2023	Asia-Pacific	estimated based on ref 38,39
hydrogen	1,600	Q1, 2023	Asia-Pacific	estimated based on ref 40

The required PCEC membrane area was calculated based on the outcomes of the Aspen Plus simulations. The base case PCEC reactor effluent stream contained 160 mol/s of hydrogen in absence of any hydrogen abstraction. For the assumed 98% hydrogen removal, this means that ca. 157 mol/s of hydrogen had to be removed by the PCEC membrane. The PCEC membrane reactor was operated at a current density of 1 A/cm<sup>2</sup>, estimated based on experimental PCEC studies available in literature.<sup>15,16</sup> With this current density and hydrogen removal rate, the membrane area required for permeation was calculated to be ca. 3000 m<sup>2</sup>. For industrial propane dehydrogenation processes, typically 17% of the reactor capacity is operating in regeneration mode.<sup>11</sup> Based on this information, the total required PCEC membrane area was determined to be ca. 3500 m<sup>2</sup>. This corresponds to ca. 80 membrane modules (see [Supporting Information F](#)). In the alternative PCEC case targeting a single-pass ethylene yield of 50% the PCEC reactor outlet only contained 129 mol/s of hydrogen. This was ascribed to smaller process stream sizes as compared to the base case PCEC process, as a result of a smaller recycle caused by the higher single-pass ethylene yield. The considered ethane-to-ethylene conversion is also much higher in the target case PCEC process, due to a lower butylene and a higher ethylene selectivity relative to the base case PCEC process, as shown in [Supporting Information D2](#). As a consequence, a smaller PCEC membrane area of about 2800 m<sup>2</sup> was required in the target case PCEC process for 98% hydrogen removal, corresponding to ca. 64 membrane modules.

**3.5. Quantification of Process Economics, Energy Usage, and Carbon Dioxide Emissions.** The outcomes of the Aspen Plus simulations (e.g., heating and cooling duties, number of distillation column stages, pump and compressor powers) were used for quantification of the capital expenditures (CAPEX), operating expenditures (OPEX), energy usage, and carbon dioxide emissions.

**3.5.1. Capital Expenditures (CAPEX).** The capital expenditures were estimated based on the factor method proposed by Towler and Sinnott.<sup>44</sup> This method uses a bottom-up approach, in which the capital investment of the process equals a summation of the capital investment per unit operation. The direct capital investment per unit operation in turn is a function of the purchased equipment costs and several compensation factors. The installation factor proposed by W.E. Hand<sup>44</sup> was used to compensate for costs related to the installation of process equipment. Besides, a material factor accounted for possible material constraints and a location factor for the geographic location of the plant in the Asia-Pacific region. In addition, the Chemical Engineering Plant Cost Index (CEPCI) corrected for the inflation. For further information on the applied factor method for the CAPEX estimation, see [Supporting Information K](#).

The capital costs of the PCEC membrane reactors were estimated by following a method proposed by Malerød-Fjeld et al.<sup>15</sup> for cost estimation of CoorsTek proton-conducting membrane reactors ([Supporting Information F](#)). In this method, the investment costs were a summation of (i) membrane reactor steel costs, (ii) hot box steel costs, (iii) stack material costs, (iv) tooling costs, and (v) additional costs. The stack material costs contained the bare costs for the electrode and electrolyte materials, as well as costs for gas manifolds, interconnects, weld connectors, and sealing rings. Besides, the tooling costs represented the depreciation of the

equipment needed for manufacturing, in which it was assumed that the equipment was fully depreciated over the process units manufactured in the plant. Lastly, the additional costs contained costs for e.g., instrumentation, tubing, and fittings.<sup>15</sup> The steel costs of the membrane reactor housing and the hot box were estimated based on the process unit dimensions and the required wall thickness.

**3.5.2. Operating Expenditures (OPEX) and Revenues.** The operating expenditures (OPEX) and revenues were calculated using a method described by Towler and Sinnott.<sup>45</sup> The OPEX consisted of the variable and the fixed production costs. The former contained costs for (i) raw materials, (ii) utilities, (iii) consumables, and (iv) effluent disposal, whereas the latter comprised costs related to (i) labor, (ii) process maintenance, (iii) property taxes, and (iv) rent of land. Besides, the revenues were comprised of contributions from the targeted ethylene product, and the hydrogen, propylene, and butylene by-products. In case all reactor heating and preheating steps were carried out electrically, then the fuel gas generated in both processes was also sold at fuel value.

The consumables contained costs for catalysts, adsorbents, and membranes. Besides, the effluent disposal expenditures covered costs for flue gas cleaning, spent caustic disposal, and wastewater treatment. The lifetime of the PCEC membranes was set equal to the lifetime of conventional alkane dehydrogenation catalysts (two years),<sup>10</sup> and it was assumed that only the membrane stack materials had to be replaced periodically. In view of the energy transition, it is expected that the carbon tax will become a more dominant factor in evaluating the viability of process alternatives. In the base case economic assessment, no carbon tax was included. Instead, the carbon tax was incorporated in the sensitivity analysis to explore the impact of penalizing carbon emissions on the profitability of the different process cases.

The profitability of the ethane SC and PCEC processes was evaluated by determining the return on investment (ROI) and the payback period. In this work, the ROI was quantified using the net annual profit and the total capital investment. The net annual profit was calculated from the gross annual profit corrected for an estimated corporate income tax of 18% for the Asia-Pacific region.<sup>46</sup> The gross annual profit was in turn calculated from the difference between the total revenues and the total production costs, including a depreciation contribution for a linear depreciation period of 15 years of the total depreciable capital. We refer the reader to [Supporting Information L and P](#) for more details on the OPEX calculations and the profitability assessment, respectively.

