

# Techno-Economic Evaluation of Palladium-Membrane Reactors for Industrial-Scale Methane Pyrolysis

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## Abstract

This study assesses the techno-economic viability of a palladium-based membrane reactor for catalytic decomposition (pyrolysis) of methane. A process simulation approach is employed to evaluate the reactor's performance and to design a complete catalytic decomposition plant. The membrane-based process is benchmarked against conventional steam methane reforming (SMR) in terms of the levelized cost of hydrogen (LCOH) production. Results indicate that the membrane reactor process achieves an approximately 5% lower LCOH than SMR, primarily due to reduced capital costs and the elimination of carbon capture and storage (CCS) requirements. Additionally, the recovery and sale of valuable carbon byproducts—such as carbon black—further improve the economic feasibility of the process. From an environmental perspective, the membrane process presents a cleaner alternative by avoiding CO<sub>2</sub> emissions and generating solid carbon instead. Overall, the palladium-based membrane reactor demonstrates strong potential as a transitional pathway toward more sustainable hydrogen production.

**Keywords:** Catalytic decomposition, Methane pyrolysis, Turquoise hydrogen, TEA, Greenhouse gas emission, Levelized cost.

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## 1. Introduction

The term "hydrogen economy" refers to the widespread adoption of clean hydrogen as a substitute for fossil fuels in energy-intensive sectors such as power generation, manufacturing, and transportation. Since hydrogen emits no carbon at the point of use, transitioning from fossil fuels to clean hydrogen can significantly reduce greenhouse gas emissions—the primary driver of global warming. A recent report by the International Renewable Energy Agency (IRENA) had highlighted that to limit global temperature rise to 1.5°C above pre-industrial levels by 2050, clean hydrogen production must increase fivefold from current levels to reach 614 million tonnes per year, representing approximately 12% of total global energy demand.<sup>1</sup>

Currently, about 92% of global hydrogen production comes from gray hydrogen derived from steam methane reforming (SMR) or coal gasification.<sup>2</sup> SMR process involves reacting high-pressure steam with methane (natural gas) at 3–25 bar and 700–1000°C in the presence of a catalyst to produce hydrogen.<sup>3</sup> Although SMR is a well-developed and widely used technology, its major drawback is the high CO<sub>2</sub> emissions it generates. On average, SMR produces approximately 12 kg of CO<sub>2</sub> per kg of hydrogen, while coal gasification emits much more at 20 kg of CO<sub>2</sub> per kg of hydrogen.<sup>4</sup>

In contrast, green hydrogen is produced through water electrolysis powered by electricity from renewable energy sources. Because the process generates little to no carbon emissions, it can be considered carbon-neutral. However, high production costs, limited infrastructure for renewable energy supply, and technological immaturity still pose significant barriers to its widespread adoption today.

A more viable near-term clean alternative is blue hydrogen, which can be readily produced by integrating steam methane reforming (SMR) or coal gasification with carbon capture and storage (CCS) or carbon capture and utilization (CCU). While green hydrogen is expected to dominate the market by 2050—accounting for up to 65% of global supply—blue hydrogen is projected to make up the remaining 35%.<sup>5</sup> However, a major challenge of the blue hydrogen production through SMR is the low concentration of CO<sub>2</sub> in the output stream, making its capture costly. To address this, ongoing research is focused on developing low-carbon hydrogen technologies that improve process efficiency while significantly reducing CO<sub>2</sub> emissions at the source.

Methane pyrolysis has recently garnered significant interest as a promising method for clean hydrogen production. In this process, methane and other hydrocarbons are thermally decomposed into hydrogen and solid carbon, following the general equation:  $C_xH_y \rightarrow x C + 0.5y H_2$  (1)

A key advantage of methane pyrolysis over SMR is its substantially lower energy requirement.<sup>6</sup> Additionally, methane pyrolysis yields solid carbon instead of CO<sub>2</sub>, effectively eliminating CO<sub>2</sub> emissions at the source. Hydrogen produced through this pyrolysis technique is known as turquoise hydrogen, which, according to a recent report by Hydrogen Europe<sup>7</sup>, has the potential to achieve the lowest clean hydrogen production cost in Europe. This is primarily because it eliminates the need for costly carbon capture while simultaneously generating valuable carbon byproducts such as carbon black, graphite, carbon nanotubes, and carbon nanofibers. The sale of these byproducts provides additional revenue, further improving the economic viability of the process. However, a major drawback of methane pyrolysis is the requirement for extremely high temperatures exceeding 1000 °C, necessitating the use of electricity or molten metal to provide the required heat.<sup>8</sup> To overcome this limitation, metal-loaded catalysts can be used to lower the decomposition temperature, such as 500–700 °C for nickel-based catalysts, 700–900 °C for iron-based catalysts, and 850–950 °C for carbon-based catalysts.<sup>9</sup>

Further advancements in the catalytic decomposition of methane (CDM) process are possible through process intensification strategy, specifically by coupling methane decomposition with hydrogen separation within a catalytic membrane reactor unit. In this approach, hydrogen generated during the catalytic reaction is continuously extracted from the gas mixture via a membrane, thereby driving higher methane conversion and improving overall efficiency. Among the various membrane materials explored, palladium (Pd)-based membranes have shown significant promise due to their high hydrogen selectivity and permeability. However, pure Pd membranes are prone to embrittlement at temperatures below 300 °C and pressures under 20 bars in hydrogen-rich environments.<sup>10</sup> Additionally, they are highly susceptible to deactivation at temperatures above 450 °C in the presence of carbonaceous impurities.<sup>10</sup> Furthermore, the high manufacturing costs of pure Pd membranes limit their commercial viability. To address these limitations of Pd membranes, they are often alloyed with other metals to enhance chemical and mechanical stability, improve resistance to contaminants, and lower production costs. For example, Pd-Cu and Pd-Au membranes demonstrate resistance to H<sub>2</sub>S and maintain stable hydrogen permeability within the 200–300 °C range.<sup>11,12</sup> Likewise, Pd-Ag membranes help mitigate embrittlement issues at temperatures below 300 °C.<sup>13</sup>

In the literature, most studies on Pd-based membrane reactors for the catalytic decomposition of methane into hydrogen have primarily focused on evaluating reactor performance under laboratory-scale conditions. For instance, Basile *et al.*<sup>14</sup> investigated the partial oxidation of

methane using Pd membrane reactors with nickel-based catalysts, achieving methane conversion rates between 45% and 56% at reaction temperatures ranging from 400 °C to 450 °C. Raybold and Huff<sup>15</sup> evaluated the performance of Pd membranes for dry reforming of methane, highlighting their effectiveness in inhibiting the reverse water-gas shift reaction through hydrogen removal. Basile *et al.*<sup>10</sup> applied a Pd–Ag membrane reactor packed with nickel-based catalysts for SMR, achieving a methane conversion of 65% and an 80% recovery of CO<sub>x</sub>-free hydrogen at 450 °C with a differential pressure of 4 bar between the retentate and permeate sides.

