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## Towards ethylene production from carbon dioxide: economic and global warming potential assessment

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### Abstract

Currently, ethylene is the most important chemical with the largest global demand: it is mainly produced by ethane or naphtha cracking but, this is characterized by significant carbon dioxide emissions. For this reason, starting from carbon dioxide and water, different routes for ethylene production have been proposed and investigated in the literature but a complete comparative analysis is missing.

In this research, we analyze ethylene production via carbon dioxide electroreduction and a methanol-to-olefin process, with methanol obtained in several ways. After the modelling of these systems, economic and environmental (in term of global warming potential) analyses are conducted to develop a comparison among the investigated processes and a conventional one based on naphtha cracking.

Results, located in the UK, show that the tandem process could be economically competitive (with the lowest production cost of 1.34 \$ per kg of ethylene), while the methanol-to-olefin process with methanol obtained from syngas (produced through carbon dioxide-water co-electrolysis) has the best advantages for carbon dioxide emissions (with the lowest impact of -3.08 kg of CO<sub>2eq</sub> per kg of ethylene). Moreover, the most preferred energy source for the electricity supply is the nuclear one with a small-scale plant because, economic and greenhouse gas emission advantages are provided while, worse conditions are obtained when solar energy is used.

Our main finding is that electrochemical processes are likely to play an important role in the future when performance improvements are realized.

**Keywords:** carbon dioxide electroreduction, methanol-to-olefin plant, ethylene, life cycle GHG assessment, modelling, economic analysis.

## **Nomenclature**

AEM, anion-exchange membrane

APEA, aspen process economic analyzer

AEL, alkaline cell

BAU, businesses as usual

BoP, balance of plant

CAPEX, capital cost

CRF, capital recovery factor

DAC, direct air capture

GHG, greenhouse gas emission

GWP, global warming potential

LCA, life cycle assessment

LCI, life cycle inventory

LCIA, life cycle impact assessment

MEA, membrane electrode assembly

MTO, methanol to olefin

NRTL, non-random two liquids

OPEX, operating cost

PEM, proton exchange membrane

PSA, pressure swing adsorption

ROI, return of investment

SRK, soave-redlich kwong

SOEC, solid oxide electrolytic cell

TRL, technology readiness level

## **Symbols**

H, annual operating time of the plant (h per year)

Levelized CAPEX, levelized capital cost (\$ per ton)

Levelized OPEX, levelized operating cost (\$ per ton)

$E_e$ , production energy consumption (kWh per kg of H<sub>2</sub>)

$Q_H$ , annual production capacity of the plant (kg of H<sub>2</sub> per year)

$\alpha$  technical learning rate (%)

## 1.Introduction

Globally, carbon dioxide (CO<sub>2</sub>) emissions were about 34.81 billion tonnes in 2020, hence there is an urgency to reduce these emissions to avoid negative phenomena such as global warming and climate change (Our World in data, 2022; Wyndorps et al., 2021). The European Union (EU), in this context, aims to reduce 80% of CO<sub>2</sub> emissions by 2050 (COM, 2011). To achieve this aim, greenhouse gases (GHGs) must be reduced in all sectors including the chemical industry which contributes about 6% to global CO<sub>2</sub> emissions (Our World in Data, 2021). Therefore, low-carbon technologies reusing CO<sub>2</sub> to produce chemicals have to be developed according to circular economy principles. Among these chemicals, methanol and ethylene have the largest global market with production capacities respectively of 145 million ton per year and 185 million ton per year in 2018 (Global Data Petrochemical, 2021). As shown by these data, ethylene is the product with the highest demand in the world as it is a building block used to produce pharmaceutical products and industrial precursors such as plastics, textiles, composites (polyethylene, ethylene dichloride, ethylene oxide, ethylbenzene, vinyl acetate, co-polymers, etc.), end products (food packaging, film, toys, food containers, bottles, pipes, antifreeze, carpets, insulation, housewares, etc.) (Berkelaar et al., 2022; Emerson, 2022). It is evident that ethylene is one of the most important organic materials: it is expected that its production will increase in the next future (the worldwide production of ethylene increased by over 15% in 2021 in comparison with 2018 (Statista, 2022)).

Currently, ethylene is mainly produced by the steam cracking of naphtha (Europe and Asia corresponding to more than 80% of total ethylene production) and natural-gas-derived ethane (North America). However, both conventional routes have both high energy requirements (up to 40 GJ heat per ton of ethylene) and CO<sub>2</sub> emissions (1.8-2 kg of CO<sub>2</sub> per kg of ethylene): it has been estimated that about 0.26 GtCO<sub>2eq</sub> were emitted to satisfy the 2021 production, accounting for about 30% of the total energy required by the chemical industry (Sisler et al., 2021; Haribal et al., 2021; Worrell et al., 2020). For these reasons, other ethylene production routes have been investigated and suggested, being based either on CO<sub>2</sub> utilization in an electrolytic cell or via methanol to be used in a methanol-to-olefin (MTO) process (Jouny et al., 2018; Chen et al., 2021). This allows the decarbonization of feedstocks and energy sources.

For CO<sub>2</sub> utilization in an electrolytic cell, known also as the CO<sub>2</sub> electrochemical reduction (CO<sub>2</sub>ER) system, CO<sub>2</sub> is directly reduced to ethylene at the cathode side and, water is oxidised at the anode side. An economic analysis of this process has been conducted in the literature by Pappijijn et al. (2020) and Orella et al., (2020) finding a production cost higher than that of the current market price, when using specific conditions for selectivity and conversion. However, an ethylene production cost lower than that of the market price has been reported in the work of Kibria et al. (2019), De Luna et al. (2019) and Jouny et al. (2018). In Kibria et al. (2019), a Faradaic efficiency of 90 %, a current density of 500 mA/cm<sup>2</sup> and an electricity cost of 0.02 \$ per kWh are assumed. The same value of Faradaic efficiency is considered in the work of De Luna et al. (2019), obtaining a production cost of 1100 \$ per ton compared to current prices which are in the range between 600 and 1300 \$ per ton. In Jouny et al. (2018) the process for ethylene production is economically feasible (net

present value is positive) when optimistic conditions are taken into account (current density of 300 mA/cm<sup>2</sup>, selectivity of 90 %, electricity price of 0.03 \$ per kWh).

The environmental analysis of the direct CO<sub>2</sub>ER route has been reported in the literature in addition to the economic analysis. Even though for Nabil et al. (2021), the electrochemical production of ethylene from CO<sub>2</sub> is one of the most compelling product in terms of global warming potential (GWP), in Pappijn et al. (2020) only the use of green electricity allows having an overall negative net CO<sub>2</sub> balance. On the other hand, in the cradle-to-gate analysis of Khoo et al. (2020) the value of GWP for a large-scale model is between 0.65-3 ton of CO<sub>2eq</sub> per ton of ethylene.

Another electrochemical process for CO<sub>2</sub> reduction has been proposed by Sisler et al. (2021) considering a tandem scheme for CO<sub>2</sub> reduction to carbon monoxide (CO) in the first stage (in a solid oxide electrolytic cell (SOEC)) and CO reduction to ethylene in the second stage (in a neutral membrane electrode assembly (MEA) or alkaline flow cell). The solution avoids CO<sub>2</sub> losses due to crossover in neutral MEAs and carbonate formation in alkaline flow cells and with an electrical energy efficiency (evaluated as Faradaic efficiency • (Thermodynamic cell voltage/Cell voltage)) of about 52 % can produce ethylene at 1000 \$ per ton.

For the MTO process, economic and environmental analyses have been conducted in the literature. In Ortiz-Espinoza et al. (2017) it is reported that this process (where methanol is obtained from syngas produced by methane steam reforming) is more profitable (a higher value of Return of Investment (ROI) is obtained for the same ethylene price in the range between 0.5 and 0.9 \$ per Ib) than the oxidative coupling of methane (OCM) process. However, the MTO is worse from an environmental point of view even though improved performance could be achieved by changing some process variables such as the recycle ratio in the methanol reactor. The economic advantages of a new MTO plant based on absorption technology in the recovery section are reported in Reyniers et al. (2017): the suggested scheme has capital costs up to 14% and operating costs up to 9% lower compared to the traditional cryogenic configuration. Another economic analysis is conducted in the work of Chen et al. (2021) finding that the MTO plant is economically profitable with a methanol price between 150 and 200 \$ per ton for which the ROI is respectively 66% and 28.7%. For a methanol price of 250 \$ per ton the ROI is negative (-8.6%).

Electrochemical and MTO processes for ethylene production are compared in Berkelaar et al. (2022) and Ioannou et al. (2020). In Berkelaar et al. (2022) the direct CO<sub>2</sub>ER to ethylene route, MTO plant with methanol from direct CO<sub>2</sub>ER, CO<sub>2</sub> hydrogenation, syngas (obtained from CO<sub>2</sub>-H<sub>2</sub>O co-electrolysis) and Fischer-Tropsch process are compared. The conducted analysis shows that the MTO plant with methanol from syngas produced from CO<sub>2</sub>-H<sub>2</sub>O co-electrolysis is the best one based on efficiency, selectivity, process complexity and thermodynamic limitations. The authors find also that electricity and CO<sub>2</sub> costs are critical for the economic analysis. As a similar work, in Ioannou et al. (2020) the following routes for ethylene production are analyzed and compared: the direct CO<sub>2</sub>ER to ethylene, MTO plant with methanol from CO<sub>2</sub> hydrogenation (green and blue hydrogen) and syngas from natural gas, naphtha cracking. These processes are classified as electro-route,

thermo-route and fossil-route. Results show that under the current scenario, CO<sub>2</sub>-based alternative solutions for ethylene production, due to high electrical energy consumption, are not economically competitive with the fossil-based production routes, although they are more environmentally friendly. The authors suggest the hybridization of CO<sub>2</sub> utilization with fossil technologies in order to combine environmental and economic benefits.

It is possible to see that comparative studies on ethylene production via alternative solutions are scarce in the existing literature. In particular, as point of weakness, all possible processes for ethylene production are not taken into account and compared together. Moreover, economic and environmental results of the electrochemical path depend on fixed assumptions and hence, a deeper analysis is required.

In this research, different and new alternative paths for ethylene production, mainly based on CO<sub>2</sub> and H<sub>2</sub>O as raw materials, are investigated considering different CO<sub>2</sub> and power sources: the electrochemical process (including the tandem process proposed by Sisler et al. (2021) and the direct CO<sub>2</sub>ER to ethylene), MTO plant with methanol obtained from CO<sub>2</sub> hydrogenation with blue and green hydrogen and from CO<sub>2</sub>ER, and an MTO process with methanol obtained from syngas produced in a SOEC for the CO<sub>2</sub>-H<sub>2</sub>O co-electrolysis. After the modelling of these processes, ethylene production cost and global warming potential are evaluated and compared together and with the businesses as usual (BAU) process, based on naphtha cracking.

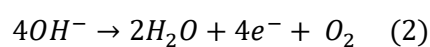
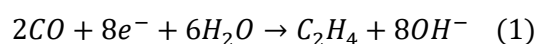
## 2. Materials and methods

In the following sections, the models used for the analyzed processes (classified into three main routes such as the electrochemical production routes, the MTO plant with methanol produced from catalytic or electrochemical reactions and the MTO plant with methanol produced from CO<sub>2</sub>-H<sub>2</sub>O co-electrolysis) are described. The methodology for economic and greenhouse gas emission analyses is also reported.

