Available online at UofKEJ Website Here
UofKEJ Vol. 13 Issue 2 pp. 23-37 (2025)

UNIVERSITY OF
KHARTOUM
ENGINEERING
JOURNAL
(UoFKEJ)

Comparison of Reactors for Hydrogen Production via Methane Steam Reforming: A Review

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ARTICLE INFO

Keywords:
Methane Steam Reforming (MSR), Fixed-Bed Reactors, Fluidized-Bed Reactors, Microreactors, Sorption-Enhanced Reactors, Membrane Reactors, Hydrogen Production.

Article History:
Received on: July, 15 2025
Accepted on: September, 25 2025

Article Type: Review Article

DOI:10.53332/uofkej.v13i2.284

ABSTRACT

Methane Steam Reforming (MSR) remains the dominant technology for hydrogen production due to its high efficiency and economic viability. This paper provides a comparative analysis of different reactors used for MSR, including fixed-bed reactors, fluidized-bed reactors, microreactors, membrane reactors, and sorption-enhanced reactors. Fixed-bed reactors are widely employed in industrial settings for their simplicity and robustness, but they face limitations s in heat transfer and equilibrium-constrained methane conversion. Fluidized-bed reactors address these issues by improving heat and mass transfer, but they introduce complexities related to catalyst attrition and operational control. Microreactors leverage their high surface area-to-volume ratio to achieve excellent heat transfer and reaction kinetics, making them ideal for small-scale and portable applications, albeit with limited throughput for large-scale operations. Sorption-enhanced reactors further enhance hydrogen production through in-situ CO_2 capture, enabling methane conversions of up to 85% and hydrogen purity exceeding 95%, though sorbent regeneration poses technical barriers. Finally, membrane reactors integrate hydrogen separation with the reforming process, shifting equilibrium towards higher methane conversion and hydrogen yield, though the high cost and stability of palladium-based membranes remain challenges. The study highlights the challenges faced by these reactor technologies, including catalyst performance, economic constraints, and scalability issues, while discussing future perspectives such as the integration of renewable energy sources, and advanced catalyst development. Advancements in these areas will be crucial for enhancing the efficiency, cost-effectiveness, and sustainability of MSR processes, paving the way for cleaner and more reliable hydrogen production.

LIST OF ABBREVIATIONS

Abbreviation	Meaning
MSR	Methane Steam Reforming
WGS	Water-Gas Shift
HTS	High Temperature Shift
LTS	Low Temperature Shift
MEA	Monoethanolamine
LH-HW	Langmuir-Hinshelwood-Hougen-Watson
DEN	Denominator
S/C	Steam-to-Methane ratio

GHSV	Gas Hourly Space Velocity
PBR	Packed Bed Reactor
PFR	Plug Flow Reactor
SE-SMR	Sorption Enhanced Steam Reforming of Methane
SERP	Sorption Enhanced Reaction Process
CMR	Catalytic Membrane Reactor
PSA	Pressure Swing Adsorption
Cat	catalyst

1. INTRODUCTION

Hydrogen plays a critical role as an energy carrier and a building block for various chemical processes, making it pivotal in clean energy and industrial applications. Hydrogen, can be classified as black, grey, blue, or green hydrogen depending on the production method [1]. Figure (1) shows the hydrogen classification based on their production source. Green hydrogen is based on the production of hydrogen from electrolysis of water [2]. Grey and Blue Hydrogen are produced from natural gas, which mainly consists of methane, through the same steam reforming process and from the same process of steam reforming, the only difference is that blue hydrogen incorporates carbon capture technologies, while grey hydrogen does not.. Black hydrogen is obtained from coal gasification [1,3].

Methane steam reforming (MSR) is a method for producing syngas (hydrogen and carbon monoxide) by reaction of hydrocarbons with water. The main purpose of this technology is hydrogen production [4], which produces nearly 48% of hydrogen globally [5], Figure 2 shows the global hydrogen production by method.

This process is particularly favored for its cost-effectiveness and scalability despite its high energy demands and carbon emissions.

Reactor design is crucial in determining the performance and viability of the MSR process. Various reactor types have been developed over the years, each offering unique advantages and limitations. This review aims to provide a comparative analysis of the most common reactors used for MSR, highlighting their design principles, performance metrics, and suitability for different industrial scenarios. It also discusses the challenges associated with these reactors.

2. BACKGROUND AND FUNDAMENTALS OF METHANE STEAM REFORMING

MSR is the dominant industrial method for hydrogen production. It involves the reaction of methane with steam at high temperatures (700°C–1000°C) and moderate pressures (3–25 bar) in the presence of a catalyst to produce hydrogen and carbon monoxide. This reaction is endothermic, requiring an external heat source. The process starts with the purification of methane (CH_4) feedstock, followed by its reaction with steam in the MSR reactor to produce hydrogen (H_2), carbon monoxide (CO), and carbon dioxide (CO_2). The intermediate gases then pass through a water-gas shift reactor, where (CO) reacts with steam to form additional (H_2) and (CO_2).

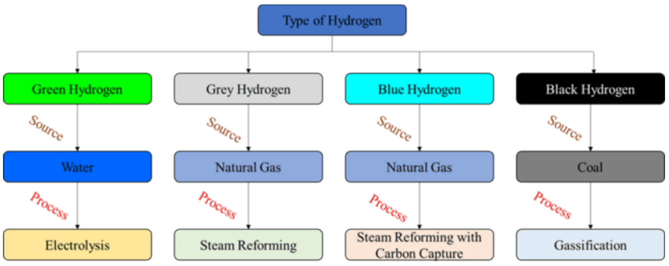

Figure 1: Hydrogen classification based on their production source [1]

Water gas shift (WGS) reactors typically operate in two modes, a high temperature shift (HTS) on a Fe/Cr catalyst at 400–500°C and a low temperature shift (LTS) on a Cu catalyst at 200°C. CO_2 produced in the reformers and WGS converters is typically removed from the process gas by chemical solvent absorption processes using solvents such as monoethanolamine (MEA) or hot Potassium Carbonate (K_2CO_3). The level of carbon oxides remaining in the hydrogen stream is reduced further by methanation which is the reverse of the steam reforming reaction and is typically carried out at 275°C resulting in hydrogen with a purity of 95–98 % [36,37].

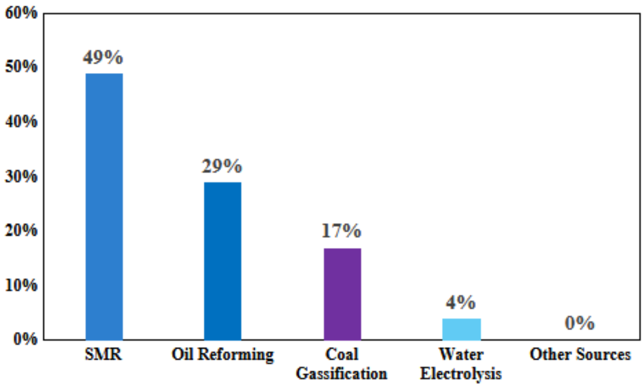

Figure 2: Global hydrogen production by method [6]

Finally, the hydrogen is purified in a separation unit for use in various applications [7]. Figure 3 shows a simple process flow diagram of MSR process.

