

BIOMETHANE-DERIVED HYDROGEN FOR PROTON EXCHANGE MEMBRANE FUEL CELLS (PEMFCs): A TECHNICAL AND ENVIRONMENTAL ANALYSIS THROUGH THE ASPEN PLUS® SOFTWARE

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DIPARTIMENTO DI
INGEGNERIA INDUSTRIALE
E SCIENZE MATEMATICHE

Energy Systems

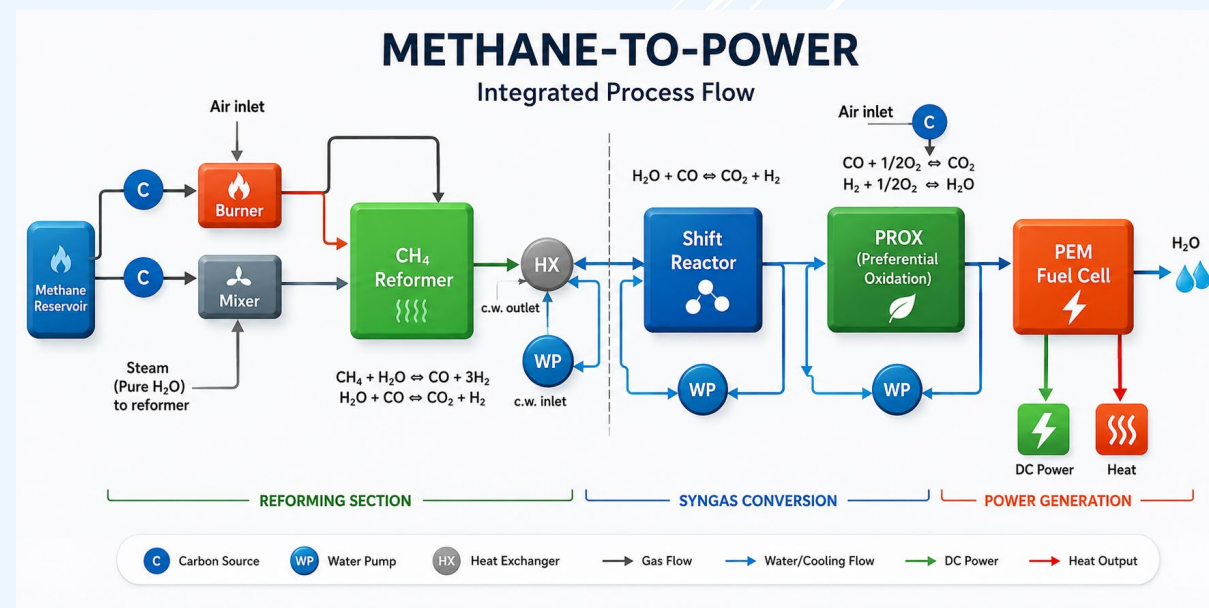
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Introduction: Integrated Biomethane-PEMFC Systems

- **Biomethane Reforming:** Produces low-carbon, dispatchable hydrogen, significantly reducing lifecycle CO_2 emissions compared to traditional fossil-based Steam Methane Reforming (SMR) [1].
- **Proton Exchange Membrane Fuel Cells (PEMFCs):** Convert hydrogen into electricity and heat with high efficiency. Their fast dynamic response and modularity make them ideal for distributed generation.
- **Thermal Integration:** The PEMFC waste heat (ca. 80°C) can be recovered to satisfy the thermal demand of the upstream anaerobic digesters (ca. 50°C), maximising overall plant efficiency.



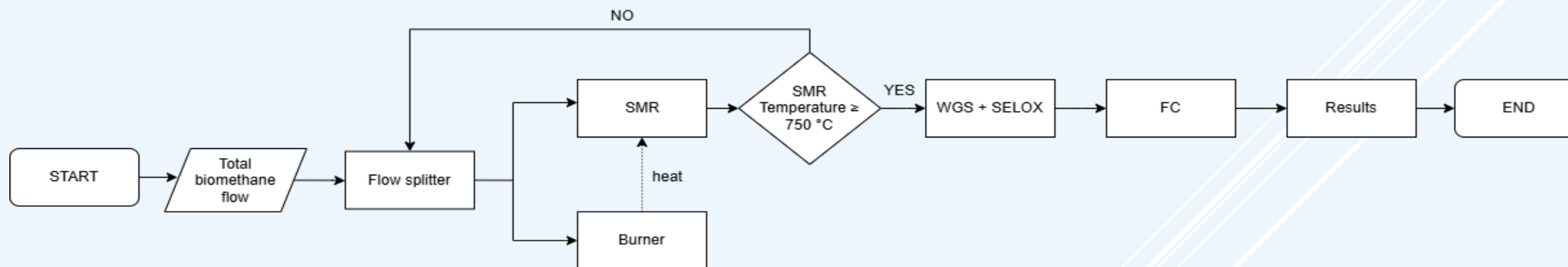
Goal of the Work

The Scientific Literature Gap: Current research typically models hydrogen production (reforming) and electrochemical conversion (PEMFCs) as separate, isolated stages.

