Techno-economic Analysis of Electrified Biogas Reforming

Diego Maporti [a], Riccardo Nardi [a], Simone Guffanti [b], Chiara Vianello [a,c], Paolo Mocellin [a,*], Gianluca Pauletto [b]

[a] Università degli Studi di Padova, Dipartimento di Ingegneria Industriale. Via Marzolo 9, 35131, Padova, Italia
[b] SYPOX, Department of Chemistry, Technical University of Munich, 88747 Garching, Germany
[c] Università degli Studi di Padova, Dipartimento di Ingegneria Civile Edile e Ambientale. Via Marzolo 9, 35131, Padova, Italia
paolo.mocellin@unipd.it

The world annual hydrogen demand continues to increase with a direct impact on the global CO_2 emissions. A potential solution is the production of CO_2-neutral hydrogen (green hydrogen) using renewable resources. In addition to electrolytic hydrogen, biogenic hydrogen can increase productivity and enable the expansion of the H_2 economy for regions with low availability of solar and wind, such as central Europe. In this work, the design of a decentralized biogas-to-hydrogen process (50 Nm^3 h^{-1} H_2 productivity) based on an electrically heated reformer was developed. An economic analysis has established the viability of this suggested production route: the Hydrogen production price remains below 6 € kg^{-1}. It results that this innovative process requires approximately 0.6 Nm^3 of biogas and 1.25 kWh of renewable electricity to produce 1 Nm^3 of hydrogen.

1. Introduction

The annual world hydrogen demand accounts for approximately 74 Mt (IEA, 2019). Hydrogen is used to produce chemicals such as ammonia and methanol and as a reagent in refineries. It is also used as fuel for energy production via directly hydrogen combustion or within fuel cells that produce electricity.

At present, approximately 90 % of the total H_2 is obtained from steam reforming of natural gas (SMR) (IEA, 2019). Usage of the standard processes to boost hydrogen production will lead to an increase in greenhouse gases (GHG) emissions. Alternative technologies are the partial oxidation (POX), the partial catalytic oxidation (CPOX), and the autothermal reforming (ATR). These processes could be coupled with carbon capture and storage (CCS), leading to blue hydrogen (French, 2020). In 2020, the European Commission published the European Hydrogen Strategy where it is clearly stated the key role that hydrogen will play as a fuel and energy carrier for the energy transition. Additionally, electrolysis, biomass gasification and biogas reforming have been identified as key production technologies (European Commission, 2020).

The present work proposes the design of a decentralized process for producing renewable hydrogen via electrified reforming of biogas. The process scheme was simulated with Aspen Plus®. The ultimate configuration produces approximately 1.6 Nm^3 h^{-1} of hydrogen from 1 Nm^3 h^{-1} of biogas made of 50:50 methane and carbon dioxide. The energy efficiency of the process is approximately 87 %.

2. Methods

As in traditional hydrogen plants, this biogas-to-hydrogen scheme also comprises three main sections: reforming, water gas-shift (WGS), and separation (Figure 1). Aspen Plus® solved the mass and energy balances using Peng-Robinson with the Boston-Mathias alpha function as the thermodynamic model. The steam reformer was modelled as a Gibbs reactor (RGibbs) working at equilibrium. The water gas shift section was modelled with two adiabatic equilibrium reactors (REquil), operating at equilibrium, where only the WGS reaction takes place. This is necessary and is commonly done to avoid the production of methane, which is thermodynamically the most favored product.

2.1 Process description

The reforming section is mainly driven by the following equilibrium reactions:

$$CH_4 + H_2O \rightleftharpoons 3H_2 + CO \tag{1}$$

$$CH_4 + CO_2 \rightleftharpoons 2H_2 + 2CO \tag{2}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{3}$$

SMR (1), dry reforming (DR) (2), and WGS (3). Both reforming reactions are endothermic with ΔH_{298} = 206 kJ mol^{-1} for SMR and 247 kJ mol^{-1} for DR (Xu and Froment, 1989), while the WGS reaction is exothermic with ΔH_{298} = -41 kJ mol^{-1}. Both reforming reactions lead to a higher number of moles. The reformer converts 0.66 kmol h^{-1} and operates at 15 bar and 950 °C with a steam to carbon ratio (S/C) of 2. Commercially Ni-based catalysts can operate under these conditions without coke formation (Lavoie, 2014). These conditions also favor a higher H$_2$/CO ratio which is essential for hydrogen production. The lower pressure compared to the typical value of approximately 30 bar is used to reduce the carbon forming potential, which is high when reforming CH$_4$, H$_2$O, and CO$_2$ mixtures. At the same time, the lower pressure enhances the conversion of methane (Seo et al., 2002), which is typical for the electrically heated SMR process.