MSR is a catalytic process that involves the reaction of methane (CH4) with steam (H2O) to produce hydrogen (H2) and carbon monoxide (CO) through the reaction:

$$CH_4+H_2O \rightarrow CO+3H_2, (\Delta H=+206\,kJ/mol) \tag{1}$$

A secondary reaction, the WGS reaction, is also utilized:

$$CO+H_2O \rightarrow CO_2+H_2, (\Delta H=-41\,kJ/mol) \tag{2}$$

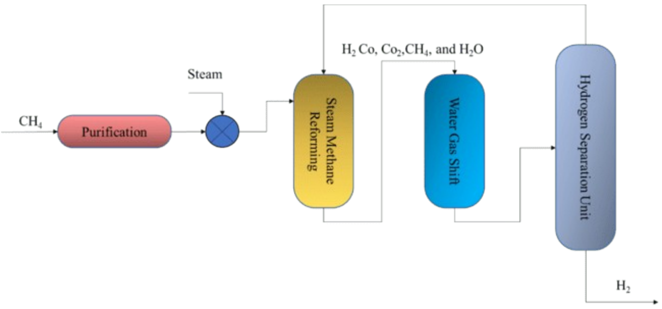

Figure 3. Diagram of traditional methane reforming unit for hydrogen production [8]

Catalyst, typically nickel-based, plays a critical role in enhancing reaction rates and reducing energy demands.

Kaihu Hou and Ronald Hughes [9] studied experimentally the mechanism and the kinetics of MSR over a commercial Ni/α-Al$_2$O$_3$ catalyst in an integral reactor under conditions of no mass/heat transfer and diffusion limitations, and they presented a comprehensive study about the possible mechanisms and kinetics rate equation using the Langmuir–Hinshelwood-Hougen-Watson (LH–HW) approach and Freundlich's adsorption concept. The following is a summary of the mechanism and rate law they have obtained:

Mechanism:

H$_2$O reacts with surface nickel atoms, yielding adsorbed oxygen atoms and gaseous hydrogen.

$$H_2O+(S)=H_2+O(S) \tag{3}$$

Where (S) is an active site on the catalyst surface.

Methane reacts with surface nickel atoms, yielding adsorbed CH$_2$ radicals and adsorbed H atoms.

$$CH_4+3(S)=CH_2(S)+2H(S) \tag{4}$$

The adsorbed radicals CH$_2$ and adsorbed oxygen react to yield adsorbed CHO and adsorbed hydrogen.

$$CH_2(S)+O(S)=CHO(S)+H(S) \tag{5}$$

Adsorbed CHO dissociates to adsorbed CO and H, or reacts with adsorbed oxygen, yielding adsorbed CO$_2$ and H in parallel.

$$CHO(S)+(S)=CO(S)+H(S) \tag{6}$$

$$CHO(S)+O(S)=CO2(S)+H(S) \tag{7}$$

Adsorbed CO reacts with adsorbed oxygen to form CO$_2$ or desorbs into the gas phase.

$$\begin{gathered} CO(S)+O(S)=CO_2(S)+(S) \\ CO(S)=CO+(S) \\ CO_2(S)=CO_2+(S) \\ 2H(S)=H_2+2(S) \end{gathered} \tag{8}$$

The rate equations are as follows:

$$r_1=\frac{k_1\left(\frac{P_{CH_4}P_{H_2O}^{0.5}}{P_{H_2}^{1.25}}\right)\left(1-\left(\frac{P_{CO}P_{H_2}^3}{K_{p1}P_{CH_4}P_{H_2O}}\right)\right)}{DEN^2} \tag{9}$$

$$r_2=\frac{k_2\left(\frac{P_{CO}P_{H_2O}^{0.5}}{P_{H_2}^{0.5}}\right)\left(1-\left(\frac{P_{CO_2}P_{H_2}}{K_{p2}P_{CO}P_{H_2O}}\right)\right)}{DEN^2} \tag{10}$$

$$r_3=\frac{k_3\left(\frac{P_{CH_4}P_{H_2O}}{P_{H_2}^{1.75}}\right)\left(1-\left(\frac{P_{CO_2}P_{H_2}^4}{K_{p3}P_{CH_4}P_{H_2O}^2}\right)\right)}{DEN^2} \tag{11}$$

` Where r$_i$ is the rate of reaction i, P$_j$ is the partial pressure of species j, and the denominator DEN is:

$$DEN=1+K_{CO}P_{CO}+K_H P_H^{0.5}+K_{H_2O}\left(\frac{P_{H_2O}}{P_{H_2}}\right) \tag{12}$$

The rate constants, k$_i$, are evaluated using Arrhenius equation:

$$k_i=A_i\exp\left(\frac{-E_i}{RT}\right) \tag{13}$$

The equilibrium constants, K$_i$, are evaluated using van't Hoff equation:

$$K_i=A(K_i)\exp\left(\frac{-\Delta H_{i,a}}{RT}\right) \tag{14}$$

Where A$_i$ and A(K$_i$) are the pre-exponential factors of reaction i, which are determined experimentally, E$_i$ is the activation energy of reaction i, R is the universal gas constant, T is absolute temperature, ΔH$_{i,a}$ is the adsorption enthalpy. Table 1 shows the values of the reactions constants.

Table 1. Activation energies, adsorption enthalpies and pre-exponential factors for MSR reactions [9]

E_1 (kJ/mol)	E_2 (kJ/mol)	E_3 (kJ/mol)	$\Delta H_{CO,a}$ (kJ/mol)	$\Delta H_{H,a}$ (kJ/mol)	$\Delta H_{H2O,a}$ (kJ/mol)
209.2	15.4	109.4	- 140.0	- 93.4	15.9
A_1	**A_2**	**A_3**	**$A(K_{CO})$**	**$A(K_H)$**	**$A(K_{H2O})$**
$5.922\text{x}10^{8}$	$6.028\text{x}10^{-4}$	$1.093\text{x}10^{3}$	$5.127\text{x}10^{-13}$	$5.68\text{x}10^{-10}$	9.251

3 TYPES OF REACTORS USED FOR MSR PROCESS

The selection of a reactor for the MSR process plays a critical role in optimizing hydrogen production. The reactor type not only determines the efficiency of the process but also impacts energy utilization, catalyst performance, and operational scalability. Various reactor configurations have been developed to address the challenges of heat transfer, reaction kinetics, and product separation. These include conventional designs like fixed-bed and fluidized-bed reactors, as well as advanced technologies such as microreactors, membrane reactors, and sorption enhanced reactors. Each reactor type offers unique advantages tailored to specific industrial needs, balancing efficiency, cost, and environmental considerations.

This section explores these reactor types, highlighting their principles, advantages, and applications in MSR.

3.1 Fixed Bed Reactor

Catalytic fixed-bed reactors are the most important type of reactors for the synthesis of large-scale basic chemicals and intermediates. In these reactors, the reaction takes place in the form of a heterogeneously catalyzed gas reaction on the surface of catalysts that are arranged [12]. Fixed-bed reactors are a widely used type of reactor in MSR.

In conventional technology, MSR is carried out using multi-tubular fixed-bed reactors [10]. High temperatures favor the process, due to the endothermicity of the reforming reactions.

3.1.1 Structure and Operation Conditions

A fixed bed reactor consists of a cylindrical vessel packed with a catalyst (Figure 4), typically nickel-based, which facilitates the endothermic reforming reactions.