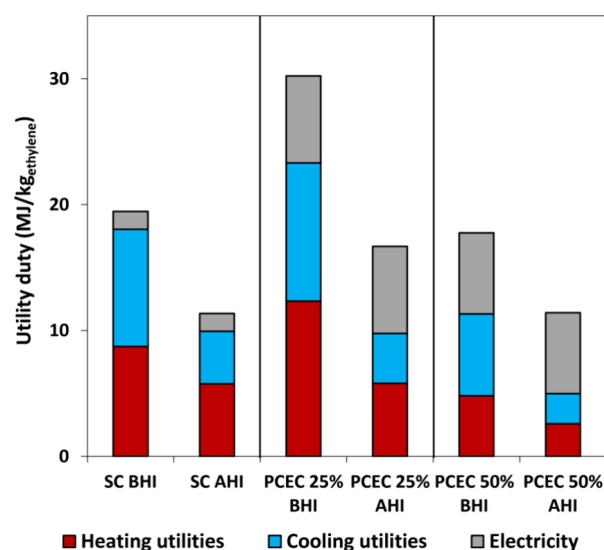
**3.5.3. Environmental Impact.** The environmental impact of the different processes was quantified by means of the carbon dioxide emissions, which comprised of contributions from (i) utility natural gas incineration, (ii) fuel gas combustion, (iii) coke combustion, (iv) electricity generation, and (v) natural gas combustion needed for steam generation. Two types of electricity were taken into consideration, namely Asia-Pacific grid electricity and fully renewable electricity. The grid electricity in the Asia-Pacific region has a carbon intensity of 532.1 gCO<sub>2</sub>/kWh,<sup>47</sup> whereas the carbon intensity of fully renewable electricity was estimated at 50 gCO<sub>2</sub>/kWh,<sup>48,49</sup> accounting for emissions related to the construction of windmills and solar panels. Two steam cracking cases were discerned, depending on whether the reactor feed and the reactor itself were heated by burning a natural gas fuel (SC fossil), or by using electricity (E-cracker, SC full electric).

Analogously, for the PCEC processes different cases were assessed in which the reactor feed and the PCEC membrane reactors were both heated by burning natural gas (PCEC fossil) or by using electricity (PCEC full electric). An additional PCEC case was included in which the reactor feed was heated by burning natural gas, while the PCEC membrane reactor was heated by operating at thermoneutral voltage (PCEC  $E_{th}$ ). In the latter case, the heat required for the dehydrogenation reactor was fully delivered by resistive Joule heating inside the PCEC membrane. It should be noted that also in the PCEC fossil cases the reactor heat partially originated from Joule heating effects. Besides, for the SC and PCEC full electric cases the fuel gas streams available within the processes were sold at fuel value and the corresponding carbon emissions were, thus, not included in that situation. More details on the calculations of the carbon dioxide emissions are available in [Supporting Information N](#).

**3.6. Process Heat Integration.** The heat integration measures implemented in the different processes were related to (i) combustion of carbon deposits, (ii) combustion of the C1 rich off-gas streams, (iii) resistive Joule heating, and (iv) heat exchange between hot and cold process streams. The latter was accomplished by means of a pinch point analysis using the FI<sup>2</sup>EPI software.<sup>50</sup> In this analysis, a minimum temperature approach of 10 °C between the hot and cold fluids was imposed. Besides, only streams with a duty of more than 1 MW were, in general, included. The only exception comprised of duties of less than 1 MW that had to be covered by one of the expensive refrigerants. Moreover, it was assumed that heat integration with the reactor blocks was practically not possible. The heat integration analysis is discussed in detail in [Supporting Information J](#). A detailed heat exchanger network was designed for the SC and PCEC base case processes. The heat exchanger network capital investment was estimated to be equal for the PCEC target case and the PCEC base case. A detailed heat exchanger design for the PCEC target case was considered to be beyond the scope of this work. The influence of heat integration within the PCEC target process on the corresponding energy usage, utility demand, and carbon emissions, was included by assuming that per heating/cooling step the same relative amount of energy could be integrated as for the PCEC base case process.

## 4. RESULTS AND DISCUSSION

**4.1. Utilities.** The available heat within the SC and PCEC processes as obtained from (i) resistive Joule heating, (ii) fuel gas combustion, and (iii) high pressure steam was in all cases used to cover part of the heating requirement. Implementation of the heat integration measures by exchanging heat between hot and cold process fluids led to considerable reductions in the required utilities for the SC and PCEC processes (see [Figure 4](#)). Notably, the utility consumption of the base case PCEC process (ca. 25% ethylene yield) was ca. 25% higher than the base case SC process, regardless of the extent of heat exchange. This was partly attributed to the great electricity demand for electrically driving the hydrogen permeation in the PCEC membrane reactor. Besides, the steam utility demand of the base case PCEC process was higher in comparison with the SC process, particularly due to the heavy C2 splitter reboiler duty. Since the inlet of the C2 splitter in the base case PCEC process contained less ethylene as compared to the SC process, due to the lower single-pass ethylene yield, a larger C2 splitter



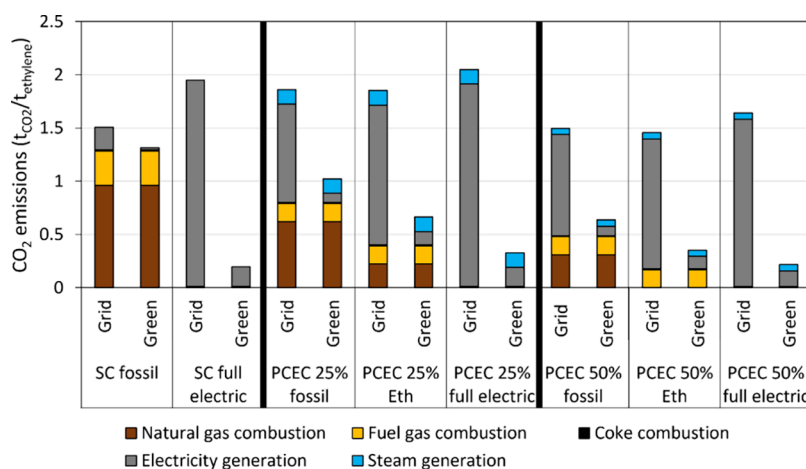
**Figure 4.** Utility duty for the fossil fuel heated ethane steam cracking (SC) and PCEC-assisted processes before heat integration (BHI) and after heat integration (AHI). Herein, heat integration only covers the exchange of heat between hot and cold process fluids; the heating utilities of the BHI cases were already corrected for the heat covered by Joule heating, fuel gas combustion, and high pressure steam. Note that the electricity contribution here contains the electricity needed for compression, pumping, and electrically driven hydrogen permeation, but excludes the possibility of electrical heating.

reboiler capacity was needed to attain the set ethylene product purity ( $\geq 99.9$  wt %).