### 2.1 Process modelling

#### 2.1.1 Electrochemical routes for ethylene production

The tandem process and the single electrolyser cell are analyzed for the electrochemical production of ethylene from CO<sub>2</sub>. The tandem process has been proposed by Sisler et al. (2021), as in Figure 1: CO<sub>2</sub> is at first reduced to CO in a solid-oxide electrolyser cell and then the produced CO is reduced to ethylene in an alkaline flow cell in a second step, avoiding CO<sub>2</sub> losses, according to the following reactions respectively for the cathode and anode side (see Eqs. 1 and 2):



A gas separation unit based on pressure swing adsorption (PSA) is present after each electrolytic cell, allowing the separation of CO, H<sub>2</sub> and ethylene. The unconverted CO is recycled so that the external CO in the feed is lower than the stoichiometric amount. Simple material and energy balances for an electrochemical process, as

reported in the Supplementary Materials, are used to model this overall system with the optimistic assumptions reported in Table 1 (Sisler et al., 2021).

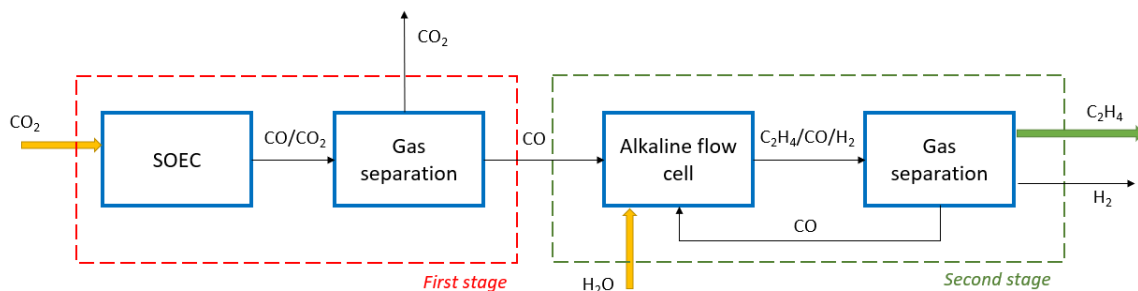


Figure 1 Scheme diagram of tandem process (Sisler et al., 2021)

Table 1 Assumption for the Tandem process (Sisler et al., 2021)

|                                       | Solid oxide electrolytic cell | Alkaline flow cell |
|---------------------------------------|-------------------------------|--------------------|
| Cell voltage (V)                      | 1.3                           | 1.8                |
| Faradaic efficiency (%)               | 100                           | 90                 |
| Current density (mA/cm <sup>2</sup> ) | 1000                          | 1000               |
| Single pass conversion (%)            | 60                            | 53                 |

A schematic diagram of the direct process reducing electrochemically CO<sub>2</sub> to ethylene is reported in Figure 2 (Jouny et al., 2018). The single electrolyser cell for the direct CO<sub>2</sub> electro-reduction to ethylene is modelled using the material and energy balances, as reported in the Supplementary materials, for an electrochemical process with the following optimistic assumptions: current density of 300 mA/cm<sup>2</sup>, cell voltage of 2 V, Faradaic efficiency of 90%, CO<sub>2</sub> conversion of 50% (Jouny et al., 2018). The cell works under alkaline conditions, because they are used by the best bench scale CO<sub>2</sub> electrolyser and this allows the use of non precious metals at the anode, making the comparison with alkaline water electrolysis appropriate. A gas separation unit, based on PSA, is present after the electrolytic cell.

Optimistic conditions, and not lab data, are assumed for both electrochemical processes because we aim to evaluate ethylene production at a large scale. Each technology is evaluated differently due to the inherent difference in the technology that follows different reactions although they produce ethylene at the end so that the same optimistic conditions could not be taken into account. In any case, in each reference, each optimistic condition is well supported. For the direct CO<sub>2</sub>ER scheme, in Jouny et al. (2018) a current density of 300 mA/cm<sup>2</sup> was assumed at cell voltage of 2 V, because fell within the range of commercial water electrolyzers. Faradaic efficiencies of 90% have been demonstrated for numerous CO<sub>2</sub> reduction products, such as CO, formic acid, and methanol, and were assumed for the analysis. Regarding CO<sub>2</sub> conversion, a value up to 35% has been reported in the literature (mostly for batch and single pass cells) so that a better electrolyzer design at a large scale and an optimistic forecast could potentially boost the CO<sub>2</sub> conversion to well over 50%. For



the tandem process, in Sisler et al. (2021), the SOEC can already operate with very high energy efficiency, so that many of its optimistic performance metrics have been measured. For the alkaline flow cell, the same comparison with alkaline anion-exchange membrane (AEM) water electrolyzers was used to obtain the optimistic current density. However, compared to the reference system, due to the limited pH gradients in the alkaline environment and the lower thermodynamic voltage of the reaction an optimistic cell voltage of 1.8 V was considered. The optimistic Faradaic efficiency was increased to 90% because recent demonstrations of CO reduction towards ethylene have reached a value of up to 72% while the conversion was increased of 10% (for the same reason discussed for the CO<sub>2</sub>ER scheme). The consideration of optimistic data helps to reduce costs up to about 15% for the direct CO<sub>2</sub>ER and up to 60% for the tandem process.

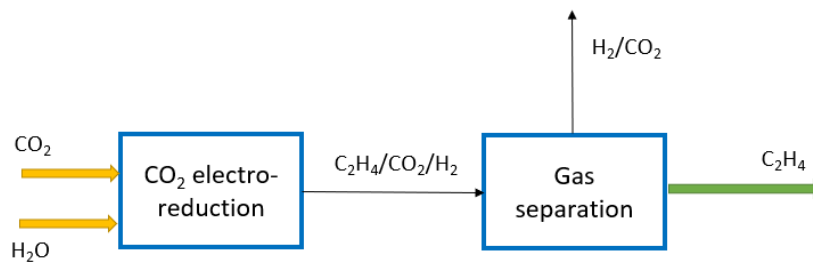


Figure 2 Scheme diagram of the CO<sub>2</sub> electrochemical reduction to ethylene process (Jouny et al., 2018)

### 2.1.2 Ethylene production with a MTO plant with methanol produced from catalytic or electrochemical reactions

The MTO plant is taken into account for ethylene production, with methanol obtained from a catalytic reaction between CO<sub>2</sub> and green or blue H<sub>2</sub> and from CO<sub>2</sub> electrochemical reduction, as in Figures 3, 4 and 5. All these sections are modelled in Aspen Plus except water and CO<sub>2</sub> electrolytic cells that are analyzed through material balances and inventory data.

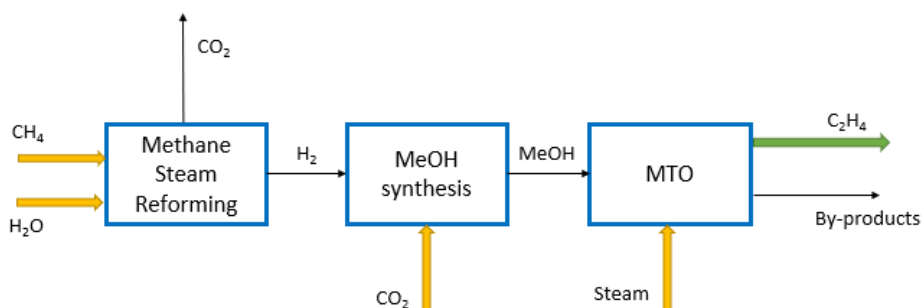


Figure 3 Scheme diagram of ethylene production through a MTO plant with methanol from a catalytic reaction between CO<sub>2</sub> and blue H<sub>2</sub> (MTO=methanol to olefin)

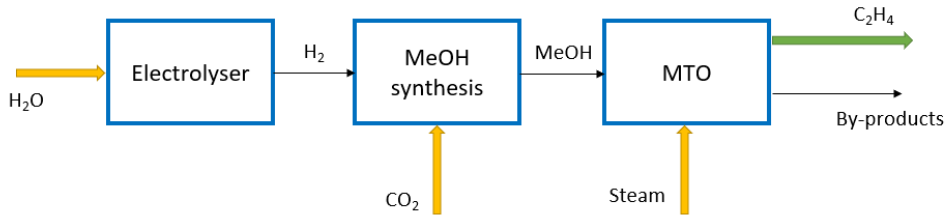


Figure 4 Scheme diagram of ethylene production through a MTO plant with methanol from a catalytic reaction between CO<sub>2</sub> and green H<sub>2</sub> (MTO=methanol to olefin; MeOH=methanol)

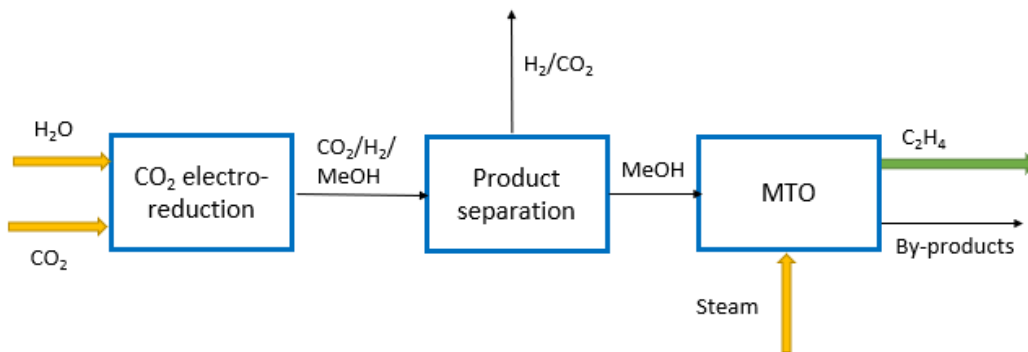


Figure 5 Scheme diagram of ethylene production through a MTO plant with methanol from the electrochemical reduction of CO<sub>2</sub> (MTO=methanol to olefin)

The blue H<sub>2</sub> is obtained from the methane steam reforming plant, reproduced in Aspen Plus as the work of Ciuchi (2019). The plant is composed of three main sections: the H<sub>2</sub> production (reformer reactor, high and low temperature water gas shift reactors and pressure swing adsorption columns), CO<sub>2</sub> capture (absorption with monoethanolamine (MEA) and stripper columns) and heat production parts. Soave-Redlich-Kwong (SRK) is used as the thermodynamic model.

The green H<sub>2</sub> is obtained from a proton exchange membrane (PEM) cell and alkaline (AEL) electrolysis process, considering the inventory data reported in Fan et al. (2022), as in Table 2.

Table 2 Assumptions for alkaline and proton exchange membrane cells for water electrolysis in green H<sub>2</sub> production (Fan et al., 2022)

|   | Alkaline cell | Proton exchange membrane cell |
|---|---------------|-------------------------------|
| Outlet pressure (bar)                                   | 1             | 30                            |
| Electricity consumption (kWh per kg of H <sub>2</sub> ) | 51            | 58                            |
| Water consumption (kg per kg of H <sub>2</sub> )        | 10            | 10                            |
| Electrolyte (KOH) (gr per kg of H <sub>2</sub> )        | 1.9           | 0                             |
| Steam (kg per kg of H <sub>2</sub> )                    | 0.11          | 0                             |
| Nitrogen (gr per kg of H <sub>2</sub> )                 | 0.29          | 0                             |

The methanol plant based on CO<sub>2</sub> hydrogenation using a highly active catalyst is modelled in Aspen Plus as the work of Kiss et al. (2016). Three sections are present: the methanol reactor with the recycle of CO, CO<sub>2</sub> and H<sub>2</sub>, a stripping column for water removal from the H<sub>2</sub> stream and the distillation column for methanol purification. The SRK thermodynamic model is used for the modelling of the first two sections while, the Non-Random Two Liquids (NRTL) is used for the distillation column. The Graaf kinetic model is taken into account for the methanol reactor (Graaf et al., 1988), characterized by the amount of catalyst (865 kg) and tube (810 with a length of 12 m) as in Kiss et al. (2016).

