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A Review: Technologies for CO_2 Capture in Hydrogen Production from Natural Gas Steam Reforming with Membrane Systems

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Abstract

Hydrogen is produced by several sources, particularly natural gas. Hydrogen production from methane steam reforming via a membrane reactor with CO_2 capture is a unique method for simultaneously producing and purifying hydrogen and obtaining clean fuel. Methane steam reforming occupies 50% of hydrogen production in the world. CO_2 capture can be divided into three fundamental types: post-, pre-, and oxy-combustion capture. However, carbon capture technologies include adsorption, absorption, membranes, cryogenic/low-temperature separation, or chemical looping combustion. MATLAB, COMSOL, Aspen Plus, and ANSYS These programs solve the governing equations for a sorbent-enhanced membrane reactor. These equations are continuity, mass, and heat transfer. We reviewed the technologies for CO_2 capture related to hydrogen production, containing the types of hydrocarbon input, methods for production, catalyst types, CO_2 capture materials, and operation conditions. Also, we summarized the technologies for CO_2 capture studies in hydrogen production from natural gas steam reforming with membrane systems.

Keywords: Hydrogen Production, CO_2 Capture, Membrane Reactor, Natural Gas Steam Reforming, Adsorption.

Introduction

The growing worldwide concerns about energy, intensified greenhouse gas emissions, constrained storage of fossil fuels, and aggravated global climate change have forced intensive developments searching for environmentally clean, sustainable, and renewable energy supply and efficient hydrogen production [1]. The primary cause of Earth's global warming is increased CO2 caused by human activity. When compared to the mid-19th century, the concentration of CO2 increased by around 38% to 403 ppm in May of 2015[2]. However, as Figure 1 indicated, based on a 2021 study by the International Energy Agency (IEA), the transportation sector generates around 25% of global CO2 emissions, while power coal is responsible for about 28% [3]. Among the various methods that could be used to reduce emissions, the most efficient and economical ways of satisfying environmental regulations are to lower the utilization of fossil fuels through enhancing process efficiency and changing to less carbon-intensive fuels (e.g., natural gas) and/or free-carbon energy sources (e.g., biomass) [4]. One approach to reducing CO2 emissions is through the use of carbon capture, utilization, and storage (CCUS) methods and technologies. By using underground storage facilities or converting them into valuable products, CCUS technologies seek to capture CO2 from major industrial sources [5]. There are several technologies available for carbon capture, including chemical adsorption, membranes, and solid sorbents. The most popular technique for post-combustion CO2 capture is chemical solvent-based adsorption because of its high CO2 removal efficiency, particularly at low partial pressure of CO_2 [6]. The pre-combustion capture method that works best is the application of solid sorbents. The majority of published papers in the open literature focus on solid sorbents at high temperatures, such as lithium zirconate(Li_2ZrO_3) [7],[8], sodium zirconate (Na_2ZrO_3) [9], [10], lithium silicate (Li_4siO_4) [11],[12] and CaO-based sorbents [13], [14]. Up to nearly 100% efficiency, the CO2 capture efficiency rises as pressure rises. The key to the membrane working effectively at greater pressures is to increase its effective permeability area [15]. This study aims to develop an understanding of techniques for capturing CO2 produced through the hydrogen production process, which can be utilized as clean energy for various applications.

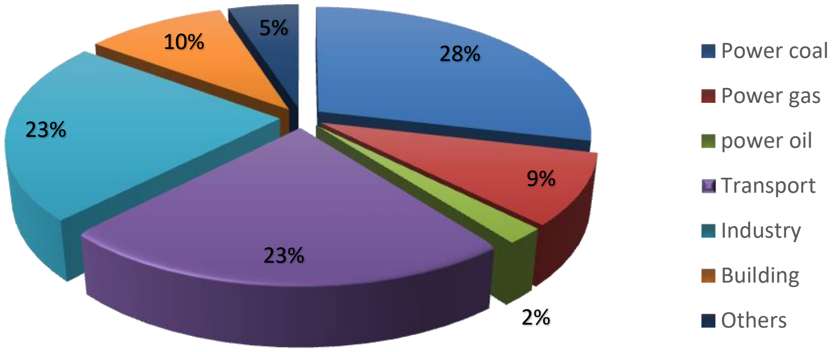


Figure 1: CO_2 emissions.

Hydrogen Production Methods

Hydrogen can be produced in a wide range of non-renewable and renewable ways, with corresponding variations in costs and carbon dioxide emissions. Though it is almost entirely dependent on the reforming and gasification of fossil hydrocarbon sources, such as coal (23%), natural gas (76%), and other sources, which generate 830 million tons of CO2 a year, the method of generating hydrogen today is by no means renewable. The substantial amount of emissions that hydrogen derived from fossil fuels releases is not good for the climate or the environment. Thus, the transition to low-carbon hydrogen production is essential [16]. Figure 2 explains the several methods for producing hydrogen.

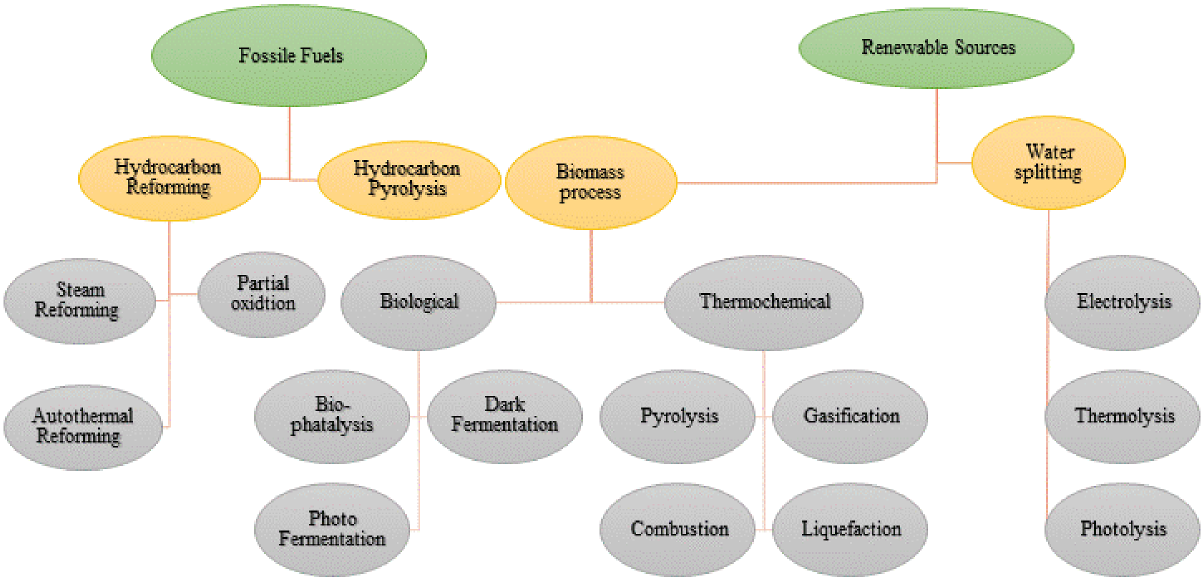


Figure 2: Hydrogen production ways [17].