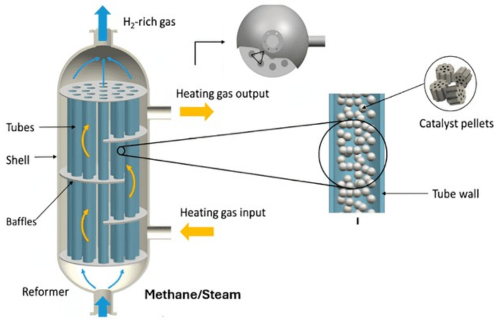

Figure 4. Multitubular fixed-bed reactor [50]

Temperature: Fixed-bed reactors typically operate between 700°C and 950°C. The reaction is highly endothermic, requiring high temperatures to drive the conversion of methane and steam into hydrogen and carbon monoxide [13,14].

Pressure: Moderate pressure is preferred for MSR reaction, because high pressure accelerates both forward and backward reactions, and integrates with downstream hydrogen purification. The pressure range is 15–30 bar [14,16].

Steam-to-Methane Ratio (S/C): Excess steam suppresses coke formation on the catalyst but increases energy consumption. The common range of Steam-to-Methane ratio for the fixed bed reactor is 2.5 – 4.0 [13,15].

Catalyst: Nickel-based catalysts supported on alumina are used. Promoters such as magnesium or calcium may be added to improve thermal stability and resistance to coking [13,15].

Gas Hourly Space Velocity (GHSV): Range is about 1000–5000 h^{-1}. It indicates the volumetric flow rate of gas relative to the catalyst volume. This is adjusted based on the reactor design and process requirements [14,16].

Heat Supply: Typically provided by radiant or convective furnaces surrounding the reactor tubes [13].

3.1.2 Thermodynamics

Methane Conversion: At industrial operating conditions (700–950°C, 15–30 bar, S/C ratio = 2.5–4.0), methane conversion typically reaches 85–95% in a fixed-bed reactor. Conversion is thermodynamically limited by equilibrium constraints [14,15].

Hydrogen Yield: Hydrogen yield is defined as moles of hydrogen produced per mole of methane fed. For a fixed bed reactor for MSR process, it usually ranges from 2.5–3.0 mol H_2/mol CH_4 depending on reactor conditions and extent of secondary reactions [13,16].

3.1.3 Material balance equation of a Fixed-Bed Reactor for MSR

The design of a fixed-bed reactor for MSR is based on the mole balance and the rate of reaction over the catalyst bed. The general equation for the design of a packed bed reactor (PBR) is applied, considering the specific reaction kinetics and catalyst behavior.

Reactor MSR is derived based on reaction kinetics

For a differential catalyst weight (dW):

$$\frac{dF_{CH_4}}{dW} = r_{CH_4} \tag{15}$$

Where: F_{CH4} is the molar flow rate of methane, W is the catalyst weight, r_{CH4} is the rate of reaction of methane (mol/kgcat-s) [17,18].

By solving the material balance equation, the total weight of catalyst will be:

$$W = \int_{F_{CH_4,\in}} F_{CH_4,out} \frac{dF_{CH_4}}{r_{CH_4}} \tag{16}$$

Energy Balance: Since MSR is highly endothermic, an energy balance is needed to determine the temperature profile along the reactor. The energy balance equation for the fixed bed reactor is:

$$\frac{dT}{dW} = \frac{-\Delta H_r r_{CH_4}}{F c_p} \tag{17}$$

Where: ΔH_r is the heat of reaction (kJ/mol), F_{total} is the total molar flow rate (mol/s), Cp is the heat capacity of the gas mixture (kJ/mol·K).

Design Considerations

Equilibrium Limitations: Methane conversion is constrained by equilibrium. operating conditions (high temperature, moderate pressure) should maximize the equilibrium constants K_i.

Catalyst Loading: The weight of the catalyst (W) must ensure sufficient residence time for the reaction to approach equilibrium.

Heat Transfer: Uniform temperature distribution is critical to avoid hotspots, which can deactivate the catalyst. For industrial fixed bed reactors, heat is usually supplied by external furnaces [13,14].

By solving the material and energy balances numerically (e.g., using finite difference methods), the reactor's length, diameter, and catalyst loading can be determined.

3.1.4 Catalyst Performance in Fixed-Bed Reactors for MSR

The catalyst used in MSR significantly influences the reactor's efficiency, product yield, and stability. Key performance metrics for catalysts in fixed-bed reactors include activity, selectivity, stability, and resistance to deactivation. Nickel-based catalysts are the most widely used for MSR due to their cost-effectiveness and high activity. Support materials like alumina (Al_2O_3) enhance dispersion, thermal stability, and resistance to sintering [14,15]. Promoters like magnesium or calcium improve resistance to carbon deposition and thermal degradation [11,19].

Catalyst performance depends on nickel particle size, dispersion on the support, and operating conditions. Smaller nickel particles generally exhibit higher activity due to increased surface area [14,15].

Deactivation: Catalysts face deactivation primarily due to: (1) Coke Formation, excessive carbon deposition blocks active sites and decreases catalytic performance. Using higher steam-to-carbon (S/C) ratios minimizes coking risk [19]. (2) Sulfur Poisoning, which is caused due to sulfur compounds in the feed that poison nickel sites [15].

Durability: Industrial MSR catalysts for fixed bed reactors are designed to operate continuously for extended periods (3–5 years). This durability depends on catalyst formulation and proper operating conditions [13,19].

3.1.5 Economic and Environmental Factors of Fixed-Bed Reactors for MSR

The economics of operating a fixed-bed reactor for MSR depend on several factors, including capital investment, operational costs, feedstock prices, and maintenance requirements.

Capital Investment: The main investment includes the reactor, heat exchangers, furnaces for external heating, and steam generation units. These components are robust to handle high-temperature and pressure conditions (700–950°C, 15–30 bar) [13,18]. High-quality materials such as heat-resistant alloys are essential to withstand thermal stress, increasing upfront costs [15].

Higher steam-to-carbon (S/C) ratios, while reducing carbon deposition, increase the cost of steam production. Therefore, optimizing the S/C ratio balances feedstock costs and reactor performance [19].

Catalyst Costs: Catalyst life (3–5 years under industrial conditions) affects replacement frequency and overall costs. Longer catalyst life reduces maintenance and operational costs [15,18].

Maintenance and Downtime: Fixed-bed reactors require periodic shutdowns for catalyst replacement and inspection, contributing to operational downtime.

Environmental Protection Costs: Stringent environmental regulations require investments in emissions control technologies, such as CO_2 capture systems. Fixed-bed reactors produce substantial CO_2, necessitating costs for mitigation technologies, which are critical for long-term sustainability [19].

3.2 Fluidized Bed Reactors

Fluidized bed reactors are gaining attention for MSR due to their unique advantages in terms of heat and mass transfer, temperature uniformity, and catalyst utilization. Unlike fixed bed reactors, where the catalyst remains stationary, fluidized bed reactors suspend catalyst particles in the gas flow, creating a fluid-like behavior that enhances reactor performance.

3.2.1 Structure and Operating Conditions

A fluidized bed reactor typically consists of a vertical cylindrical vessel equipped with a distributor plate at the bottom to ensure uniform fluidization of the catalyst particles. The reactor can operate under bubbling, turbulent, or circulating fluidized bed regimes depending on the gas velocity and particle properties. The gas flow (steam and methane) passes upward through the reactor, fluidizing the catalyst particles, which ensures gas-solid contact and uniform temperature distribution across the bed. This minimizes hot spots commonly observed in other reactor types [23,24].

