



Full Length Article

Feasibility analysis of e-Hydrogen, e-Ammonia and e-Methanol synthesis compared with methane to fuel production

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ABSTRACT

Process decarbonization is becoming one of the main requirements in the power sector, needing proper carbon capture systems or more eco-friendly technologies based on renewables. Hydrogen is the ideal solution, but its production chain has significant environmental, safety and logistical issues making its carries, such as ammonia and methanol, more suitable commercially. Starting from H₂ production paths, a feasibility analysis is presented on e-NH₃ and e-MeOH single and combined production for different flowsheets by discussing material and energy consumption. Specific electrical demands are quite high (~11–12 kWh_{el}/kg e-fuel) due to the energy-consuming electrolyser operation, which also represents more than 85 % of the total need. Nevertheless, these values balance the high fuel consumption of traditional processes based on the natural gas steam reforming (~21–31 MJ(LHV)/kg product). CO₂ emissions are minimized, permitting the CO₂ recovery from other plants in the e-MeOH synthesis as well (up to ~1.6 kg CO₂/kg e-fuel). Referring to the current renewable scenario, a hybrid plant combining ammonia and methanol production is more feasible. Indeed, the Methane to Ammonia plant coupled with the Power to Methanol one allows for halving the electrolyser size and providing an in loco CO₂ source (~0.83 kg CO₂/kg (NH₃ + MeOH)) while increasing the heat requirement (up to a 90 % increase) compared to a single-line e-fuel production. Looking at future scenarios, the electrolyser technology improvement in terms of its electrical demand and working pressure could favour e-fuel synthesis, leading to ~25 % decrease in the energy consumption and a lower number of compression steps.

1. Introduction

In the current energy scenario, hydrogen is a very promising alternative fuel due to a high energy density of around 120 MJ(LHV)/kg (three times higher than traditional fossil fuels) and without releasing GHG emissions through its oxidation, making its use feasible for multiple applications that range from the energy industry to the transportation sector [1–3]. The atomic hydrogen is extremely abundant in nature, representing around 75 % of the total amount of atoms [4]. Nevertheless, its molecular state is quite unstable in the atmosphere, though it could be extracted from some underground caves (i.e., white H₂) [5]. Hydrogen bottlenecks are correlated firstly to production and secondly to transportation and storage [6,7]. H₂ derives commonly from fossil fuel-based processes such as natural gas steam reforming and coal gasification (i.e., grey and black H₂), in rarer cases its synthesis can involve a carbon capture system (i.e., blue H₂), exploit renewable

sources (i.e., green and yellow H₂) or use nuclear energy (i.e., pink H₂) [5,8]. The second threshold is connected to the logistics because of its wide flammability region (4–75 vol% in air) and low density at room conditions, requiring its compressions up to 700 bar or its liquefaction at –253 °C with consequent safety issues [9,10]. The trending idea is the use of hydrogen through its derivatives, which are produced from hydrogen but can be transported and stored more easily and safely. These derivatives can then be used to obtain molecular hydrogen or used as a direct fuel source. The main candidates are ammonia and methanol, showing a high energy density (18.6 MJ(LHV)/kg and 20 MJ(LHV)/kg, respectively), a narrow flammability range (16–25 vol% and 6–36 vol% in air at standard conditions, respectively) and requiring mild storage conditions (room or lower temperatures) [11].

Ammonia and methanol are commonly produced using fossil fuels as the hydrogen source [12,13]. Aiming at their process decarbonization, alternative paths have been identified that involve biomass gasification

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and, above all, water electrolysis leading to the synthesis of the so-called e-fuels [14–17]. Applying both technologies allows for revamping the existing plants based on the Haber Bosch and the methanol synthesis loops. This permits eco-friendly production processes but maintains the high product yields and synthesis rates that characterize traditional reactor designs and catalysts. Focusing on e-NH₃ and e-MeOH, several plant flowsheets have been proposed with the aim of performance optimization and process emission reduction using different electrolysis technologies, such as high-temperature proton and anion-conductive solid oxide cells, proton exchange membrane cells, anion exchange membrane cells and alkaline electrolyzers [18–23]. Moreover, an external CO₂ source is needed in the case of methanol synthesis, resulting in a suitable and profitable application of the CO₂ segregated by carbon capture systems that are emerging in both industrial and transport applications [24–30]. Here, e-fuel production results in a promising solution for hard-to-abate sectors since it would permit CO₂ footprint reduction without the complete system substitution, which is not always feasible [30–32]. It is noteworthy that the origin both of the CO₂ and of the electricity influence the obtained product categorization. The resulting fuel can only be defined as “green” if the electricity is obtained using renewable resources and the CO₂ derives from a biological process or from a direct air capture plant [33], allowing for net zero emissions [34–37]. Coupling with photovoltaic and wind sources has further beneficial effects: (i) minimizing the fuel synthesis process emissions and (ii) counteracting the characteristic renewable energy fluctuations by storing the surplus into a fuel as chemical potential that can be used in a later stage. The current high electricity and electrolyser prices cause an e-fuel average costs up to 3 €/liter, which is reducing the industrial interest in these processes [38]. Here, government funding and devoted legislation are fundamental pressing points [39,40].

Despite the known variability in scale, *modus operandi*, material and energy supply [41–44], the Power to X approach is the most interesting solution at the industrial level due to, in theory, the high capacities reachable through the system modularity. Several demonstration plants started operation in last years or are under planning. Nevertheless, their annual production is still far from industrial-scale ones (Table 1), which can have a production capacity of millions of tons yearly.

The present work evaluates the feasibility of ammonia and methanol green synthesis with respect to hydrogen generation in the previously established context. The e-fuel production through low-temperature electrolysis cells coupled with renewable sources is analysed in terms of material, electricity and heat demands, comparing them with the state-of-the-art systems based on natural gas steam reforming. Still existing limits correlated to the electrolyser use at large capacities are underlined and a forecast of the reachable plant performance is presented considering the electrolysis operation improvement attended in next years, which will allow for lower consumption and higher operative

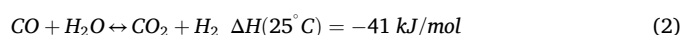
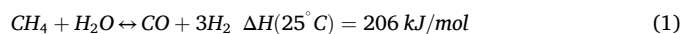
pressures. Ammonia and methanol co-production is also discussed, where the Power to Methanol process directly exploits as its reactant the CO₂ produced inside the Methane to Ammonia plant. This could overcome the still-limited CO₂ capture plants and infrastructure for its distribution. Finally, Power to Ammonia and Power to Methanol coupling is compared with respect to ammonia and methanol single-production lines.

2. Plant design for hydrogen and carriers

Focusing initially on hydrogen and then on ammonia and methanol as possible carriers, the work illustrates and compares green plant designs with the traditional ones based on fossil fuel use in terms of benefits and drawbacks. Natural gas steam reforming was taken as the reference, resulting in the most widespread plant configuration [13,54]. Proton Exchange Membrane Electrolysis Cell (PEMEC) technology was chosen for the green hydrogen production since this configuration is more mature than high-temperature solid oxide cells (technology readiness level already reaching 7–8) [55]. PEMEC higher efficiency and lifespan with a faster start-up procedure compared to alkaline cells justify its choice, despite high capital costs [56].

2.1. Hydrogen production plant

Fig. 1 illustrates the flowsheet of both the traditional (called H₂-SR) and the green (called H₂-PEMEC) processes for hydrogen production. In the first configuration, hydrogen derives from the steam reforming of natural gas (stream A) by producing a H₂-rich syngas (stream C) through an endothermic reaction performed at mild pressures for space saving (Eq. (1)). High-temperature compressed steam (stream B) is fed in excess of its stoichiometric requirement in order to guarantee a high Steam-to-Carbon ratio (S/C) and to avoid the catalyst deactivation through carbon deposition. The Water Gas Shift (WGS) reactor, set downstream the steam reforming reactor, allows to convert carbon monoxide and increase the hydrogen content in stream D (Eq. (2)).



All downstream steps are devoted to hydrogen purification. The first gas cleaning in Fig. 1A includes a flash unit to condensate water and a CO₂ separation unit. Carbon dioxide can be segregated in several ways (e.g., membrane, cryogenic, absorption technology, to name a few); however, amine-based absorption is the most suitable solution in terms of required capacities and costs for this application [57]. A further reduction of CO and CO₂ content is obtained in the Sabatier reactor through methanation

Table 1
Some working and under construction e-fuel plants.

Location	Capacity	Energy source	Electrolysis cell	Starting operation	Reference
e-Ammonia					
Perù, Cusco	<20,000 ton/y	Hydro	25 MW Alkaline	1965	[14]
Norway, Porsgrunn	20,500 ton/y	Renewable	24 MW PEM	Under construction	[45]
Morocco	183,000 ton/y	Sun	PEM	By 2026	[14]
Netherlands	75,000 ton/y	Offshore wind	Alkaline	By 2025	[46]
UAE, Abu Dhabi	200,000 ton/y	Sun	Alkaline	By 2024–2026	[47]
e-Methanol					
Iceland, Svartsengi	4000 ton/y	–	6 MW Alkaline	2011	[44]
Sweden, Luleå	350 ton/y	Blast furnace gas	Hydrogen from electrolysis and byproduct steel manufacturing	2019	[48]
Germany, Niederaussem	350 ton/y	Wind	0.6 MW PEM	2019	[48]
Denmark, Kasso	>50,000 ton/y	Sun	50 MW PEM	Under construction	[49]
Belgium, Ghent	45,000 ton/y	Wind	63 MW electrolyser	Under studied proposal	[50]
Sweden, Ørsted	50,000 ton/y	Wind + Sun	70 MW PEM	By 2025	[51]
Italy, Sicily	–	–	–	Start-up begun in 2021	[52]
Norway, Finnjord	100,000 ton/y	Hydro	Low temperature cells	Under studied proposal	[53]

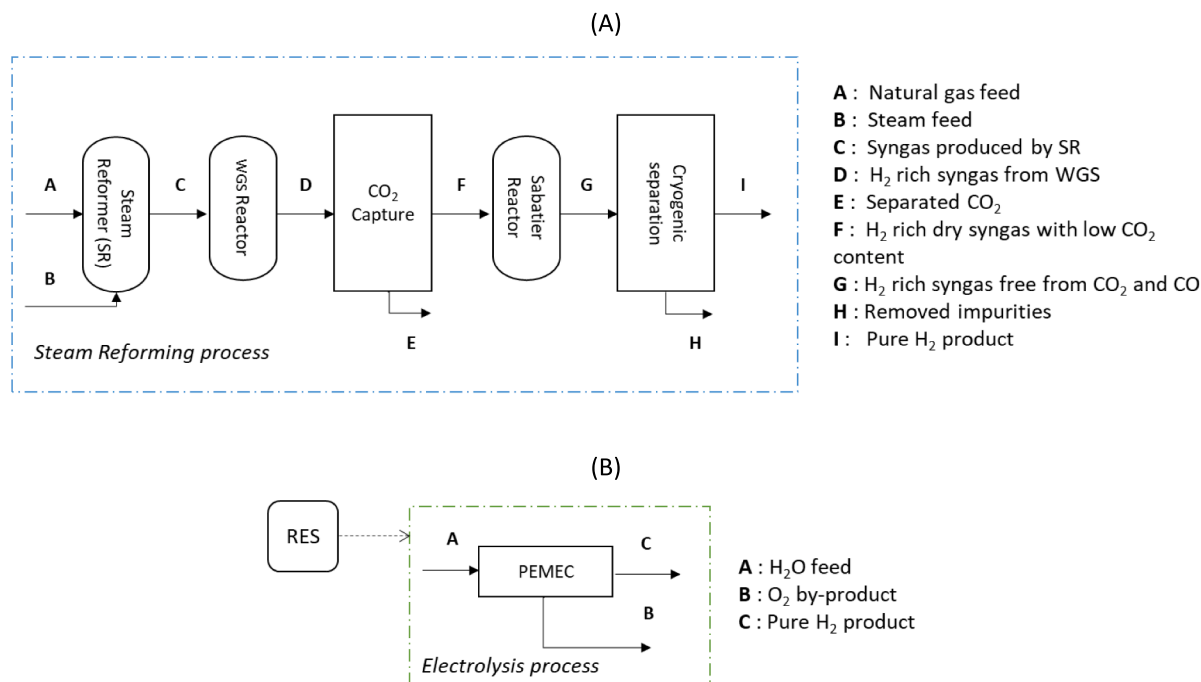
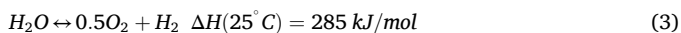


Fig. 1. Plant designs for hydrogen production referring to (A) natural gas steam reforming-based process called H₂-SR and (B) water electrolysis-based process called H₂-PEMEC.

