

Hydrogen from natural gas and biogas: Building bridges for a sustainable transition to a green economy

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ABSTRACT

Hydrogen (H_2), more than a promising solution, has been considered one of the pillars to reduce CO_2 equivalent emissions (CO_2 -eqv) in hard-to-abate sectors like transportation, petrochemical, steel, and cement. The feedstocks, the greenness of the energy consumed, the synthesis pathway, and the mitigation strategies used during its synthesis will be determinant to reduce its environmental footprint. In 2021, the production of H_2 reached 900×10^5 t; 60% of this production was synthetized from natural gas through reforming processes, which consumed 205×10^9 m³ of natural gas and 110×10^7 m³ of H_2O , and generated 556×10^6 t CO_2 and profits for 118 billion US dollars. In 2050, the Net Zero Emissions (NZE) scenario projected by the International Energy Agency (IEA) for the energy sector will demand 530×10^6 t H_2 ; 60% of this demand will be satisfied by electrolytic processes launched by green energy sources (wind, solar, hydro, and biomass) and the rest by reforming processes that use environmental mitigation technologies, like carbon capture utilization and storage (CCUS). The latter suggests that the non-renewable methane (CH_4), the biomethane (bio- CH_4), and biomass gasification processes will be key to lead the gradual decarbonizing of the economy. This work depicts the current status of mature and emerging reforming technologies to produce H_2 and focuses on the environmental implications of H_2 production from feedstocks like gas and biogas.

1. Introduction

The variation in the demand of the main energy commodities and the transition among them is a complex process that can take years and usually responds to scientific, social, economic, political, and environmental type factors (Fig. 1a) (Blazquez et al., 2020; Chlebna and Mattes, 2020; García et al., 2020; Gürsan and de Gooyert, 2021). As shown in Fig. 1 (b and c), participation of renewable sources in the primary energy mix and in the production of electricity of each country is variable (IEA, 2019; IPCC, 2021; IRENA, 2022). It is clear that the transition to sustainable and low-cost energy sources would be a key factor to boost the global economy and minimize the impacts associated with the climate change (Dawood et al., 2020; Karaca et al., 2020; Khan et al., 2021; IRENA, 2022). Limiting global warming to 1.5 °C implies a 40–60% reduction in greenhouse gas (GHG) emissions for the year 2030, and reaching net emissions close to zero by 2050 (IEA, 2019; IRENA, 2022; Pablo-Romero et al., 2021). Although the annual growth rate for atmospheric carbon dioxide (CO_2) has been kept relatively constant in the

last decade (2.4 ppm/yr), its concentration reached a record value of 419 ppm in June 2022 (GML, 2022; IPCC, 2021).

The idea of using H_2 as an energy carrier was first conceived by John Bockris in the 70s (Bockris, 2013); for its implementation it would be fundamental to produce it at a large scale from renewable and low-cost resources and to develop safe alternatives for its storage, transport, and end use (Gondal et al., 2018; IRENA, 2022; Moradi and Groth, 2019; Widera, 2020). Although technical, economic, and environmental drawbacks have been identified, H_2 remains a convenient candidate to decarbonize or at least reduce GHG emissions in strategic sectors like transportation, petrochemical, and steel industries (Dawood et al., 2020; Gondal et al., 2018; IEA, 2019; IRENA, 2022; Velazquez and Doods, 2020).

Hydrogen, more than a green fuel, is a chemical energy carrier; for this reason, it can be converted into electricity, key substances for the petrochemical industry, and multiple goods and services (Fig. 2) (Guban et al., 2020; IRENA, 2022; Karaca et al., 2020; Nuttall and Bakenne, 2020). Like any other carrier, each time it is used, its energy content is

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reduced (IRENA, 2022; Nuttall and Bakenne, 2020; Velazquez and Doods, 2020). For example, production of H₂ through electrolysis and its transformation to electricity in a combustion cell would recover 70% of the energy originally present in the H₂ (IEA, 2019).

In the literature, definitions like green H₂ refer to its production via electrolysis, using renewable electricity (IEA, 2019; IRENA, 2022; Velazquez and Doods, 2020). The grey, black, and brown H₂ reveal that the raw materials used are of non-renewable nature like gas, coal, lignite, respectively (Fig. 2). The blue H₂, although generated from gas through reforming, presents less emissions due to the implementation of CCS (carbon capture and storage) techniques. Finally, the turquoise H₂ is generated by methane (CH₄) pyrolysis, whereas the pink and yellow one is used as a label for the H₂ generated through electrolysis using nuclear energy and the reference energy mix for each country, respectively (Fig. 2) (IEA, 2019; IRENA, 2022; Velazquez and Doods, 2020).

The demand of pure H₂ is of 700×10^5 (t/yr) and has a value close to 118 billion US dollars; its market has shown a growth of 6% annually due to the demand of the industry (petrochemical, ammonia, and steel) and the transportation sector (IEA, 2019; IRENA, 2022). Of the H₂ produced each year, 96% comes from non-renewable sources like gas, petroleum, and coal (IEA, 2019; IRENA, 2019, 2022). Only the H₂ produced by methane reforming consumes 205×10^9 (m³/gas) and generates 556×10^6 (t CO₂); these exceed about 10% the emission of Germany in 2018 (IEA, 2019).

Transition to a H₂-based economy will be a complex process because, in many countries, the fossil-fuel industry must undergo a deep restructuration to endorse the shift to a greener society. Every pathway,

renewable or non-renewable, available to support the H₂ transition should consider realities like the impact of climate change in productive sectors, the availability of commodities required to produce green energy and technological devices, as well as the ability of each country to innovate, develop, and integrate value chains around green H₂ (IEA, 2022). Currently, H₂ produced from fossil fuels still needs to be greener than the electrolytic one. Nonetheless, its technological maturity and the available infrastructure, the use of carbon capture and storage, the adoption of less energy-intensive pathways, and the development of novel catalytic materials and reactors evidence the renewed interest in reforming technologies. This is why gas and biogas will play a key role in the decarbonizing of the economy in the next 50 years (Gürsan and de Gooyert, 2021; IEA, 2022; IRENA, 2022).

Previous studies discussed the potential benefits and limitations of emerging technologies to cope with the transition to a green H₂ economy. Furthermore, some works depict the current status of mature and emerging reforming technologies to produce H₂ from non-renewable resources like natural gas, coal, and oil. This work focus on the selection and study of reforming pathways that could support and lead to the decarbonizing of the economy. In this work, mature (steam methane reforming: SMR) and emerging technologies (partial oxidation: POX, catalytic partial oxidation: CPOX, autothermal reforming: ATR, dry reforming: DR, bi-reforming: BR, and tri-reforming: TR) for the production of H₂ from gas and biogas are considered. The present study not only aims at reviewing the evolution (2003–2023) in terms of technical advantages and drawbacks but also focuses on the practical implications of H₂ from gas/biogas via reforming as a transitional solution in the race

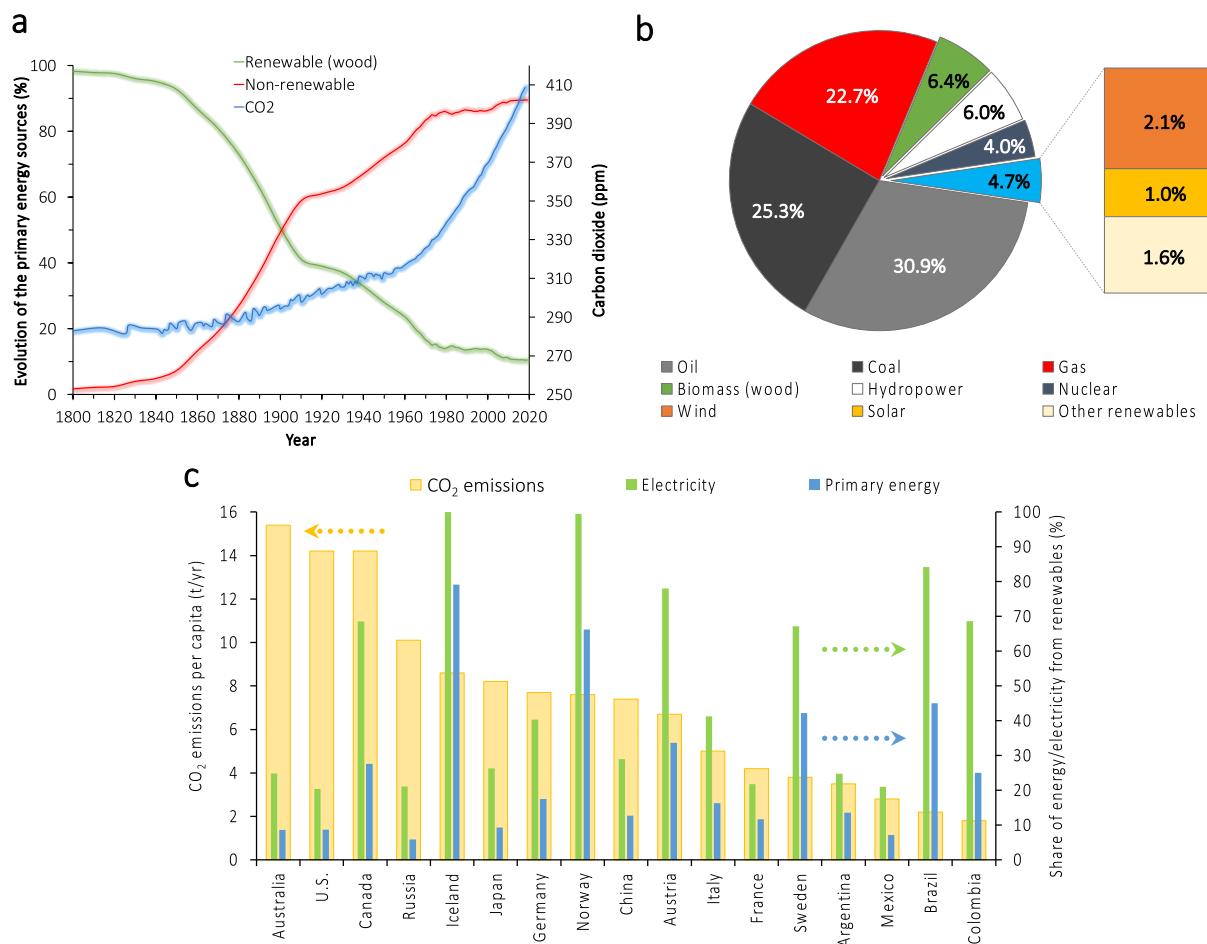


Fig. 1. General indicators on the use of energy. a) Evolution of the participation of the main commodities in the primary energy mix. b) Participation of different sources in the production of primary energy. c) Sustainability indicators for electricity production.

to decarbonize the economy. Finally, this work details, from a life cycle assessment perspective, the relevant environmental outcomes of mature and emerging reforming technologies to guide stakeholders about the impact of transitional pathways for H₂ synthesis.

1.1. Research methodology

In this work Scopus (Sc) and Web of Science (WoS, core collection) were employed to acquire the documents (articles, books, chapters of books, proceeding) required for the study. The search was conducted from 2003 to 2023. To maximize the chance of finding relevant documents, the search for the term “hydrogen” was performed within titles, abstracts, and keywords. We applied the protocol proposed by Paul et al. (2021), which consists of the following steps: i) assembling (identifying and acquiring of documents), ii) arranging (organization and screening of documents), and iii) assessing (includes valuation and reporting).

Due to the high number of documents available in Sc (1,454,917) and WoS (768,024), we screened and analyzed the preliminary mined information. Only publications in English related to the production of H₂ from natural gas and biogas were considered; the exclusion criteria reduced the number of documents to 2483 (Sc) and 2437 (WoS). The second screening allowed organizing the information as a function of the most relevant topics for the study: catalytic reforming (Sc: 158, WoS: 250), partial oxidation (Sc: 37, WoS: 163) and catalytic oxidation (Sc:

31, WoS: 75), autothermal reforming (Sc: 14, WoS: 32), dry reforming (Sc: 117, WoS: 234), bi-reforming (Sc: 6, WoS: 10), and tri-reforming (Sc: 9, WoS: 28). Regarding the environmental performance of the processes, we considered as key words each one of the production processes and the terms life cycle assessment (Sc: 1178, WoS: 1429) and environmental footprint (Sc: 1490, WoS: 898).

In the screening rounds, all duplicated documents were excluded, those not totally available were discarded, and the abstracts were reviewed to ascertain their pertinence. A co-occurrence analysis for keywords developed in VOSviewer (Van Eck and Waltman, 2010, 2014) is presented in the supplementary material (Fig. SM1); this diagram included a “thesaurus” to eliminate duplicated words. The following results can be found as supplementary material: a word cloud (Fig. SM2), top journals (Fig. SM3) and contributing countries (Fig. SM4), and the citation report retrieved from WoS (Fig. SM5). The final document included 362 references from articles (316), books (23), technical reports (15), chapters of books (7), and specialized web sites (1).

1.2. H₂ synthesis from non-renewable raw materials

Hydrogen can be produced either directly or indirectly from renewable and non-renewable resources (Fig. 3) (Abdin et al., 2020; Gondal et al., 2018; Winter, 2009; Yukesh-Kannah et al., 2021).

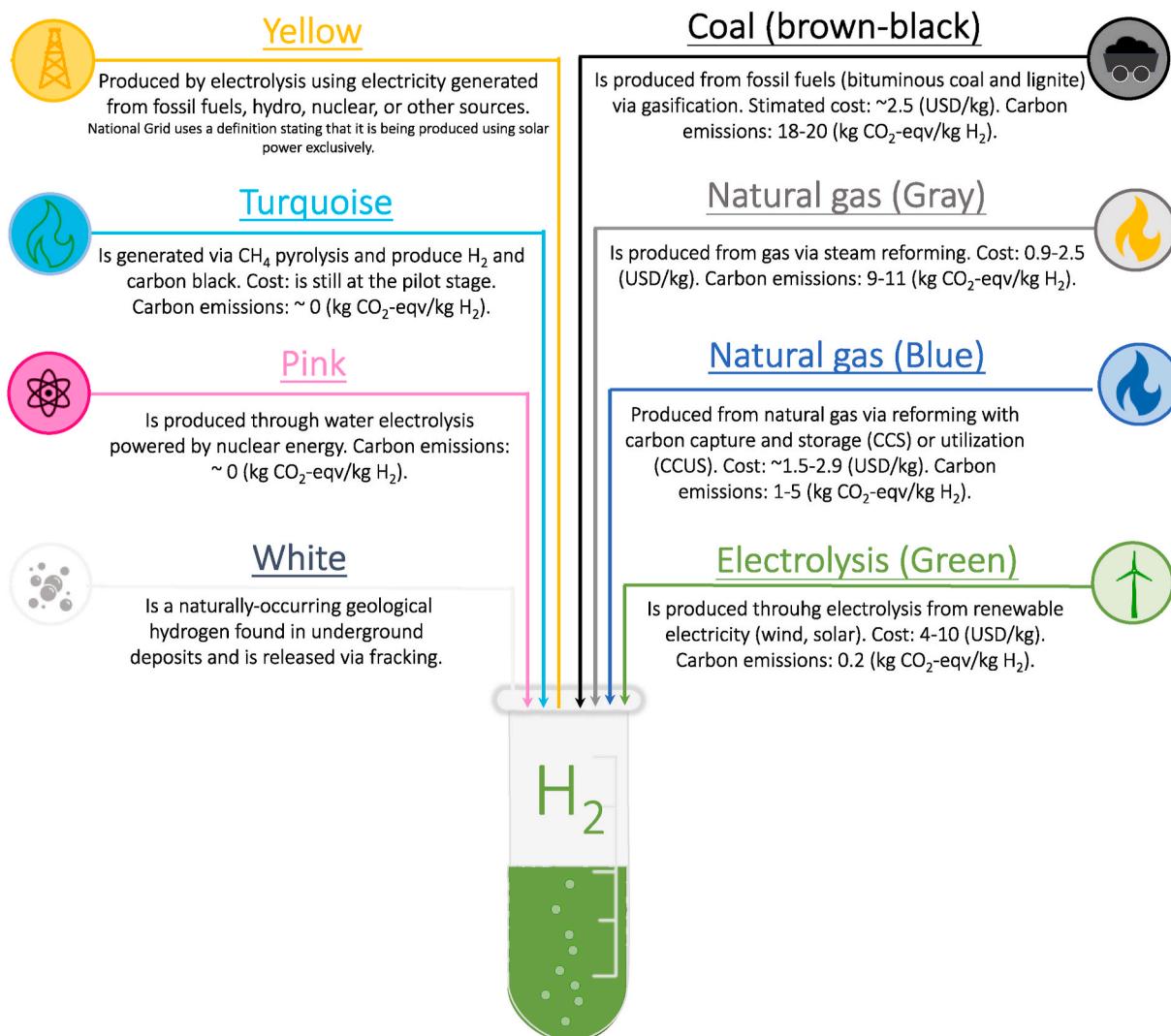


Fig. 2. Color code suggested in the literature for H₂.

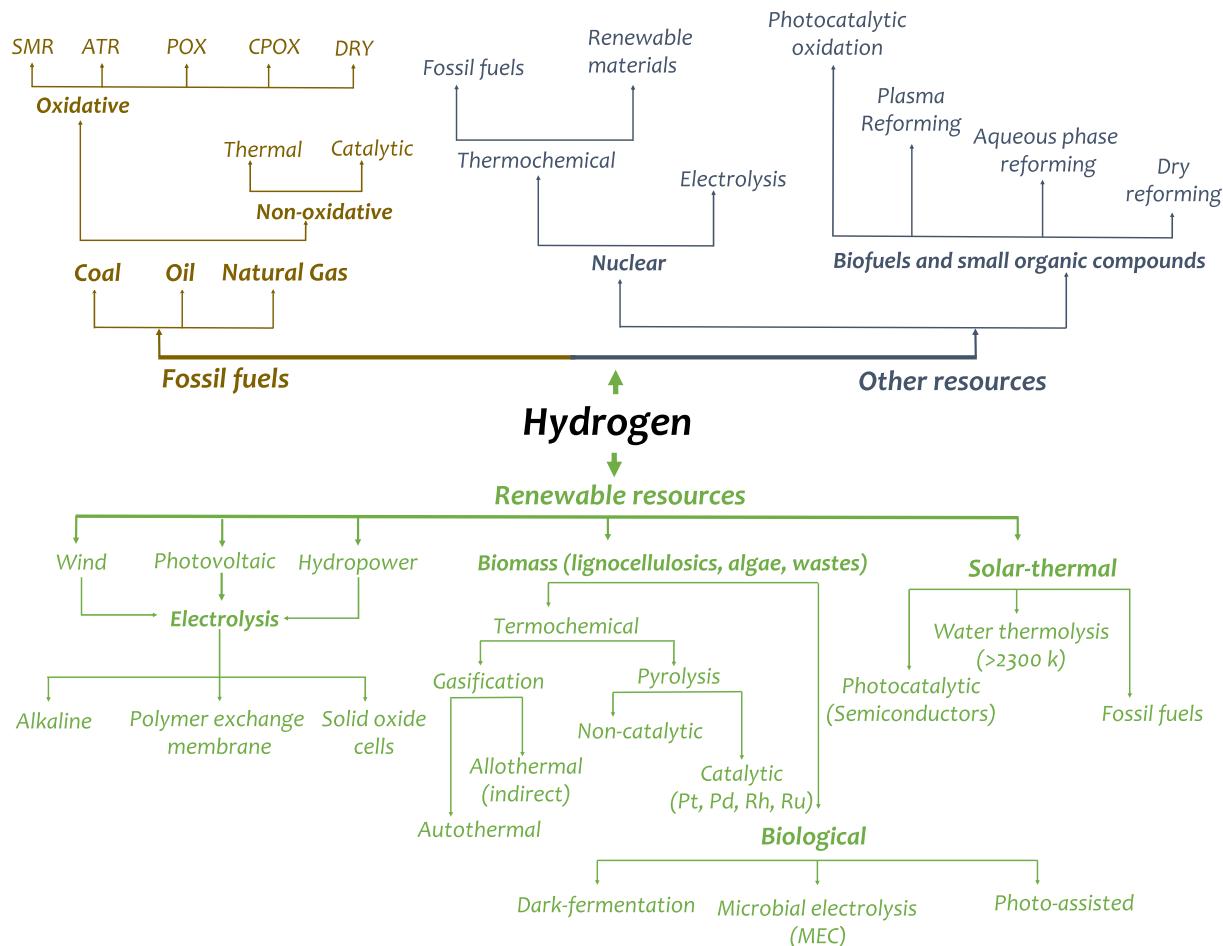


Fig. 3. Summary of alternatives for H₂ synthesis.

