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Power-to-X processes based on PEM water electrolyzers: A review of process integration and flexible operation

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ABSTRACT

Hydrogen produced with renewable electricity may be used to synthesize valuable chemical products, thus aiding the decarbonization of the chemical industry. Thanks to their fast dynamics, Polymer Electrolyte Membrane Water Electrolyzers (PEM-WEs) appear promising for coupling with fluctuating power inputs, e.g., from a grid balancing request or standalone renewable power supply. However, the flexibility of downstream synthesis processes under time-variable hydrogen flow rates is still unclear, and expensive hydrogen storage could be needed as buffer. We review the state of the technology with a focus on the potential for flexible operation of the key components of the main Power-to-X processes: hydrogen production via PEM-WEs, carbon capture, nitrogen production, and the synthesis of methane, methanol, syngas, and ammonia. Flexibility concepts of the units are described and the characteristic times for start-up and load variations, ramp rate limits, and operating ranges are collected. Opportunities for heat and mass integration are discussed.

1. Introduction

The chemical industry significantly contributes to greenhouse gas emissions because of the energy-intensive processes and reliance on fossil feedstock and energy sources. Nevertheless, most of the chemicals that are currently produced will likely be prevalent even in a low-carbon society. Therefore, the development of more sustainable production processes is essential.

Power-to-X, in which the power is obtained from renewables and the 'X' represents the final product (e-product), is a promising large-scale long-term storage technology (International Renewable Energy Agency (IRENA), 2017). This research field is extremely active (more than 200 research and development projects in Europe alone over the last 20 years (Wulf et al., 2020)) since Power-to-X aims at producing low carbon-footprint products. Several variations of "Power-to-X" can be found in literature, e.g., Power-to-Heat (Westerwalbesloh et al., 2016), Power-to-Hydrogen, Power-to-Gas (in which hydrogen is sometimes included and sometimes not), Power-to-Liquid, Power-to-Fuels, Power-to-Ammonia, and Power-to-Chemicals. The e-products can either be converted back into electricity or used for other purposes (Burre et al., 2020).

Hydrogen (H_2) is a key product or intermediate of most of the Power-to-X processes and can be produced via water electrolysis. Among the available technologies of electrolyzers, Polymer Electrolyte Membrane Water Electrolyzers (PEM-WEs) (Carmo et al., 2013) are particularly suitable for flexible operation and can provide ancillary services (Kopp et al., 2017). However, H_2 has a low volumetric energy density, is rather difficult to store on a large scale, transport, and handle, and needs a dedicated infrastructure (International Energy Agency (IEA), 2019). These limitations of H_2 as energy storage motivate its conversion to fuels/energy carriers with higher volumetric and gravimetric energy density, ideally suitable for existing infrastructure. Additionally, Power-to-X processes based on green H_2 (H_2 from renewable electricity) and its derivatives could play a role in decarbonizing sectors such as industry and transport (up to 12% and 26%, respectively, according to the scenario of the International Renewable Energy Agency to limit the temperature rise to 1.5 °C by 2050 (International Renewable Energy Agency (IRENA), 2021)).

To deal with the fluctuating nature of renewables and avoid their curtailment, a key component of many Power-to-X concepts is demand-side management (Burre et al., 2020): the production process is adapted flexibly according to the availability (or time-varying cost) of electricity and raw materials. In a Power-to-X process, fluctuating power inputs can

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Nomenclature

H	Enthalpy
MW	Molecular weight

Greek symbols

η	Efficiency

Acronyms

AEM-WE	Anion exchange membrane water electrolyzer
ASU	Air separation unit
A-WE	Alkaline water electrolyzer
CL	Chemical looping
DAC	Direct air capture
LHV	Lower heating value
MEA	Membrane electrode assembly
PEM	Polymer electrolyte membrane
PEM-WE	PEM water electrolyzer
PSA	Pressure swing adsorption
PTL	Porous transport layer
RWGS	Reverse water gas shift
SO-WE	Solid oxide water electrolyzer
TSA	Temperature swing adsorption

be handled differently according to the operation mode (steady-state vs. dynamic) of the individual process units. Every process unit (electrolyzer included) can in principle be operated at steady state by using electricity storage (Fig. 1a). Without electricity storage, at least some process units need to be operated dynamically. Tanks for raw materials or intermediates, e.g., hydrogen and carbon dioxide, are essential if their production is variable over time while the downstream synthesis process is operated steadily (Fig. 1b). To reduce the size of these expensive storages, flexible operation of the downstream conversion processes could be an alternative (Fig. 1c). Storage could be unnecessary if all units are operated flexibly, but the extent to which these processes are flexible (e.g., start-up and shutdown times, ramp rates, operating range, settling time) needs to be assessed. In case some process units are not quick enough in load following, small electric storage might be needed (Fig. 1d). However, flexible operation leads to a reduction of the capacity factor and might cause losses in efficiency, lower product quality, or increased degradation of the process units. Moreover, the mode of operation raises constraints and concerns about the integration of heat and mass at the process scale.

Recent literature includes several reviews on Power-to-X. As regards the electrochemical hydrogen production (Power-to-Hydrogen), Carmo et al. (2013) presented a comprehensive review of Polymer Electrolyte Membrane Water Electrolyzers (PEM-WEs). However, a discussion of the flexibility of PEM-WEs and their integration both in the power grid and in the synthesis of further products is largely missing. These aspects were also not covered by more recent reviews about PEM-WEs, which were focused on catalysts and materials (Shiva Kumar and Himabindu, 2019; Bernt et al., 2020; Shirvanian and van Berkel, 2020) and modeling (Abdol Rahim et al., 2016; Bensmann and Hanke-Rauschenbach, 2016; Falcão and Pinto, 2020). Furthermore, most existing works focus on the main conversion device as opposed to the additional units like the power converter or the purification units that are essential to operate the plant. Buttler and Spliethoff (2018) included relevant information about electrolysis flexibility in their comparison between the electrolyzer technologies, but a thorough discussion about the auxiliaries and the integration with further units is still missing.

Several reviews and techno-economic analyses on Power-to-X processes in which hydrogen is an intermediate product can also be found in recent literature. Götz et al. (2016), Peters et al. (2019), and Rönsch et al. (2016) conducted techno-economic reviews of Power-to-Gas and methanation. Foit et al. (2017) reviewed the Power-to-Syngas process in which the co-electrolysis technology is used. Mbatha et al. (2021) presented a thorough analysis of Power-to-Methanol technology and Pérez-Fortes et al. (2016) and Lee et al. (2020) conducted a techno-economic assessment of it. Adnan and Kibria (2020) compared different Power-to-Methanol pathways with a techno-economic analysis and a life cycle assessment. Liquid hydrocarbons were reviewed by Dieterich et al. (2020). Álvarez et al. (2017) mainly focused on catalysts for the direct hydrogenation of carbon dioxide to formic acid, methanol, and DME. Saeidi et al. (2021) reviewed catalysts, operating conditions, and reactor types for the production of methane, methanol, and heavier hydrocarbons. Power-to-Ammonia was the topic of Bennani et al. (2016) and Ikäheimo et al. (2018) analyses, while Zhang et al. (2020) compared green ammonia production pathways also including Power-to-Ammonia.

Moreover, several techno-economic comparisons between e-products are available. (Bongartz et al. (2018), for example, compared hydrogen, methane, methanol, and Dimethyl Ether (DME) for light-duty transportation. Brynolf et al. (2018) compared methane, methanol, DME, gasoline, and diesel. Tremel et al. (2015) compared green methanol, synthetic natural gas, syncrude, diesel, DME, and ammonia; methanol, methane, ammonia, and urea production processes were compared by Bargiacchi et al. (2019).

However, all the above-mentioned works focus either on the technology, cost, environmental impacts (Bargiacchi et al., 2020; Sternberg and Bardow, 2016; Koj et al., 2019), or all these aspects (Zang et al., 2021; Ince et al., 2021; Grahn et al., 2022), but not on process flexibility and process integration. Thus, we aim at complementing existing reviews on Power-to-X since this information could help answer open research questions like:

- Which parts of the process chain can be operated flexibly? How fast can these parts change the load, and which are their operating limits?
- Is storage required? And, if yes, where, and how much?
- Which are the interfaces between the process parts in terms of temperature, pressure, and purity? Should the components be heat integrated, and how is their integration affected by different time constants of the process units under dynamic operation?

Considering these questions, this article aims at (i) reviewing literature about the dynamic operation of some Power-to-X processes to determine to which extent those are flexible; and (ii) identifying potential matches and interfaces among the units. In particular, we focus on Power-to-Methane, Power-to-Methanol, Power-to-Syngas, and Power-to-Ammonia as they are the key products and/or intermediates of the chemical industry that can be synthesized from hydrogen in one step. Also, we consider the electrolysis, carbon capture, and air separation units that provide raw materials for the synthesis of these products. Process integration among different units, as well as information about process flexibility and uncertainty of resources, could then be considered in the design phase of new plants using optimization methods (Mitsos et al., 2018), thus gaining improvements in terms of flexibility, performance, and/or economic viability. The type and size of storage can also be optimized accordingly. However, providing optimal designs is not in the scope of this work because (a) they depend on project-specific details such as the flexibility of the chosen plant units, the design specifications, and the plant boundaries, e.g., heat integration with other plants, the availability of renewables, the typical power profile as input, and the local energy price; and (b) some general guidelines already exist in literature (Ausfelder et al., 2015).

The remainder of the paper is structured as follows: in Sections 2, 3, and 4, hydrogen, carbon dioxide, and nitrogen supplies are analyzed, respectively. Section 5 treats Hydrogen-to-X processes. Section 6 focuses on process integration, and, in Section 7, the conclusions are drawn.

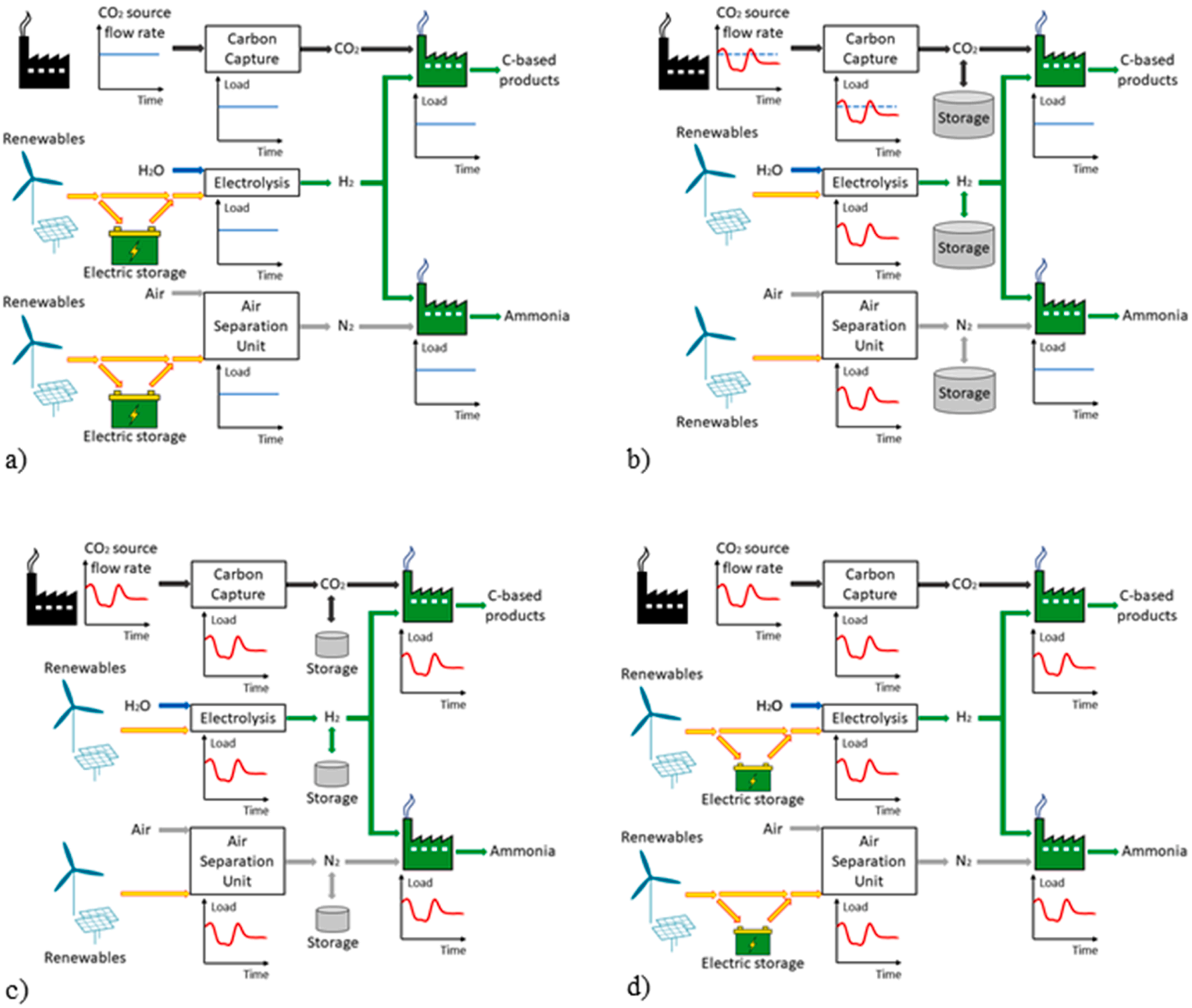

Fig. 1. Main Power-to-X operating concepts: (a) Every process unit is operated in a steady state. Constant power input is achieved by electric storage (battery). (b) The raw material production units are operated according to the input availability, while the other units are operated at steady state. Storage allows constant raw materials supply to the downstream conversion units. If the CO_2 source is steady (blue dashed line), the CO_2 storage is not needed. (c) Every process unit is operated flexibly: raw materials are produced according to the availability of the resources; the operation of the synthesis units is partially decoupled from the production of the raw materials via storage. The storage size is significantly lower than in case b); storage could even be omitted if the units are flexible enough. (d) Every process unit is operated flexibly but with smoother variations thanks to small-capacity electric storage (battery).