The WGS reaction is completed in two steps respectively, working from 330 °C to 470 °C (high-temperature WGS, HT-WGS) and from 195°C to 235 °C (low-temperature WGS, LT-WGS). The inlet temperature of the two WGS steps is in line with the requirements of commercial WGS catalysts (Johnson Matthey PLC) Fe/Cr and Cu based. An excess of water is needed to avoid hydrocarbon formation by Fischer-Tropsch reaction in the HT-WGS stage and preserve the catalyst activity in the LT-WGS. In particular, a reduction ratio below 1.9 is required at the entrance of the HT-WGS step, where the reduction ratio is defined as below :

$$R = \left(\frac{CO + H_2}{CO + H_2O}\right) \cdot \left(\frac{P}{26}\right) \tag{4}$$

where all the species are defined in volume fraction and P is the pressure in bar.

Similarly, the syngas entering the WGS must have a wet-to-dry ratio (W/D) greater than 1.3 (Johnson Matthey PLC), where the W/D ratio is given by the molar flowrate of water divided by the sum of the molar flowrates of all species excluding water. To fulfil these requirements, an injection of water downstream of the reformer has been used. Using water at 25°C as a quenching medium makes it possible to achieve the required reduction ratio and temperature needed at the entrance of the HT-WGS. Additionally, using a quench results simpler and cheaper in terms of operational and capital costs in comparison to a waste heat boiler.

The waste heat boiler for the production of the dilution steam fed to the reformer is located between the two WGS steps. The production of steam (15 atm, 255 °C) in this equipment enables cooling down the syngas to the temperature required at the inlet of the LT-WGS.

After the WGS step, the product mixture is cooled down to condense the remaining excess steam present in the H$_2$-rich syngas. After taking out the condense in a two-phase separator, the product mixture is sent to a PSA (pressure swing adsorption) unit for purification. Given the gas composition and pressure, a recovery efficiency of about 85 % with a H$_2$ purity of 99.9 % seems reasonable for an industrial PSA (Hygear, 2020). A part of the H$_2$ is left in the PSA off-gases (S-22), where unreacted CH$_4$ and CO coexist. As this stream contains an appreciable amount of energy and cannot be vented due to the presence of toxic and polluting gases, it is integrated within the process. For this purpose, it is burned with 10 % air excess and is used to preheat the reactive mixture up to 650 °C, i.e. the typical cross-over temperature for modern reformers (Rostrup-Nielsen and Christiansen, 2011). Biogas feed cannot be mixed directly with the steam arriving from the boiler to avoid partial condensation. The boiling feed water required for the correct operation of the waste heat boiler is produced by preheating pressurized demi water to near-saturation conditions. This required duty comes from the flue gases produced via combustion of the PSA off-gases.

The fermenter requires approximately 1.2 kW of thermal energy supplied as hot water at 40 °C to be able to produce 1 Nm^3 h^{-1} of biogas via anaerobic digestion (Benato and Macor, 2019). For this reason, the herein described hydrogen production plant must supply 37 kW of thermal energy. This is achieved using a water preheater exchanger and part of the duty of the water economizer where water is heated respectively to 45 °C and 170 °C. A mixture of these two streams at 50 °C (S-17 and S-18) is sent to the anaerobic digestor.

Figure 1: Process scheme of the developed biogas to hydrogen route.

2.2 Economic assessment

The described biogas-to-hydrogen process produces renewable hydrogen, which has a current market price that varies from 7 € Kg^{-1} to 9 € Kg^{-1} (IEA, 2019).

Table 1: Price of consumables and reactants used in the case study.

Chemical	Price	Reference
Biogas	0.25 € Nm^{-3}	(Benato and Macor, 2019)
Demineralized H_2O	2.7 € m^{-3}	(ICIS, 2022)
Renewable electricity	150 € MWh^{-1}	(Irena, 2021)

The capital expenditure (CAPEX) is depreciated over an operational plant lifetime of 15 years. The CAPEX for a production plant of 100 Nm^3 h^{-1} H_2 is approximately 1 M€ (Rostrup-Nielsen and Christiansen, 2011). Considering 0.77 as the scale-down factor for H_2 (Towler and Sinnot, 2008), a CAPEX of 580 K€ is reasonable for an installation of about 50 Nm^3 h^{-1}.