The total utility duty of the target case PCEC process, considering a single-pass ethylene yield of 50%, was similar to the conventional SC process ([Figure 4](#)). The heating and cooling requirements of the PCEC target case were ca. 40% lower as compared to the SC process ([Figure 4](#)), caused by the lower operating temperature of the PCEC reactor ( $T = 550$  °C) relative to the SC furnace ( $T = 850$  °C). By contrast, the PCEC target case required three to four times more electricity than conventional SC for electrochemical hydrogen separation and compression.

The electricity requirement of the SC process of 1.4 MJ/kg<sub>ethylene</sub> ([Figure 4](#)) was in line with typical values of about 1 MJ/kg<sub>ethylene</sub> reported for ethane SC processes.<sup>4</sup> The total energy input, i.e., the sum of the heating and electricity utilities, of the SC process (ca. 10.4 MJ/kg<sub>ethylene</sub>) was below the specific energy input (SEI) values typically reported for ethane SC processes (17–21 MJ/kg<sub>ethylene</sub>).<sup>4</sup> The reason for this is that the utility duty reported here was yet corrected for the heat generated from the combustion of fuel gas and the usage of high pressure steam. An overview of the distribution of the different utilities needed and the corresponding costs for the SC and PCEC process cases after heat integration is available in [Supporting Information M](#). There it is shown that the total utility costs were about one-third higher for the base case PCEC process as compared to the base case SC process, due to high electricity costs for operating the PCEC membrane reactor. By contrast, the total utility costs of the PCEC target case were ca. 10% lower relative to the SC process, due to the lower heating and cooling demand of the PCEC process, caused by the lower operating temperature of the PCEC membrane reactor ( $T = 550$  °C) in relation to the SC furnace temperature ( $T = 850$  °C). Moreover, it is demonstrated in





**Figure 5.** Carbon dioxide emissions of the ethane steam cracking (SC) process, the base case PCEC membrane-assisted process (ca. 25% ethylene yield), and the target case PCEC process (50% ethylene yield), in case the reactor feed and the reactor itself were heated by burning natural gas or fuel gas (fossil) or by using electricity (full electric). Additional PCEC cases were included in which the reactor feed was heated by burning natural gas or fuel gas, and in which the reaction heat was fully delivered via resistive Joule heating inside the PCEC membrane reactor (operation at thermoneutral voltage,  $E_{th}$ ).

Supporting Information M that the utility costs were dominated by refrigerant costs (SC and PCEC processes) and electricity costs (PCEC processes).

**4.2. Environmental Impact.** The environmental impact of the different process cases was quantified by means of the carbon dioxide emissions (see Figure 5). The obtained carbon footprint of the fossil fuel heated SC process (ca. 1.5  $t_{CO_2}/t_{ethylene}$ ), representing the conventional ethylene production method, was well in line with typical steam cracking emissions (1.0–2.0  $t_{CO_2}/t_{olefin}$ ).<sup>4</sup> This footprint was dominated by contributions from the combustion of natural gas and fuel gas (Figure 5). By contrast, the carbon footprint of the PCEC process cases was less controlled by natural gas and fuel gas incineration, since for all PCEC cases the required heat was (partially) supplied via Joule heating.

Notably, when grid electricity was utilized in the base case PCEC process (ca. 25% ethylene yield), then the carbon dioxide emissions of fossil fuel heated PCEC were ca. 24% higher compared to the fossil fuel heated SC process (Figure 5). On the contrary, the carbon emissions were 22% lower for the fossil fuel heated PCEC process compared to the fossil fuel heated SC process when green electricity was used (Figure 5). This difference was attributed to the contribution of Joule heating to the reactor heat supply. Indirect heat supply via Joule heating was only environmentally beneficial when fully renewable electricity was utilized.

The carbon dioxide emissions of the target case PCEC process (50% ethylene yield) were always lower than the carbon footprint of the base case PCEC process (Figure 5). The increase in single-pass ethylene yield from ca. 25 to 50% led to a smaller process recycle and, hence, smaller process streams. Consequently, less utilities were required for the target case PCEC process compared to base case PCEC (see Figure 4). As a result, the carbon emissions related to these utilities were also lower (Figure 5). In particular, the smaller ethane recycle stream caused a lower fired heat demand for preheating the reactor feed and a lower steam demand for distillation reboiling. For the case in which the PCEC reactor was operated at thermoneutral voltage, the energy obtained from coke and fuel gas combustion even turned out to be sufficient to cover the natural gas utility demand of target case

PCEC (Figure 5). Similar to base case PCEC, the carbon footprint of the target case PCEC was drastically reduced when using green electricity instead of Asia-Pacific grid electricity. The advantageous effect of using green electricity (50.0  $g_{CO_2}/kWh$ ) instead of fossil grid electricity (532.1  $g_{CO_2}/kWh$ ) became even more pronounced when electrifying the respective processes, as the carbon footprint reduced substantially when moving from the fossil fuel heated cases to the fully electrified cases (Figure 5).