The methanol production based on CO<sub>2</sub> electrochemical reduction is modelled with material balances for an electrochemical process as in Jouny et al. (2018) with optimistic conditions such as: a current density of 300 mA/cm<sup>2</sup>, cell voltage of 2 V, Faradaic efficiency 90%, CO<sub>2</sub> conversion 50% (as stated before, optimistic conditions are considered because a large-scale production is investigated). As for the electrolytic cell reducing CO<sub>2</sub> to ethylene, alkaline conditions are used here with non-precious metals as catalysts at the anode side. A distillation unit is present at the downstream for the recovery of methanol.

The MTO plant is modelled in Aspen Plus reproducing the work of Chen et al. (2021), considering two main sections: the reaction and conditioning section and the product separation and recovery section. In the first section the SAPO-34 catalyst is used to achieve a nearly complete methanol conversion with about 80% of carbon selectivity to ethylene and propylene. In the recovery section, in addition to ethylene other products such as light gas products, ethane, propylene, propane, C<sub>4</sub><sup>+</sup> and C<sub>5</sub><sup>+</sup> are separated. The Peng-Robinson equation of state thermodynamic model is used.

### 2.1.3 Ethylene production with a MTO process with methanol produced from CO<sub>2</sub>-H<sub>2</sub>O co-electrolysis

In this case study, the MTO process produces ethylene from methanol obtained by the syngas of a SOEC cell, based on CO<sub>2</sub>-H<sub>2</sub>O co-electrolysis, as shown in Figure 6. As mentioned, methanol is here produced by syngas while in the previous schemes, methanol is obtained via CO<sub>2</sub>ER or CO<sub>2</sub> hydrogenation distinguishing the scheme from the others. The SOEC cell is modelled in Aspen Plus as in the work of Freire Ordonez et al. (2021), by adjusting the CO<sub>2</sub> flow rate in order to have syngas with a stoichiometric number S equal to 2.03 which is suitable for the methanol synthesis as in Zhang and Desideri (2020).

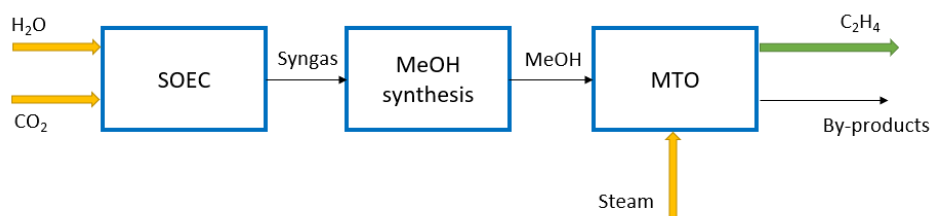


Figure 6 Scheme diagram of ethylene production through a MTO plant with methanol from syngas obtained from CO<sub>2</sub>-H<sub>2</sub>O co-electrolysis (MTO=methanol to olefin; MeOH=methanol)

The methanol process using syngas in the feed and simulated in Aspen Plus, is based on the separation of methanol and water (from unreacted gases) by condensation and on the recycle of unconverted gases (Leonzio and Foscolo, 2020). The methanol reactor is modelled as in the work of Kiss et al. (2016).

The used MTO plant is reproduced in Aspen Plus as described in section 2.1.2.

## **2.2 Economic analysis**

The economic analysis is conducted assuming that all plants are located in the UK with different CO<sub>2</sub> sources (natural gas processing/coal to chemicals, ammonia/bioethanol/ethylene oxide, methane steam reforming, iron and steel, cement, power generation and direct air capture (DAC) with a respective cost of 23.7, 35.6, 77.1, 83, 106, 88.9 and 325 \$ per ton of CO<sub>2</sub> (IEA, 2022)) and electricity (solar, wind, nuclear energy including a small modular reactor and large scale plant with a respective cost of 0.14, 0.09, 0.049 and 0.059 \$ per kWh (IRENA, 2019, NAMRC, 2022; Beis, 2016) sources. Assumptions for the economic analysis that are used in our work are the same proposed by the respective literature work taken as reference. If some assumptions are missed in the literature, we consider the most suggested and used value in other research. Regarding the analysis method, for electrolytic cells we use the same method proposed by the respective literature work with our contribution if a shortfall is present. For plants simulated in Aspen Plus (methanol, MTO, methane steam reforming) we use the economic tool of this software to have capital (CAPEX) and operating (OPEX) costs. An overview of the used methodology is reported in the Supplementary material.

### **2.2.1 Electrochemical routes for ethylene production**

The economic analysis of the two routes based on electrosynthesis is conducted considering the production of 100 tonnes/day of ethylene. CAPEX and OPEX costs are evaluated.

In the tandem process, these two terms are evaluated as reported in Sisler et al. (2021). It is assumed that the SOEC and alkaline flow cells cost 1067 and 300 \$ per kW respectively (Sisler et al., 2021). In the SOEC, the CAPEX includes the electrolyzer, gas separation unit for the cathode side and catalyst/membrane costs with their installation and balance of plant (BoP) costs. For the gas separation unit, the reference capital cost, reference capacity and scaling factor are respectively 1,990,000 \$, 1000 m<sup>3</sup>/h and 0.7 (Sisler et al., 2021). The catalyst/membrane cost is 5% of electrolyser capital cost while, the BoP is 50% of total capital (Sisler et al., 2021). The installation cost is obtained by the capital cost with a Lang Factor of 1 (Sisler et al., 2021). The OPEX includes the electricity cost for electrolyser and PSA units (consuming 0.25 kWh/m<sup>3</sup> of gases (Sisler et al., 2021)), the cost of CO<sub>2</sub> raw material and other additional operating costs related to the electrolyzer that are estimated as 10% of electricity cost (Sisler et al., 2021). For the alkaline flow cell, the same economic scheme of the SOEC is used for the evaluation of CAPEX and OPEX but, considering in addition the cost of the anolyte solution (500 \$ per ton) and water raw material (1.5 \$ per ton (Thameswaer, 2022)) feed at the anode side. The system lifetime is 20 years while, for the catalyst/membrane and electrolyte the lifetime is respectively 5 and 1 year. The overall ethylene production cost is evaluated as the sum of specific CAPEX and OPEX.

For the direct electrochemical process, the economic analysis is conducted based on the work of Jouny et al. (2018) where the electrolyser is assumed to cost 919.7 \$/m<sup>2</sup>. The overall CAPEX is provided by the sum of capital cost for the electrolytic cell, BoP (53% of electrolyser capital cost) and capital cost for the PSA unit evaluated as described in the tandem process (Jouny et al., 2018). A shortfall is present in the evaluation of operating cost in Jouny et al. (2018) so that the OPEX is obtained as the sum of direct production costs and total fixed production costs, as reported by Peters and Timmerhaus (1991), considering CO<sub>2</sub> and H<sub>2</sub>O as raw materials and the electricity consumption for the electrolyser and gas separation equipment as utilities. For the evaluation of the total levelized production cost these correlations are used (See Eqs. 3-6), assuming an interest rate of 10%, the plant lifetime of 20 years, an utilization of 95.2% and an annual production in ton per year (Moreno-Gonzalez et al., 2021).

$$\text{Levelized CAPEX} = \frac{\text{CAPEX} \cdot \text{CRF}}{\text{Annual production} \cdot \text{Utilization}} \quad (3)$$

$$\text{CRF} = \frac{\text{interest rate} \cdot (1 + \text{interest rate})^{\text{plant lifetime}}}{(1 + \text{interest rate})^{\text{plant lifetime}} - 1} \quad (4)$$

$$\text{Levelized OPEX} = \frac{\text{OPEX}}{\text{Annual production} \cdot \text{Utilization}} \quad (5)$$

$$\text{Total Levelized Production Cost} = \text{Levelized CAPEX} + \text{Levelized OPEX} \quad (6)$$

### 2.2.2 Ethylene production with a MTO plant with methanol produced from catalytic or electrochemical reactions

The economic analysis of H<sub>2</sub> production by water electrolysis is conducted according to the work of Fan et al. (2022) evaluating CAPEX and OPEX. The CAPEX is obtained by the following correlation (see Eq. 7) (Fan et al., 2022):

$$\text{CAPEX} = \text{Electrolyser cost} \cdot e^{-3\alpha} \cdot \text{Cap} \quad (7)$$

where the electrolyser capital cost is equal to 742 and 1187 \$ per kW respectively for AEL and PEM,  $\alpha$  is the technical learning rate (that considers that fact that technological progress might reduce the investment cost) equal to 12% and Cap is provided by Eq. 8 (Fan et al., 2022):

$$\text{Cap} = \frac{Q_H \cdot E_e}{H} \quad (8)$$

with  $Q_H$  the annual production capacity of the plant (kg of H<sub>2</sub> per year),  $E_e$  the production energy consumption (kWh per kg H<sub>2</sub>) and  $H$  the annual operating time of the plant. The OPEX is obtained considering the annual consumption of water, electricity, other raw materials (as in Table 2), as well as operation and maintenance cost (4% of total investment cost) (Fan et al., 2022). The H<sub>2</sub> production cost is provided as the sum of specific OPEX and CAPEX (assumed a lifetime of 20 years and an interest rate of 10% for the CRF evaluation).

The economic analysis of blue H<sub>2</sub> production by methane steam reforming is carried out by the Aspen Process Economic Analyzer (APEA) providing the values of CAPEX and OPEX while, Eqs. 1-4 are used for the

levelized cost. The lifetime of the plant is assumed to be 20 years with 8000 h/year as operating time (Ciuchi, 2019). The cost of electricity grid is assumed to be 0.251 \$ per kWh (GlobalPetrolPrice, 2022) while, the production rate is 7.27 ton of H<sub>2</sub> per h (Ciuchi, 2019).

The economic evaluation of the methanol plant based on CO<sub>2</sub> hydrogenation is conducted by APEA tool assuming an operating time of 8000 h/year (as the most used data in the literature) and a production of 11.2 ton of MeOH per h (Kiss et al., 2016). The levelized cost of methanol is evaluated with Eqs. 1-4.

The analysis of methanol production cost through CO<sub>2</sub> electrochemical reduction is carried out according to the procedure reported in Jouny et al. (2018), supposing a production rate of 100 ton/day and an operating time of 8400 h/year, as proposed by the same authors. The CAPEX is obtained by the sum of electrolyser capital cost, BoP, PSA and distillation capital costs. For the electrolyser, BoP and PSA the assumptions reported for the CO<sub>2</sub> electrochemical reduction to ethylene are considered. For the distillation unit, the product-rich electrolyte is recycled until a steady-state volume concentration of 10% methanol is reached, hence quantifying the electrolyte flow rate used for the capital cost of distillation. Assuming an electrolyte reference capacity of 1000 L/m, the distillation reference cost is \$4514670 with a capacity scaling factor of 0.7 (Jouny et al., 2018). The OPEX is evaluated as reported for the electrochemical system reducing CO<sub>2</sub> to ethylene and discussed in section 2.2.1 but, by adding the utility cost for the distillation section (the reference cost is 11,508.1 \$ per day with a reference electrolyte flow rate of 1000 L/min (Jouny et al., 2018)). The total levelized cost of methanol production is obtained from Eqs. 1-4.

The APEA tool is used to find the levelized cost of ethylene in the MTO plant, producing 46.4 ton of ethylene per h (Chen et al., 2021), in addition to the allocation by mass procedure for the specific cost.

