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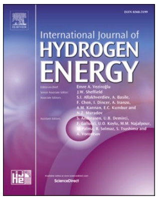

Biogas reforming as a sustainable solution for hydrogen production: Comparative environmental metrics with steam-methane reforming and water electrolysis in the Portuguese context

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ABSTRACT

This study delves into the dynamics of hydrogen production, with a specific focus on biogas reforming (BGSMR) for hydrogen generation. It compares the environmental impact of this solution with hydrogen production from natural gas-steam reforming (NGSMR) and commercial electrolysis in the Portuguese context. Various metrics, including carbon footprint, water depletion, energy utilization, and waste valorization are employed for a comprehensive comparison. The assessment explores the impact of operational parameters and different off-gas combustion scenarios, incorporating water recycling practices. Due to challenges in obtaining detailed data on the actual reforming process, the study relies on process simulation techniques, primarily using DWSIM. Commercially available data for water electrolysers were used for comparison. In the context of decarbonizing power systems, hydrogen from water electrolysis emerges as a competitive option only in a scenario where the power system is 100% reliant on renewable sources, particularly with respect to the carbon footprint metric. Biogas systems, characterized by near-zero carbon emissions, stand out as a favourable option from the near future to the long run. This research contributes valuable insights into the dynamics of hydrogen production, shedding light on environmentally viable alternatives across a range of power system scenarios.

1. Introduction

Hydrogen production at commercial scale is mainly used for ammonia production and refining crude oil [1], see Fig. 1. Reforming is still the major technology used for hydrogen production. Natural gas-steam reforming is at a high technology readiness level (TRL) 9, biogas reforming is at low TRL, whereas electrolysis is under way (TRL5 or TRL9, Table 1). Colour code for hydrogen is 'Green hydrogen' if produced using electricity from renewables; 'Grey hydrogen' if produced from methane with corresponding CO_2 emissions, 'Brown hydrogen' is produced from gasified coal, with CO_2 emissions, 'Blue hydrogen' is grey or brown hydrogen but with carbon capture and storage or usage, 'Yellow hydrogen' or 'pink hydrogen' uses nuclear electricity for electrolysis and possibly heat; 'Turquoise hydrogen' is produced from molten metal pyrolysis of methane, with solid carbon by-products [2].

In 2020, around 86.4 million tonnes of pure hydrogen were consumed worldwide. China is the world's largest producer and consumer of hydrogen. In 2020, China's usage of hydrogen amounted to some 23.9 million tonnes. Ranking second is the United States of America, accounting for 11.3 million tonnes of global hydrogen consumption [11]. If, by 2050, the world's population expands to 9.7 billion people and the global economy is nearly 150 % larger than in 2020, the demand for hydrogen will rise 6-fold (to almost 500 million tonnes).

Currently, hydrogen production is dominated by thermochemical routes such as natural gas-steam reforming (NGSMR) and coal gasification. However, there is a growing interest in low-carbon hydrogen production methods, such as gas reforming and coal gasification with carbon sequestration and storage, biological routes, and electrochemical routes.

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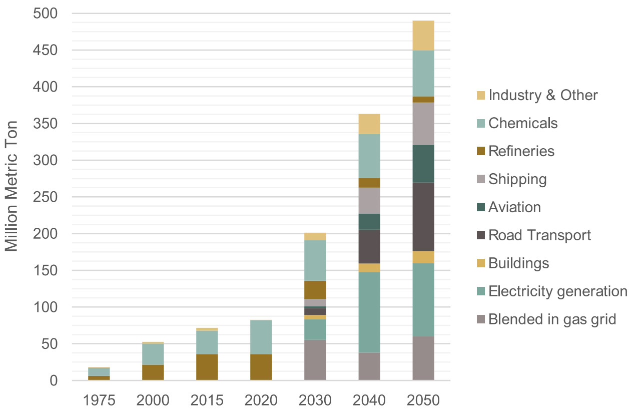

Fig. 1. Hydrogen demand and production technologies 1975–2020 (historical) and 2030–2050 (forecast) IEA [3,4].

Table 1
Technology readiness levels (TRL) of each H_2 production technology ([5–8]).

TRL[a]	Hydrogen route
9	NGSMR, Coal gasification, Alkaline/PEM electrolysis
7–8	NGSMR with CCUS, Coal gasification with CCUS
6	BGSMR
5	High Temperature Electrolysis (Solid Oxide Electrolysis Cell)
4	Biomass gasification with carbon capture and storage; Biological dark fermentation; Super critical water gasification
1–3	Photolysis; thermochemical water splitting – Water + heat; Photoelectrolysis – Water + solar

1 - Basic principles observed; 2 - Technology concept formulated; 3 - Experimental proof of concept; 4 - Technology validated in lab; 5 - Technology validated in relevant environment (industrially relevant environment in the case of key enabling technologies); 6 - Technology demonstrated in relevant environment (industrially relevant environment in the case of key enabling technologies); 7 - System prototype demonstration in operational environment; 8 - System complete and qualified; 9 - Actual system proven in operational environment (competitive manufacturing in the case of key enabling technologies; or in space).

[a] TRL Definition (Horizon 2020 European Commission).

Commercial electrolysis systems, like the H-TEC Polymer Electrolyte Membrane (PEM) 10 MW HCS[a], are available on the market. Although biological routes to hydrogen through anaerobic digestion are possible in laboratory and small pilot scale (e.g. Ref. [12]), their commercial feasibility is yet to be determined. Biogas reforming (BGSMR) with carbon capture and storage (CCUS) has the potential to be carbon negative.

Gasification of forestry biomass leftovers to syngas and reforming of organic waste biogas to hydrogen are not clearly categorized in the hydrogen colour scheme. However, since their CO_2 emissions are associated with a short carbon cycle, they can be considered as a form of blue hydrogen – reforming with carbon capture and storage.

NGSMR impact has been studied, for example, in Spath et al. (2001) [13] and Collodi et al. (2017) [14]. The latter pertains to a hydrogen production capacity of 100,000 Nm^3/h (equivalent to 89 $tonneH_2/h$) in The Netherlands, considering various options for carbon capture and storage (CCS). The focus is on the levelized cost of hydrogen, with calculations based on NG requirements for hydrogen production at 3.4 $kgNG/kgH_2$ (comprising 2.9 $kgNG/kgH_2$ for feed and 0.48 $kgNG/kgH_2$ for SMR heat). The direct CO_2 emissions of the reference system are measured at 9.9 $kgCO_2/kgH_2$. It concludes that even with CCS there is a release of 1 $kgCO_2/kgH_2$ to the atmosphere. Energy needs are 0.6 MJ/kgH_2 electricity provided by a combined heat and power (CHP) unit, and heat 22 MJ/kg provided by the NG burning. Spath et al. (2001) [13] present values of 9.17 $kgCO_2eq/kgH_2$, 14 kg_{water}/kgH_2, 3.22 $kgNG/kgH_2$ (2.9 as feed and 0.32 as fuel), 1.14 $MJ_{electricity}/kgH_2$, with off-gas combustion to heat.

The benchmark for hydrogen production within the European Emissions Trading System (EU ETS) is set at 6.84 $kgCO_2eq/kg\ H_2$, encompassing solely the direct operational emissions from natural gas-steam reforming [15]. Publications addressing the life cycle assessment (LCA) of biogas to hydrogen were examined, and a comparative analysis with the conventional process of NGSMR and water electrolyser was conducted using information retrieved from the Web of Science™ Core collection. The findings are presented in Fig. A1 of the Supplementary Material.

Cvetković et al. (2021) [16] conducted a study on a biogas upgrading and conversion to hydrogen reforming system in Serbia, utilizing literature values for upgrading and steam methane reforming (SMR). The study primarily emphasized energy requirements and assumed a ratio of 6.16 $kgCH_4/kgH_2$, with an energy input of 169 MJ/kgH_2. This input accounts for the energy contained in the biomethane during the upgrading and reforming processes. In the study by Hajjaji et al. (2016) [17], a biogas consumption rate of 8.4 $kgBG/kgH_2$ (with 6.11 kg as feed and 2.24 kg as fuel) is associated with a water consumption of 7.58 kg_{water}/kgH_2. The reforming inventory data were derived from process simulations conducted in Aspen Plus™ software, considering conditions such as 800 °C in SMR, 10 atm reactor pressure, non-upgraded biogas (60% CH_4, 35% CO_2, 3%H_2O and 2% N_2), a S:C ratio of 3, and an electricity consumption of 1.95 MJ/kgH_2 for the water pump and biogas compressor. Additionally, off-gas combustion is employed for heating purposes.

According to the CORDIS European database, two projects are aiming to deliver TRL6 systems within the research scope: the BIONICO project [18], which focuses on developing a biogas membrane reformer for decentralized hydrogen production, and the BIOROBUR^{plus} project [19,20], which is developing an advanced direct biogas fuel processor for robust and cost-effective decentralized hydrogen production. The former targeted a production capacity of approximately 100 kgH_2/day with a fluidized bed membrane reactor integrated with a separation unit and tested different biogas compositions. BIOROBUR^{plus} is a continuation of the Fuel Cell and Hydrogen Joint Undertaking (FCH JU) BioROBUR project (direct biogas oxidative steam reformer) targeting hydrogen production of 107 kg/day. The biogas origins varied from landfill gas, anaerobic digestion of organic wastes, and anaerobic digestion of wastewater-treatment sludges, with CH_4 ranging from 60 to 70 % and CO_2 ranging from 30 to 40 %.

Hydrogen can be converted to hydrogen-based fuels, including synthetic methane, methanol, and ammonia, as well as synthetic liquid fuels, which have a range of potential transport uses. In fact, ammonia is one of the prospective alternatives to hydrocarbon fuels [21] and a possible hydrogen carrier to use, for example, at maritime transportation [22]. On-board hydrogen rich syngas production though an hydrocarbon reformer is also being explored [23].