Notably, the carbon footprint of the base case SC process electrified using green electricity (ca. 0.2  $t_{CO_2}/t_{ethylene}$ ) was even lower than the green electrified base case PCEC process (ca. 0.3  $t_{CO_2}/t_{ethylene}$ , Figure 5). This difference arose from the steam utility requirement of the PCEC process. In the SC process, the amount of high pressure steam generated inside the TLE upon cooling down the hydrocarbon stream from the cracking temperature of 850 °C to ca. 300 °C was sufficient to cover the steam utility demand of the process. On the contrary, the amount of high pressure steam generated in the TLE of the base case PCEC process was more limited, due to a smaller temperature drop from the PCEC reactor temperature of 550 °C to ca. 300 °C. The steam demand of the base case PCEC process could therefore not be fully covered by internally generated steam, leading to an external steam utility demand and related carbon emissions upon generating this external steam (Figure 5).

The carbon footprint of the green electrified target case PCEC process was similar to that of the green electrified SC process (ca. 0.2  $t_{CO_2}/t_{ethylene}$ , Figure 5). This means that green electrification of conventional SC processes had comparable environmental benefits as industrial implementation of green electrified PCEC membrane reactor systems for similar ethylene product yields (ca. 50% in this comparison). It should be emphasized that the target case PCEC process considered an ethylene yield of 50% that has not been achieved yet in experimental PCEC research for this application. For currently attainable ethylene yields of ca. 25%,<sup>27</sup> the green electrified process could not outcompete green electrified SC in terms of carbon emissions (Figure 5). An ethylene yield of ca. 50% can, therefore, be regarded as a minimum threshold for industrialization of PCEC-assisted ethane dehydrogenation.



The results in Figure 5 highlight that, irrespective of the type of process case employed, renewable electricity needed to be utilized to outcompete conventional fossil fuel heated SC. For this reason, a sensitivity analysis was applied regarding the influence of the carbon intensity of the electricity on the total carbon dioxide emissions of the various process cases (see Supporting Information O3). Recall that the carbon intensity of Asia-Pacific grid electricity was 532.1 g<sub>CO2</sub>/kWh.<sup>47</sup> The full electric process cases had the lowest carbon footprint for an electricity carbon intensity of less than 200 g<sub>CO2</sub>/kWh, while the fossil fuel heated processes were more sustainable above 350 g<sub>CO2</sub>/kWh (see Supporting Information O3). The carbon emissions related to electricity generation should, thus, be lower than 200 g<sub>CO2</sub>/kWh to make electrification of SC or PCEC processes environmentally attractive. For more information on the complete carbon footprint assessment, see Supporting Information N.

#### 4.3. Process Economics. 4.3.1. Capital Expenditures.

The total investment costs of the base case PCEC process were ca. 15% higher as compared to the conventional ethane SC process (Table 2). This was particularly attributed to higher

**Table 2. Comparison of the Capital Costs between the Conventional Ethane Steam Cracking (SC) Process and the Base Case (ca. 25% Ethylene Yield) and Target Case (50% Ethylene Yield) PCEC-Assisted Ethane NODH Processes**

equipment type	capital cost (MMUSD, 2023)		
	SC	PCEC base case (25%)	PCEC target case (50%)
reactors	20	32	26
distillation columns	5	9	7
compressors and pumps	33	25	21
heat exchangers	6	7	7
flash vessels	2	3	2
other separation equipment	1	0	0
total direct investment(=ISBL <sup>a</sup> )	66	76	62
OSBL <sup>b</sup> costs (=40% of ISBL <sup>a</sup> )	27	31	25
design and engineering costs (=30% of ISBL <sup>a</sup> + OSBL <sup>b</sup> )	28	32	26
contingency charges (=10% of ISBL <sup>a</sup> + OSBL <sup>b</sup> )	9	11	9
total fixed capital investment	130	151	123
working capital	14	16	13
total capital investment	144	167	136

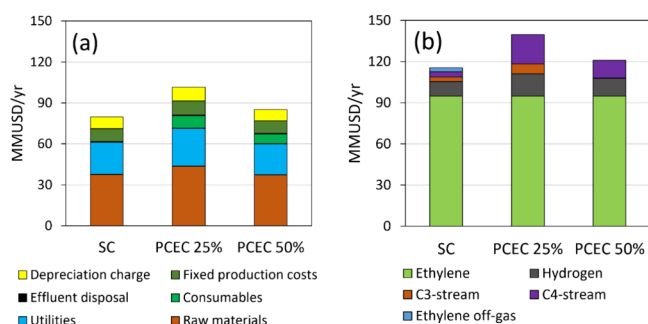
<sup>a</sup>ISBL, inside battery limits. <sup>b</sup>OSBL, outside battery limits.

reactor costs in the PCEC process. Moreover, the capital investment in distillation columns, heat exchangers, and flash vessels was higher for the base case PCEC process, due to the lower single-pass ethylene yield (ca. 25%) in comparison to the SC process (52%), resulting in a bigger recycle stream and, hence, larger equipment sizes. By contrast, when the PCEC process was operated using an ethylene yield that is similar to the SC process, as exemplified by the PCEC target case, then the total investment costs were comparable to the SC process (Table 2). Despite the higher reactor costs for the target case PCEC process relative to SC, the total capital investment of both processes was similar, due to notably lower compressor costs of the PCEC process. The latter was ascribed to the *in situ* hydrogen compression inside the PCEC membrane reactor and the higher operating pressure of the PCEC reactor (5 bar(a)) versus the SC furnace (2 bar(a)), leading to a lower demand for mechanical compression in the PCEC process.