Hydrogen Production Methods from Natural Gas

1. Steam methane reforming

Steam methane reforming (SMR) is a well-known and commonly used method for producing hydrogen; this process provides more than 80% of the hydrogen that is obtained by SMR [18], in which methane and steam interact to produce hydrogen-rich syngas [19]. In this process, high-temperature steam (700–1000 °C) is utilized to produce H_2 from natural gas, such as methane. In the presence of a catalyst, methane and steam react at a pressure of 3-25 bar to produce H_2, CO, and a tiny amount of CO_2. Steam reforming is endothermic. For the reaction to keep going, heat must be provided to the process [20]. The SMR reaction (R1) is:

$$\mathrm{CH_4 + H_2O \leftrightarrow CO + 3\,H_2} \qquad \Delta H^\circ_{298k} = 206.1\ \mathrm{KJ/mol}$$

On the other hand, about 25% of the toxic gas CO is released together with the H_2yield during reaction (R1). The water-gas shift (WGS) reaction is usually employed to further convert CO into $H_2$and a by-product, CO_2.WGS reacts efficiently only below 450 ºC; consequently, it is used to prevent producing the toxic gas, The WGS reaction (R2) is [10] :

$$\mathrm{CO + H_2O \leftrightarrow CO_2 + H_2} \qquad \Delta H^\circ_{298k} = -41.15\ \mathrm{KJ/mol}$$

Reaction (R3) can be considered as a superposition of (R1) and (R2).

$$\mathrm{CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2} \qquad \Delta H^\circ_{298k} = 165\ \mathrm{KJ/mol}$$

Reaction (R1) is endothermic, while reaction (R2) is exothermic; this means that they can't both obtain high conversion at the same temperature in a single reactor simultaneously. The membrane reactor was developed to facilitate the simultaneous operation of these two reactions (SMR and WGS) in a single reactor with enhanced □2 production and □□4 conversion. Because the membrane is made to be H_2selective, other gas components in the reactor can continue to exist while $H_2$is frequently and partially removed from the reactor through membrane permeation as shown in Figure 3.

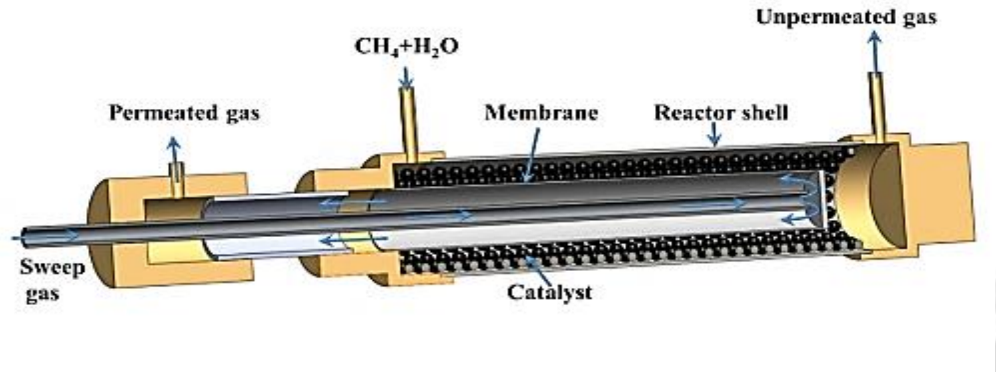


Figure 3: A membrane reactor structure for methane steam reforming [10].

The performance of the MR was investigated using three parameters, namely: methane conversion (X_{CH_4}), hydrogen recovery (HR), and permeate side hydrogen purity (HPP), which are defined [21] :

$$X_{CH_4} = \frac{Q_{CH_4}^{IN} - Q_{CH_4}^{OUT}}{Q_{CH_4}^{IN}} \times 100 \quad (1)$$

$$HR = \frac{Q_{H2}^{Permeate}}{Q_{H2}^{Permeate} + Q_{H2}^{Retentate}} \times 100 \quad (2)$$

$$HPP = \frac{Q_{H2}^{Permeate}}{Q_{Total}^{Permeate}} \times 100 \quad (3)$$

Where $Q_{CH_4}^{IN}$is the molar flow rate of methane entering the MR, and $Q_{CH_4}^{OUT}$is the outlet molar flow rate of methane. $Q_{H2}^{Permeate}$ *and* $Q_{H2}^{Retentate}$are the molar flow rates of hydrogen in the permeate and retentate sides respectively, while $Q_{Total}^{Permeate}$is the molar flow rate of all the gaseous species in the permeate side.

2. Partial oxidation

The method of partial oxidation (POX) is used to extract gray hydrogen from hydrocarbons, mainly natural gas. This technology can be regarded as mature and is available for purchase[22]. Fuel is partially burned in a reformer with a sub-stoichiometric quantity of air, which starts the reaction. In an exothermic process, partial oxidation can be carried out with or without a catalyst [23]. On the other hand, the catalyst greatly raises the reaction yield. CO is produced rather than CO_2 because only partial oxidation of the carbon occurs as a result of the sub-stoichiometric oxygen supply. Nitrogen and hydrogen are the other reaction products if air is used as a substitute for pure oxygen[22].

3. Auto-thermal reforming

The combination of SMR and non-catalytic POX is referred to as ATR. Within a single chamber, methane, oxygen, and steam react [23]. Partial oxidation is the burning of hydrocarbons in an atmosphere with less oxygen than required. The heat exchange between exothermic partial oxidation reactions and endothermic steam reforming is defined by the auto-thermal term. The combustion zone (1900°C) and the conversion zone (900°C–1100°C) are where the process occurs[24]. Methane is partially oxidized by oxygen in the reforming reactor, and the endothermic steam reforming reaction is propelled by the heat produced. The air might theoretically be utilized as an oxygen supply, but pure oxygen is used to prevent hydrogen from being contaminated with nitrogen, which is why an air separation unit (ASU) is required[19].

CO_2 Capture Methods

Carbon dioxide can be separated in power plants using three strategies: post-combustion capture, pre-combustion capture, and oxy-combustion.