Move2LowC project (https://www.move2lowc.com/; 28/10/2020-30/06/2023; Co-funded by *Programas Mobilizadores – Aviso 14/SI/2019*) is a Portuguese research project involving several Portuguese industry and university partners. Under this project, at the road transport level, the focus was on hydrogen-based biofuels ($BioH_2$) and biomethane ($BioCH_4$), which were the objects of research and innovation of sub-projects 3 and 4, respectively. $BioH_2$ and $BioCH_4$ can be produced in a variety of ways, but both molecules participate in the production of one another. $BioH_2$ can be produced from $BioCH_4$ by steam reforming (SMR) and water-gas shift (WGS), with part of the $BioCH_4$ being used to power the production system. On the other hand, $BioCH_4$ can be recovered from landfills but can also be produced by methanation from the recovery of biogenic or non-biogenic CO_2 and free CO_2 H_2 or green

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[a] HCS means Hydrogen Cube System and in this case it consists in 2 MW cubes that can be combined to form multi-MW plants.

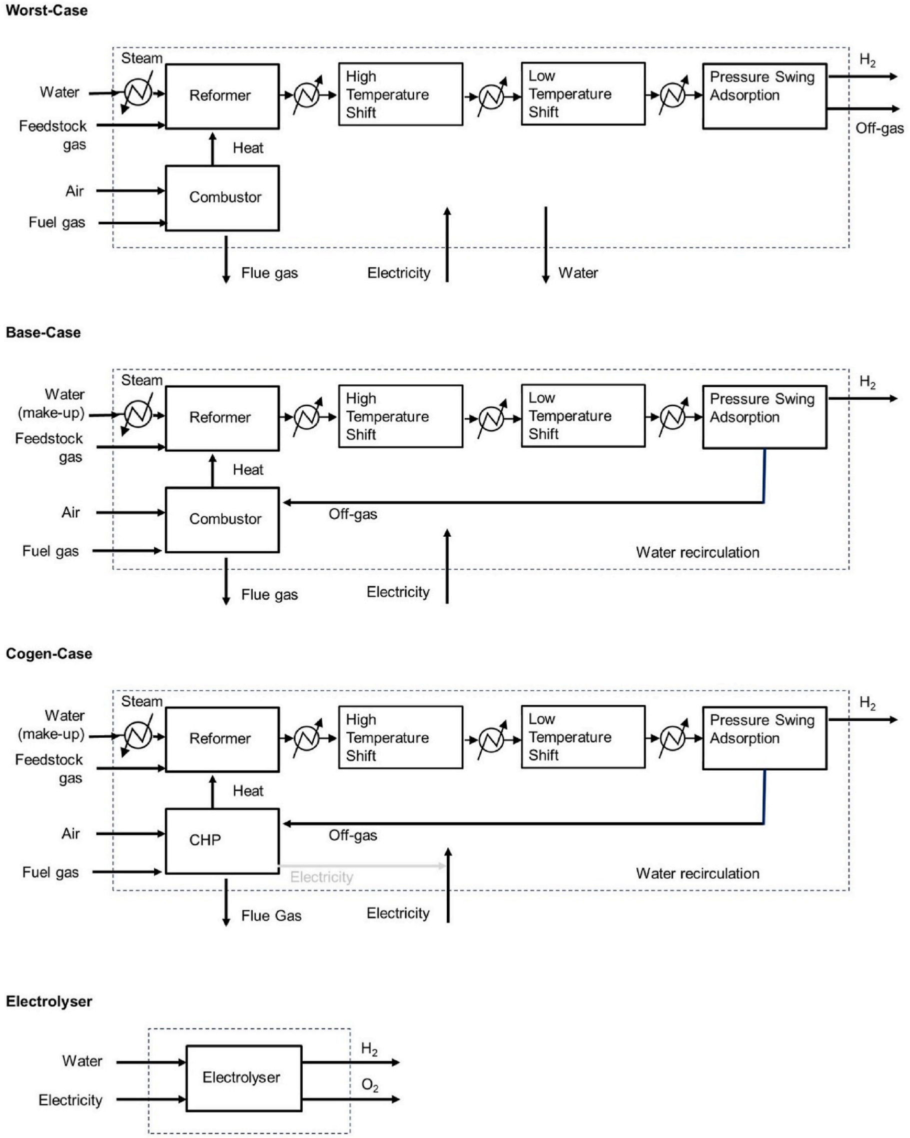


Fig. 2. Simplified block flow diagram of the hydrogen plant for each reforming scenario and water electrolysis.

Table 2
Dry feed gas composition (% v/v).

Gas	Natural gas (EU mix 2016 [9])	Biogas ([10])
CH_4	90.6	60.0
CO_2	0.7	40.0
O_2	0.0	0.0
H_2	0.3	0.0
C_2H_6	4.4	0.0
C_3H_8	1.2	0.0
Butane and C_{4+}	0.2	0.0
N_2	2.7	0.0
LHV (MJ/kg)	46.6	30[a]
gCO_2eq/MJ[c]	56.3	0.06
gCO_2/MJ	56.1	54.1[b]

[a] Dulong eq.1 or ideal gas assumption (LHV CH_4 50 MJ/kg, LHV CO_2 0 MJ/kg).
[b] Stoichiometric CO_2 and IPCC chapter 2 stationary combustion, biogenic.
[c] Biogenic CO_2 discounted as part of short carbon cycle.

H_2 (produced by water electrolyser using solar or wind electricity).

This work addresses sub-project 3, targeting a hydrogen production system of 153 kg/h, by comparing two thermochemical systems and one electrochemical system for hydrogen production in terms of their carbon footprint and resource consumption (water, feedstock and energy). Data quality within Life Cycle Assessment (LCA) is a significant issue for the future support and development of LCA as a decision support tool and its wider adoption within industry. Therefore, this work also addresses data quality and results quality by means of a qualitative “Pedigree Matrix” and by sensitivity and parametric/scenario analysis.

It is worth noting that industry estimates project Portugal’s biogas/biomethane potential to reach 0.6 billion cubic meters (bcm) by 2030, with 0.5 bcm coming from anaerobic digestion and 0.1 bcm from gasification [24], including municipal solid organic wastes, industrial wastewater, and sewage sludge. As of 2021, 0.1 bcm of biogas were predominantly utilized for electricity generation, primarily in electricity-only or combined heat and power (CHP) plants (92 %). Notably, there are no existing records of biomethane production in Portugal to date. Consequently, our analysis will consider multiple biogas origins with and without upgrading.

This research involves a comparative assessment of NGSMR, BGSMR, and electrolysis, utilizing a 0–10 scoring system for carbon footprint, water depletion, waste valorization potential, and energy consumption. The primary novelty lies in comparing fossil and non-fossil systems

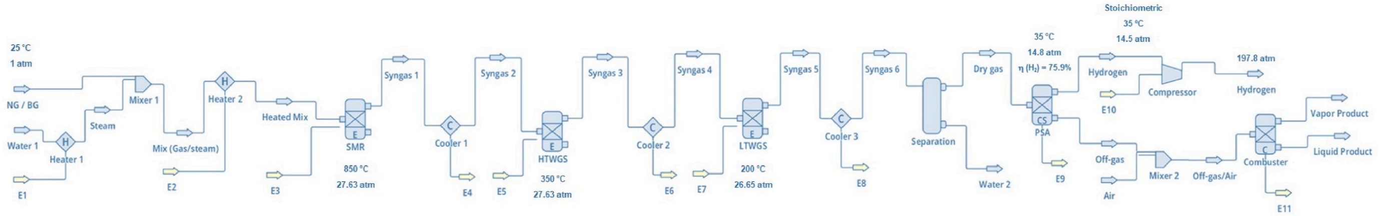
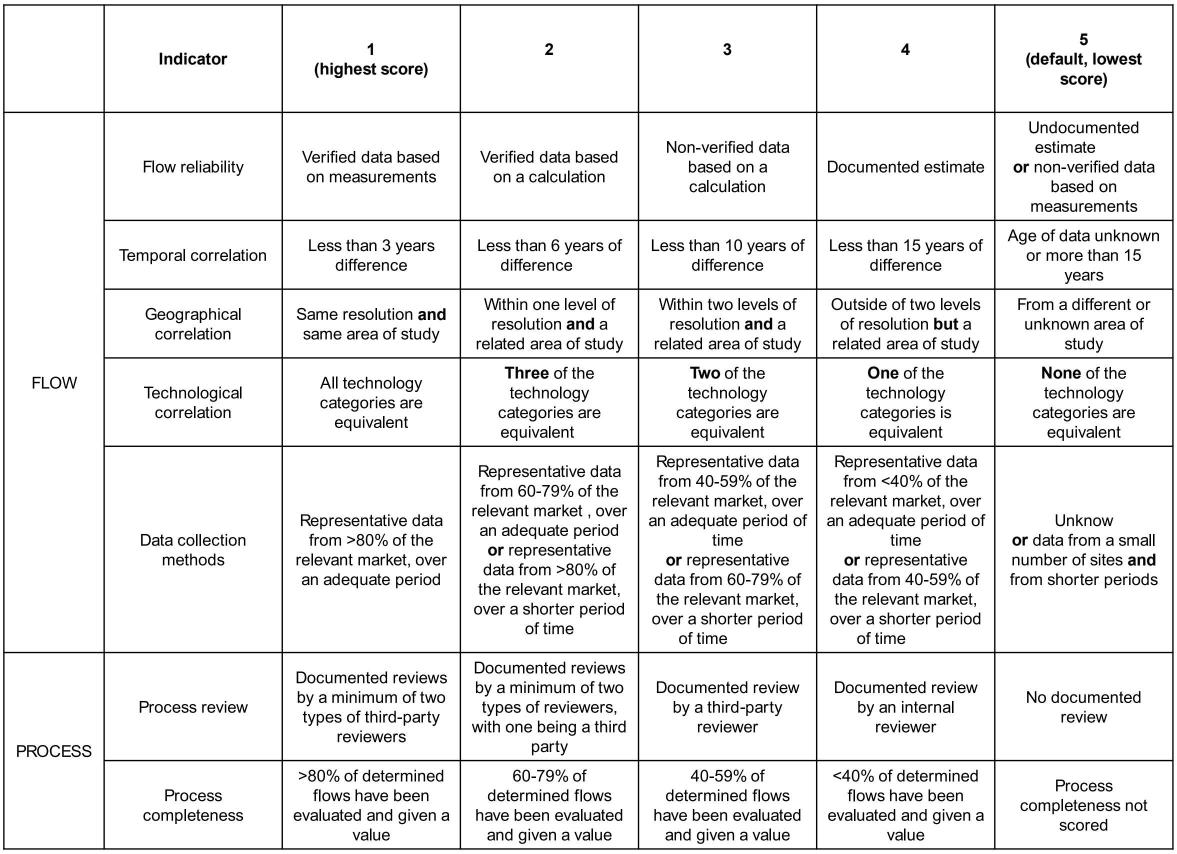


Fig. 3. Process model developed in DWSIM, detailing the process conditions.