Although the interest to produce H₂ at a large scale has been expressed since the mid 70s, its use in a mixture (H₂: 45–50%, CH₄: 28–30%, CO₂: 16–19%, CO: 1–3%) dates back to 1800 and continued until 1900 (Demirbas, 2009; Gupta, 2009; Liu et al., 2010; Sherif et al., 2014). Most of the produced H₂ is synthetized from gas (49%), liquid hydrocarbons (29%), and coal (18%) using reforming processes (Demirbas, 2009; IEA, 2019; Sherif et al., 2014).

The processes pointed out on Table 1 operate at high temperatures and pressures; however, only the used oxidant will determine whether the process is endothermic (H₂O, CO₂), exothermic (O₂), or with an almost thermo neutral effect (mixtures: O₂–H₂O and CO₂–H₂O) (Gupta, 2009; Liu et al., 2010; Sherif et al., 2014; Silveira, 2017).

1.2.1. Natural gas

The term natural gas or simply gas refers to a mixture constituted by CH₄ and to a lesser degree ethane (C₂H₆), propane (C₃H₈), isobutane (C₄H₁₀), butane (C₄H₁₀), and isopentane (C₅H₁₂) (Table 2) (Speight, 2019). Gas can be classified, according to its origin, as conventional or non-conventional; the conventional gas can be associated with petroleum (associated gas/wet gas) or contain insignificant amounts of it (non-associated gas/dry gas) (Faramawy et al., 2016; Speight, 2020). The proportion of CH₄ present in the associated gas is lower than that reported for non-associated sources, whereas the content of larger molecular weight gases is usually higher in the associated natural gas than in the non-associated one (Table 2).

The non-conventional sources of natural gas are commonly found at high depths in low porosity and low permeability formations; for this reason, these deposits must be fractured to extract the gas profitably (Shah, 2017; Speight, 2019). At least six types of non-conventional

sources are reported in the literature: i) shale gas, ii) coalbeds, iii) tight gas, iv) deep gas, v) gas in geopressured zones, and vi) gas hydrates (Faramawy et al., 2016; Speight, 2019; Viswanathan, 2017).

In 2018, the proven gas reserves attained 197×10^{12} (m³) whereas its annual production reached 3867×10^6 (m³/yr); at the rate of current consumption (3%), the reserves will be depleted in 50 years (BP, 2020; IEA, 2019). Currently, 80% of the gas demand is covered by conventional sources; however, it is expected that in the coming years the non-conventional sources will represent a much more significant share (BP, 2020; Chong et al., 2016; Speight, 2019, 2020). Fig. 4 shows the evolution of gas production and its participation in the global energy market; additionally, the insert depicts the value of the R/P (reserves-to-production) ratio and the participation of each region in the total reserves (BP, 2020). It must be pointed out that the R/P ratio establishes, for a country or a region, the duration of its reserves at the current consumption rate (BP, 2020). Natural gas has a large number of applications at the industrial level, but most of its production is aimed at the generation of electricity (48%), the chemical industry (27%), the transportation and communication sectors (11%), and for the production of energy at the residential (9%) and industrial (5%) levels (BP, 2020; IEA, 2019; Taifan and Baltrusaitis, 2016).

1.2.2. Biogas

The term biogas refers to a gaseous stream, composed mainly of CH₄, CO₂, and H₂O that is generated during the biodegradation of organic substrates in anaerobic conditions (Abbasi et al., 2012; Akunna, 2019; Rosato, 2018). Although the decomposition of organic substances generates biogas, this term is used more to denote a mixture composed of CH₄ and CO₂ (Abbasi et al., 2012; Akunna, 2019). The calorific value of

Table 1Summary of the main available processes for H₂ synthesis from methane.

Process	Operating conditions	Catalyst/support	Efficiency (%)	H ₂ :CO ratio	Investment Costs ^[1] (%)	Cost (USD/kg H ₂)	Main characteristics
Steam Methane Reforming (SMR)	T = 700–1100 °C P = 3–25 bar H ₂ O:CH ₄ = 2.5–3.0	Typical catalyst = 12–20% Ni as NiO. Typical support = α-Al ₂ O ₃ , MgAl ₂ O ₄ , ZrO ₂ . Catalyst HTS=Fe ₂ O ₃ –Cr ₂ O ₃ . Catalyst LTS = Cu-ZnO-Al ₂ O ₃	75–85%	3:1	100	1.00 ^[2] –1.50 ^[3]	Is an energy- intensive process. SMR is typically limited by mass and heat transfer. It is widely used for hydrogen production. Intensification reduces cost and improves energy use. Degradation of the catalyst due to hot spots. CO ₂ adsorption can retard the accumulation of carbon on the catalyst surface. Depending on the feedstock composition some purification steps must be performed.
Partial Oxidation (POX)	T = 1000–1500 °C P = ~1 bar	Typical catalyst: Ni and Pt. Typical support: α-Al ₂ O ₃ , MgO, CeO ₂ ,	60–75%	2:1	80–100	~1.00	Syngas production via the POX route is an established technology. Hot spots have a negative effect on the catalyst stability.
Catalytic Partial Oxidation (CPOX)	T = 700–1100 °C P = 3–25 bar	Catalyst: Ni, Pd, Pt, Rh, and Ru. Support: α-Al ₂ O ₃ , La ₂ O ₃ , CeO ₂ , ZrO ₂ .	60–75%	2:1	55–80		POX reactors have a fast start-up. High cost of pure oxygen and purification step. Developed for dealing with a variety of hydrocarbon sources. The level of sulfur must be low. Developed for dealing with a variety of hydrocarbon sources.
Autothermal Reforming (ATR)	T = 1100–2000 °C P = 80 bar H ₂ O:CH ₄ = 0.5–3.5 O ₂ :CH ₄ = 0.4–0.6	Catalyst: Ni, Pt, Co, Ru, Rh, Pd Support: α-Al ₂ O ₃ , Ce–ZrO ₂ , Ni–CeO ₂ , CeO ₂ –ZrO ₂ –SiO ₂ .	60–75%	1.1:2.1	65–80	1.90–2.5 ^[4] 5.32 ^[5]	ATR operates ideally at a thermoneutral point, neither consuming nor releasing external energy. This process may have a rapid start-up. High cost of noble metal-based catalyst. ATR combines desirable features of SMR and POX. It has a compact design. Degradation of the catalyst because of hot spots. CO ₂ adsorption can retard the accumulation of carbon on the catalyst surface.
Dry Reforming (DR)	T = 800–1100 °C P = 20–40 bar ^[6] CH ₄ :CO ₂ = 1:1	Catalyst: Ni, Co, Rh, Ru, Pt Support: α-Al ₂ O ₃ , MgO, TiO ₂ , SiO ₂ , ZrO ₂ MgAl ₂ O ₄ , MgO-γ-Al ₂ O ₃ . Promoter: Alkaline and alkaline earth metals.	60–75%	1:1	–	–	Is an energy intensive process that uses two greenhouse gases to produce hydrogen. High temperature is required to obtain a high conversion. Carbon formation, moderate selectivity and H ₂ consumption by side reactions are considered drawbacks. Promoters such as alkaline and earth metals may reduce/ avoid carbon formation.

Note: ^[1]These costs were calculated taking SMR as reference. ^[2]Without CCS. ^[3]With CCS. ^[4]Hydrogen (100 Nm³ H₂/h) production from biogas. ^[5]Hydrogen (50 Nm³ H₂/h) from biogas. ^[6]Dry reforming may occurs at 600–900 °C at atmospheric pressure.

Table 2

Typical composition of natural gas.

Compound	Formula	Composition (%)							
		Typical ^[1]	Associated ^[2]	Non-associated ^[3]	Gas hydrate ^[2]	Shale gas ^[4]	Coalbed gas ^[5]	Wellhead ^[2]	Pipeline ^[6]
Methane	CH ₄	87–96	70–98	97.9	98.6	79–96	63–99	70–98	95–98
Ethane	C ₂ H ₆	1.8–5.1	1–10	0.266	0.1	3–16	0–0.02	1–10	2–5
Propane	C ₃ H ₈	0.1–1.5	0.01–5	0.053	0.1	1–4	–	0–5	0.5–1.5
n-Butane	C ₄ H ₁₀	0.01–0.3	0.01–2	0.009	–	–	–	0–2	0.2–0.5
i-Butane	C ₄ H ₁₀	0.01–0.3	–	0.022	–	–	–	0–2	0.2–0.5
n-Pentane	C ₅ H ₁₂	0.001–0.04	0.01–1	0.002	–	–	–	0–1	–
i-Pentane	C ₅ H ₁₂	0.001–0.14	–	0.008	–	–	–	0–1	–
Carbon dioxide	CO ₂	0.1–1.0	0.01–1	0.199	0.5	5–11	0.1–15	0–3	0.5–2
Oxygen	O ₂	0.01–0.1	–	–	–	–	–	–	–
Nitrogen	N ₂	1.3–5.6	0–15	1.476	0.7	0.2–0.4	0.9–1.4	0–15	0.5–1.5
Hydrogen sulfide	H ₂ S	0.001–0.1	–	–	–	–	–	0–2	200–300 ^[6]

Note: ^[1]Viswanathan (2017); ^[2]Speight, 2019; ^[3]Cadavid and Amell, 2019; ^[4]Costa et al., 2016; ^[5]Yan et al., 2012; ^[6](μ⁸/m³).

a biogas is determined by its CH₄ content whereas the presence of impurities (CO, CO₂, N₂, H₂O, H₂S, NH₃), even in trace amounts, determines its quality and possible exploitation (Table 3) (Capa et al., 2020; Chioldo et al., 2017; Kapoor et al., 2019; Nahar et al., 2017; Rosato, 2018; Ullah-Khan et al., 2017). The calorific value of biogas (12–20 MJ/kg) is lower than that reported for CH₄ (50–55 MJ/kg), natural gas (42–55 MJ/kg), or a conditioned biogas (42–50 MJ/kg) (Wellinger et al., 2013). In developing countries, biogas is utilized without previous treatment for cooking; alternatively in industrialized

countries, biogas is conditioned to bio-CH₄ and used as fuel for cars, buses, or trucks, or to generate electricity (Nguyen et al., 2021).

As shown in Table 3, some impurities in biogas are linked to an increase in deleterious effects on human health (respiratory diseases, cardiovascular mortality), damage to ecosystems due to acidification, eutrophication, and land transformation processes (Huijbregts et al., 2017). The work performed by Macor and Benato (2020) suggests that emissions of regulated (NO_x, CO, SO_x, HCl, and particulate matter) and unregulated (polycyclic aromatic hydrocarbons, aldehydes, dioxins, and

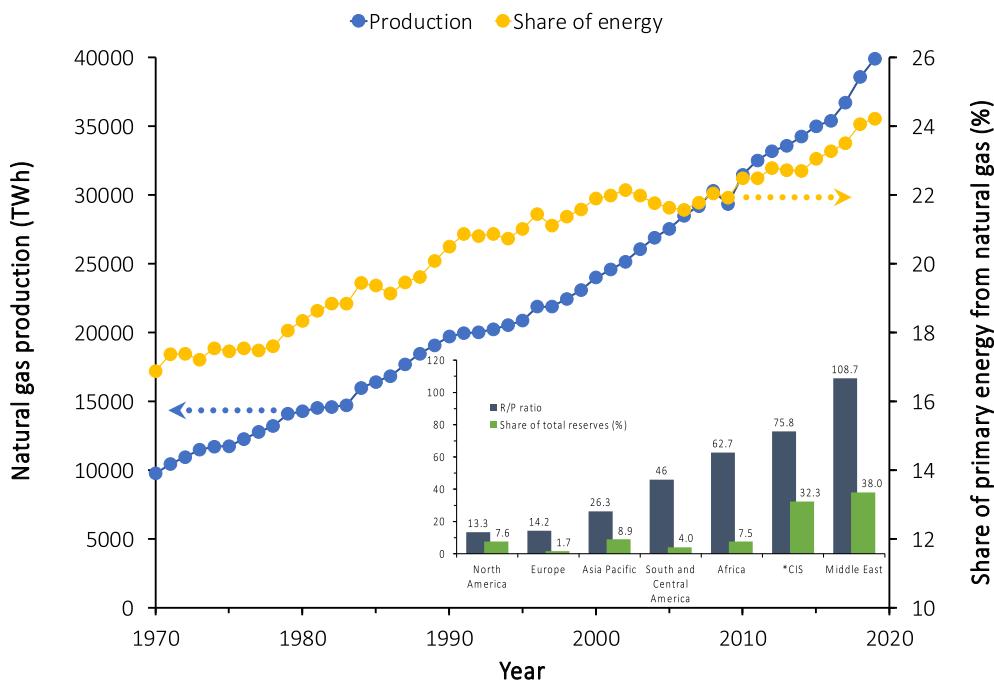
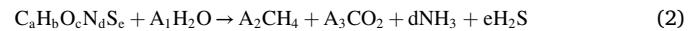
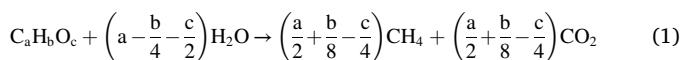


Fig. 4. Tendencies in the production and consumption of natural gas.

furans) substances is higher in combustion engines fed by biogas. On average, biogas oxidation exhausts more NO_x (3 times), CO (3 times), and formaldehydes (5 times); furthermore, the toxicity analysis of unregulated substances reveals that biogas emissions could be 10-times more toxic than natural gas (Macor and Benato, 2020). The latter is in line with the data reported for combined heat and power plants (<25 MW), where the emission level is higher than with gas engines.

The integration of conventional purification and upgrading methods (physical scrubbing, chemical absorption, membrane technologies, pressure swing absorption) to anaerobic plants led to an effective removal of impurities (mainly H_2S and CO_2) with high to medium cost (Turco et al., 2016; Yadav et al., 2022); nevertheless, membrane bio-reactors appear to be more advantageous due to the cost, simultaneous H_2S and NH_3 removal, and reduction of environmental impacts of the process due to lower energy and resources consumption (Das et al., 2022). In the literature, the contribution of biogas to sustainable development goals (SDG) is highlighted, such as SDG-6: Clean water and sanitation, SDG-7: Affordable and clean energy, SDG-9: Industry, innovation, and infrastructure, SDG-11: Sustainable cities and communities, SDG-12: Responsible consumption and production, and SDG 13: Climate action (Nadaleti et al., 2021; Cudjoe et al., 2022; Obaideen et al., 2022). In addition, several studies highlight the sustainability of biogas and H_2 supply chain (Aziz et al., 2020) and the potential of wastes to provide sustainable energy and reduce fossil fuels dependency (Nadaleti et al., 2021; Cudjoe et al., 2022).

As shown in Table 4, it is feasible to produce biogas from diverse substrates; likewise, it is possible to establish the potential of the theoretical methane production (TMP, L $\text{CH}_4/\text{g V}_S$) from a substrate based on its elemental composition using the Bushwell equation (Eq. (1)) and its extended model (Eqs. (2) and (3)), either using the composition of the organic fraction (Eq. (4)) or from the chemical oxygen demand (COD) of the substrate (Eq. (5)) (Akunna, 2019; Rosato, 2018; Weinrich, 2018). In Eq. (5), R is the universal gas constant (0.083 bar L/mol K), T is the temperature (K), P is the pressure (bar), and V_S is the amount of organic matter expressed as volatile solids (g).



$$\text{A}_1 = \left(a - \frac{b}{4} - \frac{c}{2} + \frac{3d}{4} + \frac{e}{2}\right), \text{A}_2 = \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3d}{8} + \frac{e}{4}\right), \text{A}_3 = \left(\frac{a}{2} - \frac{b}{8} + \frac{c}{4} + \frac{3d}{8} + \frac{e}{4}\right) \quad (3)$$

$$\text{TMP} = 415(\text{Carbohydrates \%}) + 496(\text{Proteins \%}) + 1014(\text{Lipids \%}) \quad (4)$$

$$\text{TMP} = \left[\frac{\text{COD}}{64 \text{ g/mol}} \right] \left(\frac{\text{RT}}{\text{PV}_S} \right) \quad (5)$$

The CH_4 and CO_2 ratio found in biogas does not depend only on the composition of the organic matter; in general, aspects like the complexity of the substrate, the presence of inhibitors, the substrate-microorganism relation, temperature, pH, and the oxidation-reduction potential also affect CH_4 production (Achinas and Euverink, 2016; Akunna, 2019; Weinrich, 2018). For example, a carbohydrate ($[\text{CH}_2\text{O}]_n$) would generate 700–800 (m^3 biogas/t V_S) with a CH_4 purity close to 55%. A protein ($\text{C}_c\text{H}_h\text{O}_o\text{N}_n\text{S}_s$) would produce around 700–800 (m^3 biogas/t V_S) with a higher (60–75%) CH_4 concentration, whereas lipids ($\text{CH}_3[\text{CH}_2]_n\text{COOH}$) usually yield higher values (1000–1400 m^3 biogas/t TS) and a CH_4 concentration close to 70% (Agabo-García et al., 2020; Deublein and Steinhauser, 2011; Nielfa et al., 2015; Weinrich, 2018). An effluent rich in fats and oils can produce more biogas (2.5–3.5 times) and presents high conversions (>90%) when it is subjected to physical (ultrasonics, microwaves, supercritical processes), chemical (acid base, enzymes), biological, and thermochemical pretreatments (Alqaralleh et al., 2016; Chowdhury et al., 2019; He et al., 2021; Rincón et al., 2016; Salama et al., 2020).

The global biogas market has an approximate value of 26 billion US dollars and is expected to reach 32 billion US dollars in 2027. In 2018, ca. $60 \times 10^3 \text{ m}^3$ biogas (35 Mtoe) were produced, the main producers being Europe (54%), Asia (30%), and the Americas (14%) (IEA, 2020; WBA, 2019; WBA, 2020). This production capacity represents roughly 6% of the biogas production potential (730 Mtoe) from crops, biomass, animal manure, the organic fraction of urban solid residues, and waste waters (Fig. 5) (IEA, 2020; WBA, 2019; WBA, 2020). Although biogas covers 0.3% of the primary consumption of global energy, it could be feasible to supply 20% of the natural gas demand (IEA, 2020; WBA,

Table 3
Typical composition of biogas.

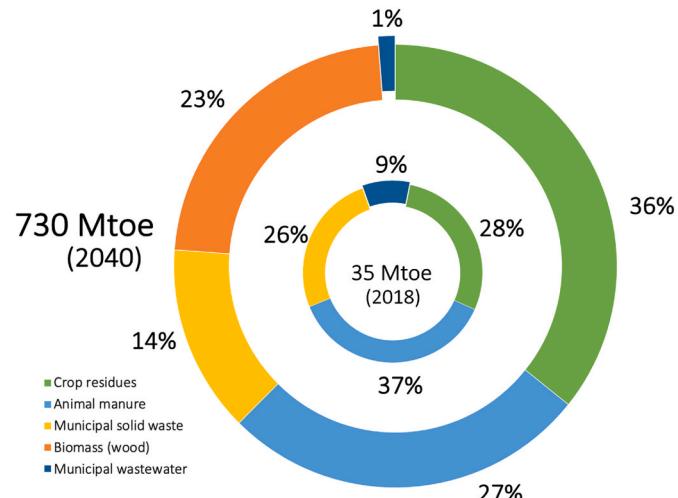
Compound	Composition (%)	Municipal wastewater ^[2]	Municipal solid waste ^[2,3]	Sugarcane vinasses ^[4]	Palm oil effluent ^[5]	Landfill ^[2,6,9]	Typical Range ^[8]	Requirements for injection in gas grids	Comments
Methane	50–77	50–60	50–60	50–70	30–65	50–75	≥97	–	–
Ethane	–	–	–	–	–	–	–	–	–
Propane	–	–	40–50	40–50	30–40	25–47	35–55	≤3	Reduces the calorific value of biogas.
Carbon dioxide	19–45	–	–	–	–	–	–	–	–
Oxygen	0.0–2.9	<1.0	<1.0	<1.0	1–5	0.0–1.0	≤1	–	–
Nitrogen	0.0–7.1	0.0–5	–	–	1–17	0–10	≤0.5	–	–
Hydrogen	0.0–0.01	0.0–1300 ^[1]	0.0–1300 ^[1]	0.0–1300 ^[1]	30–500 ^[1]	100–30,000 ^[1]	≤10 ^[1,2]	–	–
Hydrogen sulfide	0.0–4800 ^[1]	–	–	–	–	–	–	–	–
Ammonia	0.0–3.5 ^[11]	–	–	–	2.1–380 ^[12]	0.0–500 ^[12]	≤20 ^[1,2]	–	–
Carbon monoxide	0.0–0.01	–	–	–	–	0.0–0.32	0.0–0.1	–	–
Siloxanes	0.0–0.820	–	–	–	–	0.0–24 ^[11]	0.0–120 ^[11]	–	Can react with H ₂ O and O ₂ to form corrosive substances like H ₂ SO ₄ and HCl. Can transform up to silicates and micro-crystalline quartz, which are abrasive.