1. **Post-combustion carbon capture:** Carbon dioxide is captured from flue gas at low pressure (1 bar) and low CO_2content (3-20%), in general. Separation aims to capture CO_2 from a mixture mostly consisting of nitrogen and oxygen while also considering the effects of flue gas pollutants such as SO_X, NO_X, particulates [26]. Post-combustion carbon capture involves the capturing of CO_2 after fuel combustions (e.g. through the use of membrane separation, chemical looping, physical adsorption, or chemical absorption) [5].

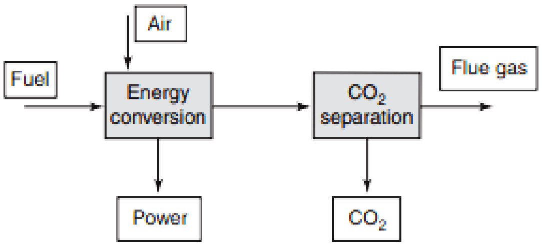


Figure 4: Post-combustion processes[26].

2. **Pre-combustion carbon capture:** Carbon dioxide is captured from a gas mixture with predominantly H_2gas at high pressure (15-40 bar) and medium CO_2content (15-40%) or carbon is produced directly from fossil fuels. In addition to the separation of CO_2 from, the feed gases also consist of CO, H_2S, as well as other Sulphur components [26]. The pre-combustion method is usually used after fuel combustions and involves oxidation (partially) or gasification of fuel materials to produce CO_2 and H_2O, in power plant processes [27].

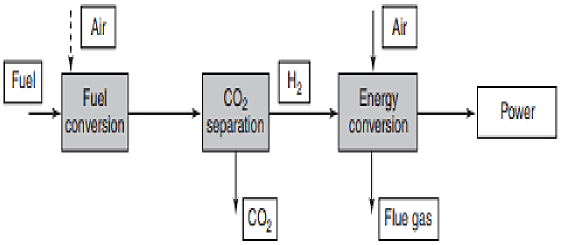


Figure 5: per-combustion processes.

3. Oxy-combustion carbon capture: An alternative method for capturing carbon from fuel gas involves altering the combustion process to increase the amount of CO_2 in the flue gas. Burning the fuel in almost pure oxygen (more than 95%) will allow you to achieve this because the exhaust that results essentially consists of CO_2 and water vapor, which can be easily separated [4][6]**.** This method integrates the pre-combustion and post-combustion capturing methods. It involves gasifying a fuel material to produce steam through oxidation, resulting in nearly pure oxygen [27]. The main advantage of oxy-fuel combustion is the absence of NO_X and SO_X components in the flue gas[28].

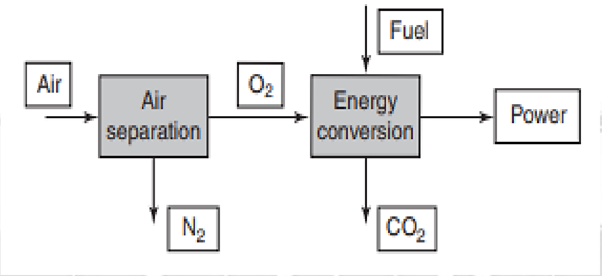


Figure 6: Oxy-combustion processes.

CO$_2$ Separation Technologies

When shifted syngas is produced, hydrogen and CO2 must be purified and separated from the other components. Crucial separating techniques for hydrogen production with CO_2capture include adsorption, absorption, membranes, cryogenic or low-temperature processes, and chemical looping combustion.

1. Adsorption: The physical process of adsorption occurs when molecules connect to surfaces that are adsorbed, usually made of solid materials [23]. Adsorbents that particularly capture CO_2 from a gas mixture, such as lithium zirconate (Li_2ZrO_3), sodium zirconate (Na_2ZrO_3), lithium silicate (Li_4siO_4) and CaO-based sorbents [29], which react with $CO_2$to generate corresponding carbonate [30].

$$Li_2ZrO_3 + \mathrm{CO_2} \leftrightarrow Li_2\mathrm{CO_3} + \mathrm{ZrO_2} \qquad \Delta\mathrm{H°}_{298\mathrm{k}} = -160\ \mathrm{KJ/mol}$$

$$Na_2ZrO_3 + \mathrm{CO_2} \leftrightarrow Na_2\mathrm{CO_3} + \mathrm{ZrO_2} \qquad \Delta\mathrm{H°}_{298\mathrm{k}} = -149\ \mathrm{KJ/mol}$$

$$Li_4SiO_4 + \mathrm{CO_2} \leftrightarrow Li_2\mathrm{CO_3} + Li_2\mathrm{SiO_3} \qquad \Delta\mathrm{H°}_{298k} = -143\ \mathrm{KJ/mol}$$

$$CaO + \mathrm{CO_2} \leftrightarrow \mathrm{CaCO3} \qquad \Delta\mathrm{H°}_{298k} = -178\ \mathrm{KJ/mol}$$

A temperature change is the preferred regeneration method for all the acceptors mentioned above. The most promising options at this time are hydrotalcite-like compounds if a pressure change regeneration arrangement is required. These materials show good kinetics and stability when exposed to $\mathrm{CO_2}$ at temperatures as high as 773 K, but their capacity is extremely low at such elevated temperatures[29]. Adsorption procedures include temperature swing adsorption (TSA), vacuum swing adsorption (VSA), pressure swing adsorption (PSA), and pressure-temperature swing adsorption (PTSA)[5]. Since the syngas is at high pressure and may change in pressure with no energy penalty, PSA is the most significant for the separation of hydrogen and CO_2 from it [23].

2. **Absorption:** To separate industrial gases by absorption, a liquid solvent must be mixed with the gas in a scrubber column, which absorbs some contaminants [23]. Liquid solvents can be divided into chemical and physical solvents. Chemical solvents that are usually used are alkanol amines, such as monoethanolamine (MEA), diethanolamine (DEA), or methyl diethanolamine (MDEA) in aqueous solution. With a purity of over 99.95%, it is estimated that the amine technique can extract between 85 and 95% of the carbon dioxide that exists in flue gas [5]. Typical reactions of CO_2 with MEA for absorbing and regenerating are as follows [31].

Absorbing reactions:

$$\mathrm{MEA} + \mathrm{H_2O} + \mathrm{CO_2} \rightarrow \mathrm{MEA\ carbonate} + \mathrm{heat}$$

Regenerating reactions:

$$\mathrm{MEA\ carbonate} + \mathrm{heat} \rightarrow \mathrm{MEA} + \mathrm{H_2O} + \mathrm{CO_2}$$

Physical solvents, as compared with chemical solvents, may dissolve $\mathrm{CO_2}$ and regenerate with a smaller heat input at higher temperatures as well as lower pressures. Usually, they facilitate the removal of $\mathrm{CO_2}$ and $\mathrm{H_2}S$ together. Conventional technologies utilizing physical solvents include the Purisol, Selexol, and Rectisol processes [23].