The use of Pd membrane reactors for CDM via pyrolysis has also been reported. Early investigations by Ishihara *et al.*<sup>16,17</sup> involved laboratory-scale experiments assessing the performance of a Ni/SiO<sub>2</sub> catalyst within a Pd–Ag membrane reactor, achieving over 99.99% hydrogen purity and enhanced methane conversion at 500 °C. Building upon this, Matsuka *et al.*<sup>18</sup> compared Pd–V alloy membranes to Pd–Ag membranes using the same Ni/SiO<sub>2</sub> catalyst. They found that a Pd-coated, 100 µm-thick vanadium-based membrane delivered methane conversion and hydrogen production rates comparable to those of a Pd–Ag membrane with a 50 µm-thick Ag layer. Subsequent efforts have then focused on developing thinner yet stable and durable membranes to maximize hydrogen permeation surface area. For instance, Maneerung *et al.*<sup>19</sup> developed an ultrathin (~1.2 µm) triple-layer hollow fiber membrane comprising an inner Pd–Ag layer, a middle support of YSZ-doped  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> ceramic, and an outer catalyst layer of Ni supported on perovskite. This configuration enhanced thermal stability and hydrogen selectivity, marking a significant advancement in membrane reactor design.

Despite numerous experimental studies on catalytic membrane reactors for methane pyrolysis using Pd-based membranes, a significant gap remains: the absence of comprehensive techno-economic evaluations for this process at an industrial scale. To address this challenge, our study adopts an integrated approach to assess both the technical and economic aspects of employing Pd-based membrane reactors for CDM. To the best of our knowledge, such a holistic assessment at a large-scale production level has not been explored in existing literature. This constitutes the primary contribution of our work to the current state-of-the-art. The remainder of this paper is organized as follows: Section 2 outlines the modeling approach for the CDM process plant using a Pd membrane reactor, including the mathematical modeling of the reactor and its simulated performance evaluation. Section 3 presents a technical analysis of the overall process plant, including material and energy balances, overall conversion rates, and energy consumption. In Section 4, we present an economic analysis of the plant and evaluate its performance across various

production scenarios, comparing it with a conventional steam methane reforming process. Finally, Section 5 summarizes our findings and presents the conclusions.

## 2. Mathematical modeling of Pd-based catalytic membrane reactor for hydrogen production

The schematic of the Pd-based catalytic membrane reactor modeled in this study employs a shell-and-tube configuration (see Figure 1). A nickel-based catalyst is placed in the shell side, where methane decomposes to produce hydrogen and carbon. The Pd membrane selectively allows hydrogen to permeate from the shell into the tube side, driven by the pressure gradient. We developed a mathematical model that integrates reaction kinetics, hydrogen flux through the membrane, and mass balances for methane, hydrogen, and carbon along the reactor's length.

In general, the decomposition of methane to hydrogen and carbon is governed by surface reactions occurring on active catalytic sites. The reaction kinetics of this process can be modelled using the following Langmuir-Hinshelwood expression<sup>20</sup>:

$$-r_{CH_4} = \frac{k \left( p_{CH_4} - \frac{p_{H_2}^2}{K_p} \right)}{\left( 1 + K_{H_2} p_{H_2}^{1.5} + K_{CH_4} p_{CH_4} \right)^2} \quad (2)$$

where:

- $r_{CH_4}$  is the decomposition rate of methane, representing natural gas,
- $k$  is the reaction rate constant, following the Arrhenius equation,
- $p_{CH_4}$  and  $p_{H_2}$  are the partial pressures of methane and hydrogen, respectively,
- $K_p$  is the equilibrium constant for the overall reaction,
- $K_{CH_4}$  and  $K_{H_2}$  are the adsorption equilibrium constants for methane and hydrogen.

Table 1 lists the kinetic parameters used in this model, adopted from Amin *et al.*<sup>21</sup>.

Hydrogen separation in a Pd-based membrane reactor follows Sieverts' law, which states that the hydrogen permeation flux is proportional to the difference between the square roots of the partial pressures on the feed and permeate sides. The general expression is:

$$J_H = \frac{D}{L} (p_H^n - p_L^n) \quad (3)$$

where:

- $J_H$  is the hydrogen flux,

- $D$  is the diffusion coefficient of hydrogen in palladium,
- $L$  is the membrane thickness,
- $p_H$  and  $p_L$  are the hydrogen partial pressures on the high-pressure (feed) and low-pressure (permeate) sides, respectively (obtained from the kinetic model),
- $n$  is the pressure exponent, typically taken as 0.5 for ideal conditions.<sup>22</sup>

The diffusion coefficient is temperature-dependent and can be expressed as:

$$D = D_0 e^{\left(\frac{-Ep}{RT}\right)} \quad (4)$$

where:

- $D_0$  is the permeation constant for hydrogen in palladium,
- $Ep$  is the permeation energy for hydrogen permeation,
- $R$  is the ideal gas constant,
- $T$  is the permeation temperature.