	Indicator	1 (highest score)	2	3	4	5 (default, lowest score)
FLOW	Flow reliability	Verified data based on measurements	Verified data based on a calculation	Non-verified data based on a calculation	Documented estimate	Undocumented estimate **or** non-verified data based on measurements
	Temporal correlation	Less than 3 years difference	Less than 6 years of difference	Less than 10 years of difference	Less than 15 years of difference	Age of data unknown or more than 15 years
	Geographical correlation	Same resolution **and** same area of study	Within one level of resolution **and** a related area of study	Within two levels of resolution **and** a related area of study	Outside of two levels of resolution **but** a related area of study	From a different or unknown area of study
	Technological correlation	All technology categories are equivalent	**Three** of the technology categories are equivalent	**Two** of the technology categories are equivalent	**One** of the technology categories is equivalent	**None** of the technology categories are equivalent
	Data collection methods	Representative data from >80% of the relevant market, over an adequate period	Representative data from 60-79% of the relevant market , over an adequate period **or** representative data from >80% of the relevant market, over a shorter period of time	Representative data from 40-59% of the relevant market, over an adequate period of time **or** representative data from 60-79% of the relevant market, over a shorter period of time	Representative data from <40% of the relevant market, over an adequate period of time **or** representative data from 40-59% of the relevant market, over a shorter period of time	Unknow **or** data from a small number of sites **and** from shorter periods
PROCESS	Process review	Documented reviews by a minimum of two types of third-party reviewers	Documented reviews by a minimum of two types of reviewers, with one being a third party	Documented review by a third-party reviewer	Documented review by an internal reviewer	No documented review
	Process completeness	>80% of determined flows have been evaluated and given a value	60-79% of determined flows have been evaluated and given a value	40-59% of determined flows have been evaluated and given a value	<40% of determined flows have been evaluated and given a value	Process completeness not scored

Fig. 4. Updated Data Quality Pedigree Matrix – Flow and process indicators [38].

within the same power system context, considering off-gas use and water recycling. Additionally, the authors successfully estimated the hydrogen production capacity in Portugal through BGSMR.

2. Materials and methods

2.1. Environmental assessment methodology

The evaluation of the systems follows the ISO 14040/44 [25,26] principles by defining the goal, scope, functional unit (FU), and impact categories.

The goal is to compare two thermochemical systems and one electrochemical system for hydrogen production in terms of their carbon footprint, and resource consumption, following an attributional approach. The scope is Gate-to-Gate, using electricity from the Portuguese National Grid in 2015, 2020 and 2050, using demineralized water, a steam methane reformer, a high-temperature and low-temperature WGS reactor, a Pressure Swing Adsorption (PSA) unit and a combustor to provide heat or “heat & electricity”. The FU is 1 kg of hydrogen (1 kg H_2). The impact category is global warming potential in 100 years (GWP100), measured in terms of CO_2eq and using the IPCC conversion factors from the 5th impact assessment report (AR5), with and without feedback, and AR6, with feedback (see Table 1 of the supplementary material). The plant is to be designed for a capacity of hydrogen production of 153 kg/h or, 8000 h of operation, 1224 tonne/year. The inventory was retrieved from Move2LowC project, literature and by using the Open Source chemical process simulator DWSIM [27]. The plant operation units and evaluation boundaries are represented in Fig. 2.

2.2. Simulation methodology: reforming processes

Due to challenges in obtaining detailed data for the actual reforming process, process simulation technique (DWSIM) was applied, except for water electrolysis, for which commercially available data was accessible. The analysis comprises three scenarios: Worst-Case, Base-Case, and Cogen-Case. The analysis encompasses three scenarios: Worst-Case, Base-Case and Cogen-Case. In the Worst-Case Scenario the PSA off-gas is emitted directly to the atmosphere, which is not common practice, but is the worst possible situation. In Base-Case, PSA off-gas is burned in a combustor for heat production, which is current practice. In Cogen-Case,

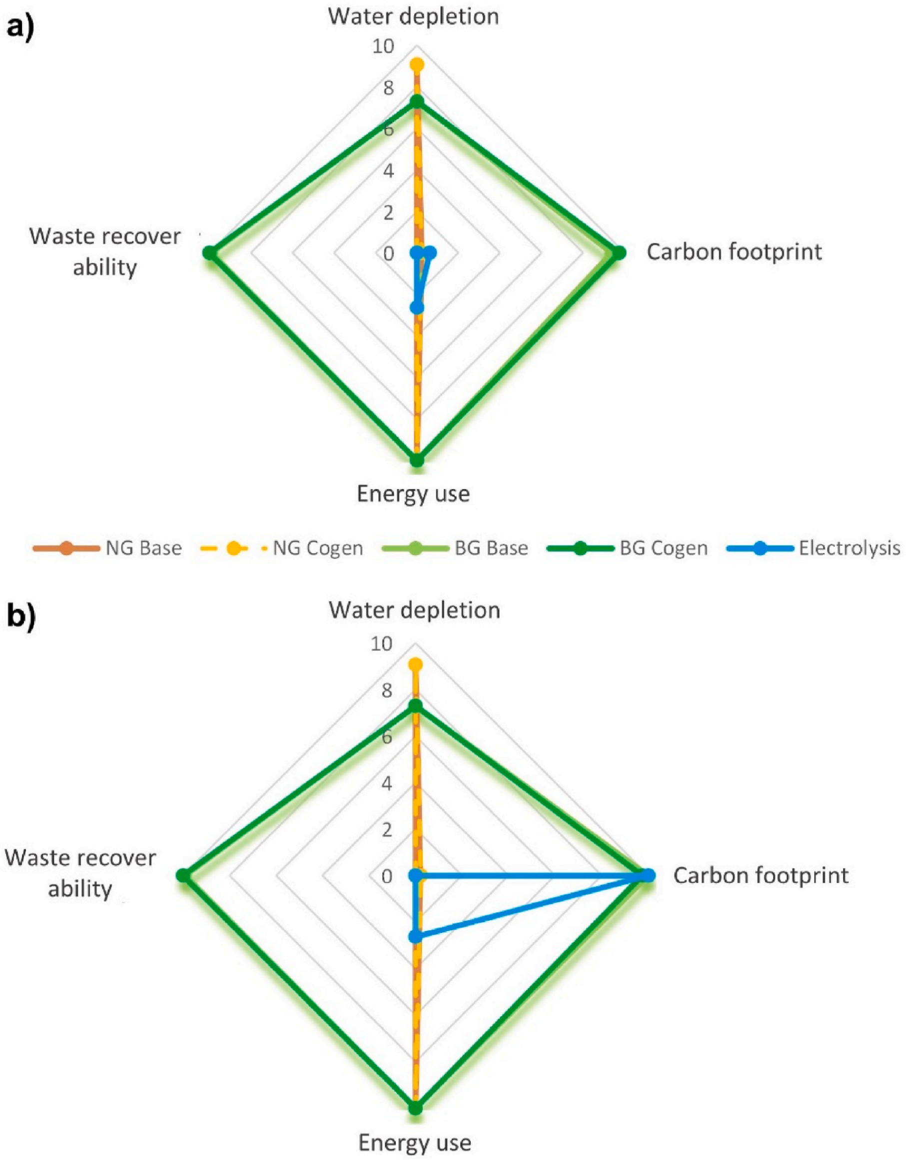


Fig. 5. Comparison of hydrogen production systems on a 0 to 10 scale for both a) 2020 and b) 2050, where a score of 10 denotes the highest performance in each indicator.

PSA off-gas is burned in the combined heat and power (CHP) production unit, which will be a future scenario. Any energy surplus would be the result of discounting the system energy needs to the energy provided by the off-gas.

Natural gas composition was retrieved from European Mix [9] and biogas composition from literature [10] (see Table 2). Natural gas burning has a Lower Heating Value (LHV) of 46.6 MJ/kg while biogas LHV can be estimated by known gas species and molar fractions or by the Dulong formula for gas [28]:

Equation 1

$$LHV\ (MJ\,/\,kg) = 38.2\ m_c + 84.9\left(m_H - \frac{m_o}{8}\right)$$

Where m_c, m_H and m_o are the carbon, hydrogen and oxygen contents in mass fraction, respectively. In our case studies this approach is consistent with the approach of assuming ideal gas behaviour and using weighted average calculations based on individual species LHV and mole fractions.

According to the sub-project 3 of Move2LowC project specifications, the objective is to produce 153 kg/h of hydrogen at a pressure of 15 bar, and then compress it to a pressure of 200 bar; The PSA H_2 recovery ratio is 75.9 % and there is an auxiliary electricity consumption of 0.3 kWh/kgH_2.