(opposite reaction of Eq. (1)), which allows to reach negligible amounts of the afore mentioned compounds but requires the consumption of a fraction of the previously produced hydrogen. The last gas cleaning step consists of a refrigeration unit that is necessary to achieve almost pure hydrogen (>99 %) by removing water and methane (stream H); it is followed by H₂ compression to reach its storage conditions (stream I).

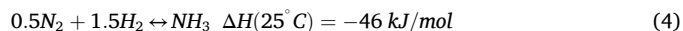
Referring to the green production process (Fig. 1B), it is based on the electrolysis of water (stream A) powered by Renewable Energy Sources (RESs). Pure hydrogen (stream C) is directly produced through water dissociation (Eq. (3)) with O₂ as a by-product, requiring just a final compression step up to the storage pressure.



2.2. Ammonia production plant

The ammonia synthesis can be schematised by two sub-blocks: one to produce the nitrogen and hydrogen reactant feed and one to obtain the liquid NH₃ through the Haber Bosh loop. Fig. 2A represents the industrial configuration, called NH₃-SR, allowing a wide range of production capacities (from small scales of 200–500 tons/day to high scales up to 4500 tons/day) [58]. The first sub-block is similar to the steam reforming process, previously described for the hydrogen synthesis, but it is based on two in series steam reforming reactors to achieve a H₂-N₂ mixture. Natural gas and steam at high temperatures and pressures (streams A and B) are fed to the first reformer, where syngas (stream C) is produced without reaching the methane complete conversion. The following unit is an autothermal reformer, where hot air (stream D) is supplied to add nitrogen and consume a fraction of the remaining methane through its partial combustion and here producing the heat required by the endothermic reforming reaction (Eq. (1)). The WGS reactor is again present to increase the hydrogen fraction, followed by several gas cleaning steps to remove all oxidised compounds (i.e., CO₂, CO and H₂O) that can poison the ammonia synthesis catalysts [59]. Unlike the H₂-SR process, the final mixture (stream I) can contain CH₄ produced by the Sabatier reactor and Ar derived from the air since they are inert in the ammonia synthesis reactor. The second sub-block includes the Haber Bosch loop, where the nitrogen and hydrogen mixture

with a molar ratio equal to 3:1 is compressed and heated before feeding to the ammonia exothermic reactor (stream J) (Eq. (4)).



Downstream, the produced ammonia is separated from the H₂-N₂-rich mixture through its liquefaction, reaching a purity of around 99.5 % (stream L). Since the yield per pass is usually low (around 20–30 %) [60], the unreacted reagents are recirculated (stream O) except for a small fraction that is purged to avoid the inert gas accumulation (stream N). A cryogenic purification step could also remove the methane downstream of the Sabatier reactor, reducing the loop purge [59]. This is a rarer plant configuration requiring further units and for this reason it was not considered in the present work.

The second configuration in Fig. 2B consists of the green ammonia production path, called NH₃-PEMEC, which uses renewables as the only energy source. In this case, hydrogen is produced by the electrolysis of water (stream A). Nitrogen derives from air (stream D) using an Air Separation Unit (ASU), which usually consists of the cryogenic distillation aiming at a high production capacity and an extremely pure N₂ stream (stream F), since oxygen can oxidise ammonia synthesis catalysts. Whereas the Haber Bosch loop includes the same unit operations described previously for the NH₃-SR case; it allows e-ammonia production with a purity of around 99.5 % again (stream I).

2.3. Methanol production plant

Fig. 3 presents two plant configurations for the methanol synthesis. The traditional path, called MeOH-SR in Fig. 3.A, can be divided into three steps: the steam reforming process, the lacking CO₂ addition from a storage tank and the MeOH under pressure loop. The steam reforming is used to produce hydrogen-rich syngas (stream C) starting from natural gas (stream A) and pressurised steam (stream B). The WGS reactor is not present downstream of the reforming unit. The gas cleaning consists of excess water removal. An external CO₂ flow (stream E) is added to reach the required Stoichiometry Ratio (StR), defined as (H₂ - CO₂)/(CO + CO₂), equal to around 2. In the following loop, the feed is compressed and heated (stream F) to favour the exothermic MeOH synthesis

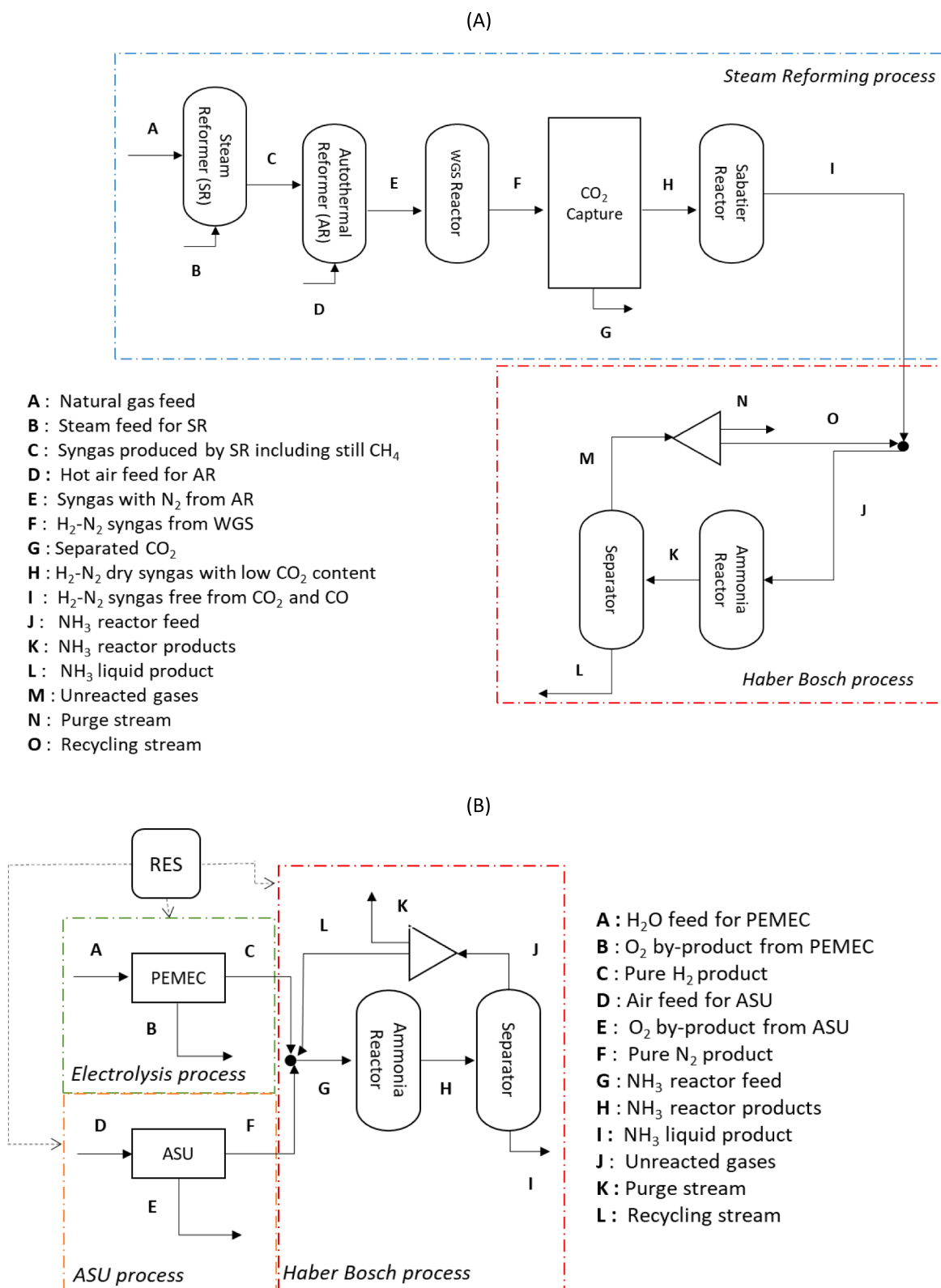
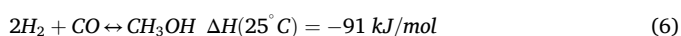
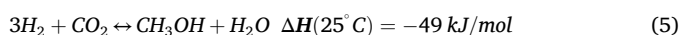


Fig. 2. Plant designs for ammonia production referring to (A) natural gas steam reforming-based process called NH₃-SR and (B) water electrolysis-based process called NH₃-PEMEC.

reactions (Eqs. (5) and (6)).



The yield per pass is about 25 % [61], requiring the recirculation of the unreacted syngas (stream K). Aiming at a purity of around 99.5 % downstream of the reactor (stream M), there are several unit operations which separate the liquid methanol from reactants and by-products,

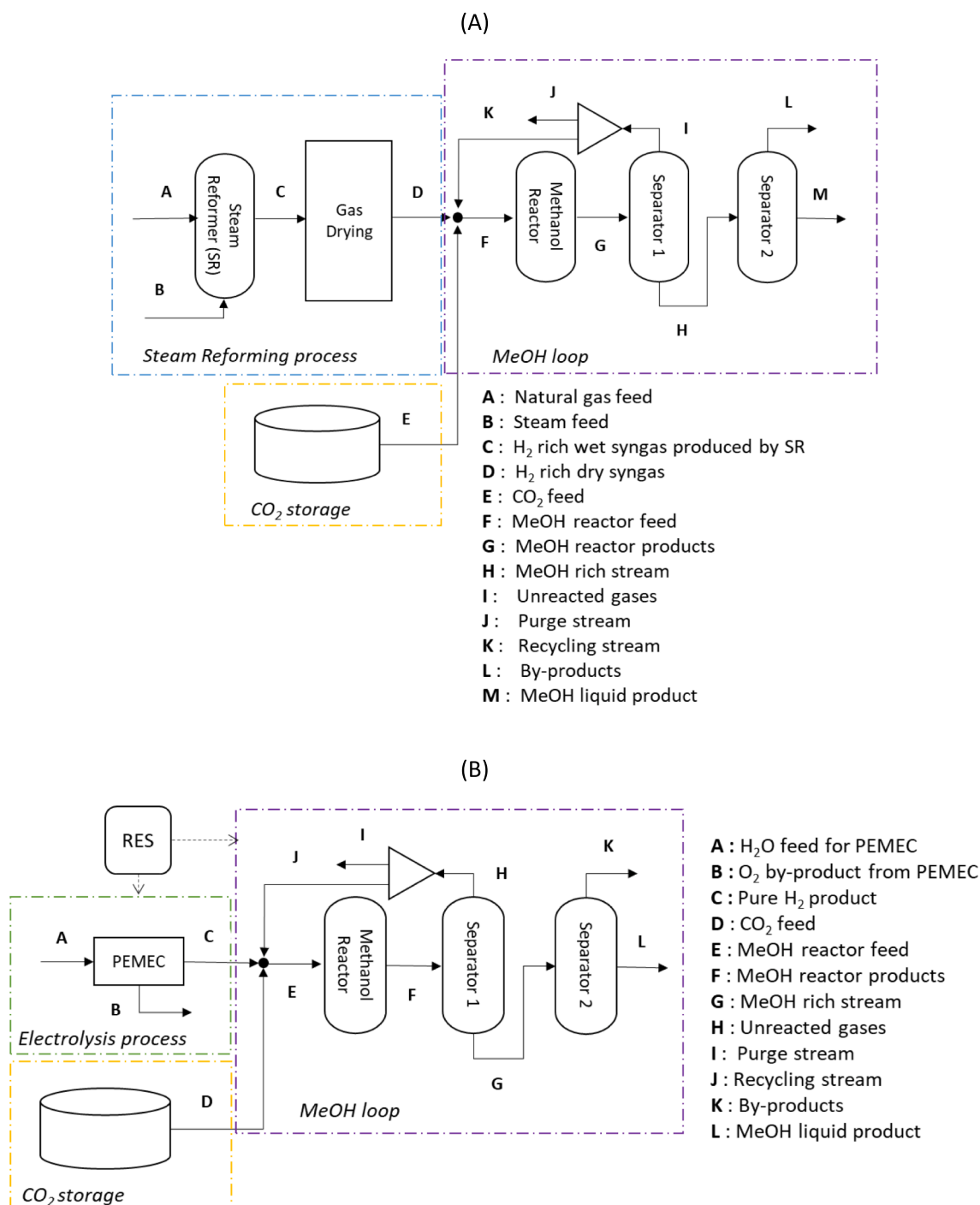
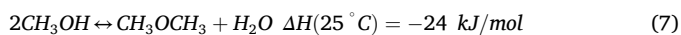


Fig. 3. Plant designs for methanol production referring to (A) natural gas steam reforming-based process with a CO₂ external source called MeOH-SR and (B) water electrolysis-based process with a CO₂ external source called MeOH-PEMEC.

such as methane and dimethyl ether (opposite reactions of Eq. (1) and (7)). It is noteworthy that, in theory, working conditions would trigger other unwanted reactions, which were not considered in the present work. Indeed, their formation can be minimised using selective catalysts and decreasing the permanence time inside the reactor in order to avoid parallel and secondary reactions, respectively [62].