2. Renewable hydrogen supply

Hydrogen can be used for several applications, e.g., in the steel and chemical industries, as a fuel for transportation, and also for heat and power generation. The International Energy Agency (IEA) (Bermudez and Hannula, 2021) estimated an overall demand for H_2 of about $9{\cdot}10^{10}$ kg in 2020. Currently, most of the hydrogen is produced from fossil fuels and only 2% via electrolysis, almost entirely in chlor-alkali electrolysis (International Energy Agency (IEA), 2019), in which hydrogen is a byproduct. In other words, dedicated water electrolysis is still negligible, around 0.1%. This is due to historical (long industrial experience in reforming and gasification) and economic reasons (high cost of electricity compared to natural gas, high cost of electrolyzers). The decarbonization potential for the industry is therefore huge but also challenging. The installed capacity of electrolyzers is still very small but expected to quickly grow (from 300 MW of installed capacity in 2020 to 54–96 GW in 2030 (Bermudez and Hannula, 2021)). To cover the current hydrogen need via electrolysis, an installed capacity of around 550 GW would be needed. This capacity will be even larger if Power-to-X processes beyond those replacing the current uses of hydrogen are to be deployed.

In the next section, an overview of the main water electrolysis technologies is provided. In Sections 2.2 and 2.3, PEM Water Electrolyzers are discussed in detail.

2.1. *Water electrolyzer technology overview*

Water molecules can be split into their constitutive elements if a proper amount of energy is provided.

$$H_2O(l) \rightarrow \frac{1}{2}O_2 + H_2$$

In water electrolysis, this overall reaction is carried out electrochemically at two electrodes, i.e., the anode and the cathode, at which oxidation and reduction reactions occur, respectively. The main water electrolyzer technologies are briefly described in the following.

Alkaline water electrolysis

Alkaline Water Electrolyzers (A-WEs) are the most mature electrolysis technology (International Energy Agency (IEA), 2019). A highly-concentrated alkaline aqueous solution (generally 20–30 wt.% of KOH (Brauns and Turek, 2020)) is fed to the cathode where water molecules are split into hydrogen molecules and hydroxide ions. At the anode, hydroxide ions are oxidized to form oxygen and water. Two main commercial versions can be identified: i) in the conventional one, a diaphragm separates the electrodes; ii) in the so-called Anion Exchange Membrane Water Electrolyzer (AEM-WE), the electrodes are divided only by a membrane. The current density range of A-WEs goes from 0.05 to only 0.70 A/cm^{-2} (Brauns and Turek, 2020), even though the range is generally more narrow (0.2–0.4 A/cm^{-2} (Carmo et al., 2013)). This drawback has been partially overcome by AEM-WEs, which can be operated up to 1.5 A/cm^{-2} (Park et al., 2019).

A-WEs have a longer lifetime and a lower capital cost than other electrolyzer technologies thanks to the absence of noble metals such as platinum and iridium (Brauns and Turek, 2020); similarly, AEM-WEs can avoid noble materials. Typically, A-WEs are more efficient than PEM-WEs (63–70% compared to 56–60% (International Energy Agency (IEA), 2019), both based on the Lower Heating Value, LHV).

Low partial-load limits (10% (International Energy Agency (IEA), 2019)) are achievable, even though the practical limits are generally higher for safety reasons (20–40% (Carmo et al., 2013)). Nevertheless, A-WEs have difficulties in tracking the power fluctuation typical of renewable power supplies such as wind power (Shen et al., 2018). This recently led to increased investments in developing other technologies, in particular PEM-WEs.

Polymer electrolyte membrane water electrolysis

Polymer electrolyte membrane water electrolyzers (PEM-WEs) were introduced in the 1960s (International Energy Agency (IEA), 2019), but a new impulse to their development can be noticed in the last few decades. The polymeric membrane divides the anode side in which water is fed and oxygen forms and the cathode side in which the produced hydrogen is collected.

Despite lower efficiency and lifespan reliability than A-WEs, their wide operating range and capability to be fast-responsive (Tremel, 2018) (see Section 2.3) make this technology extremely promising, especially if coupled with renewable sources. High operating current densities (up to 2 A/cm^2 or more) are possible. Furthermore, the estimated enhancement of the efficiency (from 56–60% to 63–68% by 2030 (International Energy Agency (IEA), 2019), based on the LHV) and the expected fall of the CAPEX prices could also make PEM-WEs cost-effective.

Solid oxide water electrolysis

Solid Oxide Water Electrolyzers (SO-WEs) are technologically less mature than the other electrolysis technologies (Millet and Grigoriev, 2013). In SO-WEs, an oxide-ion conducting ceramic material separates the anode and cathode. Water is fed to the cathodic side, where the produced hydrogen is collected.

SO-WEs do not require noble materials and are not very sensitive to impurities in the feed stream. High operating current densities have been reached experimentally (up to 3.6 A/cm^2 (Millet and Grigoriev, 2013)). Furthermore, SO-WEs are reversible and can be used as solid oxide fuel cells generating electricity.

As opposed to the other electrolyzers, SO-WEs are operated at high temperatures (800–1000 °C (Millet and Grigoriev, 2013)). On the one hand, higher temperatures reduce the amount of electricity to split water, thus enabling higher efficiencies (74–81%, based on the LHV (International Energy Agency (IEA), 2019)). On the other hand, thermal management is more complex.

Despite these appreciable features that make this technology promising, the stack lifetime is still low (International Energy Agency (IEA), 2019) and the thermal management and the scale-up of the units remain key issues.

2.2. PEM water electrolyzers: Insight into the technology

PEM-WEs are considered the most promising technology when referring to flexible Power-to-X because of their fast responsiveness and wide operating range. This section focuses on the key aspects of the technology.

PEM-WE cell

PEM-WEs have a so-called “sandwich structure” since they are composed of several layers, namely the membrane, the electrodes, the Porous Transport Layers (PTLs), and the bipolar plates.

The core of the cell is a thin (20–300 μm (Carmo et al., 2013)) polymer electrolyte membrane that separates the anode from the cathode and ideally only allows protons to cross the membrane. In reality, oxygen and hydrogen molecules, water, and cationic impurities (like Na^+, K^+, Ca^{2+}, Cu^{2+}, Fe^{3+}, and Ni^{2+}) succeed in crossing the membrane.

The membrane is coated by a conductive layer on each side acting as an electrode, in which the electrochemical reaction occurs. The union of the membrane and the electrodes is often called Membrane Electrode Assembly (MEA) or catalyst-coated membrane from the production technique (Carmo et al., 2013).

Catalysts represent one of the most challenging aspects of PEM-WEs since they must be both active and stable (Shirvanian and van Berkel, 2020). Unfortunately, only noble, scarce, and extremely expensive materials, i.e., iridium at the anode and platinum at the cathode, are highly performant in PEM-WEs. Research is active to find alternatives, recycling strategies, or at least to reduce the loadings both to lower the costs and not to have the shortage of noble materials for the expected large-scale production (Minke et al., 2021). Many studies are summarized in two recent reviews (Carmo et al., 2013; Shiva Kumar and Himabindu, 2019).

PTLs, sometimes called gas diffusion layers, aim at homogeneously distributing the reactants on the catalyst layer and efficiently evacuating the produced gasses from the reactive sites.

Bipolar plates have a threefold role in PEM-WEs: i) they transport the reactants and the products into and out of the cell, respectively, through the flow channels inside the plates, ii) they conduct electrons and heat, and iii) they physically separate adjacent cells of a stack connected in series. Parallel, single-serpentine, and multiple-serpentine flow channel layouts are the most common (Maier et al., 2021).

Stack set-up and auxiliary units

In PEM-WEs, several cells are connected in series to form a stack, and several stacks can be connected both in series and in parallel. Several additional units, e.g., pumps, sensors, valves, and power conversion and control units are essential to operate the electrolyzer (Mancera et al., 2020). A simplified scheme can be found in Fig. 2.

The pre-treatment of the feed water with ion-exchange resins plays an essential role to reduce cell poisoning. Once the MEA is contaminated, it can be partially reactivated by treatments with an H_2SO_4 solution (Wang et al., 2015; Andolfatto et al., 1994).

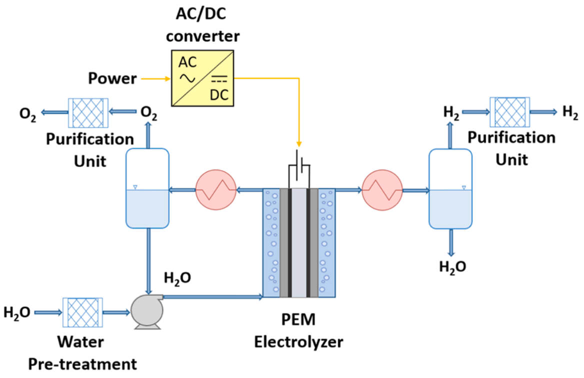

Fig. 2. Sketch of the main auxiliaries of a PEM-WE plant.

Pumps provide fresh water to the cell (generally only at the anode) in over-stoichiometric conditions to avoid membrane dehydration and entrain the produced gasses out of the cell. Water in excess also acts as a cooling medium.

The hot streams at the outlet of the cell contain two phases, i.e., liquid and gas, which are then separated. To reduce the amount of steam, the streams can be cooled down either to the ambient temperature or below, if a refrigeration cycle is used. Further purification treatments can be necessary to meet the purity specification of the hydrogen (Bensmann et al., 2016) and oxygen streams. Oxygen traces, for example, can be eliminated from the hydrogen stream via catalytic conversion as in the research facility "Energiepark Mainz" (Kopp et al., 2017). To further dry the hydrogen stream, pressure swing adsorption (PSA) or temperature swing adsorption (TSA) can be used (Tjarks et al., 2018). Extremely pure hydrogen streams ($>$ 99.999%) can be commercially achieved (Siemens Energy, 2022; Nel, 2022).

Power electronics for high-power applications and proper control systems acting on the AC/DC (or DC/DC if directly coupled with a DC power source) converter represent the key to the flexible operation of electrolyzers and the provision of ancillary services to the grid. Furthermore, if the electrolyzer is coupled to the grid via an AC-DC converter, special care needs to be paid to the power quality provided to the cell to avoid additional losses (Ruuskanen et al., 2020; Koponen et al., 2020).

Electrolyzer pressurization

The pressurization of hydrogen is a key aspect of efficient process integration. High-pressure hydrogen is needed for several applications, e.g., when feeding hydrogen into a pipeline (up to 85 bar), hydrogen for chemical synthesis processes (up to 250 bar), hydrogen storage in salt caverns underground (up to 200 bar), or hydrogen storage for hydrogen car refueling (350–700 bar).

Three main pathways can be considered to pressurize hydrogen: (i) compress hydrogen inside the PEM-WE (Fig. 3a), (ii) compress hydrogen outside the PEM-WE in an electrochemical hydrogen compressor (Fig. 3b) (Zachert et al., 2021), (iii) compress hydrogen in a mechanical (multistage) compressor (Fig. 3c). Combinations of the abovementioned methods are also possible, e.g., the first compression step inside the PEM-WE followed by a second one in a different device to reach the desired pressure. The anodic side can be also pressurized (balanced configuration) to make oxygen easier to store, but the energy demand is higher.

Determining the best alternative in terms of energy demand is not trivial. If a hybrid solution (pressurized cathode and mechanical compressor) and the hydrogen drying unit are considered, the optimal ratio between these two compression phases mainly depends on the final pressure level (Bensmann et al., 2016; Tjarks et al., 2018) and the current density (Tjarks et al., 2018). Bensmann et al. (2016) showed that the optimal cathodic pressure is lower than around 20 bar for delivery pressures up to 100 bar. Analogous findings were obtained by Tjarks et al. (2018) for delivery pressures up to 750 bar. However, it is not clear whether the positive effect of high pressure on the reduction of some overpotentials (Suermann et al., 2016) is taken into account in their evaluations. Electrochemical compression is generally not considered in these comparisons since it is a quite recent technology. Nevertheless, it is promising because it is efficient (nearly isothermal compression) and can reach high pressures (up to 1000 bar) in one stage without any moving parts (Zachert et al., 2021; Suermann et al., 2017).