Note: ^[1] ppm; ^[2] Calbry-Muzyka et al., 2022; ^[3] Precci-Lopes et al., 2022; ^[4] Nunes-Ferraz et al., 2022; ^[5] Yacob et al., 2006; ^[6] Nahar et al., 2017; ^[7] Akunna, 2019; ^[8] Deublein and Steinhauser, 2011; ^[10] Zhu et al., 2015; ^[11] mg Si/m³; ^[12] mg/m³.

Table 4
Methane production yield from different organic substrates.

Substrate	Methane yield range
Hay	350–460 ^[1]
Sunflower	154–400 ^[1]
Barley	350–660 ^[1]
Straw	242–324 ^[1]
Maize (whole plant)	175–250 ^[1]
Oats (whole plant)	240–254 ^[1]
Sugar beet (leaves)	~251 ^[1]
Banana peel	270–320 ^[1]
Potato waste	690–890 ^[1]
Vegetable waste	190–400 ^[1]
Maize silage	320–440 ^[1]
Garden wastes	250–500 ^[1]
Grass	252–296 ^[1]
Fruit	250–500 ^[1]
Municipal solid wastes	380–400 ^[1]
Newspaper	~150 ^[1]
Distillery wastes	~360 ^[1]
Sludge from distilleries	400–470 ^[1]
Palm oil mill effluent	12,000–100000 ^[2]
Domestic sewage	71–100 ^[2]
Water hyacinth	220–235 ^[1]
Fats and oils	330–715 ^[1]
Animal fat	1000 ^[1]
Abattoir wastes	275–550 ^[1]
Olive mill wastewaters	325–470 ^[1]
Cheese whey	420 ^[1]
Waste activated sludge + fat and oil	310–490 ^[1,3]
Waste activated sludge + fat and oil	390–673 ^[1,3]
Used vegetable oil	650 ^[1]
Slaughterhouse wastewaters	562–777 ^[2]
Olive mill wastewater	315–470 ^[1]
Olive mill wastewater	220–390 ^[1,3]
Chicken	90–150 ^[1]
Pig	210–385 ^[1]
Cow	120–150 ^[1]

Note: ^[1] (m³ CH₄/t VS). ^[2] (m³ CH₄/t COD). ^[3] Thermophilic condition (T: 55 °C). ^[4] Hyper-thermophilic condition (T: 70 °C).



1Mtoe=11.63 TWh=39652608.7 MMBTU=1.11 Gm³ natural gas

Fig. 5. Participation of diverse organic byproducts in the production of energy.

2020). The fixed and operational costs per unit of produced energy depend on the used technology and the region where the project is developed (IEA, 2020; WBA, 2020). It must be noted that the average price of natural gas is 0.23 USD/m³ (6.8 USD/MMBTU); however, bio-CH₄ is more expensive than natural gas in some regions (IEA, 2020). The average cost of biogas production technologies lie in the range of 0.11–0.71/m³ (3–20 USD/MMBTU). It is expected that, by 2040, more

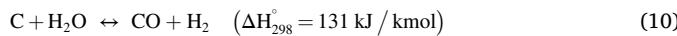
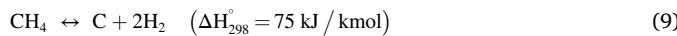
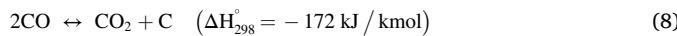
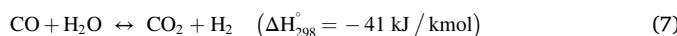
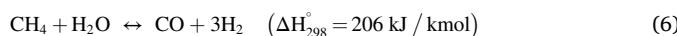
than 1000 Mtoe (11,630 TWh) be generated with a production cost below 0.33 USD/m³ (15 USD/MMBTU) (IEA, 2020; WBA, 2020).

2. Hydrogen production processes

2.1. Steam methane reforming (SMR)

Steam methane reforming (SMR) dates back to 1924 and is the most used process at an industrial level for the synthesis of H₂ due to its efficiency, low cost, and technological maturity (IEA, 2020, 2022; IRENA, 2022; Rostrup-Nielsen and Christiaensen, 2011). Methane possesses a tetrahedral structure with four equivalent bonds (C–H), which turns it into a poorly reactive molecule; for this reason, its transformation to H₂ is performed at high temperatures to warrant high efficiencies (IEA, 2019; Liu et al., 2010). The efficiency of the reforming reaction depends on the temperature (T), pressure (P), and the steam-to-carbon (S/C) ratio, among others (IEA, 2019; IRENA, 2019; Liu et al., 2010; Navarro et al., 2007; Rostrup-Nielsen and Christiaensen, 2011).

The SMR is constituted by four stages: i) pre-treatment of the raw material; ii) reaction of CH₄ with water (Eq. (6)); iii) the water gas shift reaction (WGSR), which is reversible and slightly exothermal (Eq. (7)); and iv) the purification of the obtained product (Fig. 6). It is worth mentioning that Eq. (6) suggests an S/C ratio equal to 1; in practice this ratio can vary between 2.5 and 3.0 to minimize the formation of carbon on the catalyst (Eqs. (8)–(10)) (Ghosh and Prelas, 2011; Liu et al., 2010; Navarro et al., 2007).



An SMR process at an industrial level (500×10^2 – $300 \times 10^3 \text{ Nm}^3 \text{ H}_2/\text{h}$) frequently uses a tube-shield type oven, the tubes are filled with a nickel catalyst (12–25% Ni as NiO) supported on alumina (Al₂O₃), which also contains promoters (Ca, K, La, Ce, Ru) that reduce the

formation of carbon and poisoning of the catalyst with sulfide (Ghosh and Prelas, 2011; Liu et al., 2010; Navarro et al., 2007; Rostrup-Nielsen and Christiaensen, 2011). The carbonaceous and sulfured materials can affect the catalytic activity of Ni; nonetheless, it is the most used catalytic material at the industrial level because it is less expensive than alternatives like Co, Rh, Ru, Pt, and Pd (Ghosh and Prelas, 2011).

The formation of the carbonaceous material (Eqs. (8) and (9)) occurs when a hydrocarbon or the carbon monoxide (CO) itself reacts with a transition metal (Liu et al., 2010; Navarro et al., 2007); carbon can be found as fibers or tubular filaments (resembling whiskers) that contain a small Ni particle in their upper part (Ghosh and Prelas, 2011; Liu et al., 2010; Rostrup-Nielsen and Christiaensen, 2011). These structures are generated at high temperatures (1000 °C) and, because of their hardness, can cause rupture of the catalyst and an increase in the pressure drop inside the reactor (Ghosh and Prelas, 2011; Navarro et al., 2007; Rostrup-Nielsen and Christiaensen, 2011). At temperatures below 1050 °C, the formation of a polymeric film on the catalyst is possible, causing a progressive loss of its activity (Navarro et al., 2007).

Production of H₂ through SMR (Fig. 6) is usually performed at high temperatures (800–950 °C) and pressures (20–30 bar). To reduce the CO concentration to less than 0.1% (vol.) and improve H₂ conversion, two additional reactors, named HT-WGS (water-gas shift) and LT-WGS, are used (Fig. 6). The reactor HT-WGS operates at 300–350 °C and uses a catalyst constituted by iron oxides (Fe₃O₄: 95%, Cr₂O₃: 5%), conversely, in the LT-WGS reactor, operational temperature is much lower (200–250 °C) and it uses copper and zinc oxides (CuO: 15–30%, ZnO: 30–60%) as catalysts (Bagheri, 2017; Ghosh and Prelas, 2011; Liu et al., 2010; Navarro et al., 2007).

To limit the impact of natural restrictions (e.g., thermodynamic, kinetic, and heat transfer) imposed on the reforming process, some modifications have been made to the design and operation. The most significant advances involve: i) use of palladium-based membrane membranes for H₂ recovery, ii) packed-bed membrane reactors, iii) fluidized-bed membrane reactors (Basile et al., 2015; De Falco et al., 2013; Julianelli et al., 2021), iv) recovery of partially transformed compounds (CO, CO₂, CH₄) (Capa et al., 2020; Lee et al., 2021; Wu et al., 2020; Yan et al., 2020), and the development of microreactors (Ferreira-Aparicio et al., 2005; Murphy et al., 2013). Table 5 depicts a series of promising alternatives to improve the performance of gas reforming processes at low temperatures (600–700 °C), minimize the impact of

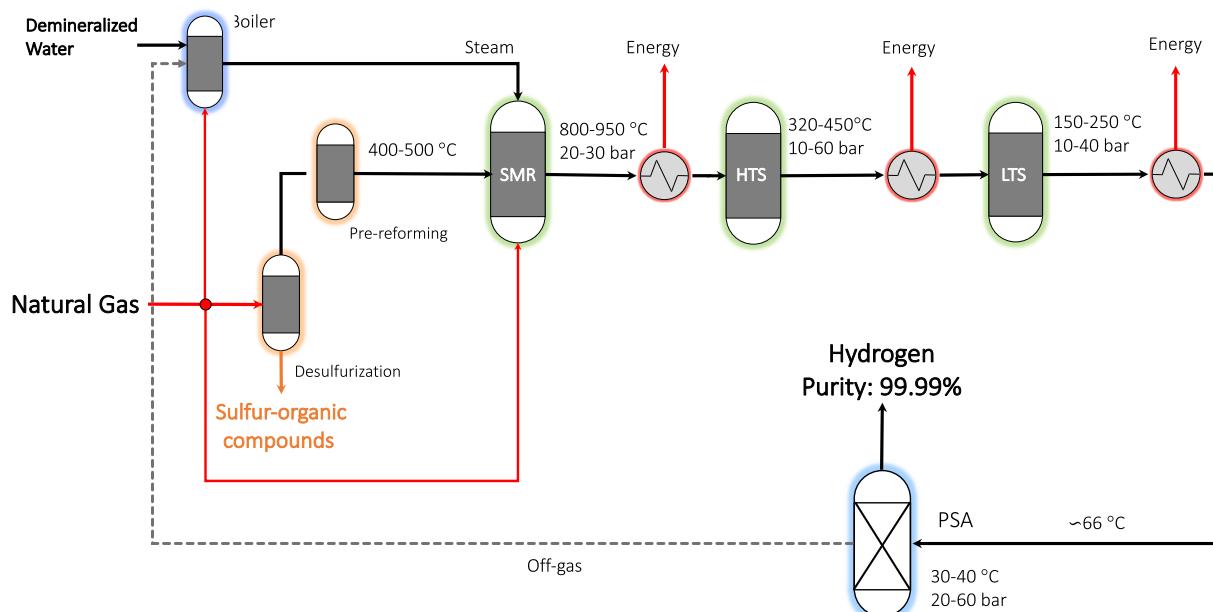


Fig. 6. H₂ production through steam methane reforming (SMR).

Table 5

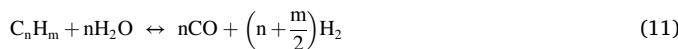
Available alternatives to improve the efficiency of catalytic reforming processes.

Standard process	Description of the improvement	Advantage	Disadvantage	Source
Steam Methane Reforming (SMR)	Palladium-based membrane technology	Can be used to process natural gas and biogas. Increases the recovery of H ₂ (40–60%). Good resistance to H ₂ S. Binary (Pd–Au, Pd–Cu) and ternary (Au–Pt–Ag) alloy membranes show superior permeability and high resistance to H ₂ S. Integration of reaction and separation in a single unit may lead to lower costs. Presence of other hydrocarbons (ethane, propane, and butane) increase H ₂ production.	Composition of biogas (CO ₂ and CH ₄ content) may vary substantially and affect process performance. H ₂ S may affect membrane and catalyst stability, membrane cost, and lifetime. Techno-economic analyses are usually performed at laboratory scale. H ₂ is obtained at low pressure (<3 bar).	Iulianelli et al. (2021); Basile et al., 2015; Bruni et al., 2019
	Sorption enhanced steam reforming, SESR	Can be used to process natural gas and biogas. High H ₂ purity (>98%) and high H ₂ yield (>90%) can be obtained. A wide number of materials can be used in CO ₂ sorption (CaO, dolomite, lithium-based sorbents, alkali-metal ceramics). Sorption allows lower temperatures in the reformer (550–650 °C). Integration of oxygen transport membrane-hydrogen transport membrane may reduce investment and operational cost. Partial oxidation and steam reforming can occur in the same reactor. The United States Department of Energy predicted that H ₂ production cost could be reduced 15–20% (compared to the SMR process)	Technoeconomic analyses at laboratory scale suggest higher production cost (4–6 \$kg/H ₂). H ₂ is obtained at low pressure (<3 bar).	Capa et al., 2020; Yan et al., 2020; Lee et al. (2021)
	CO ₂ -permselective membrane reactor	CO ₂ removal promotes water-gas shift reaction increasing H ₂ yield. High pressure H ₂ can be generated if a pressurized feed is used. No extra WGS unit is required for the process.	Fabrication of thin ceramic-carbonate membranes can be considered complicated. Some ceramic-carbonate membranes could present low mechanical strength. Techno-economic analysis are usually performed at laboratory scale. H ₂ is obtained at low pressure (<3 bar).	Dat-Vo et al. (2021); Wu et al. (2020)
	Chemical looping	H ₂ production using chemical looping utilizes the same principles as chemical looping combustion. H ₂ synthesis can be performed using chemical looping reforming (CLR) or chemical looping hydrogen production (CLH). Allows CO ₂ capture with a low energy penalty. Energy required for the reforming reaction is provided by the solids circulating in the chemical looping combustion system. Carbon capture and H ₂ yield increase at high temperature in the fuel.	Selection of the oxygen carrier is critical for the performance of the process. Therefore, thermodynamic, cost, nontoxicity and sustainability properties should be considered.	Pans et al., 2013; Xu et al., 2019; Stenberg et al. (2021)

corrosion, and reduce installation costs (Bruni et al., 2019; Dat-Vo et al., 2021; De Falco et al., 2013; Murphy et al., 2013; Yan et al., 2020).

The content of high molecular weight hydrocarbons (C₂–C₅) in the natural gas and the reforming of complex substrates (high-sulfur fuels, naphtha) and renewable materials (glycerol, bio-oil) can make it necessary to include a pre-reforming stage to avoid that these substances, much more reactive than CH₄ deactivate the reforming catalyst (Fig. 6) (García-Gómez et al., 2021; Ghosh and Prelas, 2011; Moreira et al., 2019; Subramani et al., 2015). Although renewable materials like bio-oil reforming reached remarkable results in terms of H₂ production and substrate conversion, Ni catalyst usually undergo rapid deactivation because aromatic compounds favor coke deposition on Ni sites (García-Gómez et al., 2021).

In the catalytic pre-reforming, the higher molecular weight substances are transformed into CH₄, H₂, CO, and CO₂ (Eq. (11)) whereas the sulfur traces can be reduced by adsorption (Moreira et al., 2019; Sperle et al., 2005). The pre-reforming is a key step because it increases the efficiency of the process, reduces the size of the reforming unit, and allows operating with a wider range of feedstocks (Subramani et al., 2015). A pre-reforming reactor uses a Ni catalyst supported by alumina and operates at intermediate temperatures (350–550 °C) (Sperle et al., 2005). Recently, different groups have evidenced the potential of modified catalytic systems (Co-based catalysts, Ni–Ru catalysts, Ni-MO_x, M = Mg, Cr, Ce) and low cost materials (Fe/bio-char, dolomite: CaMg(CO₃)₂) to hinder deactivation by coke and increase the stability of the reformer (García-Gómez et al., 2021; Liu et al., 2019; Moreira et al., 2019).



It must be pointed out that the reforming process analyzed in this section can be applied to raw materials like bio-CH₄ (CH₄: 95% and CO₂: 5%), bio-oils, glycerol, liquefied petroleum gas, associated gas, and higher hydrocarbons (Choi et al., 2017; García-Gómez et al., 2021; Uskov et al., 2019). For synthetic mixtures of biogas (CH₄: 40–60% and CO₂: 60–40%), it can be stated that CH₄ conversion will depend on the temperature, the (S/C) and (CO₂/CH₄) ratios, the type of catalyst, the applied preparation method, the used supports and promoters (Capa et al., 2020; Chouhan et al., 2019; Tuna et al., 2018). The presence of CO₂ in the biogas contributes to the production of carbon monoxide (CO); suggesting a tendency to the formation of carbonaceous materials on the catalyst (Ahmed et al., 2015; Janajreh et al., 2021).

Low concentrations of sulfured compounds and light hydrocarbons accelerate the deactivation process of the catalyst and reduces up to 50% the CH₄ conversion in short times (<50 h) (Chioldo et al., 2017). At low concentrations of H₂S, direct adsorption of the sulfur species on the catalytic material blocks the active sites in a reversible way whereas high concentrations lead to the formation of metal sulfides, reducing the regeneration capacity of the catalyst (Jangam et al., 2021; Nirmal-Kumar et al., 2021) Some studies show that an increase in temperature, metal loading, and the partial pressure of the reacting gases will mitigate the damage in Ni catalysts (Capa et al., 2020; Chioldo et al., 2017; Chouhan et al., 2019; Roy et al., 2018). Although H₂S and CO₂ are ubiquitously present in biogas streams, sorption-enhanced steam reforming (SESR) and membrane reactors appear to be attractive ways to produce high purity H₂. Sorption performed with CaO-based materials allows the use of biogas with a highly variable content of CO₂ (5–50%) without affecting the purity (>98% vol) or the H₂ yield (>91%) (Capa et al., 2020; Dang et al., 2022). Alternatives like desulfurization and catalyst regeneration, tailor-made catalyst with improved resistance

to sulfur, and selection of the best reactor and operating conditions are considered attractive to increase sulfur tolerance (Janajreh et al., 2021).

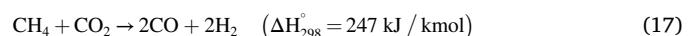
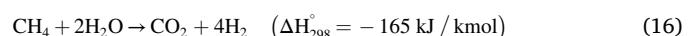
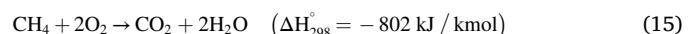
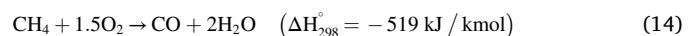
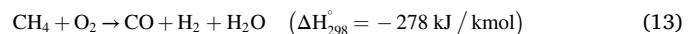
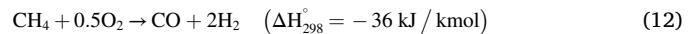
The use of mathematical models suggests that the catalytic steam biogas reforming (SBR) could reach energetic efficiencies (75%) similar to those obtained with SMR; however, operating costs (SBR: 0.14 US \$/kWh vs. SMR: 0.08 US\$/kWh) and the carbon footprint (20 kg CO₂-eqv/kg H₂) suggest the need to improve critical activities of the H₂ production system (Ferreira-Madeira et al., 2021). It should be noted that process performance (hydrogen yield, H₂ cost, and carbon footprint) is highly dependent on the characteristics of the raw material, the reforming process, and the electricity mix of the country (Ramírez-Díaz et al., 2022). Biodegradable and waste materials can easily be used to produce H₂ from biogas reforming with low carbon footprints (3.5 kg CO₂-eqv/kg H₂) and high ecological efficiencies (89%) (Cvetkovic et al., 2022). There are also reports on the feasibility of reforming the biogas produced in landfills and anaerobic reactors; nevertheless, the reforming efficiencies are considerably lower (36%) than those reported for natural gas (72%) (Janajreh et al., 2021). Cvetkovic et al. (2021), evidenced that although the system is not sustainable from the energy point of view due to the natural gas consumption in the reformer, inclusion in the life cycle analysis of economic and social aspects related to this type of processes would improve the environmental performance. It must be noted that many of the conditions described for the production of H₂ from natural gas are applicable for its synthesis from biogas.