To account for the mass and energy balances of the membrane reactor, Equations (5) to (8) are applied. The total mass flow rate of any stream entering or leaving the membrane reactor is calculated by multiplying its total molar flow rate by the sum of the products of each component's mole fraction and molecular weight. The mass balance on the shell side of the membrane reactor is given by:

$$\dot{m}_{in,S} = \dot{m}_{out,S} + J_H + RateShell \quad (5)$$

where:

- $\dot{m}_{in,S}$  is the inlet mass flow rate on the shell side (e.g., sweep gas),
- $\dot{m}_{out,S}$  is the outlet mass flow rate on the shell side, reduced by hydrogen permeation to the tube side,
- $J_H$  is the hydrogen mass flux leaving the shell,
- $RateShell$  is the net mass change due to reactions occurring on the shell side (based on methane decomposition kinetics).

Similarly, the mass balance on the tube side is:

$$\dot{m}_{in,T} + J_H = \dot{m}_{out,T} \quad (6)$$

where:

- $\dot{m}_{in,T}$  is the inlet mass flow rate on the tube side,

- $\dot{m}_{out,T}$  is the outlet mass flow rate on the tube side, increased by the permeated hydrogen,
- $J_H$  is the hydrogen mass flux entering the tube side.

The steady-state energy balance for the membrane reactor accounts for heat transfer between the tube and shell sides, as well as the enthalpy carried by permeating hydrogen. The reactor is assumed to operate under steady-state conditions, with no mass and energy accumulation. The shell-side energy balance can be expressed as:

$$\dot{n}_{S,in}H_{S,in} + \dot{Q}_{Duty} + \dot{Q}_{iso} = \dot{n}_{S,out}H_{S,out} + \dot{Q}_{flux} \quad (7)$$

where:

- $\dot{n}_{S,in}$  and  $\dot{n}_{S,out}$  are the inlet and outlet molar flow rate on the shell side,
- $H_{S,in}$  and  $H_{S,out}$  are the inlet and outlet molar enthalpy on the shell side,
- $\dot{Q}_{flux}$  is the enthalpy flux due to permeating species,
- $\dot{Q}_{Duty}$  is the heat transfer rate between shell and tube sides,
- $\dot{Q}_{iso}$  is the auxiliary heating term to maintain isothermal operation.

The isothermal term  $\dot{Q}_{iso}$  represents the external heat required to maintain constant shell-side temperature, i.e.,  $T_{S,out} = T_{S,in}$ .

In the same way, the energy balance on the tube side is described as:

$$\dot{n}_{T,in}H_{T,in} + \dot{Q}_{flux} = \dot{n}_{T,out}H_{T,out} + \dot{Q}_{Duty} \quad (8)$$

where:

- $\dot{n}_{T,in}$  and  $\dot{n}_{T,out}$  are the inlet and outlet molar flow rate on the tube side,
- $H_{T,in}$  and  $H_{T,out}$  are the inlet and outlet molar enthalpy on the tube side.

We implemented the above equations for the Pd-based membrane reactor in AVEVA Process Simulation software to evaluate its performance. Within the shell, the reaction kinetics (as described in Equation 2) are applied, while a heater unit simulates heat input from furnace fuel

combustion to maintain isothermal conditions in the reactor. Table 2 summarizes the reactor parameters used in the model.

Figure 2 highlights key simulation results, illustrating product composition profiles along the reactor length at operating temperatures ranging from 500 °C to 650 °C. As shown in the figure, methane conversion and hydrogen separation efficiency increase with temperature, reaching a maximum at 650 °C. Accordingly, hydrogen flux to the tube side also improves as the temperature rises. Based on these results, 650 °C was selected as the optimal operating temperature, as it offers the highest conversion and separation efficiency without compromising membrane performance. The figure also shows a progressive decrease in methane concentration along the reactor due to the decomposition reaction. Additionally, hydrogen concentration in the shell side is significantly lower than in the tube side, reflecting the continuous permeation of hydrogen through the membrane.

### 3. Process Plant Design and Configuration

We propose a process flowsheet for the methane decomposition plant comprising four key stages (see Figure 3): methane preheating, furnace heating, methane decomposition, and carbon byproduct separation. The plant is designed to produce approximately 1.5 tonnes of hydrogen per hour (36 tonnes per day). At this capacity, an estimated 10 membrane reactors are required, with a methane feed rate of 6,272 kg/h for centralized hydrogen production.

Our feasibility assessment of the methane decomposition plant involves several key steps. First, a conceptual design of the plant is developed using AVEVA Process Simulation, with the Pd-membrane reactor adapted from the software's built-in model. The process is simulated using a thermodynamic package based on the Peng–Robinson equation of state, which is well-suited for the high-temperature and high-pressure conditions of the membrane reactor decomposition process. In this case, default thermodynamic parameters from the AVEVA databanks are utilized. Next, we perform an economic assessment to estimate both the capital and operating costs of the proposed plant. Based on these costs, we calculate the levelized cost of hydrogen (LCOH) production. The economic performance of the decomposition plant is then compared with that of conventional steam methane reforming, which has also been modeled using AVEVA software.

As shown in Figure 3, the process begins with preheating the natural gas (methane) feed stream through a combination of furnace heating and heat recovery from process streams. This heat integration is essential to achieve the high temperatures required for efficient conversion in

the membrane reactor, as methane decomposition is an endothermic reaction. In the proposed setup, the Pd-based membrane reactors are housed within a furnace (B1), which burns methane fuel (Stream 15) to raise the temperature of the incoming methane feed (Stream 1) to the target of 650 °C. Additionally, the furnace flue gas is utilized to preheat both the methane feed and the combustion air, further improving thermal efficiency.

Hydrogen generated on the shell side of the membrane reactor permeates through the membrane into the tube side (Stream 5). This product stream is first heat-exchanged with the methane fuel stream (Stream 16) and then cooled using cooling water in cooler E5. It is subsequently compressed to a higher pressure in compressor K2 and further cooled in cooler E6. The purpose of these compression and cooling steps is to condition the hydrogen product to match the pressure and temperature of a conventional SMR process.

