CHEMICAL ENGINEERING TRANSACTIONS
VOL. 114, 2024
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Petar S. Varbanov, Min Zeng, Yee Van Fan, Xuechao Wang

ISBN 979-12-81206-12-0; **ISSN** 2283-9216
DOI: 10.3303/CET24114058

Green Hydrogen Production based on Biogas Reforming Integrated with Membrane-based CO_2 Capture

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Renewable energy sources and the Carbon Capture, Utilization and Storage (CCUS) technologies are foreseen to play a fundamental role in an overall decarbonized economy in view of achieving the global climate neutrality. This work evaluates the technical and environmental implications of the green hydrogen production from biogas reforming process integrated with CO_2 capture using membrane-based systems. The evaluated concepts have a capacity of 100 MW_{th} green hydrogen with pre-combustion and post-combustion CO_2 capture. The mass and energy balances of decarbonized biogas reforming design were then used to quantify the key performance indicators. For comparison reasons, the biogas reforming process without decarbonization feature and with CO_2 capture based on chemical gas-liquid absorption were considered as benchmark cases. Detailed techno-economic and environmental analysis underlines the promising potential of green hydrogen production based on biogas reforming integrated with membrane-based CO_2 capture feature: high cumulative energy efficiency (about 55 - 60 %), low specific CO_2 emissions (down to 2 kg/MWh as process emission and negative emissions for the overall decarbonized biogas reforming system), co-generation capability of green hydrogen and decarbonized power as well as positive key economic indicators (e.g., specific investment cost, operational cost, levelized hydrogen production cost etc.) compared to the current fossil-based state of the art systems.

1. Introduction

One of the most important environmental problems is related to greenhouse gas (GHG) emissions, which cause global warming and climate change (Asghar et al., 2021). Reduction of GHG emissions is of paramount importance for achieving climate neutrality. Integrating the renewable energy sources and the CCUS technologies will result in energy conversion systems with overall negative carbon emissions (CO_2 is removed from the atmosphere, therefore reducing its concentration), which are required for climate neutrality (Quang et al., 2023). Lately, the biogas production and its utilisation attracted large consideration as a promising renewable source and an efficient way of various bio-based wastes transformation into energy carriers/chemicals (e.g., heat, power, hydrogen). Furthermore, green hydrogen (produced from renewable energy sources - Hermesmann and Müller, 2022) is seen as a promising energy carrier for decarbonizing a wide range of global economy sectors (e.g., heat and power production, transport, metallurgy, chemistry, cement, buildings etc.).
This work evaluates the main technical and environmental implications of green hydrogen production based on biogas reforming with membrane-based CO_2 capture. As industrial relevant production capacity, a 100 MW thermal high purity hydrogen (>99.95 % vol.) was chosen considering the current sizes of conventional hydrogen production units as well as the biogas availability. The pre-and post-combustion CO2 capture was done using membrane gas separation as a promising energy- and cost-efficient decarbonization technology (Han and Ho, 2021). Various technological process options were evaluated e.g., conventional and autothermal reforming systems, pre- and post-combustion CO_2 capture using membranes as the gas separation technology (Giordano et al. 2019). As benchmark cases, the biogas reforming processes without CO_2 capture and with CO_2 capture based on chemical gas-liquid absorption (using Methyl-Di-Ethanol-Amine - MDEA) were considered for comparison. For an overall technical and environmental assessment, various relevant process engineering tools were used: conceptual design, process flow modelling and simulation using ChemCAD, mass and energy integration analysis, model validation by comparing the simulation results with experimental/industrial data, etc.

Paper Received: 20 June 2024; Revised: 23 October 2024; Accepted: 17 November 2024
Please cite this article as: Cormos C.-C., Petrescu L., Cormos A.-M., 2024, Green Hydrogen Production based on Biogas Reforming Integrated with Membrane-based CO_2 Capture , Chemical Engineering Transactions, 114, 343-348 DOI:10.3303/CET24114058

The relevant research novelty of the proposed work can be evaluated considering the following key elements: implementation of an integrated techno-economic and environmental assessment methodology and evaluation of the possibility that the innovative membrane-based decarbonized biogas reforming process delivers a sustainable energy- and cost-effective green hydrogen with higher energy conversion yields and negative CO_2 emissions when compared to state-of-the-art biogas reforming with and without CO_2 capture (reference cases).