3. **Membrane separation:** Membranes are semi-permeable barriers composed of numerous substances that, through a wide range of strategies, can separate different compounds from a mixture [32]. Membranes are often mentioned as possible methods in post-combustion separation [33]. Permeate refers to the part of the feed that gets beyond the membrane, and retentate refers to the part that doesn't. Essential characteristics of membranes include great mechanical stability, high selectivity, high flux, cheap cost, high chemical stability, and high-cost stability [23]. For hydrogen production with CO_2 capture, both hydrogen and CO_2-selective membranes are relevant. CO_2-selective membranes are favored for processes that operate at ambient or sub-ambient temperatures since they are often constructed on rubbery polar polymers. On the other hand, rigid glassy polymers or ceramic and metallic materials are the traditional basis for H_2-selective membranes, which are suited for operations at

elevated temperatures. It has been suggested that these various membrane material types may be employed in syngas applications requiring CO_2separation, such as H_2production plants[34].

4. **Cryogenic/low-temperature separation:** Several species from the gas mixture, such as $CO_2$are liquefied by chilling in a cryogenic process through two or three successive stages of compression, cooling, expansion, and phase separation[3]. Hydrogen separation requires cooling the gas mixture to cryogenic temperatures (<150 °C). Different temperature ranges allow contaminant gases to condense, whereas hydrogen stays in the gas phase[23]. Cryogenic separation is used commercially for waste gas streams that contain more than 90% CO_2 because the technique is only profitable above this concentration [33].

5. **Chemical Looping Combustion (CLC) and Calcium Looping Process (CLP):** Chemical looping technology is a novel technique in the carbon capture sector. This approach to removing carbon dioxide from fossil fuel power plants has the potential to be the most effective and economical one [32]. Instead of applying pure oxygen directly for combustion, as in the case of oxy-fuel combustion, a metal oxide is used as an oxygen carrier. While the fuel is oxidizing to produce CO_2 and water, the metal oxide is converted to metal during the process. After that, the metal undergoes one more stage of oxidation and is recycled. While pure CO_2 can be obtained without requiring energy for separation, water, a by-product of the process, can be easily removed by condensation. Numerous low-cost metal oxides, such as Fe_2, NiO, CuO, and Mn_2O_3 are appropriate for this technique[35]. The calcium looping process is another type of chemical looping. The reversible reaction between carbon dioxide and calcium oxide is the basis of the process. The reaction of connecting CaO and CO_2 is called carbonation [5].

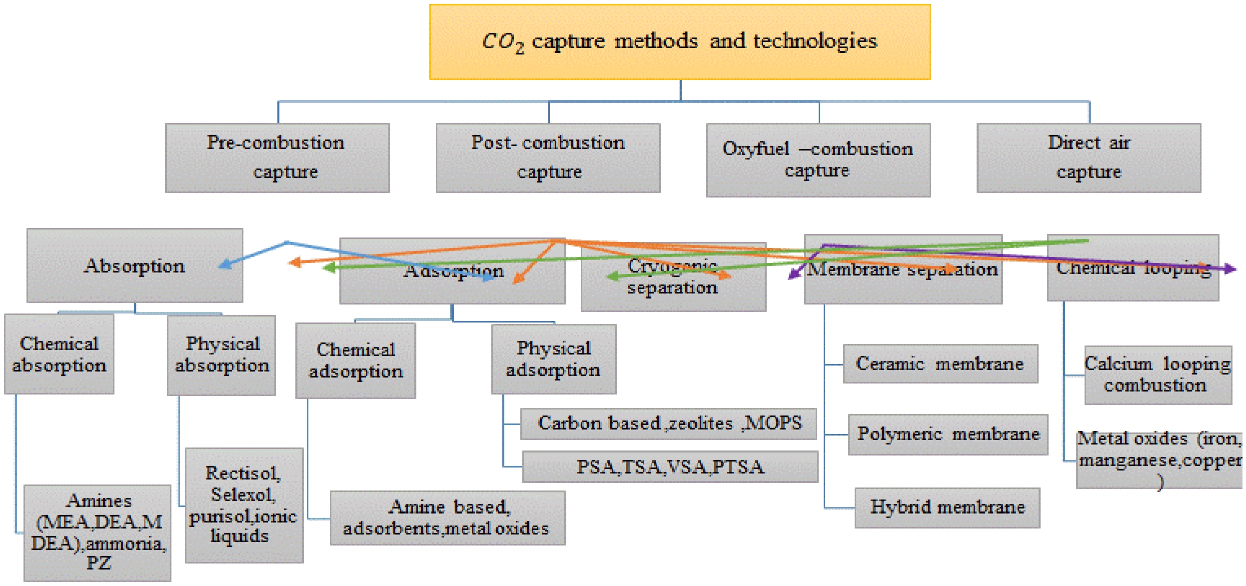


Figure 7: CO_2 capture methods and technologies [36],[33].

Governing Equations

The governing equations of the model consist of the continuity equation (Eq. (4)), the momentum balance equation (Eq. (5)), and the species transport-reaction equation (Eq. (6))[14]:

$$\nabla\left(\varepsilon\cdot u\cdot\rho_f\right)+\frac{\delta}{\delta t}\left(\varepsilon\cdot\rho_f\right)=\pm S_i \tag{4}$$

$$\nabla\left(\varepsilon\cdot u\cdot\rho_f\cdot u\right)+\frac{\delta}{\delta t}\left(\varepsilon\cdot\rho_f\cdot u\right)=-\nabla P-\beta\cdot u+\nabla\tau+\rho_f\cdot g \tag{5}$$

$$\begin{aligned}\nabla\left(\varepsilon\cdot u\cdot\rho_f\right)+\frac{\delta}{\delta t}\left(\varepsilon\cdot\rho_f\right)\\ &=-\nabla\left(\rho_f\cdot D_{i.e}\cdot\nabla m_i\right)+(1\\ &-\varepsilon)\rho M_i\sum_i V_{ij}R_{WGS}\pm S_i-(1\\ &-\varepsilon)\rho M_i\sum_j V_{ij}R_{Ads}\end{aligned} \tag{6}$$

In the equations reported above, i is the chemical component (i $= CH_4, H_2O.$ CO, H_2 *or* CO_2) , j is the reaction number (j = 1, 2, 3, or 4) and β is the friction coefficient given by the following equation (ε = 0.6 and d_p = 5 mm):

$$\beta=\frac{150\mu_f(1-\varepsilon)^2}{\varepsilon\cdot d_p^2}+\frac{1\cdot 75(1-\varepsilon)\rho_f}{\varepsilon^3 d_p}|u| \tag{7}$$

R_{WGS} is the reaction rate of WGS and R_{Ads}adsorption rate of carbon dioxide. Tables 2 and 3 summarize the reaction rates and their related kinetic, equilibrium, and adsorption constants.