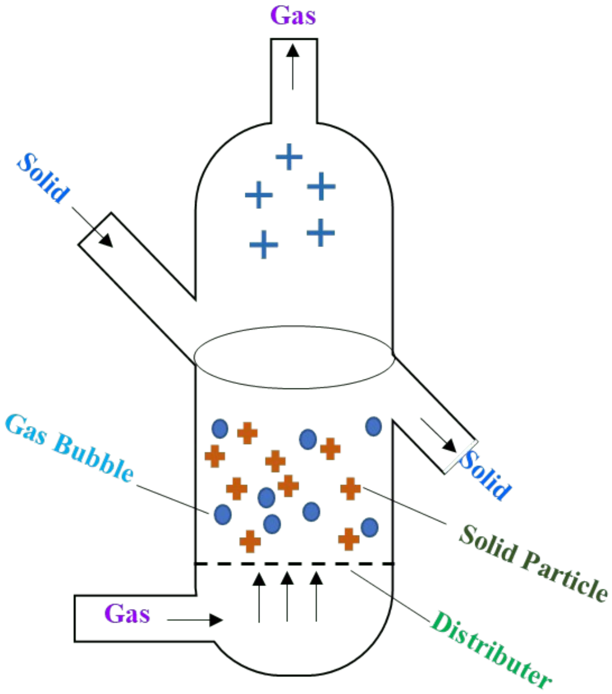

Figure 5. Fluidized bed reactor

Temperature: Fluidized bed reactors for MSR operate at 500–900°C to ensure the reaction progresses favorably. The uniform temperature profile within the fluidized bed minimizes hotspots, which are common in fixed bed reactors [4,9].

Pressure: Operating pressures typically range from 1–25 bar, depending on the downstream hydrogen application and reactor design. Higher pressures favor hydrogen adsorption but reduce methane conversion due to equilibrium limitations [13,18].

Steam-to-Methane Ratio (S/C): The S/C ratio is maintained between 2.5 and 5 to minimize carbon deposition on the catalyst while optimizing hydrogen production. Higher ratios reduce the risk of coke formation but increase energy requirements for steam generation [13,22].

Catalyst: Nickel-based catalysts supported on alumina are used. Catalyst particle sizes typically range from 50–200 µm to ensure good fluidization and activity [13,21].

Gas Velocity: The superficial gas velocity is adjusted to maintain the catalyst in a fluidized state. Typical values range from 0.1 to 1 m/s, depending on particle size and density [18,21]. Proper velocity ensures efficient gas-solid contact, enhancing reaction rates and product yield.

Heat Supply: External furnaces or internal heat exchangers supply heat to sustain the endothermic MSR reaction [18,22].

3.2.2 Thermodynamics

The dynamic nature of a fluidized bed reactor provides an advantage in approaching thermodynamic limits compared to fixed-bed reactors. The uniform temperature distribution minimizes hot spots, which can favor undesired reactions like coke deposition. Additionally, fluidization enhances the effectiveness factor of the catalyst, allowing for higher reaction rates and improved yields under near-equilibrium conditions [5,18].

Methane Conversion: The fluidized state ensures excellent mixing and heat transfer, reducing temperature gradients and achieving high methane conversions, typically 90% [18,24]

Hydrogen Yield: For a fluidized bed reactor for MSR process, the hydrogen yield usually is about 3 mol H_2/mol CH_4 depending on reactor conditions and extent of secondary reactions [1].

3.2.3 Material balance equation of a Fluidized-Bed Reactor for MSR

Fluidized bed reactors for MSR are designed based on principles of mole balance, considering the unique fluidization behavior. The design incorporates aspects of gas-solid interactions, bed hydrodynamics, and reaction kinetics.

Reactor Material balance equation: The material balance equations are coupled and solved over the reactor height or catalyst weight using numerical methods.

$$\frac{dX}{dW}=\frac{-r^{'}CH\,4\left(Ci\left(X\right),T\,,P\right)}{F\,CH\,4{,}0} \qquad (18)$$

$$\int_{0}^{X}\frac{dX}{r_{CH_4\left(X\,,T\,,P\right)}}=\frac{W}{FCH\,4{,}0} \qquad (19)$$

$$\frac{FCH\,4{,}0\,X}{\left(-rCH\,4\right)} \qquad (20)$$

The integration is typically performed as:

$$\int_{0}^{L}\frac{dC_{CH_4}}{r_{CH_4}}=C_{CH_4,\in-C_{CH_4,OUT}} \qquad (21)$$

Where L is the reactor height (m) [24,26].

Bed Hydrodynamics: In a fluidized bed, gas flows through the bed, creating both bubbles and emulsion phases.

Energy Balance: Like fixed bed reactors, heat must be supplied to maintain the reaction temperature. By taking account into the flow pattern of gaseous feed, the energy balance for a fluidized bed reformer is written as:

$$\frac{dT}{dz}=\frac{-\Delta H_r r_{CH_4}}{\rho_g C_p U_g} \qquad (22)$$

Where: T: Reactor temperature (K), ΔHr: Reaction enthalpy (J/mol), ρg: Gas density (kg/m³), Cp: Heat capacity of the gas mixture (J/mol·K), Ug: Superficial gas velocity (m/s) [5,6].

3.2.4 Catalyst Performance

In fluidized bed reactors, the catalyst must withstand attrition due to particle movement, maintain activity under high temperatures, and resist deactivation caused by coke formation [24]. As in fixed bed reactors, Nickel-based catalysts are also used for fluidized bed reactors for MSR.

The activity of the catalyst in a fluidized bed is influenced by temperature and Steam-to-Carbon (S/C) Ratio. Higher temperatures increase reaction rates but can lead to sintering of the active phase. Operating within the range of 500–900 °C balances activity and stability and maintaining an S/C ratio of 2–3 also reduces coke formation, ensuring prolonged catalyst life [5,18,25,26]

3.2.5 Economic and Environmental Factors of Fluidized-Bed Reactors for MSR

Fluidized bed reactors offer several economic advantages over other reactor types for MSR, particularly in terms of operational efficiency, scalability, and catalyst utilization. However, they also involve specific cost challenges.

Capital Investment: Fluidized bed reactors are compact and provide high volumetric efficiency, resulting in reduced construction costs compared to large fixed-bed reactors [25].

Operating Costs: The enhanced heat and mass transfer in fluidized bed reactors lowers energy costs, as uniform temperatures reduce the need for external heat input. Catalyst particles experience attrition and need to be replaced or regenerated periodically, contributing to operating costs [26].

Environmental Protection: Fluidized bed reactors do not inherently reduce CO_2 emissions compared to fixed-bed reactors, but can be adapted to include CO_2 capture technologies, potentially reducing emissions [5,26].

Coke Formation and Disposal: The continuous particle movement in fluidized bed reactors helps prevent excessive coke deposition, which reduces the need for frequent disposal of spent catalyst [27].

3.3 Micro Reactors

Micro-reactors are compact reactors with characteristic dimensions on the millimeter or sub-millimeter scale. These reactors have characteristics such as enhanced heat and mass transfer, precise reaction control, and reduced material and energy consumption. For MSR, micro-reactors offer an innovative solution to produce hydrogen efficiently, especially for small-scale [28,29].

3.3.1 Structure and Operation Conditions

Micro-reactors are designed with high precision to optimize heat and mass transfer for efficient MSR. The key structural features include:

Micro-Channels: Micro-reactors consist of numerous parallel micro-channels with dimensions ranging from 100 micrometers to a few millimeters. These channels are typically etched or fabricated in materials such as stainless steel, ceramics, or silicon [28]. However, micro-reactors used for hydrogen production differ in whether the catalyst is packed within the channels or coated on the walls [1]. The uniform distribution of the catalyst ensures efficient methane conversion [30].