The remaining unreacted methane and carbon byproducts (Stream 7) are next sent to a cyclone separator (CS1) to mechanically separate solid carbon from the gas mixture. To prevent the accumulation of CO<sub>2</sub>—present in the natural gas feed—a CO<sub>2</sub> removal membrane unit (CO<sub>2</sub> MEM) is installed downstream of the cyclone. The resulting product stream (Stream 11) from the CO<sub>2</sub> MEM is then split into two parts: one stream (Stream 13) is recycled and mixed with the methane feed for reuse in the decomposition process, while the other (Stream 12) is combined with the methane fuel stream (CH<sub>4</sub> Burner) for furnace combustion.

The overall methane conversion achieved by the membrane reactors is 77.3%. The plant's energy requirements are met through a combination of natural gas combustion in the furnace and electricity from the grid. As shown in the figure, the furnace provides the necessary heat for both the membrane reactors and the heat exchanger units (E1, E2, and E4). Additionally, compressors K1 and K2 are powered by electricity from the grid. The material balance of the process streams and the plant's utility requirements are summarized in the supplementary information.

#### **4. Economic Analysis**

A detailed assessment was conducted to evaluate the economic performance of the proposed methane decomposition, or membrane cracking (MC), plant in comparison with a conventional steam methane reforming (SMR) plant—both designed for a hydrogen production capacity of 36 tonnes per day. For this comparison, the SMR simulation model available in AVEVA was adapted to fit our specific context.

In the SMR process, methane (natural gas) reacts with high-pressure steam over a Ni/MgAl<sub>2</sub>O<sub>4</sub> catalyst to produce syngas, a mixture of H<sub>2</sub>, CO, and CO<sub>2</sub>. The syngas is then processed through a series of water-gas shift reactors—first at high temperature, then at low temperature—to convert most of the CO into additional H<sub>2</sub> and CO<sub>2</sub> as the byproduct. The resulting gas stream is next sent to an amine capture unit for CO<sub>2</sub> removal. Finally, hydrogen is separated from the remaining gas mixture using pressure swing adsorption. We modeled the SMR plant using AVEVA software, and for simplicity, the adsorption unit was represented as a component splitter in the simulation. The reader is referred to the Supporting Information for the flowsheet of the SMR plant modeled in AVEVA.

Our analysis shows that the fixed capital investment (FCI) for the proposed MC plant is significantly lower—USD 18.7 million—compared to USD 36.3 million for the conventional SMR plant. A detailed breakdown of the cost calculation is provided in the supplementary information. The substantially lower capital cost of the MC plant is mainly due to its simpler process configuration, requiring fewer reaction steps than SMR. Furthermore, unlike SMR, the MC plant does not require a CO<sub>2</sub> capture system, which further reduces costs. Including working capital (WC), the total capital expenditure (CAPEX) for the MC plant is USD 23.3 million, compared to USD 45.4 million for the SMR plant. It is important to note that, for this analysis, the hydrogen delivery pressure of the MC plant was set to match that of the SMR plant, which typically operates at around 20 bar. If such a high delivery pressure were not required, the MC plant's capital cost could be significantly reduced by lowering compressor requirements.

Figure 4 compares the operating expenses (OPEX) of the MC plant and the SMR plant, highlighting their distinct cost profiles. The utility cost for the SMR plant is significantly higher at USD 18.7 million, compared to USD 11.9 million for the MC plant. This is due to the energy-intensive nature of the reforming process and the substantial steam requirements. However, the MC process incurs higher raw material costs—USD 26.1 million for methane feed and fuel—versus USD 16.3 million for the SMR process. This reflects the greater methane consumption per unit of hydrogen produced in the membrane cracking process.

The two processes have comparable manpower costs, both at approximately USD 1.9 million. However, the maintenance cost for the SMR plant is nearly twice as high, at USD 3.6 million, compared to USD 1.9 million for the MC plant, due to the latter's simpler equipment requirements. As shown in the figure, the SMR process also incurs a transport and storage cost of USD 1.4 million for the captured CO<sub>2</sub>, representing the expense of transporting it from the amine unit to

storage sites. In this calculation, we assumed CO<sub>2</sub> shipping and storage costs of USD 24 and USD 16 per tonne, respectively<sup>23</sup>. Overall, the total OPEX of the MC plant (USD 41.8 million) is nearly the same as that of the SMR plant (USD 41.9 million).

In terms of energy performance, the MC plant is more efficient, consuming 44 MJ/kg H<sub>2</sub> compared to 56 MJ/kg H<sub>2</sub> for SMR, a 21% reduction. This improved energy efficiency is due to the MC process's simpler reaction pathway, which directly cracks methane into hydrogen and solid carbon, avoiding the need for energy-intensive steam generation and CO<sub>2</sub> capture.

Overall, the levelized cost of hydrogen (LCOH) for the MC plant is USD 3.38 per tonne of H<sub>2</sub>, approximately 5% lower than the SMR plant's LCOH of USD 3.57 per tonne. This underscores the economic advantage of the MC process over SMR. In addition, the membrane-based MC process offers lower operational complexity, as it adopts a modular configuration that can be easily scaled up or down based on production requirements. From an environmental perspective, the MC process provides a key benefit by producing solid carbon instead of direct CO<sub>2</sub> emissions, making it a cleaner alternative to conventional SMR.

As economic viability of the MC process plant is greatly reliant on operating variables, it is important to perform a sensitivity analysis study to investigate the impact of these variables so that strategies towards reducing the risk to economic feasibility of the process can be identified. For this case, we perform sensitivity analysis to examine the impact of variation in cost components on the LCOH value.

Figure 5 illustrates the sensitivity of the LCOH to variations in natural gas price, catalyst price, membrane price, and the selling price of carbon black. Among these factors, LCOH shows the strongest positive correlation with the price of natural gas (methane). Our analysis identifies natural gas cost as the primary driver of hydrogen production costs—any increase in methane price could lead to a sharp rise in LCOH. This finding underscores the critical importance of securing a stable and competitively priced natural gas supply for the plant. Price volatility in the natural gas market poses a significant economic risk and could undermine the financial viability of the membrane-based hydrogen production process.

Catalyst cost has a comparatively smaller impact on the LCOH. Although catalysts contribute to the overall operating expenses, their influence is secondary to that of natural gas. This suggests that while reducing catalyst consumption or developing cheaper, longer-lasting catalysts is beneficial, the potential cost savings are limited compared to those achievable through lower natural gas prices.