The second flowsheet in Fig. 3B represents the green alternative called MeOH-PEMEC. It is constituted by three main sub-blocks powered by RESs: the water (stream A) electrolyser unit producing pure hydrogen

(stream C), the CO₂ (stream D) storage unit and the MeOH under pressure loop producing methanol at around 99.5 % purity degree (stream L).

2.4. Ammonia and methanol co-production plant

Coupling ammonia with methanol production has several benefits, such as CO₂ emission reduction, CAPEX and OPEX decrease and production flexibility [63,64]. This solution has already been presented on the market combining steam reforming-based synthesis paths [65,66]. Nevertheless, some more eco-friendly alternatives are being studied,

where biomass gasification and water electrolysis can be the hydrogen sources and CO_2 is recovered by carbon capture units [67,68]. The methanol synthesis becomes a possible profitable application for the CO_2 utilization on a large scale. Recently, a plant configuration has been reported that proposes the ammonia synthesis from water electrolysis and ASU, using the pure oxygen derived from air separation for an autothermic steam reforming reactor [69–71]. The obtained syngas has a higher CO- CO_2 content and a StR suitable for the methanol synthesis, favouring the methane partial oxidation.

Two possible flowsheets are presented: (i) a hybrid solution merging a traditional and a green production line with CO_2 internal use called NH_3 – MeOH SR Hybrid, (ii) a plant based only on green hydrogen production recovering CO_2 externally called NH_3 – MeOH PEMEC Hybrid. The first case shown in Fig. 4A combines the Methane to Ammonia approach with the Power to Methanol one. Natural gas, steam and air (stream A) are fed to two in series steam reforming reactors to obtain a hydrogen- and nitrogen-rich mixture (stream B) for the Haber Bosch process that produces pure liquid ammonia (stream D). The CO_2 recovered from the syngas cleaning (stream C) becomes the reagent in

the MeOH loop, after mixing with the hydrogen produced by water electrolysis (stream F), to obtain liquid methanol (stream H). The second case shown in Fig. 4B is based on a single electrolyser that provides hydrogen to both carrier synthesis lines (streams F and G), requiring an ASU for pure nitrogen production (stream D) and a CO_2 storage tank (stream H).

2.5. Working conditions and assumptions

A feasibility analysis of all previously discussed plant designs was performed by DWSIM, an open-source process simulation software [72], allowing a quantitative characterization of the material and energy consumption. Moreover, the heat integration was also evaluated assuming 20 degrees as the minimum temperature gradient between hot and cold streams. Knowing the maximum and minimum temperatures of the plant, the net heat flux ϕ for each temperature range ΔT was computed by algebraically summing the enthalpic fluxes of all heating and cooling currents included in this step (Eq. (8)).

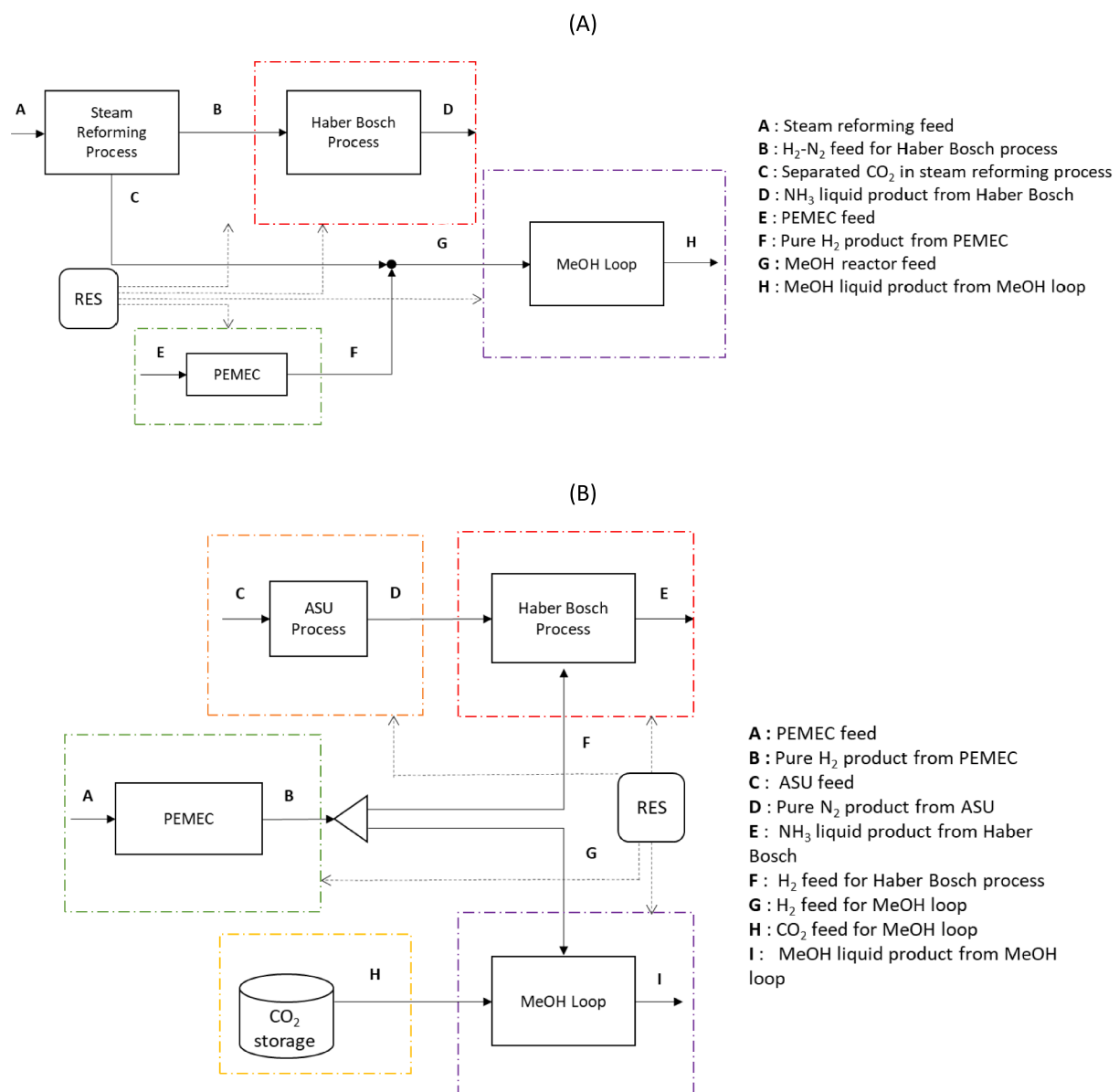


Fig. 4. Plant designs for ammonia and methanol co-production referring to (A) plant coupling Methane to Ammonia with Power to Methanol called NH_3 – MeOH SR Hybrid and (B) plant coupling Power to Ammonia with Power to Methanol called NH_3 – MeOH PEMEC Hybrid.

$$\phi_i = \left(\sum_{j=1}^{N_{hot}} W_j c_{pj} - \sum_{j=1}^{N_{cold}} W_j c_{pj} \right) \Delta T_i, \forall i = \text{number of temperature ranges} \quad (8)$$

Where W is the flowrate, c_p the specific heat and N the stream number. A positive value means a heat surplus, while a negative value means a heat deficit. The cumulative heat flux $\check{\phi}$ was computed considering surplus and deficit from ranges at higher temperatures (Eq. (9)) and here evaluating the required heat integration.

$$\check{\phi}_{i+1} = \check{\phi}_i + \phi_i, \forall i = \text{number of temperature ranges} \quad (9)$$

The reactor working conditions are reported in Table 2. The NH_3 synthesis occurred at 500 °C and 200 bar [12], while the methanol synthesis needed milder working conditions, resulting in 220 °C and 80 bar. Referring to the reforming process, two reformers in the NH_3 -SR case had different working temperatures: the first was set at 750 °C while the second reached 970 °C under an autothermic behaviour with air oxidation inside [35,73]. H_2 -SR and MeOH-SR plants consist of a single reforming working at a fixed temperature of 980 °C to favour the methane complete conversion [74]. In all cases, the reforming pressure was set to 35 bar to reduce space issues. It is noteworthy that the first approximation considered available steam at high temperatures and pressures (@ 360 °C and 35 bar). Following, the steam production consumption was also added to the analysis. WGS and Sabatier reactors worked at a temperature of 200 °C and 300 °C, respectively, and at the same pressure of the reformer to minimise the pressure variations. The PEM electrolyser was modelled by a reactor with a fixed water conversion at 80 °C and 30 bar, assuming an electrical consumption of ~55 $\text{kWh}_{el}/\text{kg H}_2$ (Begin of Life) and a heat loss of ~9 $\text{kWh}_{th}/\text{kg H}_2$ [75,76]. The reactant purification steps were simulated by imposing the separation efficiency. Referring to the amine absorption technology [77], the CO_2 capture efficiency in H_2 -SR and NH_3 -SR cases was ~95 % requiring 0.09 $\text{kWh}_{el}/\text{kg CO}_2$ as the electrical work and 0.98 $\text{kWh}_{th}/\text{kg CO}_2$ as the reboiler duty. While air distillation was considered as the ASU reference, allowing the N_2 complete separation from oxygen and argon by consuming ~0.5 $\text{kWh}_{el}/\text{kg}$ of liquid N_2 [78]. Looking at target products (Table 2), hydrogen was obtained at a purity higher than 99 %, a pressure of 100 bar and room temperature [10]. Liquid ammonia at purity levels higher than 99 % was refrigerated up to -34 °C at 1.3 bar [79]. Whereas fuel grade methanol was assumed to be in liquid phase at atmospheric conditions [80], fixing a water content lower than 0.05 wt % with possible traces of other organic compounds [28].

3. Results and discussion

A technical feasibility analysis of three H_2 -based fuels was performed looking at the material and the energy demand characterizing the production processes using both fossil fuels and renewables (i.e., e-fuel synthesis). All these cases assumed an equal involved hydrogen flowrate, as the hydrogen synthesis was considered the basic scenario. Note that the following tables and figures report the most relevant results; for more details, refer to Supplementary Materials, which list the properties of each stream in the analysed flowsheets.

Comparing the H_2 -SR process with the H_2 -PEMEC system, the main

benefits and weaknesses of a traditional vs. a green production are already evident. In the H_2 -SR traditional process, the hydrogen is produced by the natural gas steam reformer, obtaining a 43 vol% H_2 -rich mixture that is further enriched by the water gas shift reaction up to 49 vol% H_2 and by several purification steps, finally reaching 93 vol% H_2 . The cooling step allows for the hydrogen to undergo a complete purification (>99 vol% H_2). Significant fuel and steam supplies are needed, resulting in 3.3 Nm^3 fuel/kg H_2 and 12.9 kg $\text{H}_2\text{O}/\text{kg H}_2$, respectively. On the other hand, the electricity demand is minimum by exploiting a thermochemical process: 0.7 $\text{kWh}_{el}/\text{kg H}_2$ for the initial compression of the natural gas, the purification and the final compression of the produced hydrogen. Green H_2 electrochemical synthesis has a simple design involving just a PEM water electrolysis module, which produces pure dry hydrogen at mild pressures. Water consumption is quite comparable in two cases, with a bit higher value using an electrolyser; nevertheless, this last technology requires a high purity degree feed. The H_2 -PEMEC plant is dominated by the electricity demand of the electrolyser that leads globally to 55.7 $\text{kWh}_{el}/\text{kg H}_2$, resulting only competitive in the case of low-cost available electricity. However, the heat management line is easier and lower temperatures are involved (electrolyser works below 100 °C) with respect to the steam reformer process, where a temperature near 1000 °C is forced to guarantee a quite complete methane conversion (around 98 %). The H_2 -SR plant is further penalised in standalone applications without a steam stream already available, resulting in a penalization of around 0.8 $\text{kWh}_{th}/\text{kg steam}$ (@ 35 bar and 360 °C).