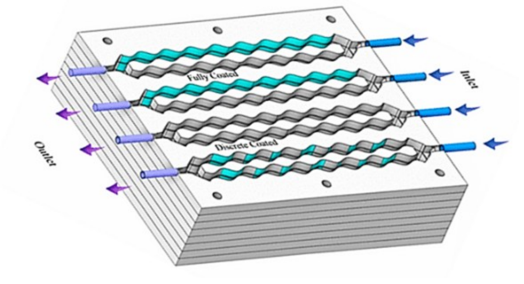

Figure 6. Wall-coated micro reactor for MSR process, Chen et al. (2019) [35]

Heat Exchanger Integration: Micro-reactors are integrated with micro-scale heat exchangers to manage the endothermic nature of the MSR reaction. Heat exchangers ensure a uniform temperature profile, minimizing hot spots and enhancing overall efficiency [32].

Temperature: Operating temperatures range from 600°C to 800°C, depending on the catalyst and design [30].

Pressure: Micro-reactors typically operate at 1 to 10 atm. Higher pressures enhance hydrogen yield and methane conversion but may increase the complexity of reactor fabrication and operation [33].

Steam-to-Methane Ratio (S/C): The S/C ratio is maintained between 2:1 and 3:1 to suppress coke formation and optimize reaction kinetics. The uniform catalyst distribution in micro-reactors ensures efficient utilization of steam and methane [32,33]

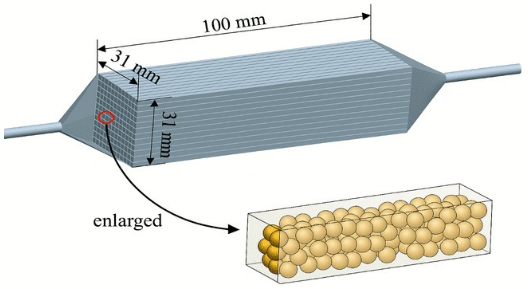

Figure 7. Packed bed micro reactor for MSR process, Wang, J et al [37]

Catalyst: The catalysts used must resist deactivation due to coking and thermal sintering. Noble metal-based catalysts (e.g., rhodium, platinum) are often used, although nickel-based catalysts are also common for their cost-effectiveness [28,30]

Gas Velocity: Typical values range from 0.1 to 10 m/s depending on the reactor design and operating conditions.

3.3.2 Thermodynamics

Methane Conversion: Micro-reactors can achieve high methane conversion rates, typically exceeding 90%, due to their small dimensions and high surface-to-volume ratio. This ratio ensures excellent contact between the gaseous reactants and the catalyst, improving reaction kinetics and reducing diffusion limitations. Optimal conversion occurs at elevated temperatures (850°C) and steam-to-carbon (S/C) ratios of 2:1 or higher, which suppress coke formation and maximize methane reforming efficiency [29,31]. Both statements are correct in context, but they highlight different aspects of steam methane reforming (SMR) in micro-reactors. The first statement, which notes that operating temperatures range from 600 °C to 800 °C depending on the catalyst and design, is accurate for micro-reactors. This is because their enhanced heat and mass transfer characteristics allow the reforming process to proceed effectively at somewhat lower temperatures compared to large-scale reactors.

The second statement, which indicates that optimal conversion occurs at elevated temperatures of around 850 °C and steam-to-carbon (S/C) ratios of 2:1 or higher, is also valid. However, it applies more generally to conventional SMR processes or larger reactor systems, where such conditions are needed to maximize methane conversion, increase hydrogen yield, and suppress coke formation.

Hydrogen Yield: Hydrogen yield in micro-reactors for MSR can reach up to 3 moles of H_2 per mole of CH_4, depending on operating conditions.

3.3.3 Material balance equation of a Micro-Reactor for Methane Steam Reforming

The material balance equation for a micro-reactor used in MSR is affected by reaction kinetics, heat transfer, and flow dynamics. The micro-reactor operates as a plug flow reactor (PFR) with negligible axial mixing. So, the material balance equation is written as:

$$\frac{dF_{CH_4}}{dV}=r_{CH_4} \tag{23}$$

Energy Balance: Like fixed bed and fluidized bed reactors, heat must be supplied to maintain the reaction temperature. The energy balance for a micro reactor is written as:

$$\frac{dT}{dV}=\frac{-\Delta H_r r_{CH_4}}{F c_p} \tag{24}$$

Pressure Drop: Due to the compact design and small channel dimensions of micro reactors, the pressure drop is significant and is calculated using the Ergun equation [36]:

$$\frac{dP}{dL}=\frac{150\mu(1-\epsilon)^2}{\epsilon^3 d_p^2}u+\frac{1.75\rho(1-\epsilon)}{\epsilon^3 d_p}U_g{}^2 \tag{25}$$

Where :P: pressure (Pa), L: reactor length (m), μ: dynamic viscosity (Pa·s), ϵ: void fraction, dp: particle diameter (m), Ug: superficial velocity (m/s), and ρ: density of the gas mixture (kg/m³).

3.3.4 Catalyst Performance in Microreactors for MSR

Enhanced Reaction Rates: Microreactors demonstrate significantly higher catalytic performance due to their excellent heat and mass transfer characteristics. The small dimensions of the microchannels reduce transport resistances, leading to uniform temperature profiles and enhanced reaction kinetics. Studies indicate that the use of microreactors improves methane conversion efficiency compared to conventional reactors [1].

Microreactors typically operate at temperatures between 600°C and 800°C and moderate pressures. Optimizing catalyst properties such as dispersion, particle size, and support material is crucial for achieving optimal performance [33].

3.3.5 Economic and Environmental Considerations of Micro reactors for MSR

Lower Operating Costs: Micro-reactors offer improved thermal efficiency due to their excellent heat and mass transfer properties, resulting in lower energy consumption compared to traditional reactors. This efficiency reduces fuel costs in hydrogen production [29,30]

Capital Costs: The initial fabrication cost of micro-reactors is high due to the precision manufacturing required for microchannels and catalytic coating or packing [29,31].

Catalyst Usage: For the thin wall coated micro-reactors, catalyst material requirements are less than other reactors, leading to cost savings in precious metals like rhodium or platinum [31,32].

Maintenance: Micro-reactors experience less coke deposition due to efficient heat distribution, which reduces downtime and maintenance costs. However, replacing or recoating catalysts in microchannels can be challenging and may require specialized equipment [32,33].

Lower Carbon Footprint: By maximizing heat recovery and minimizing energy wastage, micro-reactors reduce CO_2 emissions compared to conventional reactors [29].

Integration with Renewable Energy: Micro-reactors can be paired with renewable hydrogen production methods, such as electrolysis or biogas reforming. This integration enhances sustainability and reduces reliance on fossil-based methane [33,34].

3.4 Sorption-Enhanced Steam Methane Reforming

The Sorption-Enhanced Steam Methane Reforming (SE-SMR) method is a procedure that combines the methane reforming process with the collection of carbon dioxide (CO_2) within the same reactor. During the process, methane reacts with water vapor in the presence of a catalyst, while a solid sorbent such as calcium oxide (CaO) captures the carbon dioxide CO_2 generated, forming calcium carbonate ($CaCO_3$) [40]. In Sorption-Enhanced Steam Methane Reforming (SE-SMR) of biogas, methane reacts with steam over a Ni-based catalyst to produce hydrogen and carbon dioxide. To enhance hydrogen yield, a CO_2 sorbent such as CaO is added, which captures CO_2 in situ and shifts the equilibrium toward hydrogen formation. However, several factors must be considered for effective integration. First, CaO can react with steam to form $Ca(OH)_2$, influencing sorbent activity and long-term stability. Second, the removal of CO_2 helps suppress the disproportionation reaction ($CO_2 + C \rightarrow 2CO$), which otherwise contributes to carbon deposition on the catalyst surface. Third, the overall adsorption capacity of CaO determines how much CO_2 can be effectively captured before sorbent regeneration is required. Furthermore, the addition of sorbent dilutes the Ni catalyst, necessitating a larger reactor volume to maintain performance. Finally, the system's design becomes more complex due to sorbent handling, regeneration, and integration challenges.