The sensitivity analysis also indicates that membrane cost has a relatively minor impact on the LCOH. Even with an increase in membrane cost, the LCOH rises only slightly. This suggests that investing in the development of new Pd-based membranes—despite potentially higher material costs—can be justified if they offer improved hydrogen separation efficiency, as the performance gains may offset the additional expense.

In this study, we consider carbon black as the by-product of the MC process, which can be sold to enhance the economic feasibility of the plant. The sensitivity analysis highlights a strong correlation between the selling price of carbon black and reductions in LCOH. We also calculate the required carbon black prices at various recovery rates to achieve breakeven hydrogen production. The result is shown in Figure 6. Assuming 100% recovery of carbon black, the breakeven point is reached at a selling price of USD 1096.1 per tonne. Given that the current market price of carbon black ranges from USD 1200 to 1900 per tonne<sup>24</sup>, the MC plant is expected to generate a substantial profit. As the recovery rate decreases, the selling price of carbon black must increase to offset the shortfall. The figure indicates that, to reach breakeven at typical market prices of USD 1,200 to 1,900 per tonne, a recovery rate of approximately 60% to 70% is required.

We also conducted a sensitivity analysis comparing the economics of SMR and MC plants across various production scenarios (Table 3). For the SMR plant without CCS and with no carbon tax, its LCOH is USD 2.37 per kg H<sub>2</sub>. When a carbon tax of USD 100 per tonne of CO<sub>2</sub> is applied, the LCOH of the SMR plant without CCS increases to USD 2.82 per kg H<sub>2</sub>. However, this remains 21% lower than the LCOH of the SMR plant equipped with a CCS unit.

In our analysis, the MC base case plant refers to a membrane plant with a 12-month membrane lifetime and no recovery or sale of carbon black. Although such a membrane lifetime may be optimistic, we also evaluated scenarios with shorter lifetimes (6, 3, and 1.5 months) alongside different carbon black recovery rates. The results show that with each halving of membrane lifetime, the LCOH increases only marginally, by about USD 0.08 per kg H<sub>2</sub>. Furthermore, we evaluated scenarios with a 6-month membrane lifetime combined with 25% and 50% carbon black recovery, assuming a conservative market value of USD 1,200 per tonne. At 25% recovery, the LCOH decreases to USD 2.54 per kg H<sub>2</sub>, representing a 25% reduction from the base case. With 50% recovery, the LCOH drops further to USD 1.61 per kg H<sub>2</sub>, which is lower than that of the SMR plant without CCS.

Overall, this analysis highlights that the economic viability of the MC plant depends not only on the efficiency of hydrogen production but also on the quantity of recoverable carbon byproduct

that can be sold. Therefore, future research should focus on enhancing both membrane performance and the efficiency of the recovery of high-value carbon products to help overcome the economic challenges of the methane decomposition process.

## **5. Conclusions**

This study presents a techno-economic analysis of a Pd-based membrane reactor for commercial-scale methane pyrolysis, designed to produce 36 tonnes of hydrogen per day. Compared with SMR, the proposed membrane reactor process proves more cost-effective, achieving a 5% lower levelized cost of hydrogen.

The economic viability of hydrogen production using Pd-membrane can be further improved by accounting for revenue from carbon black sales. The analysis shows that with 100% recovery, the hydrogen production cost reaches break-even at a carbon black price well below the current market range. However, with only 10% recovery, the required break-even price far significantly exceeds current market levels.

Despite the promising results of the proposed membrane process, this study has several limitations that point to opportunities for future research. The analysis assumes membrane and catalyst replacement cycles of 12 months and 30 days, respectively. While this assumption is reasonable for preliminary evaluation, experimental validation is necessary to assess the long-term stability and degradation behavior of both components under carbon deposition.

Moreover, our simulation excludes the operating costs associated with downtime from membrane and catalyst replacement, as well as the membrane's operational cycle time, assuming these factors to be negligible. Future cost analyses should revisit this simplification to improve accuracy.

Finally, although the membrane process appears to outperform SMR both economically and environmentally, it is important to acknowledge that SMR is a mature and commercially established technology. In contrast, the Pd-membrane process has only been demonstrated at the experimental scale. To address this gap, a pilot-scale demonstration is crucial for identifying practical limitations not captured by simulation and for validating the scalability of the technology to commercial levels.

## **Supporting Information:**

Process stream and utility data for a heat-integrated methane decomposition plant; CAPEX, OPEX, and LCOH for methane decomposition plant; Screenshot of the steam methane reforming plant model developed using AVEVA software; CAPEX, OPEX, and LCOH for stream methane reforming plant with and without carbon capture and storage requirements.

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#### **Notes:**

The authors declare no competing financial interest.

#### **Acknowledgements:**

The authors would like to thank Low-Carbon Energy Research (LCER), Singapore for financial support.

## Declaration of generative AI and AI-assisted technologies in writing

During the preparation of this work, the authors used ChatGPT versions 4 and 5 to improve grammar and sentence structure for better readability. All content generated using this tool was subsequently reviewed and edited by the authors, who take full responsibility for the final manuscript.

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Table 1. Reaction kinetic parameters.

| Constant   | Parameter of Arrhenius Equation                                | Value    |
|------------|----------------------------------------------------------------|----------|
| $k$        | $A$ (mmol <sub>CH<sub>4</sub></sub> /g <sub>ni</sub> /min/atm) | 4.64E+07 |
|            | $E$ (kJ/mol)                                                   | 88       |
| $K_{H_2}$  | $A_{H_2}$ (atm <sup>-1.5</sup> )                               | 2.00E-08 |
|            | $\Delta H_{H_2}$ (kJ/mol)                                      | 144      |
| $K_{CH_4}$ | $A_{CH_4}$ (atm <sup>-1</sup> )                                | 3.75E-05 |
|            | $\Delta H_{CH_4}$ (kJ/mol)                                     | 56       |
| $K_p$      | -                                                              | 0.42     |

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Table 2. Membrane reactor parameters.