Table 2: The reaction rate equations of steam methane reforming and CO_2 capture [10],[50],[51].

Steam Methane Reforming (SMR): $\mathbf{CH_4+H_2O\leftrightarrow CO+3\,H_2}$	$\mathbf{r_1=\frac{k_1}{P_{H_2}^{2.5}}\frac{\left(P_{CH_4}P_{H_2O}-\frac{P_{H_2}^3\,P_{CO}}{K_{e1}}\right)}{DEN^2}}$
Water Gas Shift Reaction (WGS): $CO+H_2O\leftrightarrow CO_2+H_2$	$r_2=\frac{k_2}{P_{H_2}}\frac{\left(P_{CO}P_{H_2O}-\frac{P_{H_2}P_{CO_2}}{K_{e2}}\right)}{DEN^2}$
Direct Steam Reforming Reaction (DSR): $CH_4+2H_2O\leftrightarrow CO_2+4H_2$	$r_3=\frac{k_3}{P_{H_2}^{3.5}}\frac{\left(P_{CH4}P_{H_2O}^2-\frac{P_{H_2}^4\,P_{CO_2}}{K_{e3}}\right)}{DEN^2}$
CO_2Adsorption Reaction: $CaO+CO_2\leftrightarrow CaCO3$	$r_4=\frac{\eta}{M_{CaO}}k_4(X_{Max}-X)(\upsilon_{CO2}-\upsilon_{CO2.eq})$

$\mathrm{DEN} = 1 + K_{CO}P_{CO} + K_{H_2}P_{H_2} + K_{CH_4} + K_{H_2O}\frac{P_{H_2O}}{P_{H_2}}$
$X_{Max} = 96.34\exp\left(-\frac{12171}{T}\right)4.49\exp(\frac{4790.6}{T})$
$\upsilon_{CO2} = \frac{F_{CO2}}{F_{total}}$ $\upsilon_{CO2.eq} = 4.137 \times 10^7\exp(-\frac{20474}{T})$

The mass flow of species across the dense Pd-Ag membrane is clarified by the source/sink term defined in Eq. (8), and the H_2flux is given by Eq. (9) applying Richardson's formula [14]:

$$S_i = \frac{A \cdot J_i\ M_i}{V} \tag{8}$$

$$J_{H_2} = \frac{P_{e_0} \cdot \exp(\frac{-E_{H_2}}{RT})(P^{0.5}_{H_2.retentate} - P^{0.5}_{H_2.permeate})}{\delta} \tag{9}$$

Because Ni-based catalyst is inexpensive and has a high CH_4conversion ,it was the most commonly used catalyst in palladium SMR reactors.

Table 3: The reaction constants of the process [50],[52].

Kinetic-constant coefficients:	$\mathbf{k_1 = 4.22 \times 10^{15}exp(-\frac{240100}{RT})}$
	$k_2 = 1.96 \times 10^6\exp(-\frac{67130}{RT})$
	$k_3 = 1.02 \times 10^{15}\exp(-\frac{243900}{RT})$
	$k_4 = 0.35$
Equilibrium constants:	$K_{e1} = 1.198 \times 10^{13}\exp(-\frac{26830}{RT})$
	$K_{e2} = 1.767 \times 10^{-2}\exp(\frac{4400}{RT})$
	$K_{e3} = 2.117 \times 10^{11}\exp(-\frac{22430}{RT})$
Adsorption constants:	$k_{CH4} = 6.65 \times 10^{-4}\exp(\frac{38280}{RT})$
	$k_{H2O} = 1.77 \times 10^5\exp(-\frac{88680}{RT})$
	$k_{H2} = 6.12 \times 10^{-9}\exp(\frac{82900}{RT})$
	$k_{CO} = 8.23 \times 10^{-5}\exp(\frac{70650}{RT})$

The mass and energy balances are shown below (Eqs. (10)- (12)) [50]:

$$\frac{dF_{i.ret}}{dw} = \sum \varphi_i r_j - r_{i.perm} \tag{10}$$

$$\frac{dF_{i.perm}}{dw} = \sum \pm r_{i.perm} \tag{11}$$

$$\frac{dT}{dw} = \frac{U_{a.c}\,(T_a - T) - \sum r_j \times H_j + (U_{a.R} \times \left(\frac{1}{\frac{1}{W} + \frac{1}{\varepsilon_{gas}} - 1}\right) \times (T_a^4 - T^4)}{\sum F_{i.ret} \times C_{P,i}} \tag{12}$$

The paper's primary goal is to evaluate CO2 capture technologies for hydrogen production in order to reduce CO2 emissions and provide usable, clean fuel for usage in many applications. This study contains the types of hydrocarbon input, methods for production, catalyst types, and CO2 capture materials, as well as the operation conditions. The review will focus on the technologies for CO2 capture in hydrogen production by natural gas steam reforming with membrane systems.

Ghasemzadeh et al.;[14] used a 2D model for a hybrid sorption-enhanced membrane reactor (HSE-MR) for hydrogen production during the WGS reaction. Only hydrogen can pass through the Pd-Ag membrane. A catalyst/sorbent weight ratio of 1/12 was used.H2 recovery was 24% at 1 bar, 51% at 10 bar, and the CO conversion was 90.3% at 1 bar, 99.9% at 10 bar, and 573 K. Through CFD evaluation, it was demonstrated that the HSE-MR system achieved better CO conversion and hydrogen recovery during the WGS reaction than the SER and MR methods. Using COMSOL multiphysics modeling.

Subraveti et al.;[53] The VSA process was simulated utilizing a one-dimensional, non-isothermal mathematical model that was developed by solving mass, momentum, and energy using three different adsorbents in this process, namely, Zeolite 13X, UTSA-16, and IISERP MOF2, which are optimized to reduce the CO_2 capture cost. To evaluate and compare the best techno-economic performances of VSA technology for three adsorbents, (MEA)-based absorption technology was utilized as a baseline situation. Looking at the results, it can be concluded that the four-step VSA process with IISERP MOF2 is greater than the other two adsorbents. It has the lowest CO_2 capture cost of 33.6 € per tonne of CO_2avoided and the lowest CO_2 avoided cost of 73.0 € per tonne of CO_2avoided. UTSA-16 and Zeolite 13X produced CO_2avoided costs per tonne of CO_2 avoided of 104.9 and 90.9 €, respectively. Using MATLAB software.