Proposed Approach

- **End-to-End Simulation:** Develop a single Aspen Plus® model integrating the entire pathway-from biomethane reforming to power and heat generation.
- **Direct Coupling:** Seamlessly link thermochemical hydrogen production with a scientific literature-validated PEMFC model.
- **System-Level Assessment:** Evaluate overall energy performance using a thermodynamic approach, creating a practical tool for preliminary design and techno-economic analysis.

Methodology - Flowchart



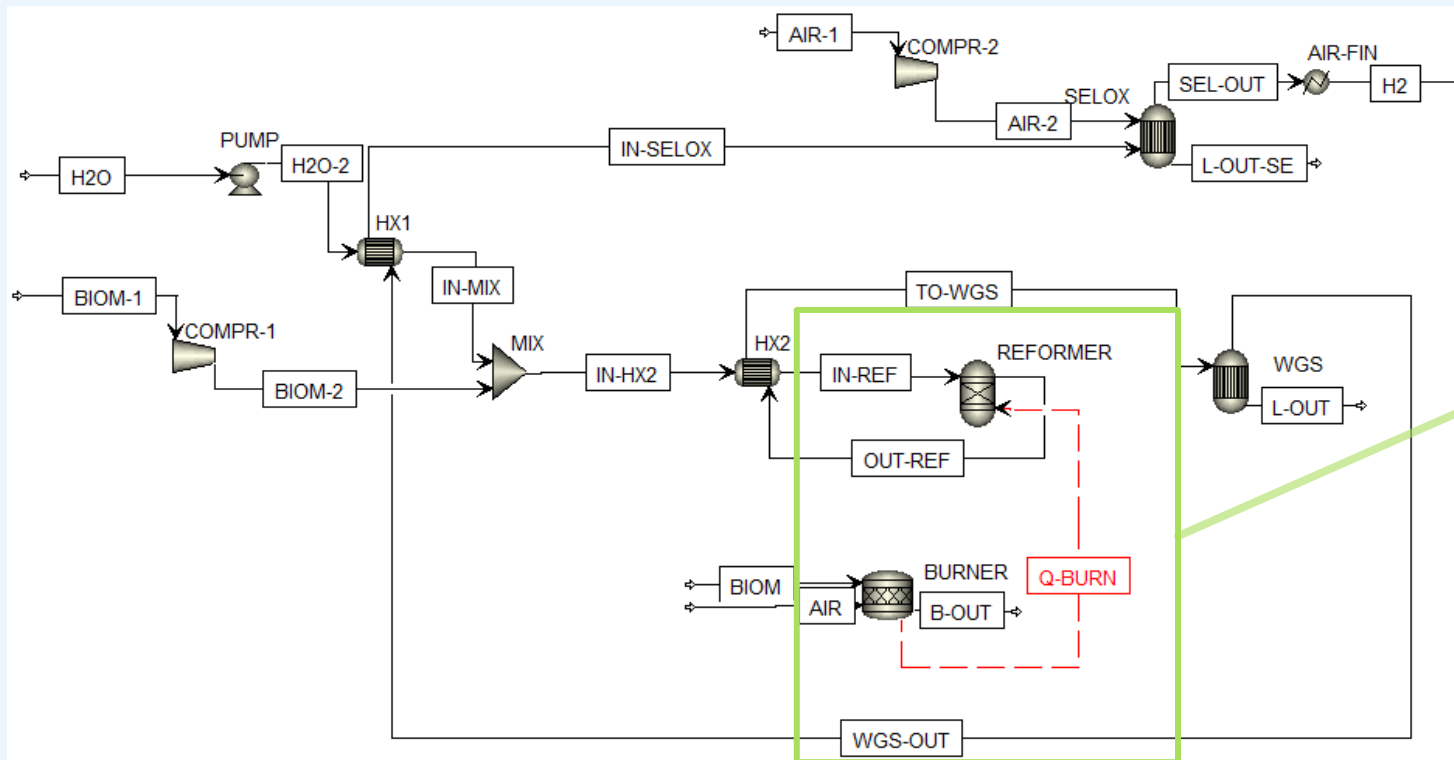
Plant Layout & Flow Splitting

- **Total Input:** A constant biomethane stream of 150 Nm³/h is partitioned into a process feed (BIOM-1) and an auxiliary burner fuel (BIOM).
- **Thermal-Driven Logic:** The split ratio is driven by the reformer's heat demand, ensuring it operates above the 750°C threshold.

Mass Balance Results

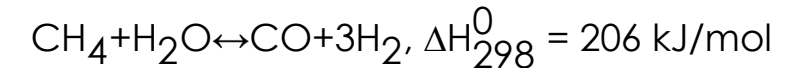
- **Burner Demand (BIOM):** To satisfy the thermal requirement, the actual burner fuel needed is 65 Nm³/h (factoring in a 90% burner efficiency).
- **Process Feed (BIOM-1):** The remaining 85 Nm³/h is routed directly to the SMR for hydrogen production.