This method allows for greater methane conversion and hydrogen production due to the continuous elimination of CO_2, and includes lower energy consumption, reduction of CO_2 emissions and simplification of processes by integrating carbon capture in the reactor, surpassing traditional reforming processes and making it a sustainable and attractive alternative to produce clean hydrogen [40,41].

3.4.1 Structure and Operation Conditions

The combination of reversible chemical reactions within sorption of a product improves the conversion of reactants and consequently, due to the removal of the product from the reaction zone, the purity of the target product in the effluent stream can also be improved. This integrated process comprising both chemical reaction and removal by adsorption processes is called reactive adsorption process or sorption-enhanced reaction process (SERP) [43,44].

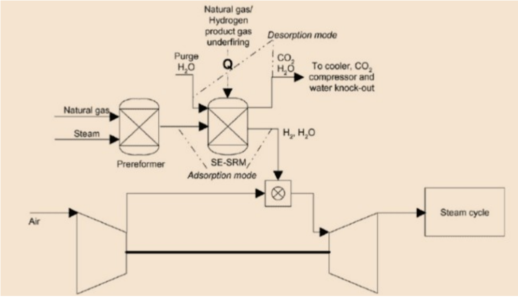

Figure 8. Sorption-enhanced steam-methane reformer (SE-SMR). [42]

The following table shows the different operating conditions of SE-SMR

3.4.2 Thermodynamics

Methane Conversion: SE-SMR can achieve methane conversions up to 85% under specific operating conditions. **Hydrogen Yield:** The process can produce hydrogen with purities up to 95%, significantly higher than traditional steam methane reforming [52].

3.4.3 Economic and Environmental Considerations of SE-SMR

Since this process in the reactor works at high temperatures, it requires the consumption of a lot of energy, which represents significant expenses, although it is being studied to use renewable energy, with respect to the cost of the reactor materials, the SE-SMR reactors are more complex than those of conventional reforming, increasing capital cost by up to 30% compared to conventional systems. [40]

Environmental factors: This reactor, using a solid sorbent such as CaO to form $CaCO_3$, can reduce direct CO_2 emissions into the environment, as it can capture up to 90% - 95% of the CO_2 generated in the process, thus preventing it from accumulating in the atmosphere, contributing greatly to the carbon footprint, although it can also generate secondary solid waste from the replacement of the adsorbents used [40].

3.5 Membrane Reactors

A membrane reactor is a multifaceted vessel used to produce chemicals. Hydrogen is produced in two systems: conventional reactors and membrane reactors, which separate and purify hydrogen in a single vessel. There are many types of membrane reactors depending on their design, such as catalytic membrane reactor (CMR), fixed bed membrane reactor, and fluidized bed membrane reactor [47].

These reactors use the combination of chemical reaction and simultaneous separation in a single system. It is widely used for hydrogen production because it improves reaction efficiency by selectively removing the hydrogen produced through a permeable membrane. This results in a higher conversion of the reactant and a more efficient operation than other reactors, reduced operating costs by combining the chemical reaction and separation, and production of purer hydrogen [46]. Figure (9) shows a schematic of the packed bed membrane reactor.

Table 2. Summary of reactor types employed to carry out the SESMR process and their main operating conditions [40]

Catalyst	Sorbent	SESMR Conditions	Regeneration Conditions
Ni-based commercial (1.5 g in packed-bed)	CaO-$Ca_{12}Al_{14}O_{33}$ (85:15 wt)	550–650 °C, 1 atm, 11–44 ml min^{-1} CH_4, S/C = 3.4	-
Ni-$NiAl_2O_4$ (10 wt% NiO)	CaO-$Ca_{12}Al_{14}O_{33}$ (90:10 wt)	600–700 °C, 1 atm, 760 h^{-1} CH_4, 30 cm^3 bed volume, S/C = 1.6–5	-
Ni-CaO-$Ca_{12}Al_{14}O_{33}$ (10 wt% Ni) (0.2 g in packed-bed)	CaO-$Ca_{12}Al_{14}O_{33}$ (15, 30, 45, 54 wt% of free CaO)	650 °C, 1 atm, 2 Nml min^{-1} CH_4, 12 Nml min^{-1} inert gases, S/C = 3	-
Ni/Mg-Al catalyst (atomic ratio 0.5:2.5:1) (1 g in packed-bed)	CaO-$Ca_9Al_6O_{18}$ (80 wt% of CaO)	550–650 °C, 1 atm, 12.8–19.3 ml min^{-1} CH_4, S/C = 3–5	800 °C, 1 atm, 20 vol% H_2 in N_2
Ni-based commercial (3 g in packed-bed)	CaO-$Ca_{12}Al_{14}O_{33}$ (85:15 wt)	650 °C, 1 atm, 11 ml min^{-1} CH_4, 25 ml min^{-1} He, S/C = 3.4	850 °C, 1 atm, He
Ni-based commercial (3 g in packed-bed)	CaO-$Ca_{12}Al_{14}O_{33}$ (75:25 wt)	630 °C, 1 atm, 70 ml min^{-1} CH_4, S/C = 3	780 °C, 1 atm, N_2
Ni-hydrotalcite (1.6 g in packed-bed)	CaO-$Ca_{12}Al_{14}O_{33}$ or limestone (6 g in packed-bed)	550 °C, 1 atm, 0.51 ml^{-1} total CH_4, 10 vol% dry CH_4 in N_2, S/C = 4	750 °C, 1 atm, 0.81 min^{-1} N_2
Ni-based commercial (2214 g in fluidized bed)	Calcined dolomite (886 g in fluidized bed)	600 °C, 1 atm, steam, Superficial velocity = 3.2 mm/s inlet CH_4, S/C = 3	850 °C, 1 atm, N_2

3.5.1 Structure and Operation Conditions

Types of Membrane

Depending on the substance used to manufacture the membrane, which has a high hydrogen permeability, there are two different varieties, and they are divided into two categories

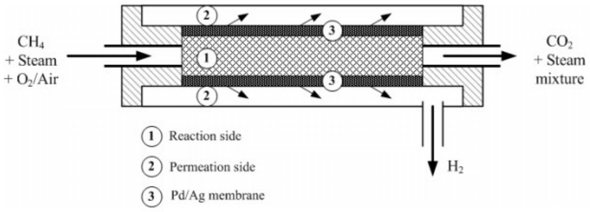

Figure 9 : Schematic of the packed bed membrane reactor. [46]

Polymeric Membrane: The use of polymeric membranes in commercial gas separation processes is common. Glass and rubber polymeric membranes are two different types of polymeric membranes.

Metallic Membrane: Dense membranes made of palladium, platinum, nickel and the metallic elements in the III-V bands of chemical elements have theoretically unlimited selectivity as they can transport hydrogen in a dissociated form [47].