Ghungrud et al.;[54] investigated sorption-enhanced steam methane reformation using hybrid materials consisting of Ni, Co, and hydrotalcite in an experimental system. The use of multifunctional hybrid materials shows promise for low-temperature on-site CO_2 capture and high-purity hydrogen production. These materials were directed to as $Ni_{10}Co_{30}$/HTlc (or HM_1) and $Ni_{20}Co_{20}$/HTlc (or HM_2) In order to enhance the composite material's basicity and thermal stability, Ce species were subsequently added to these substances. Strongly basic sites for CO_2 adsorption were created by the stimulation with Ce, which enhanced the generation of H_2 . Specifically, Ce-HM_1 exhibited the highest breakthrough time (45 min) and adsorption capacity (1.74 mol CO_2/kg sorbent), whereas Ce-HM_2 exhibited a breakthrough time of 30 min and adsorption capacity (1.51 mol CO_2/kg sorbent), producing >90 mol% H_2 at T =773 K, P = 0.1 MPa, S/ C= 6, and gas hourly space velocity or GHSV=3600 mL/(g-h).

A. Outman et al.;[55] used a conversion-type reactor for hydrogen production via steam methane reforming and CO_2capture, Aspen HYSYS V12.1 was used to evaluate and simulate the catalytic membrane reactor in a steady-state model with varying steam-to -carbon ratios (S/C=1–10). Hydrogen production increased in conjunction with the rise in the S/C ratio. The most efficient solvent for this carbon capture system is determined by simulating three absorbents (MDEA, MEA, and propylene carbonate), where 98.8% of the CO_2 can be adsorbed by this system.

Ji et al.;[10] utilized a CFD model for the steam reforming of methane in the sorption-enhanced membrane reactor (SEMR) using a Ni/Al_2O_3 catalyst and Na_2ZrO_3 as CO_2sorbent. This reactor increases reaction rates, CH_4 conversion, and H_2 yield in addition to lowering the CO_2 fraction and improving the production of hydrogen. 20% of the volume is estimated to be occupied by the sorbent Na_2ZrO_3. Compared to the conventional membrane reactor, the CO fraction level was lowered by 1 order of magnitude in the sorption-enhanced membrane reactor, reducing the chance of H_2 permeation decay. At the output, H_2 fraction is 80.79% mol, reducing outlet CO_2 and CO by more than 95%. Use the ANSYS software.

Wu et al.;[56] A CO_2-permselective membrane reactor was experimentally evaluated for enhancing hydrogen production by the steam reforming of methane (SRM) with CO_2- capture .A ceramic-carbonate dual-phase membrane with a two-layered asymmetric wall structure builds up the membrane reactor. The samarium-doped ceria (SDC) layer forms a thin (~150μm) CO_2-permselective SDC/molten-carbonate dual-phase layer after molten carbonate infiltration, with a small amount of bismuth-yttrium-samarium oxide (BYS) to the support layer to render it non-wettable. The membrane reactor's output product composition shows that the removal of CO_2 in situ efficiently encourages the conversion of water to gas shift in SRM, hence enhancing the yield of hydrogen. utilizing Ni /SiO_2 as a catalyst. 90% hydrogen yield and 84% CO_2 recovery are achieved by the membrane reactor operating at 900 °C and 1 atm of feed pressure.

Lee et al.;[13] A numerical evaluation of five different reactors, an MR with counter-current flow, a PBR, an MR with co-current flow, a SEMR with co-current flow, and a SEMR with counter-current flow, has been carried out utilizing 1-D modeling for reactor design. Because of its inexpensive nature and excellent reactivity, CaO was added as an adsorbent. Based on the process simulation H_2 production rates in a PBR, MR, and SEMR have been determined to be 0.012, 0.011, and 0.012 mol/s, whereas CO_2 emission rates at 773 K were estimated to be 0.003, 0.004, and 0.002 mol/s. A MR had the lowest unit H_2 production cost when compared to the other reactors, as the economic study revealed that the unit H_2 production costs for a PBR, MR, and SEMR were 4.53, 1.98, and 3.04 $ kg H_2^{-1}, respectively. Using Aspen Plus® software.

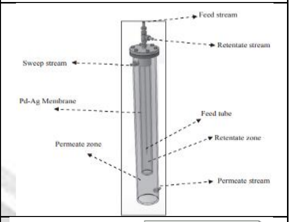
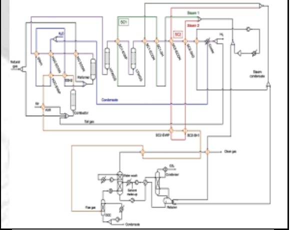
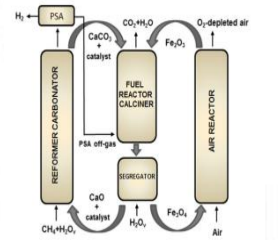
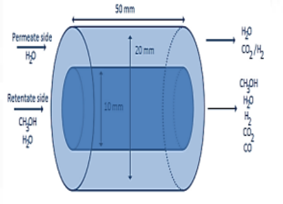
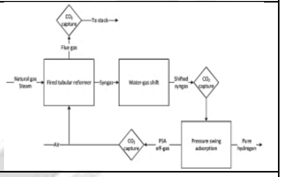
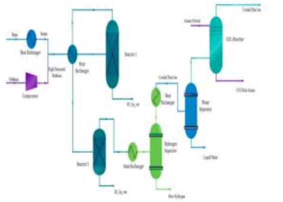
Bang et al.;[57] A Pd-Cu catalytic membrane reactor integrated with PSA via a WGS reaction for hydrogen production was investigated both mathematically and experimentally. By adding additional adsorption beds, the PSA techniques' ability to recover and purify H_2can be improved. The catalytic MR experiments took place using a combination of CO, H_2, and CO_2 (65: 30: 5 vol %) at 300–350 °C and 6–10 bar. As permeate H_2 is a product, the sweeping gas that was used in this process was H_2 . For the WGS process in the developed MR, a commercial high-temperature shift (HTS) catalyst (Sud-Chemie Catalysts, Japan) that included chromium oxide (Cr_2O_3), chromium trioxide (CrO_3), aluminum oxide (Al_2O_3),), and copper oxide (CuO)was used. The investigation showed that H2 was recovered from the retentate using layered two-bed and arranged four-bed PSA techniques . The adsorption beds were filled with activated carbon on the bottom and zeolite 13X on the top at a ratio of 6:4. Zeolite 13X was utilized to adsorb CO, while activated carbon was primarily used to absorb CO_2 in the layered bed. Using a four-bed PSA with integrated Pd-Cu catalytic MR, it was possible to achieve H_2 values of over 99.9991%, 91.37% recovery, and 8.67 ppm CO. The recovery for H_2 produced with less than 0.2 ppm CO was decreased to 85.99% with 0.15 ppm CO.