Table 2 shows that the main contributors to the capital investment of the SC and PCEC processes were the reactor and compressor equipment. The compressor costs were independent of whether the reaction and (pre)heating steps within the processes were operated using electrical heat or heat generated by burning fossil fuels. However, the reactor equipment costs might differ per heating method, as e.g., electrification of cracking equipment could lead to a considerable reduction in the required equipment size.<sup>51,52</sup> On the contrary, electrification is anticipated to be accompanied by additional expenditures on heating elements and power management (transformers, etc.).<sup>51</sup> Due to this current uncertainty, it was assumed in this work that the CAPEX of the electrically heated processes equals the CAPEX of the corresponding fossil fuel heated process cases.

The capital investment of the distillation columns and heat exchangers in this work (Table 2) were relatively marginal as compared to values typically reported in literature for alkane dehydrogenation processes.<sup>53</sup> The olefin/paraffin separator (including condenser and reboiler) often even covers 40% of the total direct investment.<sup>53</sup> However, due to the relatively small olefin production capacity selected in this work (100 ktpa) as compared to the typical production capacity of alkane dehydrogenation plants (ca. 400–1000 ktpa),<sup>54</sup> the distillation column diameters were comparably small here, allowing for relatively thin walls and, hence, relatively low steel costs. Moreover, the cryogenic distillation steps in this ethane dehydrogenation study were carried out using refrigerants at subzero temperatures, whereas distillation columns in propane and butane dehydrogenation plants are commonly operated using cooling water.<sup>55</sup> The use of relatively cheap cooling water for condensation was not possible for the ethane dehydrogenation processes simulated here, as the temperatures of the overhead streams to be condensed were too low ( $T$ :  $-20$  to  $20$  °C). However, the advantage of using more expensive refrigerants ( $T$ :  $-150$  to  $-25$  °C) was the large temperature gap between the refrigerant and the overhead stream to be condensed. Consequently, the driving force for condensation was large, leading to low condenser investment costs as compared to typical cooling water-based propane and butane dehydrogenation processes. Analogously, the temperature gap between the low pressure steam utility ( $T$ :  $125$  °C) and the distillate bottom streams to be reboiled ( $T$ :  $-30$  to  $20$  °C) was much larger for the ethane dehydrogenation processes simulated here as compared to typical propane and butane dehydrogenation processes (reboiler  $T$ :  $50$ – $60$  °C). The required reboiler heat exchange areas and corresponding reboiler capital costs were, therefore, also lower in this work as compared to typical propane and butane dehydrogenation processes, even after applying material factors for the operation at subzero temperatures in the distillation section.

**4.3.2. Operating Expenditures.** The operating expenditures (OPEX) of the different processes were quantified for the fossil fuel heated cases. The total OPEX of the base case PCEC process was ca. 30% higher compared to the SC process (Figure 6a). This was attributed to higher costs for raw materials, utilities, and consumables. The raw material costs were higher for the base case PCEC process, due to the lower ethylene selectivity of that process relative to the SC process (63% versus 80%, respectively). Besides, the utilities were more expensive for the base case PCEC process, since the energy duty to be covered by utilities was higher compared to the SC process (see Figure 4). Moreover, the costs for consumables



**Figure 6.** (a) The total production costs and (b) the total revenues for the conventional ethane steam cracking (SC) process and the base case (ca. 25% ethylene yield), and target case (50% ethylene yield) PCEC processes.

were considerably higher for the base case PCEC process than for the SC process, due to the periodic replacement of the membrane stack materials. The membrane lifetime was set equal to the lifetime of the dehydrogenation catalyst of two years in this analysis. Marginal over/underpredictions of the PCEC membrane replacement frequency could strongly impact the total operating costs, as the consumables are a major contributor to the total PCEC OPEX (Figure 6a).

In contrast to the base case PCEC process, the operating costs of the target case PCEC process were more comparable to conventional SC (Figure 6a). Solely the expenditures on consumables were significantly higher for the target case PCEC compared to SC, due to periodic replacement of the membranes. It should be noted that the share of raw material costs to the total OPEX of the SC and PCEC processes (ca. 50%, Figure 6a) was small relative to typical values of bulk chemical production processes (ca. 80%).<sup>45</sup> This is in agreement with previous ethane steam cracking process simulation studies.<sup>55,56</sup> The lower share of raw material costs to the total OPEX was particularly caused by the high refrigerant utility costs in the different processes, which was associated with the cryogenic operation of the separation train.

Despite the higher OPEX of the PCEC processes compared to the SC process (Figure 6a), the yearly revenues were also higher for both PCEC process cases (Figure 6b). This was due to the larger amount of valuable hydrogen, C3, and C4 byproducts generated in the PCEC processes. The *in situ* hydrogen separation inside the PCEC reactor allowed for facile hydrogen isolation. Besides, the simulated PCEC process dealt with a higher C3 and C4 selectivity, as adopted from the work by Wu et al.,<sup>27</sup> relative to the simulated SC process. The profitability of the different processes was investigated for situations in which the revenues obtained from selling the C3 and C4 byproducts were included or excluded to evaluate the process viability when aiming at ethylene production (Table 3, see Supporting Information P for more details). When including the C3 and C4 revenues, the profitability of the SC and PCEC processes was comparable in terms of return on investment (ROI) and payback time (Table 3), since the higher operating costs of the PCEC processes (Figure 6a) were compensated by the higher revenues (Figure 6b). The profitability of particularly the base case PCEC process declined when only including the ethylene revenues (Table 3), as this process case heavily relied on incomes from the C3 and C4 byproducts (Figure 6b). By contrast, the viability of the SC and target case PCEC processes, which both dealt with similar product distributions, was also comparable when only

**Table 3. Return on Investment (ROI) and Payback Period of the Ethane SC Process and the Base Case and Target Case PCEC-Assisted Ethane Dehydrogenation Processes, Excluding Carbon Taxation<sup>a</sup>**

	SC	PCEC base case (25%)	PCEC target case (50%)
When including revenues obtained from selling C3 and C4 byproducts:			
ROI	20.3%	18.8%	21.6%
payback period	4 years	5 years	4 years
When excluding revenues obtained from selling C3 and C4 byproducts:			
ROI	14.7%	4.7%	13.8%
payback period	6 years	19 years	7 years