| Parameter                                                       | Value   | Units |
|-----------------------------------------------------------------|---------|-------|
| Length of reactor                                               | 0.6     | m     |
| Tube diameter                                                   | 50.4    | cm    |
| Shell diameter                                                  | 269.7   | cm    |
| Membrane thickness                                              | 0.002   | mm    |
| Size Factor: Fraction of the membrane reactor occupied by tubes | 0.7     | -     |
| Shell in mass flowrate                                          | 1375.1  | kg/h  |
| Tube in mass flowrate                                           | 196     | kg/h  |
| Shell inlet temperature                                         | Varying | °C    |
| Tube inlet temperature                                          | 24.9    | °C    |
| Shell inlet pressure                                            | 20      | bar   |
| Tube inlet pressure                                             | 1       | bar   |
| Shell side catalyst void fraction                               | 0.87    | -     |

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Table 3. LCOH values for various hydrogen production scenarios.

| Plant | Scenario                                                                                  | LCOH<br>(\$USD/kg) |
|-------|-------------------------------------------------------------------------------------------|--------------------|
| SMR   | Without CCS and no carbon tax                                                             | 2.37               |
|       | Without CCS and a carbon tax of USD 100 per tonne                                         | 2.82               |
|       | With CCS unit                                                                             | 3.57               |
| MC    | Base case with membrane lifetime of 12 months and without carbon black recovery           | 3.38               |
|       | Membrane lifetime of 6 months and without carbon black recovery                           | 3.46               |
|       | Membrane lifetime of 3 months and without carbon black recovery                           | 3.54               |
|       | Membrane lifetime of 1.5 months and without carbon black recovery                         | 3.62               |
|       | Membrane lifetime of 6 months and 25% carbon black recovery, valued at USD 1200 per tonne | 2.54               |
|       | Membrane lifetime of 6 months and 50% carbon black recovery, valued at USD 1200 per tonne | 1.61               |

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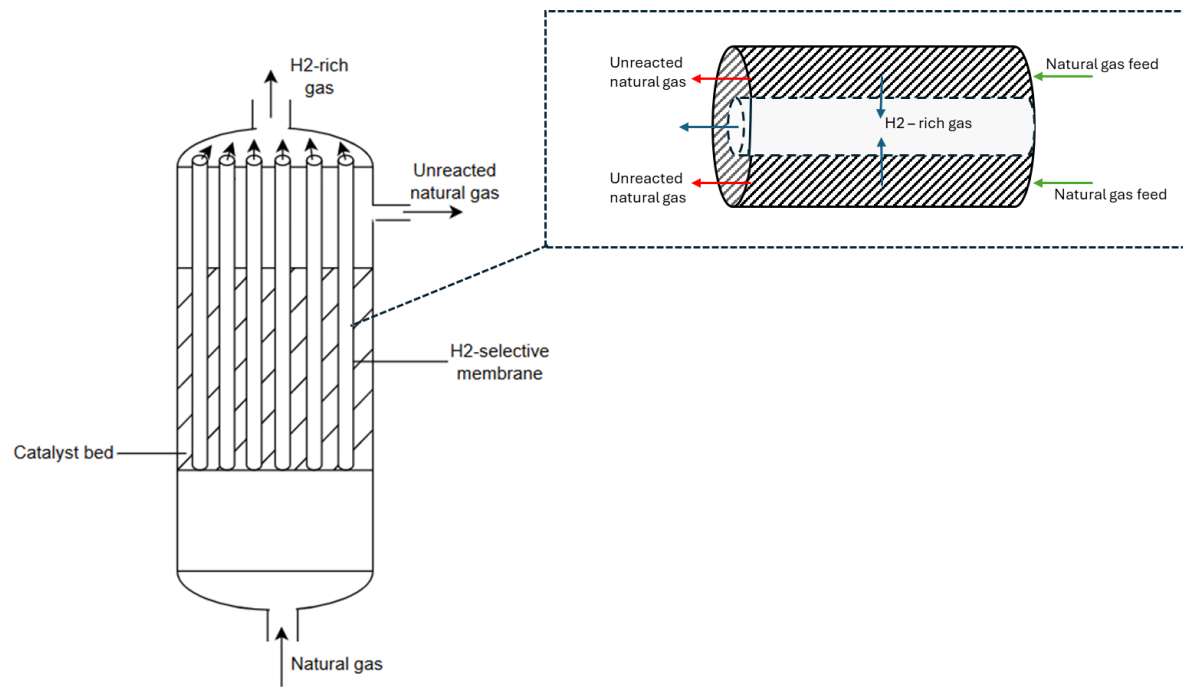


Figure 1. Membrane reactor schematic.