2.2. Partial oxidation (POX)

Partial oxidation (POX) is a process developed more than 100 years ago for the production of syngas. Vandever and Parr noted that when replacing air with oxygen (O₂), the efficiency of the syngas production process improved notably (Keiski et al., 2011; Milner-Elkharrout et al., 2020). In POX, the reaction between the feedstock (generally CH₄) and O₂ is accomplished at high temperatures (1000–1500 °C), short contact times (10^{-4} - 10^{-2} s), and at atmospheric pressure (~1 bar)

(Nourbakhsh et al., 2018; Sengodan et al., 2018; Welya et al., 2012). POX requires a pre-treatment stage of the raw material and a reaction system in which an O₂ is used to oxidize partially CH₄ (Fig. 7). The generated syngas follows a similar route to that described for SMR (Sengodan et al., 2018; Welya et al., 2012).

In POX, the H₂/CO ratio varies between 1.7 and 1.8 and efficiencies can reach 70–80%; this route can be coupled to Fischer-Tropsch processes for the synthesis of hydrocarbons (gasolines, diesel) and chemical products (olefins, methanol, and ethanol) (Milner-Elkharrout et al., 2020; Nourbakhsh et al., 2018; Ul-Hasnain et al., 2021). Equations (6), (7), (12)–(17) represent the possible reactions that occur during syngas production via POX (Liu et al., 2010; Milner-Elkharrout et al., 2020; Sengodan et al., 2018). For practical uses, all the reactions that involve O₂ are considered irreversible (Rostrup-Nielsen and Christiaensen, 2011).



Among the main advantages of POX are: i) the reaction system is smaller; ii) it can use gaseous, liquid hydrocarbons, and coal as raw material; iii) due to operational factors, this process does not lead to the generation of sulfur (SO_x) and nitrogen (NO_x) oxides (Milner-Elkharrout et al., 2020; Ul-Hasnain et al., 2021). The process has the following disadvantages: i) higher energy consumptions, ii) high operating temperatures lead to coking, hotspot, and sintering of the catalyst, and iii)

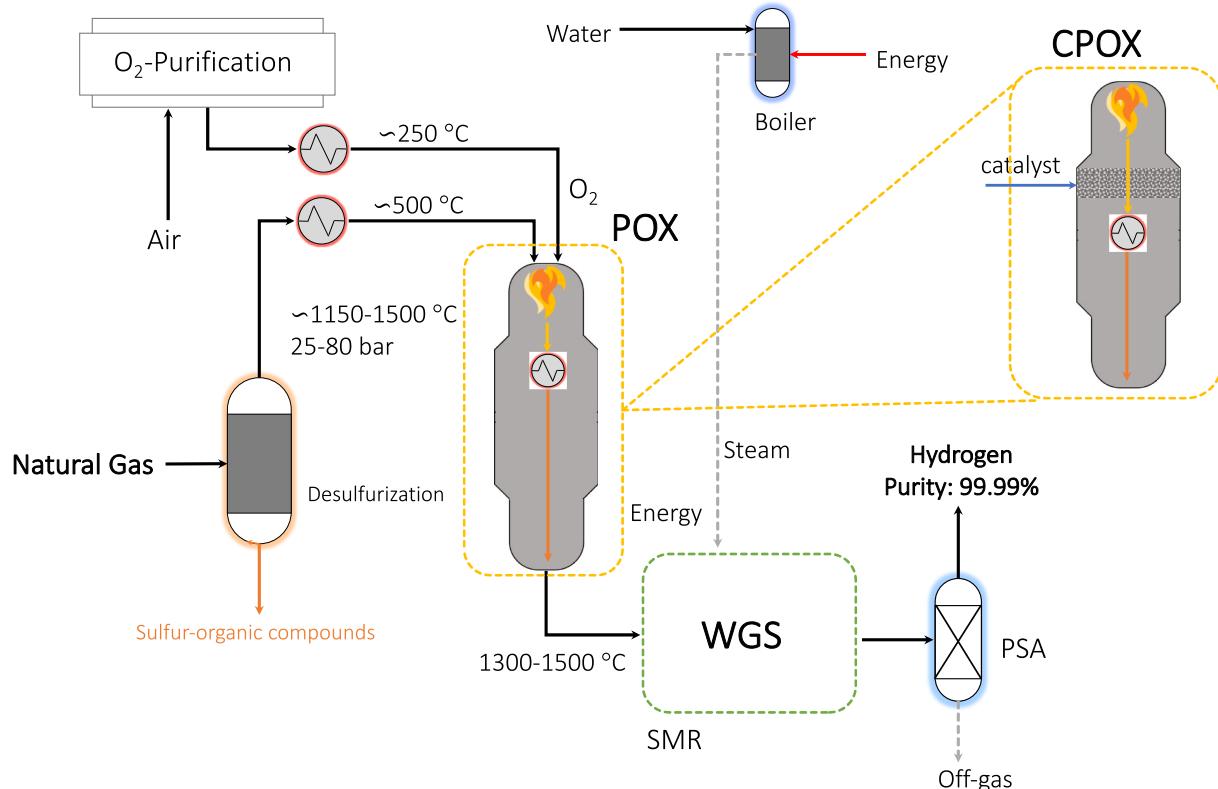


Fig. 7. H₂ production through partial (POX) and catalytic partial oxidation (CPOX).

the O₂ production and purification units increase the installation and operational costs of the process (Al-Musa et al., 2014; Gupta, 2009; Kumar et al., 2021; Milner-Elkharouf et al., 2020; Sengodan et al., 2018).

Compared to other processes, POX presents a lower H₂ yield; for example, SMR leads to relatively high H₂ concentrations (70–80%) whereas the yields observed with POX are much lower (40–50%). POX tends to generate soot, and factors like a less stable flame and slower kinetics complicate the design of the reaction systems (Dobrego et al., 2008a; Ersoz et al., 2006; Nourbakhsh et al., 2018); however, the use of inert media (Al₂O₃, SiO₂, ZrO₂, and SiC foams) favors the reaction rate (Al-Hamamre et al., 2009; Dobrego et al., 2008a). In addition, when inert media are used, like Al₂O₃ and ZrO₂, no appreciable amount of soot is observed and conversion is correlated with the maximal temperature reached in the bed (Al-Hamamre et al., 2009; Dobrego et al., 2008a). When Cerium (CeO₂) is used as promoter, the catalytic system increases its thermal stability and resistance to coke formation; this is because ceria-type promoters enhance oxygen mobility due to their capacity to store and release O₂ during the reaction (Fazlakeshteli et al., 2022; Ul-Hasnain et al., 2021). Compared to monometallic, bimetallic catalysts (Ni and noble metals) promoted by CeO₂ show higher methane conversion at lower temperatures (550 °C) (Fazlakeshteli et al., 2022).

The use of air is convenient because it reduces installation costs; however, the N₂ concentration in the generated syngas can be high (60%) (Dobrego et al., 2008b; Ersoz et al., 2006; Zhang et al., 2021). In contrast to the catalysts-assisted processes, POX can handle relatively high sulfur contents (above 50 ppm), which favors the use of less expensive and more complex raw materials (Cao et al., 2010; Wang et al., 2019). Considering that the natural gas will continue to be important in the global energy market, POX becomes of great interest due to its energy efficiency and its higher flexibility for the handling of complex raw materials (Cao et al., 2010; Fazlakeshteli et al., 2022; Liao et al., 2019; Zhang et al., 2021). POX has proven efficient for the production of gas-to-liquid products (GTL) at an industrial level, as evidenced by projects in Malaysia (84 t/h) and Qatar (836 t/h); nonetheless, the global market remains to be dominated by SMR. Although POX can be carried out in different types of reactors (gas turbines, fixed bed, fluidized bed, entrained flow reactors, and micro-reactors), the selection of the reactor is tied to the characteristics of the feedstocks and the target products (Cornelissen et al., 2006; Keiski et al., 2011; Marín et al., 2019; Svensson et al., 2013).

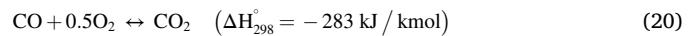
The reverse-flow POX reactor, a type of fixed reactor that combines in one processing unit the reaction and the transfer of energy, has shown a great potential due to its energy efficiency (Marín et al., 2019; Wang et al., 2019). In these systems, a bed filled with inert material with a high thermal capacity absorbs the energy generated by the reaction, which is then used to raise the temperature of the gas that enters the system (Lee and Hwang, 2016; Marín et al., 2019; Svensson et al., 2013; Wang et al., 2019). The use of a fixed or fluidized medium is key to store transitorily the energy required for the process, ensure flame stability, and achieve high conversions (Mujeebu, 2016; Schoegl et al., 2009; Toledo et al., 2009). For POX, the most notable challenges are related to the handling of extreme temperature and pressure conditions, explosion risks, fragilization of the medium, soot formation, and the costs associated to the O₂ production process (Keiski et al., 2011; Marín et al., 2019; Nourbakhsh et al., 2018; Svensson et al., 2013; Wang et al., 2019). Mathematical models highlight that H₂ yield is reduced with an increase in the CO₂ content of the biogas; CO₂ has a significant impact on the operating temperature and the conversion of the WGS reaction (Eq. (7)). Nourbakhsh et al. (2018) pointed out that steam injection and high temperatures reduce carbon formation and enhance H₂ production—Tezel et al. (2020) indicated that an over 93% conversion of methane in synthetic biogas mixtures (CH₄, CO, CO₂, N₂, and H₂) was observed at 750 and 850 °C.

2.3. Catalytic partial oxidation (CPOX)

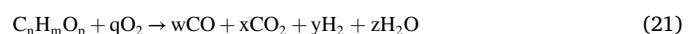
Catalytic partial oxidation (CPOX) incorporates a catalyst to favor the efficiency and energy consumption of the process (Fig. 7) (Mosayebi, 2020; Pauletto et al., 2021). Theoretically, it could be accomplished at relatively low temperatures (700–1000 °C) and pressures (Arku et al., 2018; Chen et al., 2018; Huang et al., 2016; Mosayebi, 2020; Pauletto et al., 2021; Sengodan et al., 2018). In practice, the main products (H₂-CO) usually oxidize, therefore, the reaction must be performed at 900 °C (Aasberg-Petersen et al., 2011; Mosayebi, 2020; Pauletto et al., 2021). In contrast to POX and ATR, the reaction is of the catalytic type and, hence, occurs without a flame (Dias and Assaf, 2008; Keiski et al., 2011). Due to the characteristics of the fuel/oxidant mixture, for safety reasons, it is necessary to limit the reaction temperature, especially at high pressures (Aasberg-Petersen et al., 2011). During POX, an equilibrium between the fuel and the oxidant must be warranted to avoid incomplete oxidation (CO and H₂) or complete oxidation (CO₂ and H₂O) of the raw material. This makes it difficult to control the temperature within the reaction system and leads to the formation of carbon deposits. (Cheekatamarla and Finnerty, 2008; Dias and Assaf, 2008; Figen and Baykara, 2018; Silva et al., 2009).

The CPOX can be catalyzed by transition or noble metals. Transition metals like Ni and Co supported on different oxides (Al₂O₃, CaO, SiO₂, CeO₂, TiO₂, ZrO₂) have been proven to be efficient from a technical and economical point of view. Noble metals (Ir, Pd, Pt, Rh) are more attractive because they present a higher catalytic activity, can operate at lower temperatures, and are less susceptible to be deactivated (Dias and Assaf, 2008; Figen and Baykara, 2018; Huang et al., 2016; Khajenoori et al., 2013; Luo et al., 2018; Milner-Elkharouf et al., 2020; Silva et al., 2009). Although Ni and Pd tend to form carbon deposits, Rh, Ru, Ir, and Pt show high activity during their operation (Dias and Assaf, 2008; Figen and Baykara, 2018; Khajenoori et al., 2013). The chosen support has a notable effect on catalyst stability; for example, the Pt/Al₂O₃ and Pt/ZrO₂ are deactivated whereas the Pt/CeZrO₂ remains stable during the reaction because of the number of oxygen vacancies caused by the addition of Zr (Figen and Baykara, 2018; Silva et al., 2009; Warren and Scheffe, 2018).

Nickel is preferred due to its high activity, selectivity, and low cost; additionally, its deactivation, due to carbon or sulfide formation, can be reduced using CeO₂, ZrO₂, Y₂O₃/ZrO₂, TiO₂/ZrO₂, NiO/MgO/ZrO₂, and Nb₂O₅/ZrO₂ (Boukha et al., 2018). CPOX can use gaseous and liquid hydrocarbons; its H₂/CO ratios are close to 2, whereas the production efficiencies and selectivities are in the order of 70–80% (Silva et al., 2009; Warren and Scheffe, 2018). The main observed reactions during CPOX of CH₄ include the following equations (7), (8), (11)–(20) (Arku et al., 2018; Mosayebi, 2020; Smith and Shekhawat, 2011)



For the CPOX catalyzed by Ni, the increase in the number of carbons leads to higher H₂ yields (Eq. (21)), notwithstanding, the soot formation is more marked in hydrocarbons like ethane (C₂H₆) and propane (C₃H₈) (Arku et al., 2018). For liquid fuels (ethanol: C₂H₅OH; isoctane: C₈H₁₈; hexadecane: C₁₆H₃₄, kerosene, diesel, and jet fuel), the highest energetic efficiencies (ThE) and H₂ yields (H₂Y) were obtained for ethanol (ThE: 82%, H₂Y: 94%) and the lowest for diesel (ThE: 70%, H₂Y: 80%). An increase in the number of carbons in the fuel and the presence of complex substances reduce the efficiency of the process (Arku et al., 2018; Cheekatamarla and Finnerty, 2008).



The operational conditions of CPOX allow it to be coupled to fuel cells (solid oxide fuel cells, SOFCs) for electricity generation (Arku et al., 2018; Boukha et al., 2018; Cheekatamarla and Finnerty, 2008;

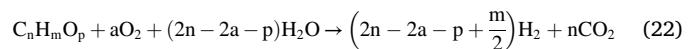
Milner-Elkharouf et al., 2020). The SOFCs result advantageous because they operate at high temperatures (800–1000 °C), are not affected by the presence of CH₄ and CO, and can be used for the production of electricity at small and large scales. For these systems, energetic efficiencies of 60% have been reported and a daily reduction in H₂ yield below 0.7% (Milner-Elkharouf et al., 2020). Integration of SOFCs with CPOX could raise those efficiencies up to 85% (Cheekatamarla and Finnerty, 2008; Milner-Elkharouf et al., 2020).

2.4. Autothermal reforming (ATR)

The autothermal reforming (ATR) was developed between 1930 and 1950 for the synthesis of ammonia and it combines two processes (SMR and POX) or (POX and DR) in a reactor (Araújo et al., 2021; Carapellucci and Giordano, 2020; Fan et al., 2021; Rostrup-Nielsen and Christiaensen, 2011). The combination of endothermal (SMR, DR) and exothermal (POX) paths enables the production of an adjustable H₂/CO ratio, by changing the H₂O/O₂ ratio of the feed and reducing the energy demand of ATR (Araújo et al., 2021; Luneau et al., 2017; Rau et al., 2019; Rosha et al., 2019). An ATR for the production of syngas is composed of a burner, a combustion chamber, and a catalytic bed (Chen et al., 2010; Murmura et al., 2016; Rostrup-Nielsen and Christiaensen, 2011). When the reforming and combustion reaction occur simultaneously on a catalytic bed, the resulting reactor is more compact and is quite attractive to be used in fuel cells; on the other hand, when reactions occur in well-differentiated sections, for example POX followed by SMR, these systems are better suited for the production of liquid fuels (Aasberg-Petersen et al., 2003; Nahar et al., 2017).

The possibility to make O₂ react with a fuel facilitates the generation of the energy required for the reforming (Eq. (22)); the latter is very desirable at the industrial level because it would lead to a thermo-neutral process (Araújo et al., 2021; Chen et al., 2010; Murmura et al., 2016; Rau et al., 2019; Rosha et al., 2019; Sepehri and Rezaei, 2017). Furthermore, its efficiency, smaller size, low operation temperature, and fast start-up make ATR attractive for the development of decentralized and low scale systems (Cao et al., 2009; Ersoz et al., 2006; Halabi et al.,

2008; Rau et al., 2019; Wang, 2008).



As the number of carbon atoms increases in the fuel, the amount of O₂ required for the process also increases (Eq. (22)); nonetheless, the O/C ratio (ca. 0.7) at which the equilibrium occurs between the endothermal and exothermal reactions (thermo-neutrality) is similar for various fuels (CH₄, bioCH₄, C₂H₆, C₃H₈, C₈H₁₈, C₁₄H₃₀, C₁₆H₃₄) (Rau et al., 2019; Shilov et al., 2022; Wang, 2008). The ATR can operate in a wide range of conditions, but the literature indicates that the ratios O/C: 0.7–1.0, S/C: 1.5–2.0, and intermediate temperatures (700–800 °C) lead to optimal performances (Feio et al., 2008; Wang, 2008).

As shown in Fig. 8, the reformer operates at variable temperatures (900–1150 °C) and pressures (1–80 bar) and uses as oxidant O₂, O₂-enriched air, or air (Araújo et al., 2021; Feio et al., 2008; Luneau et al., 2017; Rau et al., 2019; Rosha et al., 2019). Although the use of CPOX is optional in ATR, catalytic processes usually have higher energetic efficiencies (Araújo et al., 2021). ATR produces synthesis gas with a H₂/CO ratio close to 2, which makes it very attractive for the Fischer-Tropsch synthesis (Araújo et al., 2021; Luneau et al., 2017; Rau et al., 2019; Rosha et al., 2019). In the ATR, the following reactions could occur (Eqs.: 6–10, 12–20) (Feio et al., 2008; Ghosh and Prelas, 2011; Murmura et al., 2016; Rostrup-Nielsen and Christiaensen, 2011).

In the ATR, part of the raw material is oxidized to give rise to products like H₂O and CO₂; the remaining fuel is transformed to syngas by the reforming reactions of H₂O and CO₂ (Araújo et al., 2021; Gao et al., 2008; Murmura et al., 2016; Nahar et al., 2017; Wang, 2008). An ATR process uses catalysts (e.g., Ni, Pt, Pd, Rh, Ru) and supports (Al₂O₃) similar to those used in SMR; due to the high operating temperatures it is necessary to use materials with high thermal stability (Dias and Assaf, 2008; Gao et al., 2008; Kim et al., 2013; Navarro et al., 2007). Taking as reference the CH₄ conversion, Rh becomes very attractive for ATR; however, the cost does not make it adequate for its industrial use (Sepehri and Rezaei, 2017; Sepehri et al., 2018).

Conventional catalysts (Ni-Al₂O₃) can undergo deactivation by H₂S,

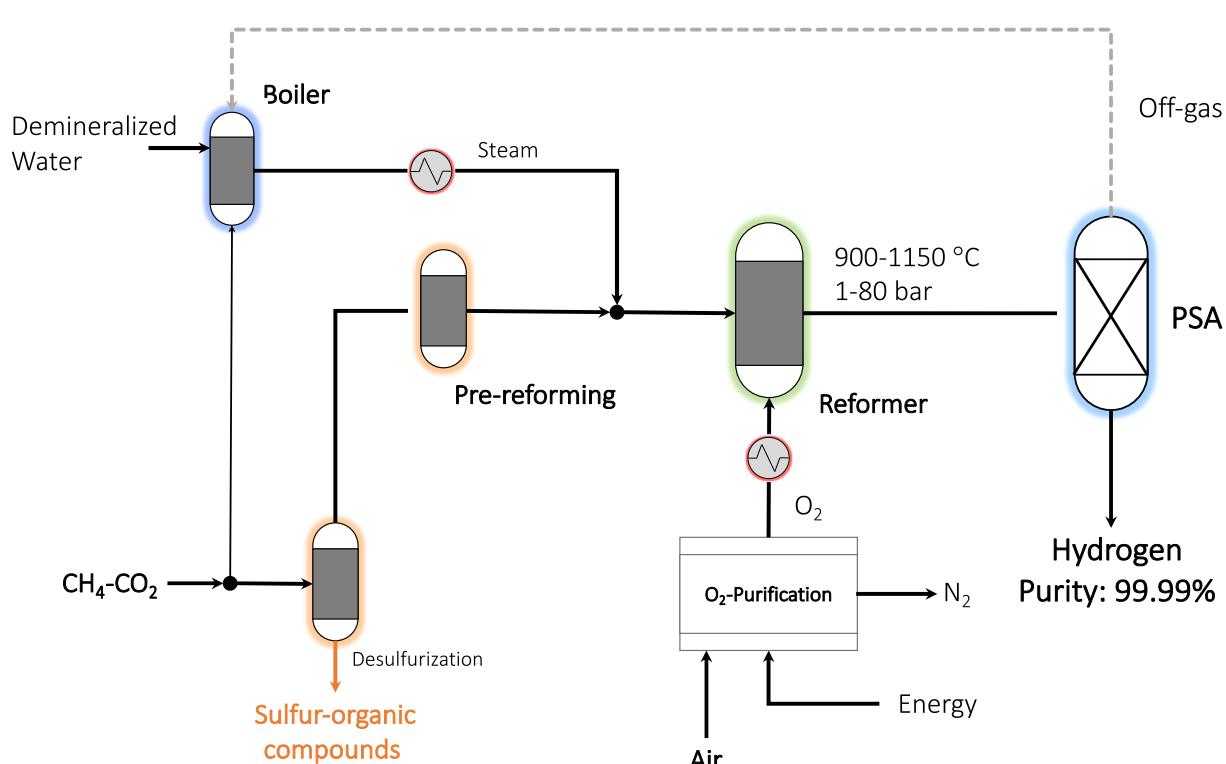


Fig. 8. Autothermal reforming (ATR) of methane.

sintering of the active phase, and soot formation (Gao et al., 2008; Kim et al., 2013; Liu et al., 2010); this type of deactivation can be reduced through the incorporation of promoters (Rh, Pd, Ru) and the selection of an appropriate support (CeAl₂O₃, CeZrO₂). The latter results in a better balance between the capacity of the support to transfer O₂ and metal dispersion (Dias and Assaf, 2008; Ruiz et al., 2008; Sepehri and Rezaei, 2017; Sepehri et al., 2018).