The cathodic pressure of PEM-WEs affects not only the energy demand but also hydrogen crossover backward to the anode Trinke et al. (2016). High amounts of hydrogen at the anode reduce the faradaic efficiency (Yodwong et al., 2020; Tijani and Rahim, 2016) and pose safety issues since the flammability threshold of hydrogen in oxygen is low (4 vol.% (Carmo et al., 2013)). Thicker membranes (Trinke et al., 2016; Scheepers et al., 2020) and the introduction of a third electrode inside the membrane to force the conversion of the crossing hydrogen into water or hinder hydrogen crossover (Klose et al., 2018) can avoid this risk. If the compression of hydrogen is carried out in an electrochemical compressor afterward, the hydrogen crossover is not a safety issue anymore since there is no oxygen at the anode, but the reduction of the efficiency still stands.

2.3. Flexible operation of PEM-WEs

In Power-to-X, the renewable power input is variable over time, thus flexible operation must be considered (see Section 1). The following paragraphs deal with flexibility aspects of PEM-WEs; the key parameters of their flexibility are then summarized in Table 2.

Start-up and shutdown

Start-ups and shutdowns for PEM-WEs could be quite frequent if the electrolysis unit is directly coupled with renewables. It has been experimentally tested that PEM-WEs have short start-up and shutdown times (minute scale (Kopp et al., 2017)). However, the effects of their flexible and alternating operation on cell degradation are still unclear. Furthermore, shutdown and idle phases can be critical; having small bias currents and low cell voltages instead of idle periods seems to reduce degradation (Weiß et al., 2019), as for A-WEs.

Load changes

PEM-WEs have an extremely wide operating range (5–100 % (Siemens Energy, 2022)). Operation at loads higher than the nominal is also possible (150 % (Kopp et al., 2017)- 160 % (International Energy Agency (IEA), 2019)), but only for short periods because of cooling reasons (Kopp et al., 2017).

Several dynamic models have been built to assess how flexible and fast-responsive PEM-WEs could effectively be, and which ancillary services they could provide. Gusain et al. (2020) built a simplified PEM-WE model to show that PEM-WEs can provide ancillary services on large scale. They also pointed out that degradation phenomena over time should be taken into account for long-term assessments to avoid overestimating the real flexibility (Gusain et al., 2020). Alshehri et al. (2019) showed that PEM-WEs can participate in the European electrical ancillary markets and, by providing primary regulation, can contain frequency unbalance even in a low-inertia grid. Veerakumar et al. (2020), using a synthetic model of the north Netherland network for the year 2030, showed that a properly controlled large-scale electrolyzer (300

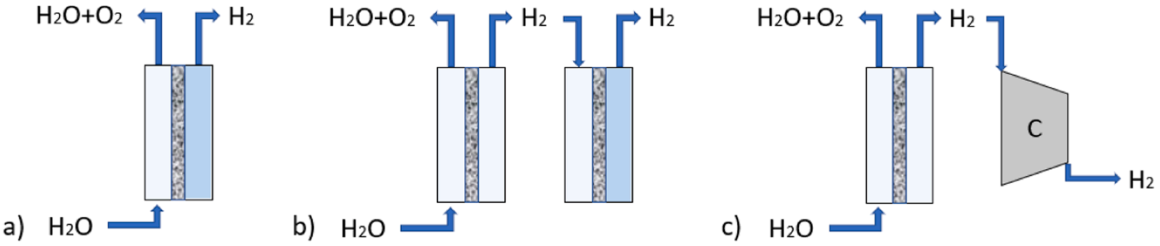

Fig. 3. Alternatives for the pressurization of hydrogen: (a) hydrogen is produced and pressurized in the PEM-WE; (b) hydrogen is produced in a PEM-WE and then electrochemically compressed in a different device; (c) hydrogen is produced in a PEM-WE and then mechanically compressed. (Note: the darker color represents a pressurized side, if any).

MW PEM-WE) can quickly damp frequency unbalances. Furthermore, the use of small-scale PEM-WEs aggregated in virtual power plant concepts can enhance grid flexibility (De Corato et al., 2020).

PEM-WEs flexibility has been tested not only via dynamic models but also experimentally. Koponen et al. (2017) showed that their small-size PEM-WE (4.5 kW) was not able to follow extremely fluctuating power profiles due to the ramp limit (0.4 %/s (Koponen et al., 2017)); this problem can be solved by coupling the electrolyzer with a fast-responsive storage like a supercapacitor (Koponen et al., 2017). Some industrial-scale products can reach 10 %/s as ramp rate instead (Siemens Energy, 2022). For a medium-size pilot plant (4 MW) (Kopp et al., 2017), it was experimentally shown that ancillary services up to primary control reserve can be provided, but the economic profitability of having such a high responsivity is still under debate (Kopp et al., 2017; Guinot et al., 2015).

3. Carbon dioxide supply

To reduce the environmental impact of the chemical industry, alternative carbon sources to fossil fuels are necessary for the production of carbon-based chemicals. Carbon dioxide is the considered carbon feedstock in the following sections.

3.1. CO_2 sources

Carbon dioxide sources can be classified into three main categories, i.e., biogenic, fossil-based, and air. Apart from the CO_2 that can be separated from air, most of the sources have an anthropogenic-related origin. The International Renewable Energy Agency (IRENA) estimated that the net worldwide CO_2 emissions were around 37 Gt/y in 2020 (International Renewable Energy Agency (IRENA), 2021). In order to reduce these emissions, carbon capture and utilization is a promising solution in the medium-to-long term (International Renewable Energy Agency (IRENA), 2021). Since the current CO_2 demand (0.04 Gt in 2020 (International Renewable Energy Agency (IRENA), 2021)) is much lower than the potential availability, a classification of which CO_2 sources are more environmentally favorable to be captured is important. Von Der Assen et al. (2016) ranked the current CO_2 sources according to an environmental merit-order. Even though carbon capture requires substantial amounts of energy, they verified that carbon capture reduces CO_2 emissions compared to the status quo without capture for all the analyzed sources (power plants, hydrogen, ammonia, ethylene oxide, pulp and paper, steel and iron, cement plants, refineries and gas processing plants, and direct air capture) (Von Der Assen et al., 2016). The largest reduction can be obtained from hydrogen (from fossil fuels like methane), ammonia, and ethylene oxide production processes (Von Der Assen et al., 2016). Other authors (Bargiacchi et al., 2020) confirmed that carbon dioxide from hydrogen production plants has the lowest cradle-to-gate impact. Romeo and Bailera (2020) also pointed out the necessity of the right choice of the carbon source. Capturing CO_2 from power plants that use fossil fuels to then convert it into methane with green hydrogen is not worthwhile in absence of H_2 storage: the electricity demand of the electrolyzer would be at least 3 times higher than the nominal production of the power plant (Romeo and Bailera, 2020).

Capturing CO_2 from point sources is less energy-demanding than Direct Air Capture (DAC) because of the low concentration (around 400 ppm). However, DAC has a negative value of CO_2 emissions (Von Der Assen et al., 2016; Deutz and Bardow, 2021), it will be an available process even in a low-carbon economy; furthermore, it is geographically unconstrained, thus allowing to convert captured CO_2 with green hydrogen into valuable chemicals where the renewable plant is located without transporting electricity.

3.2. Carbon capture technologies

According to the position in which the carbon capture unit is placed in plants, a general classification of pre-combustion, oxy-combustion, and post-combustion is done (Cuéllar-Franca and Azapagic, 2015; Lyons et al., 2021). In pre-combustion capture, a carbon-based material is first converted into a suitable intermediate product from which CO_2 is then separated. In post-combustion capture, CO_2 is captured from the flue gas after the combustion. In oxy-combustion, carbon and hydrogen atoms are oxidized in pure oxygen (and recycled flue gas) instead of air; as nitrogen and argon are not present in the mixture, an almost pure CO_2 stream (after water condensation) is obtained. Oxy-combustion could be interesting especially if coupled with electrolysis: the main side product of water electrolysis is oxygen that could be used to substitute the combustion air. Several benefits can be named such as no nitrogen oxides emissions, the absence of the energy-intensive carbon capture unit, and a lower need for oxygen purification (hydrogen traces in oxygen provide additional thermal energy when burned).

Several carbon capture technologies are available, e.g., chemical absorption, chemical adsorption, PSA, selective membranes, and cryogenic separation (Cuéllar-Franca and Azapagic, 2015; About CCUS International Energy Agency (IEA), 2021). Further separation concepts with lower technological readiness levels have been proposed like the use of molten carbonate fuel cells (Lewandowska-Bernat and Desideri, 2018) and biological capture methods, e.g., dedicated microalgae plantations where microalgae grow by capturing CO_2 from flue gas (Cuéllar-Franca and Azapagic, 2015; Roh et al., 2020) to be then used as biomass feedstock.

Absorption in monoethanolamine (C_2H_7NO) solutions is the most mature carbon capture technique. Furthermore, the relatively low temperature for solvent regeneration (lower than 150 °C) makes this technology particularly suitable for heat integration with several exothermic downstream synthesis processes. Monoethanolamine is also considered the benchmark for new carbon capture solvents because they are cheap, stable, and fast-reactive. However, they require a significant amount of thermal energy for regeneration (stripping phase), and their corrosivity and viscosity limit the CO_2 mass fraction in aqueous solutions to 40% (Lee et al., 2016). Other solvents, e.g., ammonia (Yu et al., 2013) and piperazine (Gaspar et al., 2017) have been proposed as alternatives, but none of these outperforms monoethanolamine overall. Finally, the choice of solvent also depends on the partial pressure of carbon dioxide in the gas (Herzog, 2003).

Since absorption and stripping are exothermic and endothermic reactions, respectively, inter-cooling of the absorber and inter-heating of the stripper enhance the capture rate and reduce the thermal duty. There is much interest in optimizing carbon capture via monoethanolamine solutions. For example, a reduction of the thermal duty from 3.8 MJ/kg CO_2 to 3.1 MJ/kg CO_2 was achieved with the introduction of an absorber inter-cooling, a stripper inter-heating, and a CO_2-rich feed split before thermal regeneration (Li et al., 2016). That value was further improved up to 2.2 MJ/kg CO_2 by Lee et al. (2016) by solving a superstructure optimization problem.

Adsorption on solid materials, generally CaO-based, is another mature technology. These sorbents can be used for carbon capture both in pre-conversion and post-conversion configurations. CaO sorbents have a high theoretical CO_2 sorption capacity (Yoon and Lee, 2019) enabled by chemical adsorption according to the following reaction:

$$\mathrm{CaO(s)} + \mathrm{CO_2} \leftrightarrow \mathrm{CaCO_3(s)},$$

where CO_2 is captured at around 650 °C at atmospheric pressure and desorbed at around 950 °C, then requiring an energy input.

Research on solid sorbent materials for carbon capture is still active. ZrO_2-modified CaO materials, for example, were proven to enhance the sorbent stability over time without highly affecting the sorption capacity (Yoon and Lee, 2019), and the NiCaO material, despite a lower sorption capacity, was proven to release methane at 500 °C (Bin Jo et al., 2020a, 2020b) or carbon monoxide at 700 °C (Bin Jo et al., 2020b) if fluxed with hydrogen. The latter could be an interesting alternative for producing syngas (see Section 5.3).

3.3. Flexible operation of carbon capture units

Flexible operation of carbon capture units would allow adapting the absorption and desorption rates according to the availability of the carbon source or demand of the downstream process, thus reducing the need for storage. However, it could complicate heat integration with other processes. The next paragraphs deal with the flexibility of carbon capture plants via chemical absorption as the most established technology. The key parameters of their flexibility are then summarized in Table 2.

Start-up

Two main start-up procedures are mentioned in literature (Gaspar et al., 2015a). In the first, air substitutes the flue gas in the first phases of the start-up; in the latter, the flue gas enters the absorber directly and the monoethanolamine flow rate is adjusted consequently. Gaspar et al. (Gaspar et al., 2015a) simulated the second procedure and noted that, after around 20–30 min, the CO_2 removal factor is approximately at the design value. However, some residual fluctuations of the control variables remained, and longer times would be needed to reach the steady-state.

Load changes

As regards the operating load range, a properly designed control system seems able to handle wide variations (50–130% (Gaspar et al., 2015a)) of the flue gas flow rate while keeping the CO_2 removal factor almost constant. The main risk of a further extension of the load range is flooding or drying of the columns.