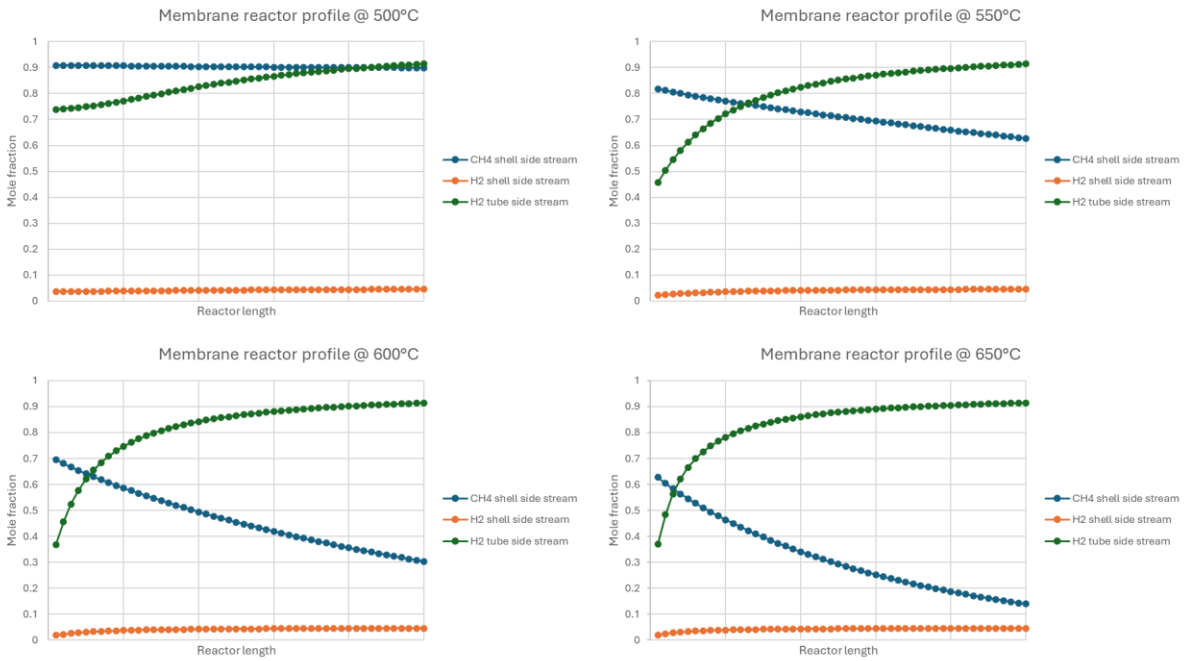


Figure 2. Concentration profile along the membrane reactor length at varying temperatures.

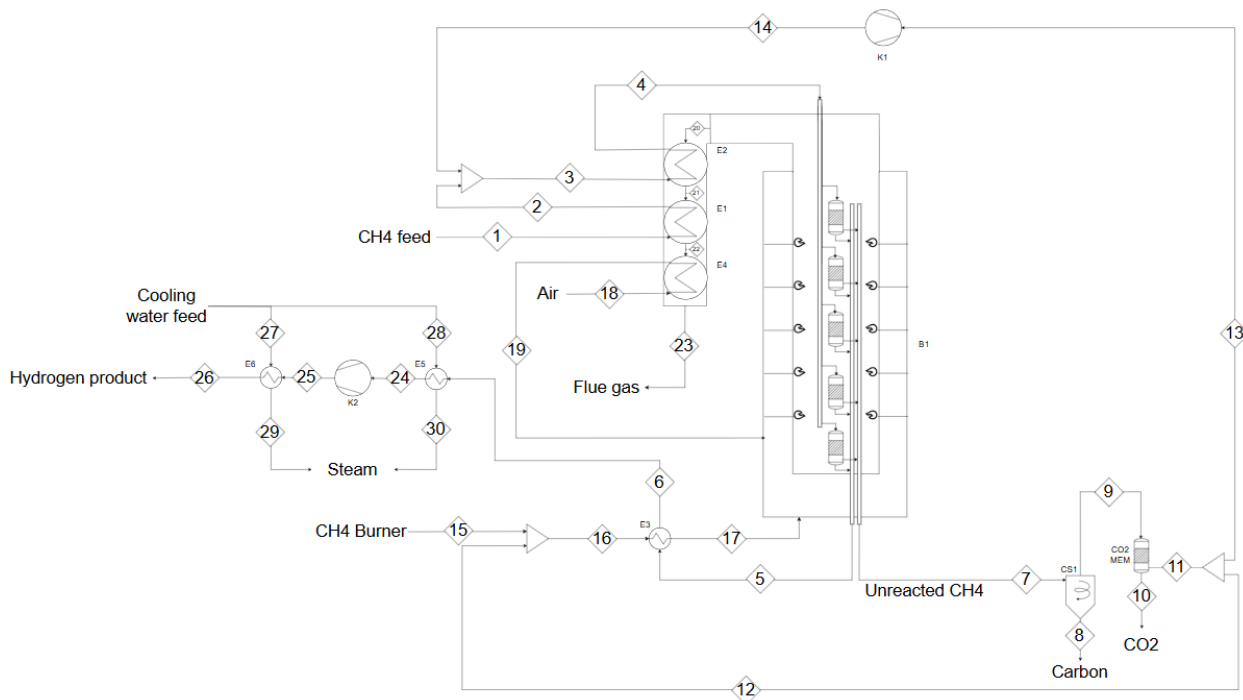
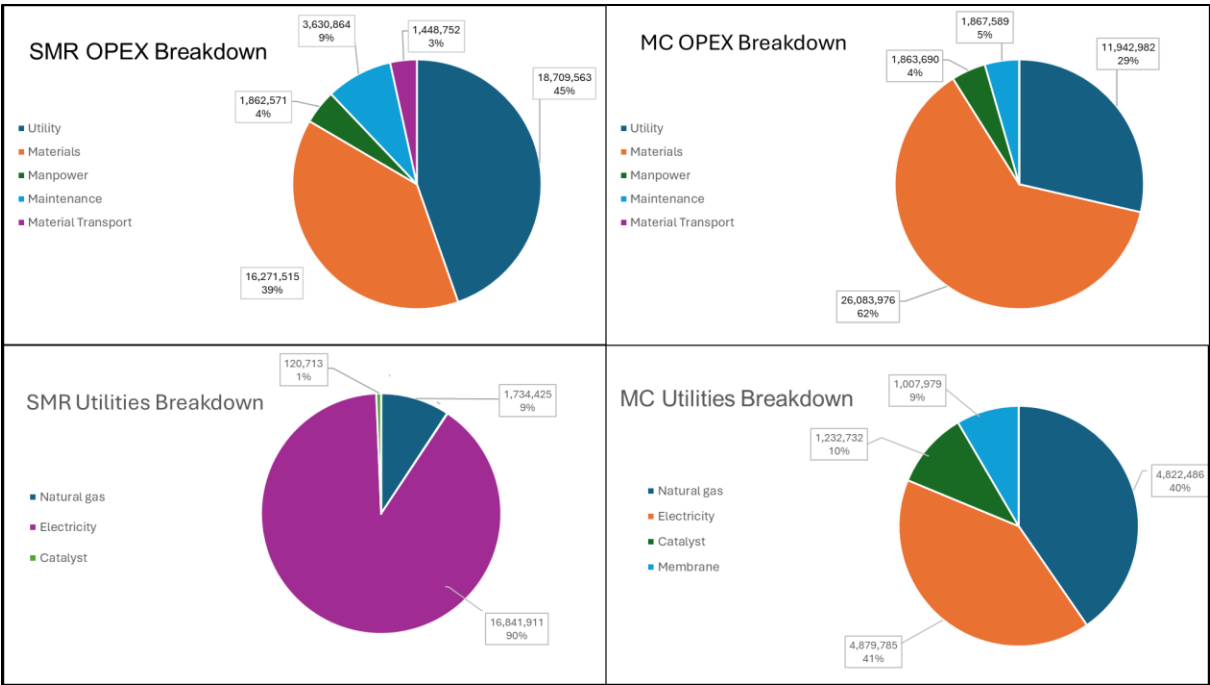