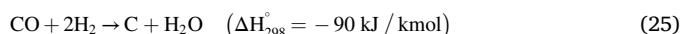
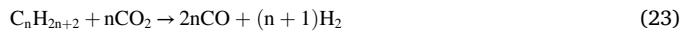
The addition of CeO₂ favors the mobility of the lattice oxygen, which reduces the formation of carbon deposits on the catalyst (Cao et al., 2009; Sepehri and Rezaei, 2017). Although ATR is not currently a mature or predominant alternative, some projects, like the BioRobur, have demonstrated their technical feasibility for the synthesis of H₂ at a pre-commercial level (100 Nm³ H₂/h) from the biogas generated by renewable sources (landfills, municipal solid waste, agroindustry by-products) (Montenegro-Camacho et al., 2017; Rau et al., 2019). Currently, its production costs are not favorable (6 USD/kg H₂), but its environmental footprint and the incentives created by different governments could tilt the balance in its favor.

Finally, it must be pointed out that biogas is a very complex stream due to the amount of impurities/contaminants; therefore, deactivation of the catalyst, usually nickel, can be fast (H₂S) or slow (NH₃) due to the formation of nickel oxides (NiO, Ni₂O₃, NiAl₂O₄) (Luneau et al., 2017; Yin et al., 2020). For ATR, the consequences of those substances are much more severe because the deactivation is irreversible (Yin et al., 2020).

2.5. Dry reforming (DR)

Dry reforming is a H₂ production process that uses hydrocarbons (CH₄, C₂H₆, C₃H₈, and C₄H₁₀) as raw materials and CO₂ as an oxidizing agent (Eq. (23)) (Aziz et al., 2019; Chaghouri et al., 2022; Su et al., 2022). The DR process of CH₄ (Eq. (17)) is of great interest because it would allow transforming two GHG in synthetic fuels, solvents, and ammonia; furthermore, DR could be 20% less expensive than SMR, which is a reference route at the industrial level (Gao et al., 2020; Jin et al., 2021; Vo et al., 2022). The DR (ΔH_{rxn} : 247 kJ/mol, Eq. (17)) is a more endothermal reaction than SMR (ΔH_{rxn} : 206 kJ/mol, Eq. (6)) and ATR, which must be performed at high temperatures (630–1000 °C) (Akansu et al., 2022; Gao et al., 2020; Gomes-Oliveira et al., 2022). Above 900 °C the predominant products are CO and H₂; nonetheless, the catalyst could be deactivated through sintering (Akansu et al., 2022; Charisiou et al., 2018; Pakhare and Spivey, 2014).

In DR, coke formation is associated to the Boudouard (Eq. (8)) and methane decomposition reactions (Eq. (9)). At high temperatures, parallel reactions (Eqs. (6), (16) and (24)) also occur varying the H₂ concentration; therefore, the possibility of obtaining H₂/CO ratios below 1 is evident (Eqs. (17), (23)–(25)); the latter would be attractive for the synthesis of methanol, acetic acid, and dimethyl ester through a Fischer-Tropsch process (Akansu et al., 2022, 2022de Araújo Moreira et al., 2021; Jang et al., 2019). When the CO₂/CH₄ ratio is close to 1, basically CO and H₂ are generated; an increase in this ratio favors the formation of CO and reduces that of H₂ (Aziz et al., 2019; Gao et al., 2020; Jang et al., 2019; Jin et al., 2021).



The DR can also be accomplished using noble metals (mainly Pd, Pt, Rh, Ru) as catalysts, which offer high catalytic activity and stability (Charisiou et al., 2018; Schiaroli et al., 2019); however, these are not viable at the industrial level due to their costs (Abdullah et al., 2017; Gao et al., 2020; Jang et al., 2019; Jin et al., 2021; Li et al., 2020b). On average, Ni-based catalysts are 100-times cheaper than noble metals but

are more prone to deactivate in a short period of time (Charisiou et al., 2018; Schiaroli et al., 2019). Metal catalysts (transition metals: Ni, Fe, Co) show comparable activities but they are more prone to form coke on their surface (Abdullah et al., 2017; Al Abdulghani et al., 2020; Ali et al., 2020; Chen et al., 2020; Gao et al., 2020; Li et al., 2020a). The use of bi-metallic catalysts (Ni-M, M: Cu, Ru, Pd, Ag, Pt, Au) is quite appealing because it would increase the reducibility of Ni, diminishing carbon formation on the catalyst (Abdullah et al., 2017; Dehimi et al., 2020; Gould et al., 2015). Promoters are used to reduce the sintering of the active species (structural) or to provide additional active sites (chemical) that improve the catalyst's performance (Abdullah et al., 2017; Jang et al., 2019; Li et al., 2020a).

The adequate support and promoters selection (Ce, Ca, K, Cu, V) is a key factor to reduce the deactivation of the catalyst, because they provide properties like reducibility (CeO₂, Nb₂O₅, Ta₂O₅, TiO₂; ZrO₂), alkalinity (CaO, BaO, Na₂O, K₂O, La₂O₃, MgO), and the capacity to store oxygen (TiO₂, CeO₂, CeO₂–ZrO₂) (Akansu et al., 2022; Aziz et al., 2019; Chein and Fung, 2019; Jang et al., 2019; Jin et al., 2021; Li et al., 2020a; Pizzolitto et al., 2019). Metallic promoters like K, Cu, Au, and V are of great interest because they reduce the deactivation caused by sintering and carbon formation (Abdullah et al., 2017; Gould et al., 2015). The use of low Rh concentrations (0.1% w) fosters the dispersion of Ni and reduces the formation of coke on the catalyst (de Araújo Moreira et al., 2021). Likewise, the use of V₂O₅ as a promoter in Rh/SiO₂ systems increases the catalytic activity up to 20 times due to the improvement in Rh dispersion (Abdullah et al., 2017; Pakhare and Spivey, 2014). Schiaroli et al. (2019) evidenced that the addition of Rh and steam to the feed is highly effective to decrease carbon formation while Charisiou et al. (2018) stated that metal oxides (La₂O₃ and CeO₂) induce modifications on the catalytic surface, increasing its catalytic activity.

Most of the available studies use synthetic mixtures of biogas as raw material for DR, incorporating, in some cases, variable amounts of impurities; notwithstanding, from the point of view of the sustainability of the process, the use of the generated biogas from renewable resources is quite attractive (Elsayed et al., 2018; Jiang et al., 2021; Pakhare and Spivey, 2014; Parente et al., 2020; Ugarte et al., 2017). Hajizadeh et al. (2022) evidenced the feasibility of integrating anaerobic digestion with dry reforming; the process could produce 8.1 (kg H₂/h) with energetic efficiencies of 73%. The authors showed the advantages of using methane for H₂ synthesis instead of combustion. Gomes-Oliveira et al. (2022) proposed ideal ranges for CO₂ (50–60%) and CH₄ (40–50%) during the reforming of a synthetic mixture of biogas at a pilot scale (0.57 m³/h). These operational conditions lead to high conversion of reactants (CH₄: 99%, CO₂: 97%), high selectivity to H₂ (42–50%) and CO (49–58%), and relative low coke formation.

A biogas current usually has a CH₄/CO₂ ratio greater than 1, which can lead to operational difficulties due to the need to recover the excess CH₄; furthermore, this excess is an important disadvantage because it may increase the formation of carbonaceous materials (Akansu et al., 2022; Charisiou et al., 2018; Schiaroli et al., 2019). Although H₂S affects the efficiency of the process, this impact would be reduced by the development of new catalytic materials (noble metals, transition metals, rare earth, supports, promoters), optimization of the synthesis of the catalyst and of the operational conditions, and the introduction of modifications to the reaction system (Calgaro et al., 2021; Elsayed et al., 2018; Jiang et al., 2021). Table 6 summarizes some promising alternatives to improve the performance of the dry CH₄ and biogas reforming.

2.6. Bi-reforming (BR) and tri-reforming (TR) of biogas

The impact that energy consumption and coke formation has on the DRM efficiency is well known since the 30s; however, some authors suggest that injecting H₂O and O₂ could be an effective measure to assure the thermal neutrality of the DRM reaction and to supply part of the required raw materials needed for the reforming (Lima et al., 2020; Mallikarjun et al., 2020; Moura et al., 2021; Minette and De Wilde,

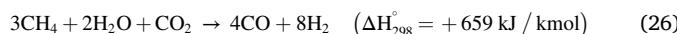
Table 6

Technological options to increase the efficiency of the dry reforming processes.

Standard process	Description of the improvement	Advantage	Disadvantage	Source
Dry reforming	Membrane reactors	H ₂ separation shifts the reaction equilibrium forward and inhibits the competing WGS reaction. This technology avoids the use of additional purification processes. Membrane reactors allow transformation/extraction of one or more products by using a selective barrier. Membrane reactors are made from different materials to fit requirements of experimental conditions.	Sulfur compound can cause corrosion in pipelines as well as catalyst and membrane poisoning. High price of membrane materials is considered the bottleneck for large-scale applications. Life span is reduced by pinhole formation and cracking. Non-commercial technology.	Gallucci et al., 2008; Garcia-Garcia et al., 2013; Sumrunronnasak et al., 2016; Parente et al., 2020
	Micromoreactors	Highly efficient for multiphase reactions because of their large surface to volume ratio and excellent mass and heat transfer performance. Compared to fixed bed reactors, micromoreactors have high conversion (>90%) of CH ₄ and CO ₂ . Presence of O ₂ improves the catalytic activity and stability of the process. Higher selectivity than conventional fixed bed reactors. Micromoreactors could be made in different materials.	Reactor blockage can reduce the performance of the process. Sulfur deposition decreases reagent conversion even at low concentrations of H ₂ S (1–10 ppm). Deactivation may be reversible/irreversible; it depends on the composition of the catalyst. Non-commercial technology.	Behroozsaran and Pour, 2014; Rezaei and Moradi, 2018; Fukuda et al. (2021); Basuni et al. (2021).
	Chemical looping	The process has been widely studied and applied in the last decades. The H ₂ produced is never in contact with CO ₂ avoiding the reverse water gas shift reaction. Selectivity and production of H ₂ is higher. Reduces the impact of catalyst deactivation and the adjustment of the H ₂ /CO ratio (above 1) which is critical for the final application of the syngas produced.	In the presence of higher hydrocarbons, carbon deposition is significant. The selection of an appropriate oxygen carrier is critical for process performance. High thermal stability and resistance to sintering is highly desirable. Fe-based materials are highly efficient for chemical looping in a wide range of conditions (700–1800 °C) but tend to form oxide layers that slow down the reaction. Non-commercial technology.	Löfberg et al. (2017); Ugarte et al. (2017). Ugwu et al. (2019) Tian et al. (2020)
Microwave-assisted reforming		Microwave (MW) heating systems offer higher heating rates, low equipment size, safe operation, and a better control of heating. MW can preserve catalyst stability in reforming reactions due to its ability to remove coke deposition. MW systems can be easily installed and integrated into existing plants. Low carbon formation. Ceramics are an excellent microwave absorbing material that could achieve uniform heating of the catalyst	Heat transfer control plays an important role in dry reforming of methane. Catalyst and supports used in DR usually show low microwave absorption. Commercial applications are not available. A simple and accurate device for measurement of the catalyst temperature is not available. Non-commercial technology.	Zhang et al., 2018; Tan et al., 2019; Fidalgo et al., 2011; Garcia et al. (2021); Alawi et al., 2020
Plasma-based reforming: Non-thermal: 150–450 °C		Low carbon formation. Can operate at low temperature/ambient pressure with a low energy input. Plasma has a synergic effect on the catalytic process because it reduces the energetic barrier of some reactions. Several alternatives are available to produce plasma: gliding arc discharge, dielectric barrier discharge, corona discharge, radio frequency discharge, atmospheric pressure glow discharge, and low-energy pulsed discharge. CO ₂ and CH ₄ can be dissociated easily. In the presence of noble gases dissociation of CH ₄ and CO ₂ is faster.	Carbon formation still occurs mainly due to the Boudouard reaction and methane cracking. For higher CH ₄ /CO ₂ feed ratios many side reactions can occur. Plasma can cause a change in the physico-chemical characteristics of the catalyst. Compared to thermo-catalytic processes, CH ₄ /CO ₂ conversion observed in plasma technologies are lower. Energy cost is the main concern of the process. Non-commercial technology.	Yap et al., 2018; Wang et al., 2019; Cheng et al., 2020; Martin del campo et al., 2021.
Plasma-based reforming: Thermal: 400–1000 °C		Low carbon formation. In thermal plasma process, reaction rates of raw materials are higher than non-thermal, therefore high conversions are expected. Methane decomposition is driven by temperature. In thermal processes, reaction completes quickly (few milliseconds)	High-energy consumption to ionize the raw materials. High temperature can lead to carbon formation. Non-commercial technology.	Tao et al., 2008; Yan et al., 2010; Chung and Chang, 2016; Scapinello et al. (2017)

2021; Siang et al., 2019). The previous combination is interesting because it would also limit the formation of coke on the catalyst (Entesari et al., 2020; Blumberg et al., 2019; Kumar et al., 2016; Li et al., 2015). In CH₄ bi-reforming, CO₂ and H₂O combine to form syngas (Eq. (26)) with an H/C ratio close to 2 (this ratio is usually termed metgas), which is very adequate for the production of methanol through the Fischer-Tropsch synthesis (Chein et al., 2017; Dan et al., 2020; Singh et al., 2018; Singha et al., 2016; Zhao et al., 2017).

Bi-reforming is a very endothermal reaction, which reduces significantly its environmental performance (Lima et al., 2020; Moura et al., 2021); to this regard, Olah et al. (2013, 2015) suggest the combustion of CH₄ would generate the reagents (CO₂-H₂O) and the necessary energy for the bi-reforming reaction to take place (Eq. (26)). The increase in temperature rises the conversion of CH₄ and CO₂ to reach 86% and 79%, respectively; it must be noted that the increase in the reaction temperature, from 830 to 910 °C, has an insignificant effect on the H₂/CO ratio (Moura et al., 2021; Olah et al., 2015). Thermodynamic analyses suggest that when bi-reforming operated at atmospheric pressure and temperatures close to 900 °C, the production of metgas without the generation of coke would be viable (Entesari et al., 2020; Moura et al., 2021). Mathematical models reveal the feasibility of these alternatives; nonetheless, the presence of impurities and the variability observed in the composition of the raw biogas leads to the deactivation of the catalyst (Blumberg et al., 2019; Moura et al., 2021).



High operating temperatures (700–1000 °C) and coke formation will demand the following attributes for the catalytic material: i) thermal stability of the support, ii) high resistance to sintering, and iii) high activity during long operation times. In the bi-reforming (Eqs. (6), (17) and (26)) and tri-reforming (Eqs. ((6), (12), (17) and (27))) processes, Ni and noble metals (Pt, Pd, Ru, Rh) are also used, but the latter are not very practical due to their cost (Aziz et al., 2019; Kumar et al., 2015; Li et al., 2020a; Singh et al., 2018). The use of Ni and Co (NiO/MgO, CoO/MgO) and promoters like Ce and La has been effective to limit coke formation, enhance selectivity, and improve conversion of the raw

materials (Aziz et al., 2019; Entesari et al., 2020; Izquierdo et al., 2017; Kumar et al., 2015; Lima et al., 2020; Mallikarjun et al., 2020). Cerium (CeO₂) is considered an efficient promoter in bi-reforming because its redox properties allow storage/delivery of oxygen that is used for coke gasification; however, the combination of CeO₂/ZrO₂ is highly recommendable because its positive effect on oxygen storage capacity, thermal stability, and metal dispersion (Entesari et al., 2020; Izquierdo et al., 2017; Lima et al., 2020). As indicated in Table 7, the performance of a bi- or tri-reforming process is tied to the properties of the used catalytic system (catalyst, support, promoter), of the chosen reactor, the applied operational strategies, and the variability of the feedstock, among others (Anchieta et al., 2019; Elsayed et al., 2018; García-Vargas et al., 2015; He and de Wilde, 2021; Kumar et al., 2016; Li et al., 2015; Lima et al., 2020; Siang et al., 2019). The variability of the reforming conditions hinders identifying the most suitable catalytic system for large-scale applications (Blumberg et al., 2019; Lima et al., 2020; Moura et al., 2021); however, characteristics like the low cost, high thermal and catalytic stability, and its capacity to store oxygen are determinants for its selection (Table 7).

In tri-reforming (Eq. (27)), the reference technologies (SMR, POX, and DR) are combined to generate syngas at intermediate temperatures (700–900 °C) and atmospheric pressure (Osat and Shojaati, 2022; Schmal et al., 2018; Singha et al., 2016; Wachter et al., 2020, 2021). It should be noted that high pressure does not favor this process, but high pressure is required in large-scale processes to favor the downstream use of the produced syngas (Jang and Han, 2022). Tri-reforming can generate highly flexible H/C ratios (1.5–2) because it is possible to adjust the molar ratio of four reagents (CH₄, CO₂, H₂O, and O₂) in a single process (Bertoldi et al., 2022; Izquierdo et al., 2017; Kantserova et al., 2018; Khademi et al., 2021). Some studies emphasize the positive effect of side feeding the reagents, particularly O₂, in methane conversion (99.9%, 5% higher to other reactors), selectivity, and the activity of the catalyst (Alipour and Khademi, 2020; Khademi et al., 2021; Jang and Han, 2022).

Nickel-based catalysis are extensively used for tri-reforming of methane (Fedorova et al., 2020; Anchieta et al., 2022) and synthetic biogas (Veiga et al., 2021); this is due to the activity and low cost of this

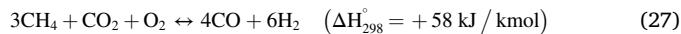
Table 7
Catalytic materials used in methane, bi- and tri-reforming processes.