3.1. Ammonia and methanol single production

Ammonia and methanol are alternative fuels that derive from hydrogen produced by steam reforming or water electrolysis coupled with a high temperature and pressure synthesis loop. As shown in Table 3, hydrogen and other reactant production has a significant influence on the whole process due to a high fuel demand due to steam reforming in NH_3 -SR and MeOH-SR cases and a high electricity requirement for e-fuels in NH_3 -PEMEC and MeOH-PEMEC cases.

In detail, ammonia derives from high-purity hydrogen and nitrogen reacted in the Haber Bosch loop (Eq. (4)). In the NH_3 -SR these reactants are obtained by two reforming reactors permitting to simplify the process design with respect to the NH_3 -PEMEC, where the water electrolysis module works in parallel to the air cryogenic distillation columns to have a final H_2/N_2 molar ratio equal to around 3. The needed natural gas is high since it is the source for H_2 as well as for the heat stabilizing the second autothermic reformer. Consequently, both air and steam flows increase by around 80 % and 30 %, respectively, in NH_3 -SR compared with NH_3 -PEMEC, to have a complete methane conversion and a steam-to-carbon ratio higher than four. It is noteworthy that NH_3 -PEMEC does not only need less air, but all the oxygen present in the feed can be recovered at a high purity degree allowing ~1.25 Nm^3 $\text{O}_2/\text{kg NH}_3$ as a co-product from the air separation unit (around 15 %) and the water electrolysis (around 85 %). Another difference between traditional and green paths consists of purification steps, since the PEMEC directly produces a pure hydrogen stream while the reformer generates syngas with a significant amount of H_2O , CO e CO_2 . Water can be recovered by its condensation (~0.45 kg $\text{H}_2\text{O}/\text{kg syngas}$), while CO_2 is captured by

Table 2
Main working conditions of analysed case-studies.

Working Condition	Reforming Reactor	PEMEC	WGS Reactor	Sabatier Reactor	Ammonia Reactor	MeOH Reactor
Temperature [°C]	750–980 (NH_3 -SR) 980 (H_2 -SR and MeOH-SR)	80	200	300	500	220
Pressure [bar]	35	30	35	35	200	80
Feed composition	S/C = 4.7	Pure water	Crude syngas	Clean syngas	$\text{H}_2/\text{N}_2 \approx 3$	StR ≈ 2
H_2 purity degree			>99 % @ 100 bar and 20 °C			
NH_3 purity degree			>99 % @ 1.3 bar and -34 °C			
MeOH purity degree			>99 % @ 1.3 bar and 20 °C			

Table 3

Comparison of ammonia and methanol production processes: Steam Reforming (SR) vs. PEM Electrolysis Cell (PEMEC).

Process	NH ₃ – SR	NH ₃ – PEMEC	MeOH – SR	MeOH – PEMEC
Product	NH ₃		MeOH	
Fuel specific consumption [Nm ³ _{fuel} /kg _{product}]	0.97	–	0.67	–
Air specific consumption [Nm ³ _{air} /kg _{product}]	1.63	0.90	–	–
Inlet water specific consumption [kg _{H₂O} /kg _{product}]	3.80 @ 35 bar & 360 °C	2.94 @ room conditions	2.57 @ 35 bar & 360 °C	3.37 @ room conditions
H ₂ derivative specific production [kg _{product} /Nm ³ _{H₂}]	0.38	0.47	0.44	0.41
Specific O ₂ production [Nm ³ _{O₂} /kg _{product}]	–	1.25	–	1.22
Specific electrical demand [kWh _{el} /kg _{product}]	2.49	11.40	0.14	12.23
Specific hot external demand [kWh _{th} /kg _{product}]	0.77	0.06	1.82	0.13
Specific cold external demand [kWh _{th} /kg _{product}]	6.11	3.30	3.23	3.19

amine-based absorption (~0.25 kg CO₂/kg syngas). The final Sabatier reactor generates methane by consuming H₂, CO and CO₂, resulting in a 4 vol% CH₄ mixture fed to the loop. Working conditions for the Haber Bosch process are the same in both considered flowsheets (@ 200 bar and 500 °C); nevertheless, a higher H₂ conversion is obtained in NH₃-PEMEC (93 % vs. 79 %) producing 20 % more of ammonia under an equal feed because of a pure H₂-N₂ mixture reagent. The off-gases are consequently different, since in the NH₃-SR case they contain up to 12 vol% CH₄, while in the NH₃-PEMEC plant hydrogen exceeds 77 vol%. Varying composition leads to doubling the heating value of the mixture in this second case (~24 MJ(LHV)/kg).

Referring to the electrical demand (Table 3), the PEMEC requires ~10.5 kWh_{el}/kg NH₃ with just ~0.8 kWh_{el}/kg NH₃ for the air separation unit and the synthesis loop. Focusing on the Haber Bosch process contribution, compression work is needed for both the fresh feed and the recirculated, unreacted gas stream. NH₃-PEMEC value equal to ~0.4

kWh_{el}/kg NH₃ is significantly lower than the ~2.3 kWh_{el}/kg NH₃ of the natural gas-based plant. This variation is partially due to recycling. The inert presence (i.e., Ar and CH₄) makes the ammonia purification step more difficult since it requires lower pressures in the final refrigeration separator (19 bar in NH₃-SR vs. 100 bar in NH₃-PEMEC) and consequently more electric work for the reagent recompression. Moreover, under equal H₂-N₂ reactant amounts, a higher ammonia production obtained in the NH₃-PEMEC case decreases its specific consumption value. Referring to hydrogen synthesis steps in the NH₃-SR plant, the natural gas compression is quite negligible evaluating the gas cleaning as more energy-consuming (above all due to amine-based absorption).

Considering the thermic aspect (Fig. 5A), NH₃-SR and NH₃-PEMEC designs show significantly different heat demands resulting mainly influenced by the applied processes for the hydrogen production. In the NH₃-SR case, the first isothermal reforming reactor has to maintain a working temperature of around 750 °C. This hot requirement can be partially satisfied by cooling the syngas leaving the second autothermal reformer at 970 °C (the only stream at higher temperatures) and partially using an external hot source (~0.8 kWh_{th}/kg NH₃). There would be a higher demand (~1.6 kWh_{th}/kg NH₃), if steam was not available as here assumed. Amine based absorbent regeneration has a high heat consumption; however, its working temperatures below 130 °C permit to maximise the internal heat recovery in this case. The cooling in syngas cleaning and liquid ammonia separation steps leads to heat recovery, by treating high flowrates due to both nitrogen presence and water surplus fed to the reforming. Ammonia synthesis, WGS and Sabatier reactors are all exothermic units that can provide heat for the amine regeneration and their feed pre-heating. Total cold requirement of NH₃-SR is ~6.1 kWh_{th}/kg NH₃. It is noteworthy that most heat is available at temperatures below 100 °C, here it cannot be used to produce steam. In NH₃-PEMEC all main unit operations are exothermic. The ammonia synthesis loop provides heat at quite high temperatures (a 15 % higher thermal power with respect to the NH₃-SR case due to a higher conversion), which allows for heating the reactant mixture. Here the hot external need is minimised at ~0.06 kWh_{th}/kg NH₃. Whereas the water electrolyser releases low-temperature heat that can be narrowly used within the plant itself.

Methanol production needs hydrogen and carbon-based sources (i.e., CO and CO₂) with a stoichiometric ratio of around 2. In both analysed flowsheets, an external CO₂ source is introduced since (i) the steam reforming syngas is lacking resulting in a StR of 2.9 and (ii) the PEMEC technology is not mature for co-electrolysis operation at commercial level [81]. Here the added CO₂ represents 7 % and 30 % of the mixture fed to the loop in MeOH-SR and MeOH-PEMEC, respectively. Fixed the same hydrogen amount, the natural gas demand is lower than both the H₂-SR case (around 5 % decrease), without consuming a H₂ fraction in

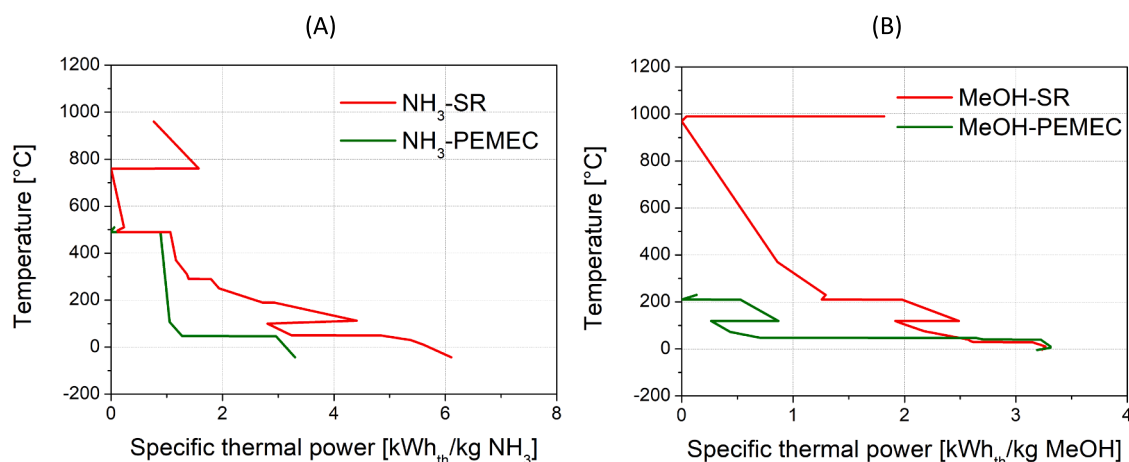


Fig. 5. (A) Ammonia and (B) methanol synthesis grand composite curves comparing Steam Reforming (SR) and PEM Electrolysis Cell (PEMEC) based processes.

the Sabatier reactor, and the NH₃-SR one (around 20 % decrease) using a single isothermal reformer. Note that a configuration with two in-series reforming steps, as in the NH₃-SR plant, would decrease the syngas stoichiometric ratio up to 2.3, but pure oxygen would be required to avoid the nitrogen accumulation. Comparing the water specific consumption in Table 3, the MeOH-PEMEC value is higher than the MeOH-SR one in view of fewer amounts of natural gas (without the reactor heating as in the NH₃-SR case) and here of steam; moreover, water is the only hydrogen source in the MeOH-PEMEC process. The hydrogen total conversion is 76 % and 89 % for MeOH-SR and MeOH-PEMEC systems, respectively, since the second has a lower purge. However, a bit higher value of the per pass conversion characterises the MeOH-SR plant since the feed contains more CO (17 vol% CO₂ and 6 vol% CO) which reacts producing further methanol (Eq. (6)). The CO content is < 2 vol% in the MeOH-PEMEC loop, deriving only from the water gas shift reaction developed directly within the MeOH reactor. In the Haber Bosch process, ammonia and unreacted gases are detected at the outlet without involving secondary reactions. Differently, some by-products can be produced in the methanol. Since the commercially used selective catalysts minimize their formation, a limited number of secondary reactions were applied in this analysis showing visible effects on the plant performance only correlated to methanation. Indeed, it favours the methane accumulation, which is also partially due to its presence in the inlet fed syngas. Again, in the e-fuel synthesis path, the water electrolysis permits pure oxygen as a by-product, resulting in ~1.22 Nm³ O₂/kg MeOH. Looking at purged off-gases, MeOH-SR and MeOH-PEMEC configurations have quite similar compositions containing between 76–79 vol% H₂. A similar heating value of ~20 MJ(LHV)/kg is detected in both cases, which is comparable to ammonia process results.

Referring to Table 3, the MeOH-SR plant has a negligible electrical demand since it does not require any purification for CO₂ removal. All consumption of steps upstream the methanol loop is due to natural gas and CO₂ pre-compression, representing about 17 % of the total required electricity. The synthesis loop is also less energy-consuming than the Haber Bosch one due to a lower working pressure (80 bar for MeOH vs. 200 bar for NH₃). Moreover, the recycled stream does not have to be expanded at low pressures to favour the product separation, reducing the number of compression steps. As in NH₃-PEMEC, the highest consumption of the green system depends on the electrolyser operation that needs ~12 kWh_{el}/kg MeOH. Aiming at the operative pressure reduction for safety and economic issues, more effective catalysts for methanol synthesis could work up to 40–50 bar [82], which would minimize the compression within the loop feeding directly a syngas at 35 bar from the steam reformer or hydrogen at 30 bar from the PEMEC. However, the influence of working pressures within the loop would be minimal on the total electricity demand, above all in the MeOH-PEMEC process.