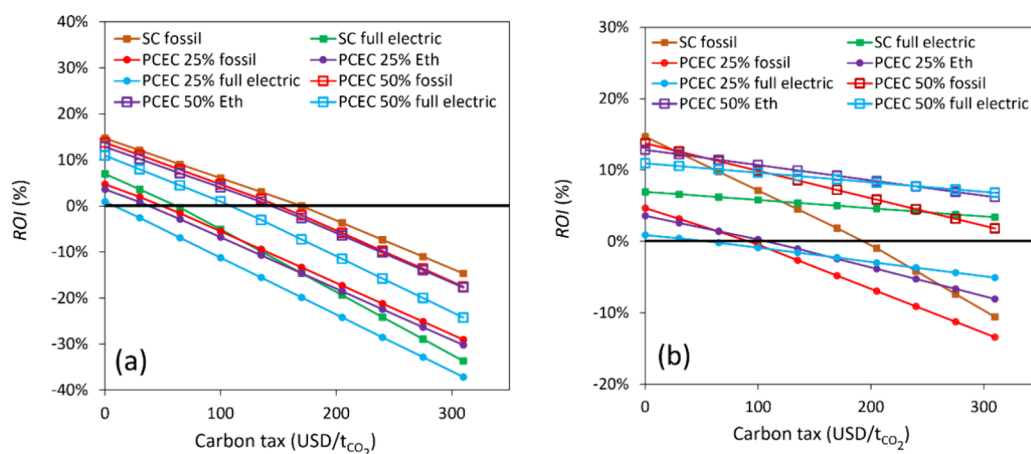
<sup>a</sup>A distinction was made between situations in which the revenues obtained from selling C3 and C4 byproducts were included or excluded. See Supporting Information P for more details.

including ethylene revenues (Table 3). Note that the results in Table 3 considered a grid electricity price of 60 USD/MWh. However, green electricity is often cheaper than average grid electricity.<sup>42</sup> A sensitivity analysis revealed that, when including C3 and C4 product revenues, the base case PCEC process became more profitable than the SC process if the electricity price was lower than ca. 50 USD/MWh (see Supporting Information O2).

**4.3.2.1. Carbon Tax.** In view of resolving the global climate crisis, increased carbon taxes are expected to be levied on the emission of greenhouse gases like carbon dioxide by the chemical industry. For this reason, the potential impact of variations in the carbon tax on the profitability of the SC and PCEC processes was investigated in this work (see Figure 7). The revenues obtained from selling C3 and C4 byproduct streams, which were particularly significant for the base case PCEC process (Figure 6b), were excluded from this analysis to highlight the process profitability when aiming at ethylene production.

In the case of Asia-Pacific grid electricity (Figure 7a), all the considered process cases became substantially less viable with increasing carbon tax, as all these cases coped with considerable carbon dioxide emissions (see Figure 5). Notably, the SC and PCEC full electric cases that required a substantial amount of relatively expensive electricity (60 USD/MWh), were consistently the least profitable ones (Figure 7a). Moreover, the base case PCEC process (ca. 25% ethylene yield) was barely profitable, even in absence of carbon taxation and irrespective of the heating method. This is again an indication that higher ethylene yields are needed to make PCEC-assisted ethane NODH industrially attractive. Compared to base case PCEC, the target case PCEC process was significantly more lucrative, as it dealt with (i) a lower capital investment (Table 2), (ii) lower utility costs (Figure 6a), and (iii) lower raw material costs (Figure 6a). The utility costs were lower, partly due to the lower fired heat and steam demand in preheating and reboiling, and partly due to lower refrigerant costs in the cryogenic distillation columns. Besides, the raw material costs were lower, due to more efficient usage of the fresh ethane reactant when operating at a higher single-pass ethylene yield.

When fully renewable electricity was used (Figure 7b), then all full electric cases were significantly less penalized by the imposed carbon tax, as these cases had a considerable smaller carbon footprint (see Figure 5). The SC and target case PCEC full electric cases remained lucrative up to the highest



**Figure 7.** Influence of the levied carbon tax on the return on investment (ROI) of the different process cases (a) when Asia-Pacific grid electricity was used and (b) when fully renewable electricity was utilized. SC, ethane steam cracking process; PCEC, PCEC-assisted ethane dehydrogenation process;  $E_{th}$ , PCEC operation at thermoneutral voltage. The results presented here excluded the revenues obtained from selling C3 and C4 byproducts.

considered carbon tax and became more profitable than their fossil fuel heated alternatives above a carbon tax of ca. 100 USD/ $t_{CO_2}$  (Figure 7b). This thereby illustrates that for the price (60 USD/MWh) and carbon intensity (532.1  $g_{CO_2}/kWh$ ) of the electricity considered in this work, a carbon tax of more than 100 USD/ $t_{CO_2}$  is recommended to be levied to stimulate process electrification. Interestingly, the green electrified target case PCEC process was more profitable than the green electrified SC process (Figure 7b). This difference was ascribed to excessive electricity costs for the green electrified SC process, where in this case expensive electricity was utilized to heat the reactor inlet to the cracking temperature of 850 °C. One needs to note that the ROI values of the full electric cases in Figure 7b are pessimistic estimations, as they were determined using an overestimated electricity price of 60 USD/MWh, i.e., the current grid electricity price. Green electricity can be generated at lower prices than those herein considered.<sup>42</sup> In summary, to environmentally and financially outcompete fossil fuel-based SC and PCEC processes, fully renewable electricity needs to be utilized and a carbon tax of more than 100 USD/ $t_{CO_2}$  needs to be imposed (Figure 7b).