2. Process design, main assumptions, model validation and thermal integration analysis

The conceptual design of green hydrogen production based on biogas reforming with membrane pre- and post-combustion CO_2 capture is presented in Figure 1. The design is similar to the conventional methane steam reforming concept with CO_2 capture feature to be applied in ammonia/fertilizer industry (IEAGHG, 2017).

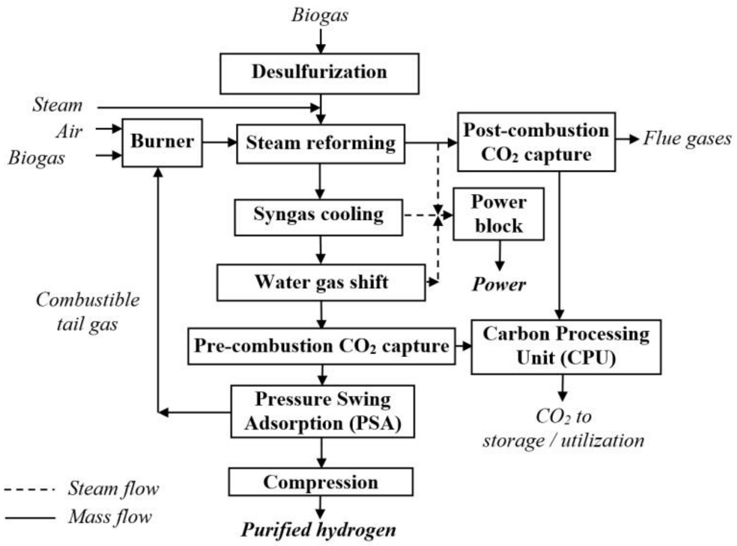

Figure 1: Green hydrogen production plant based on biogas reforming with membrane-based CO_2 capture

Table 1 shows the key design assumptions of green hydrogen plant based on biogas reforming with membrane-based CO_2 capture unit. The whole plant concept was modeled and simulated using ChemCAD. The simulation results were compared to relevant experimental / industrial data in view of validation (IEAGHG, 2017). For this purpose, key performance indicators of various plant sub-systems were used (e.g., biogas conversion rate, water gas shift conversion yield, CO_2 capture rate etc.). Furthermore, the evaluated design was optimized in view of efficiency utilization of energy within the plant by the heat integration analysis using Pinch method (Smith, 2016). Figure 2 shows the Composite Curves for the overall system, including heat recovery and power block.

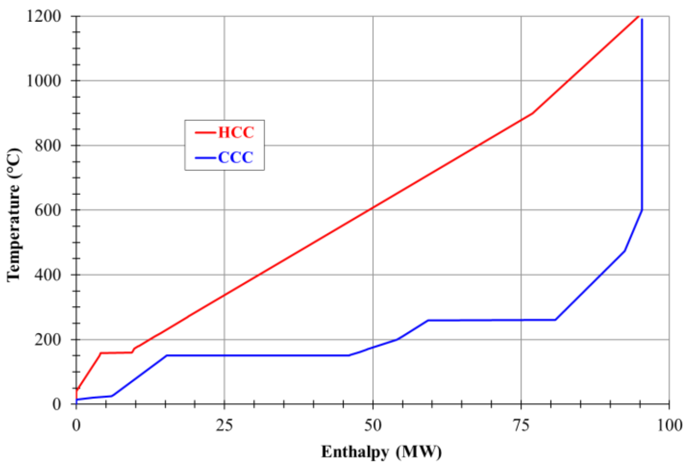

Figure 2: Thermal integration analysis of biogas-based green hydrogen production plant