Hydrogen production significantly influences the heat demand of the process (Fig. 5.B). In details, the specific hot requirement of the MeOH-SR plant is higher than the NH₃-SR plant value. Indeed, a single isothermal reactor working at 980 °C is used, which means an external hot supply of ~1.8 kWh_{th}/kg MeOH (2 kWh_{th}/kg MeOH without available steam at high temperatures and pressures), lacking a hotter process stream. At lower temperatures, the hot heat demand is completely satisfied by cooling the outlet syngas and by the exothermic methanol synthesis providing ~0.5–0.7 kWh_{th}/kg MeOH. Differently from the NH₃ production, the methanol purification consists of distillation column separation where the reboiler heat is provided by the internal recovery. Specific cold demand is halved with respect to the ammonia production plant value. Referring to the MeOH-PEMEC plant, it is almost thermally self-sufficient requiring just ~0.13 kWh_{th}/kg MeOH for the MeOH loop reactant final heating. The electrolyser dissipates heat, although it has limited uses. Comparing two methanol synthesis paths, below room conditions a bit higher hot demand is visible in the MeOH-PEMEC plant due to a higher CO₂ feed that has to be pre-heated assuming its liquid storage.

According to the previous results, both ammonia and methanol are

promising hydrogen carriers since their synthesis requires some further unit operations (i.e., high temperature and pressure loops) that do not make their production so much more penalized with respect to pure H₂ yet, showing a minor weight on the global process consumption. Focusing above all on e-fuels due to the industrial application decarbonization need, in all cases the high specific electricity demand is correlated to the electrolyser operation that increases by changing from ammonia and methanol to hydrogen due to the compound different weights. In order to have an effective comparison with the steam reforming-based processes, the plant global energy consumption E_{tot} was calculated by summing the energy content of natural gas used as the process reactant to the electrical work (Eq. (10)).

$$E_{tot} = \frac{\sum P_{el} + N_{NG}LHV_{NG}}{N_{e-fuel}} \quad (10)$$

where P_{el} is the electrical power, N_{NG} the natural gas flowrate, LHV_{NG} the Lower Heating Value of the natural gas and N_{e-fuel} the produced e-fuel flowrate. As shown in Fig. 6, NH₃-SR production requires ~12.1 kWh_{tot}/kg NH₃ (~80 % due to natural gas demand of the steam reforming and ~20 % due to the electrical work of other unit operations) compared with ~11.4 kWh_{tot}/kg NH₃ of NH₃-PEMEC (~92 % due to the electrolysis electricity demand and ~8 % due to the electrical work of other unit operations). In summary, the electrolyser has a higher energy weight with respect to the steam reforming, but it is balanced by a less energy-consuming Haber Bosch loop in view of a higher pressure of the recycling. Referring to the methanol synthesis, MeOH-PEMEC has a higher value, obtaining ~12.2 kWh_{tot}/kg MeOH with respect to ~6.8 kWh_{tot}/kg MeOH of the MeOH-SR plant, since a lower natural gas amount is required and the loop consumption does not differ between MeOH-SR and MeOH-PEMEC, differently from ammonia cases (Table 3).

Beyond the energy consumption, another key point to be considered is the environmental impact due to CO₂ emissions, which leads to the most significant benefit of e-fuel synthesis (Fig. 7). Indeed, the NH₃-SR plant releases ~1.65 kg CO₂/kg NH₃ just due to the syngas purification, assuming high-temperature compressed steam is already available. The NH₃-PEMEC system has zero emissions, substituting fossil fuels with renewables as the energy source. The methanol production uses all CO₂ produced within the process itself and recovers also the CO₂ separated by other plants, resulting in one of its more promising application fields. In the MeOH-SR case, the required CO₂ amount is minimum (~0.42 kg CO₂/kg MeOH), whereas it becomes significant in the MeOH-PEMEC plant reaching ~1.60 kg CO₂/kg MeOH.

3.2. Ammonia and methanol co-production

The first weakness to large-scale e-fuel production is the electricity

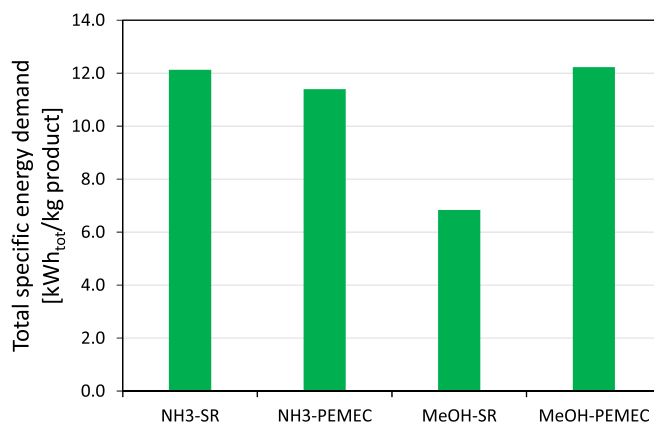


Fig. 6. Comparison of plant specific energy consumption for ammonia and methanol production processes.

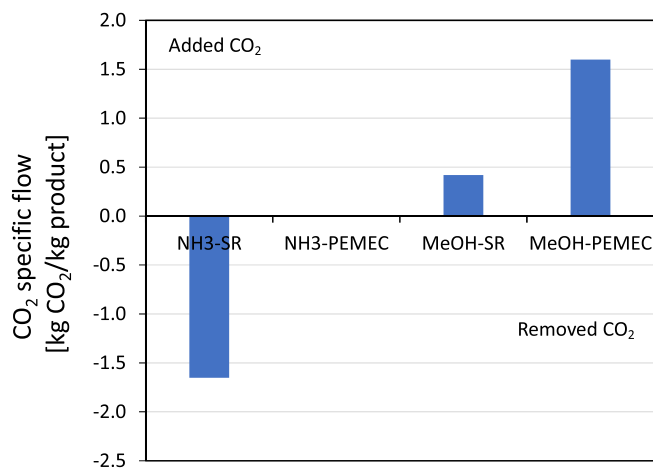


Fig. 7. Removed CO₂ (as negative values) and added CO₂ (as positive values) as a function of produced ammonia and methanol in different plant designs.

consumption, which cannot be satisfied by the current renewable installed capacity. Another severe limit is the actual commercial electrolyser size that is unable to cope with a high worldwide ammonia and methanol demand as chemicals and fuels. Multimegawatt systems should be available to permit a production of hundreds of tons, as in fossil-fuel-based operating processes [14,83]. Moreover, in the MeOH case, CO₂ storage or a proper supply infrastructure should be introduced for a continuous plant operation (existing storage sites exploit mainly geological formations [84]). Since both points have still not reached the required technological development, a hybrid plant combining traditional and green synthesis paths for ammonia and methanol co-production can be an effective solution during the on-going energy transition. Indeed, the coupling of methanol and ammonia plants allows to reduce the electrolyser size. Here H₂ supply is guaranteed by both steam reforming and water electrolysis, obtaining in loco direct CO₂ production and oxygen as a by-product. Coupling the Methane to Ammonia with the Power to Methanol approach, there is no net emission since the CO₂ separated by the H₂/N₂ mixture upstream the Haber Bosch loop is used as a reactant for the methanol synthesis, obtaining ~1.08 kg MeOH/kg NH₃.

If a biofuel substituted the natural gas, the produced ammonia and methanol could be effectively defined as green chemicals according to the legislation in force [85–88]. The current biofuel market is not sufficient to satisfy process demand; however, an average growth of ~11 % per year could gradually solve this threshold [89]. As underlined in Table 4 and assuming biomethane feed, the fuel specific consumption of the steam reforming reactor is ~0.51 Nm³ fuel/kg NH₃ + MeOH, which results lower than the single production plant operations obtaining two products in the hybrid case. Water is necessary in almost equal amounts for both the steam reforming and the electrolysis operations. The specific total energy consumption is equal to ~12.8 kWh_{tot}/kg (NH₃ + MeOH) distinguishing ~5.2 kWh(LHV)/kg (NH₃ + MeOH) due to the fuel use and ~7.6 kWh_{el}/kg (NH₃ + MeOH) as the electrical work. In this last term, the main contribution is correlated to the electrolyser, representing ~83 % of the overall inlet electricity. The plant needs ~0.8 kWh_{th}/kg (NH₃ + MeOH) and ~4.5 kWh_{th}/kg (NH₃ + MeOH) as the hot and the cold external demands, respectively (Fig. 8). The steam reforming technology requires additional heat to guarantee an isothermal operation, which cannot be provided by the MeOH synthesis line working always at lower temperatures and leads to an increase in the effective fuel consumption. Excluding the steam reforming operation, two process coupling allows for an optimised internal heat recovery that satisfies both the heat for the amine absorbent regeneration in the NH₃ synthesis line and for the reboilers of the methanol distillation columns.

Table 4

NH₃ and MeOH co-production processes with respect to single green product plants, considering bio methane as steam reforming feed in NH₃-MeOH SR Hybrid solution and an equal hydrogen distribution between two synthesis lines in NH₃-MeOH PEMEC Hybrid solution.

Process	NH ₃ – MeOH SR Hybrid	NH ₃ – MeOH PEMEC Hybrid	NH ₃ – PEMEC	MeOH – PEMEC
Product	NH ₃ + MeOH	NH ₃ + MeOH	NH ₃	MeOH
Fuel specific consumption [Nm ³ _{fuel} /kg _{product}]	0.51	–	–	–
Inlet water specific consumption [kg _{H₂O} /kg _{product}]	3.59 (51 % NH ₃ – 49 % MeOH)	3.14 (50 % NH ₃ – 50 % MeOH)	2.94	3.37
CO ₂ specific flow [kg _{CO₂} /kg _{product}]	–0.83	+0.74	–	+1.60
Net CO ₂ specific production [kg _{CO₂} /kg _{product}]	–	–	–	–
MeOH specific production [kg _{MeOH} /kg _{NH₃}]	1.08	0.87	–	–
Specific electrical demand [kWh _{el} /kg _{product}]	7.60 (16 % NH ₃ – 84 % MeOH)	11.78 (52 % NH ₃ – 48 % MeOH)	11.40	12.23
Specific energy demand [kWh _{tot} /kg _{product}]	12.81 (50 % NH ₃ – 50 % MeOH)	11.78 (52 % NH ₃ – 48 % MeOH)	11.40	12.23
Specific hot external demand [kWh _{th} /kg _{product}]	0.83	0.03	0.06	0.13
Specific cold external demand [kWh _{th} /kg _{product}]	4.51	3.18	3.30	3.19

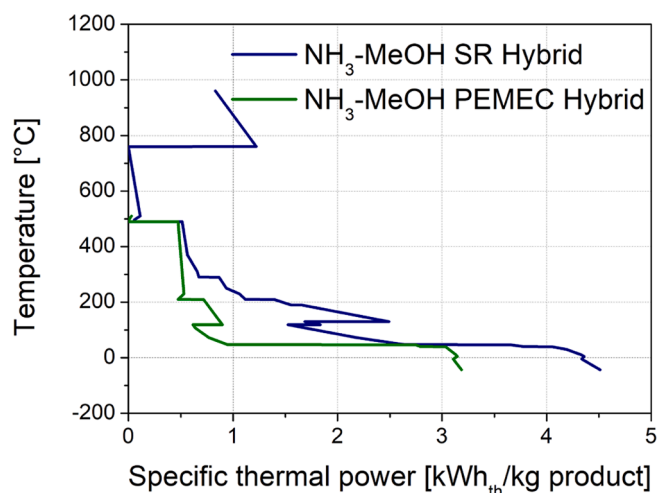


Fig. 8. Grand composite curves comparing Steam Reforming (SR) and PEM Electrolysis Cell (PEMEC) based hybrid processes.