Methodology - Hydrogen Production Section



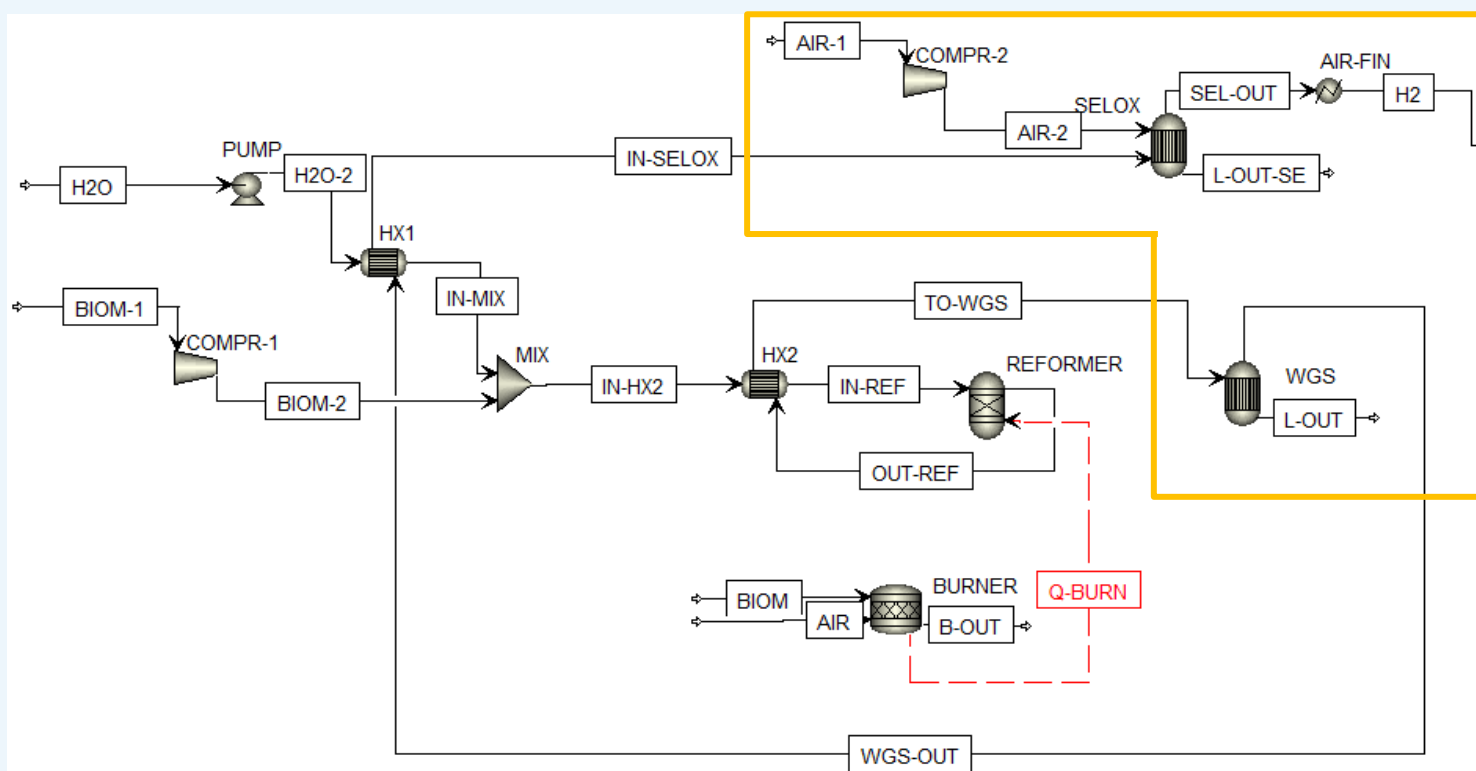
Steam Methane Reforming (SMR)

- **Primary Conversion:** The biomethane feed reacts with steam to produce a hydrogen-rich syngas.



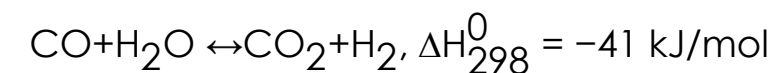
- **Operating Conditions:** The endothermic reaction is thermally sustained by the burner, strictly maintaining temperatures above 750°C to ensure high conversion efficiency.

Methodology - Hydrogen Production Section

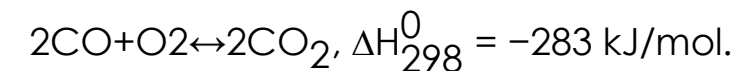


Syngas Purification

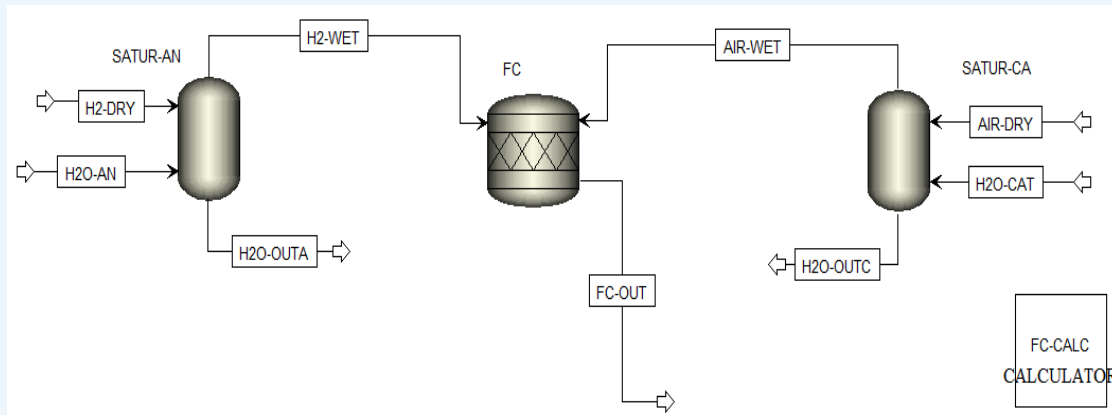
- **Water Gas Shift (WGS):** Reacts carbon monoxide with steam, drastically reducing CO while maximising total H₂ yield.