### **2.2.3 Ethylene production with a MTO plant with methanol produced from CO<sub>2</sub>-H<sub>2</sub>O co-electrolysis**

For the economic analysis of an SOEC system, the specific electricity consumption is evaluated from the work of Freire Ordonez et al. (2021) and it is equal to 6.38 MWh per ton of syngas. This enables evaluation of the electricity consumption of the simulated electrolyser cell producing 18.9 ton of syngas per h (Zhang and Desideri, 2020). The electrolyser cost is based on Freire Ordonez et al. (2021) considering a reference cost of  $1.48 \cdot 10^6$  \$ per MW, a reference size of 1 MW and a scaling factor of 0.65. As a shortfall is present in the reference work, CAPEX and OPEX are obtained according to the methodology suggested by Peters and Timmerhaus (1991).

The economic analysis of methanol and MTO plants is carried out through the APEA tool in Aspen Plus and already discussed.

### **2.3 Life cycle of greenhouse gas emissions**

The analysis of greenhouse gas (GHG) emissions of processes producing ethylene is conducted according to the principles of Life Cycle Assessment (LCA) with the following standard phases as suggested by the ISO

14040: goal and scope definition, life cycle inventory (LCI), life cycle impact assessment (LCIA) and interpretation (ISO 14040, 2009; ISO 14044, 2006).

Regarding the first phase of LCA, the aim of the analysis is to evaluate and compare GHG emissions of the proposed ethylene production routes at different CO<sub>2</sub> and electricity sources. In view of this, the LCA is conducted considering 1 kg of ethylene as the functional unit (the reference to which all inputs and outputs of the specific process are related) and cradle-to-gate system boundaries (the use of ethylene is not taken into account during the evaluation of the environmental burden but, only all processes from raw material extraction up to the production of ethylene are considered). An allocation by mass is assumed in processes (MTO and tandem) where ethylene is not the unique product and the geographical location was chosen as UK.

In the second phase of LCA, inventory data are evaluated. The inventory data (consisting of material and energy balances based on 1 kg of produced ethylene) for all investigated processes are reported in the Tables 3-13 and are obtained from modelling studies as described in section 2.1, since these are unavailable in Ecoinvent.

Table 3 Inventory data for the SOEC electrolyser in tandem process (all heating in the process can be provided by recycled heat of up and down stream processes and for this reason an external heat in the input is not considered in the inventory data. This explains the fact that the electricity consumption for the electrolyser is lower than the heating value of CO (10 GJ/ton)) (Sisler et al., 2021)

| <b>Inputs</b>             |                       |
|---------------------------|-----------------------|
| CO <sub>2</sub>           | 1.57ton per ton of CO |
| Electricity-electrolyser  | 8.96GJ per ton of CO  |
| Electricity-PSA           | 1.31 GJ per ton of CO |
| <b>Outputs</b>            |                       |
| CO                        | 1 ton                 |
| CO <sub>2</sub> emissions | 0.62ton per ton of CO |

Table 4 Inventory data for the alkaline flow cell in tandem process (Sisler et al., 2021)

| <b>Inputs</b>            |                              |
|--------------------------|------------------------------|
| CO                       | 1.06ton per ton of ethylene  |
| H <sub>2</sub> O         | 2.57ton per ton of ethylene  |
| Electricity-electrolyser | 55.13GJ per ton of ethylene  |
| Electricity-PSA          | 2.53 GJ per ton of ethylene  |
| <b>Outputs</b>           |                              |
| Ethylene                 | 1 ton                        |
| H <sub>2</sub>           | 0.032ton per ton of ethylene |

Table 5 Inventory data for the direct CO<sub>2</sub>ER route (Jouny et al., 2018)

| <b>Inputs</b>             |                               |
|---------------------------|-------------------------------|
| CO <sub>2</sub>           | 6.27 ton per ton of ethylene  |
| H <sub>2</sub> O          | 2.52 ton per ton of ethylene  |
| Electricity electrolyser  | 25.73 MWh per ton of ethylene |
| Electricity PSA           | 750 kWh per ton of ethylene   |
| <b>Outputs</b>            |                               |
| Ethylene                  | 1 ton                         |
| H <sub>2</sub>            | 0.046 ton per ton of ethylene |
| CO <sub>2</sub> emissions | 3.13 ton per ton of ethylene  |

Table 6 Inventory data for the hydrogen production through the methane steam reforming plant simulated in Aspen Plus (Ciuchi, 2019)

| <b>Inputs</b>             |                                       |
|---------------------------|---------------------------------------|
| Natural gas               | 3.12 ton per ton of H <sub>2</sub>    |
| Water                     | 8.76 ton per ton of H <sub>2</sub>    |
| Electricity               | 0.00346 kWh per ton of H <sub>2</sub> |
| Cooling water             | 1742 ton per ton of H <sub>2</sub>    |
| Steam LP                  | 2.11 ton per ton of H <sub>2</sub>    |
| Steam MP                  | 10.00 ton per ton of H <sub>2</sub>   |
| Fuel                      | 0.0008 ton per ton of H <sub>2</sub>  |
| <b>Outputs</b>            |                                       |
| CO <sub>2</sub> emissions | 3.79 ton per ton of H <sub>2</sub>    |
| Hydrogen                  | 1 ton                                 |

Table 7 Inventory data for methanol production through carbon dioxide hydrogenation with blue hydrogen simulated in Aspen Plus (Kiss et al., 2016)

| <b>Inputs</b>   |                             |
|-----------------|-----------------------------|
| CO <sub>2</sub> | 1.53 ton per ton of MeOH    |
| H <sub>2</sub>  | 0.21 ton per ton of MeOH    |
| Electricity     | 0.00029 kWh per ton of MeOH |
| Cooling water   | 458 ton per ton of MeOH     |
| Steam LP        | 0.95 ton per ton of MeOH    |
| <b>Outputs</b>  |                             |
| MeOH            | 1 ton                       |



Table 8 Inventory data for the MTO plant simulated in Aspen Plus (Chen et al., 2021)

| <b>Inputs</b>             |                                |
|---------------------------|--------------------------------|
| MeOH                      | 6.04ton per ton of ethylene    |
| Steam-raw material        | 1.51 ton per ton of ethylene   |
| Electricity               | 0.00025kWh per ton of ethylene |
| Cooling water             | 797ton per ton of ethylene     |
| Steam LP                  | 2.14ton per ton of ethylene    |
| Steam MP                  | 0.07ton per ton of ethylene    |
| <b>Outputs</b>            |                                |
| Ethylene                  | 1 ton                          |
| CO <sub>2</sub> emissions | 0.0018ton per ton of ethylene  |
| By-products               | 1.63ton per ton of ethylene    |

Table 9 Inventory data for hydrogen production through water electrolysis (Fan et al., 2022)

| Electrolyser                                      | AEL     | PEM   |
|---|---------|-------|
| <b>Inputs</b>                                     |         |       |
| Electricity (kWh per ton of H <sub>2</sub> )      | 0.051   | 0.048 |
| Water (ton per ton of H <sub>2</sub> )            | 10      | 10    |
| Electrolyte (KOH) (gr per ton of H <sub>2</sub> ) | 0.0019  | 0     |
| Steam (ton per ton of H <sub>2</sub> )            | 0.11    | 0     |
| Nitrogen (gr per ton of H <sub>2</sub> )          | 0.00029 | 0     |
| <b>Outputs</b>                                    |         |       |
| Hydrogen (ton)                                    | 1       | 1     |

Table 10 Inventory data for methanol production through carbon dioxide hydrogenation with green hydrogen simulated in Aspen Plus (Kiss et al., 2016) (Differences are due to the pressure level of H<sub>2</sub> from the cells)

| <b>Inputs</b>                         |            |            |
|---------------------------------------|------------|------------|
| H <sub>2</sub> source                 | <b>AEL</b> | <b>PEM</b> |
| CO <sub>2</sub> (ton per ton of MeOH) | 1.41       | 1.53       |
| H <sub>2</sub> (ton per ton of MeOH)  | 0.19       | 0.21       |
| Electricity (kWh per ton of MeOH)     | 0.00054    | 0.00013    |
| Cooling water (ton per ton of MeOH)   | 502        | 434        |
| Steam LP (ton per ton of MeOH)        | 0.8        | 0.91       |
| <b>Outputs</b>                        |            |            |
| MeOH (ton)                            | 1          |            |

Table 11 Inventory data for methanol production through carbon dioxide electrochemical reduction (Jouny et al., 2018)

| <b>Inputs</b>             |                           |
|---------------------------|---------------------------|
| CO <sub>2</sub>           | 2.74 ton per ton of MeOH  |
| H <sub>2</sub> O          | 1.10 ton per ton of MeOH  |
| Electricity electrolyser  | 11.53 MWh per ton of MeOH |
| Electricity PSA           | 236 kWh per ton of MeOH   |
| <b>Outputs</b>            |                           |
| MeOH                      | 1 ton                     |
| H <sub>2</sub>            | 0.02 ton per ton of MeOH  |
| CO <sub>2</sub> emissions | 1.37 ton per ton of MeOH  |

Table 12 Inventory data for the SOEC cell for carbon dioxide water co-electrolysis simulated in Aspen Plus (Freire Ordonez et al., 2021; Zhang and Desideri, 2020)

| <b>Inputs</b>    |                               |
|------------------|-------------------------------|
| CO <sub>2</sub>  | 1.30 ton per ton of syngas    |
| H <sub>2</sub> O | 1.62 ton per ton of syngas    |
| Electricity      | 0.00639 kWh per ton of syngas |
| <b>Outputs</b>   |                               |
| Syngas           | 1 ton                         |

Table 13 Inventory data for methanol production from syngas simulated in Aspen Plus (Leonzio and Foscolo, 2020)

| <b>Inputs</b>  |                            |
|----------------|----------------------------|
| Syngas         | 1.60ton per ton of MeOH    |
| Electricity    | 0.00016kWh per ton of MeOH |
| Cooling water  | 233ton per ton of MeOH     |
| Steam LP       | 1.07ton per ton of MeOH    |
| Steam HP       | 0.60ton per ton of MeOH    |
| <b>Outputs</b> |                            |
| MeOH           | 1 ton                      |

These foreground inventories are combined with data collected from Ecoinvent for the background process in order to quantify the LCIs of each production process. At this stage, carbon footprints of CO<sub>2</sub> from different sources are taken from Muller et al. (2020) where in the multifunctionality this parameter for the CO<sub>2</sub> feedstock is evaluated through the substitution method, keeping the carbon footprint of the main product of the CO<sub>2</sub> source unchanged. In this way all emission reductions are credited to the CO<sub>2</sub> feedstock. As a result, the CO<sub>2</sub> feedstock has negative carbon footprints even for fossil CO<sub>2</sub>. In their work (Muller et al., 2020), having conducted a cradle-to-gate analysis, a negative value of carbon footprints means a reduction of emissions and not their removal. However, the substitution method is neither applicable nor needed for CO<sub>2</sub> from a direct capture system because other products besides CO<sub>2</sub> feedstock are not produced.

In the following phase of LCA, i.e. LCIA, the global warming potential (GWP) is evaluated through two different steps: classification and characterization. In these steps, the LCI results are generated and organized into the impact category and then into the impact indicator at the midpoint level using the Environmental Footprint 2.0 method, recommended by the European Commission's Joint Research Centre (European Commission, 2018) by using SimaPro software (version 9.1.1.7) interfaced with the Ecoinvent database. At this first level of study, we are neglecting the analysis of other impact categories which could be investigated in future studies.

In the last stage of LCA, i.e. the interpretation, results obtained in the previous phase are discussed and compared together and with the literature.