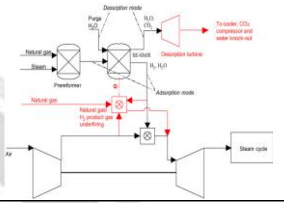
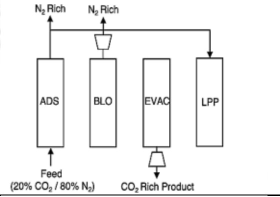
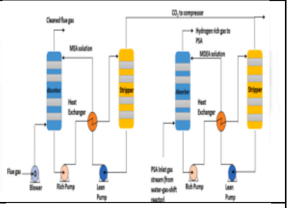
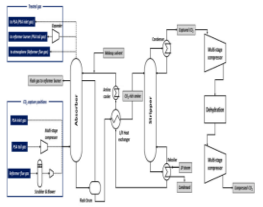
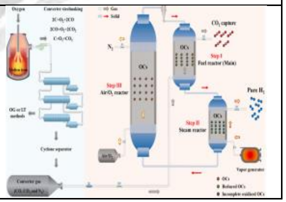
Alrashed et al.; [58] Aspen Custom Modeler (ACM) built a 1D pseudo-homogenous model with a S/C ratio of 3 in order to compare traditional and Pd-Au membrane steam methane reforming (SMR) methods. At 30 bar and 550 ˚C, the membrane SMR method was used. The typical SMR process operates at 900 ˚C and 23 bar at the reforming reactor, where it performs better. The VSA unit was used to remove CO_2 from the other gases. The remaining separated gases are recycled back into the process, and the VSA produces a 90.8% recovered CO_2 stream. The results of this study reveal that, in comparison to the conventional SMR process, the membrane reactor SMR method has a greater methane conversion and hydrogen yield by 4% and 20%, respectively. Additionally, it provides a 10% increase in process energy efficiency compared to the traditional method, which lowers the cost of producing hydrogen. The costs for producing hydrogen with membrane SMR and conventional techniques were found to be 2.87 and 4.54 $/kg H_2 , respectively.

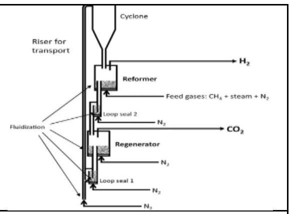
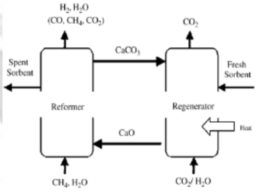
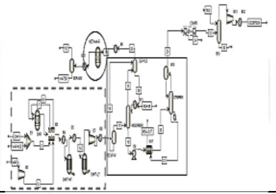
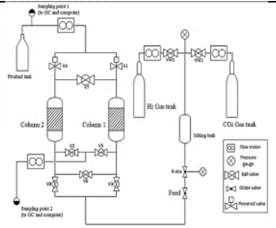
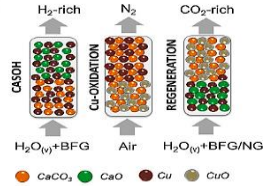
Abbasi et al., [59] Applying a steady-state, one-dimensional heterogeneous catalytic reaction model, the effectiveness of chemical looping combustion (CLC) in a steam reformer with Pd-Ag hydrogen perm-selective membranes (CLC-SRM) support for CO2 capture and hydrogen synthesis was investigated. With AR operating in the rapid fluidization regime and FR operating in the bubbling fluidization regime, CLC is composed of two interconnected fluidized bed reactors. NiO18-αAl2O3 particles have been used as oxygen carriers in CLC. In contrast to a conventional steam reformer (CSR), the simulation results of the CLC-SRM show an increase in methane conversion and hydrogen production of 7.54% and 25.48%, respectively.

Joo et al., [60] designed a 1D model integrating the on-site SMR process for blue hydrogen production with the HFMMs. The SMR-HFMM model was developed and implemented using three possible locations for CO2 capture: dry syngas, PSA tail gas, and flue gas. Five significant performance elements were also used to assess the HFMMs' performance. Every scenario demonstrated excellent CO2 capture performance, and workable values for the quantity of HFMMs were also suggested. The study suggested that on-site SMR with the HFMM process might one day provide an answer to the CO2 emission issue facing on-site SMR facilities.

Table 4: Summarized technologies for CO_2 capture in hydrogen production studies.

No.	Ref.	Technique	Production Method	Condition	feedstock	Catalyst & CO_2 capture Material	Study type	Configuration
1	[14]	HSEMR (Pd-Ag)	Steam reforming	T=573K P=(1-10)bar	Methanol	$Cu/ZnO/Al_2O_3$&K_2CO_3	Numerical study	
2	[61]	chemical absorption	Steam reforming	T=1050℃ S/C=3-5	Methane	-& CESAR1	Numerical study	
3	[62]	Adsorption (PSA)+CLC	Steam reforming	T=670℃ P=1 bar S/C=2.5	Methane	Ni/Al_2O_3 &CaO/Fe_2O_3	Experimental study	
4	[63]	FBMR	Steam reforming	T=453-513K P=1-3 bar S/C=1.5	Methanol	Ni/Al_2O_3 &porous membrane filled with ionic liquids-ILs	Experimental and Numerical study	
5	[64]	chemical absorption	Steam reforming	T=125℃ S/C=2.83	Methane	Ni &MDEA	Numerical study	
6	[65]	Adsorption	Steam reforming	T=650℃ P=1bar S/C=3	Methane	Ni/ Cao $-Ca_{12}Al_{14}$	Numerical study	-
7	[55]	chemical absorption	Steam reforming	T=800 − 1000℃ P=14-20 atm S/C=1-10	Methane	-&MDEA, MEA, Propylene carbonate	Numerical study	