The LCA inventory in terms of mass inflows/outflows and energy inflows/outflows was retrieved from process simulation using DWSIM software, see Fig. 3. DWSIM is as Open-Source Chemical software. DWSIM simulates the following chemical reactions in the reforming reactor (SMR) – Equations 2, 3 and 4 – and water-gas shift reactors (WGSR) – Equation 4. Different studies consider different sets of chemical reactions for reforming we move forward with these equations and compare the outcomes with literature for validation/verification (see Supplementary Material, Fig. A4).

Equation 2

$$CH_4 + H_2O \leftrightarrow CO + 3\ H_2\ (206\ kJ\,/\,mol)$$

Equation 3

$$C_2H_6 + 2\ H_2O \leftrightarrow 2\ CO + 5\ H_2\ (\ 346\ kJ\,/\,mol)$$

Equation 4

Table 3
Life Cycle Inventory of NGSMR for the production of 1 kg of H_2 . S:C = 3 (see Fig. 3).

Process	Inputs			Outputs		
	Stream	Value	Units	Stream	Value	Units
Heater 1	Water 1	11.620	kg	Steam	11.620	kg
	E1 (Heat)	49.529	MJ			
Mixer 1	Steam	11.620	kg	Mix NG/ Steam	15.261	kg
	NG National EU-mix	3.772	kg			
Heater 2	Mix NG/ Steam	15.261	kg	Heated mix	15.261	kg
	E2 (Heat)	10.137	MJ			
NGSMR	Heated mix	15.261	kg	Syngas 1	15.261	kg
				CH_4	0.741	
				C_2H_6	0	
				H_2O	7.379	
				CO	2.859	
				CO_2	2.992	
				H_2	1.131	
				N_2	0.156	
	E3 (Heat)	35.121	MJ			
Cooler 1	Syngas 1	15.261	kg	Syngas 2	15.261	kg
	CH_4	0.741		CH_4	0.741	
	C_2H_6	0		C_2H_6	0	
	H_2O	7.379		H_2O	7.379	
	CO	2.859		CO	2.859	
	CO_2	2.992		CO_2	2.992	
	H_2	1.131		H_2	1.131	
	N_2	0.156		N_2	0.156	
				E4 (Heat)	21.713	MJ
HTWGS	Syngas 2	15.261	kg	Syngas 3	15.261	kg
	CH_4	0.741		CH_4	0.742	
	C_2H_6	0		C_2H_6	0	
	H_2O	7.379		H_2O	5.814	
	CO	2.859		CO	0.423	
	CO_2	2.992		CO_2	6.819	
	H_2	1.131		H_2	1.306	
	N_2	0.156		N_2	0.156	
				E5 (Heat)	3.325	MJ
Cooler 2	Syngas 3	15.261	kg	Syngas 4	15.261	kg
	CH_4	0.742		CH_4	0.742	
	C_2H_6	0		C_2H_6	0	
	H_2O	5.814		H_2O	5.814	
	CO	0.423		CO	0.423	
	CO_2	6.819		CO_2	6.819	
	H_2	1.306		H_2	1.306	
	N_2	0.156		N_2	0.156	
				E6 (Heat)	6.203	MJ
LTWGS	Syngas 4	15.261	kg	Syngas 5	15.261	kg
	CH_4	0.742		CH_4	0.742	
	C_2H_6	0		C_2H_6	0	
	H_2O	5.814		H_2O	5.571	
	CO	0.423		CO	0.045	
	CO_2	6.819		CO_2	7.414	
	H_2	1.306		H_2	1.333	
	N_2	0.156		N_2	0.167	
				E7 (Heat)	0.533	MJ
Cooler 3	Syngas 5	15.261	kg	Syngas 6	15.261	kg
	CH_4	0.742		CH_4	0.742	
	C_2H_6	0		C_2H_6	0	
	H_2O	5.571		H_2O	5.571	
	CO	0.045		CO	0.045	
	CO_2	7.414		CO_2	7.414	
	H_2	1.333		H_2	1.333	
	N_2	0.167		N_2	0.167	
				E8 (Heat)	20.018	MJ
Separation	Syngas 6	15.261	kg	Dry gas	9.729	kg
	CH_4	0.742		CH_4	0.742	
	C_2H_6	0		C_2H_6	0	
	H_2O	5.571		H_2O	0.057	
	CO	0.045		CO	0.045	
	CO_2	7.414		CO_2	7.395	
	H_2	1.333		H_2	1.333	
	N_2	0.167		N_2	0.167	
				Water	5.532	kg
PSA	Dry gas	9.729	kg	Off-gas	8.729	kg
	CH_4	0.742		CH_4	0.742	
	C_2H_6	0		C_2H_6	0.395	
	H_2O	0.057		H_2O	0.057	
	CO	0.045		CO	0.045	
	CO_2	7.395		CO_2	7.395	
	H_2	1.333		H_2	0.333	
	N_2	0.167		N_2	0.167	
				H_2	1.000	kg
				E9 (Heat)	0.097	
Compressor	H_2	1.000	kg	H_2	1.000	kg
	E10 (Electricity)	6.645	MJ			
Mixer 2	Off-gas	8.729	kg	Off-gas/Air	33.114	kg
	CH_4	0.742		CH_4	0.742	
	C_2H_6	0.395		C_2H_6	0.395	
	H_2O	0.057		H_2O	0.057	
	CO	0.045		CO	0.045	
	CO_2	7.395		CO_2	7.395	
	H_2	0.333		H_2	0.333	
	N_2	0.167		N_2	18.574	
				O_2	5.630	
				Ar	0.336	
	Air	24.383	kg			
	N_2	18.418				
	O_2	5.630				
	Ar	0.336				
Combustion	Off-gas/Air	33.114	kg	Vapour Product	28.446	kg
	CH_4	0.742		H_2O	0.053	
	C_2H_6	0.395		CO_2	9.482	
	H_2O	0.057		N_2	18.575	
	CO	0.045		O_2	0.000	
	CO_2	7.395		Ar	0.336	
	H_2	0.333				
	N_2	18.574				
	O_2	5.630				
	Ar	0.336				
				Liquid Product	4.668	kg
				H_2O	4.668	
				CO_2	0.020	
				E11 (available for 100 % Heat or 35 %electricity & 50 % heat)	89.250	MJ

$$C_3H_8 + 3\,H_2O \leftrightarrow 3\,CO + 7\,H_2\ (\,499\ kJ\,/\,mol)$$

Equation 5

$$CO + H_2 \leftrightarrow C + H_2O\ (-171\ kJ\,/\,mol)$$

Equation 6

$$CO + H_2O \leftrightarrow CO_2 + H_2\ (-41\ kJ\,/\,mol)$$

N_2 and other gases that are not in Equations 2 to 6 are considered

Table 4
Life Cycle Inventory of BGSMR for the production of 1 kg of H_2. S:C = 3 (see Fig. 3).

Process	Inputs			Outputs		
	Stream	Value	Units	Stream	Value	Units
Heater 1	Water 1	11.082	kg	Steam	11.082	kg
	E1 (Heat)	47.238	MJ			
Mixer 1	Steam	11.082	kg	Mix BG/ Steam	20.420	kg
				CH_4	3.290	
				H_2O	11.082	
				CO_2	6.048	
	BG	9.337	kg			
	CH_4	3.290				
	CO_2	6.048				
Heater 2	Mix BG/ Steam	20.420	kg	Heated mix	20.420	kg
	CH_4	3.290		CH_4	3.290	
	H_2O	11.082		H_2O	11.082	
	CO_2	6.048		CO_2	6.048	
	E2 (Heat)	15.166	MJ			
BGSMR	Heated mix	20.420	kg	Syngas 1	20.420	kg
	CH_4	3.290		CH_4	0.643	
	H_2O	11.082		H_2O	8.114	
	CO_2	6.048		CO	4.629	
				CO_2	6.037	
				H_2	0.997	
	E3 (Heat)	37.426	MJ			
Cooler 1	Syngas 1	20.420	kg	Syngas 2	20.420	kg
	CH_4	0.643		CH_4	0.643	
	H_2O	8.114		H_2O	8.114	
	CO	4.629		CO	4.629	
	CO_2	6.037		CO_2	6.037	
	H_2	0.997		H_2	0.997	
				E4 (Heat)	24.098	MJ
HTWGS	Syngas 2	20.420	kg	Syngas 3	20.420	kg
	CH_4	0.643		CH_4	0.643	
	H_2O	8.114		H_2O	5.627	
	CO	4.629		CO	0.761	
	CO_2	6.037		CO_2	12.114	
	H_2	0.997		H_2	1.276	
				E5 (Heat)	5.275	MJ
Cooler 2	Syngas 3	20.420	kg	Syngas 4	20.420	kg
	CH_4	0.643		CH_4	0.643	
	H_2O	5.627		H_2O	5.627	
	CO	0.761		CO	0.761	
	CO_2	12.114		CO_2	12.114	
	H_2	1.276		H_2	1.276	
				E6 (Heat)	6.917	MJ
LTWGS	Syngas 4	20.420	kg	Syngas 5	20.420	kg
	CH_4	0.643		CH_4	0.643	
	H_2O	5.627		H_2O	5.192	
	CO	0.761		CO	0.086	
	CO_2	12.114		CO_2	13.174	
	H_2	1.276		H_2	1.324	
				E7 (Heat)	0.951	MJ
Cooler 3	Syngas 5	20.420	kg	Syngas 6	20.420	kg
	CH_4	0.643		CH_4	0.643	
	H_2O	5.192		H_2O	5.192	
	CO	0.086		CO	0.086	
	CO_2	13.174		CO_2	13.174	
	H_2	1.324		H_2	1.324	
				E8 (Heat)	19.730	MJ
Separation	Syngas 6	20.420	kg	Dry gas	15.267	kg
	CH_4	0.643		CH_4	0.643	
	H_2O	5.192		H_2O	0.066	
	CO	0.086		CO	0.086	
	CO_2	13.174		CO_2	13.148	
	H_2	1.324		H_2	1.324	
				Water	5.153	kg
PSA	Dry gas	15.267	kg	Off-gas	14.267	kg
	CH_4	0.643		CH_4	0.643	
	H_2O	0.066		H_2O	0.066	
	CO	0.086		CO	0.086	
	CO_2	13.148		CO_2	13.148	
	H_2	1.324		H_2	0.324	
				H_2	1.000	kg
				E9 (Heat)	0.039	MJ
Compressor	H_2	1.000	kg	H_2	1.000	kg
	E10 (Electricity)	6.645	MJ			
Mixer 2	Off-gas	14.267	kg	Off-gas/Air	36.730	kg
	CH_4	0.643		CH_4	0.643	
	H_2O	0.066		H_2O	0.066	
	CO	0.086		CO	0.086	
	CO_2	13.148		CO_2	13.148	
	H_2	0.324		H_2	0.324	
				N_2	16.967	
				O_2	5.186	
				Ar	0.310	
	Air	22.463	kg			
	N_2	16.967				
	O_2	5.186				
	Ar	0.310				
Combustion	Off-gas/Air	36.730	kg	Vapour Product	32.360	kg
	CH_4	0.643		H_2O	0.064	
	H_2O	0.066		CO_2	15.019	
	CO	0.086		N_2	16.967	
	CO_2	13.148		O_2	0.000	
	H_2	0.324		Ar	0.310	
	N_2	16.967				
	O_2	5.186				
	Ar	0.310				
				Liquid Product	4.370	kg
				H_2O	4.343	
				CO_2	0.027	
				E11 (available for 100 % Heat or 35 %electricity & 50 % heat)	82.843	MJ