### **3. Results and discussion**

#### **3.1 Results of process modelling**

All simulations in Aspen Plus are validated by respective references in the literature (Ciuchi (2019) for the methane steam reforming plant, Kiss et al. (2016) for the methanol plant with CO<sub>2</sub> hydrogenation, Chen et al. (2021) for the MTO plant and Leonzio and Foscolo (2020) for the methanol plant with syngas as feed). After the validation of the models, from the modelling of each process, material and energy balances are determined. Table 14 reports the overall material and energy balances (classified as raw materials, utilities and outputs

relative to 1 tonne of ethylene production) of the investigated processes. It is clear that the major differences in the mass and energy balances come from the used technology for ethylene production.

CO<sub>2</sub> and process water are the two main important raw materials to be considered. The process with the highest CO<sub>2</sub> consumption for 1 tonne of ethylene production (16.55 ton of CO<sub>2</sub> per ton of ethylene) is the MTO with methanol from the CO<sub>2</sub>ER system. On the other hand, the tandem process consumes only 1.66 ton of CO<sub>2</sub> per ton of ethylene, the lowest value among all studied processes. Another process with a significant CO<sub>2</sub> consumption is the MTO plant with methanol from CO<sub>2</sub>-H<sub>2</sub>O co-electrolysis: in this case CO<sub>2</sub> is transformed to syngas and after that into methanol for ethylene production. Regarding water consumption, MTO plants have values higher than those of electroreduction routes (the lowest value equal to 2.52 ton of H<sub>2</sub>O per ton of ethylene is for the pure CO<sub>2</sub>ER process).

Other raw materials are steam, methane, electrolyte (KOH) and nitrogen, all used in the MTO plant options. However, it is evident that electrochemical routes (tandem and direct CO<sub>2</sub>ER), based only on CO<sub>2</sub> and water, have lower consumptions of raw materials compared to MTO processes, despite higher amounts of electricity consumption. In fact, the highest value of electricity consumption is for the direct CO<sub>2</sub>ER route (95.33 GJ per ton of ethylene) while, the lowest value of electricity consumption is for the MTO plant using blue H<sub>2</sub> (0.02 GJ per ton of ethylene). The highest value of the electricity consumption for the electrochemical route is due to the fact that electricity is the only driver in this route that is based on a non-spontaneous reaction so that more energy in input is required. In any case, the order of magnitude of the electricity consumption ratio between electrochemical and MTO routes is the same of that suggested by Ioannou et al. (2020). On the other hand, MTO plants have other utilities as inputs, such as cooling water, steam at medium pressure (MP), steam at low pressure (LP), steam at high pressure (HP) and fuel.

CO<sub>2</sub> emissions are present for all analyzed processes with the highest and lowest value respectively for the MTO plant with methanol from CO<sub>2</sub>ER (8.27 ton of CO<sub>2</sub> per ton of ethylene) and other MTO plants (0.0018 ton of CO<sub>2</sub> per ton of ethylene). In the tandem process, 0.66 ton of CO<sub>2</sub> per ton of ethylene (0.62 ton of CO<sub>2</sub> per ton of CO) are emitted because in the SOEC the CO<sub>2</sub> conversion is not total but it is set to 40 % (Sisler et al., 2021).

For future research, it is suggested to consider the recycle of the emitted CO<sub>2</sub> in these processes with a once-through scheme and verify how this influences on the results. In addition to CO<sub>2</sub> emissions and the main product, by-products are present as outputs. Hydrogen (in tandem and direct CO<sub>2</sub>ER processes respectively of 0.032 and 0.046 ton per ton of ethylene) and other by-products (for the MTO plant equal to 1.63 ton per ton of ethylene and including ethane, propylene, propane, C<sub>4</sub><sup>+</sup> and C<sub>5</sub><sup>+</sup>) are obtained.

Table 14 Overall material and energy balances for the investigated processes (CO<sub>2</sub>ER=CO<sub>2</sub> electrochemical reduction; MTO=methanol to olefin; MeOH=methanol; AEL=alkaline cell; PEM=proton exchange membrane cell; LP=low pressure; MP=medium pressure; HP=high pressure)

|              |  | Tandem | Direct CO <sub>2</sub> ER to ethylene | MTO with MeOH from blue H <sub>2</sub> | MTO with MeOH from green H <sub>2</sub> (PEM) | MTO with MeOH from green H <sub>2</sub> (AEL) | MTO with MeOH from CO <sub>2</sub> ER | MTO with MeOH from CO <sub>2</sub> -H <sub>2</sub> O co-electrolysis |
|--------------|--|--------|---------------------------------------|--|---|---|---------------------------------------|--|
| Raw material | CO <sub>2</sub> (ton per ton of ethylene)            | 1.66   | 6.27                                  | 9.24                                   | 9.24  | 8.52  | 16.55                                 | 12.56  |
|              | Water (ton per ton of ethylene)                      | 2.57   | 2.52                                  | 11.11                                  | 12.68   | 11.48   | 6.64                                  | 15.66  |
|              | Steam (ton per ton of ethylene )                     | 0      | 0                                     | 1.51                                   | 1.51  | 1.51  | 1.51                                  | 1.51   |
|              | CH <sub>4</sub> (ton per ton of ethylene )           | 0      | 0                                     | 3.96                                   | 0   | 0   | 0                                     | 0  |
|              | Electrolyte (KOH) (kg per ton of ethylene)           | 0      | 0                                     | 0                                      | 0   | 2.18  | 0                                     | 0  |
|              | Nitrogen (kg per ton of ethylene)                    | 0      | 0                                     | 0                                      | 0   | 0.33  | 0                                     | 0  |
| Utilities    | Electricity (GJ per ton of ethylene)                 | 68.55  | 95.33                                 | 0.02                                   | 0.22  | 0.22  | 0.26                                  | 0.23   |
|              | Cooling water (ton per ton of ethylene )             | 0      | 0                                     | 5773                                   | 3418  | 3829  | 797                                   | 2204   |
|              | Steam LP (ton per ton of ethylene )                  | 0      | 0                                     | 10.55                                  | 7.64  | 7.10  | 2.14                                  | 8.60   |
|              | Steam MP (ton per ton of ethylene )                  | 0      | 0                                     | 12.75                                  | 0.07  | 0.07  | 0.07                                  | 0.07   |
|              | Steam HP (ton per ton of ethylene )                  | 0      | 0                                     | 0                                      | 0   | 0   | 0                                     | 3.62   |
|              | Fuel (ton per ton of ethylene )                      | 0      | 0                                     | 0.001                                  | 0   | 0   | 0                                     | 0  |
| Output       | Ethylene (ton)                                       | 1      | 1                                     | 1                                      | 1   | 1   | 1                                     | 1  |
|              | H <sub>2</sub> by-product (ton per ton of ethylene ) | 0.032  | 0.046                                 | 0                                      | 0   | 0   | 0                                     | 0  |
|              | CO <sub>2</sub> emissions (ton per ton of ethylene ) | 0.66   | 3.13                                  | 4.8                                    | 0.0018  | 0.0018  | 8.27                                  | 0.0018   |
|              | Other by-products ton per ton of ethylene )          | 0      | 0                                     | 1.63                                   | 1.63  | 1.63  | 1.63                                  | 1.63   |

### 3.2 Results of economic analysis

In the economic analysis the levelized production cost of ethylene for all analyzed routes is evaluated as reported in Figures 7, 8 and 9 for different CO<sub>2</sub> and electricity sources.

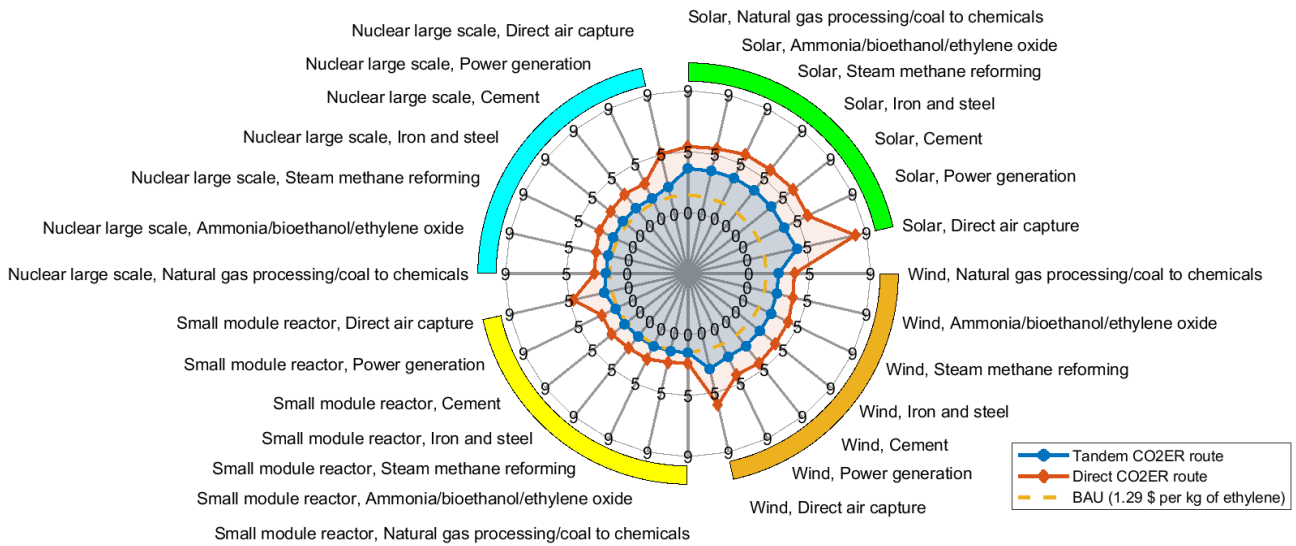


Figure 7 Ethylene production cost for the electrochemical routes at different CO<sub>2</sub> and electricity sources and comparison with the BAU process (BAU=business as usual)

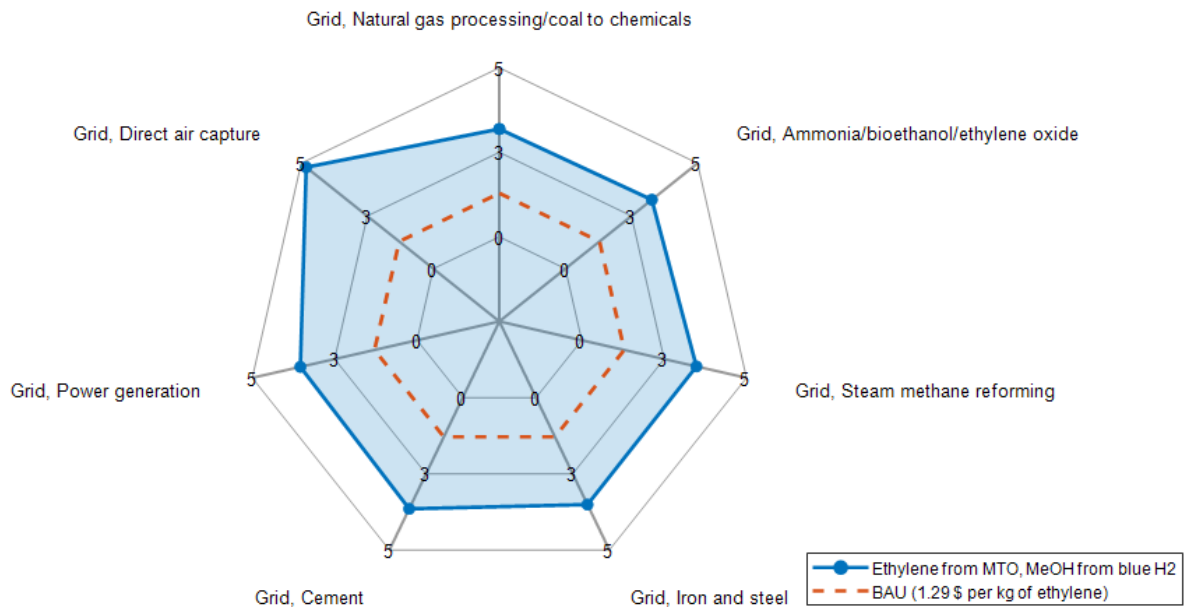


Figure 8 Ethylene production cost for the MTO plant with methanol from blue H<sub>2</sub> and comparison with the BAU process (BAU=business as usual)