Table 1: Key design assumptions

Plant component	Design characteristics
Biogas composition and thermal properties	Biogas composition (volumetric): 59.75 % CH_4, 40.00 % CO_2, 0.20 % N_2, 0.04 % O_2, 725 ppm H_2S Lower calorific value (LHV): 17.58 MJ/kg
Biogas desulphurization unit	Adsorption on ZnO bed Desulfurization efficiency: >99 %
Biogas reforming unit	Reactor operating temperature & pressure: 900 °C & 30 bar Reactor model: Gibbs Reactor thermal mode: heat transfer Pressure drop: 1 bar
Catalytic water gas shift unit	Two adiabatically operated shift reactors (high & low temperature) Steam to CO molar ratio: 3 Conversion yield: 98 %
Membrane-based pre-combustion CO_2 capture unit	H_2-selective membrane CO_2 removal rate: 96 % Membrane permeance data: H_2 - 300, CO_2 - 10, CO - 4, N_2 - 2, Ar - 2, CH_4 - 2, H_2O - 10,000 Pressure ratio: 5 - 10
Membrane-based post-combustion CO_2 capture unit	CO_2-selective membrane CO_2 removal rate: 98 % Membrane permeance data: CO_2 - 1075, N_2 - 1.1, O2 - 1.05, H_2O - 0.01 Pressure ratio: 10
Heat recovery and steam-based power block	Steam conditions: 475 °C & 48 bar / 220 °C & 3 bar Steam turbine efficiency: 85 % Condenser pressure: 0.045 bar
CO_2 processing unit (drying and compression)	Final delivery pressure: 120 bar Compressor efficiency: 85 % Moisture removal unit: TEG (Tri-ethylene-glycol) CO_2 composition (vol. %): > 95 % CO_2, < 2,000 ppm CO, < 250 ppm H_2O, < 100 ppm H_2S, < 4 % non-condensable gases
Heat exchangers	Pressure drops: 4 % of inlet pressure Minimum temperature difference: $\Delta T_{min.}$ = 10 °C

3. Techno-economic and environmental evaluation methodology

Following the overall process flow modelling and simulation of the green hydrogen production plant through biogas catalytic reforming with membrane-based CO_2 capture, the overall mass & energy balances are used to calculate the key techno-economic and environmental indicators. The following performance indicators are used in accordance with the validated methodology in the field (IEAGHG, 2017):

- Hydrogen thermal efficiency ($\eta_{Hydrogen}$) is defined as the ratio of hydrogen output and biogas input:

$$\eta_{Hydrogen} = \frac{Hydrogen\ thermal\ output}{Biogas\ thermal\ input} * 100 \quad (1)$$

- Net electrical efficiency (η_{Power}) is defined as the ratio of net power output and biogas thermal input:

$$\eta_{Power} = \frac{Net\ power\ output}{Biogas\ thermal\ input} * 100 \quad (2)$$

- Overall energy efficiency ($\eta_{Overall}$) is defined as the sum of hydrogen thermal and net power efficiencies:

$$\eta_{Overall} = \eta_{Hydrogen} + \eta_{Power} \quad (3)$$

- CO_2 capture rate ($\eta_{CO2\ capture\ rate}$) is defined as the percentage ratio of capture carbon from biogas input:

$$\eta_{CO2\ capture\ rate} = \frac{Captured\ CO_2\ molar\ flow}{Inlet\ biogas\ carbon\ molar\ flow} * 100 \quad (4)$$

- Specific CO_2 emission (SE_{CO2}) is defined as the ratio of emitted CO_2 and combined energy output:

$$SE_{CO_2} = \frac{Emitted\ CO_2\ mass\ flow}{Hydrogen\ thermal\ output\ +\ Net\ power\ output} * 100 \quad (5)$$

- Capital cost of a specific plant sub-system (C_E) is calculated with the cost correlation method as follow:

$$C_E = C_B * (\frac{Q}{Q_B})^M \quad (6)$$

- Specific investment cost (SIC) is defined as the ratio of capital investment and overall combined energy output:

$$SIC = \frac{Total\ capital\ investment\ cost}{Hydrogen\ thermal\ output\ +\ Net\ power\ output} \quad (7)$$

- Operational & maintenance (O&M) costs account both fixed (e.g., labour, maintenance, administrative costs) and variable (e.g., biogas, catalysts, membrane, chemicals etc.) components.
- Levelized cost of hydrogen (*LCOH*) is defined as the ratio of annualized capital investment and operational & maintenance costs and the hydrogen thermal output:

$$LCOH = \frac{(Annualized\ capital\ investment\ cost\ +\ Operational\ \&\ Maintenance\ cost)}{Hydrogen\ thermal\ output} \quad (8)$$

Table 2 presents the main economic assumptions used in the present work (Cormos et al., 2022).