- **Selective Oxidation (SELOX):** Selectively oxidises the residual CO, ensuring an ultra-pure H₂ stream to protect the PEMFC catalyst.



Methodology - PEMFC Flowsheet



Operating Conditions:

- The cell is modeled at **3 bar** and **80°C** to replicate the experimental literature setup.

Flowsheet Implementation:

- **Humidification Control:** Two gas saturators (SATUR-AN, SATUR-CA) ensure precise Relative Humidity regulation.
- **Core Reactor:** The stoichiometric reactor (FC) simulates the global electrochemical conversion with a fuel utilisation factor **U_f = 0.85** [2].
- **The Interface (FC-CALC):** A dedicated Calculator Block extracts thermodynamic data (partial pressures, temperatures, flows) and links them directly to the custom electrochemical sub-model.

Methodology - PEMFC Electrochemical Sub-Model

Global Cell Voltage: The actual cell voltage is computed by subtracting the main overpotentials from the theoretical Nernst potential:

$$V_{\text{cell}} = E_{\text{Nernst}} - V_{\text{act,c}} - V_{\text{act,a}} - V_{\text{Ohm}} - V_{\text{conc}}$$

Reversible Nernst Potential E_{Nernst} : Accounts for the operating temperature and reactant partial pressures:

$$E_{\text{Nernst}} = E_0(T) + \frac{R \cdot T}{n \cdot F} \ln\left(\frac{P_{\text{H}_2} \cdot P_{\text{O}_2}^{0.5}}{P_{\text{H}_2\text{O}}}\right)$$

V_{cell} [V]	Actual cell voltage
E_{Nernst} [V]	Reversible Nernst potential
$E_0(T)$ [V]	Standard reversible potential at temperature T
$V_{\text{act,a}}, V_{\text{act,c}}$ [V]	Anodic/Catodic activation overpotential
V_{Ohm} [V]	Ohmic overpotential
V_{conc} [V]	Mass transport overpotential
T [K]	Operating temperature
R [J/(mol·K)]	Universal gas constant
F [C/mol]	Faraday constant
$P_{\text{H}_2}, P_{\text{O}_2}, P_{\text{H}_2\text{O}}$ [atm]	Partial pressure of reactants and product
n [-]	Number of electrons exchanged
i [A/cm ²]	Operating current density
α_a, α_c [-]	Anodic / Cathodic charge transfer coefficient
$i_{0,a}, i_{0,c}$ [A/cm ²]	Anodic / Cathodic exchange current density
i_L [A/cm ²]	Limiting current density
R_{cell} [Ω·cm ²]	Cell resistance

Methodology - PEMFC Electrochemical Sub-Model

Activation Overpotentials: Represent the chemical energy barrier that must be overcome to start the electrochemical reactions at the electrodes' surface:

$$V_{\text{act},c} = \frac{R \cdot T}{a_C \cdot n \cdot F} \cdot \ln\left(\frac{i}{i_{0,c}}\right)$$

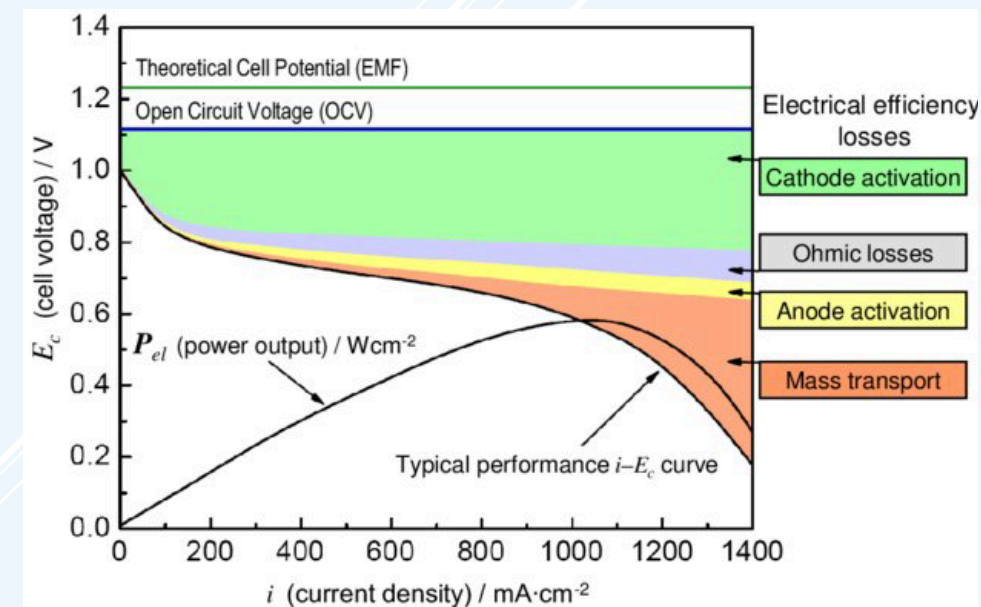
$$V_{\text{act},a} = \frac{R \cdot T}{a_A \cdot n \cdot F} \cdot \ln\left(\frac{i}{i_{0,a}}\right)$$