Several studies about flexible operation of carbon capture can be found in the literature. This includes models to investigate the solvent loss for entrainment and degradation (Dickinson et al., 2015), load changes (Gaspar et al., 2015a, 2015b, 2016a), variation of the carbon dioxide content in the flue gas (Gaspar et al., 2016b), insufficient steam at the reboiler for regeneration (Gaspar et al., 2015b), and integration of a tank (Gaspar et al., 2017). Most of the abovementioned simulative studies are comparisons of two solvents, i.e., monoethanolamine and piperazine. Plants using monoethanolamine solutions provide faster responses (up to 2–3 times faster) both for step (Gaspar et al., 2016a, 2016b) and a ramp (Gaspar et al., 2015b, 2016a) variations, but still on the order of magnitude of 1–2 h (Gaspar et al., 2016a). Other studies instead show shorter settling times for plants using monoethanolamine solutions (around 0.2–0.5 h) (Gaspar et al., 2015a, 2016b). Similar settling times were found by Mostafa et al. (2021) for the absorber. Furthermore, monoethanolamine and piperazine provide inverse response behavior under certain step changes in the desorber, thus making control more challenging (Gaspar et al., 2017, 2016b). The slower settling times (around 6 h (Mostafa et al., 2021)) of the desorption phase could be a bottleneck unless solvent storage is used (Gaspar et al., 2015a).

Experimental tests were carried out at the amine-based carbon capture test rig at the Klemetsrud waste incinerator in Oslo (Fagerlund et al., 2021). However, these tests were focused more on the pollutants emissions and solvent degradation than the assessment of the unit flexibility. Fagerlund et al. (2021) remarked that sudden variations of the load or high presence of dust in the flue gas result in higher emissions of amines in the flue gas.

Alternative designs or additional units could make carbon capture more flexible. Having smaller carbon capture units in parallel, for example, could enhance capture flexibility (Yu et al., 2013), and could be particularly suitable when the processed gas flow rate is high. Flue gas bypass and solvent storage tanks (Fig. 4) could also enhance the carbon capture unit efficiency and flexibility in off-design conditions (Gaspar et al., 2017, 2015a, 2016c). In particular, storing CO_2-rich solvent in a tank instead of CO_2 in a pressurized vessel might be advantageous. This decoupling technique could be particularly suitable in case the heat for stripping is provided by the downstream process because the operation of stripping can be matched to the downstream one. However, the costs would unavoidably be higher because of the tank inventories and the additional amount of solvent.

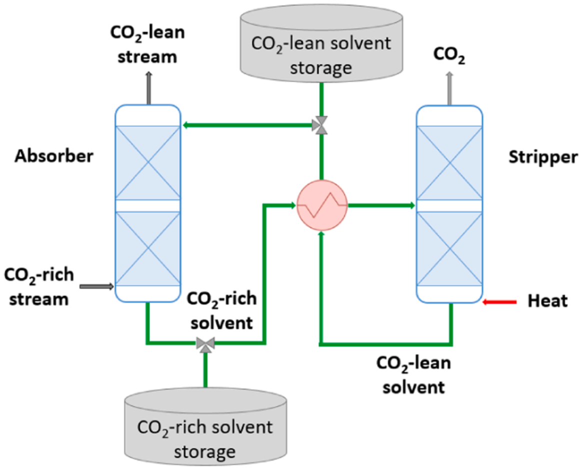

Fig. 4. Simplified sketch of a carbon capture unit (absorption via solvent) with solvent storage.

4. Nitrogen supply

Nitrogen is a key molecule for the synthesis of ammonia, urea, and their derivatives. Although nitrogen is the main component of air and, thus, abundantly available, its separation is highly energy-demanding.

4.1. Nitrogen separation technologies

The nitrogen separation processes can be divided into two categories: cryogenic and non-cryogenic (Smith and Klosek, 2001). The latter category includes PSA (Haering, 2008), absorption, and selective membranes. Membranes and PSA processes, the most common non-cryogenic units, are generally used at smaller scales (lower than 5000 Nm^3/h) and achieve slightly lower nitrogen purities and yields (Smith and Klosek, 2001; Haering, 2008).

Cryogenic Air Separation Units (ASUs) are the most efficient and cost-effective technology to produce large amounts of gases (Smith and Klosek, 2001; Haering, 2008) with an extremely high purity level (higher than 99.9% (Smith and Klosek, 2001; Haering, 2008)).

Since cryogenic ASUs can supply large amounts of high-purity nitrogen, which is required for the conventional Haber-Bosch synthesis (Osman et al., 2020) (see Section 5.4), they will be considered as the reference production process later on.

The design of ASUs depends on which gas is the main product: nitrogen, oxygen, or argon. Their design should also consider the operation mode since some design choices can limit flexibility (Cao et al., 2015). In cryogenic ASUs (see Fig. 5), warm and cold sections can be distinguished. The former includes the units for compression, pre-cooling, drying, and purification of incoming air. The latter includes the heat exchanger network, turbines, rectification unit, and storage, and it is characterized by temperatures lower than -170 °C (Haering, 2008). The rectification unit is a double-column system, the configuration of which changes depending on the delivery pressure for nitrogen (Haering, 2008). Heat integration is a key point for the efficiency of the overall liquefaction process. The produced nitrogen, as well as the oxygen, is generally stored in liquid form.

4.2. Flexible operation of ASUs

Since electricity is the main energy input of ASUs (Haering, 2008), demand-side management for these processes could be a way to reduce

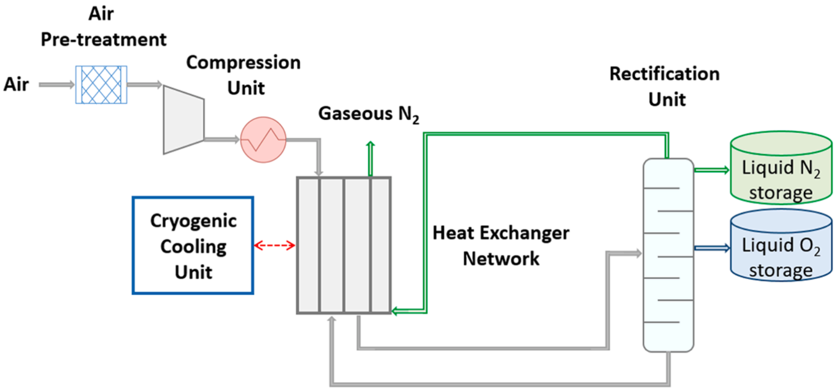

Fig. 5. Simplified sketch of an ASU with storage of liquid products.

the renewable curtailment and make the ASU more economically profitable by exploiting electricity price fluctuations. The next paragraphs deal with flexibility aspects; the key parameters are then summarized in Table 2.

Start-up and shutdown

Cryogenic ASUs have longer start-up times compared with non-cryogenic units like membranes and PSA (hours vs. minutes (Smith and Klosek, 2001; Haering, 2008)). As regards warm start-up, in which the cryogenic plant is turned on from ambient conditions, about 4–5 h are necessary to reach the steady-state condition (Kender et al., 2019). Cold start-ups, in which at least some parts of the cryogenic plant are still at low temperatures, are shorter. Caspari et al. (2020), for example, optimized the cold start-up procedure in silico with and without liquid assist operation, a start-up technique that uses products stored at cryogenic temperatures. The use of the already produced liquid product turned out to shorten the start-up period from around 1.5 h to around 0.5 h (Caspari et al., 2020).

For ASUs, the shutdown time is quite short: once the compressor is turned off, the mass flow rates approach zero in about 5 min while the column dries in about one hour, even though this time highly depends on the geometry of the column internals (Kender et al., 2019).

Load changes

Cryogenic ASUs have generally a lower load range (60–100 %) compared with non-cryogenic units like membranes and PSA (30–100%) (Haering, 2008). However, since one of the most critical components for the operating range is the train of centrifugal compressors, further extension of the operating range and improvement of the off-design efficiency could be obtained, e.g., by varying the rotating speed (He et al., 2018) and/or using variable inlet guide vanes (Frank et al., 2021), also with adjustable blade geometry (Frank et al., 2022).

Some studies about the flexibility of ASUs can be found in literature. Caspari et al. (2019a) modeled a complete ASU with an auxiliary liquefier, which allows the production of large liquid quantities, and a liquid assist operation, which allows liquefying even when the liquefaction unit is temporarily not active. The possibility of storing liquid nitrogen offers a further degree of freedom for demand-side management since nitrogen can be produced under favorable conditions (or renewable energy availability) and supplied when needed after vaporization (Haering, 2008; Cao et al., 2016).

The control of transients is particularly important to avoid the violation of constraints like purity (Cao et al., 2016) and have smother profiles. Caspari et al. (2019b), for example, showed that the economic nonlinear model predictive control (eNMPC) can optimize the operation by reducing the operating costs without violating the product purity constraints. Different control schemes, e.g., a two-layer control (Schäfer et al., 2018), can also reduce transient times and, thus, increase economic savings while avoiding constraint violations. Step variations without proper control should be avoided because of the flooding risk in the rectification columns (Cao et al., 2015). Transient times are relatively long, especially if a step variation is performed; Cao et al. (Cao et al., 2015) estimated a settling time of around 0.5 h for a step-up variation of 20%.

5. Hydrogen-to-X

Green hydrogen can be converted into a wide variety of useful chemicals by reacting with raw materials like carbon dioxide or nitrogen. Flexible operation of the downstream conversion processes could increase the use of renewable electricity in the process (even though most of the electricity is used to run the electrolyzer, e.g., more than 90% in Power-to-Ammonia plants (Morgan et al., 2017)) and reduce the size and cost of storage tanks (see Section 1), but it would reduce the capacity factor of the plant. Therefore, economic evaluations have to be carried out (Brynolf et al., 2018). Still, it should be assessed to what extent downstream processes are flexible.

To try to answer this question, some of the main one-step products from hydrogen are analyzed, namely methane, methanol, syngas, and ammonia. The choice of these chemicals is motivated by their wide utilization and the medium-to-high technological readiness level of the related Power-to-X processes. In fact, demonstration plants for Power-to-Methane at the MW scale have been built (Wulf et al., 2020). Power-to-Methanol technology is at the commercialization phase already (Carbon Recycling International (CRI), 2022). A 150 kW Power-to-Syngas plant with a solid oxide electrolyzer to synthesize liquid fuels via the Fischer-Tropsch process was built (Wulf et al., 2020), while we are not aware of demonstration plants that produce syngas via RWGS. Power-to-Ammonia plants also started to be built on large scales (a 5000 t/y e-ammonia production plant is expected to be operating in 2023 (Skovgaard Energy, 2022)).

Furthermore, the synthesis processes of these chemicals have a high theoretical conversion efficiency (see Table 1), which means that most of the chemical energy in hydrogen can be stored in the product. The theoretical conversion efficiency in terms of lower heating value (η_{LHV}) is calculated as follows (Tremel et al., 2015):

$$\eta_{\mathrm{LHV}} = \frac{p \cdot \mathrm{MW_P} \cdot \mathrm{LHV_P}}{h \cdot \mathrm{MW_{H_2}} \cdot \mathrm{LHV_{H_2}}},$$

Table 1
Hydrogen content and theoretical conversion efficiency in terms of LHV for the considered products.

	Molecular weight	LHV	η_{LHV}
Methane	16 kg/kmol	50.0 MJ/kg	0.833
Methanol	32 kg/kmol	19.9 MJ/kg	0.884
Syngas (ranging from pure H_2 to pure CO)	2–28 kg/kmol	120.0–10.1 MJ/kg	1–1.178
Ammonia	17 kg/kmol	18.6 MJ/kg	0.878

where MW_P and LHV_P are the molecular weight and the lower heating value of the product P, p and h are the stoichiometric numbers of the direct synthesis reaction for the product and hydrogen, respectively. The theoretical conversion efficiency can be higher than one only if the reaction is endothermic, as for syngas production via Reverse Water Gas Shift (RWGS).

5.1. Methane

Power-to-Methane (often also called Power-to-Gas) is gaining a growing interest, as proven by the more than thirty projects founded in Europe in the last decade (Bailera et al., 2017). The produced e-methane can be injected, stored, and distributed in the existing infrastructure, and then converted to heat and electricity or used as fuel. Methane synthesis can be catalyzed both chemically and biologically (Götz et al., 2016). The first case requires high-activity and selective catalysts; the second requires microorganisms that are able to convert CO_2 and H_2. Given such catalysts or microorganisms, methane production is a highly efficient one-step process; this makes its production cheap and competitive compared to other alternatives like methanol (Uebbing et al., 2019).

5.1.1. Catalytic methane production

Two process routes are possible for catalytic methanation: direct and indirect. In the direct one, the most common, CO_2 is hydrogenated to produce methane. In the indirect one, CO_2 is reduced to carbon monoxide in a Reverse Water Gas Shift (RWGS) step (also see Section 5.3.1), which is then converted to methane. Direct electrochemical synthesis from water and carbon dioxide is also an interesting alternative (de Vasconcelos and Lavoie, 2019).

Reaction and operating conditions

The synthesis reaction in which carbon dioxide is directly hydrogenated to form methane is known as the Sabatier reaction:

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O.$$

The reaction is exothermic and a typical temperature range is 200–550 °C (Götz et al., 2016); the operating range depends on the catalyst. Several metals such as Ni, Ru, Pt, and Co can be used as catalysts (Rönsch et al., 2016). Nickel is the most used because of its activity, but it risks being poisoned if the feed contains contaminants such as sulfur (Gaikwad et al., 2020). The reaction can be carried out in a wide pressure range (1–100 bar (Götz et al., 2016)). High pressures enhance the conversion according to Le Chatelier's principle. The feed typically has a stoichiometric CO_2:H_2 ratio (Götz et al., 2016).