Palladium-free Membranes: Palladium is a particularly desirable material for metal-based membranes because it is highly selective towards hydrogen and allows the synthesis of pure hydrogen. However, palladium is expensive. Due to their lower cost and strong hydrogen permeability, Group 5 metals with a body-centered cubic structure, such as tantalum, vanadium, and niobium, present a viable alternative to platinum [48].

Palladium membranes: Palladium-based membranes for hydrogen purification provide the highest selectivity and penetration due to their special permeation mechanism [50]. A dense palladium-based membrane (2–50 μm) can be employed to separate pure hydrogen [46].

Operation Conditions for Hydrogen Production:

Temperature: Operating temperatures range from 850°C to 950°C, depending on the catalyst and design [46].

Pressure: Membrane-reactors typically operate at 15 to 30 bar in view of thermodynamic limitations and downstream compression requirements [46].

Steam-to-Methane Ratio (S/C): The S/C ratio is maintained typically between 2 to 5 depending on the end use.

Catalyst: The choice of catalyst for membrane reactors in MSR is crucial to achieving efficient reforming. The most used catalysts include Ni-based catalysts, which are typically supported on alumina (γ-Al_2O_3) or other stable supports. Sometimes catalysts are supported with metals like Cerium (Ce) or Magnesium (Mg) to improve stability and activity [53].

Gas Hourly Space Velocity (GHSV): Typical values range from 500 – 10,000 h^{-1} depending on operating conditions and membrane performance. Lower GHSV may favor higher conversion but reduces throughput. Higher GHSV increases productivity but could limit conversion unless membranes remove hydrogen efficiently [54].

3.5.2 Thermodynamics

Methane Conversion: The range of methane conversion is 80–95% at optimized conditions. A study of Hu et al.(2014) showed that at 600°C and 5 bar, a Pd-based membrane reactor achieved 95% methane conversion compared to a conventional fixed-bed reactor [55].

Hydrogen Yield: Hydrogen yield is significantly enhanced in membrane reactors due to selective hydrogen extraction through the membrane. The yield is close to 100% of the theoretical maximum under ideal conditions. Hydrogen recovery rates of 70–90% are common in practical systems. A study by Dolan et al. (2010) reported hydrogen yields of 85% with a Pd-Ag membrane reactor operating at 600°C and 10 bar [56].

3.5.3 Material balance equation of a Membrane-Reactor for Methane Steam Reforming

The mole balance of hydrogen is written as:

$$\frac{dF_{H_2}}{dz}=r_{H_2}-\frac{J_{H_2}A_m}{V_{cat}} \tag{26}$$

Where: F_{H2}: molar flow rate of hydrogen, z: axial distance in the reactor, r_{H2}: rate of hydrogen production from kinetics, J_{H2}: hydrogen permeation flux through the membrane, A_m: membrane surface area per unit reactor volume, and V_{cat}: catalyst bed volume.

The hydrogen permeation flux J_{H2} follows Sievert's Law for palladium-based membranes:

$$J_{H_2}=k_p\left(P^{0.5}_{H_2,reaction\,side}-P^{0.5}_{H_2,permeate\,side}\right) \tag{27}$$

Where k_p is the Permeation constant

3.5.4 Economic and Environmental Considerations of Membrane reactors for MSR

Capital Costs: Membrane materials (e.g., Pd-alloy membranes) are expensive due to palladium cost [57]. Reactor integration reduces equipment costs by eliminating downstream hydrogen purification steps like Pressure Swing Adsorption (PSA) [54].

Operational Costs: Lower operating temperatures reduce heating costs compared to conventional steam reforming (>700°C) [53]. Membrane fouling and poisoning can add to maintenance costs [56].

CO_2 Emissions Reduction: Operating at lower temperatures reduces energy demand and associated CO_2 emissions [54].

Efficiency Improving: Integration of reaction and separation increases hydrogen recovery while reducing methane slip [58 - 60].

Waste Minimization: High methane conversion leads to lower unconverted methane emissions [56].

To tie the reactor-by-reactor discussion together, the summary below compares MSR reactor options through the lens of cost, efficiency, and scalability to guide practical technology selection.

Across the five options, think of **fixed-bed** as the proven workhorse, **fluidized-bed** as the better heat manager, **microreactors** as the precision tool for small/modular plants, **SE-SMR** as reforming with built-in CO_2 capture, and **membrane reactors** as reforming with built-in hydrogen purification. Each one trades capital cost, running cost, hydrogen output, and ease of scale in different ways.

Cost lens. Fixed-beds are simplest to build at large scale but pay for high-temperature furnaces and steady steam use. Fluidized-beds can trim energy use thanks to uniform temperatures, yet add costs for solids handling and catalyst make-up. Microreactors often have the **highest cost per unit of hydrogen** (precision fabrication, coatings), even if the absolute plant cost is small. SE-SMR usually raises up-front cost versus conventional (extra sorbent inventory and regeneration hardware), trading CAPEX for lower downstream separation and lower CO_2 fees. Membrane reactors concentrate cost in the membranes themselves (especially Pd-based), with ongoing expense tied to membrane care and replacement; they may save on or shrink PSA and some compression.

Efficiency & product quality. Fixed-beds deliver reliable, high conversion but are ultimately limited by reaction equilibrium at the chosen temperature and pressure. Fluidized-beds push closer to those limits thanks to excellent mixing and temperature control, which also helps keep coking in check. Microreactors excel at heat and mass transfer, enabling high per-volume productivity and stable operation at somewhat lower temperatures for a given performance target. SE-SMR boosts **apparent** conversion and hydrogen purity by removing CO_2 in-situ, shifting the reaction toward more H_2. Membrane reactors selectively bleed out hydrogen as it forms, raising single-pass conversion and yielding very high purity streams directly from the reactor.

Scalability, reliability, and emissions. Fixed-beds scale straightforwardly to world-scale units and are mechanically simple, but require planned outages for catalyst change-outs and are carbon-intensive without capture. Fluidized-beds scale well too and are resistant to hot spots, though they demand competence in solids handling and accept some catalyst attrition. Microreactors "scale by numbering-up," making them ideal for distributed or flexible production but not yet the natural choice for very large complexes. SE-SMR simplifies the overall CO_2 picture at the source—high capture potential with fewer downstream steps—while introducing sorbent management and regeneration as new reliability tasks. Membrane reactors reduce or replace downstream purification and can cut energy use, but long-term performance hinges on protecting membranes from sulfur, particulates, and carbon.

Based on these trade-offs, the following choices are generally recommended. For bankable, world-scale plants with familiar equipment and supply chains, selection of **fixed-bed** designs is favored, optionally paired with external CO_2 capture. Where thermal management or coking is the main constraint and solids-handling capability is available, **fluidized-bed** designs are preferred for their temperature uniformity and potentially lower operating cost. For decentralized or modular production in which fast start-up, turndown, and compact footprint are valued, **microreactors** are recommended despite higher specific capital cost. Where policy or contracts place a premium on in-reactor CO_2 capture and high hydrogen purity, **SE-SMR** is justified even with added complexity. When ultra-high hydrogen purity and high single-pass conversion are prioritized and membrane budgets and protection can be ensured, **membrane reactors** are considered attractive. In practice, the strongest overall results are often obtained from **hybrid trains**, for example, fixed- or fluidized-bed reforming combined with capture, or a membrane polishing step—so a blended design is frequently preferred over any single reactor type.