**4.4. Perspective and Industrial Guidelines.** The PCEC-assisted ethane dehydrogenation process was simulated in this work based on two distinct product distributions. In the base case, the product distribution employed in the model was obtained from experimental studies on PCEC-assisted ethane NODH,<sup>27</sup> which concerned a single-pass ethylene yield of ca. 25%. In the second case, a higher targeted single-pass ethylene yield of 50% was applied to examine the potential impact of industrial usage of PCEC membranes on a process dealing with an equal ethylene yield as conventional SC. In this work, we showed that the base case PCEC process had higher capital costs (Table 2), higher operating costs (Figure 6), higher energy usage (Figure 4), and a greater carbon footprint (Figure 5) than conventional SC. This was all attributed to the existence of larger process streams and process units in the base case PCEC process as compared to the SC process, which is linked to the lower single-pass ethylene yield (25% vs 52%). As a result, the PCEC process was barely profitable for an ethylene yield of ca. 25% (Figure 7). On the contrary, the PCEC process could become financially and environmentally

competitive with the SC process if it would be operated with an ethylene yield of about 50% (Figures 5 and 7). Moreover, a sensitivity analysis revealed that the biggest energy savings in the PCEC process were achieved when increasing the single-pass ethylene yield from ca. 25% (26.9 MJ/kg<sub>ethylene</sub>) to ca. 50% (19.9 MJ/kg<sub>ethylene</sub>, see Supporting Information O1). The energy savings were more marginal upon further increasing the ethane-to-ethylene conversion, as a minimum amount of energy was needed for operating the dehydrogenation reaction, heating, and mass circulation, regardless of the ethylene yield employed.

Despite the uncertainty in the obtained carbon emission and cost values, it is clear that higher ethylene yields need to be achieved in experimental PCEC research for ethane NODH applications to brighten the industrial perspective of this technology. To this end, a better understanding of the reaction mechanisms taking place under various conditions in PCEC systems for ethylene production would help in steering the product distribution. A key challenge will be to ensure system stability at high ethylene yields, as higher olefin and lower hydrogen concentrations generally boost carbon deposition.<sup>57</sup> In particular, the PCEC membrane lifetime needs to be similar or longer than the dehydrogenation catalyst lifetime, as the PCEC membrane replacement was found to be a major contributor to the operating costs for an equal catalyst and membrane lifetime of two years (Figure 6a).

A possible way to mitigate carbon deposition in PCEC systems is by making use of the co-ionic properties of solid oxide electrolyzer cells. Morejudo et al.<sup>16</sup> demonstrated for the related methane dehydroaromatization reaction that cotransport of  $O^{2-}$  ions in the direction opposing proton transport assists in improving PCEC stability, caused by oxidation of carbon deposits induced by well distributed injection of oxygen to the reaction zone. This counter-current flow of  $O^{2-}$  through the solid electrolyte could originate from the steam cosupply that is inevitably needed for optimal membrane operation. Besides, the direct steam cosupply on the PCEC reaction side could help avoiding coke formation, despite the possible steam reforming reactions. Additionally, avoiding the use of Ni in PCEC electrode materials could help in improving PCEC stability, as Ni is known to boost carbon deposition.<sup>58</sup> The Ni could e.g., be replaced by other metals (e.g., Cu, Ag) or redox



active metal oxides.<sup>59</sup> Also note that sulfur removal in process pretreatment steps will be essential to avoid possible sulfur poisoning of PCEC materials operating in hydrocarbon-rich atmospheres. Lastly, operation at lower temperatures could minimize issues related to mismatches in thermal expansion coefficients of the different PCEC layers and would thermodynamically be beneficial to diminish coke formation, although this might require higher PCEC voltages to attain certain hydrogen removal rates and ethylene yields.

Another important parameter in PCEC systems is the applied current density. A current density of 1.0 A/cm<sup>2</sup> was selected in this work as a realistic estimation for industrial PCEC reactors, based on current densities achieved in lab scale PCEC systems.<sup>15,16</sup> Upon increasing the current density, the PCEC reactor capital investment would reduce due to a reduction in required membrane area, while the energy consumption would increase for a constant area specific resistance (ASR). A sensitivity analysis of the applied current density revealed that the optimum in the trade-off between minimizing membrane area and minimizing energy consumption was obtained for a current density of 1.0 A/cm<sup>2</sup> (see Supporting Information O4). The current density used in this work is therefore also proposed to be used in future PCEC research. Moreover, upon increasing the ASR, the required voltage for a given current density and thereby the required energy input will increase, which leads to a less profitable process if electricity is expensive (>50 USD/MWh, see Supporting Information O5). If the electricity price would become as low as the natural gas price (ca. 16 USD/MWh), the profitability of the PCEC process was found to become independent of the ASR.

In this contribution, we further demonstrated that fully renewable electricity needs to be utilized upon process electrification to potentially reduce the process carbon footprint (Figure 5). Specifically, the carbon intensity of the electricity needs to be below 200 g<sub>CO2</sub>/kWh to ecologically justify process electrification (Supporting Information O3). Otherwise, the use of direct fossil fuel heat is ecologically friendlier than the use of electrical heat. Moreover, to make electrified processes more profitable than their fossil fuel-based alternative, green electrical heat should become cheaper per MWh than fossil fuel heating, and a carbon tax of more than 100 USD/t<sub>CO2</sub> should be imposed (Figure 7b). The latter emphasizes that governments can play a pivotal role in electrifying the chemical industry.