Ohmic Overpotential: Accounts for resistive losses from proton transport through the membrane and electron conduction across the cell's conductive components:

$$V_{\text{Ohm}} = R_{\text{cell}} \cdot i$$

Mass Transport Overpotential: Occurs when reactants are consumed at the electrode faster than they can be supplied from the gas phase:

$$V_{\text{conc}} = -\frac{R \cdot T}{n \cdot F} \cdot \ln\left(1 - \frac{i}{i_L}\right)$$



Methodology - PEMFC Electrochemical Sub-Model

Cell Specifications:

Physical and geometric properties were defined using values directly from the reference experimental setup [3].

Parameter	Symbol	Value	U.M.
Active area	A_{act}	51.84	cm ²
Membrane thickness	δ	127	μm
Anodic/cathodic Pt loading	L_{Pt}	0.4	mg _{Pt} /cm ²

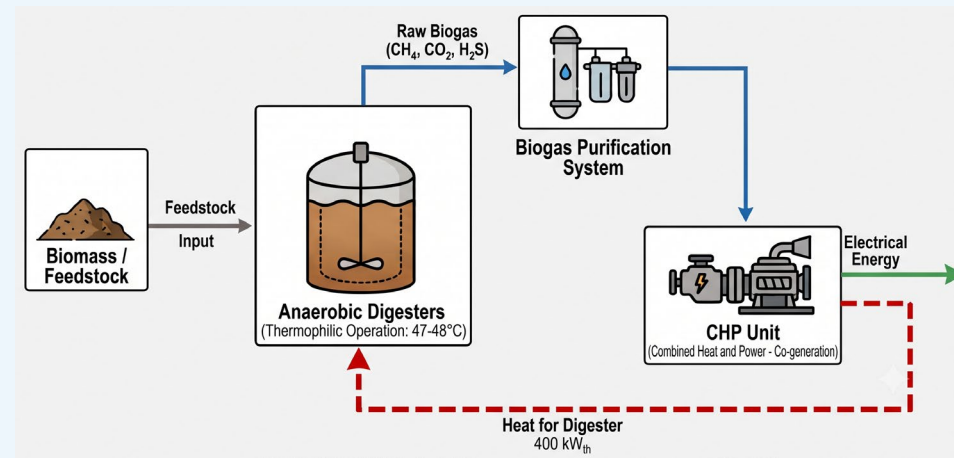
Calibrated Parameters (Python Curve-Fitting)

Since complex kinetic and ionic parameters are highly specific, they were estimated by minimising the deviation between the theoretical voltage equations and the experimental polarisation curve.

Parameter	Symbol	Value	U.M.
Cathodic charge transfer coefficient	a_c	0.5	-
Reference cathodic exchange current density	$i_{0ref,c}$	$9.8 \cdot 10^{-9}$	A/cm ²
Membrane ionic conductivity	σ	0.072	S/m

Case Study

Reference Facility



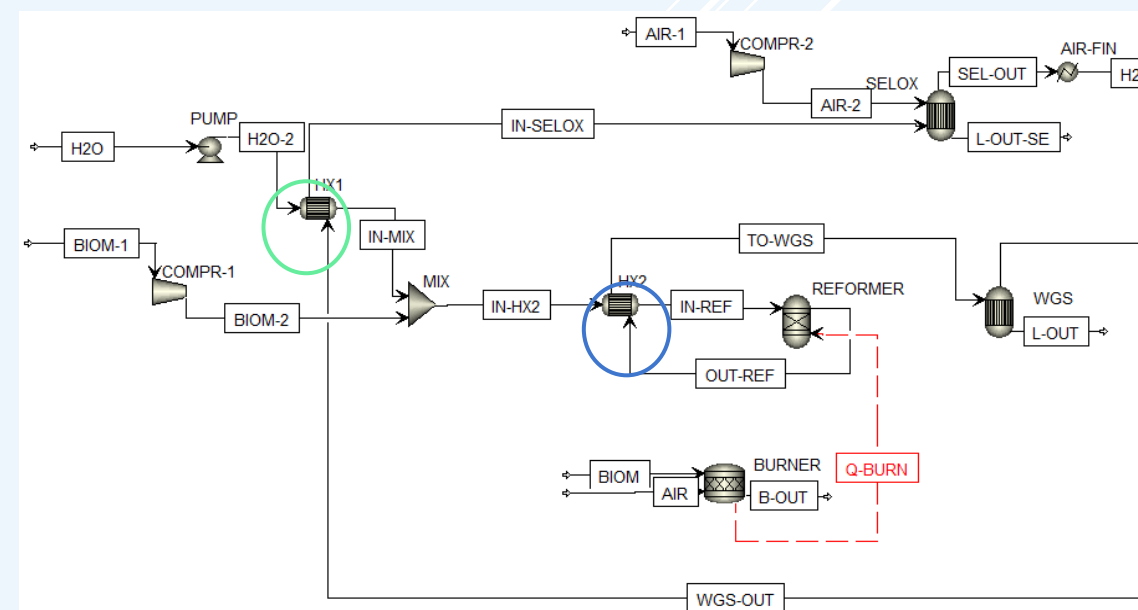
Core Operating Regimes:

- **System Pressure:** Pressurised to **3 bar** across the plant and fuel cell to align with PEMFC experimental validation.
- **Stack Temperature:** Fixed at **80°C**, reflecting typical low-temperature PEMFC operation.
- **Steam-to-Carbon (S/C) Ratio:** Fixed at **3 S/C** within the reforming section to optimise H₂ yield and strictly prevent carbon deposition [4].

Case Study

Thermal Cascade Strategy

- **Core Heating:** Burner exhaust (800°C) drives the SMR endothermic reaction.
- **High-T Recovery (HX2):** Raw syngas cooling (774°C → 149°C) directly pre-heats the mixed feed entering the reformer.
- **Low-T Recovery (HX1):** Shifted syngas cooling (263°C → 135°C) vaporises and pre-heats the incoming water feed.
- **Final Conditioning:** All purified target streams are stabilised at 80°C for stack injection.

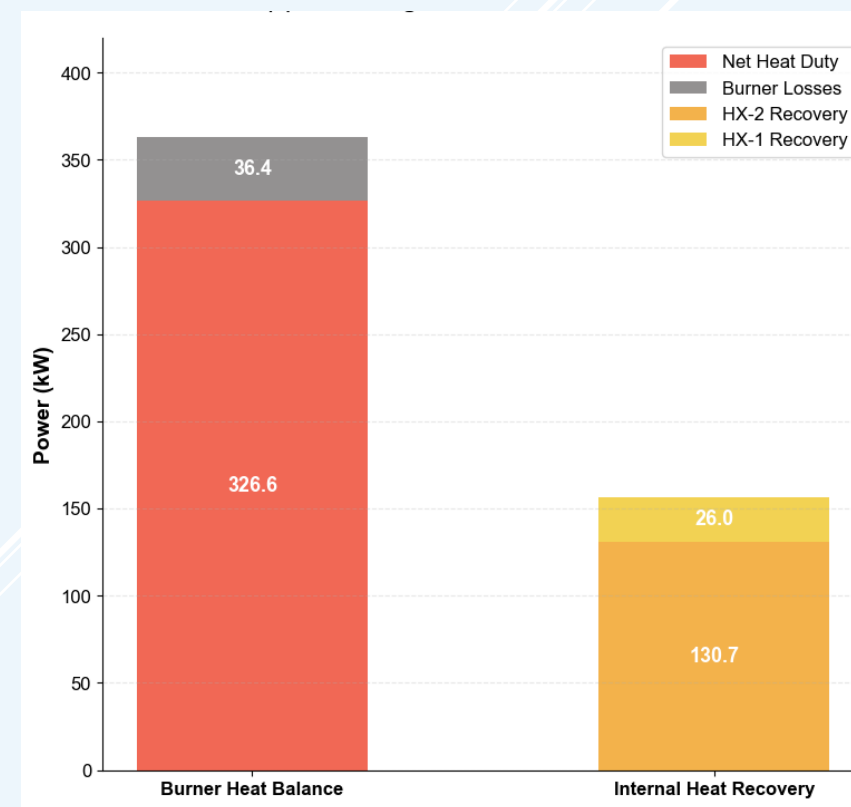


Results and Comments - Reforming Section

- **External Heat Supply:** The endothermic SMR reaction is sustained by an external burner processing the auxiliary biomethane fuel.
- **Net SMR Heat Duty:** 326.6 kW.
- **Total Combustion Heat:** 363.0 kW, assuming a **90%** burner **efficiency**.