High CO_2 conversion rates are achievable and recycle streams are generally not needed. The selectivity of methanation is very high but small amounts of side-products like CO, C_2H_6, CH_3OH, C_2H_4, and DME are produced (Jürgensen et al., 2015). Among these, carbon monoxide is the main side-product, but high pressures (e.g., 10 bar) strongly hinder its formation (Jürgensen et al., 2015). Increased pressure also reduces the risk of carbon deposition (Jürgensen et al., 2015).

Reactor configurations and process concepts

For the methanation of both CO_2 and CO, multiple reactor types have been proposed, e.g., fixed-bed, fluidized-bed, three-phase, and structured reactors (Götz et al., 2016). Thermal management is a key point for all methanation reactors, especially when CO is used due to the higher exothermicity (Lefebvre et al., 2015). Beyond the risk of thermal runaway, hot spots could damage the catalyst and compromise the reactor performance. The risk of hotspot formation can be reduced by introducing a diluent, at the expense of having larger components. A common diluent is methane itself (e.g., when using CO_2 from biogas), which luckily hardly affects carbon dioxide conversion (Jürgensen et al., 2015). The injection of fresh reactants at the inlet of each reactor (Gaikwad et al., 2020) or an inhomogeneous catalyst distribution over the reactor can also be beneficial (Zimmermann et al., 2022).

One of the most widely used configurations consists of multiple adiabatic fixed-bed reactors with intercooling since it avoids excessive temperature rises (Held et al., 2020). El Sibai et al. (2015) economically optimized a multiple adiabatic fixed-bed reactor, also taking into account the downstream separation units to meet purity specifications. They found that a configuration with three reactors with two intercoolers for water condensation was optimal.

Cooled reactors allow the reduction of the number of reactors and intercooling steps, but insufficient heat removal can cause hot spots. High-temperature-resistant diathermic oil can be used for this purpose (Gaikwad et al., 2020). Other reactors like fluidized-bed reactors avoid the problem of hot spots thanks to the high degree of mixing, but friction and attrition have to be considered (Held et al., 2020).

Further reactor types with a lower technological readiness level have been proposed, e.g., hydrophilic membrane reactor (El Sibai et al., 2017) and the sorption enhanced synthesis (Wei et al., 2021) that aim at removing steam *in situ*.

Regardless of the reactor type, the methane stream has to be purified. Most of the water can be separated via condensation. If there are strict purity constraints on methane, as for injecting methane into the gas grid, further purification is needed to remove the small amount of unreacted CO_2 and the residual water. A compression unit is usually included to reach the desired delivery pressure.

Finally, the direct integration of carbon capture and methanation could also be an alternative, e.g., if a Ni/CaO adsorbent is fluxed with hydrogen at a relatively low temperature (500 °C) (Bin Jo et al., 2020a; Bin Jo et al., 2020b).

5.1.2. Biological methane production

Specific species of microorganisms (methanogens) can convert CO_2 and H_2 into methane in a biological reactor (Götz et al., 2016). Recent studies (Bensmann et al., 2014; Luo et al., 2012) have shown that the direct injection of hydrogen into the anaerobic digester, which produces biogas (a mixture of CO_2 and CH_4), promotes the conversion of the residual CO_2 into methane since hydrogenotrophic bacteria are present. Up to 90% of the injected hydrogen can be converted into methane, thus increasing methane production by over 20%, although the increase of pH causes partial inhibition of methanogenesis from biomass (Luo et al., 2012). This limitation can be overcome by feeding biogas and hydrogen in a different reactor.

On the one hand, the low temperatures (< 100 °C) and pressures ($<$ 10 bar), as well as the high selectivity of biological methanation reactors are very attractive; on the other hand, biological processes are complex and difficult to operate. Furthermore, they have a lower space-time yield (Götz et al., 2016). Biological methanation from biogas is, therefore, an option for small-medium size plants because this is the common size for anaerobic digesters (Götz et al., 2016).

However, the economic viability of biological methanation is uncertain. The cost of biological methanation plants from biogas was found to be higher than the catalytic ones by Uebbing et al. (2020), who solved a superstructure optimization problem. Nevertheless, further configurations could be considered, e.g., the direct injection of hydrogen in the anaerobic digester.

5.1.3. Flexible operation of methanation plants

Taking into account the operation of the plant substantially complicates the plant design phase, but improves its off-design behavior. To this end, approaches like multi-period design optimization (Zimmermann et al., 2022) or integrated process design and control (Fischer and Freund, 2020) were proposed for methanation. Optimal sizing that considers both storage and plant has also been recently proposed (Gorre et al., 2019).

Dynamic evaluations in the literature generally focus on the reactor behavior and only a few, e.g., Uebbing et al. (2019), also considered the purification units. Several aspects of the dynamics of reactors such as start-ups, shutdowns, step tests, and ramp tests are reviewed in the following, and the key parameters are collected in Table 2.

Start-up and shutdown

Bremer et al. (Bremer et al., 2017) proposed a 2D dynamic model of the first block of a fixed-bed reactor with a cooling jacket to investigate and optimize the start-up procedure. The examined start-up procedure starts with a temperature step in the cooling stream that temporarily heats the reactants (Bremer et al., 2017). One of the main results is that the time to reach the steady state is much higher than the residence time because of thermal inertia (around 500 s vs around 5 s (Bremer et al., 2017)).

Jürgensen et al. (2015) simulated the warm start-up of a cooled reactor in Aspen Dynamics starting from a standby mode in which only hydrogen was fed into the reactor, and they validated the model against experimental data. They showed that the steady state is reached after around 5–6 times the residence time in the reactor, and that, during this period, the product purity requirements are not met. If the CO_2 source is biogas, the impure methane can be recycled back into the biogas reactor (Jürgensen et al., 2015). Similarly, Matthischke et al. (2018) investigated the warm start-up behavior of a fixed-bed reactor, both in adiabatic and cooled configurations with a recycle. They showed that the cooled reactor is faster than the adiabatic reactor in case of a warm start from 280 °C (around 200 s vs around 400 s (Matthischke et al., 2018)) because less energy is necessary to heat the reactor.

The period after which a warm start-up is still possible was identified by Rönsch et al. (2017) for a carbon monoxide methanation reactor with insulation. After four hours, the simulated temperature fell below 550 K and made the start-up problematic since the reaction cannot start again unless the reactants are heated (Rönsch et al., 2017; Sun and Simakov, 2017).

The temperature of the reactor also plays a relevant role during the shutdown of the plant and idle periods. Before the shutdown, the reactor has to be fluxed with an inert gas like nitrogen or hydrogen (Götz et al., 2016; Rönsch et al., 2017), and the temperature of the reactor should not fall below 503 K (depending on the catalyst) to avoid catalyst deactivation (Rönsch et al., 2017). These aspects complicate the intermittent use of the reactor, thus flexible but continuous operation should be preferred.

Biological reactors are less suitable for frequent start-ups and shutdowns than catalytic reactors since these reactors are characterized by long characteristic times. Immediate shutdowns of these plants are possible but the restart could take more than 500 h (Götz et al., 2016).

Load changes

The reactor concept affects the minimum allowable load and flexibility. For both adiabatic fixed-bed and cooled reactors, it has been identified as 40% of the nominal load (Gorre et al., 2019), in contrast to 10–20% for a three-phase reactor (Götz et al., 2016).

The inlet temperature of the reactants is one of the most important variables to be controlled in methanation, especially if flexible. This temperature affects the position of the temperature peak in the reactor (Sun and Simakov, 2017), and the stability of the reaction. For the methanation reactors, in fact, a temperature hysteresis cycle exists: the ignition temperature is higher than the extinction temperature of the reaction and, therefore, a bi-stability region exists. Sun and Simakov (2017) claimed that it would be better to avoid the bi-stability operating region for practical applications since sudden variations of the feed temperature could cause the extinction of the reaction. However, the stable operating region, hence flexibility, can be extended with a suitable control system, e.g., a cooling jacket with controlled coolant temperature or mass flow rate (Bremer and Sundmacher, 2019).

Several factors can affect the settling time after load variations. Matthischke et al. (2016) pointed out that thermal inertia causes slower temperature responses than concentration responses (Matthischke et al., 2016). Because of the importance of thermal inertia, even the design of the catalyst particles affects the dynamic behavior

Table 2
Summary of the main flexibility parameters for the considered processes (Note: Syngas is missing here in lack of data).

	PEM Water Electrolyzer	Carbon capture with monoethanolamine	Cryogenic Air Separation Unit	Methane synthesis (catalytic*)	Methanol synthesis	Ammonia synthesis
Load range (relative to the nominal load)	0–160% (International Energy Agency (IEA), 2019)***	50 (Gaspar et al., 2015a; Mostafa et al., 2021) -130% (Gaspar et al., 2015a)	60–100% (Haering, 2008)	40–100% (Götz et al., 2016; Gorre et al., 2019)	20–100% (Dieterich et al., 2020) 10–120% (BSE Engineering, 2022)**	60–100%; 10–100 % (Rouwenhorst et al., 2019)**
Max ramp rates	3.3%/s (Kopp et al., 2017)**-10%/s (Siemens Energy, 2022)	N.A.	N.A.	> 3%/min (Gorre et al., 2019); 4%/min (Matthischke et al., 2016)**	5–13%/min (Dieterich et al., 2020) or higher (BSE Engineering, 2022)**	20%/h (Armijo and Philibert, 2020)
Settling times	Few seconds (Kopp et al., 2017)**	1–2 h (Gaspar et al., 2016a)	0.5 h (Haering, 2008)	Few minutes (Herrmann et al., 2022)**	<1 min (Manenti et al., 2013)	from 0.5–1 h to 4 h (Araújo and Skogestad, 2008)
Cold start-up time	Few minutes (Kopp et al., 2017; Siemens Energy, 2022)** (Koponen et al., 2017)	20–60 min for absorption (Gaspar et al., 2015a) Up to 6 h for stripping (Mostafa et al., 2021)	0.5–2 h (Haering, 2008; Caspari et al., 2020)	Few minutes (Bremer et al., 2017)	N.A.	Several days (Morgan et al., 2017); Around 12 h for new design (NEL Hydrogen, 2022).
Warm start-up time	< 1 min (Kopp et al., 2017)**	N.A.	About 4 h (Kender et al., 2019)	200–400 s (Matthischke et al., 2018)	N.A.	N.A.

* Fixed-bed reactor. Other reactor types have different flexibility parameters.

** From experimental tests. (In absence of this symbol **, data are from simulations, or their origin is not known).

** Operation at loads higher than the nominal one is possible, but only for short periods because of cooling reasons (Kopp et al., 2017).

NA Data Not Available.

(Zimmermann et al., 2020).

Moreover, recycles, although generally not needed for the methanation reactor, could offer a further degree of freedom for transients and more robustness to the variation of the mass flow rate. Faster load variations can then be achieved by adjusting the recycle ratio (Matthischke et al., 2016). Recycles can contribute to extending the reactor flexibility and the operating range by reducing the risk of temperature hot spots and catalyst deactivation. Similarly, catalyst dilution over the reactor has been experimentally proven on a lab-scale (around 10 kW capacity) fixed-bed reactor to reduce temperature peaks (Herrmann et al., 2022) and potentially extend the operating range.

Several studies, both simulative and experimental, on load changes of methanation plants can be found for different reactor types. Matthischke et al. (2016) experimentally investigated the performance of a lab-scale fixed-bed reactor without recycle under ramp variations of the inlet flow. Ramp rates up to around 4%/min were used (Matthischke et al., 2016). Similar ramp rates (around 3%/min) were suggested to be suitable to load changes without affecting the gas quality at the outlet of the reactor in a different study (Gorre et al., 2019).

A reactor with alternating cooling and reaction channels was simulated by Kreitz et al. (2020) under variable hydrogen feed flow rates. Though the CO_2 flow rate was modified proportionally to the hydrogen flow rate, the purity requirements were not always met in their study (Kreitz et al., 2020). Thus, they suggested inserting a purification unit, modifying the reactor design, or controlling other variables, e.g., the coolant temperature (Kreitz et al., 2020).

Lefebvre et al. (2015) experimentally investigated a lab-scale slurry bubble column reactor, a promising alternative to the adiabatic fixed-bed reactor, under flexible operation since the nearly isothermal temperature profile avoids the risk of hot spots. It was noticed that the settling time changes if the step-change of the gas velocity is positive or negative (around 10 and 40 min, respectively (Lefebvre et al., 2015)); a similar behavior was experienced by Herrmann et al. (2022) in a lab-scale fixed-bed reactor. Hervy et al. (2021) experimentally tested the flexibility of a demonstration-scale (400 kW capacity) fluidized bed reactor by varying pressure, reaction temperature, and H_2:CO_2 inlet ratio and showed that a stable regime and maximum conversion were reached in less than 30 min after the variation.