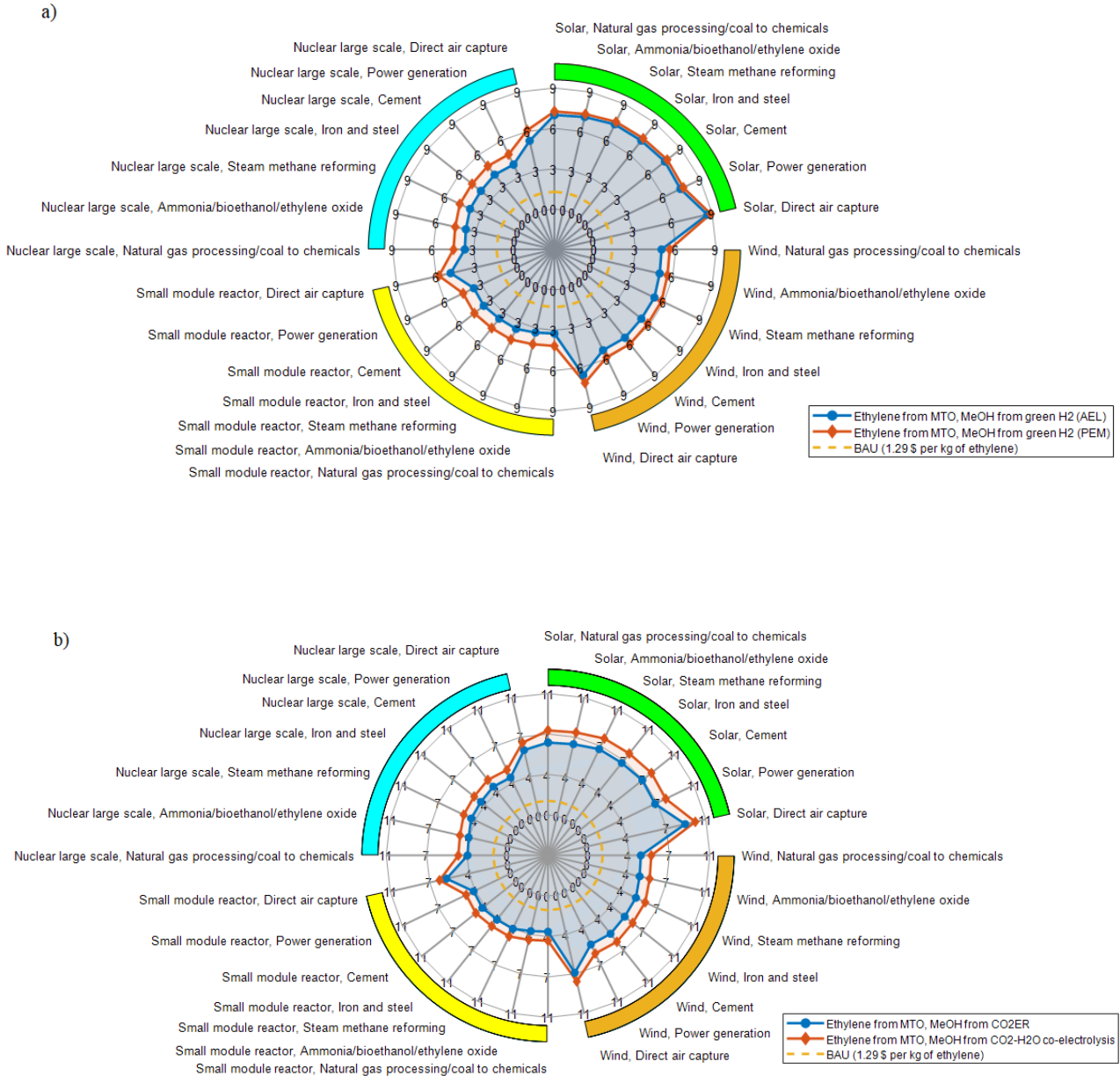


Figure 9 Ethylene production cost for the MTO process with methanol from, a)  $\text{CO}_2$  hydrogenation with green  $\text{H}_2$  (PEM and AEL), b)  $\text{CO}_2\text{ER}$  and  $\text{CO}_2\text{-H}_2\text{O}$  co-electrolysis and comparison with the BAU process (BAU=business as usual; MTO=methanol to olefin; MeOH=methanol;  $\text{CO}_2\text{ER}=\text{CO}_2$  electrochemical reduction)

Among these, Figure 7 shows the ethylene production cost for the electrochemical routes (tandem and direct  $\text{CO}_2\text{ER}$  processes): lower costs are determined for the tandem system with values in a range between 1.34 and 3.74 \$ per kg of ethylene. On the other hand, for the direct electrochemical reduction of  $\text{CO}_2$  to ethylene the cost ranges between 2.11 and 8.18 \$ per kg of ethylene. The higher range cost obtained for the direct  $\text{CO}_2\text{ER}$  route is due to the higher  $\text{CO}_2$  flow rate needed in the feed (6.27 ton per ton of ethylene) and overall electricity consumption (95.33 GJ per ton of ethylene) as already reported in Table 14. In fact, these two factors contribute to the increase of operating costs. Although the direct  $\text{CO}_2\text{ER}$  process has a lower CAPEX compared to the

tandem process (154 \$ per ton of ethylene vs 270 \$ per ton of ethylene), OPEX are higher and influences the total cost in a significant way. More optimization studies should be conducted in order to optimize the direct electrochemical conversion in order to reduce operating costs.

In both study cases, the lowest price is obtained when CO<sub>2</sub> comes from natural gas processing/coal to chemicals source while using a small modular nuclear reactor as an electricity source. The highest price, on the other hand, is produced with CO<sub>2</sub> from a DAC system while using solar energy for electricity.

Figure 8 shows the ethylene production cost using a MTO plant with methanol from the catalytic reaction between CO<sub>2</sub> and blue H<sub>2</sub> at different CO<sub>2</sub> sources and with electricity from the UK grid. The cost has values between 3.19 and 4.81 \$ per kg of ethylene when CO<sub>2</sub> comes from natural gas processing/coal to chemicals sources and DAC processes respectively.

Figure 9 reports the ethylene production cost when the MTO plant is used and with methanol from the catalytic reaction between CO<sub>2</sub> and green H<sub>2</sub> (obtained in PEM and AEL electrolyzers) (Figure 9a), from the direct electrochemical reaction of CO<sub>2</sub> and syngas produced in a SOEC for CO<sub>2</sub> and H<sub>2</sub>O co-electrolysis (Figure 9b). The cost is evaluated at different CO<sub>2</sub> and electricity sources. Among these processes, the cost range is between 3.25 and 8.64 \$ per kg of ethylene for the MTO plant using methanol from hydrogenation with green H<sub>2</sub> produced in AEL electrolyzers. Here, the lowest cost is obtained when CO<sub>2</sub> is captured from natural gas processing/coal to chemicals sources and electricity is extracted from small modular nuclear reactors. On the other hand, the highest cost is when CO<sub>2</sub> is obtained from DAC plants and solar energy is exploited for electricity. In a similar process but, with H<sub>2</sub> from a PEM water electrolyser, the specific cost to produce ethylene ranges between 4.17 (CO<sub>2</sub> from natural gas processing/coal to chemicals sources and electricity from small nuclear plants) and 8.89 \$ per kg of ethylene (CO<sub>2</sub> from DAC plant and electricity from solar energy). The higher range cost obtained for the MTO plant with methanol produced by CO<sub>2</sub> hydrogenation with PEM is due to the higher OPEX compared to the same system but using the AEL. In fact, as shown in Table 14, the process based on PEM has higher CO<sub>2</sub> (9.24 ton per ton of ethylene), water (12.68 ton per ton of ethylene) and steam LP (7.64 ton per ton of ethylene) consumptions.

A wider range exists for the production cost of ethylene in MTO plant with methanol from the electrochemical reduction of CO<sub>2</sub>: 3.24 and 9.08 \$ per kg of ethylene, for the same electricity and CO<sub>2</sub> sources considered in the previous processes.

The highest production cost, equal to 10.02 \$ per kg of ethylene, in Figure 9b is for the MTO plant with methanol obtained by syngas (produced with CO<sub>2</sub>-H<sub>2</sub>O co-electrolysis). This cost is incurred when CO<sub>2</sub> is captured from the atmosphere and the electricity is from solar energy. For the same process, the lowest production cost is 4.06 \$ per kg of ethylene (CO<sub>2</sub> from natural gas processing/coal to chemicals sources and electricity from small modular reactors). Comparing these last two processes, the MTO plant with methanol from syngas has a higher OPEX that increase the overall ethylene production cost. A higher OPEX is due to a higher consumption of water, cooling water and steam, despite of the lower CO<sub>2</sub> consumption.



Overall, the results show that in order to decrease the production cost, CO<sub>2</sub> should be captured from natural gas processing/coal to chemicals sources while electricity should be produced in small scale nuclear plants, due to the very convenient price of CO<sub>2</sub> and electricity (although the GWP is much higher compared other cases) (IEA, 2022; NAMRC, 2022). The DAC process and solar energy both have still higher costs (Ioannou et al., 2020; IRENA. 2019; Leonzio et al., 2022a,b).

A conventional process for ethylene production is naphtha cracking with a cost of 1.29 \$ per kg of ethylene (Iannou et al., 2020; ICIS, 2022). The market price of ethylene fluctuates with time, but in this analysis a reference price of 1.29 \$ per kg of ethylene is considered and all costs of ethylene will be compared to this reference cost.

A secondary process that could be considered as reference for ethylene production is that based on MTO plant with methanol obtained from syngas produced by methane steam reforming.

Table 15 reports the discussed cost ranges for each process and a comparison with both naphtha cracking process and the second reference process (here the simulation for the MTO plant and the market methanol price (Methanex, 2023) are considered). It is evident that, considering uncertainties in the economic analysis, only the tandem process in cases with lower costs is competitive with the traditional method of ethylene production (in the absence of high costs for CO<sub>2</sub> emissions) and that based on MTO with methanol from syngas. The economic profitability of ethylene production via the tandem route has been demonstrated by Sisler et al. (2021), suggesting that it has more promise for producing low-cost ethylene due to its efficient use of energy and CO<sub>2</sub>. Other process schemes for ethylene production that are analyzed in this research and based on MTO plant with methanol from CO<sub>2</sub> hydrogenation of green H<sub>2</sub> have a cost higher compared to that of the current production, as already found by Ioannou et al. (2020). The costs of the of CO<sub>2</sub>ER to ethylene route in comparison current prices are in line with the work of Pappijin et al. (2020), Ioannou et al. (2020) and Orella et al., (2020). For other systems producing ethylene a comparison with market prices has not been presented in the literature.