Next to electrochemical ethane NODH, the main alternative routes for green ethylene production encompass (i) electrochemical ethane oxidative dehydrogenation (ODH), (ii) bioethanol dehydration, (iii) electrochemical CO<sub>2</sub> reduction, and (iv) electrical steam cracking. The electrochemical ethane ODH route is technologically undesired, because of the risk for hydrocarbon overoxidation and the facile generation of explosive atmospheres in ethane ODH conditions.<sup>60</sup> Besides, the bioethanol dehydration route is financially unattractive, as the high costs of the ethanol feedstock raise the ethylene production costs via this route.<sup>60</sup>

Ethylene production via CO<sub>2</sub> reduction appears the other most competitive route for green ethylene production. The CO<sub>2</sub>-to-ethylene approach has the clear advantage of using CO<sub>2</sub> as feedstock, potentially allowing for net zero emissions. In contrast, electrochemical ethane NODH needs to be combined with depolymerization strategies to establish circular production pathways. However, CO<sub>2</sub> is a highly stable

molecule that is hard to convert. Moreover, electrochemical conversion of CO<sub>2</sub> to ethylene is hindered by a limited olefin selectivity of typically less than 60%.<sup>60</sup> Due to this low ethylene selectivity, a lot of energy in the CO<sub>2</sub> reduction process is lost in generating byproducts.<sup>61</sup> Additionally, the CO<sub>2</sub> reduction process suffers from a high capital investment, as only a limited part of the total electrolyzer area is effectively utilized for ethylene production.<sup>61</sup> Therefore, the CO<sub>2</sub> reduction route primarily requires an improvement in ethylene selectivity to become competitive with conventional ethane SC. Without further improvements in ethylene yield in the CO<sub>2</sub> reduction and electrochemical ethane NODH routes, electrification of ethane steam cracking seems the most promising direction for green ethylene production. But, as pointed out in this techno-economic study on ethane NODH and in a previous techno-economic study on CO<sub>2</sub> reduction to produce ethylene,<sup>61</sup> a substantial decrease in grid electricity price is needed to create the incentive for process electrification, regardless of the target green ethylene production route.

Apart from the performance requirements and financial constraints of PCECs, several other technological challenges need to be considered before PCEC membrane reactors can be implemented on an industrial scale. Since ethylene is an essential building block for the chemical industry with a market size around 200 billion USD in 2023,<sup>2</sup> possible green alternative production processes need to be scalable to plants with ethylene production capacities in the range 100–1000 ktpa. For this reason, PCEC systems need to become available in enormous amounts to enable integration with ethylene production facilities. Because of this, non-noble and nonrare elements should be applied in PCEC systems to lower the capital investment of PCEC membrane reactors.<sup>60</sup> Furthermore, a closer look needs to be taken at the synthesis routes of the various PCEC materials. Currently, most of the PCEC electrode and electrolyte materials are obtained from energy and labor intensive lab-scale synthesis methods. Eventually, these synthesis methods need to be scalable to industrial production facilities and the required chemical elements for the PCEC electrode and electrolyte materials need to be abundantly available to satisfy industrial scale ethylene production. An additional challenge lies in the continuous usage of renewable electricity. We confirmed in this work that green electricity needs to be used to minimize carbon emissions in electrified ethylene production processes (Figure 5). However, it is questionable whether green electricity can be delivered continuously, as e.g., solar and wind power will not be permanently available. Moreover, electrification of large scale ethylene production processes will put an enormous pressure on the electricity grid. There is a heavy responsibility on governments to facilitate the electrification of the chemical industry by expanding the electricity grid around chemical plants.

Ultimately, electrification of ethylene production processes—whether through the industrial implementation of PCEC membranes or the electrification of conventional steam crackers—could reduce the carbon footprint from ca. 1.5 t<sub>CO2</sub>/t<sub>ethylene</sub> (SC fossil) to ca. 0.2 t<sub>CO2</sub>/t<sub>ethylene</sub> (see Figure 5). The global ethylene market size was around 200 billion USD in 2023.<sup>2</sup> For a polymer-grade ethylene price of ca. 950 USD/t<sub>ethylene</sub>, this leads to a global annual production of about 210 million ton of ethylene. A reduction in carbon footprint of ca. 1.3 t<sub>CO2</sub>/t<sub>ethylene</sub> thus, corresponds to a saving in carbon dioxide emissions of ca. 270 million tons, which is ca. 0.7% of

the global carbon dioxide emissions,<sup>62</sup> if all ethylene production processes worldwide would be replaced by these green electrified alternatives.

## 5. CONCLUSIONS

The potential of applying ceramic proton-conducting electrolysis cell (PCEC) membranes in ethylene production processes was explored in this work. To this end, a PCEC-assisted ethane dehydrogenation process was compared to a conventional ethane steam cracking (SC) process in terms of process economics, energy usage, and carbon footprint. The results indicated that the PCEC process could only be financially and environmentally competitive with conventional SC in the case of similar ethylene yields (ca. 50%). For currently achievable ethylene yields using PCEC technologies of ca. 25%, the capital investment and carbon emissions of the PCEC process were too excessive to outcompete electrified ethane SC. The total energy usage, utility demand, and capital investment were substantially higher for the ca. 25% ethylene yield PCEC case as compared to the 50% case, due to larger process streams and process units as a result of the lower single-pass yield. The results further highlighted that carbon emissions could be reduced from ca. 1.5  $t_{\text{CO}_2}/t_{\text{ethylene}}$  to ca. 0.2  $t_{\text{CO}_2}/t_{\text{ethylene}}$  when employing green electrified SC or PCEC processes instead of conventional fossil fuel-based SC, but only if fully renewable electricity was utilized. Moreover, a carbon tax of more than 100 USD/ $t_{\text{CO}_2}$  would need to be imposed to make the green electrified SC and PCEC processes more viable than their fossil-based counterparts. Lastly, technological challenges related to the attainable ethylene yield, PCEC stability, large scale sustainable production of PCECs, and the continuous availability of green electricity were identified as hurdles that need to overcome in facilitating the industrial implementation of PCECs for green ethylene production.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.4c08549>.

Background information of the process simulations, encompassing (i) process design basis, (ii) process flow diagrams and stream tables, (iii) equipment design, (iv) heat integration, and (v) tables containing the results of the CAPEX, OPEX, energy usage, and carbon emission calculations (PDF)

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## Notes

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