The dynamic behavior of a simplified model of a reactor under periodic inputs was investigated in silico by Güttel (2013). The reactor was able to self-stabilize and damp the fluctuation amplitude, especially if its period was lower than the residence time (Güttel, 2013).

As regards flexible operation of biological methanation processes, the only dedicated study we are aware of is the step test analysis by Bensmann et al. (2014). The results of this simulative analysis showed that the reactor has slow dynamics (multiple days to reach the new steady state), and that, during transients, it can operate for a certain period in conditions that are unfeasible at steady state (Bensmann et al., 2014). However, the high volumes and the slowness of biological reactors could also be positive aspects if coupled with a high-frequency fluctuating hydrogen production: The biological process could potentially work almost steadily if the mean hydrogen feed rate over a certain period is constant since the large volume of the reactor behaves as hydrogen storage and damps fluctuations.

5.2. Methanol

Methanol is one of the most produced chemicals since it can be used as raw material for the synthesis of other chemicals (e.g., formaldehyde, formic acid, and acetic acid) and fuels (e.g., dimethyl ether), and its demand is expected to grow (International Energy Agency (IEA), 2019). With its high energy density in terms of volume (nearly 80 % more than liquid hydrogen), its simple handling due to its liquid form, and relatively easy synthesis, methanol represents one of the most investigated uses of green hydrogen. Furthermore, it could be used as a storage medium since high-purity hydrogen can be obtained back from methanol, e.g. electrochemically (Pethaiah et al., 2020).

5.2.1. Methanol production

Methanol can be produced from carbon dioxide and hydrogen either directly or indirectly. In the indirect route, carbon dioxide is reduced to carbon monoxide in a Reverse Water Gas Shift (RWGS) step (also see Section 5.3.1) and then converted to methanol. This process is also known as CAMERE (CArbon dioxide hydrogenation to form MEthanol via a REverse-water-gas-shift reaction) process (Joo et al., 1999) and aims at using the consolidated know-how of methanol production from syngas. The direct pathway allows producing methanol in one step with obvious benefits in terms of plant complexity, higher energy efficiency, and better economic feasibility (Anicic et al., 2014); thus, it is the main focus of this section.

Reaction and operating conditions

Methanol synthesis from H_2 and CO_2 is an exothermic catalytic reaction that can be described by the following kinetic network: (i) carbon dioxide hydrogenation, (ii) reverse water gas shift, (iii) carbon monoxide hydrogenation:

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O$$

$$CO + 2H_2 \leftrightarrow CH_3OH$$

The operating temperature ranges between 220 °C and 280 °C (Nestler et al., 2020) depending on the catalyst. Since the overall number of moles decreases from the inlet to the outlet, high pressures allow higher conversions. The operating pressure generally ranges between 50 bar and 100 bar.

Other than CO, CH_4, and H_2O, further components such as ethers, formiates, aldehydes, and ketones, which are not generally included in the reaction scheme, form in traces and are removed via distillation. The amount of these side-products for the one-step route is lower than for the CAMERE process because of the lower reaction exothermicity that leads to fewer hot spots (Nestler et al., 2020; Pontzen et al., 2011). However, the equilibrium conversion for the CAMERE process is higher than for the one-step process since part of the water is removed from syngas before entering the methanol reactor.

Reactor configurations and process concepts

The reactor for methanol production has generally a multi-tube design. The reactor is cooled by evaporating water on the shell side. The generated steam can be exported for heat integration.

Since the one-pass conversion for methanol is low, a relevant fraction of unreacted gasses is recirculated after the separation of crude methanol (a mixture of methanol and water) via condensation. Recycle streams are bigger in the one-step process than in the CAMERE one because of the lower conversion per pass, which has clear implications on the size and costs of the unit. Methanol is then separated from water via distillation to meet the purity requirements (generally higher than 99%.wt). The higher water content in crude methanol of the one-step process increases the thermal duty of the distillation unit. Nevertheless, the direct pathway is still more efficient (Anicic et al., 2014) and does not need the RWGS unit.

Alternative reactor concepts at an early research stage are studied to increase the conversion per pass. Selective *in-situ* removal of the reaction products, like water, is beneficial to shift the equilibrium toward the products. Selective water removal would be particularly effective, especially for the one-step process where the water content is particularly high (also 30–40% (Pontzen et al., 2011)). A commercial copper-based catalyst combined with a 3 Å molecular sieve for water removal was also proven to be suitable for selective *in-situ* water adsorption during gas-phase synthesis and increase methanol production (Maksimov et al., 2021). Unfortunately, steam removal via adsorption cannot occur steadily because of the saturation of the sorbent; hence the need for scheduling a periodical desorption phase. These drawbacks can be overcome if steam removal is performed via water perm-selective membranes (Samimi et al., 2018).

5.2.2. Flexible operation of methanol plants

In the following paragraphs, the studies about the flexibility of methanol processes are reviewed, and the key parameters are summarized in Table 2.

Start-up and shutdown

Start-up and shutdown processes of methanol plants are rarely discussed in literature. During the start-up, the reactor has to be heated e.g. via steam, but, to the best of our knowledge, there is no information about the time that is needed. Neither the effects of frequent start-ups are reported in literature since the conventional plants were traditionally operated at steady state. However, it is mentioned that the catalyst suffers from deactivation, especially during idle periods, and it takes more than three days to fully recover its performance from 90% of its activity (Dieterich et al., 2020).

Load changes

Dieterich et al. (2020) reported that some commercial plants have a wide operating range (20–100%); lower part-load limits might be problematic because the higher residence time inside the reactor could increase the risk of hotspot formation (Manenti and Bozzano, 2013). Nevertheless, this is generally not the case for reactors cooled via water evaporation because of the excellent heat transfer coefficient (Dieterich et al., 2020).

Several setups under different operating regimes have been investigated to assess the influence of some variables and novel operating strategies. Manenti et al. (2013) noted from their model of a cooled fixed-bed reactor that a step variation of the shell temperature significantly affects the performance, while a step variation of the feed temperature does not. Furthermore, the settling times for step changes are on the minute scale (Manenti et al., 2013). This short time scale makes methanol plants fast-responsive; these can change their load with high ramp rates (5–13 %/min) (Dieterich et al., 2020).

Seidel et al. (2021) optimized a dynamic model of an isothermal reactor with respect to two objective functions (methanol outlet flow rate and methanol yield based on the total carbon in the feed) by simultaneously and periodically varying the CO concentration in the feed and the total feed flow rate. They showed that this periodic feeding improved the average performance over a period compared with the steady-state operation. For this evaluation, a kinetic model validated against experimental data of dynamic tests (Seidel et al., 2018) was embedded in the model to better predict the catalyst dynamics.

A similar strategy was previously proposed by Velardi and Barresi (2002) for a ring-reactor concept in which the feed stream is fed into one of the three adiabatic reactors without intercooling connected in series. Periodically shifting the feed position forces the reactor network to work in transient. This strategy would allow to use the catalyst uniformly, exploit catalyst thermal inertia to heat the reactants, and enhance the methanol concentration (Velardi and Barresi, 2002; Mancusi et al., 2011). Furthermore, Velardi and Barresi (2002) noted in their simulations that short switching times for the variation of the feed position are beneficial in terms of conversion. Nevertheless, proper switching times and controllers are required to keep the reaction in the stability domain and avoid its extinction (Mancusi et al., 2011).

As an alternative to periodic feeding, fresh feed streams can be injected along the reactor (or between the reactors if in series) to cool the mixture and promote the endothermic RWGS reaction without having too much methane as a by-product (Mignard and Pritchard, 2008).

Other types of reactor networks, e.g., modular reactors in which some reactors can be bypassed in case of reduced feed rates, may offer additional flexibility but also cause higher capital costs (Mbatha et al., 2021).

The presence of distillation units in conventional methanol production is likely to be a bottleneck for faster transients without affecting the methanol purity. This problem could be partially circumvented with the introduction of a tank for crude methanol that decouples the reactor from the purification process (Ausfelder et al., 2015). At the same time, this would make heat integration more complex and expensive (Chen and Yang, 2021) because additional tanks and controllers would be required.

5.3. Syngas

Syngas, a mixture mainly composed of carbon monoxide and hydrogen, is an important intermediate for several chemical synthesis processes, e.g., Fischer-Tropsch and methanol synthesis. Nowadays, syngas is predominantly produced from fossil fuels, i.e., via methane steam reforming or coal gasification, but its production from CO_2 might be an alternative.

5.3.1. Syngas production

Syngas can be produced either chemically or electrochemically. CO_2 electrolyzers can produce syngas with a different H_2:CO ratio according to the operating conditions (Foit et al., 2017; Haas et al., 2018; Dittrich et al., 2019). In the chemical pathway instead, syngas is produced via Reverse Water Gas Shift (RWGS) by reducing CO_2 to CO via hydrogenation. The H_2:CO ratio of syngas depends on the requirements of the downstream synthesis process, e.g., around 2:1 for methanol, DME, or Fischer-Tropsch synthesis. The chemical route to syngas will be the focus of the following paragraphs.

Reaction and operating conditions

Carbon dioxide reduction occurs chemically through the RWGS reaction:

$$CO_2 + H_2 \leftrightarrow CO + H_2O$$

As the RWGS reaction is endothermic, high temperatures are necessary to shift the equilibrium towards products. If the reactor is operated with conventional catalysts below 600 °C, methanation occurs instead of RWGS. Above 700 °C, the main product is carbon monoxide and only traces of methane are produced at atmospheric pressure. Though the equilibrium yield of the RWGS reaction does not depend on pressure (equimolar reaction), the formation of side products like methane does. At high pressures, methanation is relevant at higher temperatures; therefore, the operating temperature of RWGS should be even higher (at least 800 °C) (Kaiser et al., 2013), making heat integration with other process units challenging (see Section 6.1).

Historically, Fe_2O_3/Cr_2O_3 catalyst has been used for RWGS. Several studies on catalysts were carried out to improve both the selectivity and the yield, and to achieve a reasonable conversion rate at lower temperatures while avoiding methanation. A quite recent and detailed review of catalysts and kinetic mechanisms was carried out by Daza and Kuhn (Daza and Kuhn, 2016).

Reactor configurations and process concepts

The main RWGS reactor technologies are fixed and fluidized beds. Typically, the fixed-bed reactor is preferred because of its simple design, but it has some drawbacks such as the need to shut down the plant for replacement of the degraded catalyst and a slower response under flexible operation (González-Castaño et al., 2021).

Fixed-bed reactors can be both adiabatic and heated. In adiabatic reactors, the inlet gas is at high temperatures (up to 1000 °C) and it gradually cools down (e.g., to around 800 °C) during the conversion since the reaction is endothermic (Kaiser et al., 2013). The achieved CO_2 conversion is around 80% and the residence time could be lower than 0.1 s, thus allowing high mass flow rates in compact devices. In heated reactors, heat flux and the outlet temperature can be used to optimize the conversion. Achieving high CO_2 conversion is possible via stream recycling. The crude syngas at the outlet of the reactor is first dehydrated via condensation, and then partially recycled back to the reactor. The feed of over-stoichiometric hydrogen, which should be added to adjust the H_2:CO ratio anyway, helps to reduce the recycle streams. CO_2 and side products are still present in the produced syngas and further separation processes might be needed. Membranes and adsorption methods are generally preferred over absorption and cryogenic methods (Maggi et al., 2020). However, CO_2 removal is not always essential since several downstream processes, e.g., methanol synthesis, can tolerate and/or convert CO_2.

RWGS in chemical looping (RWGS-CL) is an alternative RWGS technology. The hydrogen and carbon dioxide streams are fed into different chambers of the reactor. Hydrogen oxidation and carbon dioxide reduction occur on a catalyst matrix (generally solid iron): hydrogen is oxidized by subtracting oxygen atoms from the iron matrix; carbon dioxide is reduced by inserting oxygen atoms into the matrix. The two streams are then periodically inverted. The unreacted carbon dioxide is then separated from carbon monoxide and re-fed into the reactor; the unreacted hydrogen is dehydrated and recycled into the reactor or mixed with the CO stream to adjust the composition of syngas.

RWGS-CL circumvents the formation of side products like methane since hydrogen and carbon dioxide are not in contact (Daza and Kuhn, 2016). Furthermore, it is particularly suitable for the production of almost pure carbon monoxide (Wenzel et al., 2017a) since there is no direct addition of hydrogen, and the carbon dioxide can be separated, e.g., via membranes. The energy demand for CO_2 separation from the syngas in RWGS-CL is lower than in common RWGS (Wenzel et al., 2017a), though it is a less mature technology.

Wenzel et al. (2017b) experimentally investigated an isothermal RWGS-CL with a modified iron oxide oxygen carrier material and proposed a kinetic model for the temperature range 750–850 °C. Research on catalysts for RWGS-CL is very active. For example, the use of BaFe-hexaferrite allows stable operation at 350–450 °C (Utsis et al., 2020). The best design for a RWGS-CL reactor is also an object of interest (Wenzel et al., 2018).