Table 15 Comparison between the ethylene production cost of proposed and conventional routes (CO<sub>2</sub>ER=CO<sub>2</sub> electrochemical reduction; MTO=methanol to olefin; MeOH=methanol; AEL=alkaline cell; PEM=proton exchange membrane cell)

| Process  | Min production cost (\$ per kg of ethylene) | Max production cost (\$ per kg of ethylene) |
|--|---|---|
| Tandem   | 1.34  | 3.74  |
| Direct CO <sub>2</sub> ER to ethylene                                | 2.11  | 8.18  |
| MTO with MeOH from blue H <sub>2</sub>                               | 3.19  | 4.81  |
| MTO with MeOH from green H <sub>2</sub> (PEM)                        | 3.25  | 8.64  |
| MTO with MeOH from green H <sub>2</sub> (AEL)                        | 4.17  | 8.89  |
| MTO with MeOH from CO <sub>2</sub> ER                                | 3.24  | 9.08  |
| MTO with MeOH from CO <sub>2</sub> -H <sub>2</sub> O co-electrolysis | 4.06  | 10.02                                       |
| Naphtha cracking   | 1.29  | 1.29  |
| MTO with MeOH from methane steam reforming                           | 1.48  | 1.48  |

### 3.3 Results of GHG emission analysis

The global warming potential impact category is evaluated for the analyzed processes, as shown in Figures 10, 11 and 12.

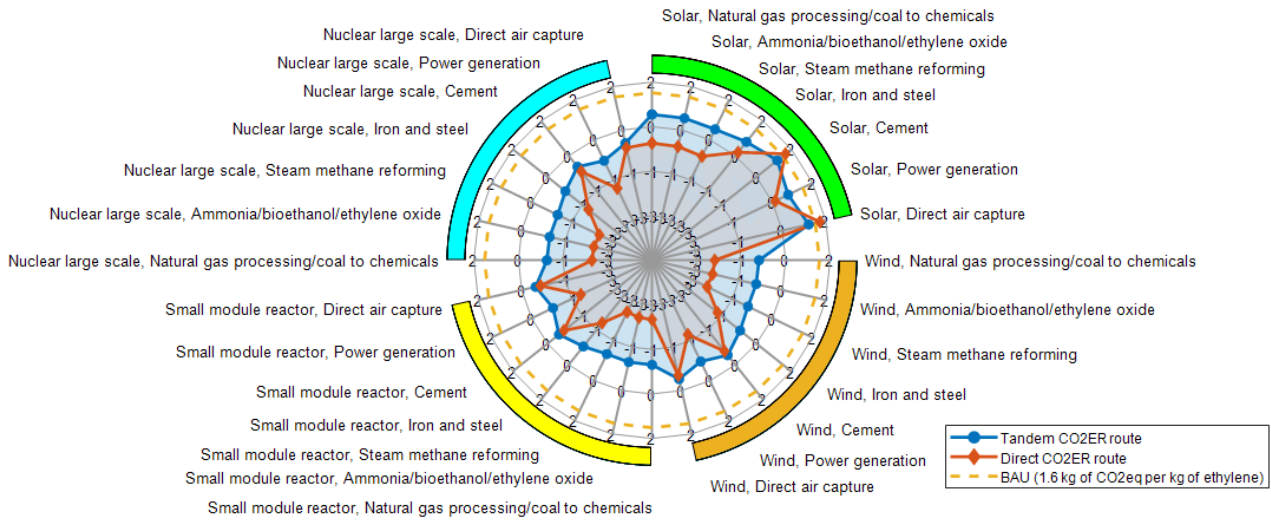


Figure 10 Global warming potential for the electrochemical routes at different CO<sub>2</sub> and electricity sources and comparison with the BAU process (BAU=business as usual; CO<sub>2</sub>ER=CO<sub>2</sub> electrochemical reduction)

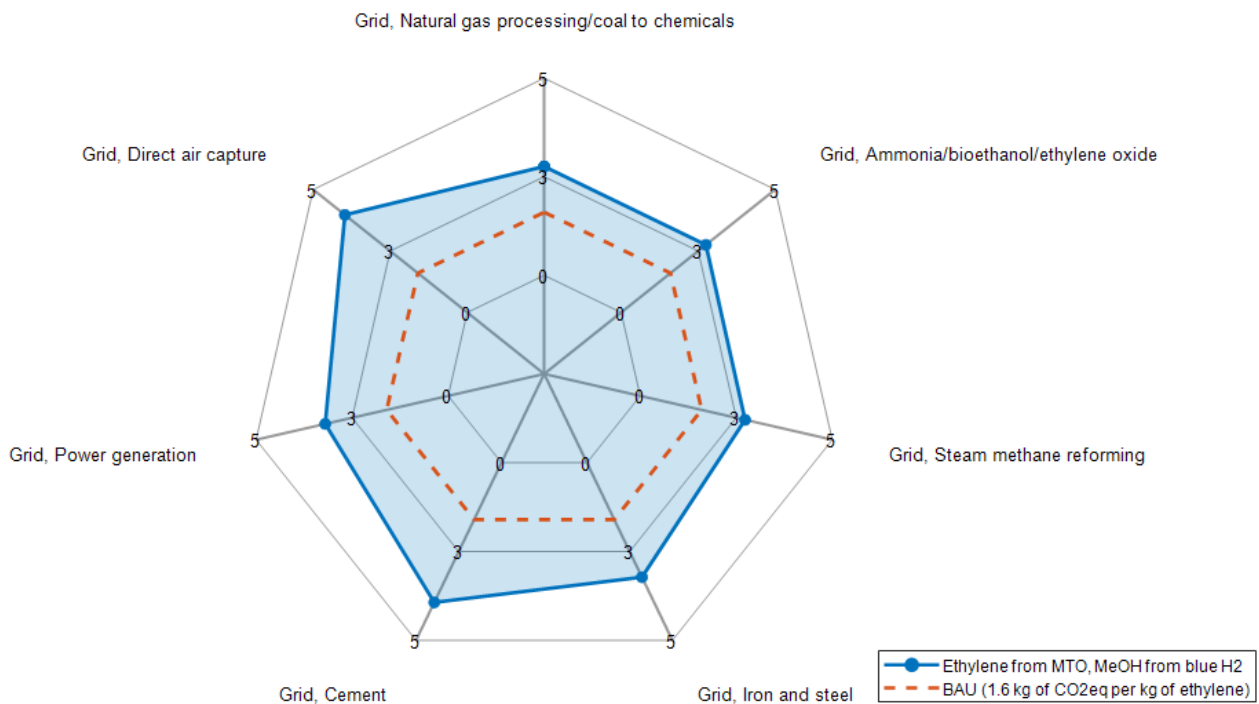


Figure 11 Global warming potential for the MTO plant with methanol from blue H<sub>2</sub> and comparison with the BAU process (BAU=business as usual; MTO=methanol to olefin; MeOH=methanol)

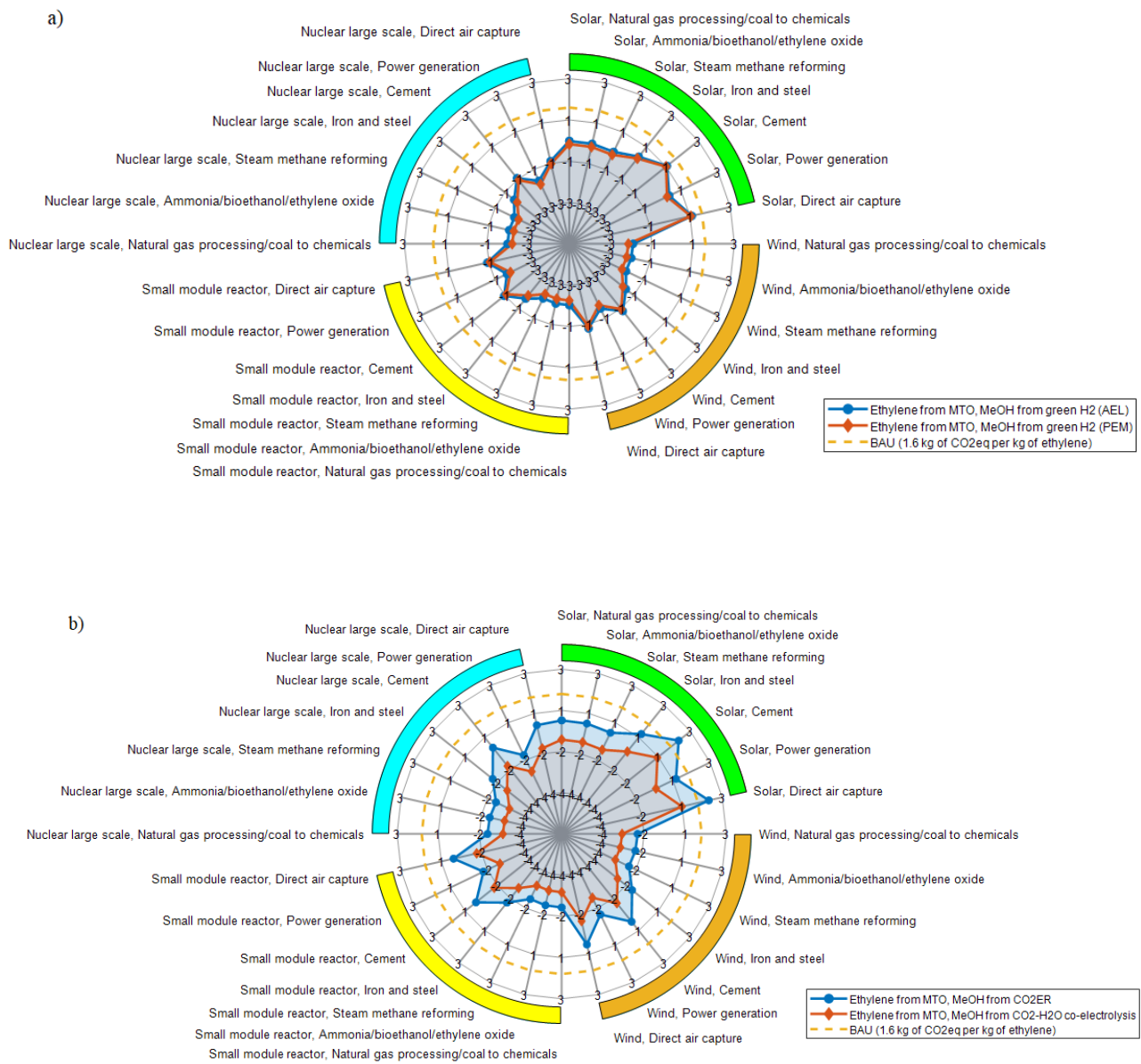


Figure 12 Global warming potential for the MTO process with methanol from a) CO<sub>2</sub> hydrogenation with green H<sub>2</sub> (PEM and AEL), b) CO<sub>2</sub>ER and CO<sub>2</sub>-H<sub>2</sub>O co-electrolysis and comparison with the BAU process (BAU=business as usual; MTO=methanol to olefin; MeOH=methanol; CO<sub>2</sub>ER=CO<sub>2</sub> electrochemical reduction; AEL=alkaline cell; PEM=proton exchange membrane cell)

Among these Figures, in Figure 10 results for the two electrochemical routes are reported for different CO<sub>2</sub> and electricity sources: the direct and tandem CO<sub>2</sub>ER to ethylene system enables negative values of global warming potential meaning a mitigation of CO<sub>2</sub> because, a cradle-to-gate analysis is conducted. In fact, for the direct process, the lowest achieved value is -2.52 kg of CO<sub>2</sub>eq per kg of ethylene when CO<sub>2</sub> is captured from a methane steam reforming plant and electricity is obtained by nuclear energy (small nuclear reactors). On the other hand, for the same process, the highest value is 1.78 kg of CO<sub>2</sub>eq per kg of ethylene obtained from CO<sub>2</sub> captured in a DAC system and electricity from solar energy. In addition to the pure CO<sub>2</sub>ER, the GWP of the

tandem process is shown in Figure 10: it has overall a higher environmental impact (in term of CO<sub>2</sub> emissions) compared to the direct CO<sub>2</sub> electrochemical reduction to ethylene with a range of GWP between -0.771 kg of CO<sub>2eq</sub> per kg of ethylene (when CO<sub>2</sub> is captured from a methane steam reforming plant and electricity is obtained by small nuclear reactors) and 1.35 kg of CO<sub>2eq</sub> per kg of ethylene (CO<sub>2</sub> from DAC with electricity from solar energy). The better performance of the direct CO<sub>2</sub>ER is due to the higher CO<sub>2</sub> consumption, as already discussed, resulting in a more negative carbon footprint of the feedstock compared to the other system. It is evident that in this case the feed has the highest influence on GWP.