4. CHALLENGES AND FUTURE PERSPECTIVES

The implementation of various reactor technologies for MSR faces several challenges, while advancements in research present promising future perspectives. Fixed-bed reactors, although widely used, struggle with heat transfer limitations, catalyst deactivation, and equilibrium constraints that limit methane conversion efficiency. Fluidized-bed reactors, while improving heat and mass transfer, face challenges such as catalyst attrition, operational complexity, and difficulties in scale-up. Microreactors, despite offering excellent heat and mass transfer properties, are limited by their small throughput, restricting their feasibility for large-scale hydrogen production. For membrane reactors, the high cost and limited long-term stability of palladium-based membranes remain significant barriers to widespread adoption, alongside issues with membrane fouling and scalability. Similarly, sorption-enhanced reactors face challenges related to sorbent regeneration, thermal stability, and process integration on an industrial scale. Future research efforts should focus on improving catalyst performance, developing cost-effective and durable membrane materials, and enhancing sorbent regeneration techniques. Innovations in process intensification, such as integrating renewable energy sources (e.g., solar or biogas) into MSR systems, can reduce carbon emissions and improve sustainability.

Biogas integration into Sustainable Resource Management (SRM) begins with collecting organic waste such as food scraps, crop residues, or manure. This material is fed into an anaerobic digester, where microbes break it down in the absence of oxygen, producing a mixture of methane and carbon dioxide. The captured methane, which would otherwise escape into the atmosphere, is then purified and used as a renewable fuel for electricity, heating, or transport. The remaining digestate can be applied as organic fertilizer. This process reduces reliance on fossil fuels, prevents landfill methane emissions, and closes the loop in sustainable waste management. Additionally, advancements in nanotechnology and reactor design, such as scalable microreactor systems and hybrid membrane-sorption technologies, hold the potential to overcome current limitations and achieve higher efficiency, lower costs, and reduced environmental impact. Ultimately, the development of more efficient and sustainable reactor technologies will be critical for meeting the increasing global demand for clean hydrogen production while addressing economic and environmental concerns.

5. COMPARATIVE ASSESSMENT OF MSR REACTOR TECHNOLOGIES

Methane steam reforming (MSR) remains the primary pathway for industrial hydrogen production; however, reactor design plays a crucial role in determining efficiency, scalability, and sustainability. Table 3 summarizes the comparative performance of major reactor types.

Fixed-bed reactors are the industrial standard, valued for their robustness and maturity. They can achieve 85–95% methane conversion but are constrained by equilibrium limits and CO_2 emissions unless paired with capture systems. While capital investment is high due to the requirements for materials and furnaces, their reliability makes them the baseline technology.

Fluidized-bed reactors enhance heat and mass transfer, achieving approximately 90% conversion with improved catalyst utilization. Their compact design lowers construction costs, but the attrition of catalyst particles and the complexity of scale-up remain challenges. Environmentally, they do not inherently reduce CO_2, but are adaptable for capturing integration.

Microreactors excel in kinetics and heat management, often achieving conversions exceeding 90% on a laboratory scale. They offer low operating costs and reduced CO_2 emissions due to thermal efficiency but are limited to small-scale or portable applications because of high fabrication costs and low throughput.

Sorption-enhanced reactors (SE-SMR) integrate CO_2 capture directly into the reformer, achieving up to 85% methane conversion and hydrogen purity above 95%. They can capture 90–95% of process CO_2, making them highly attractive for the production of clean hydrogen. However, higher capital costs (approximately 30% higher than conventional systems) and the need for sorbent regeneration pose technical and economic challenges.

Membrane reactors combine reforming and hydrogen separation in a single unit, achieving conversion rates of 80–95% and yields approaching the theoretical maximum. They are efficient, compact, and reduce CO_2 emissions by lowering process temperatures. Nonetheless, the high cost and long-term stability of palladium membranes remain critical bottlenecks.

Overall, fixed-bed reactors continue to dominate large-scale production, but fluidized-bed and membrane reactors offer pathways to greater efficiency and improved integration with carbon management. Microreactors are ideal for niche, distributed applications, while sorption-enhanced systems show promise for carbon-neutral hydrogen but need further advancements in sorbent technology. Future research should focus on balancing cost, scalability, and environmental performance, with hybrid designs and renewable integration providing promising options.

CONCLUSION

Methane Steam Reforming (MSR) is carried out in various types of reactors, each offering distinct advantages and limitations. Fixed-bed reactors are the most widely used in industrial MSR processes due to their simple design, high thermal efficiency, and robust catalyst performance. However, fixed-bed reactors often face limitations in heat transfer and methane conversion due to equilibrium constraints. On the other hand, fluidized-bed reactors improve heat and mass transfer, ensuring uniform temperature distribution and better catalyst utilization, which enhances methane conversion. Despite these advantages, fluidized-bed reactors are more complex and prone to catalyst attrition. Micro-reactors offer unique advantages due to their small scale, high surface area-to-volume ratio, and enhanced heat and mass transfer rates. These features enable precise temperature control, rapid reaction kinetics, and efficient catalyst utilization, making microreactors ideal for small-scale hydrogen production and portable applications. However, their limited throughput poses challenges for large-scale operations. Therefore, the selection of reactor type depends on factors such as process efficiency, capital and operating costs, and the desired hydrogen purity, with advancements in membrane, sorption, and microreactor technologies offering promising pathways for future MSR optimization. Sorption-enhanced reactors incorporate in-situ CO_2 capture, further shifting the reaction equilibrium, resulting in significantly higher methane conversion (up to 85%) and hydrogen yield with purities exceeding 95%. While this reactor type offers exceptional performance, challenges remain in sorbent regeneration and integration with industrial-scale systems. Therefore, the selection of reactor types depends on factors such as process efficiency, capital and operating costs, and the desired hydrogen purity. Lastly, membrane reactors integrate reaction and hydrogen separation in a single unit, shifting the equilibrium towards higher hydrogen production while achieving near-complete methane conversion. These reactors, however, face economic challenges due to the high cost of palladium-based membranes and long-term membrane stability issues.

Table 3 summarizes the key features, advantages, and limitations of the reactors used for the MSR process:

Table 3. The comparison results between MSR reactors

Reactor Type	**Key Features**	**Advantages**	**Limitations**
Fixed Bed	– Limited heat transfer. Stationary catalyst bed. – Widely used in industrial MSR processes.	– Simple design and operation. – Robust and reliable. – High thermal efficiency.	– Limited heat transfer. – Equilibrium constraints reduce methane conversion.
Fluidized Bed	– Fluidized catalyst particles. – Enhanced heat and mass transfer.	– - Uniform temperature distribution. - Better catalyst utilization. - Improved methane conversion.	– Complex operation. – Catalyst attrition. – Challenges in scale-up.
Micro	– High surface area-to-volume ratio. – Small-scale systems.	– Enhanced heat and mass transfer. – Rapid reaction kinetics. – Suitable for portable applications.	– Limited throughput for large-scale operations. – High manufacturing costs.
Sorption Enhanced	—In-situ CO_2 capture. – Shifts equilibrium for higher H_2 production.	– Enhanced heat and mass transfer. – Rapid reaction kinetics. – Suitable for portable applications.	– Limited throughput for large-scale operations. – High manufacturing costs.
Memb-rane	– Integration of reaction and hydrogen separation. – Selective H_2 permeation.	– Near-complete methane conversio – High hydrogen yield. – Process intensification.	– High cost of palladium-based membrane – Membrane stability and fouling issues.

ACKNOWLEDGMENT

The authors express gratitude for the assistance of Dr. Mohamed Mozahar at King Fahd University of Petroleum & Minerals (KFUPM).

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