The following economic indicators are used for comparison:
- the Operating Expenditure (OPEX) considering 8000 h y^{-1} of operation
- the hydrogen production cost (HPC) (Eq. 5)

$$HPC \ [€ \ kg^{-1}] = OPEX \ [€] + \frac{CAPEX[€]}{years[y]} \cdot \left(H_{2prod}[kg \ h^{-1}] \cdot hours[h]\right)^{-1} \tag{5}$$

- the yearly profit (Eq. 6):

$$Profit \ [€ \ y^{-1}] = \left(H_{2prod}[kg \ h^{-1}] \cdot hours[h] \cdot H_{2price}[€ \ kg^{-1}]\right) - OPEX \ [€] - \frac{CAPEX[€]}{years \ [y]} \tag{6}$$

- the % of OPEX defined as

$$\%opex = OPEX \ [€] \cdot \left(OPEX \ [€] + \frac{CAPEX[€]}{years[y]}\right)^{-1} \tag{7}$$

Since the recovery of the PSA is the most important factor affecting the H2 productivity, the abovementioned parameters are calculated for a recovery ranging between 85 % and 75 % to investigate more pessimistic scenarios. Moreover, a sensitivity analysis on the above-described economic indicators has been performed.

The cost of biogas and electricity have been varied respectively from 0.2 € Nm^{-3} to 0.3 € Nm^{-3} and from 0.05 € kWh^{-1} to 0.20 € kWh^{-1}. The cost of demineralized water is maintained constant.

2.3 Key performance indicators

The primary indices used for assessing the process performance are the following:
- methane conversion in the reformer,
- H_2/CO selectivity in the WGS section,
- H_2 production to biogas ratio,
- specific electricity consumption,
- process efficiency based on LHV of reagent and products, electricity consumptions, with and without considering the thermal integration of the process with the fermenter.

3. Result

3.1 Mass balance and energy requirements

Process mass balances refers to a plant that produce 50 Nm^3 h^{-1} hydrogen (4.5 kg h^{-1}) (Table 2).

Table 2: Mass balance of the developed biogas to hydrogen process.

Stream	S-4	S-5	S-6	S-7	S-9	S-11	S-12	S-24	S-28
Temperature [°C]	650	950	332	470	236	50	50	1010	55
Mole Flow [kmol h^{-1}]	2.72	4.04	5.63	5.63	5.63	4.02	2.23	2.81	68.5
Mass Flow [kg h^{-1}]	65.3	65.3	94.0	94.0	94.0	64.9	4.50	96.2	1233.6
Mole Fraction									
H_2O	0.50	0.25	0.46	0.33	0.29	0.01	0.00	0.17	1.00
CO_2	0.25	0.09	0.07	0.20	0.24	0.33	0.00	0.48	0.00
CH_4	0.25	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H_2	0.00	0.42	0.30	0.43	0.47	0.65	1.00	0.00	0.00
CO	0.00	0.24	0.17	0.04	0.00	0.01	0.00	0.00	0.00
N_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.34	0.00
O_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00

The process uses 30.9 Nm^3 h^{-1} (40.8 kg h^{-1}) of biogas (50% CH_4, 50% CO_2) and 53.3 kg h^{-1} of water for hydrogen production. The economic assessment does not consider the additional water used as a medium to integrate the hydrogen-producing plant and the fermenter.

Energy requirements for the different equipment are reported in Table 3, together with an indication of whether the equipment is thermally integrated or not. Almost all the units are integrated except the reformer and the biogas compressor that use external electricity. This equipment uses respectively 57 kW and 6 kW. The H_2O preheater (approximately 30 kW) and the water economizer (approximately 7 kW) supply the thermal energy necessary in the thermophilic digester that produces biogas. Under average year operations, the thermal consumption of the digester is 0.73 kWh per 1 Nm^3 H_2 produced.

Table 3: Energy requirements for the different equipment of the biogas to hydrogen process.