As shown in Figure 11, higher values of GWP are obtained for the MTO plant with methanol produced by CO<sub>2</sub> hydrogenation with blue H<sub>2</sub>: 3.97 kg of CO<sub>2eq</sub> per kg of ethylene are when CO<sub>2</sub> is captured from the atmosphere and UK electricity grid is used. For this process, the lowest value of GWP is 2.73 kg of CO<sub>2eq</sub> per kg of ethylene, by capturing CO<sub>2</sub> from a methane steam reforming plant.

In Figure 12, results for the other MTO plants are shown: it is evident that the lowest GWP impact is for the MTO with methanol obtained by CO<sub>2</sub>-H<sub>2</sub>O co-electrolysis (Figure 12b). Here the GWP is in a range between -3.08 kg of CO<sub>2eq</sub> per kg of ethylene (CO<sub>2</sub> from methane steam reforming plant and electricity from a small-scale nuclear plant) and 0.655 kg of CO<sub>2eq</sub> per kg of ethylene (CO<sub>2</sub> from a DAC system and electricity from solar energy). On the other hand, the highest value of GWP in Figure 12b is for the MTO plant with methanol from CO<sub>2</sub>ER that incurs 2.2 kg of CO<sub>2eq</sub> per kg of ethylene with CO<sub>2</sub> captured from the atmosphere and electricity from solar energy. For the same process, the lowest GWP impact of -2.24 kg of CO<sub>2eq</sub> per kg of ethylene is obtained with CO<sub>2</sub> captured from methane steam reforming plant and electricity from small modular reactors. Despite of a higher CO<sub>2</sub> consumption (16.55 ton per ton of ethylene) in the feed for the MTO plant with methanol produced via CO<sub>2</sub>ER, a higher CO<sub>2</sub> emission (8.27 ton per ton of ethylene) causes a higher environmental impact compared to the MTO plant with methanol from syngas.

-2.3 and 1.04 kg of CO<sub>2eq</sub> per kg of ethylene is the GWP range for the MTO plant using methanol from the CO<sub>2</sub> hydrogenation with green H<sub>2</sub> (PEM). In this range, -2.3 kg of CO<sub>2eq</sub> per kg of ethylene are for the case in which CO<sub>2</sub> is from a methane steam reforming plant and electricity is from nuclear energy (small modular reactors) while 1.04 kg of CO<sub>2eq</sub> per kg of ethylene are produced by using CO<sub>2</sub> from a DAC system and electricity from solar energy. For the same process but, with H<sub>2</sub> produced in an AEL cell, the climate change is between -2.07 kg of CO<sub>2eq</sub> per kg of ethylene (CO<sub>2</sub> from a methane steam reforming plant and electricity from small-scale nuclear plant) and 1.09 kg of CO<sub>2eq</sub> per kg of ethylene (CO<sub>2</sub> from DAC plants and electricity from solar energy).

Comparing the results for these two last processes with those of the MTO plant with methanol from syngas, it is possible to see that better performances are for the second mentioned system: for the same amount of CO<sub>2</sub> emitted, a higher amount of CO<sub>2</sub> feedstock ensures better environmental conditions.

Overall, results show that the lowest GWP impact is ensured by using CO<sub>2</sub> captured from a methane steam reforming plant and electricity produced by nuclear energy, in particular small modular reactors. On the other

hand, the highest GWP impact is caused by using CO<sub>2</sub> from a DAC plant and electricity from solar energy. These results are technically in agreement with the work of Muller et al. (2020) finding that the CO<sub>2</sub> capture from ammonia plant (then from a methane steam reforming plant) leads to the lowest carbon footprint of the CO<sub>2</sub> feedstock. However, this result does not agree from the point of view of the European Union legislation because other CO<sub>2</sub> sources are preferred for fuel synthesis (McQuillen et al., 2022).

Table 16 shows the GWP range for the investigated processes and the comparison with the GWP impact of the conventional process based on naphtha cracking which is equal to 1.6 kg of CO<sub>2eq</sub> per kg of ethylene (Iannou et al., 2020) and that based on MTO plant with methanol from methane steam reforming with a GWP of 2.15 kg of CO<sub>2eq</sub> per kg of ethylene (obtained from SimaPro considering the new defined MTO plant and the conventional methanol flow rate as in the Ecoinvent database).

Considering the lowest value of GWP in that range, all processes for ethylene production except the MTO plant with methanol from blue hydrogen are more environmentally friendly compared to the traditional one and the process based on MTO with methanol from methane steam reforming. The environmental benefit of the CO<sub>2</sub>ER to ethylene route has been also reported by Pappijn et al. (2020), especially when renewable energies are used for electricity generation. In Ioannou et al. (2020), a better performance of the direct electrochemical reduction route and the MTO plant with methanol from green H<sub>2</sub> is achieved compared to the naphtha cracking. For the other alternative plants, a comparison with the BAU has not been conducted in the literature so far.

In any case, in our results, the best process with the lowest value of GWP value is the MTO plant with methanol obtained from syngas from CO<sub>2</sub>-H<sub>2</sub>O co-electrolysis in a SOEC. Another competitive process is the direct CO<sub>2</sub>ER for which a proper optimization could ensure good performances as well the best process. An optimization of the operating conditions (increase of CO<sub>2</sub> conversion and consumption with a recycle of emissions and reduction of consumed electrical energy) must be focused on later studies. Negative values of GWP can be achieved by all investigated processes but not by the tandem system and MTO plant using blue hydrogen that should be optimized in future research in order to reduce their environmental burden.

Table 16 Comparison between the global warming potential of proposed and conventional routes for ethylene production (CO<sub>2</sub>ER=CO<sub>2</sub> electrochemical reduction; MTO=methanol to olefin; MeOH=methanol; AEL=alkaline cell; PEM=proton exchange membrane cell)

| Process  | Min global warming potential (kg of CO <sub>2</sub> eq per kg of ethylene) | Max global warming potential (kg of CO <sub>2</sub> eq per kg of ethylene) |
|--|--|--|
| Direct CO <sub>2</sub> ER to ethylene                                | -2.5   | 1.8  |
| Tandem   | 0.8  | 2.3  |
| MTO with MeOH from blue H <sub>2</sub>                               | 2.7  | 4.0  |
| MTO with MeOH from green H <sub>2</sub> (PEM)                        | -2.3   | 1.0  |
| MTO with MeOH from green H <sub>2</sub> (AEL)                        | -2.1   | 1.1  |
| MTO with MeOH from CO <sub>2</sub> ER                                | -2.2   | 2.2  |
| MTO with MeOH from CO <sub>2</sub> -H <sub>2</sub> O co-electrolysis | -3.1   | 0.7  |
| Naphtha cracking   | 1.6  | 1.6  |
| MTO with MeOH from methane steam reforming                           | 2.15   | 2.15   |

### 3.4 Best ethylene production routes

From the above results it is determined that the best process for ethylene production from an economic point of view is the tandem one. On the other hand, the MTO plant with methanol obtained from syngas from CO<sub>2</sub>-H<sub>2</sub>O co-electrolysis is the best process for a GWP point of view.

It can be supposed that the use of only electrical energy and the high electrical energy efficiency make the tandem process the most favorable in the economic analysis (a lower value of OPEX is ensured). Moreover, only 1.66 ton of CO<sub>2</sub> per ton of ethylene are required by this process reducing in this way the OPEX (in particular the expenditure for raw materials) in comparison with other investigated routes characterized by higher CO<sub>2</sub> consumptions.

Regarding the MTO plant integrated into a SOEC, it can be supposed that a relative high CO<sub>2</sub> consumption in the feed and the lowest value of CO<sub>2</sub> emissions make the process the best one in the GHG emission analysis. It can be underlined that the MTO plant with methanol from CO<sub>2</sub>ER has the highest CO<sub>2</sub> consumption (16.55 tonne<sub>CO<sub>2</sub></sub>/tonne<sub>Ethylene</sub>) but in this case a relative high emission of CO<sub>2</sub> (8.27 ton of CO<sub>2</sub> per ton of ethylene) is present making the process not favorable for the GWP point of view.

Results suggest that these new technologies could be competitive and better compared to the conventional thermos-routes in the next future.

CO<sub>2</sub> consumption and emission and energy consumptions as well are important factors able to provide economic and GWP benefits. It is convenient to have low values for CO<sub>2</sub> emissions and energy consumption in order to have low costs and GHG emission burdens. On the other hand, for CO<sub>2</sub> consumption a trade-off should be achieved: a high value causes a high OPEX but a low value of global warming potential if the overall process is efficient from an environmental point of view. Future research should be conducted on

electrochemical reduction routes taking into account these factors influencing costs and impact on the environment.

#### 4. Conclusions

The research introduces a comparative analysis of all ethylene production routes investigated in the literature. The alternative production paths, starting from two important molecules such as CO<sub>2</sub> and H<sub>2</sub>O, are based on CO<sub>2</sub> electroreduction (direct and tandem processes) and on MTO plant (with methanol from different production ways such as CO<sub>2</sub> hydrogenation, syngas and CO<sub>2</sub>ER), while the fossil-based ethylene production based on naphtha cracking is taken as a reference.

In the first stage, the modelling of each process according to the literature is carried out considering the optimistic conditions for electrochemical processes although, electrolytic cells for CO<sub>2</sub> reduction are currently characterized by a low value of technology readiness level (TRL). In the second stage, the economic profitability in terms of ethylene production cost and the environmental impact in terms of global warming potential are evaluated and compared.

The economic analysis shows that only the tandem process in cases with lower costs (cheaper CO<sub>2</sub> sources and electricity from nuclear energy at a small-scale) is competitive with the conventional production of ethylene. The production cost for the tandem process is in the range between 1.34 and 3.74 \$ per kg of ethylene compared to a current market price of 1.29 \$ per kg of ethylene. However, the most convenient ethylene production from a GWP point of view is that based on the MTO plant with methanol produced from syngas obtained in the CO<sub>2</sub>-H<sub>2</sub>O co-electrolysis. In this case, the GWP can achieve a value of -3.08 kg of CO<sub>2eq</sub> per kg of ethylene (CO<sub>2</sub> from methane steam reforming plant and electricity from a small modular reactor), while the corresponding figure for naphtha cracking is 1.6 kg of CO<sub>2eq</sub> per kg of ethylene. It is evident that, the most preferred energy source for the electricity supply is the nuclear one with a small-scale plant because, economic and environmental (in term of GHG emissions) advantages are provided.

Moreover, as the MTO plant with methanol from CO<sub>2</sub>-H<sub>2</sub>O co-electrolysis and the tandem one are the best processes, it is evident that the electrochemical route starting from two abundant raw materials (CO<sub>2</sub> and H<sub>2</sub>O), could potentially have an important role inside the chemical industry, being competitive with conventional production processes.

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