Overcome the current technical thresholds thanks to the electrolyser performance improvement, the renewable energy spread and sharing, the carbon capture and storage system increase [90–94], a more sustainable co-production process could use only e-hydrogen feeding both lines and exploit an external CO₂ supply (~0.74 kg CO₂/kg (NH₃ + MeOH)). In such a system, water is the only H₂ source, but its demand is comparable to the previously discussed hybrid solution. The methanol to ammonia ratio is a bit lower than the NH₃-MeOH SR Hybrid value due to

a higher hydrogen conversion in the Haber Bosch loop when a pure H₂-N₂ mixture is fed. Referring to the electricity consumption, the electrolyser alone needs ~11.2 kWh_{el}/kg (NH₃ + MeOH) leading to total energy consumption quite comparable to the steam reforming-based hybrid plant (with a minimum improvement computing ~8 % decrease). Working always below ~500 °C, the hot requirement is just due to the Haber Bosch reactant final heating step (~0.03 kWh_{th}/kg (NH₃ + MeOH)). Whereas the cold need results quite similar to the single line productions referring to the same electrolyser working (~3.2 kWh_{th}/kg (NH₃ + MeOH)), but it is lower than the NH₃-MeOH SR Hybrid case, where the hot outlet syngas temperature has to be reduced at atmospheric conditions for cleaning purposes (Fig. 8). The heat produced by PEMEC, working at 80 °C, has again minimum applications within the plant itself.

Fig. 9 depicts the energy consumption in terms of power and heat using different H₂ percentages in the NH₃-MeOH PEMEC Hybrid design. The electricity-specific consumption shows an increasing trend as the methanol plant capacity rises. This is mainly due to a lower output flowrate than the ammonia plant one, despite equal hydrogen fed to both cases. The system thermal operation is mainly influenced by working temperature ranges, which are greater in the case of the NH₃ production line, requiring both a higher reaction temperature and a lower storage temperature. The specific hot requirement has a slightly decreasing profile by reducing the ammonia line capacity, since less reactant has to reach 500 °C in the Haber Bosch loop. Nevertheless, since the methanol synthesis path cannot use the heat available from NH₃-based mixture cooling, the hot need increases again at very low ammonia production. The cold-specific demand has a constant profile except for an increasing ammonia synthesis capacity, when the effects due to NH₃ liquefaction below room temperature are more evident.

3.3. Influence of attended electrolyser performance improvement

In all discussed “green” flowsheets, significant penalizations are due to firstly the electrolyser energy consumption and secondly the required high pressures within the synthesis loops. Nevertheless, in the future, PEMEC system performance should improve from the current value of more than 55 kWh_{el}/kg H₂ to 51 kWh_{el}/kg H₂ by 2026 and up to 46 kWh_{el}/kg H₂ in the following [90]. Consequently, the e-fuel production should have a significant decrease in the electricity demand, making the Power to X technology more and more feasible. For instance, reducing of 5 kWh_{el}/kg H₂ and of 10 kWh_{el}/kg H₂ the PEMEC consumption means a ~9 % and a ~17 % lower electrical demand, respectively (Fig. 10). Moreover, alternative high-performing cell configurations should be

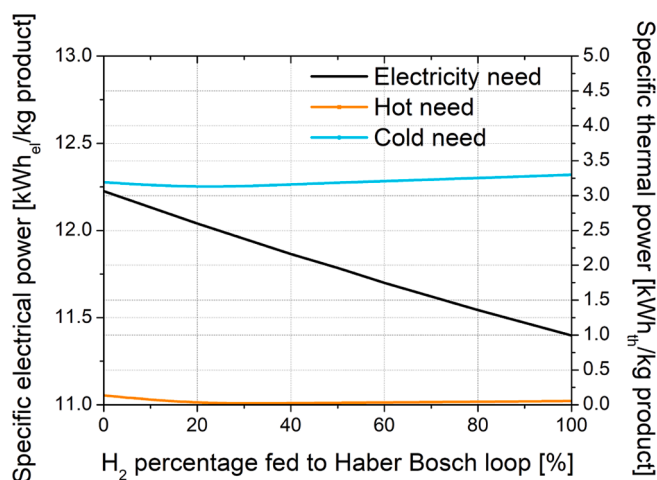


Fig. 9. Sensitivity analysis on NH₃-MeOH PEMEC Hybrid plant varying hydrogen feed distribution in two production lines (considering an increasing NH₃ plant capacity).

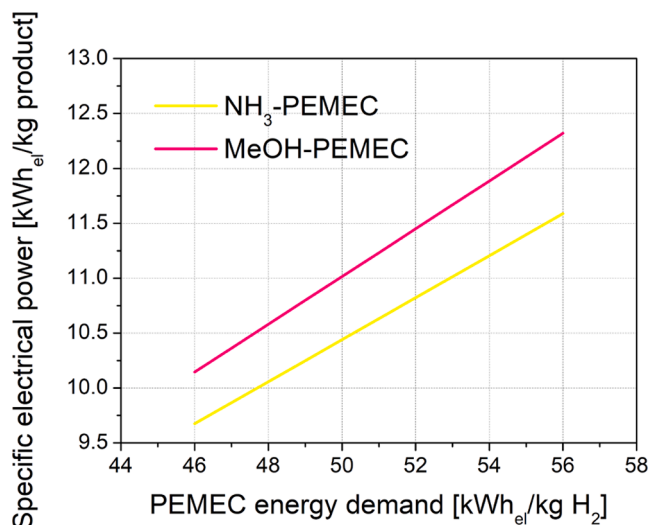


Fig. 10. Sensitivity analysis on NH₃-PEMEC and MeOH-PEMEC single plants due to PEMEC energy consumption reduction.

ready for commercial applications, such as solid oxide cells (<42 kWh_{el}/kg H₂) and anionic exchange membrane cells (<50 kWh_{el}/kg H₂) [55,95,96]. Assuming the most optimistic value equal to 40 kWh_{el}/kg H₂, the NH₃ synthesis would require 8.5 kWh_{el}/kg NH₃ (vs. actual 11.4 kWh_{el}/kg NH₃) and the methanol synthesis 8.8 kWh_{el}/kg MeOH (vs. actual 12.2 kWh_{el}/kg MeOH).

Another PEMEC improvement involves the working pressure. Indeed, this electrolyser is characterised by a differential pressure operation (just the anode side under pressure), which allows to avoid both the inlet water pressurization pump and the outlet hydrogen mechanical compression. However, this operation still has significant issues correlated to the membrane mechanical stability, requiring its thickness to increase. The possible hydrogen diffusion from the anode to the cathode reduces the production capacity as well as increases the risk of oxygen mixing beyond the flammability range [97]. According to reference theoretical studies [98,86], the hydrogen delivery pressure could reach up to 200 bar with the consequent energy consumption penalization yet (~10 % increase). Assuming this operation is possible, PEMEC technology would provide hydrogen already ready for both Haber Bosch and MeOH loops with a relevant simplification of the plant flowsheet. Fig. 11 reports the NH₃-PEMEC and MeOH-PEMEC consumption values at variable hydrogen delivery pressures. The electricity demands have a minimum profile in view of two balancing effects: the gas compression and the water electrolysis power. Knowing the predominant weight of the electrolyser, the optimum (i.e., the lowest demand) characterises a PEMEC operation ranging between 30–50 bar. The increases are due to the produced hydrogen compression at lower pressures and to the electrolyser major demand at higher ones. Referring to the specific e-fuel production, the MeOH-PEMEC case working at 80 bar should have the main benefits. Varying the compression step number influences also the plant thermic behaviour upstream the loop, since produced hydrogen is at higher pressures but at lower temperatures. This allows for lower specific external cold requirements by enhancing the internal heat exchange. For instance, an atmospheric electrolyser application results in a value of ~4 kWh_{th}/kg product, which decreases below ~3 kWh_{th}/kg product at the highest considered pressure. Hot need profiles do not have any significant variation.

4. Conclusion

A technical feasibility assessment of e-fuel production through low-temperature electrolysis cells (PEMECs- Proton Exchange Membrane Electrolysis Cells) was performed. Green synthesis paths were compared

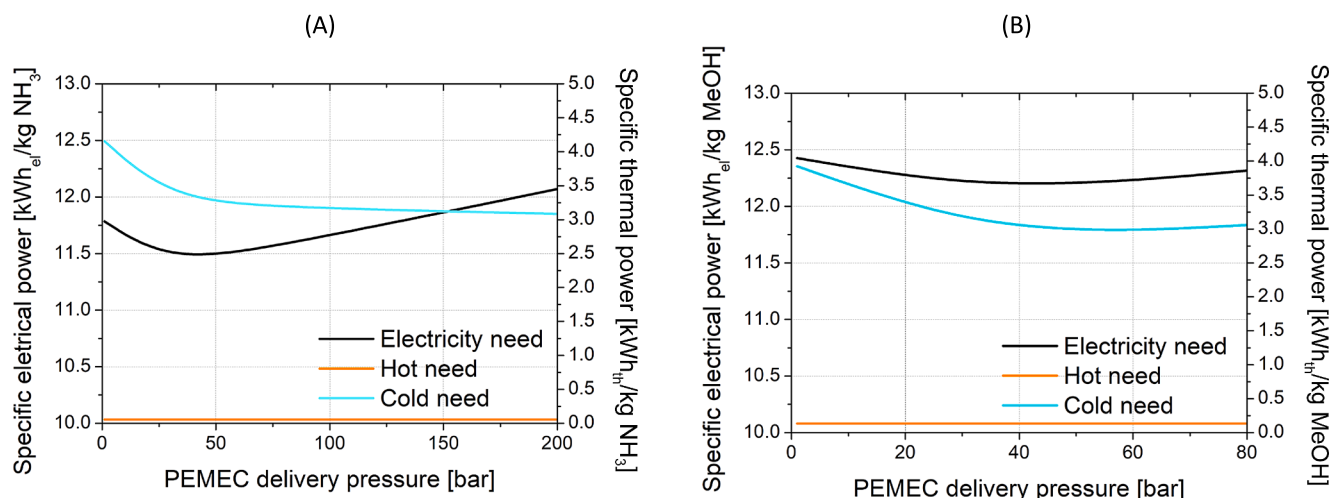


Fig. 11. Sensitivity analysis on (A) NH₃-PEMEC single plant and (B) MeOH-PEMEC single plant changing the PEMEC delivery pressure.

with steam reforming-based processes, starting with hydrogen as the base case and then focusing on ammonia and methanol as its possible carriers. Their production is not energetically penalised with respect to the H₂ case, despite the needs of unit operations involving high pressure and temperature loops for synthesis, reactant recycling and pure product separation. Indeed, the main plant consumption is correlated to the hydrogen production steps. Referring to the energy requirements including fuel and electricity demand, NH₃-SR and NH₃-PEMEC plants have quite similar performance: ~ 12.1 kWh_{tot}/kg NH₃ vs. ~ 11.4 kWh_{tot}/kg NH₃. Indeed, the PEMEC high electricity consumption is counterbalanced by a lower compression work within the Haber Bosch loop in the NH₃-PEMEC case. Moreover, a high fuel amount is needed in two in-series reformers of the NH₃-SR case, where the natural gas is used as both hydrogen and heat sources. Whereas the MeOH-PEMEC needs ~ 12.2 kWh_{tot}/kg MeOH with respect to ~ 6.8 kWh_{tot}/kg MeOH of the MeOH-SR plant, due to less natural gas consumed in the MeOH-SR using a unique non-adiabatic reformer. The green production paths are attended to have significant improvements thanks to a lower PEMEC consumption (around 46 kWh_{el}/kg H₂) and a higher delivery pressure (up to 50–80 bar), which could permit a 10 % decrease in the plant consumption. Both e-processes have zero net carbon emissions with e-MeOH synthesis consuming also CO₂ derived from other systems, resulting in the driven key favouring their industrial application. Ammonia and methanol co-production was also investigated, considering firstly a hybrid plant that couples Methane to Ammonia with Power to Methanol as a possible intermediate solution to cope with the current lack of a proper CO₂ infrastructure and high-capacity electrolyzers. After technological improvements, a more high-performance solution results in a co-production plant exploiting only the PEMEC unit as the hydrogen source, which permits ~ 11.8 kWh_{el}/kg product with a minimum external heat requirement.

Starting from this analysis focusing mainly on the flowsheet design and referring to state-of-the-art features for the different involved unit operations, a more detailed simulation could be applied for each of them. Production efficiency could be differentiated depending on used catalysts, here requiring the introduction of specific kinetics studies. Moreover, other electrolyzers working at both low and high temperatures could be introduced, comparing their consumption, balance of plant and possible internal heat recovery. Finally, alternative technologies could be studied for the air separation step in the ammonia synthesis line, considering the limited production capacity of the current e-fuel synthesis that would make the use of selective membranes and adsorbent beds more suitable than cryogenic distillation.