inert in this context, and they are assumed to exit the system through the PSA off-gas. A simplified model without equation 4 and 5 is also tested. The SMR and WGS reactors are modelled as isothermal and in equilibrium. The Peng-Robinson (PR) thermodynamic model is used in the DWSIM package [27]. The limitation of the thermodynamic simulation is not considering reactor design, number of tubes, pressure drop in the packed bed, catalyst type, catalyst particle height, catalyst bulk density, catalyst particle hole diameter and number of holes. Therefore, for example, the influence of using Ni-based and Pd–Au composite membrane reactor [29] or pressure drop [30,31] could not be assessed. The combustor for PSA off-gas cogeneration was assumed to be in stoichiometric combustion conditions with ideal air (N_2: 78.1 %; O_2: 20.9 %; Ar: 1 %). Combustor efficiency for heat was considered 100 %. CHP efficiency for heat production was considered to be 50 % and for electricity 35 % [32].

The components considered are: one vapour-liquid separator, two heaters, three coolers, one SMR, 2-stage WGS, one PSA, one combustor (see Fig. 3). Additionally, the simulation was performed under steady state conditions according to the following assumptions.

- NG, BG and water enter the process at 25 °C and 1 atm;
- Air is inserted in the system at 35 °C and 14.80 atm;

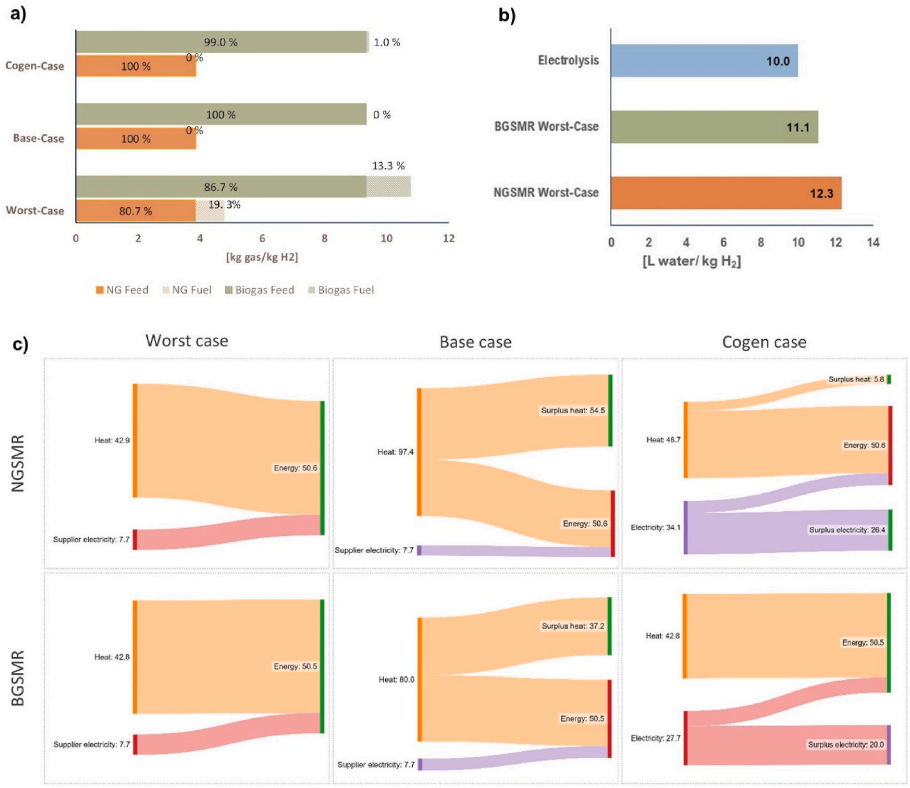


Fig. 6. Resource consumption, including a) Gas (with CH_4) consumption for SMR and heat generation, b) Demineralized water consumption, and c) Energy consumption (heat and electricity) along with Surplus Energy (heat in the Base-Case and electricity in the Cogen-Case). The Sankey diagram was generated using SankeyMATIC© for visual representation.

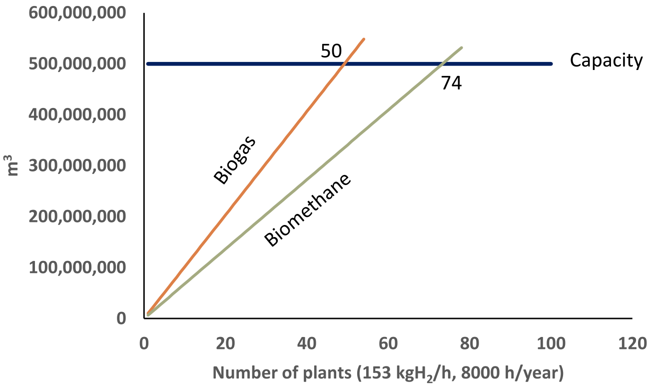


Fig. 7. Portuguese BG capacity and BGSMR plant capacity.

Steam-to-carbon ratio (S:C) is by default 3, and is defined as the number of water molecules to the number of carbon atoms.

No experimental data was available, nevertheless the results were also compared with a similar analysis to hydrogen production with different reactor temperatures and difference S:C ratios [17] and for a different biogas compositon.

2.3. Water electrolysis: benchmark data

Water electrolysis has already reached the commercial stage, facilitating the availability of data on demineralized water consumption and electricity consumption. Consequently, the authors chose to survey the market rather than resorting to the complex simulations used for the reforming systems.

According to the mass balance, the minimum demineralized water required per kilogram of hydrogen is 9 L/kgH_2.

Equation 7

$$H_2O + electricity \rightarrow H_2 + {}^{1}\!/\!{}_{2}\ O_2$$

By using the ideal gas law,

Equation 8

$$PV = \frac{mRT}{M}$$

where P stands for pressure, V for volume, m the mass of the gas, R = 8.314 kJ/(kmol•K), T is the temperature in K and M is the molar mass (2 kg/kmol for H_2). For 1 m^3, at 273 K and 100 kPa, the amount of H_2 is 0.088 kg. According to H-TEC PEM electrolyser manufacturer (see supplementary material), the energy consumption is 4.7 kWh/Nm^3 or 53.4 kWh/kgH_2 or (multiplying by 3.6 MJ/kWh) 192 MJ/kgH_2.

In the literature for other PEMs we have retrieved a demineralized water consumption of 10–11 L/kgH_2 [33–35] and an electricity consumption of 51–80 kWh/kgH_2 [33,36].

For comparing carbon footprint and water consumption of the hydrogen production technologies (SMR and water electrolyser), 10 LH_2O/kgH_2 and 54 kWh/kgH_2 were used as the parameters for PEM electrolysers.

2.4. Comparative analyses: pedigree matrix and sensitivity analyses

The ISO 14044 [26] standard does not specify to which component, or level, data quality analysis should be applied. Inventory data qualitative assessment, reflecting the data quality is based on the updated Pedigree Matrix as defined by USEPA [37]. It covers data quality at the flow and the process level. Flow level indicators address source reliability, temporal, geographic, and technological correlation and data sampling methods. The process level indicators address the level of

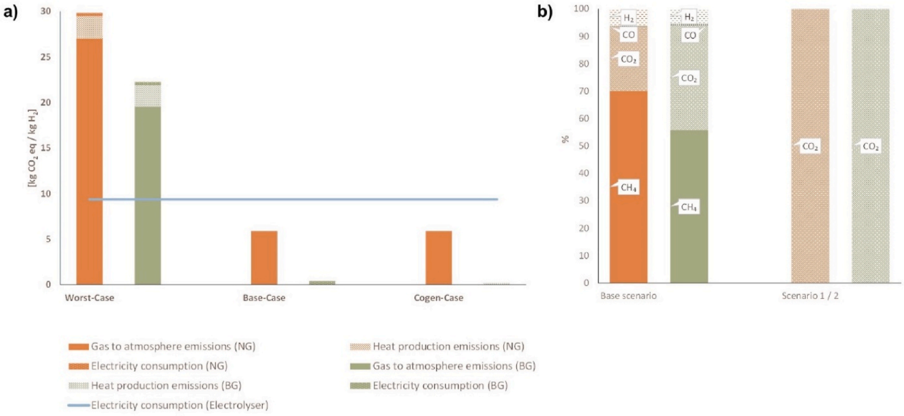


Fig. 8. Results utilizing IPCC AR6 with feedback and the 2020 Portuguese electricity emission factor: a) GWP100 as CO_2eq divided into indirect and direct emissions for the Worst-Case Scenario (indirect from electricity consumption and direct emissions from off-gas release to the atmosphere), Base-Case Scenario (indirect from electricity consumption and direct emissions due to off-gas combustion for heat), and Cogen-Case Scenario (off-gas combustion in CHP); b) Contribution of each global warming gas to carbon footprint; biogenic emissions from the biogas system are discounted as part of the short carbon cycle.

review the unit process has undergone and completeness of the unit process. The items and available scores are as in Fig. 4.