Table 2: Main economic assumptions

Biogas cost	4.50 €/GJ
Boiler feed water cost	0.15 €/t
Cooling water cost	0.01 €/t
Cooling water treatment cost	0.003 €/m^3
BFW and process treatment cost	95.00 k€/month
Membrane cost	50 €/m^2
Reforming and water gas shift catalysts cost	2.5 M€/y
Direct productive personnel number	60
Annual direct labor cost per person	48.00 k€/y/person
Administrative costs, share of direct labor cost	30 %
Plant maintenance costs, share of capital cost per year	3 %
Plant capacity factor	7,884 h/y
Discount rate	8 %
CO_2 transport and storage cost	15 €/t
Carbon emission tax	0 €/t
Construction period	2 years
Capital cost share per each construction year	40 %, 60 %
Plant operation life	25 years

4. Results and discussions

The following case studies of green hydrogen production based on biogas catalytic steam reforming were evaluated:

- Case 1: Biogas catalytic reforming without CO_2 capture (benchmark);
- Case 2: Biogas catalytic reforming with pre-combustion CO_2 capture with MDEA (benchmark);
- Case 3: Biogas catalytic reforming with pre-combustion CO_2 capture with membranes;
- Case 4: Biogas catalytic reforming with pre- and post-combustion CO_2 capture with membranes.

For the investigated green hydrogen production plant based on biogas catalytic steam reforming with and without CO_2 capture capability, the main technical and environmental performance results are presented in Table 3. The auto-thermal biogas reforming technology using oxygen was also evaluated and the overall energy efficiency was lower than the conventional biogas steam reforming technology (65 vs. 70 % for the concepts without carbon capture feature). Between the two membrane-based concepts (Cases 3 and 4) there is a significant difference in terms of the carbon capture rates (55 vs. 99 %) as well as in terms of overall energy balance. Case 4 is almost totally decarbonized but it requires power import from the grid (the available heat within the plant is not enough for a positive energy balance as in other cases). The decarbonized green hydrogen production plants using membrane separation technology have high overall energy efficiency (about 55 - 60 %). The fully decarbonized concept (Case 4) using both pre- and post-combustion CO_2 capture by membrane separation technology has near zero plant sourced CO_2 emissions (about 2 kg/MWh). Considering the fact that biogas is a renewable energy source, the fully decarbonized concept, which uses both membrane-based pre- and post-combustion capture configurations (Case 4) has negative CO_2 emissions of about -468 kg/MWh.

Table 3: Technical performance indicators for green hydrogen production based on biogas reforming

Performance indicator	Units	Case 1	Case 2	Case 3	Case 4
Biogas input	t/h	31.16	31.16	35.80	35.80
Biogas lower calorific value	MJ/kg	17.58	17.58	17.58	17.58
Biogas thermal input	MW_{th}	152.16	152.16	174.82	174.82
Steam turbine output	MW_e	10.20	7.65	15.46	15.46
Expander output	MW_e	0.48	0.20	0.15	0.15
Gross power output	MW_e	10.68	7.85	15.61	15.61
Ancillary power consumption	MW_e	4.12	6.75	10.95	20.20
Hydrogen thermal output	MW_{th}	100.00	100.00	100.00	100.00
Net power output	MW_e	6.56	1.10	4.66	-4.59
Hydrogen thermal efficiency	%	65.72	65.72	57.20	57.20
Net electrical efficiency	%	4.31	0.72	2.66	-2.62
Overall energy efficiency (hydrogen + power)	%	70.03	66.44	59.86	54.58
CO_2 capture rate	%	0.00	64.70	55.50	99.60
Specific CO_2 emissions (plant level)	kg/MWh	470.60	175.20	240.78	2.25

Table 4 shows the total capital investment cost, specific capital investment cost, operational & maintenance (O&M) cost as well as the levelized cost of green hydrogen for the assessed biogas reforming concepts with and without CO_2 capture feature. The fully decarbonized biogas reforming concept (Case 4) shows the highest hydrogen production cost mainly due to the membrane-based post-combustion CO_2 capture unit from flue gases. It can be noticed that the green hydrogen production cost from biogas is not very high compared with the current natural gas-based hydrogen prices of around 50 - 60 €/MWh (IEAGHG, 2017). Considering the fact that this technology is using renewable energy sources coupled with CO_2 capture capability, the techno-economic and environmental advantages are very promising for developing low carbon applications.