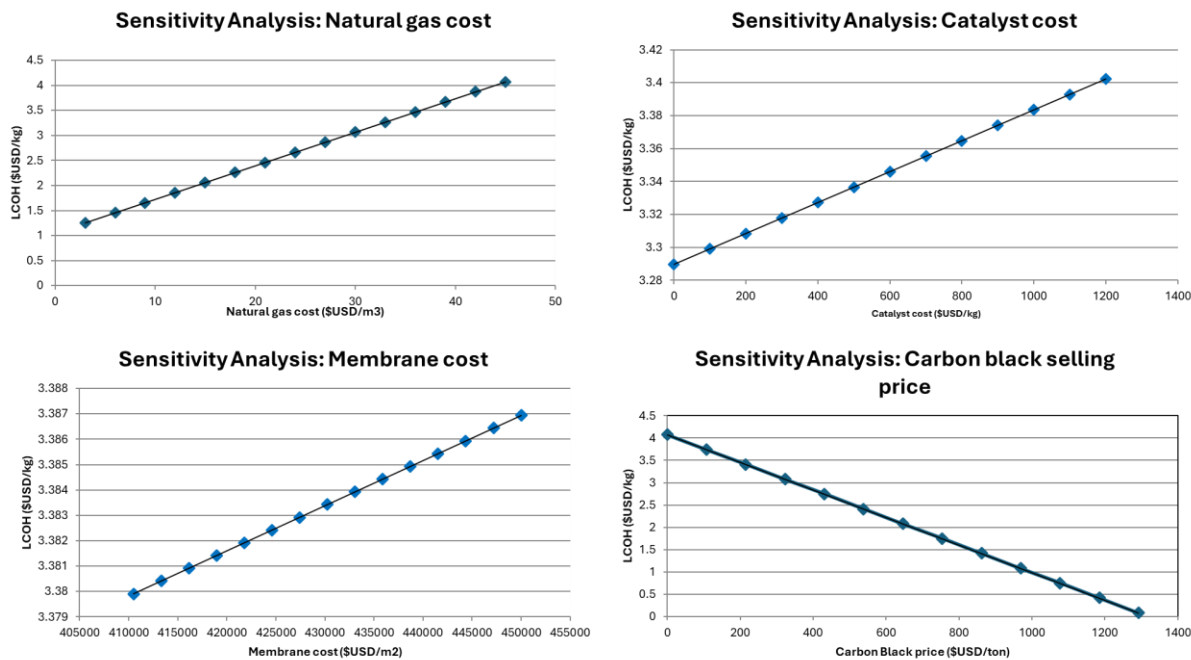
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Figure 4. Operating and utility cost breakdown for SMR and MC processes.



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Figure 5. Sensitivity analysis results.

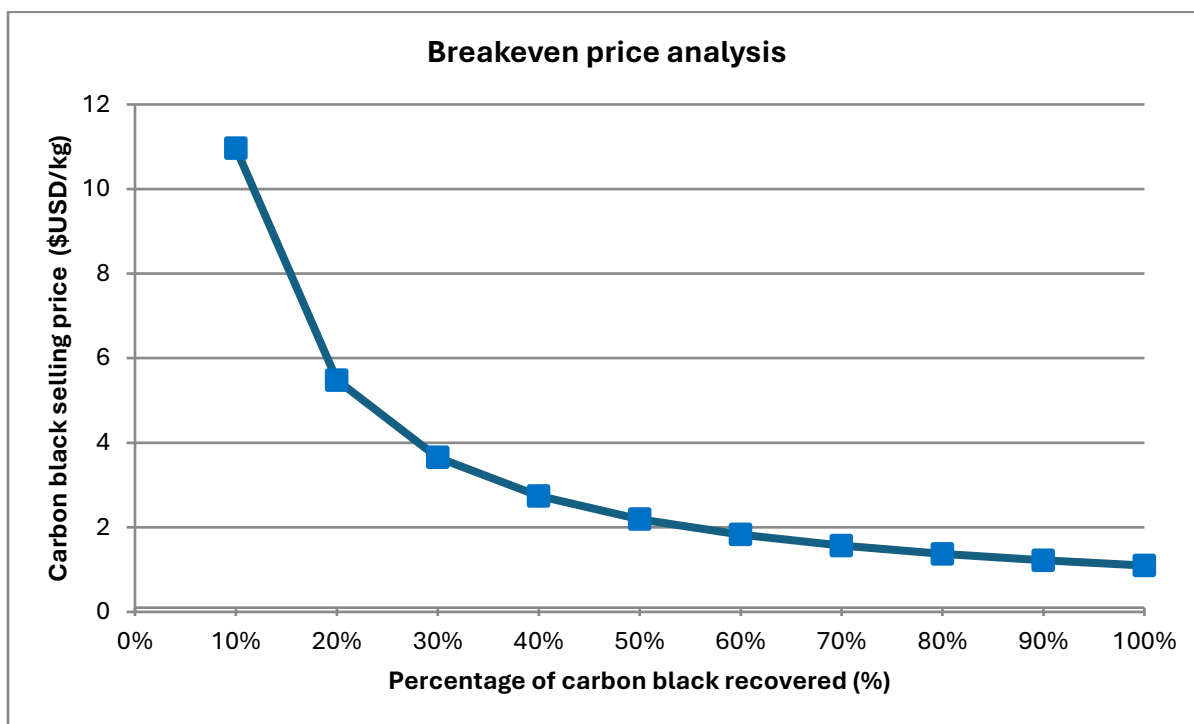


Figure 6. The required carbon black price for breakeven hydrogen production.