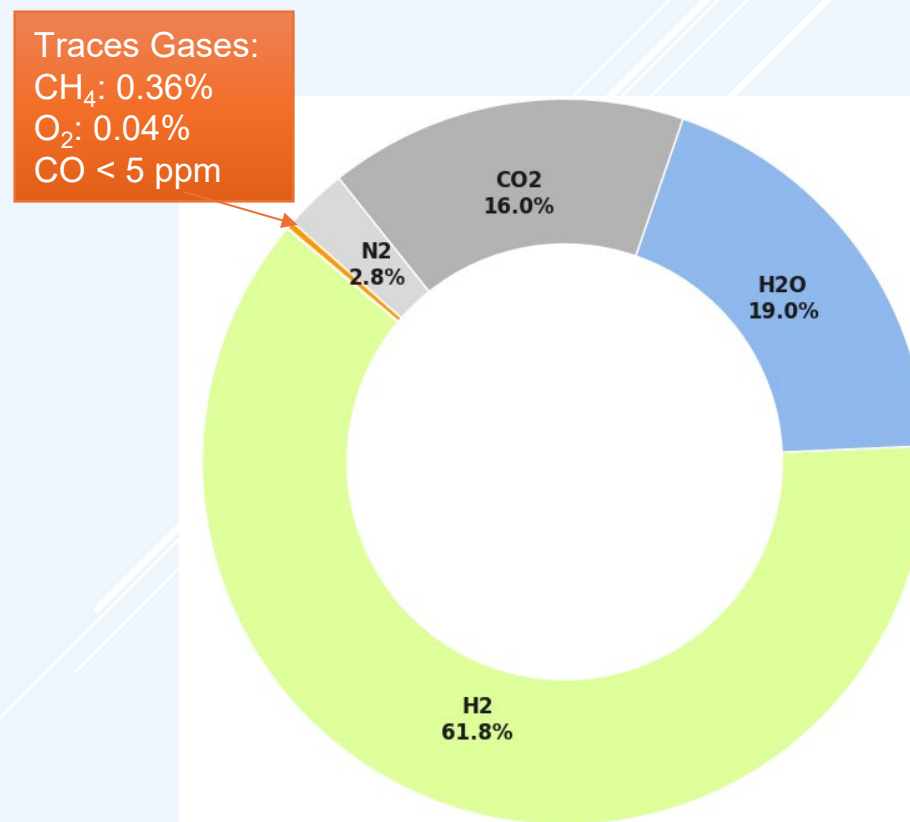
Two-Stage Heat Recovery Cascade

- **HX-1 (Water Preheating):** Recovers **26.0 kW** by cooling the hot syngas from the SELOX unit, raising the water feed temperature from 25°C to 125.1°C.
- **HX-2 (Process Mixture Preheating):** Recovers **130.7 kW** by cooling the high-temperature raw syngas exiting the reformer (from 773.8°C to 148.6°C), heating the feed mixture from 88.7°C to 138.6°C before it enters the SMR.



Results and Comments - Anode Feed Composition

- **Stream Characteristics (25°C, 3 bar).**
- **Flow Rates: 211 m³/h (291 kg/h).**
- **H₂ & Self-Humidification:** High hydrogen yield (**61.8%**) with a 19.0% steam fraction to ensure optimal PEMFC membrane hydration without external management.
- **Conversion Efficiency:** Minimal residual CH₄ confirms a reforming conversion rate of roughly **97%**.
- **SELOX Purification:** CO is strictly reduced **below 5 ppm** to prevent anode poisoning. N₂ (2.8%) and O₂ traces act as inert byproducts from the required SELOX air injection.



Results & Comments - PEMFC Electrical & Thermal Performance

Electrical Balance

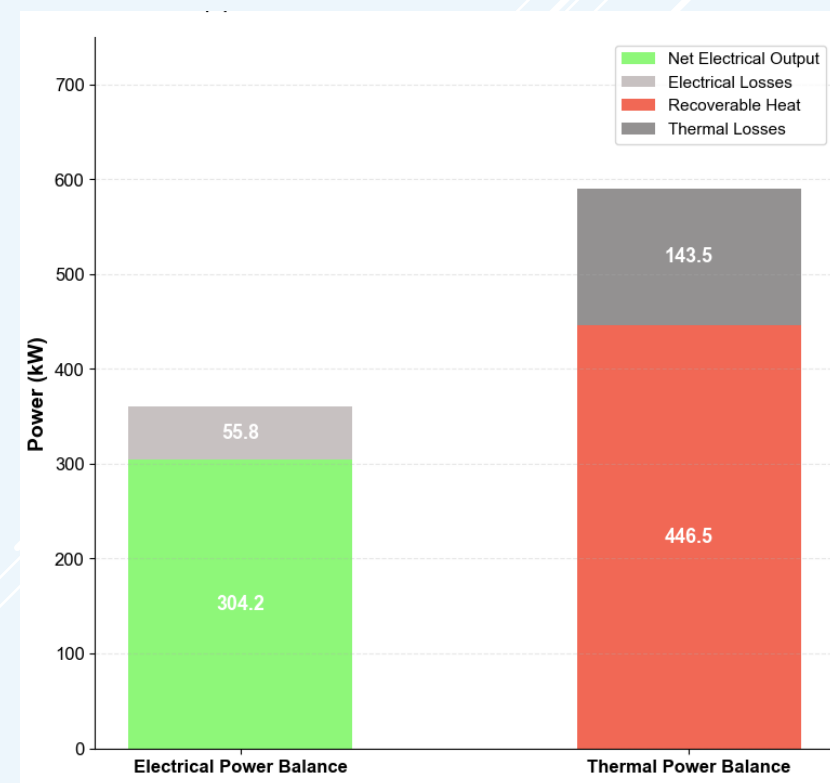
- **Gross Stack Output: 360 kW.**
- **Parasitic Loads (Compression):** 55.8 kW total (COMPR-1: 4.5 kW | COMPR-2: 1.0 kW | COMPR-3: 50.3 kW).
- **Net Electrical Power: 304.2 kW.**

Thermal Balance and Integration

Total Heat Generation: 590 kW.

Net Recoverable Heat: 446.5 kW (applying an 85% overall CHP efficiency).

Digester Integration: Fully satisfies the nominal thermal demand of the anaerobic digesters (400 kW), providing a critical safety margin to compensate for increased environmental heat losses during winter.