Table 4: Economic performance indicators for green hydrogen production based on biogas reforming

Performance indicator	Units	Case 1	Case 2	Case 3	Case 4
Capital investment cost	M€	103.79	150.26	138.78	260.97
Specific capital investment cost	€/kW net	973.96	1,486.28	1,326.06	2,735.22
Operational & maintenance cost	€/MWh	34.57	42.76	41.22	45.55
Levelized cost of hydrogen (LCOH)	€/MWh	46.67	66.20	62.70	89.05
	€/GJ	12.96	18.38	17.41	24.73
	€/kg	1.55	2.20	2.09	2.96

A relevant tool used to forecast the economic behaviour of the project is the cumulative cash flow analysis. This analysis (Figure 3) shows the overall profitability of evaluated concepts as well as the payback time (13 years).

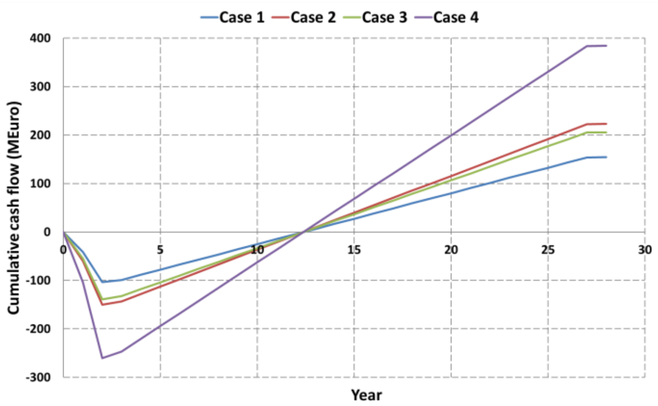

Figure 3: Cumulative cash flow analysis

Sensitivity analysis of various key techno-economic parameters (such as the capital investment and operational & maintenance costs, biogas price, interest rate and plant availability factor as shown in Turton et al., 2018) were assessed for the illustrative concept of biogas reforming with pre- and post-combustion CO_2 capture (Case 4) as presented in Figure 4. The most important influence is noticed for the capital cost, biogas price, interest rate and availability factor. The operational & maintenance costs have the smallest influence.

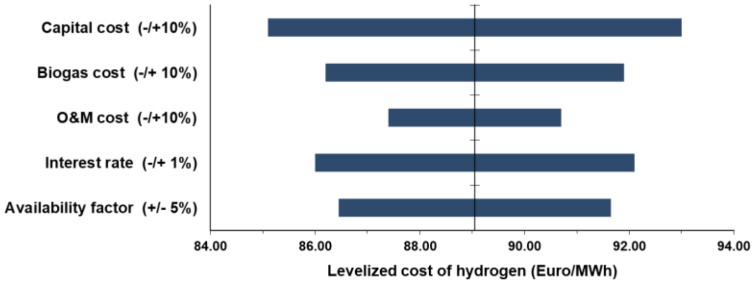

Figure 4: Sensitivity analysis of the levelized cost of hydrogen (Case 4)

5. Conclusions

The present work evaluates the main techno-economic and environmental performance indicators of the green hydrogen production with 100 MW thermal plant capacity based on biogas catalytic steam reforming with CO_2 capture using membrane gas separation technology. Two membrane-based concepts were evaluated: one design with pre-combustion CO_2 capture only which treats the shifted syngas in view of decarbonization (overall carbon capture rate 55 %) and one design with pre- and post-combustion CO_2 capture for almost total decarbonization of the process (carbon capture rate 99 %). The overall energy efficiency of both membrane-based cases is high (55 - 60 %). As the detailed techno-economic evaluation shows, the membrane-based decarbonization technology is very efficient (at least for the pre-combustion CO_2 capture configuration which takes advantage of high CO_2 partial pressure in the syngas to be treated as presented by Cormos et al. (2022). Green hydrogen production based on biogas catalytic reforming have higher costs compared to conventional fossil-based concepts but considering the potential ofdelivering negative CO_2 emissions for the whole biogas chain they are verypromising as future energy applications for achieving the climate neutrality.

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