CRediT authorship contribution statement

Fiammetta Rita Bianchi: Writing – review & editing, Writing – original draft, Software, Methodology, Data curation, Conceptualization. **Riccardo Rizzo:** Writing – review & editing, Writing – original draft, Software, Methodology, Data curation. **Lucia Cardona:** Writing – review & editing, Writing – original draft, Software, Methodology, Data curation. **Dario Bove:** Writing – review & editing, Supervision, Software, Methodology, Conceptualization. **Fabio Cannizzaro:** Writing – review & editing, Supervision, Conceptualization. **Luca Bonardi:** Writing – review & editing, Supervision, Conceptualization. **Ezio Palmisani:** Writing – review & editing, Supervision, Conceptualization. **Barbara Bosio:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

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Declaration of competing interest

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

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuel.2024.133938>.

Data availability

The authors confirm that the data supporting the findings of this study are available within the article.

References

- [1] Kovač A, Paranos M, Marciuš D. Hydrogen in energy transition: a review. *Int J Hydrogen Energy* 2021;46:10016–35. <https://doi.org/10.1016/j.ijhydene.2020.11.256>.

- [2] Fonseca JD, Camargo M, Commenge JM, Falk L, Gil ID. Trends in design of distributed energy systems using hydrogen as energy vector: A systematic literature review. *Int J Hydrogen Energy* 2019;44:9486–504. <https://doi.org/10.1016/j.ijhydene.2018.09.177>.
- [3] Moriarty P, Honnery D. Prospects for hydrogen as a transport fuel. *Int J Hydrogen Energy* 2019;44:16029–37. <https://doi.org/10.1016/j.ijhydene.2019.04.278>.
- [4] Nationalgrid. What is hydrogen?, (2023). [https://www.nationalgrid.com/stories/energy-explained/what-is-hydrogen#:~:text=Hydrogen is a clean alternative,and%2C of course%2C human \(accessed October 13, 2023\)](https://www.nationalgrid.com/stories/energy-explained/what-is-hydrogen#:~:text=Hydrogen is a clean alternative,and%2C of course%2C human (accessed October 13, 2023)).
- [5] Incer-Valverde J, Korayem A, Tsatsaronis G, Morosuk T. “Colors” of hydrogen: Definitions and carbon intensity. *Energy Convers Manag* 2023;291:117294. <https://doi.org/10.1016/j.enconman.2023.117294>.
- [6] Armaroli N, Balzani V. The hydrogen issue. *ChemSusChem* 2011;4:21–36. <https://doi.org/10.1002/cssc.201000182>.
- [7] Abdalla AM, Hossain S, Nisfindy OB, Azad AT, Dawood M, Azad AK. Hydrogen production, storage, transportation and key challenges with applications: A review. *Energy Convers Manag* 2018;165:602–27. <https://doi.org/10.1016/j.enconman.2018.03.088>.
- [8] Moreno-Brieva F, Guimón J, Salazar-Elena JC. From grey to green and from west to east: The geography and innovation trajectories of hydrogen fuel technologies. *Energy Res Soc Sci* 2023;101. <https://doi.org/10.1016/j.erss.2023.103146>.
- [9] Aziz M, TriWijayanta A, Nandiyanto ABD. Ammonia as effective hydrogen storage: A review on production, storage and utilization. *Energies* 2020;13:1–25. <https://doi.org/10.3390/en13123062>.
- [10] Andersson J, Grönkvist S. Large-scale storage of hydrogen. *Int J Hydrogen Energy* 2019;44:11901–19. <https://doi.org/10.1016/j.ijhydene.2019.03.063>.
- [11] Djermouni M, Ouadha A. Thermodynamic analysis of methanol, ammonia, and hydrogen as alternative fuels in HCCI engines. *Int J Thermofluids* 2023;19:100372. <https://doi.org/10.1016/j.ijtf.2023.100372>.
- [12] Rouwenhorst KHR, Krzywda PM, Benes NE, Mul G, Lefferts L. Ammonia Production Technologies, Techno-Economic Challenges Green Ammonia. as an Energy Vector 2021:41–83. <https://doi.org/10.1016/B978-0-12-820560-0.00004-7>.
- [13] Tabibian SS, Sharifzadeh M. Statistical and analytical investigation of methanol applications, production technologies, value-chain and economy with a special focus on renewable methanol. *Renew Sustain Energy Rev* 2023;179:113281. <https://doi.org/10.1016/j.rser.2023.113281>.
- [14] IRENA and AEA, Innovation Outlook: Renewable Ammonia, 2022.
- [15] Smith C, Hill AK, Torrente-Murciano L. Current and future role of Haber-Bosch ammonia in a carbon-free energy landscape. *Energy Environ Sci* 2020;13:331–44. <https://doi.org/10.1039/c9ee02873k>.
- [16] M. Institute, Renewable Methanol, (n.d.). <https://www.methanol.org/renewable/> (accessed June 22, 2023).
- [17] Mbatha S, Everson RC, Musyoka NM, Langmi HW, Lanzini A, Brilman W. Power-to-methanol process: A review of electrolysis, methanol catalysts, kinetics, reactor designs and modelling, process integration, optimisation, and techno-economics, *Sustain. Energy Fuels* 2021;5:3490–569. <https://doi.org/10.1039/d1se00635e>.
- [18] Sun Z, Zhang Y, Huang H, Luo Y, Lin L, Jiang L. Modeling and simulation of dynamic characteristics of a green ammonia synthesis system. *Energy Convers Manag* 2024;300:117893. <https://doi.org/10.1016/j.enconman.2023.117893>.
- [19] Pagani G, Hajimolana Y, Acar C. Green hydrogen for ammonia production – A case for the Netherlands. *Int J Hydrogen Energy* 2024;52:418–32. <https://doi.org/10.1016/j.ijhydene.2023.06.309>.
- [20] Lin H, Zhang MH, Singh Chauhan B, Elsiddeh AMA, Abdelghany Elkotb M, Zhu P, et al. Comprehensive analysis of a novel power and methanol coproduction process using landfill gas reforming and renewable hydrogen generation by an alkaline electrolyzer. *J Clean Prod* 2023;418:138131. <https://doi.org/10.1016/j.jclepro.2023.138131>.
- [21] Fogel S, Unger S, Hampel U. Dynamic system modeling and simulation of a power-to-methanol process based on proton-conducting tubular solid oxide cells. *Energy Convers Manag* 2024;300:117970. <https://doi.org/10.1016/j.enconman.2023.117970>.
- [22] Fogel S, Unger S, Hampel U. Operating windows and techno-economics of a power-to-methanol process utilizing proton-conducting high temperature electrolyzers. *J CO2 Util* 2024;82:102758. <https://doi.org/10.1016/j.jcou.2024.102758>.
- [23] Li Q, Khosravi A, Farsaei A, Sun L. Thermodynamics, economic and carbon emission analysis of power-to-methanol process through alkaline electrolysis and monoethanolamine (MEA) carbon capture. *Chem Eng Sci* 2024;293:120029. <https://doi.org/10.1016/j.ces.2024.120029>.
- [24] Global CCS Institute. *The Global Status of CCS. Special Report: Introducing Industrial Carbon Capture and Storage*; 2016.
- [25] Risso R, Cardona L, Archetti M, Lossani F, Bosio B, Bove D. A Review of On-Board Carbon Capture and Storage Techniques: Solutions to the 2030 IMO Regulations. *Energies* 2023;16. <https://doi.org/10.3390/en16186748>.
- [26] Cooper R, Bove D, Audasso E, Ferrari MC, Bosio B. A feasibility assessment of a retrofit Molten Carbonate Fuel Cell coal-fired plant for flue gas CO2 segregation. *Int J Hydrogen Energy* 2021;46:15024–31. <https://doi.org/10.1016/j.ijhydene.2020.09.189>.
- [27] Strojny M, Gladysz P, Hanak DP, Nowak W. Comparative analysis of CO2 capture technologies using amine absorption and calcium looping integrated with natural gas combined cycle power plant. *Energy* 2023;284. <https://doi.org/10.1016/j.energy.2023.128599>.
- [28] Hou R, Fong C, Freeman BD, Hill MR, Xie Z. Current status and advances in membrane technology for carbon capture. *Sep Purif Technol* 2022;300:121863. <https://doi.org/10.1016/j.seppur.2022.121863>.
- [29] Audasso E, Bosio B, Bove D, Arato E, Barckholtz T, Kiss G, et al. The Effects of Gas Diffusion in Molten Carbonate Fuel Cells Working as Carbon Capture Devices. *J Electrochem Soc* 2020;167:114515. <https://doi.org/10.1149/1945-7111/aba8b6>.
- [30] Bosio B, Archetti M, Audasso E, Bove D. Process analysis of a molten carbonate fuel cell on-board application to reduce vessel CO2 emissions. *Chem Eng Process - Process Intensif* 2023;190:109415. <https://doi.org/10.1016/j.cep.2023.109415>.
- [31] Prussi M, Chiaramonti D. Alternative fuels for hard-to-abate sectors: A carbon intensity assessment. *J Phys Conf Ser* 2022;2385. <https://doi.org/10.1088/1742-6596/2385/1/012044>.
- [32] Thonemann N, Maga D. Life Cycle Assessment of Steel Mill Gas-Based Methanol Production within the Carbon2Chem® Project. *Chem-Ing-Tech* 2020;92:1425–30. <https://doi.org/10.1002/cite.202000051>.
- [33] d’Amore F, Nava A, Colbertaldo P, Visconti CG, Romano MC. Turning CO2 from fuel combustion into e-Fuel? Consider alternative pathways. *Energy Convers Manag* 2023;289:117170. <https://doi.org/10.1016/j.enconman.2023.117170>.
- [34] Saygin D, Bianco H, Boshell F, Cordonnier J, Rouwenhorst K, Lathwal P, et al. Ammonia Production from Clean Hydrogen and the Implications for Global Natural Gas Demand. *Sustainability* 2023;15:1623. <https://doi.org/10.3390/su15021623>.
- [35] El-Shafie M, Kambara S. Recent advances in ammonia synthesis technologies: Toward future zero carbon emissions. *Int J Hydrogen Energy* 2023;48:11237–73. <https://doi.org/10.1016/j.ijhydene.2022.09.061>.
- [36] Adnan MA, Kibria MG. Comparative techno-economic and life-cycle assessment of power-to-methanol synthesis pathways. *Appl Energy* 2020;278:115614. <https://doi.org/10.1016/j.apenergy.2020.115614>.
- [37] Bos MJ, Kersten SRA, Brilman DWF. Wind power to methanol: Renewable methanol production using electricity, electrolysis of water and CO2 air capture. *Appl Energy* 2020;264:114672. <https://doi.org/10.1016/j.apenergy.2020.114672>.
- [38] D’Adamo I, Gastaldi M, Giannini M, Nizami AS. Environmental implications and leveraged cost analysis of E-fuel production under photovoltaic energy, direct air capture, and hydrogen. *Environ Res* 2024;246:118163. <https://doi.org/10.1016/j.envres.2024.118163>.
- [39] Birel T, Breeman GE, van Buitenen A, Vijver MG. Defueling the impasse: EU political discourse on e-fuels. *Energy Policy* 2024;187:114022. <https://doi.org/10.1016/j.enpol.2024.114022>.
- [40] Kountouris I, Langer L, Bramstoff R, Münster M, Keles D. Power-to-X in energy hubs: A Danish case study of renewable fuel production. *Energy Policy* 2023;175:113439. <https://doi.org/10.1016/j.enpol.2023.113439>.
- [41] MacFarlane DR, Cherepanov PV, Choi J, Suryanto BHR, Hodgetts RY, Bakker JM, et al. A Roadmap to the Ammonia Economy. *Joule* 2020;4:1186–205. <https://doi.org/10.1016/j.joule.2020.04.004>.
- [42] Olabi AG, Abdelkareem MA, Al-Murisi M, Shehata N, Alami AH, Radwan A, et al. Recent progress in Green Ammonia: Production, applications, assessment; barriers, and its role in achieving the sustainable development goals. *Energy Convers Manag* 2023;277:116594. <https://doi.org/10.1016/j.enconman.2022.116594>.
- [43] Chen C, Yang A. Power-to-methanol: The role of process flexibility in the integration of variable renewable energy into chemical production. *Energy Convers Manag* 2021;228:113673. <https://doi.org/10.1016/j.enconman.2020.113673>.
- [44] Marlin DS, Sarron E, Sigurbjörnsson Ó. Process Advantages of Direct CO2 to Methanol Synthesis. *Front Chem* 2018;6:1–8. <https://doi.org/10.3389/fchem.2018.00446>.
- [45] Linde Engineering to Build 24 MW PEM Electrolyzer Plant for Yara, (2022). https://www.linde-engineering.com/en/news_and_media/press_releases/news20220128.html.
- [46] Ørsted&Yara, Ørsted and Yara seek to develop groundbreaking green ammonia project in the Netherlands, (2020). <https://www.yara.com/corporate-releases/orsted-and-yara-seek-to-develop-groundbreaking-green-ammonia-project-in-the-netherlands/> (accessed September 1, 2023).
- [47] Kezad Group, AED3.67 bn ‘Helios Industry’ Plant to Export Green Ammonia from Abu Dhabi, (2021).
- [48] B. Stefansson, Low carbon intensity and green methanol: Iceland and beyond, (n.d.).
- [49] A. Habibic, World’s 1st large-scale e-methanol project to fuel Maersk’s boxships, (2022). <https://www.offshore-energy.biz/worlds-1st-large-scale-e-methanol-project-to-fuel-maersks-boxships/> (accessed June 27, 2023).
- [50] North CCU Hub, Innovation, (n.d.). <https://northcchub.eu/north-c-methanol/> (accessed June 27, 2023).
- [51] A. Habibic, Ørsted breaks ground on Europe’s largest e-methanol plant, (2023). <https://www.offshore-energy.biz/orsted-breaks-ground-on-europes-largest-e-methanol-plant/> (accessed June 27, 2023).
- [52] MethaNet, (n.d.). <https://www.methanet.org/en/progetti-e-obiettivi/> (accessed June 27, 2023).
- [53] Carbon Recycling International, The Finnford e-methanol project: commercial scale e-methanol production in Norway, (n.d.). <https://www.carbonrecycling.is/finnfjord-emethanol> (accessed June 27, 2023).
- [54] R. ROBERT, LIFE CYCLE EMISSIONS OF HYDROGEN, (2020).
- [55] Bianchi FR, Bosio B. Operating Principles. Performance and Technology Readiness Level of Reversible Solid Oxide Cells, *Sustainability* 2021;13:4777. <https://doi.org/10.3390/su13094777>.
- [56] Grigoriev SA, Fateev VN, Bessarabov DG, Millet P. Current status, research trends, and challenges in water electrolysis science and technology. *Int J Hydrogen Energy* 2020;45:26036–58. <https://doi.org/10.1016/j.ijhydene.2020.03.109>.
- [57] Czarnota R, Knapik E, Wojnarowski P, Janiga D, Stopa J. Carbon dioxide separation technologies. *Arch Min Sci* 2019;64:487–98. <https://doi.org/10.24425/ams.2019.129364>.
- [58] thyssenkrupp Uhde, Building the world’s largest ammonia plants, with high capacities and low energy consumption, (2022). <https://www.thyssenkrupp-uhde.com/en/products-and-technologies/fertilizer-technologies/ammonia-plants>.