Strategies used to improve the process' performance	Bi-reforming	Tri-reforming
Catalysts: Must have the following characteristics; low cost, activity, selectivity and stability at high temperatures (700–1000 °C). Nickel (Ni): Is the most used active phase due to its low cost; however, it tends to form coke.	Small amounts of Rh and Pd improve the dispersion and reducibility of NiO, which increases the resistance to sintering and coke formation. The use of transition-metal carbides (Mo ₂ C) could lead to similar results at a lower cost (Li et al., 2015). The use of Pt-Pd-doped Ni-Mg catalysts supported with CeO ₂ -ZrO ₂ has allowed performing bi-reforming at lower temperatures (450–600 °C) (Elsayed et al., 2018). The use of CeO ₂ , ZrO ₂ , and La ₂ O ₃ , the metal dispersion improvement, the use of materials at a manometric scale (core-shell, nanotubes) would reduce coke formation and sintering (Singh et al., 2018; Cunha et al., 2020; Lima et al., 2020). The better operational conditions of temperature (800–850 °C) and pressure (1 bar) suggest conversions of CH ₄ (60–90%) and CO ₂ (40–60%) (Singh et al., 2018; Cunha et al., 2020; Lima et al., 2020; Mallikarjun et al., 2020). The use of pyrochlores (A ₂ B ₂ O ₇ , A: element of the lanthanide series, B: transition metal) improves the metal-support interaction increasing the resistance to coke formation (Kumar et al., 2016).	Simultaneous impregnation of Ni-Mg, instead of successive ones improves the catalytic activity, increases stability, and reduces coke formation (García-Vargas et al., 2015). The use of ionic liquids improves the activity of Ni-ZrO ₂ systems due to their impact on the morphology, the acid-base properties, and the dispersion of the metal (Anchieta et al., 2019).
Supports: The main characteristics of this type of materials are: low cost, high thermal stability, high specific surface area, high alkalinity, and capacity to store oxygen. The most used materials are: Al ₂ O ₃ , SiO ₂ , MgO, CeO ₂ , ZrO ₂ , TiO _x , carbon-based support, and its mixtures. The elements of the lanthanide series have been applied efficaciously as promoters/supports/catalysts of bi- and tri-reforming processes to minimize/eliminate the formation of coke.	The presence of B (3%) can suppress/reduce the diffusion of carbon in the lattice structure of nickel, inducing a coke formation of 4% after 24 h of operation at 800 °C (Siang et al., 2019).	Synthesis of mesoporous Ni-SiO ₂ and Ni-MgO systems improves metal dispersion and increases the metal-support interaction (Yoo et al., 2015; Fedorova et al., 2020). The latter has proven effective to reduce the formation of coke in short reaction periods (10–20 h). The use of carbon nanomaterials (tubes, fibers, spheres) allows generating stable H ₂ /CO (1.5) ratios for up to 44 h (Kozonoe et al., 2020).
Promoters: These substances improve the performance of the catalytic material because the increase the activity and stability of the catalyst and reduce coke formation. The most used promoters include elements of the group s (Na, K, Ca, Mg) and d (Zr, La, Ce, Pt, Rh) of the periodic table.		In a tri-reforming process (Ni-CeO ₂) an increase in La concentration (0–10%) improves the metal dispersion and increases the catalytic activity (Pino et al., 2011). The presence of alkaline supports favors the adsorption and dissociation of CO ₂ , which would minimize the coke formation (Pino et al., 2011; García-Vargas et al., 2015). For Ni-Mo-carbides systems, the presence of Mg and K can reduce the conversion of CH ₄ -CO ₂ and the yield of H ₂ .

metal. As in other reforming processes, the addition of promoters (CeO_2 , ZrO_2 , MgO) and mixed promoters ($\text{ZrO}_2\text{-CeO}_2$, $\text{La}_2\text{O}_3\text{-CeO}_2$) with basic properties provides an increase in activity and stability of the catalytic system (Kim et al., 2019). In tri-reforming, coke formation could be prevented/reduced by improving the dispersion of the catalyst, reducing the particle size, and improving the interaction of the metal-support pair (Ancheta et al., 2019; Kumar and Pant, 2020; Mallikarjun et al., 2020; Schmal et al., 2018; Singh et al., 2018; Zhao et al., 2017).

The use of micro-reactors and the inclusion of bi-metallic catalysts could have a large impact on the performance of the tri-reforming process (Pt-metal, metal: Pt, Pd, Co, Mo, Fe, Re, Y, Cu, Zn) because these systems have less pressure losses, improve mass and energy transfer, and increase the catalytic activity (Izquierdo et al., 2017). The use of compound materials (Pt–Ni, Pd–Ni) provides a better response to the presence of H_2S ; it should be noted that the recovery of the catalytic activity takes time and requires a combination of oxidation (H_2O) and reduction (H_2) stages (Kantserova et al., 2018). During tri-reforming, the H_2/CO ratio can be adjusted (1.7–2.7) by modifying the temperature and the CH_4 , CO_2 , and H_2O content (Lima et al., 2020; Singha et al., 2016; Siang et al., 2019).

The presence of H_2O is positive because it reduces coke formation to less than 1%; the latter is attributed to the increasing impact of the SMR within the production process (Alipour and Khademi, 2020; Kumar et al., 2016; Khademi et al., 2021; Lima et al., 2020; Siang et al., 2019; Singha et al., 2018). Tri-reforming reduces the magnitude of the catalyst deactivation and energy consumption thanks to the incorporation of H_2O and O_2 to the reaction medium (Singha et al., 2016). Although reforming reactions (Eqs. (6), (12), (15) and (17)) and that of coke formation (Eqs. (8)–(10)) are well-known for tri-reforming, the thermodynamic behavior is still uncertain due to the complexity of the reactions (Alipour and Khademi, 2020; Jang and Han, 2022; Zhang et al., 2014).



Currently, tri-reforming is not commercially available; notwithstanding, the laboratory-scale results suggest that the development of materials (catalysts, supports, and promoters) and the energy integration (Chein and Hsu, 2018; Ding et al., 2019; Pashchenko, 2018; Swirk et al., 2020; Wachter et al., 2020, 2021) of the processes forecast a promising future for these technologies. Mathematical models disclose the potential of biogas sources (wastewaters, landfills, biomass) to produce raw materials for methanol synthesis and high value chemicals (Chein et al., 2021; dos Santos et al., 2018; Furtado-Amaral et al., 2020). The literature proposes strategies such as energy integration and intensification of bi- and tri-reforming processes to increase their environmental performance. For example, mathematical models indicate that chemical-looping is an attractive alternative to reduce CO_2 emissions and the energy losses of the bi-reforming process. Co-injections of reagents allow obtaining flexible ratios (H_2/CO), although this strategy could favor coke formation (He and de Wilde, 2021). Rahnama et al. (2014) indicate that it is feasible to couple SMR (endothermic) with tri-reforming (exothermic) and generate a biogas stream with variable H_2/CO ratios.

Instead of fixed beds, the use of fluidized reactors would lead to improvements in the efficiency of CH_4 and CO_2 conversion; besides the lesser pressure losses and the better temperature distribution would make them attractive for their industrial application (Khajeh et al., 2014). The reagent injection strategy has a significant impact on the useful life of the catalyst and CO_2 conversion during H_2 synthesis for H_2/CO ratios close to 1.2; for ratios equal to 2, the applied strategy has no appreciable impact (Alipour and Khademi, 2019). Likewise, the thermochemical recovery is a technique of interest for tri-reforming because it reduces the size of the reformer, increases the CH_4 conversion, and reduces coke formation (Wachter et al., 2020). Table 7 summarizes some of the most important characteristics of catalysts,

supports, and promoters used in bi- and tri-reforming of CH_4 .

3. Environmental analysis of hydrogen production processes

The transforming energy scenario (TES) proposed by the International Renewable Energy Agency (IRENA) intends to maintain the global temperature increase under 2 °C by 2050 (IRENA, 2020, 2022). This implies a reduction in the consumption of coal, oil, and gas by 2050 of 87, 70, and 41%, respectively (IRENA, 2020, 2022), and the adoption of greener practices and sustainable energy sources in hard-to-abate sectors (electricity, transportation, iron and steel, petrochemical processes) (Rasul et al., 2022). Unfortunately, the global socio-economic scenario evidences an increase in non-renewable energy use; therefore, the expected rise in the Earth's temperature will be higher (3–6 °C) (Rasul et al., 2022).

Currently, 120×10^4 (t/yr) of green H_2 are produced, the proposed TES will require 250×10^5 and 160×10^6 (t H_2 /yr) for 2030 and 2050, respectively. This represents a constant growth of the installed capacity for electrolysis, 50–60 GW per year, until reaching 1700 GW in 2050. For this reason, the demand for renewable electricity will rise from 0.26 TWh (2016) to 7500 TWh (2050); the required estimated investment for TES is set to reach 110 trillion US dollars in 2050, and green and blue H_2 will supply 8% of the total energy consumption (IRENA, 2020, 2022). The technical and economic complexities of the aforementioned scenario suggest the need to support this transition with low impact alternatives that take into account one of the main bottlenecks, consumption of electricity. Table 8 evidences the relevant role of electrolysis as a source of green H_2 to cover the future needs of society; however, the environmental footprint depends on the energy mix used for the production of H_2 (Gerloff, 2021). An energy mix with a strong component of non-renewable raw materials (coal, gas, and oil) could give rise to significant emissions of GHGs (20–34 kg $\text{CO}_2\text{-eqv}/\text{kg H}_2$), whereas the use of electrolytic processes driven by wind or solar energy would lead to emissions at a lower range (0.1–2.0 kg $\text{CO}_2\text{-eqv}/\text{kg H}_2$) (Table 8). As suggested in the literature, electrolysis will be the dominant pathway for H_2 synthesis by 2050 because of its lower carbon footprint, the cost reduction associated with economies of scale, the increase in electrolyzer performance, the feasibility of recycling the valuable components (Ni, Pt, Ir), and the expected reductions in the consumption of renewable and non-renewable resources (water, electricity, precious metals, steel) (Badgett et al., 2021; Rasul et al., 2022; Zhao et al., 2020).

3.1. Available technologies for the reduction of the carbon footprint of hydrogen

In the long term, electrolytic processes will replace the non-renewable H_2 needed to decarbonize the global economy; nonetheless, it is convenient to identify which options could warrant the generation of H_2 without adding more GHG to the atmosphere (Badgett et al., 2021; IRENA, 2019; Rasul et al., 2022). The literature points to at least three routes for the utilization of the CO_2 generated in some H_2 processes: i) carbon capture and storage (CCS), ii) carbon capture and utilization (CCU), and iii) biomass-based synthesis (BIO) (Aresta et al., 2013, 2014; Artz et al., 2018; Gabrielli et al., 2020; Greig and Uden, 2021; Terlouw et al., 2021). These alternatives would ease the recovery and utilization of the CO_2 emitted during the generation of electricity from non-renewable sources (coal, oil, and gas) in industrial processes with an intensive use of fossil fuels (petrochemistry, cement, and steel), or from atmospheric CO_2 (Table 9) (Gabrielli et al., 2020; Greig and Uden, 2021). CCS uses four basic systems to capture CO_2 : i) capture from industrial process streams, ii) post-combustion capture, iii) oxy-fuel combustion capture, and iv) pre-combustion capture (Table 9) (Cuéllar and Azapagic, 2017; IPCC, 2005; Suicmez, 2019).

CCS is used practically in all continents in thermoelectric power plants, the cement, oil, and gas industries (GCCSI, 2021; Kawai et al., 2022; Loria and Bright, 2021; Nagabhushan et al., 2021); however, the

Table 8Available technological alternatives for the generation of green H₂.

Technology	Process description	Advantages	Disadvantages	Source
Alkaline water electrolysis (AWE) ¹	Is a mature technology that uses KOH (25–30% weight) or NaOH as electrolyte for the generation of O ₂ in the anode ($4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$) and of H ₂ ($4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2$) in the cathode. The process operates at relatively low temperatures (60–80 °C). Pressure varies between 6 and 30 bar. Current densities (0.2–0.4 A/cm ²), voltages (1.8–2.4 V), and reported consumptions (4–7 kWh/Nm ³) suggest that production capacities close to 800 (Nm ³ /h) can be achieved. The production system could generate H ₂ (99.8%) and O ₂ (99.7%) and have a useful life time close to 90,000 h. The efficiency of the process can vary between 70 and 89%.	The use of high operational pressures would reduce the economic and environmental costs associated with the product compression and storage stages. The carbon footprint of the processes driven by renewable energies like solar and wind is usually below 1.0 kg CO ₂ -eqv/kg H ₂ .	The carbon footprint of the process is determined by the raw materials used for the generation of electricity. When in the energy grid raw materials like carbon and petroleum predominate, the carbon footprint (20–30 kg CO ₂ -eqv/kg H ₂) can be significantly higher than that reported for natural gas (9–12 kg CO ₂ -eqv/kg H ₂) or coal (14–19 kg CO ₂ -eqv/kg H ₂) reforming processes. The released O ₂ is not utilized. Consumption of energy in electrolytic processes is of 2–33 times higher than the calculated theoretical value. It is possible that explosive H ₂ /O ₂ mixtures be generated.	Shi et al., 2020; Amini-Horri and Choolaei, 2019
Polymer electrolyte membrane electrolyzers (PEME) ¹	Electrodes use noble metals like Pt and Ir. Electrons released by the oxidation of H ₂ O ($\text{H}_2\text{O} \rightarrow 0.5\text{O}_2 + 2\text{H}^+ + 2\text{e}^-$) are used to reduce protons ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$) in the cathode. H ⁺ are led towards the cathode through a solid polymer electrolyte whereas the e ⁻ make it through an external circuit. It can operate at low temperatures (60–80 °C) and pressures (<30 bar). The current densities (0.6–2.0 A/cm ²), the cell voltages (1.8–2.2 V), and energy consumptions (4–7 kWh/Nm ³) suggest that production capacities of 30 (Nm ³ /h) can be reached. The system could generate H ₂ (99.999%) and have a useful life time of ca. 20,000 h. The efficiency of the process can vary from 80 to 90%.	The use of this type of technologies would reduce 75% the CO ₂ emissions if the system uses electricity from renewable routes.	The most used metals (Pt, Rh, Rb, Pd, Au and their oxides) are much more expensive than those used in AWE. The direct or indirect use of H ₂ O could be a disadvantage in a world scenario of water scarcity. Although seawater could be a raw material of great interest, phenomena like evolution of Cl ⁻ and corrosion would limit its use.	Barejš et al. (2019)
Solid oxide electrolyzers (SOEs) ¹	Can operate at variable temperatures (300–900 °C and relatively low pressures (<30 bar). The current densities (0.3–1.0 A/cm ²), the cell voltages (1.0–1.3 V), and the reported energy consumptions (2.5–3.5 kWh/Nm ³) suggest that production capacities below 10 (Nm ³ /h) can be reached. The efficiency of the process can exceed 90%. It is still in the research and development stage.	Although Pt electrodes are quite electroactive, good performances have been evidenced with lower cost electrodes (stainless steel, Ni and Mo). The use of high temperatures could reduce up to 25% the consumption of electricity; for this reason, the costs of the produced H ₂ are lower.	Selecting membranes of great chemical and thermal stability is key for the efficiency of the process. The most active materials (Pt, Au, Ru, Ag) are expensive and scarce, which limits their application at a large scale. Some studies have shown that it is feasible to integrate these H ₂ production systems into nuclear and electrical power plants. The direct or indirect consumption of H ₂ O could be a disadvantage. Although seawater could be a raw material of great interest, phenomena like evolution of Cl ⁻ and corrosion would limit its use.	Al-Zahrani and Dincer, 2018; Liu et al., 2021

Note: In an electrolytic process, the production of 1 Nm³ H₂ (0.09 kg H₂) consumes directly 1 L of fresh H₂O but its consumption could range widely (9–120 L H₂O/kg H₂) due to the indirect consumption of the process (electricity production, cooling, etc.).

installed capacity until 2020 was relatively low, around 400×10^5 t CO₂/yr (GCCSI, 2021; IPCC, 2005). It should be noted that CO₂ emissions were increased to 36.3 Gt (36.3 billion/t); therefore, by 2050 more than 2000 facilities (70–100 per year) should be in operation to meet the goals of the Paris Agreement (GCCSI, 2021).

Considering exclusively 7887 fixed sources with an emission capacity above 100×10^3 t CO₂/yr, it would be possible to capture 0.3% of the 134×10^8 t CO₂ generated per year (GCCSI, 2021; Nagabhusan et al., 2021). The production of electricity concentrates 78% (105×10^8 t CO₂/yr) of the emissions and 63% of the sources (4942) with an emission capacity greater than 100×10^3 t CO₂/yr (IPCC, 2005).

The recovery efficiencies reported by the electrical sector are high (85–95%) but they consume important percentages of the generated energy (10–40%); for example, a power plant that uses natural gas consumes less energy (11–22%) than one that uses coal (24–40%) (IPCC, 2005). Although these technologies can lead to controversies by their economic and environmental cost (Arning et al., 2019; Kawai et al., 2022; Nagabhusan et al., 2021); these routes would allow the industry to reduce CO₂ emissions close to zero faster with lower investment costs (20–30%). In this regard, experts claim that carbon capture in geological

sequestration sites (saline formation and depleted fields) can be done securely; up to date, 26 facilities have stored underground more than 300×10^3 t CO₂ (Loria and Bright, 2021; Nagabhusan et al., 2021).

Although knowledge gained will allow to reduce cost and risks, a large number of projects must be developed to make a significant impact on climate change (Loria and Bright, 2021; Nagabhusan et al., 2021). CCS has as disadvantages its relatively high costs (cement: 60–120, electricity: 50–100, hydrogen: 60–120, iron and steel: 40–100 USD/t CO₂) and the high energy consumption (250–300 kWh/t CO₂) for the compression, transport, and injection of CO₂. In mature processes, like SMR, the reduction of the energy efficiency would reach 6%; which would entail the use of renewable energy to reduce the carbon footprint.

In 2050, CCUS would be responsible for a sixth of the reduction of CO₂ emissions (Arning et al., 2019; GCCSI, 2021; Suicmez, 2019; Waxman et al., 2021). Application of CCUS has been quite limited because of the lack of government incentives, making it unprofitable to adopt this technology (Ochu and Friedmann, 2021; Victor and Nichols, 2022; Yao et al., 2018); nevertheless, it is expected that the strategies focus on private capital (through capital incentives, revenue treatments) to decarbonize critical sectors of the economy (Ochu and Friedmann,

Table 9Processes used to reduce the carbon footprint during H₂ synthesis.

Technology	Process description	Source	
CCS CCS is a mature technology (+80 years) applied in diverse sectors and with CO ₂ abatement capacity reaching 400 × 10 ⁵ t CO ₂ /year.	Capture from industrial process streams post-combustion capture oxy-fuel combustion capture pre-combustion capture	It is an alternative with an efficiency of 80–90% that allows eliminating CO ₂ from process currents using a solvent (chemical or physical) or a solid material (zeolites or activated carbon). It is used for the purification (upgrading) of natural gas and biogas. The process requires large amounts of energy for the separation of CO ₂ . The membrane (polymeric, metallic, and ceramic) separation processes are considerably efficient and present lower energy consumption. They are still in developing stages, and only a few projects operate at a commercial level. Combustion gases are passed through process units in which the generated CO ₂ is eliminated. Like the previous process, it presents high energy consumptions and the separation efficiency is quite variable (85–99%). The cost of this alternative can vary from 20 to 70 USD/t CO ₂ captured. It requires the use of oxygen (instead of air) for the fuel oxidation. The resulting mixture contains CO ₂ y H ₂ O; for this reason, a reduction in temperature allows condensing the water and generating a CO ₂ -rich current. It allows removing the CO ₂ from a raw material before its combustion. Requires large amounts of energy, but in contrast to post-combustion, it is more efficient because the CO ₂ is more concentrated (15–50% vol.) and at higher pressures (20–70 bar) and temperatures (190–220 °C). When using chemical and physical solvents, its cost can reach 60 USD/t CO ₂ captured. Its efficiency has been tested at a pilot scale.	Jackson and Brodal, 2019; Schmelz et al., 2020; IEA, 2019,2020; Belaissaoui and Favre, 2018; Gabrielli et al. (2020)
CCUS: Is a process capable of scavenging temporarily CO ₂ . A large amount of available alternatives are mature technologies.	Urea production CO (NH ₂) ₂	It is a mature technology for the exploitation of CO ₂ with a demand (120 Mt/year) that increases 3% annually. The process uses 0.74 t CO ₂ /t CO(NH ₂) ₂ and presents a CO ₂ conversion close to 88%. Urea is synthesized from CO ₂ and NH ₃ in a two-stages process at high temperature and pressure (~185 °C, ~150 bar). Stage 1: 2NH ₃ + CO ₂ <→ NH ₂ -COONH ₄ , stage 2: NH ₂ -COONH ₄ <→ CO(NH ₂) ₂ + H ₂ O	Artz et al., 2018; Gabrielli et al., 2020
	Methane production (methanation): Sabatier synthesis	It is an alternative capable of transforming H ₂ and CO ₂ into CH ₄ . It is an exothermal process (ΔH_{rxn}^o : 165 kJ/mol) accomplished at high temperature (250–550 °C) and low pressures (5–10 bar) on different catalysts (Ni, Rh, Ru, Co, Fe, Mo). CO ₂ conversion is close to 100%. The process involves a high consumption of electricity (15 MWh/t produced); for this reason, it could increase the CO ₂ emissions if non-renewable energy sources are used. The reaction has been tested for the production of CH ₄ from coal or as a support medium for the spatial missions of NASA.	
	Hydrocarbons production: Fischer-Tropsch synthesis	This route has been used since 1930 and it is used at a large scale for the transformation of syngas to light hydrocarbons (gasoline, alcohols, oils). It is performed at different temperature ranges (200–250 °C and 300–350 °C) and varied pressures (20–40 bar) on different catalysts (Ru, Co, Fe, Mo). The process employs 2.6 t CO ₂ /t produced and presents a CO ₂ conversion close to 52%. It can be coupled to biomass gasification process for the synthesis of hydrocarbons. The process presents a high consumption of electricity (7 MWh/t produced); for this reason, it could increase the CO ₂ emissions if renewable energy sources are not used.	
	Methanol production: CH ₃ OH	In this process that operates at a large scale, (CO + 2H ₂ <→ CH ₃ OH) syngas is made to react on a catalyst of (CuO/ZnO/Al ₂ O ₃) in a varied range of temperature (250–350 °C) and pressure (50–100 bar). The hydrogenation process of CO ₂ (CO ₂ + 3H ₂ <→ CH ₃ OH + H ₂ O) uses 1.4 t CO ₂ /t produced, but it is 2–2.5 times more expensive than the route that uses syngas. The cost of H ₂ produced electrolytically is one of the barriers that makes it, at the level of models, poorly competitive at a large scale.	Boretti, 2013; Nyári et al., 2020.