Finally, promising outcomes could also come from the integration of the carbon capture process with the carbon dioxide reduction one. For example, some adsorbent materials, e.g., Ni/CaO can capture carbon dioxide and release carbon monoxide with good selectivity if treated with hydrogen at temperatures around 700 °C (Bin Jo et al., 2020b).

5.3.2. *Flexible operation of syngas plants*

To our knowledge, the behavior of conventional RWGS units under flexible operation has not yet been treated in the literature. This is likely since syngas is a gaseous intermediate, thus more difficult to store. Therefore, flexible operation of syngas production is likely only an option if the downstream process that converts syngas also operates flexibly.

Despite the lack of studies about flexible RWGS, a few considerations can be done. Since the process is endothermic, the flexible operation should not lead to hot spots at partial load. However, high conversion rates due to higher residence times could lead to an excessive lowering of temperature in the reactor, which could lead to catalyst deactivation. Thermal management could thus be a crucial factor, especially if heat is provided by another process. Furthermore, the presence of a recycle is likely to allow an extension of the operating range, a shortening of transient times, and a damping of fluctuations in analogy with flexible methanation (Section 5.1.3).

In contrast, some information is available about the flexibility potential of RWGS-CL reactors, which are an intrinsically dynamic technology: The yield changes over time even for steady feed streams since the catalyst matrix gradually saturates (Wenzel et al., 2018).

RWGS-CL reactors could be particularly promising for the conversion of green hydrogen thanks to their inherent decoupling of hydrogen conversion and carbon monoxide generation. To ensure the continued operation of the system, the only requirement is that the number of oxygen atoms deposited by carbon dioxide in the matrix is equal to the number of oxygen atoms captured by hydrogen at the moment in which the feed streams are switched. This constraint can still be met if the hydrogen flow rate is variable over time (e.g., according to the availability of renewable electricity): only the integral stoichiometric ratio between carbon dioxide and hydrogen over a phase duration, and not the instantaneous stoichiometric ratio, must be constant. Thus, in case of temporary hydrogen shortage, hydrogen could be used to adjust the H_2:CO ratio of syngas instead of also feeding the RWGS-CL reactor to remove oxygen from the matrix. This technology could potentially deal with variable hydrogen production without the need for hydrogen storage.

5.4. *Ammonia*

Ammonia is one of the most produced chemicals around the world and its production is expected to further grow by 2030 (International Energy Agency (IEA), 2019). Ammonia is widely used in several sectors, e.g., agriculture, plastics production, carbon capture, the capture of nitrogen oxides ($DeNO_x$), refrigeration, and pharmaceuticals (Bennani et al., 2016), and has recently gained attention as possible energy storage (Wang et al., 2017) and energy carrier. Furthermore, ammonia is stable and easy to handle and store as a liquid (Bennani et al., 2016). Its energy density both per unit volume and mass is relatively high and it can be converted back to hydrogen, directly used in fuel cells or as a fuel (Valera-Medina et al., 2018).

5.4.1. *Ammonia production*

Ammonia production is highly energy-consuming (around 2% of the global energy demand (Valera-Medina et al., 2018)) and it is nowadays based on fossil fuels, generally steam reforming of natural gas, while production from green hydrogen is just 0.5% of the total production (Valera-Medina et al., 2018). In the future, green hydrogen could replace hydrogen from steam reforming. The direct electrochemical synthesis of ammonia is also an alternative, but it is less mature (Rouwenhorst et al., 2021; Wu et al., 2021); the latest advances are summarized in a recent review (Ghavam et al., 2021).

In the following paragraphs, the main aspects of the Power-to-Ammonia concept in which hydrogen is electrochemically produced are analyzed.

Reaction and operating conditions

The state-of-art ammonia production is based on the Haber-Bosch process in which hydrogen exothermically reacts with nitrogen to produce ammonia:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

Ammonia synthesis generally occurs at high temperatures (623–823 K) and pressures (100–250 bar) in the gas phase (Valera-Medina et al., 2018). The exothermicity of the reaction implies that lower temperatures are beneficial in terms of equilibrium conversion, but the reaction rates would be slow (Al-Zareer et al., 2019). The reaction generally occurs over Fe-based catalysts; Ru-based catalysts were also proven to be active at milder operating conditions but they are much more expensive (Nishi et al., 2019). Furthermore, impurities, especially oxygen, can poison the catalysts (Grundt and Christiansen, 1982; Morgan et al., 2014). High-purity hydrogen ($>$ 99.999 mol%) and nitrogen ($>$ 99.99 mol%) are required (Morgan et al., 2017). For this reason, nitrogen is generally provided by a cryogenic ASU. The replacement of hydrogen from steam reforming with hydrogen from electrolysis would even reduce the complexity of the plant since hydrogen from steam reforming has to be highly purified.

Reactor configurations and process concepts

Because of the exothermicity of the ammonia synthesis, the reactors have to be cooled. Proper thermal management avoids thermal runaways or instabilities, catalyst deactivation, and reaction extinction. Multiple-bed adiabatic reactors with intercooling stages are generally used for ammonia synthesis (Rouwenhorst et al., 2021). These reactors have a minimum temperature limit in order to have a thermally self-sustaining reaction and avoid its extinction (Cheema and Krewer, 2018). The temperature of each bed can also be optimized; the first bed generally operates at high temperatures (550–550 °C) while the others at milder conditions (Rouwenhorst et al., 2021).

Other less mature reactor concepts like chemical looping (Rouwenhorst et al., 2021; Lee Pereira et al., 2020), enhanced ammonia synthesis via absorption (Palys et al., 2018; Malmali et al., 2018), or 'subzero' reactors without catalyst and with an operating temperature below 0 °C (Al-Zareer et al., 2019) have been proposed.

Since conversion per pass is around 25%, large recycles of unreacted gasses are needed (Morgan et al., 2017; Rouwenhorst et al., 2021). To separate ammonia from unreacted gases, the stream at the outlet of the reactor is cooled at low temperatures (generally lower than -10 °C (Rouwenhorst et al., 2021; Fuhrmann et al., 2013)). High ammonia purity can be obtained ($>$ 99.5%) (Morgan et al., 2017). Ammonia is often stored as a liquid (-33 °C at nearly atmospheric pressure (Morgan et al., 2017)) in tanks in large chemical plants. A cryogenic plant is therefore needed to both cool down the stream and condense the boiloff.

The production of ammonia is possible both in remote places, e.g., islands (Morgan et al., 2014) but also close to industrial parks, which would allow exporting excess heat to other processes or to generate electricity with small-scale power plants (Zhang et al., 2020).

5.4.2. *Flexible operation of ammonia plants*

Ammonia plants have been historically designed for steady-state operation. This fact could affect their state-of-the-art flexibility potential and off-design performance compared with the plants that have been designed by taking into account different working points via the combined design and scheduling (Allman et al., 2019) or the uncertainty of inputs, e.g., power availability (Verleysen et al., 2020).

In the following paragraphs, flexibility aspects of ammonia plants are reviewed, and the key parameters are summarized in Table 2.

Start-up and shutdown

Start-up and shutdown are generally avoided in conventional ammonia plants because of the long times that are needed. These procedures can take several days (Morgan et al., 2017; Armijo and Philibert, 2020). The main reason for the long start-up time is the need of achieving high-purity reactants from the steam reforming and ASU. Furthermore, some time is needed to regenerate the catalyst (oxidized during the shutdown) with hydrogen or syngas (Fuhrmann et al., 2013); this reactivation process can also take 24–30 h (Fuhrmann et al., 2013; Reese et al., 2016).

Since the steam reforming unit is substituted by the PEM-WE in Power-to-Ammonia, the start-up procedure, at least to get pure reactants, could speed up. Significantly shorter start-up procedures (around 12 h and 10 min for cold and warm start-ups, respectively) are claimed for the first large-scale dynamic e-ammonia production plant that will be built in 2023 at Lemvig in Denmark (NEL Hydrogen: Danish dynamic ammonia production is world first, 2022).

Load changes

Large-scale conventional ammonia plants were proven to have an operating range of 60–100% (Ostuni and Zardi, 2012). Lower partial loads have been achieved by reducing the stream fraction that is purged (Verleysen et al., 2021) to accumulate inert gas in the reactor and avoid its overheating. A similar idea was proposed and patented by Ammonia licensor Casale SA (Ostuni and Zardi, 2012): The increase of inert gasses in the reactor by adding argon or nitrogen in excess allows lowering the minimum operating limit down to around 10% of the nominal capacity with only a little increase of the specific energy consumption for ammonia (Ostuni and Zardi, 2012).

Two further load variation techniques have also been proposed, namely, pressure variation and loop parallelization (Rouwenhorst et al., 2019). However, the variation of the pressure of the reaction unit can cause fatigue stress, while loop parallelization is expensive in terms of equipment (Rouwenhorst et al., 2019).

Operation with H_2:N_2 ratios different from the stoichiometric one is possible, even though this causes bigger recycles due to the unreacted gases. Cheema and Krewer (Cheema and Krewer, 2018) showed in their simulative case study that the operating H_2:N_2 ratio range is wide (from 0.4 to 3.2), thus allowing the operation even in case of hydrogen shortage.

As regards the characteristic times to change the load, only little information is present in literature. Armijo and Philibert reported a typical ramp rate value of around 20 %/h of the nominal load (Armijo and Philibert, 2020). Low ramp rates might be due to long settling times. Long settling times (from 0.5–1 h to 4 h (Araújo and Skogestad, 2008)) were also found by Araújo and Skogestad (Araújo and Skogestad, 2008), who modeled an ammonia plant in Aspen Dynamics to test some control strategies in case of disturbances and variations.

6. System perspective: Process integration and flexibility

In the previous sections, we analyzed individually the production of the three considered raw materials, i.e., hydrogen, carbon dioxide, and nitrogen, and their main one-step conversion processes. A similar approach is often found in literature; most studies propose thorough models of just one process step or component by moving the others outside the system boundaries. In contrast, considering heat integration and interfaces between the process steps in terms of temperature, pressure, and purity levels of streams could significantly change the optimal design and make Power-to-X processes even more promising.

6.1. *Process integration for Power-to-X*

Only a few analyses of integrated Power-to-X processes can be found in literature. Adelung et al. (2021) built a model of a Power-to-Liquid process including the electrolyzer, the CO_2 absorption unit, an oxygen burner, and an RWGS unit to maximize the power-to-liquid efficiency by varying the operating conditions and performing heat integration among the units via pinch analysis. Similarly, Marchese et al. (2021) presented an Aspen Plus model including a DAC unit, an RWGS unit, and a Fischer-Tropsch process to assess different configurations for the off-gas recirculation.

A few more process integration and optimization examples can be found for other processes, e.g., methanol. Heat integration between the one-step methanol production process and the carbon capture unit allowed the reduction of 36% of its net thermal demand in Van-Dal et al.́ s case study (Van-Dal and Bouallou, 2013). Chen and Yang (2021) instead optimized the levelized cost of methanol for a Power-to-Methanol concept in which both the electrolyzer and the methanol plant were operated flexibly.

However, most of these simulation-based studies neither consider nor optimize several heat and material interfaces that would improve the efficiency of the overall process. In the following paragraphs, we highlight the main interfaces between the units that should be considered for the analyzed Power-to-X concepts.

6.1.1. *Material streams interfaces*

Purity levels at the interface should be determined by the downstream process/catalyst tolerance. High-purity hydrogen, for example, might be unnecessary in processes in which it is mixed with a carbon dioxide stream that has still some residual water. Oxygen, even if in traces, should be removed from the hydrogen stream in case of risk of catalyst poisoning.

Temperature levels at the interfaces also play a relevant role, especially in energetic and economic evaluations. Some heat exchangers, e.g., intercoolers at the last stage of compression, might be unnecessary if the stream has to be heated afterward.

Also, the operating pressures of the units, e.g., the electrolyzer (see Section 2.2) might be different according to the delivery pressure and the objective function. The optimal delivery pressure itself at which the product synthesis occurs might change if the pressurization unit is considered in a design optimization problem. For example, for a given synthesis process, high pressures may improve the conversion, thus reducing the size of the conversion unit, but they increase the size and operating costs of the compression unit. The choice of the optimal operating pressure is even more important in case of side-product formation or further processing of the product, as for the syngas production via RWGS (see Section 5.3.1) for a Fischer-Tropsch plant.

Finally, side-products of the units could also play a relevant role in improving both efficiency and economic profitability. Oxygen, the main side-product of water electrolysis and ASUs, could be either sold or used for other applications, e.g., wastewater treatment plants (Ausfelder et al., 2015), peroxides products (Ausfelder et al., 2015), medical purposes (Kato et al., 2005), blast furnaces for steel production (International Energy Agency (IEA) 2019), or chlorine production via chlor-alkali electrolysis in the oxygen-mode to reduce the power demand (Brée et al., 2019; Roh et al., 2019a; Brée et al., 2020; Roh et al., 2019b). Furthermore, oxygen could enrich or replace the combustion air of C-based fuels, e.g., biomass, to reduce equipment size and ease CO_2 capture (see Fig. 6). A fraction of the produced oxygen could also be used to oxidize purge streams, which are always present in chemical plants. In this way, heat can be recovered and CO_2 easily captured, thus reducing the direct CO_2 emissions of the process. Argon, another side-product of ASUs, could be stored and used to extend the load range of ammonia plants (see Section 5.4.2) instead of using one of the other two reactants in excess.