Unit	Energy requirements, kW
Compressor	5.9 (not integrated)
Biogas preheater	3.0 (integrated)
Reformer	56.6 (not integrated)
Mixture preheater	14.8 (integrated)
Quench	24.8 (integrated)
Waste heat boiler	15.4 (integrated)
H_2O preheater	29.7 (integrated)
H_2O economizer	11.6 (integrated)

3.2 Key performance indicators

According to Table 4, the methane conversion is equal to 97 %; thus, a minimal amount of methane remains unreacted and leaves the PSA in the off-gases stream. The process leads to syngas with an H_2/CO ratio of approximately 1.7. This ratio is unusual for a traditional H_2 production plant based on SMR, but it is related to the high concentration of CO_2 present in the biogas feed. In particular, not only SMR but also DR take within

the e-SMR. For this reason, in the herein described process, it is crucial to push the WGS reaction using both high and low-temperature steps. The reached CO conversion is higher than 98%. Assuming that the PSA has an H_2 recovery efficiency of 85%, the process produces approximately 1.6 Nm^3 of H_2 per 1 Nm^3 of fed biogas. Compared to a biogas reforming configuration, the H_2 productivity is increased by approximately 60 % (1.6 Nm^3 vs 1.0 Nm^3). This is possible because no biogas is fed to the burners and because the water gas shift is pushed. At the same time, approximately 1.25 kWh of electricity is used in the e-SMR to compensate for the reaction endothermicity.

Table 4: Key performance indicators of the developed biogas to hydrogen process.

Parameter	Value
CH_4 conversion [%]	97.3
H_2/CO selectivity [%]	98.0
H_2/biogas ratio [-]	1.65
Specific power in the reagents [kWh Nm^{-3} biogas]	4.91
Specific external energy demand [kWh Nm^{-3} biogas]	2.03
Specific external energy demand [kWh Nm^{-3} H_2]	1.25
Specific energy in the products [kWh Nm^{-3} biogas]	4.86
Specific energy to fermenter [kWh Nm^{-3} biogas]	1.20
Thermal efficiency without fermenter [%]	70.0
Thermal efficiency with fermenter [%]	87.3

The thermal efficiency of the process is approximately 70% without considering the integration of the thermal energy between the hydrogen-producing plant and biogas digester. If this integration is completed, the efficiency increases to 87%, comparable to a large-scale centralized SMR (Rostrup-Nielsen and Christiansen, 2011). Considering that the efficiency of traditionally biogas plants that produce electricity (2 kW_{el} per 1 Nm^3 of biogas) using an internal combustion engine and an alternator is approximately 35%, the described H_2 production route is twice higher (Benato and Macor, 2019). Therefore, considering the renewable energy market related to the biogas section within Italy, it will be possible to increase the energy production from 8.3 TWh to 16.6 TWh.

3.3 Economic analysis

The economic indexes (Table 5) show the economic feasibility of the process based on the selling price of the green hydrogen of about 7 € Kg^{-1}. The operating costs account for approximately 75 % of the hydrogen production costs. It is evident how the recovery of the PSA is a crucial parameter and strongly influences the profit of the process. On the other hand, for all possible values of this parameter, the process stays profitable.

Table 5: Economic parameters for the biogas-to-hydrogen process for the investigated PSA recovery range.

Economic indexes	85 % recovery	80 % recovery	75 % recovery
H_2 productivity [Nm^3 h^{-1}]	50	47.1	44.1
OPEX [€ y^{-1}]	137000	137000	137000
% OPEX	78	78	78
H_2 production cost [€ kg^{-1}]	4.9	5.19	5.54
Profit [€ y^{-1}]	76000	61000	46000

Figure 2 shows the influence of the electricity price on the H_2 production cost (left) and the related annual profit (right) at different biogas prices. Within the considered range for electricity price (50 € MWh^{-1} to 200 € MWh^{-1}), the hydrogen production cost doubles from 4 € kg^{-1} to 6 € kg^{-1}.

The reported biogas to hydrogen process becomes economically unattractive when electricity costs more than 200 € MWh^{-1}. Indeed, even at the lower biogas price, the H_2 production cost is higher than the selling price. At the same time, such a high electricity price is unrealistic for renewable electricity already produced at prices well below 100 € MWh^{-1} (IRENA, 2021).