2021; Victor and Nichols, 2022).

This technology can be adapted to existing power plants to generate gaseous products like H₂ or CH₄, but the most attractive option, due to its maturity and profitability, is injecting CO₂ to enhance oil recovery (Kawai et al., 2022; Quarton and Samsatlí, 2020; Yao et al., 2018). On the other side, it is feasible to synthesize hydrocarbons from H₂ and CO₂ (Fischer-Tropsch), which would improve the profitability of the CCUS processes and would create a market of more sustainable products. As shown in Table 9, methanol (CH₃OH), CH₄, and urea (CO(NH₂)₂) are raw materials of interest that can be synthesized from the direct

hydrogenation of CO₂; these routes are not profitable when compared to their direct competitors due to their costs and their raw material, crude oil (Quarton and Samsatlí, 2020; Ren et al., 2023)

The biomass-based synthesis (BIO) uses the biomass produced sustainably to generate raw materials and capture the atmospheric CO₂ (Gabrielli et al., 2020). Ideally, in this type of processes, the residual biomass will be used to generate the required energy for the productive processes. The biomass is constituted by cellulose (40–50%), hemicellulose (20–30%), and lignin (20–40%). Lignin represents only 40% of the energetic content of the biomass and can be gasified (500–800 K)

and then be transformed, through Fischer-Tropsch synthesis, in liquid fuels.

The annual production of biomass reaches 170 billion tons, of which only 5% is used; on the other hand, only 2% of the more than 500×10^5 t of pulp produced by the paper industry is used for the generation of higher added value products, the remainder is used as fuel (Ahlström et al., 2022; Gabrielli et al., 2020; Mika and Csefalvay, 2018). Lignocellulosic materials and algae can give rise to platform products like organic acids (formic, lactic, levulinic, propionic, succinic, fumaric), alcohols (methanol, ethanol, ethylene glycol, and propylene glycol), biofuels, proteins (*Spirulina* and *Chlorella*), and aldehydes (furfural and hydroxymethylfurfural). Interestingly, algae possess the ability to use CO₂/NOx as raw material and to grow in a wide range of aquatic habitats. In general, varied conversion processes (chemical, thermochemical, biochemical, etc.) are used to reduce costs and increase flexibility (raw materials, fuels, and electricity) of the biomass transformation processes (Mika and Csefalvay, 2018; Upton and Kasko, 2016)

3.2. Life cycle analysis (LCA) applied to the production of hydrogen

The idea of using LCA to determine the sustainability of diverse production processes is based on the possibility of identifying the activities that present the most number of interactions with the environment (Hauschild et al., 2018; Masilela and Pradham, 2021). An LCA is a tool that identifies and quantifies, through a rigorous analysis along the useful life of a project or product, the impacts caused by those interactions; besides, it facilitates the decision making by those responsible for public policies using a tool supported on the available scientific knowledge (Atia et al., 2020; Mahmud et al., 2021; Sadhukhan et al., 2021).

The emissions reported in the environmental categories used by the impact analysis method will depend on the raw material, the chosen technology, the applied contamination abatement processes, and the properties of the final product (Borole and Landfield, 2019; Cvetkovic et al., 2021; Dufour et al., 2012; Hajjaji et al., 2016a; Karaca et al., 2020; Salkuyeh et al., 2017; Siddiqui and Dincer, 2019; Valente et al., 2019a; Verma and Kumar, 2015). Taking into account the similarities observed in some studies on the environmental footprint of H₂, the information depicted on Table 10 was grouped considering the following aspects: i) Tools and impact analysis methods used, ii) origin of data (primary-secondary), iii) functional unit, objective and duration of the project, iv) required raw materials and characteristics of the produced H₂, and v) limitations of the study (Table 10). Impact categories and their indicators at the midpoint level are summarized and explained in Table SM1.

Although in many of the analyzed studies, an LCA was performed defining each of the five aspects of interest previously mentioned; in most cases, GHG emissions are considered an element to assess the environmental performance (Cho et al., 2022; Diab et al., 2022; Oni et al., 2022). Compared with other environmental categories, global warming is easier to be interpreted by different types of audiences, it presents less uncertainties due to the lower amount of substance involved in the model and because its effect on the environment has been assessed for decades (Hauschild et al., 2018). In most studies, important categories (e.g., acidification, eutrophication, ozone depletion, ecotoxicity, among others) are left in the background, which limit appreciably the assessment of the process' sustainability. Regardless of the used raw material, consumption of energy (mainly steam and electricity) and the reagent (natural gas, catalyst) are the activities with the highest impact on the categories used to analyze the performance of the processes (Dufour et al., 2012; Siddiqui and Dincer, 2019) (Table 9).

In the SMR, CO₂ emissions come from the operation (72%) and the construction/dismantling of the process (25%) (Borole and Landfield, 2019; Cetinkaya et al., 2012). Depending on the energy source and the chosen technology, the carbon footprint of SMR varies considerably. Oni et al. (2022) concluded that 25 (t H₂/h) could emit up to 6.7 (kg

CO₂-eqv/kg H₂) whereas ATR leads to about 3.9 (kg CO₂-eqv/kg H₂). Cho et al. (2022) mentioned that the emissions from 33 SMR facilities were between 9.4 and 11.2 (kg CO₂-eqv/kg H₂) when direct and upstream emissions were considered. Steam reforming is a mature technology, in terms of technology readiness; therefore, incorporating carbon abatement technologies could reduce GHGs by 45–85% and increase the leveled cost of H₂ between US\$0.2 and 0.7/kg H₂ (Katebbeh et al., 2022; Navas-Anguita et al., 2021). This suggests, at least for a transition, the feasibility of this alternative to produce H₂.

Coal gasification is an alternative that provides 18% of the world's H₂ production. In coal gasification, consumption of raw materials is responsible for 97% of CO₂ emissions, whereas the extraction and transportation processes represent the remaining 3% (Cetinkaya et al., 2012). The footprint for gasification, considering mining, preparation, transportation, and H₂ production, compression and transportation, falls between 22 and 52 (kg CO₂-eqv/kg H₂). With CCS, the footprint could be reduced (50–75%) but the H₂ price would rise to US\$1.4–2.1/kg H₂; therefore, CCS will increase the cost of the H₂ produced from coal by 45–50% (Li et al., 2022). The use of coke oven gas (COG) evidences the large number of by-products that can be transformed to H₂. The LCA performed by Li and Cheng (2020) indicates that it is feasible to obtain lower environmental footprints (14 kg CO₂-eqv/kg H₂) than those obtained in coal gasification processes. The authors also point out that the CO₂ emissions are concentrated in the production stage (85%) and that this route could be a potential competitor for the coal gasification processes due to its lower energy consumption (35%), CO₂ emissions (37%), and installation costs (28%).

Susmozas et al. (2013) concluded that residual biomass is a sustainable source of raw materials and energy for H₂ synthesis with a low non-renewable energy demand but categories like land use, acidification, eutrophication present relatively higher impacts than those observed for the SMR. Compared to coal gasification, energy use and GHGs emissions for H₂ from corn straw is reduced 75% and 90%, respectively (Li et al., 2020a). In this latter study, carbon dioxide emissions were distributed as follows: raw material preparation and transportation (40%), production stage (31%), and purification-transportation (29%).

Valente et al. (2019b) showed the environmental advantages of biomass gasification over SMR in aspects like child labor, carbon emissions, and acidification; however, the economic and social impacts of the process are matters of interest because SMR outperforms gasification in health expenditure, gender wage gap, and leveled cost. Regarding biomass gasification, studies concluded that it leads to lower emission of carbon dioxide and reduced requirements of non-renewable energy sources (Kalinkci et al., 2012; Wu et al., 2023). Reforming of biomass presents lower emissions and, hence, a relatively smaller impact on categories like abiotic depletion, GWP, ODP, and POFP. According to Amaya-Santos et al. (2021), gasification of urban solid wastes, followed by a reforming process, would be environmentally attractive considering the reduction in GHG emissions (−5.4 kg CO₂-eqv/kg H₂), a value that is far lower than that reported for SMR (1.9 kg CO₂-eqv/kg H₂), ATR (1.7 kg CO₂-eqv/kg H₂), or H₂ production via electrolysis, considering the energy mix of the country of reference (0.3 kg CO₂-eqv/kg H₂) or renewable sources like wind (0.6 kg CO₂-eqv/kg H₂) or photovoltaic (2.9 kg CO₂-eqv/kg H₂). These authors indicate that the use of this type of materials generates slightly higher emissions of acidifying substances (11%) than those generated by SMR, but significantly lower than those caused by electrolytic processes driven by electricity based on non-renewable sources (74%) or solar energy (54%).

Gasification of biomass and wastes via thermochemistry has allowed mitigating the impact caused by the use of non-renewable raw materials; the bio-CH₄ generated in these processes is subjected to a reforming process and part of the generated carbonaceous material is used to improve the energetic performance of the process (Wijayasekera et al., 2022). Koroneos et al. (2004, 2008) analyzed the performance of several H₂ production processes and indicated that its production from solar

Table 10Life cycle analysis applied to different processes for H₂ production.

Study description	Analysis tool, origin of data, and functional unit (FU)	General comments	Source
This study approaches different processes (SMR, gasification, alkaline electrolysis) for the production of H ₂ using different energy sources of raw materials (solar, wind, biomass, hydraulic).	Used software was not specified. Impacts analysis method considered: the GEMIS model developed by the Otto-Institute (Germany) was used. The LCA considered raw materials, industrial services and reagents, liquefaction (-253 °C) and H ₂ transport. The used data are from secondary sources. The selected FU was the production of 1 MJ of energy (purity of H ₂ is not specified). Studied environmental categories were GWP, AP, EP, and WS.	The lowest emission of global warming potential (GWP) substances come from electrolytic process that use wind, solar, and hydraulic energy. The categories with the highest relative impact (70–90%) in the environmental category of all the studied alternatives were: GWP, AP, and EP. The manufacture of photovoltaic panels and their low efficiencies are responsible of the low environmental performance of this type of renewable technologies for the production of H ₂ .	Koroneos et al. (2004)
This study analyzed the environmental performance of two routes (gasification-reforming and gasification-generation of electricity-electrolysis) for the production H ₂ from biomass.	Used software not specified. Impacts analysis method considered: Eco-indicator 95 method. The LCA considered raw materials, industrial services and reagents, liquefaction (-253 °C) and H ₂ transport. The used data come from secondary sources (GEMIS). The selected FU was the production of 1 MJ of energy (purity of H ₂ is not specified). Studied environmental categories were GWP, AP, EP, and WS.	Gasification-generation of electricity-electrolysis is more sustainable because it generates all the electricity required by the process. LCA indicates that at least 93% of all the consumed energy must have a renewable origin, whereas in the gasification-reforming process it is about 54%. The acidification and eutrophication processes reduce the environmental performance of the studies processes. When compared to the gasification-reforming process, it is observed that the electrolysis process reduces 88% the GHG emissions. The activity that impacts the most the performance of the reforming process is the use of electricity generated from non-renewable sources.	Koroneos et al. (2008)
This study analyzed the environmental performance of two routes (thermal and autocatalytic decomposition of CH ₄) for the production of H ₂ from natural gas. The study assesses the efficiency of SMR coupled to CCS.	Used software: SimaPro (v7.1). Impacts analysis method considered: Eco-indicator 95 method. The selected FU was the production of 1 Nm ³ H ₂ (Purity: 99.99%). The used data come from reports of specialized literature. The study considered the following environmental categories: GWP, TAP, ODP, EP, WS, SM, and TS. The stages/activities of the process considered in the LCA include: raw materials, energy consumption, production process, and construction materials.	The use of CCS coupled to SMR effectively diminishes the CO ₂ emissions (from 0.0 to 0.35 kg CO ₂ -eqv/Nm ³ H ₂). Nonetheless, in other environmental categories (TAP, TS, and WS) a considerable increase in contaminant emissions was observed. The latter is attributed to the consumption of electricity of non-renewable origin in the CO ₂ capture and compression processes.	Dufour et al. (2009)
The study assessed the environmental performance of the following H ₂ production processes: thermochemical (Cu–Cl and sulfur-iodine water splitting), high temperature water electrolysis, SMR and hydrogen production from renewable sources (biomass- based electrolysis).	Used software is not mentioned, but the authors indicate that the required information for the calculations of emission of GWP and AP categories come from data reported in the literature. Impacts analysis method considered: Campo, 2021 and Eco-indicator 95 methods. The selected FU was the production of 1 kg H ₂ (Purity: not specified). Used data come from reports of specialized literature. The LCA considered the extraction and transportation of raw materials (including nuclear for the thermochemical process), equipments, construction materials, energy, operation, and dismantling of the project.	The use of nuclear energy has a positive impact in the reduction of emissions in GWP and AP categories. Compared with SMR, the thermochemical cycles reduce the emissions of these categories 96 and 87%, respectively. Considering globally the categories taken into account by the Eco-indicator 95, the best environmental performances are depicted by the thermochemical cycles and the processes that use renewable energies.	Ozbilen et al. (2011)
Study description	Analysis tool, origin of data, and functional unit (FU)	General comments	Source
The study compares the environmental performance of a conventional process with CCS (SMR-CCS) to alternatives that are still in developing stages (water photosplitting, water electrolysis, solar two-step thermochemical cycles and automaintained methane decomposition) for H ₂ synthesis.	Used software: SimaPro (v7.1). Impacts analysis method considered: IPCC-2007, the study also considered CED and CExD. The selected FU was the production of 1 Nm ³ H ₂ (Purity: 99.99%). The used data come from reports of the specialized literature and from the EcoInvent database. The LCA is focused on the required raw materials and the operation of the process because the studied processes are still under development.	The use of non-renewable electricity makes electrolysis the alternative with the worst performance in the category GWP (2.5 kg CO ₂ -eqv/Nm ³ H ₂). Electrolysis driven by solar energy, the thermochemical processes, and the SMR-CCS present up to 80% reduction in emissions. The reforming processes (automaintained) and the electrolytic (photosplitting) reduce 70 and 90% the GHG emissions, respectively. Photosplitting and electrolytic processes driven by renewable energies have primary energy consumptions below 2 (MJ/Nm ³ H ₂); that is, consume less energy (90%) for their operation.	Dufour et al. (2012)
This study assessed the environmental performance of five alternatives for the production of H ₂ (SMR coal gasification, water electrolysis via wind and solar electrolysis, and thermochemical water splitting with a Cu–Cl cycle).	Used software is not mentioned. Impacts analysis method considered: is not mentioned, but the study determines the emissions of contaminants associated to the following environmental categories: GWP and AP. The selected FU was the production of 1 kg H ₂ (Purity: not specified). Data used come from reports of the specialized literature. The LCA considers the extraction and transportation of raw materials (including nuclear fuel for the thermochemical process), equipments, construction	Considering GWP, processes present the following performance: SMR (11.9), coal gasification (11.3), water electrolysis via solar energy (2.4), water electrolysis via wind energy (0.97), and water splitting (0.12 kg CO ₂ -eqv/kg H ₂). The construction materials of the solar panels and their low efficiencies increase the emissions of electrolysis driven by solar energy. Due to its production capacity and low emissions, the thermochemical cycle is more attractive as a H ₂ source. Of the CO ₂ emissions, 55% correspond to the processing of	Cetinkaya et al. (2012)

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Table 10 (continued)

Study description	Analysis tool, origin of data, and functional unit (FU)	General comments	Source
This study considers on thermochemical cycle o (Sulfur-iodine cycle) for H ₂ production in Mexico, using as energy source a nuclear power plant	materials, energy, operation, and dismantling of the project.	nuclear materials, whereas the remainder corresponds to the construction-operation of the nuclear power plant (17%) and the H ₂ (24%) plant. The environmental footprint of the process was 0.30 (kg CO ₂ -eqv/kg H ₂); 66% of emissions come from the nuclear plant and the rest from the H ₂ (33%) production process. When the energy comes from an external nuclear power plant, emissions reach 0.45 (kg CO ₂ -eqv/kg H ₂). The use of an energy mix dominated by non-renewables increases the CO ₂ emissions to 10.5 (kg CO ₂ -eqv/kg H ₂). Emissions are comparable to other nuclear energy-assisted processes (4.1 kg CO ₂ -eqv/kg H ₂).	Giraldi et al. (2012)
This study analyzed the performance of two biomass gasification reactors (pine Wood) (DG: Downdraft Gasifier and CFBG: Circulating Fluidized Bed Gasifier) for H ₂ production	Used software: SimaPro (v.2). Impacts analysis method was not specified, but uses the climate change category to assess the environmental performance of the process. The selected FU was the production of 1 kg H ₂ (purity is not indicated). The required information was extracted from the EcoInvent database. The LCA considers the procurement of the nuclear fuel and the required industrial services for the operation of the thermochemical cycles and the nuclear power plant. The used data come from secondary sources. Used software was not mentioned. Impacts analysis method considered was not mentioned but the authors used the GHG emissions (GWP) to assess the environmental performance of the processes. The CHPP was also used to relate the energy contained in the product and the used raw materials. The selected FU was the production of 1 (MJ/s) (99.9% vol). The used data are from secondary sources. LCA considered the pre-treatment of the biomass, H ₂ production, and its use in cars that use fuel cells (PEM).	The activities that consume most of the required energy by the process are the compression and transport of H ₂ . The CFBG system (17.1 g CO ₂ -eqv/s) presents higher GHG emissions than the DG (6.3 g CO ₂ -eqv/s). The previous values are equivalent to those reported in wind energy-driven (8–9 g CO ₂ -eqv/s) or solar-driven (15 g CO ₂ -eqv/s) electrolytic processes but are much lower than values reported for SMR (100 g CO ₂ -eqv/s). The values calculated for the CHPP were 5.7 (CFBG) and 11.4 (DG), indicating a significant incorporation of renewable energy to the final product.	Kalinci et al. (2012)
This study assessed the environmental efficiency of an indirect gasification of biomass process (poplar) and the catalytic reforming of the biogas generated by H ₂ production. Results were compared with those obtained with SMR.	Used software: SimaPro (v7.1). Impacts analysis method considered: Campo, 2021 . Inventory analysis was performed with the GREET software. The selected FU was the production of 1 kg H ₂ (99.9% vol). The used data come from secondary sources (models-simulations in Aspen Plus). The study considered the following environmental categories: GWP, TAP, ODP, EP, ADP, POFP, LC, and CED.	Compared to SMR, the use of gasification leads to less emissions in categories like GWP, ADP, ODP, PFOP, and CED but increases them in LC, AP, and EP. The estimated carbon footprint is close to 0.4 (kg CO ₂ -eqv/kg H ₂) whereas that estimated for SMR reaches 11.5 (kg CO ₂ -eqv/kg H ₂). Sustainability of the process depends on the analyzed environmental category and, depending on the region or country of reference, it could lead to different decisions. The category LC (tied to the land use) is the main disadvantage associated with the use of biomass.	Susmozas et al. (2013)
The study assessed the performance of three sources of raw materials (natural gas, biogas, and bioethanol produced from wheat) for the production of H ₂ , using three production processes: catalytic reforming (SMR), partial oxidation (POX), and autothermal reforming (ATR).	Used software: SimaPro (v.7.1). Impacts analysis method considered: Campo, 2021 and Eco-indicator 99. The selected FU was the production of 1 kg H ₂ (purity is not specified). The study considered the following environmental categories: GWP, ADP, AP, EP, ODP, HTP, METP, TETP, and FETP. The used data come from secondary sources (models-simulations in Aspen Plus). The LCA considered procurement or raw materials, transport, production process, and distribution of the product. The LCA did not consider construction materials, dismantling of the power plant, and recycling of the catalyst.	Conventional production processes (SMR: 11.2, ATR: 10.8, and POX: 10.7 kg CO ₂ -eqv/kg H ₂) presented the worst performance in GWP. The use of bio-CH ₄ reduces the emissions in the category GWP almost 50% (SMR: 4.8, ATR: 4.9, and POX: 4.8 kg CO ₂ -eqv/kg H ₂). Ethanol steam (9.2) and autothermal (8.8 kg CO ₂ -eqv/kg H ₂) reforming lead to lower carbon footprints than those obtained with SMR. The most adequate raw material (bio-CH ₄) allowed reducing emissions in all environmental categories. The use of bio-ethanol increases the emissions in the following categories: GWP, ADP, AP, EP, ODP, METP, TETP y FETP.	Hajjaji et al. (2013)
The objective of the study was to compare the environmental footprint of a natural gas reforming process for H ₂ production using chemical looping gas conversion (S2), SMR with CCS (iron-based chemical looping) (SMR-CCS, S3), and a conventional (SMR, S1).	Used software: GaBi (v.6). Impacts analysis method considered: Campo, 2021 . The selected FU was the production of 1 MW of H ₂ (purity is not specified). Data come from secondary sources (ChemCAD v6.0.1 simulations). The study considered categories: GWP, ADP, AP, EP, ODP, HTP, METP, TETP, and FETP. The LCA considered the supply chain and the reforming process (SMR). CCS included transport, compression, and injection of the captured CO ₂ .	The use of SMR (S1) led to the highest GHG emissions (20.9 kg CO ₂ -eqv/kg H ₂) whereas the implementation of strategies for the absorption of CO ₂ reduced the emissions for the S2 (7.1 kg CO ₂ -eqv/kg H ₂) and S1 (14.7 kg CO ₂ -eqv/kg H ₂) systems. In S1, 81% of the footprint comes from the H ₂ production and transport processes. S2 recovers 99% of the CO ₂ generated, whereas S3 recovers 69%. Energy consumptions increased the precursors of contaminants like AP (547%), EP (1400%), HTP (727%), and TETP (2260%). Production of biomass, its transport and processing are the activities with the highest relative impact (>99%) in all studied environmental categories. When considering only GWP, the advantages of bio-H ₂ are overwhelming (0.3 kg CO ₂ -eqv/kg H ₂); however, in categories like AP, EP, and POFP, reductions are less significant. Despite replacing the non-renewable energy source, the impact on the land use and possible on the water, would be aspects that could reduce its sustainability in a long term.	Petrescu et al. (2014)
The study assessed the production potential of bio-H ₂ from residual biomass gasification (vineyard waste)	Used software: SimaPro (v.8). Impacts analysis method considered: Campo, 2021 . The study considered the following environmental categories: GWP, ADP, AP, EP, ODP, POFP, LC, and CED. The selected FU was the production of 1 kg H ₂ (purity is not specified). The used data come from secondary sources (models-simulations in Aspen Plus).	Production of biomass, its transport and processing are the activities with the highest relative impact (>99%) in all studied environmental categories. When considering only GWP, the advantages of bio-H ₂ are overwhelming (0.3 kg CO ₂ -eqv/kg H ₂); however, in categories like AP, EP, and POFP, reductions are less significant. Despite replacing the non-renewable energy source, the impact on the land use and possible on the water, would be aspects that could reduce its sustainability in a long term.	Martín-Gamboa et al. (2016)