Quantitative results variation was evaluated, in the Cogen-Case scenario, by varying feed gas composition, i.e., using several natural gas, several biogas and one biomethane, by adding a biogas upgrading unit. Steam-to-carbon ratio (S:C) was varied from 1 to 5 at SMR, even though the value of 1 may cause coke formation problems it is useful to observe the trend and compare with other studies [17]. Moreover operating temperature conditions of the SMR was varied (750 °C–950 °C).

Portuguese electricity mix has shown variations over the years [39] and it is anticipated to become nearly carbon-neutral by 2050 [40]. The composition of the electricity generation mix (as indicated in the supplementary materials for the years 2015, 2020, and 2050, with emission intensities of 328 gCO_2eq/kWh, 175 gCO_2eq/kWh and 0 gCO_2eq/kWh, respectively) has discernible influence on the outcomes, including those for the Global Warming Potential over a 100-year period (GWP100) of the electrolyser.

Conversion factors from the IPCC report for CO_2eq emissions (AR5 with and without feedback and AR6 with feedback included, as detailed in supplementary material) were employed to assess their impact on results, primarily attributed to CH_4 emissions (both fossil and biogenic).

NG origin determines its composition and the same applies to BG. NG in Europe has several origins: Russia, Algeria, Netherlands, etc. Concentrations of BG components (methane, carbon dioxide, nitrogen, and oxygen) vary according to the BG source: landfill, dairy waste, food waste [41]. The gas upgrading may be realized by means of several technologies, e.g. according to Ref. [42]: alkaline with regeneration, high pressure water scrubbing, bottom ash scrubbing, pressure swing adsorption, membrane separation and cryogenic separation. Per 1 tonne of CO_2 removed and for 98% biomethane purity, the electricity consumption of the processes varies between 120 and 354 kWh and water consumption between 0 and 129 L, with a CH_4 loss of 0.1–3.5%. The average values were used to include in the LCA of biogas system to run a scenario with a stream of 98% CH_4, 2% CO_2 and CH_4 loss of 1.8 %.

3. Results

This section shows the results obtained for the following simulation conditions: NG and BG, SMR at 850 °C, IPCC AR6, 2020. DWSIM verification was made via literature [17] for $S:C = 3$, 10 atm, BG composition in %v/v 60 CH_4, 35 CO_2, $3H_2O$ and 2 N_2 and is in Fig. A4 of the Supplementary Material. DWSIM reproduces well the literature findings using ASPEN except for reactor temperatures higher than 1050 °C, which falls outside our analysis scope.

The sensitivity analysis to NG and BG composition and inclusion/exclusion of C_3H_8 reforming and H_2 reaction with CO to form graphite (equation 4 and 5); SMR temperature (750 °C – 950 °C); S:C (1–5); IPCC CO_2 equivalency factors (AR5, AR6, with and without feedback) and Portuguese electricity generation mix (2015, 2020, 2050) is presented in the discussion section, for the Cogen-Case scenario. It is noteworthy that a S:C ratio of 1 is improbable in a realistic scenario, as it may result in coke formation. Nevertheless, it was employed in this assessment for comparison purposes.

The metrics carbon footprint, water depletion, energy utilization and ability to valorise waste were used to compare the three hydrogen production systems, see.

Fig. 5. It is interesting the BGSMR system ability to valorise waste, as biogas comes from anaerobic digestion/landfill of wastes. In fact, hydrogen electrolysis in competitive only in a 100 % renewable power system in 2050 and only for the carbon footprint metric, with all the BG systems having near zero carbon emissions (<0.16 kg CO_2eq/kgH_2). Both Base-Case and Cogen-Case are better in the long run, unless electrolysis could use wastewater streams, and will be less energy demanding.

3.1. *Inventory retrieved from DWSIM*

The simulation results allowed to obtain a complete inventory for mass and energy flows presented in Table 3 for natural gas to hydrogen and in Table 4 for biogas to hydrogen. The water-to-carbon ratio is consistent at 3 ($S:C = 3$) in both cases. For NGSMR, it is calculated as water/(CH_4+C_2H_6), and for BGSMR, it is determined as water/CH_4.

3.2. *Resource consumption*

Demineralized water, external/internal heat and external/internal electricity consumption and feedstock consumption are depicted in Fig. 6.

In Worst-Case scenario the energy consumption is provided externally and no water is recycled. In Base-Case the off-gas combustion provides the heat needs and surplus heat that can be sourced as district heating, decreasing the gas needs to produce hydrogen, and recycling water. In Cogen-Case Scenario, the off-gas in a CHP unit provides all the electricity needs with surplus that can be dispatchable with a little amount of heat surplus in the NG case. For BG a small amount of heat must still be provided by burning additional BG. The electrolyser energy needs are much higher (190 MJ/kgH_2) as well as non-recyclable water (10 L/kgH_2).

Other studies refer to 7.58 kg_{water}/kgH_2 for a biogas consumption of

Table 5
Pedigree Matrix for SMR inventory data.

Unit	Flow reliability	Temporal correlation	Geographical correlation	Technological correlation	Data collection methods	Process review	Process completeness	Observations
Heater 1								
Water flow	3	1	1	1	5	4	1	Simulation DWSIM
Energy flow	3	1	1	1	5	4	1	
Mixer 1								
Steam	3	1	1	1	5	4	1	Simulation DWSIM
NG or BG	3	1	1	1	5	4	1	
Heater 2								
Energy flow	3	1	1	1	5	4	1	Simulation DWSIM
Mix NG/steam	3	1	1	1	5	4	1	
SMR								
Mix NG/steam	3	1	1	1	5	4	1	Simulation DWSIM
Syngas 1	3	1	1	1	5	4	1	
Energy flow	3	1	1	1	5	4	1	
Cooler 1								
Syngas 1	3	1	1	1	5	4	1	Simulation DWSIM
Energy flow	3	1	1	1	5	4	1	
Syngas 2	3	1	1	1	5	4	1	
HTWGS								
Syngas 2	3	1	1	1	5	4	1	Simulation DWSIM
Syngas 3	3	1	1	1	5	4	1	
Cooler 2								
Syngas 3	3	1	1	1	5	4	1	Simulation DWSIM
Energy flow	3	1	1	1	5	4	1	
Syngas 4	3	1	1	1	5	4	1	
LTWGS								
Syngas 4	3	1	1	1	5	4	1	Simulation DWSIM
Syngas 5	3	1	1	1	5	4	1	
Cooler 3								
Syngas 5	3	1	1	1	5	4	1	Simulation DWSIM
Energy flow	3	1	1	1	5	4	1	
Syngas 6	3	1	1	1	5	4	1	
Separation gas/liquid								
Syngas 6	3	1	1	1	5	4	1	Simulation DWSIM
Liquid	3	1	1	1	5	4	1	
Dry gas	3	1	1	1	5	4	1	
PSA								
H_2	3	1	1	1	5	4	1	Simulation DWSIM
Off-gas	3	1	1	1	5	4	1	
Compressor								
Electricity flow	3	1	1	1	5	4	1	Simulation DWSIM; Electricity from national Portuguese mainland 5-year moving average production
Indirect CO_2eq emissions	3	1	4	1	5	4	1	
H_2	3	1	1	1	5	4	1	
Combustor Heat/CHP								
NG, BG and/or off-gas	3	1	1	1	5	4	1	Simulation DWSIM
Direct CO_2eq emissions	3	1	1	1	5	4	1	

Table 6
Pedigree Matrix for Electrolyser inventory data.