The H_2 production cost strongly depends on electricity (43 % of the total cost using the price reported in Table 1), while biogas has a much smaller influence. Moreover, it is also clear that for prices above 100 € MWh^{-1}, the electrification of high-temperature thermochemical processes, such as SMR, is not convenient (Mion et al., 2022). Under these renewable energy prices, traditional fired configurations are economically favored (Roelofse et al., 2020).
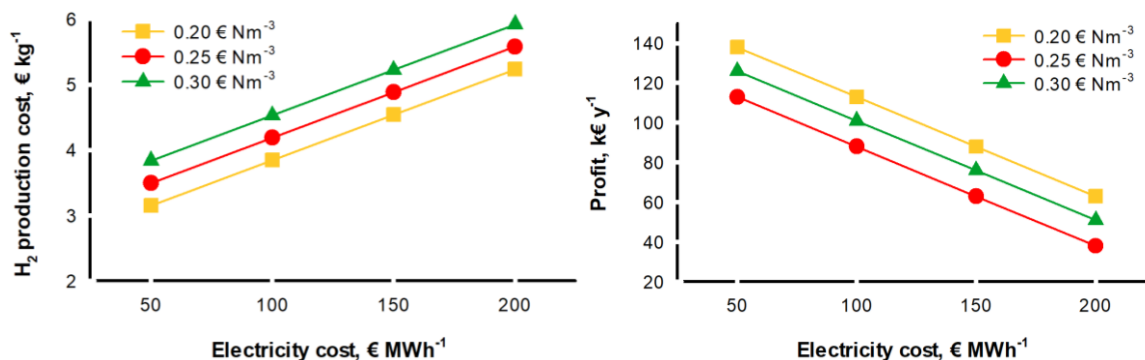
Figure 2: Effect of the electricity price on the H_2 production cost (left) and the annual profit (right) at different biogas prices.

4. Conclusions

The present work proposes the design of a decentralized biogas-to-hydrogen process (50 $Nm^3\,h^{-1}$) based on an electrically heated reformer. The reforming section runs at 15 bar, 950 °C and a steam-to-carbon ratio of 2, and it is followed by a two-steps water gas shift at an inlet temperature of 330 °C and 194 °C respectively. Under these conditions, the process achieves a methane and carbon monoxide conversion of 97% and 98%, respectively, ensuring an H_2/CO ratio for the syngas of approximately 1.7.

This innovative route requires approximately 0.6 Nm^3 of biogas and 1.25 kWh of renewable electricity to produce 1 Nm^3 of hydrogen. Its thermal efficiency is about 70%, which is higher than that of a conventional plant burning biogas in a thermal engine. The thermal efficiency is increased to 87% if the hydrogen-producing plant and biogas digester are fully integrated, making it comparable to a large-scale centralized SMR.

According to the economic analysis, the suggested decentralized biogas-to-hydrogen route is viable and provides hydrogen at a price below 6 € kg^{-1}.

References

Benato, A., Macor, A., 2019, Italian Biogas Plants: Trend, Subsidies, Cost, Biogas Composition and Engine Emissions. Energies 2019, 12 (979).

European Commission, 2020. A hydrogen strategy for a climate-neutral Europe.

French, S., 2020. The Role of Zero and Low Carbon Hydrogen in Enabling the Energy Transition and the Path to Net Zero Greenhouse Gas Emissions, Johnson Matthey Technol. Rev., 64(3), 357-370.

Hygear, 2020 (https://hygear.com/technologies/hy-pure/, accessed 01.07.2022)

IEA, 2019. The Future of Hydrogen, Paris.

IRENA, Power Generation Costs, 2021 (www.irena.org/costs/Power-Generation-Costs, accessed 15.03.2022).

ICIS, 2022. Independent commodity Intelligence services (https://www.icis.com/explore/, accessed 01.07.2022)

Johnson Matthey PLC, (www.alfa.com/media/HiFUEL_Base_Metal_Water_Gas_Shift_Catalysts.pdf, accessed 15.03.2022).

Lavoie, J.M., 2014. Review on dry reforming of methane, a potentially more environmentally friendly approach to the increasing natural gas exploitation. Frontiers in Chemistry, Front Chem. 2014 Nov 11;2:81.

Mion, A., Galli F., Mocellin P., Guffanti S., Pauletto, G., 2022, Electrified methane reforming decarbonises methanol synthesis, Journal of CO2 Utilization, 58, 101911.

Roelofse, O., Somers, K., Speelman, E., Witteveen, M., 2020. Plugging in: What electrification can do for industry. McKinsey & Company.

Rostrup-Nielsen, J., Christiansen, J.L., 2011. Concept in syngas manufacture, Imperial College Press, London, UK.

Seo, Y.S., Shirley, A., Kolaczkewski, S.T., 2002. Evaluation of thermodynamically favourable operating condition for production of hydrogen in three different reforming technologies, Journal of Power Sources, 108, 213-225.

Towler G.,Sinnot R.,2008, Chemical Engineering Design Principles Practice and Economics of Plant and Process Design, Butterworth-Heinemann (Elsevier),San Diego,USA.

Xu, J., Froment, G.F., 1989. Methane steam reforming, Methanation and Water-Gas Shift: 1. Intrisic Kinetics, AIChe Journal, 35(1).