Study description	Analysis tool, origin of data, and functional unit (FU)	General comments	Source
The study assessed through LCA the environmental performance of an electrolytic process (alkaline) for H ₂ production, driven by renewable electricity (wind turbines) in Canada.	Used software was not specified. The impacts analysis method was not specified, but the study uses the climate change category to evaluate the environmental performance of the process. The used data come from secondary sources. The LCA considered the construction of the equipment (turbines), the construction materials, the operation, compressions and transport of H ₂ and dismantling of the project.	The environmental footprint of the process is of 0.68 (kg CO ₂ -eqv/kg H ₂). Compared to SMR (12 kg CO ₂ -eqv/kg H ₂) this process would reduce in 94% the CO ₂ emissions. Operation of the power plant is responsible for 65% of the carbon footprint, whereas the electrolytic process, the compression, and transport of H ₂ account for 7, 22, and 6%, respectively.	Ghandehari and Kumar (2016)
The study assessed the environmental performance of H ₂ production from biogas (farm waste) using catalytic reforming.	Used software: SimaPro (v.8). Impacts analysis method considered: IPCC, 2021. The selected FU was the production of 1 kg H ₂ (purity is not specified). The study considered the following environmental categories: GWP, ODP, HTPC, HTPNc, PMP, IRP, POP, AP, TEP, FEP, MEP, FETP, LUP, ADP, CED, and NRE. The used data come from secondary sources and the Eco-Invent database. The LCA considered the construction and dismantling of the project.	Biogas reforming could generate H ₂ with an environmental footprint (5.6 kg CO ₂ -eqv/kg H ₂) quite lower than that reported for conventional processes like: SMR (11 kg CO ₂ -eqv/kg H ₂), gasification/reforming of biomass (2 kg CO ₂ -eqv/kg H ₂), and electrolysis (32 kg CO ₂ -eqv/kg H ₂). The production process of biogas and H ₂ concentrate most of the contaminating emissions. The construction and dismantling of the project are not environmentally significant. Some environmental categories present a significant reduction in the emissions of contaminants (ODP, HTP, POF, FETP, ADP).	Hajjaji et al. (2016a)
This study assessed the environmental performance of H ₂ production from biogas ATR. The biogas was generated from an agroindustrial substrate (poultry fat).	Used software: SimaPro (v.7.3). Impacts analysis method considered: Campo, 2021. The study considered the following environmental categories: GWP, ADP, AP, EP, ODP, and POFP. The selected FU was the production of 1 kg H ₂ (purity is not specified). The LCA considered the construction of the equipments, construction materials, the operation, compression and transport of H ₂ , and dismantling of the project.	The proposed process recovered as H ₂ , 52% of the energy that entered the process. Although this is low compared to SMR (70–80%), the process allows re-valorizing agroindustrial byproducts (148 mol H ₂ /kg poultry fat). Critical activities were energy consumption (thermal and electric: 60–90%) and transport (10%). The footprint of the generated H ₂ was of 9.12 (kg CO ₂ -eqv/kg H ₂), 85% of this footprint is associated with the reforming process of the raw material	Hajjaji et al. (2016b)
Five routes for H ₂ synthesis were studied: electrolysis, biomass and coal gasification, gas, ethanol, and methanol reforming.	Used software: GaBi. Impacts analysis method considered: Campo, 2021. The inventories analysis was performed with the GREET software. The selected FU was the production of 1 kg H ₂ (purity is not specified). The used data come from reports of specialized literature. The study assessed the environmental performance of the process in function of the following environmental categories: AP, GWP, HTP, POP, and EP.	The estimated emissions for the processes (kg CO ₂ -eqv/kg H ₂) were: electrolysis (28.6), coal gasification (23.7), methanol reforming (17.9), gas (13.8) and methanol (12.2), biomass gasification (4.4). The observed low environmental performances for the electrolytic process in most environmental categories are because the energy mix for the production of energy depends on non-renewable sources.	Siddiqui and Dincer (2019)
Study description	Analysis tool, origin of data, and functional unit (FU)	General comments	Source
The study developed an LCSA (Life Cycle Sustainability Assessment) of H ₂ production from biomass (poplar). The study assessed sustainability considering economic, social, and environmental aspects.	Used software was not indicated. Impacts analysis method was not specified, but the analysis included three dimensions: environmental (GWP, AP), economic (levelized cost), and social (child labor, gender wage gap, and health expenditure). The selected FU was the production of 1 kg H ₂ (purity: 99.9% vol, 200 bar, and 25 °C). The required information was retrieved from the Ecoinvent database (v3). The LCSA considered the culture, transport and milling of the biomass, reforming and purification of H ₂ , compression of H ₂ .	The study demonstrates the significant advantage of biomass gasification (GWP: 0.18 kg CO ₂ -eqv/kg H ₂) compared to mature technologies (SMR: 11.4 kg CO ₂ -eqv/kg H ₂). However, the social performance was worst, 2–3 times that calculated for SMR. The biomass transformation processes require more labor hours and resources to generate 1 kg of H ₂ . Hence, poor performances are observed in indicators like: health expenditure, gender wage gap, and levelized cost. Finally, the levelized cost of gasification is higher (3.59 Euros) than that determined for the SMR (2.17 Euros).	Valente et al. (2019b)
The objective of the study was to perform an environmental, technical, and economic analysis of a biomass process (corn straw) followed by tri-reforming for the production of H ₂ .	Used software: GaBi (v.7.3). Impacts analysis method was not specified, but the study uses the GWP category and energy consumption (EC _{c,om}) to determine the environmental performance of the process. The selected FU was the production of 1 kg H ₂ (purity is not specified). The used data come from secondary sources (models-simulations in Aspen Plus). The LCA considered the gasification, reforming, purification, and electricity production. The study also considered the flows of material and the required energy for the production and transport of the biomass.	The study evidences the feasibility and lesser impact of producing H ₂ from biomass, due to the increase in production generated by the use of tri-reforming. The energy consumption of the process (113 MJ/kg H ₂) is distributed as follows: biomass production-transport (45%), gasification-tri-reforming (34%), and purification-transport of H ₂ (21%). Emissions in the GWP category (5 kg CO ₂ -eqv/kg H ₂) are distributed as follows: biomass production-transport (33%), gasification-tri-reforming (41%), and purification-transport of H ₂ (26%).	Li et al. (2020a)
The efficiency of a bio-H ₂ production process from the gasification of urban solid wastes was assessed	Used software: GaBi. Impacts analysis method considered: Environmental Footprint 3.0. Inventories analysis was performed with the GREET software. The selected FU was the production of 1 MW _{HHV} of H ₂ (Purity: >99.97, Pressure: 300 bar, transport grade). The used data come from primary and secondary sources. The study considered the following environmental	Production of H ₂ from gasification (−5.4 CO ₂ -eqv/kg H ₂) presents significantly lower GHG emissions than those reported for SMR (1.9), ATR (1.7), and an electrolytic process (11.1). The sources of acidifying substances (SO _x and NO _x) are from the combustion processes. Electrolytic processes driven with a non-renewable energy mix increase the emissions of contaminants. The gasification	Amaya-Santos et al. (2021)

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Table 10 (continued)

Study description	Analysis tool, origin of data, and functional unit (FU)	General comments	Source
	categories: GWP, TAP and FAP, FEP, FETP, and POF.	process, the SMR, and water electrolysis driven by wind-energy reduce the 76% the emissions of acidifying substance.	

Note: LCA: Life Cycle Assessment; GEMIS: Global Emission Model for Integrated Systems; GHGs: Greenhouse Gases; FU: Functional Unit; SMR: Steam Methane Reforming; CCS: Carbon Capture and Storage; CED: Cumulative Energy Demand; CExD: Cumulative Exergy Demand; CHPP: Coefficient of Hydrogen Production Performance; PEM: Proton Exchange Membrane; GWP: Global Warming Potential; TAP: Terrestrial Acidification Potential; ODP: Ozone Depletion Potential; TS: Toxic Substances; WS: Winter Smog; SM: Summer Smog; EP: Eutrophication Potential; HTP: Human Toxicity non-cancer; HTPc: Human Toxicity cancer; METP: Marine Eutrophication; TETP: Terrestrial Ecotoxicity Potential; FETP: Freshwater Ecotoxicity Potential; LC: Land Use.

energy is less sustainable than mature processes like SMR, biomass reforming, and electrolytic processes that use energy sourced from wind and water; for SMR, the impact is dominated by GHG emissions (48%), emission of acidification precursors (35%), eutrophication (5%), and particulate matter emission (13%). The manufacture of solar panels and their low H₂ yields lead to a poor performance of the photovoltaic systems. Gasification, followed by the generation of electricity, and electrolysis are more sustainable than the gasification/reforming processes when the processes are energetically self-sustainable (Koroneos et al., 2008). For these authors, the SMR presents a low environmental performance in terms of energy consumption by the compression and purification processes that make it necessary to use electricity from the local grid.

Use of green electricity is mandatory to provide H₂ with low carbon emissions; for instance, an electrolytic process driven by solar or wind energy has emissions lower than 1.0 kg CO₂-eqv/kg H₂, whereas one using electricity generated from non-renewable sources like coal, oil, and gas could emit between 20 and 30 kg CO₂-eqv/kg H₂ (Ghandehariun and Kumar, 2016; Siddiqui and Dincer, 2019; Verma and Kumar, 2015). Green synthesis technologies (electrolysis, production from algae) can have higher footprints than those observed in processes like SMR, when the energy mix depends strongly on fossil resources (Cetinkaya et al., 2012; Ghokar et al., 2021; Siddiqui and Dincer, 2019). The contribution of non-renewables to the local or regional energy mix increases (3–5 times) the emissions of SO₂, NO_x, particulate matter, and toxic substances over those reported for SMR (Siddiqui and Dincer, 2019); nonetheless, the use of CCS could reduce CO₂ emissions from 18 to 0.91 kg CO₂-eqv/kg H₂ (Verma and Kumar, 2015).

Taking SMR as reference, the use of nuclear energy for the electrolytic generation of H₂ would reduce one-third of the CO₂ emissions and one-sixth that of acidification processes precursor substances (SO_x and NO_x) (Karaca et al., 2020; Utgikar and Thiesen, 2006). The use of nuclear clear energy for H₂ production via water splitting (Cu–Cl cycle) leads to higher environmental footprints (0.8 kg CO₂-eqv/kg H₂) than those reported for electrolytic processes driven by wind energy (0.6 kg CO₂-eqv/kg H₂) (Hacatoglu et al., 2012). Karaca et al. (2020) concluded that H₂ produced through electrolysis (conventional, high temperature, 3–4–5-step Cu-cycles) powered by nuclear energy leads to low carbon footprints (0.5–1.4 kg CO₂-eqv/kg H₂). Giraldi et al. (2012) indicated that CO₂ emissions can reach low values (0.30 kg CO₂-eqv/kg H₂) when using nuclear energy, whereas the use of an energy mix rich in fossil fuels can increase CO₂ emissions up to 10.5 kg CO₂-eqv/kg H₂.

Ozbilen et al. (2011) point out another advantage of using nuclear energy to power thermochemical cycles that is the noticeable reduction of acidifying substance (SO_x-NO_x) emissions; indicating that a thermochemical process (Cu–Cl cycle) could emit 1.8 g SO₂-eqv, whereas other technologies like SMR (15 g SO₂-eqv) and those driven by solar energy (2.6 g SO₂-eqv) or biomass (29 g SO₂-eqv) could increase them. Cetinkaya et al. (2012) also point out the remarkable reduction in CO₂ emission observed in nuclear energy-assisted processes, which are below those reported for SMR (~12 kg CO₂-eqv/kg H₂) and quite similar to those obtained through electrolytic processes driven by wind (~1 kg CO₂-eqv/kg H₂) or solar (~2.4 kg CO₂-eqv/kg H₂) energy.

Valente et al. (2021a) also described the good environmental performance of H₂ produced from nuclear energy (thermochemical cycles and electrochemical processes at low and high temperatures) in terms of CO₂ and acidifying substance emissions. The authors mention that when other sustainability indicators (for instance, CO₂ emissions, acidification, child labor, leveled cost, and health expenditure) are taken into account, alternatives like electrolysis and biomass gasification reveal a better performance than SMR in the first three categories, whereas SMR exceeds the renewable routes of the two last indicators previously mentioned (Valente et al., 2021b). Although nuclear energy reduces the emissions in environmental categories of interest for humankind (GWP, HTP, ODP); aspects related to the processing, utilization, and fuel disposal act as barriers for their implementation (Bhandari et al., 2014; Karaca et al., 2020).

3.3. Practical implications of this work

By 2050, the TES proposed by IRENA (2020) suggests that cumulative investment will reach 110 trillion US dollars, whereas a deeper decarbonizing, to reach near zero emissions, will require about 130 US\$. Noteworthy, the transition to a more renewable society results in a payback of 50–142 trillion US dollars in reduced externalities related to climate change. Although the determination of the carbon's costly legacy possesses numerous sources of uncertainty, the expected global cost of one ton of CO₂ emitted in 2020 will vary between \$12 and \$64.

Hydrogen from gas/biogas via reforming is a transitional solution in the race to decarbonize the economy. The main challenges, in the considered reforming technologies, is the development of highly selective catalysts with a notorious resistance to sintering and deactivation caused by coke and sulfur compounds. The best choice should also consider operating factors like energy use and the sustainability of the energy grid to decrease the carbon footprint of the process; therefore, thermoneutral processes with green electricity-powered CCUS are favorable for H₂ synthesis.

The contribution of electricity to GHGs emissions differs significantly among processes and is intrinsically linked to the participation of renewable energy sources in the local energy grid (Table 10). Gasification and biogas reforming without CCS usually led to CO₂ emissions between 1 and 5 kg CO₂-eqv/kg H₂; this is very promising due to the readiness level of these technologies. Up to date, the main drawbacks of reforming rely in the low sustainability (greenness) of the energy grid and the limited capacity for carbon capture and storage.

As evidenced in the revised studies, it is difficult to overcome the greenness of the H₂ produced by electrolysis; nevertheless, the processes should be driven by a sustainable energy grid to justify their selection for H₂ production. In electrolysis, the environmental impact of electricity could be reduced by using an energy grid with a low footprint (wind:11, hydropower: 12, geothermal: 38, solar: 45 g CO₂/kWh). Nowadays, less than 40% of the electricity produced comes from low carbon sources.

A significant increase in electrolyzer manufacturing is required to accomplish the goal established in the TES proposed by IRENA. Although this work and the analyzed ones are not enough to promote “the alternative” to drive the transition to green H₂, data gathered offer

useful information to identify pros and cons of the available mature technologies; however, it is necessary to incorporate additional tools to analyze the techno-economic performance and the sustainability of mature and emerging pathways.

4. Conclusions

The reports by international institutes evidence the relevance of limiting the increase of global temperature to 1.5 °C. This challenge poses the need to implement an energy transition, use of renewable raw materials in more activities, development of green production processes, and sustainable use of the natural resources. IEA proposes seven pillars to decarbonize the energy sector by 2050: i) Energy efficiency, ii) behavioral changes, iii) electrification, iv) renewables, v) bioenergy, vi) hydrogen and hydrogen-based fuels, and vii) carbon capture utilization and storage (CCUS). By 2030, 70% of the more than 200×10^6 t H₂ produced will be supplied by renewable sources like electrolysis driven by renewable energies and non-renewable ones that use CCUS. For 2050, it is expected that 530×10^6 t H₂ be produced by technologies with a carbon footprint close to zero.

Currently steam methane reforming (SMR) is a mature, efficient (85%) technology that has been proven at a large-scale (500×10^2 - 300×10^3 Nm³ H₂/h), generating at least 60% of the H₂ consumed worldwide. Notwithstanding, the operational conditions (700–1000 °C), the limited availability of gas reserves (ca. 52 years), and its carbon footprint (9–12 kg CO₂-eqv/kg H₂) have compromised its contribution to the sustainability of humankind. The present study evidences the importance of using CH₄ and bio-CH₄ in steam reforming processes; however, the impact of energy consumption (mainly steam and electricity) on sustainability is clear, because they dominate a good part (70–80%) of CO₂ equivalent emissions to the environment. In general, most studies evidence the relevance of using CCS to reduce the carbon footprint (80–90%) of the SMR process. On the other hand, autothermal reforming (ATR), dry reforming (DR), bi-reforming and tri-reforming promise reductions of the impact in terms of energy consumption, deactivation of the catalyst, and, at the same time, to generate syngas currents with more flexible C/H ratios. Although these alternatives do not yet depict a noticeable maturity, some of the developed models evidence their technical feasibility for the synthesis of H₂.

This study also evidenced the relevant role played by alternatives like biomass gasification, thermochemical cycles driven by nuclear energy and, finally, the electrolytic processes driven by solar and wind energy. Despite the evident advantages of electrolytic processes, it must be emphasized that the energy mix of a country or region conditions the environmental performance; for this reason, it will be necessary to count upon truly renewable energy sources to relish all environmental advantages. Nowadays, a large amount of studies is available that assess in great detail the environmental processes through an LCA; despite the rigor and degree of detail, most studies use secondary sources (laboratory-scale models and simulations) to complete key stages of the LCA, like inventory analyses. The reviewed studies point out the advantage of H₂ as energy carrier and, in turn, confirm the relevance of searching for alternate H₂ sources to comply with the Paris Agreement and reach a harmonized decarbonizing of energy sources.

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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Appendix A. Supplementary data

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