Unit	Flow reliability	Temporal correlation	Geographical correlation	Technological correlation	Data collection methods	Process review	Process completeness	Observations
Electrolyser								
Water flow	1	1	1	1	5	4	1	Data from manufacturer and literature; Electricity from national Portuguese mainland 5-year moving average production
Energy flow	1	1	1	1	5	4	1	
H_2	1	1	1	1	5	4	1	
Indirect CO_2eq emissions	1	1	4	1	5	4	1	

8.4 kgBG/kgH_2 (6.11 as feed, 2.24 as fuel) whereas the reforming inventory data are obtained from process simulation in Aspen Plus™ software [17], 800 °C SMR, 10 atm reactor, a ratio S:C = 3 and 1.95 MJ/kgH_2 for water pump and biogas compressor, with off-gas combustion to heat. Regarding NG, the NREL study of 2001 [13] reports a reactor pressure of 26 atm (no operating temperature specified nor S:C

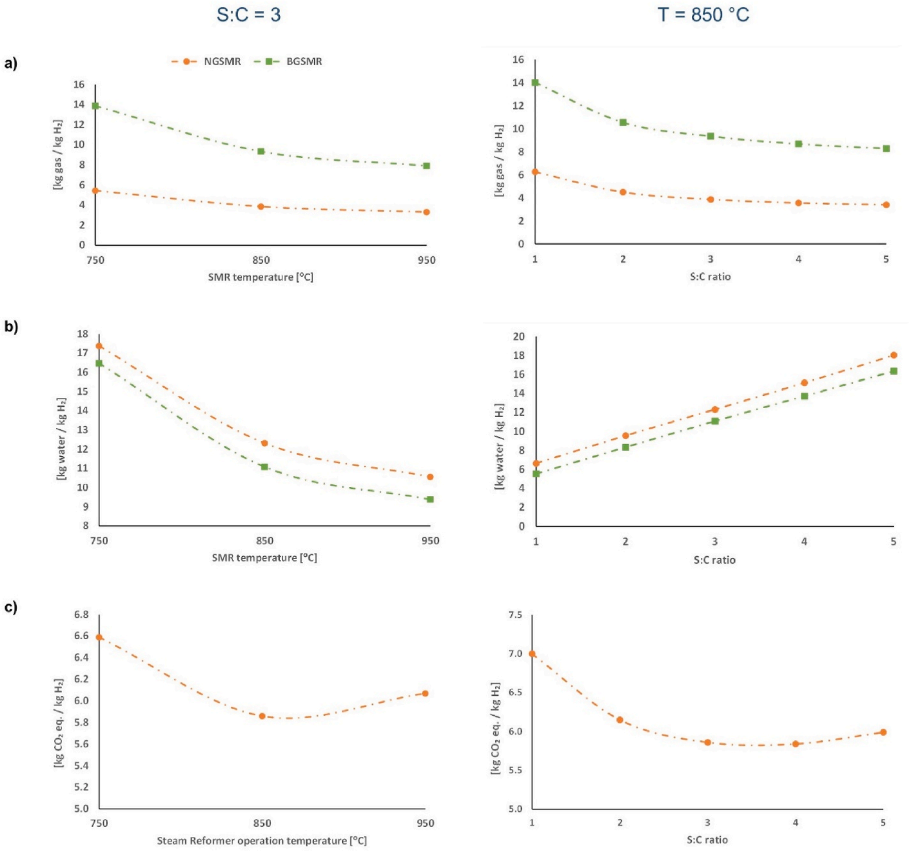


Fig. 9. Influence on gas consumption (a), initial water consumption (b), carbon footprint (c) of SMR temperature with a S:C ratio of 3 – left, and S:C ratio at 850 °C – right.

Table 7
Influence of the number of stages WGSR.

	NGSMR			BGSMR		
	kg_{gas}/kgH_2	kg_{water}/kgH_2	$kgCO_{2eq}/kgH_2$	kg_{gas}/kgH_2	kg_{water}/kgH_2	$kgCO_{2eq}/kgH_2$
1 stage WGS	3.93	12.53	10.23	9.67	11.48	0.00
2 stage WGS	3.88	12.39	10.11	9.34	11.08	0.00
Variation (%)	−1.1	−1.1	−1.2	−3.5	−3.5	NA

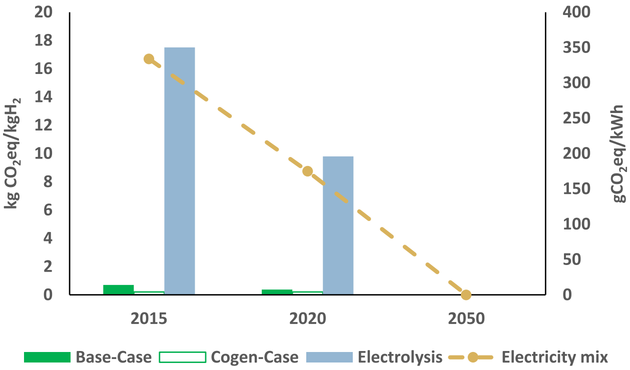


Fig. 10. Influence of electricity generation mix (emission factor for electricity impact see supplementary material) in BSMR and Electrolysis.

ratio), presenting values of 14 kg_{water}/kgH_2, 3.22 $kgNG/kgH_2$ (2.9 as feed and 0.32 as fuel), 1.14 $MJ_{electricity}/kgH_2$, with off-gas combustion to heat. In fact, after converting our conditions to the same of this study we obtained the same outcomes (see verification at the supplementary Data).

In another study [14], incorporating cogeneration, the natural gas to hydrogen ratio is reported as 3.4 $kgNG/kgH_2$ (86 % as feedstock, 14 % as fuel), with emissions of 9 $kgCO_2/kgH_2$. However, the study lacks detailed information on water balances, does not specify CO_2 equivalents, and provides no details on the conversion efficiency of the cogeneration unit to heat. Additionally, crucial data such as the steam-methane reactor operating temperature is not mentioned, making a direct comparison with the Cogen-Case challenging. Furthermore, the methane content in natural gas used in the referred study is lower than in the present work, introducing potential variations in the results.

Considering a BG (60% CH_4), the yearly production of 1224 tonne H_2, needs 9.3 kg BG per each 1 kg of H_2 or 11,383 tonne BG. With density of 1.1 kg/m^3, it amounts to an yearly demand of 11 million m^3 BG. Portuguese capacity of 0.5 bcm (maintaining 0.1 bcm for CHP [24]), would leverage the production of 50 hydrogen plants with the same yearly production (see Fig. 7), which amounts to an annual hydrogen production capacity of 61 ktonne. If BG with 98% CH_4 is considered (biomethane) with density of 0.7 kg/m^3, we could have 73 plants and hydrogen production capacity of 90 ktonne.

3.3. Carbon footprint

Simulation results from this work are depicted in Fig. 8. The reviewed studies for biogas reforming [17] and for natural gas-steam reforming [13] estimated a global warming potential of, respectively, 13.43 kg biogenic CO_2/kgH_2 and 9.17 kg CO_2eq/kgH_2. These values

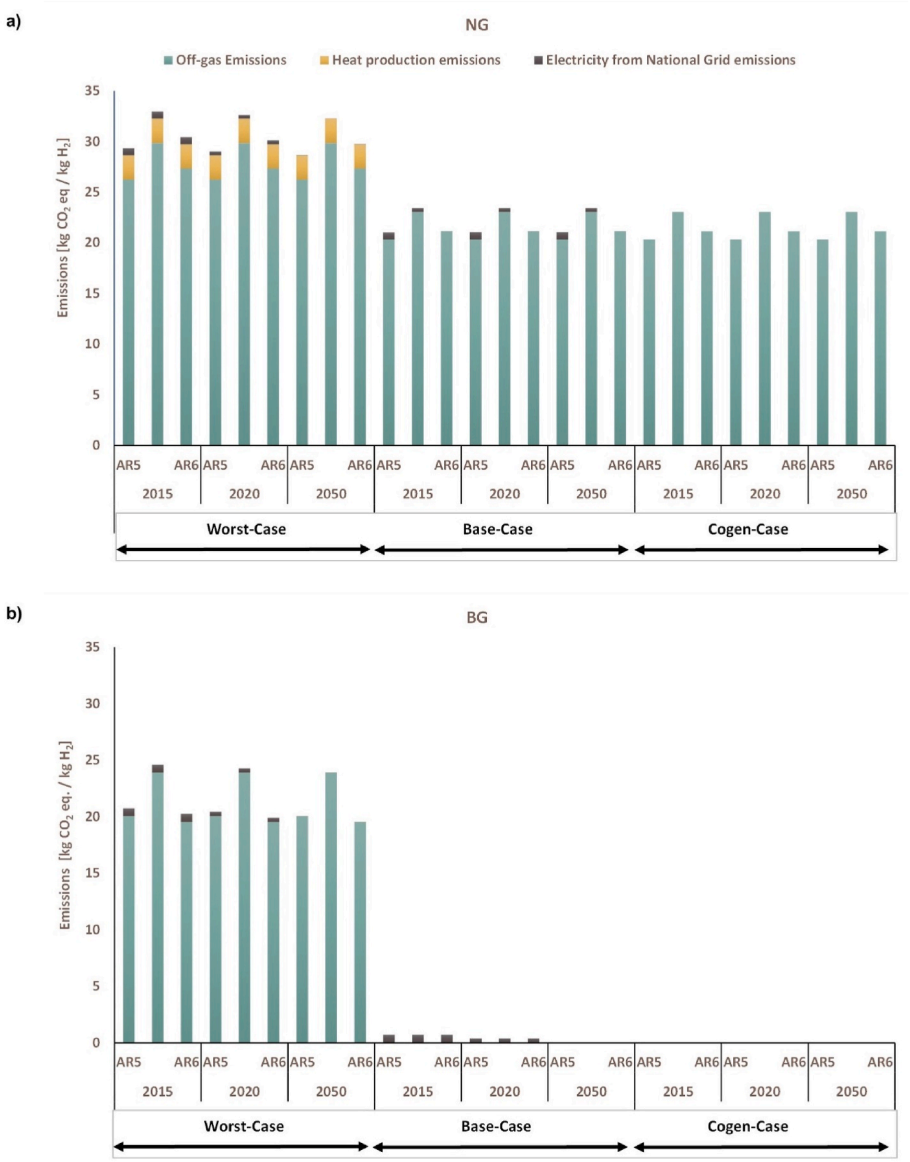


Fig. 11. Influence of IPCC equivalency factors a) Natural gas system b) Biogas system.

cannot be compared directly with our simulation outcomes due to different assumptions, e.g. different gas feed compositions, different S:C ratio, different reactor temperatures, different electricity generation mixes and CO_2 equivalency factors from prior IPCC reports. The European Emissions Trading System (EU ETS) benchmark [15] for hydrogen production is 6.84 $kgCO_2eq/kgH_2$ and covers only direct operational emissions of natural gas-steam reforming, i.e. a different boundary (our study comprehends indirect emissions from electricity generation). Our benchmark update, including cogeneration, marks at 5.9 $kgCO_2eq/kgH_2$, favouring the NG system.