6.1.2. Heat streams interfaces

Heat integration is essential for achieving high energy efficiencies. Several options are available among the units of the considered Power-to-X processes, but challenges arise in case of flexible operation and/or the presence of intermediate storage; thus, specific studies should be carried out.

The temperature of the exothermic reaction of both methane and methanol (see Table 3) allows exporting heat to other units, e.g., to the stripper of the carbon capture unit (temperatures around 120 °C), the distillation column for methanol purification (temperatures around 100 °C), or the temperature swing absorption unit for the purification of gases (the temperature depends on the adsorbent material and the component that has to be removed). For some energy-demanding applications like carbon capture stripping, heat from the reactor might not be sufficient. However, additional heat could be provided by other units or burning purge streams.

High-temperature heat from the ammonia reactor could be exported to other processes or used for power generation (Zhang et al., 2020). An example of deep heat and material integration was proposed by Wang et al. (2020); they modeled an efficient Power-to-X process in which ammonia and nitric acid are co-produced.

The large amount of low-temperature heat from the electrolyzer is instead more difficult to use. The electrolyzer could be coupled, for example, with an anaerobic digester, in which the produced biogas is upgraded to methane via hydrogenation (see Section 5.1.2), or low-temperature district heating.

As regards conventional RWGS, the high temperature for the endothermic reactor makes heat integration more challenging. Most common downstream processes using syngas, e.g., a Fischer-Tropsch process, cannot provide such high-temperature heat. Also, the heat from the combustion of purge streams would not likely be sufficient to run the RWGS. Alternatives could come from biomass combustion, new catalysts that are performant even at lower temperatures, electric heating, or completely different technologies, e.g., co-electrolysis.

Among the considered processes, only ammonia plants have a cryogenic cooling demand for separating and storing ammonia; this could be supplied via heat integration with the ASU.

6.2. Flexibility of Power-to-X

Despite the experience gained in the existing Power-to-X plants, dedicated experimental studies of their overall flexibility are still missing. However, as shown in the previous sections, each unit of the considered Power-to-X concepts is suitable for flexible operation, but with different characteristic times and operating ranges (see Table 2). In particular, the electrolysis unit can handle highly fluctuating power profiles while all the other units are at least one order of magnitude slower. This means that the less-responsive unit slows the variation of the load of the electrolyzer unless tanks for raw materials are considered (see Fig. 1c). In fact, storage can decouple the operation of fast-responsive units like the electrolyzers from the less-responsive ones and damp high-frequency fluctuations. Nevertheless, it must be mentioned that the values reported in Table 2 are for state-of-the-art processes. Several possible solutions on different length scales (from the catalyst to the plant scale) could be considered to enhance flexibility (Riese and Grünewald, 2020). Furthermore, novel optimal designs that integrate also information about operation and uncertainties (Mitsos et al., 2018), e.g., the electricity availability and price, could make

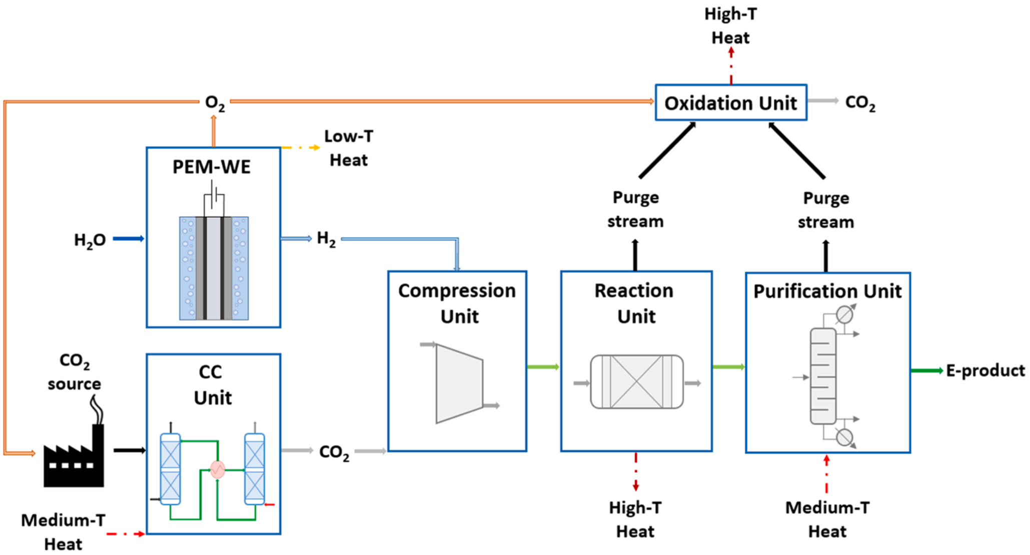

Fig. 6. Simplified sketch of a Power-to-X plant with an exothermic reaction unit for C-based chemicals production. The use of oxygen both for the purge stream oxidation and in the upstream unit that provides CO_2 is shown. The recycling of the additional CO_2 stream from the oxidation unit, as well as heat integration among the units, is instead not shown.

Table 3
Summary of the main characteristics and possible interfaces of the process units of Power-to-X.

	PEM Water Electrolyzer	Carbon capture with monoethanolamine	Cryogenic Air Separation Unit	Methane synthesis (catalytic)	Methanol synthesis	Syngas synthesis, (conventional RWGS)	Ammonia synthesis
Input stream	Water	Flue gas after combustion	Air	Syngas/CO_2-H_2 mixture	Syngas/CO_2-H_2 mixture	CO_2-H_2 mixture	N_2-H_2 mixture
Input stream quality	High purity water	No specific requirements	–	No poisonous components for the catalyst	No poisonous components for the catalyst	No poisonous components for the catalyst	> 99.999 mol% H_2 > 99.99 mol% N_2 (Morgan et al., 2017)
Output stream quality	99.999 mol% H_2 when oxygen traces and water are removed	> 98% (Mostafa et al., 2021) CO_2 stream saturated by steam with monoethanolamine traces	> 99.99 mol% N_2 with traces of oxygen and argon (1–100 ppm) (Haering, 2008)	The achieved purity depends on the requirements. High purity if the residual CO_2 and H_2O are removed	The achieved purity depends on the requirements. High purity (> 99.9%) if CO_2 and H_2O are removed via distillation	The achieved composition depends on the requirements.	Anhydrous NH_3 at 99.5 %, with water and process machine oil traces (Morgan et al., 2017)
Side-products	Oxygen	–	Oxygen, Argon	–	–	–	–
Typical operating temperature range	50–80 °C (International Energy Agency (IEA), 2019)	40–60 °C for the absorber Around 120 °C for the stripper (Lee et al., 2016)	-193 to -173 °C (Haering, 2008)	300–550 °C (Götz et al., 2016)	220–280 °C (Nestler et al., 2020)	700–1000 °C (Daza and Kuhn, 2016)	350–550 °C (Valera-Medina et al., 2018)
Typical operating pressure range	1–30 bar (Carmo et al., 2013) 30–100 bar (International Energy Agency (IEA), 2019)	1–3 bar	4–9 bar in the rectification section (Haering, 2008)	1–100 bar (Götz et al., 2016)	50–100 bar (Nestler et al., 2020)	1–10 bar	100–250 bar (Valera-Medina et al., 2018)
Relevant energy inputs	Electricity: 4.2–5.6 kWh/Nm^3 H_2 (Carmo et al., 2013)	Electricity: 80–130 kJ/t CO_2 (Lee et al., 2016) Heat: 2.2–3.8 GJ/t CO_2 (Lee et al., 2016)	Electricity: 0.15–0.25 kWh/m^3 N_2 at 8 bar (Haering, 2008)	–	Electricity for the compression of the reactants; Heat for the distillation unit	Heat for the endothermic reaction	Electricity for the compression of the reactants and for the refrigeration unit

Power-to-X processes more flexible and economically viable.

Among the considered Power-to-X routes, Power-to-Methane and Power-to-Methanol are the most flexible both in terms of operating range and possible ramp rates; thus, these plants may handle quite variable fluctuating inputs, and a relatively small storage capacity for raw materials would be needed.

Despite storage might not be needed in fast-responsive plants, it could still play a role in the reduction of operating costs and tackling variability. The reactants could be produced in excess and stored during cheap electricity price hours or renewables availability to be then converted into chemicals at a later time. However, the best configuration (Fig. 1c, d) highly depends on the case study, plant location, and considered costs for storage. Despite this key role, the optimization of storage capacity in Power-to-X concepts has been considered in only a few recent works (Osman et al., 2020; Gorre et al., 2019; Chen and Yang, 2021; Li et al., 2020).

Finally, dedicated studies and experimental works on the flexibility of entire Power-to-X processes should be carried out to assess and eventually exploit the real potential of these technologies. In fact, the different operating ranges of the units affect the flexibility of the whole Power-to-X plant, as shown by Herrmann et al. (2020) for a Power-to-Methane case study without storage. Also, the role of process integration between the units should be investigated because it could affect flexibility and operation in off-design conditions.

7. Conclusions

Power-to-X is a promising pathway to bring renewables into different industry sectors, provide long-term high-capacity energy storage, and support grid stability. In this article, technologies for key components of such Power-to-X systems were reviewed: the production of hydrogen via PEM-WEs, provision of CO_2 and N_2 as additional raw materials, and the main one-step Hydrogen-to-X processes, i.e., methane, methanol, syngas, and ammonia production. Particular attention was paid to the capability of these processes to be operated flexibly and the perspective of integrating processes to achieve higher efficiencies and cost-effectiveness.

From the analysis, the following conclusions can be drawn and open research questions raised:

- PEM water electrolyzers, if equipped with suitable power electronics, can be flexibly operated up to providing ancillary services. Further research is needed to reduce noble metals loadings and costs, improve their efficiency, and shed light on degradation under flexible operation.
- The investigation of the flexibility of Hydrogen-to-X processes is still at an early stage. Most of the works are simulative while only a few are experimental, which means that the validity of some of the findings should still be assessed experimentally. Under this caveat, the main parameters of the flexibility of the plant units at the current state have been summarized in Table 2, and some interesting aspects can be pointed out:
  - Chemical e-methane production seems to be suitable for flexible operation even on a short timescale (minutes) if care is paid to the thermal management of the reactor because of the risk of hot spots and reaction extinction. Warm and cold start-ups can be potentially carried out in a few minutes; however, their impact on catalyst deactivation should be investigated.
  - Biological methanation is not suitable for quick load variations of the methane production rate. However, the large size of reactors could serve as buffer in case of fluctuating hydrogen production if the reaction time of the biological system is much higher than the time of fluctuations.
  - E-methanol processes are suitable for flexible operation. Storing crude methanol and operating the distillation column as steadily as possible could be an interesting option to still meet the purity

  requirements and quickly vary the feed flow rate of the reactants. In that case, the main problem would be due to the typical heat integration between the reboiler and the reactor. Also, frequent idle periods and start-ups do not seem appropriate since the catalyst suffers from deactivation.
  - Literature about the flexibility of e-syngas plants is almost absent since it is an intermediate product and it is not easy to store as a gas. Nevertheless, some technologies like RWGS-CL could be suitable for variable H_2 inputs. However, flexible operation of the e-syngas production should be considered together with the downstream synthesis process since syngas is not the final product.
  - E-ammonia production with conventional designs seems to be less flexible than the other processes because of the longer transients. Furthermore, it is not particularly suitable for frequent start-ups because of the long periods for reactivation of the catalyst and meeting the purity targets.
- The considered Power-to-X processes are, therefore, suitable for flexible operation to some extent, and can deal with renewables. Further research on catalysts, process designs, and process control could increase this potential. Their flexibility could reduce the need for storage of raw materials and enhance the economic competitiveness of these processes, especially if information about flexible operation is already considered in the design phase of the whole Power-to-X plant. The economic viability of these routes compared to the traditional fossil-based ones remains the main obstacle to real implementation.
- Only a few studies consider process integration among different units of Power-to-X plants. A plant design that optimizes heat integration among the units and the stream interfaces (e.g., purity, temperatures, and pressures) could lead to more efficient and competitive configurations than those that have been analyzed to date. For this purpose, the main opportunities for heat and stream integration have been highlighted.
- For integrated processes, flexible operation is even more challenging. Therefore, optimal solutions need to be identified and also investigated experimentally to assess their viability.

CRediT authorship contribution statement

Simone Mucci: Writing – original draft, Conceptualization, Investigation, Visualization. **Alexander Mitsos:** Writing – review & editing, Conceptualization, Funding acquisition. **Dominik Bongartz:** Writing – review & editing, Conceptualization, Funding acquisition, Supervision, Project administration.

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.

Data availability

No data was used for the research described in the article.

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