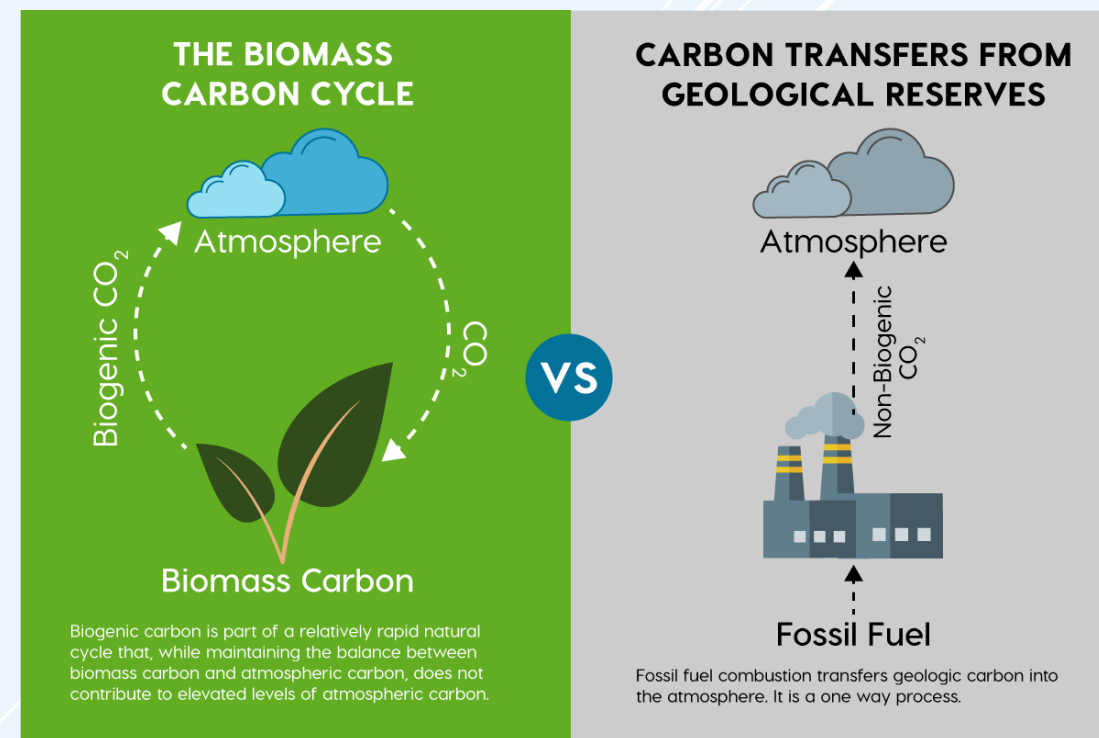
Results & Comments - Environmental Analysis

Carbon Mass Balance and IPCC Guidelines

- **Complete Oxidation:** Both the burner combustion and the SMR chemical conversion lead to the complete oxidation of the inlet carbon (1 mole of $\text{CH}_4 \rightarrow 1$ mole of CO_2).
- **Emission Factor:** Consequently, both processes adopt the same IPCC default emission factor for natural gas: **56.1 kg CO_2 /GJ** [5].

Energy Conversion and Avoided Emissions

- **Energy Input:** The total biomethane input of 150 Nm^3/h corresponds to a primary energy substitution of **5.295 GJ/h**.
- **Biogenic Carbon:** Since the feedstock is 100% biomethane, the CO_2 released is biogenic.
- **Total GHG Mitigation:** **297.1 kg CO_2 /h** avoided, which translates to **ca. 2,376 tons of CO_2 per year**.



Conclusions

Integrated Plant Simulation with High-Efficiency Cogeneration

- **Net Electrical Power:** 304.2 kW delivered for plant or grid use.
- **Thermal Self-Sufficiency:** 446.5 kW of recoverable heat fully satisfies the digesters' demand, providing a critical buffer for winter thermal peaks.

Environmental Mitigation

- **Net-Zero Footprint:** Complete substitution of 150 Nm³/h of fossil natural gas with biogenic carbon.
- **Decarbonisation:** Ca. 2,376 tons of CO₂ emissions avoided annually (8,000 operating hours).

Future Developments

- **Biomethane Plant Integration:** Full integration of the biomethane plant section into the current model.
- **CO₂ Capture System:** Development of an advanced CO₂ capture system integrated into the model for reforming off-gases.

Acknowledgements

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- [3] Wang L., Husar A., Zhou T., Liu H., A parametric study of PEM fuel cell performances. *Int J Hydro Energy* 2003;28:1263-72.
- [4] Zolghadri S., Kiani M.R., Kamandi R., Rahimpour M.R., Enhanced hydrogen production in steam methane reforming: comparative analysis of industrial catalysts and process optimization. *J Energy Inst* 2024;113:101541.
- [5] IPCC, 2006 IPCC Guidelines for National Greenhouse Gas Inventories. Prepared by the National Greenhouse Gas Inventories Programme, Eggleston H.S., Buendia L., Miwa K., Ngara T., Tanabe K. (eds). Hayama, Japan: IGES; 2006.

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