4. Discussion

The lack of reproducible data and confidence in results is still an issue in the LCA community and is crucial for the sake of transparency in the decision-making process. The EPA Guidance on Data Quality Assessment for Life Cycle Inventory Data is followed by applying the Pedigree Matrix at the flow and process levels, see Table 5 and Table 6. Flow level indicators address source reliability, temporal, geographic, and technological correlation and data sampling methods. The process level indicators address the level of review the unit process has undergone and completeness of the unit process.

One of the issues impacting the reliability of LCA results is uncertainty which may be very high, underestimated or, very often, simply ignored [43]. Representing the results as point values is misleading. Following an attributional LCA approach, the authors identified the main parametric/scenario analysis sources as being: Feed gas composition, SMR temperature, Water/carbon ratio, IPCC CO_2 equivalency factors AR5, AR6 and Portuguese electricity generation mix 2015, 2020, 2050. Fig. 9 shows the influence of SMR temperature and S:C ratio.

Higher temperatures translate into higher energy needs but also tend to produce more hydrogen. The NG carbon footprint is thus a compromise between these factors. BG carbon footprint is zero, because is only emits biogenic carbon, that follows fossil NG carbon trend The increase of the steam/methane ratio favours the hydrogen production, but demineralized water consumption increases which is a drawback regarding initial resource consumption. A good compromise among hydrogen production, water consumption and global warming minimum is for 850 °C and S:C = 3. Water-gas shift reactor stage increase (from 1 to 2) is beneficial for hydrogen production lowering the gas and water consumption to produce 1 kg of hydrogen together with a decrease of the carbon footprint. However, the gain (variation) is

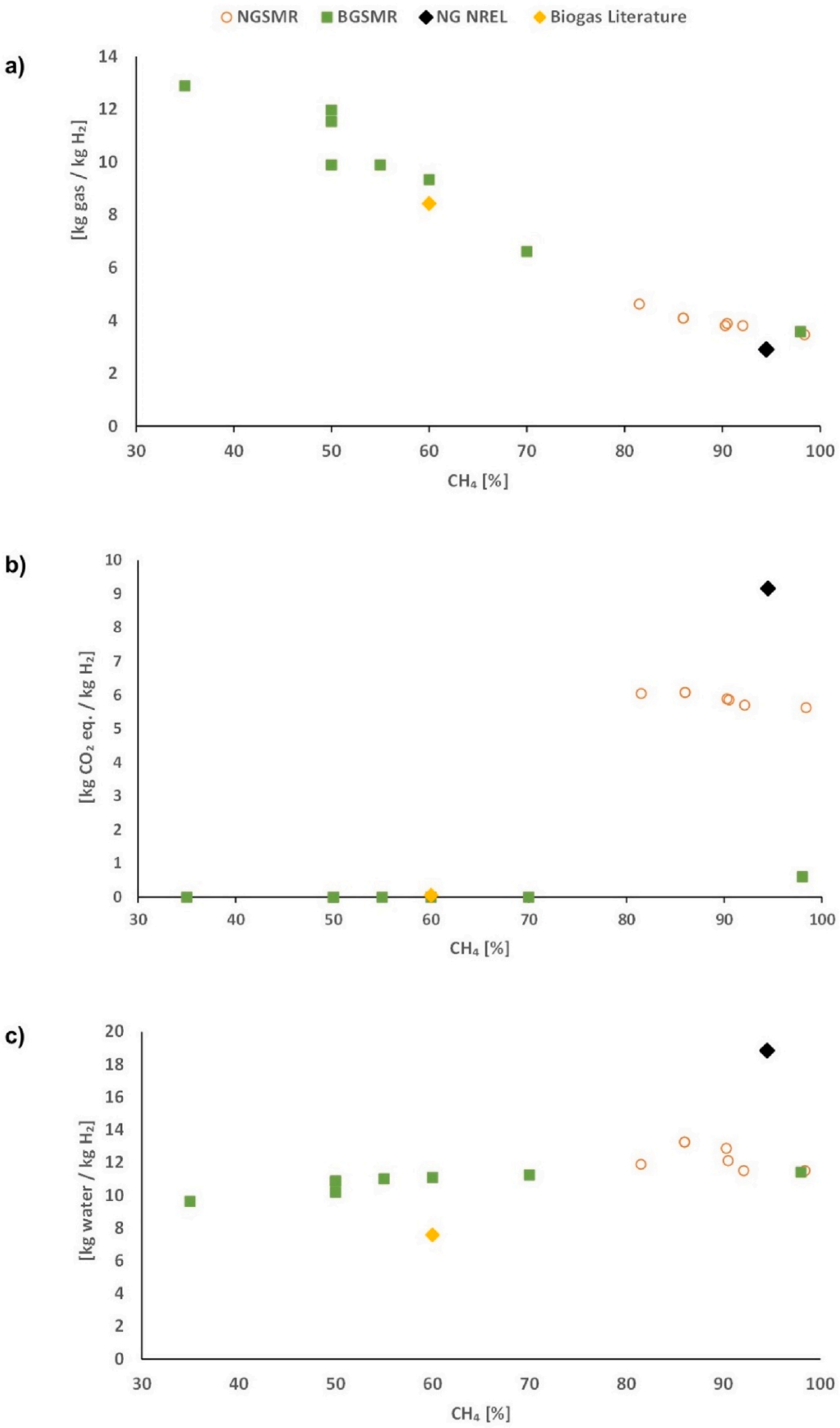


Fig. 12. Influence of inlet gas composition on gas consumption (a), carbon footprint (b) and initial water consumption (c).

marginal as can be seen in Table 7. The influence is higher in biogas systems with lower CH_4 content than natural gas.

The exclusion of the C_3H_8 reforming reaction and H_2 reaction with CO forming graphite (equations 4 and 5) did not alter the main results thus one can infer a simplified model would be suitable for the intended analysis.

The electricity consumption of SMR systems is notably lower compared to the electrolysis system. Consequently, it is expected that the electricity mix will induce a higher variation in the latter, as depicted in Fig. 10. BGSMR with off-gas combustion is projected to rank higher than electrolysis, demonstrating a lower global warming potential for electricity emission factors exceeding 8 g CO_2eq/kWh. Notably, the European Union's 2021 emission factor of 298 g CO_2eq/kWh will further amplify the environmental impact of hydrogen production via electrolysis using grid electricity. The imperative use of renewables is underscored for achieving environmental competitiveness with biogas SMR.

Fig. 11 presents the influence of CO_2 equivalency emission factors. It is quite interesting to observe that its influence is in the Worst-Case scenario, the higher the CH_4 emission in off-gas release to atmosphere the higher the impact of using other CO_2eq factors other than IPCC AR6 with feedback (see Fig. 8b). Combustion of NG also releases more CH_4 than biogas and off-gas and thus the first system is more impacted. Nevertheless, the main conclusions regarding both SMR systems and electrolysis remain unchanged.

Fig. 12 shows the influence of the amount of CH_4 present in the feed gas and its origin (fossil or non-fossil). The higher the percentage of methane the less gas is needed as feed to produce the same amount of hydrogen. Biogenic CO_2 emissions are discounted for biogas and therefore its global warming potential is much lower than fossil natural gas. One can observe three points for three types of biogases that albeit having different global compositions do present the same percentage of CH_4 (e.g., 50 %), but different needs of feed to produce the same amount of H_2. This is due to the percentage of CO_2 in the feed gas, that alters the equilibrium constant of the reaction (see Equation 2-4). In terms of H_2 production, a lower content of CO_2 in the biogas can increase the efficiency of CH_4 conversion, raising the quantity of H_2 produced, and, consequently, lowering the gas needs as input. Upgrading biogas to biomethane, has an extra water demand of 0.14 L/kgH_2 (calculations at the Supplementary material), an extra electricity consumption of 0.5 kWh/kg H_2 (1.9 MJ/kgH_2) that could be provided by the surplus electricity and an extra carbon footprint, due to methane losses at the upgrading unit, of 0.6 kg CO_2eq/kgH_2. This implies that incorporating a biogas upgrading unit would sustain the favourable performance of BGSMR compared to the electrolysis system.

5. Conclusions

DWSIM enables to simulate mass and energy balances of steam methane reforming to hydrogen and off-gas combustion to energy (heat or heat & electricity). This approach was necessary due to lack of real operating data and to pre-estimate the impact of the project on climate change. Moreover, it was necessary to compare fossil and non-fossil thermochemical systems with electrochemical system in terms of carbon footprint, water depletion, energy consumption and ability to recover waste streams.

The optimization of the BGSMR system combining minimum global warming potential, minimum demineralized water consumption and maximum hydrogen production is for upgraded biogas to biomethane, a vapour-carbon ratio of 3 and SMR temperature near the 850 °C. The decarbonization of the power systems (electricity mix with zero carbon intensity) will favour both electrolyser and BGSMR systems but the ability to recover waste, consume less energy and deplete less water make the BGSMR more appealing in the near future to the long run.

As far as waste is concerned, the Portuguese biogas/biomethane potential could cover the production of up to 61–91 ktonnes of hydrogen per year (50–74 plants, respectively, with 153 khH_2/hour capacity working 8000 h/year). If credits are given to heat/electricity surplus the BGSMR system might even be carbon negative.

A techno-economic analysis considering oxygen production by electrolysis as an added-value co-product (8 kg O_2 for each 1 kg H_2) would bring more insight on which system would be preferable to use not only from the environmental point of view but also from the economical/market needs point of view.

Furthermore, investigating the influence of selecting specific chemical reactions in reforming, such as those involving graphite formation and C_3H_8, in comparison to alternative reactions, could present an intriguing avenue for future research.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijhydene.2024.04.113.

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