- [59] Pattabathula V, Richardson J. Introduction to ammonia production. *Chem Eng Prog* 2016;112:69–75.
- [60] K.H.R. Rouwenhorst, P.M. Krzywda, N.E. Benes, G. Mul, L. Lefferts, Ammonia Production Technologies, Elsevier Inc., 2021. doi: 10.1016/b978-0-12-820560-0.00004-7.
- [61] Yang C, Ma Z, Zhao N, Wei W, Hu T, Sun Y. Methanol synthesis from CO₂-rich syngas over a ZrO₂ doped CuZnO catalyst. *Catal Today* 2006;115:222–7. <https://doi.org/10.1016/j.cattod.2006.02.077>.
- [62] A. de Klerk, Transport fuel: Biomass-, coal-, gas- and waste-to-liquids processes, Elsevier Ltd, 2020. doi: 10.1016/B978-0-08-102886-5.00010-4.
- [63] Pravin Prashant, KBR, Johnson Matthey to license ammonia-methanol co-production process technology, (2020).
- [64] Palone O, Gagliardi GG, Mechelli M, Cedola L, Borello D. Techno-economic analysis of sustainable methanol and ammonia production by chemical looping hydrogen generation from waste plastic. *Energy Convers Manag* 2023;292. <https://doi.org/10.1016/j.enconman.2023.117389>.
- [65] A.R. Reserved, KBR-JM MeOH NH₃ Co-production • KBR + JM Introductions • Grass Roots Co-Production • Q & A, (2020).
- [66] N. Ketov, UCC SHCHEKINOAZOT LAUNCHES METHANOL AND AMMONIA CO-PRODUCTION PLANT LICENSED BY HALDOR TOPSOE, (2018). <https://www.topsoe.com/blog/ucc-shchekinoazot-launches-methanol-and-ammonia-co-production-plant-licensed-by-haldor-topsoe>.
- [67] Tso WW, Doga Demiran C, Powell JB, Pistikopoulos EN. Toward Optimal Synthesis of Renewable Ammonia and Methanol Processes (RAMP). Elsevier Masson SAS 2018. <https://doi.org/10.1016/B978-0-444-64241-7.50279-2>.
- [68] Zang G, Sun P, Elgowainy A, Wang M. Technoeconomic and Life Cycle Analysis of Synthetic Methanol Production from Hydrogen and Industrial Byproduct CO₂. *Environ Sci Technol* 2021;55:5248–57. <https://doi.org/10.1021/acs.est.0c08237>.
- [69] Process for the co-production of methanol and ammonia in parallel, 2019.
- [70] Nowicki DA, Agnew GD, Irvine JTS. Green ammonia production via the integration of a solid oxide electrolyser and a Haber-Bosch loop with a series of solid electrolyte oxygen pumps. *Energy Convers Manag* 2023;280. <https://doi.org/10.1016/j.enconman.2023.116816>.
- [71] Bianchi FR, Bosio B. Modelling of green ammonia production based on solid oxide cells as electrolyser and oxygen separator for Haber-Bosch loop decarbonization. *Int J Hydrogen Energy* 2024. <https://doi.org/10.1016/j.ijhydene.2024.07.047>.
- [72] DWSIM – Open-Source Chemical Process Simulator, (n.d.). <https://dwsim.org/> (accessed September 19, 2024).
- [73] Lee K, Liu X, Vyawahare P, Sun P, Elgowainy A, Wang M. Techno-economic performances and life cycle greenhouse gas emissions of various ammonia production pathways including conventional, carbon-capturing, nuclear-powered, and renewable production. *Green Chem* 2022;24:4830–44. <https://doi.org/10.1039/d2gc00843b>.
- [74] Ren BP, Xu YP, Huang YW, She C, Sun B. Methanol production from natural gas reforming and CO₂ capturing process, simulation, design, and technical-economic analysis. *Energy* 2023;263:125879. <https://doi.org/10.1016/j.energy.2022.125879>.
- [75] Cummins, HyLYZER® WATER ELECTROLYZERS, (n.d.). doi: <https://www.cummins.com/sites/default/files/2021-08/cummins-hylyzer-1000-specsheet.pdf>.
- [76] H-TEC SYSTEMS, (n.d.). <https://www.h-tec.com/en/products/> (accessed April 20, 2024).
- [77] Ahn H, Luberti M, Liu Z, Brandani S. Process simulation of aqueous MEA plants for postcombustion capture from coal-fired power plants. *Energy Procedia* 2013;37:1523–31. <https://doi.org/10.1016/j.egypro.2013.06.028>.
- [78] Wu Y, Xiang Y, Cai L, Liu H, Liang Y. Optimization of a novel cryogenic air separation process based on cold energy recovery of LNG with exergoeconomic analysis. *J Clean Prod* 2020;275:123027. <https://doi.org/10.1016/j.jclepro.2020.123027>.
- [79] O. Elishav, B. Mosevitzky Lis, A. Valera-Medina, G.S. Grader, Storage and Distribution of Ammonia, Elsevier Inc., 2020. doi: 10.1016/B978-0-12-820560-0.00005-9.
- [80] Methanol U.S. federal grade specification O-M-232, (2016).
- [81] Kowalski A, Faber G, Cave E. PEM CO₂ electrolyzers from an industrial perspective. *Curr Opin Green Sustain Chem* 2023;39:100702. <https://doi.org/10.1016/j.cogsc.2022.100702>.
- [82] L. Yang, X. Ge, Chapter Three - Biogas and Syngas Upgrading, in: *Adv. Bioenergy*, 2016; pp. 125–188. doi: 10.1016/bs.aibe.2016.09.003.
- [83] KBR, Petrochemical Processes 2010, (2010) 121 a 131.
- [84] Yang B, Shao C, Hu X, Ngata MR, Aminu MD. Advances in carbon dioxide storage projects: assessment and perspectives. *Energy Fuels* 2023;37:1757–76. <https://doi.org/10.1021/acs.energyfuels.2c03826>.
- [85] International Renewable Energy Agency (IRENA) and Methanol Institute, INNOVATION OUTLOOK, RENEWABLE METHANOL, (2021). ISBN 978-92-9260-320-5.
- [86] Hancke R, Holm T, Ulleberg Ø. The case for high-pressure PEM water electrolysis. *Energy Convers Manag* 2022;261. <https://doi.org/10.1016/j.enconman.2022.115642>.
- [87] Samuel MS, Prabakaran Sudhakar M, Santhappan JS, Ravikumar M, Kalaiselvan N, Mathimani T. Ammonia production from microalgal biosystem: Present scenario, cultivation systems, production technologies, and way forward. *Fuel* 2024;368. <https://doi.org/10.1016/j.fuel.2024.131643>.
- [88] Ostadi M, Bromberg L, Cohn DR, Gençer E. Flexible methanol production process using biomass/municipal solid waste and hydrogen produced by electrolysis and natural gas pyrolysis. *Fuel* 2023;334. <https://doi.org/10.1016/j.fuel.2022.126697>.
- [89] IEA, Tracking Clean Energy Progress 2023, 2023. <https://www.iea.org/reports/tracking-clean-energy-progress-2023>.
- [90] Hydrogen and Fuel Cell Technologies Office, Technical Targets for Proton Exchange Membrane Electrolysis, (2022). <https://www.energy.gov/eere/fuelcells/technical-targets-proton-exchange-membrane-electrolysis>.
- [91] Bove D, Audasso E, Barckholtz T, Kiss G, Rosen J, Bosio B. Process analysis of molten carbonate fuel cells in carbon capture applications. *Int J Hydrogen Energy* 2021;46:15032–45. <https://doi.org/10.1016/j.ijhydene.2020.08.020>.
- [92] Sarker AK, Azad AK, Rasul MG, Doppalapudi AT. Prospect of Green Hydrogen Generation from Hybrid Renewable Energy Sources: A Review. *Energies* 2023;16:1–17. <https://doi.org/10.3390/en16031556>.
- [93] Pursiheimo E, Holttinen H, Koljonen T. Inter-sectoral effects of high renewable energy share in global energy system. *Renew Energy* 2019;136:1119–29. <https://doi.org/10.1016/j.renene.2018.09.082>.
- [94] Okoye-Chine CG, Otun K, Shiba N, Rashama C, Ugwu SN, Onyeaka H, et al. Conversion of carbon dioxide into fuels - A review. *J CO₂ Util* 2022;62:102099. <https://doi.org/10.1016/j.jcou.2022.102099>.
- [95] Noor Azam AMI, Ragunathan T, Zulkefli NN, Masdar MS, Majlan EH, Mohamad Yunus R, et al. Investigation of Performance of Anion Exchange Membrane (AEM) Electrolysis with Different Operating Conditions. *Polymers (Basel)* 2023;15. <https://doi.org/10.3390/polym15051301>.
- [96] Pozio A, Bozza F, Nigliaccio G, Platter M, Monteleone G. Development perspectives on low-temperature electrolysis. *Energia, Ambient e Innov* 2021;66–71. <https://doi.org/10.12910/EA12021-014>.
- [97] Hancke R, Ulleberg Ø, Skattum R, Torp V. High Differential Pressure PEM Water Electrolysis System. *Laboratory* 2019:1–10.
- [98] IRENA, Green Hydrogen Cost Reduction: Scaling up Electrolysers to Meet the 1.5°C Climate Goal, International Renewable Energy Agency, 2020. www.irena.org/publications.