8	[54]	Adsorption	Steam reforming	T =773 K P = 1 bar S/C= 6	Methane	$Ni_{10}Co_{30}$/ HTIc and $Ni_{20}Co_{20}$/ HTIc	Experimental study	-
9	[66]	Adsorption	Steam reforming	T=550℃ S/C=4 CaO=0.5 - 4.5	Acetic acid	Ni/ $Ce_xZr_{1-x}O_2$ -CaO	Experimental study	-
10	[67]	Adsorption	Steam reforming	T=400 °C P= 17 bar S/C=3	Methane	- & Hydrotalcite	Numerical study	
11	[68]	Adsorption	Steam reforming	T=650 °C P= 1 bar S/C=3.4	Methane	Ni/Cao $- Ca_{12}Al_{14}$	Experimental study	-
12	[53]	Adsorption 4-step VSA	Steam reforming	T=353.15 K P=1.02 bar	Methane	- & Zeolite 13X, UTSA-16, and IISERP MOF2	Numerical study	
13	[69]	chemical absorption	Steam reforming	T=100-125°C	Methane	MEA - & and MDEA	Numerical study	
14	[70]	chemical absorption	Steam reforming	P=1-1.3 bar CO2= 21-22%	Methane	-& MDEA/PZ and MEA	Numerical study	
15	[71]	Adsorption	Steam reforming	T=925℃ 100 vol% CO2	Methane	Ni/ Cao $/Ca_{12}Al_{14}O$	Experimental study	-
16	[72]	CLC	Steam reforming	T=650℃	LDG	Ni and Mg & wt%$Ce_{0.75}Zr_{0.25}O_2$ $/Fe_2O_3$	Experimental study	

17	[73]	Adsorption	Steam reforming	T=575°C P=1 bar S/C=4	Methane	NiO/$NiAl_2O_4$&CaO	Experimental study	
18	[51]	Adsorption	Steam reforming	T=923-1023°C P=1-35 bar S/C=3-7	Methane	Ni/ Al_2O_3 &CaO	Numerical study	-
19	[74]	Adsorption	Steam reforming	T=600°C P=1.031 bar S/C=3	Methane	Ni/Dolomite	Experimental study	
20	[75]	Adsorption	Steam reforming	T=650°C P=1bar S/C=4	Methane	Ni/ $MgAl_2O_4$ $- Al_2O_3$& C $- Ca_{12}Al_{14}$	Numerical study	-
21	[76]	Chemical absorption	Auto-Thermal Reforming	T=1200K P=40 atm	Methane	Fe-Cr oxide& MEA	Experimental Study	
22	[77]	Adsorption PSA	Steam reforming	T=30°C P=3bar	Methane	-&PKS activated carbon	Experimental study	
23	[78]	Adsorption	Steam reforming	T=923°C P=0.1MPa S/C=4	Methane	Ni/ CaO $- Ca_5Al_6O_1$	Experimental study	-
24	[79]	Ca–Cu chemical looping	Steam reforming	T=600-650°C P=5bar S/CO=2	BFG	CuO/ Al_2O_3 &CaO	Experimental study	

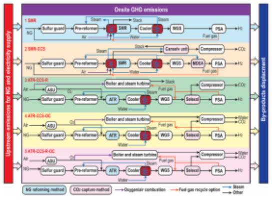
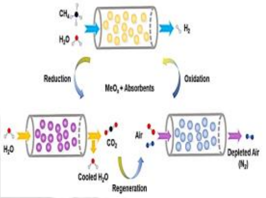
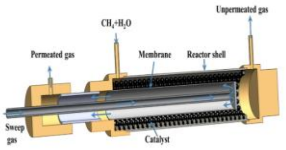
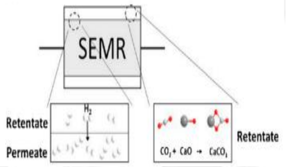
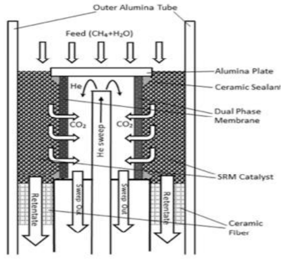
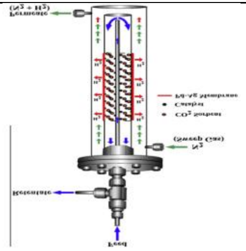
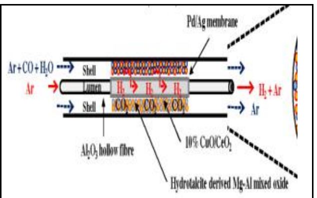
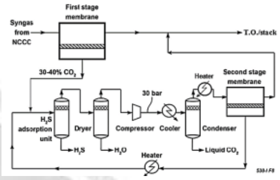
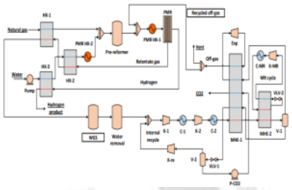
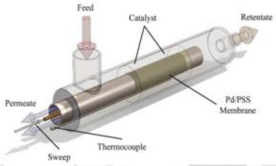
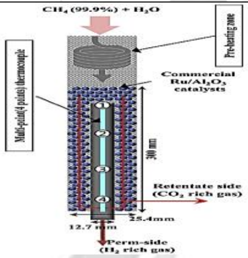
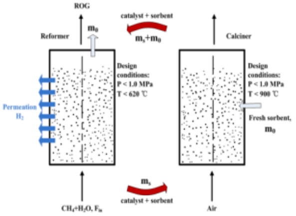
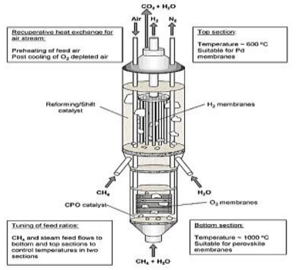
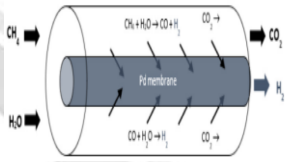
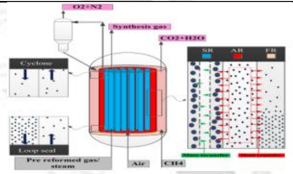
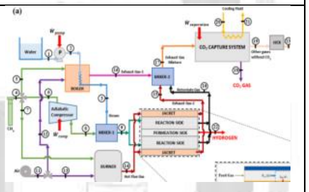
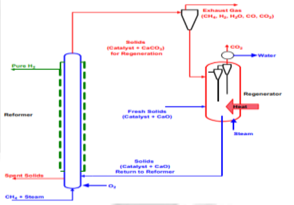
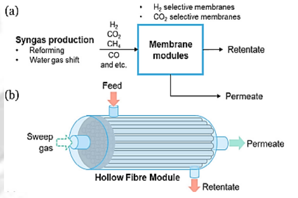
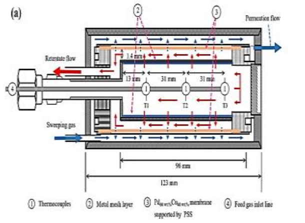
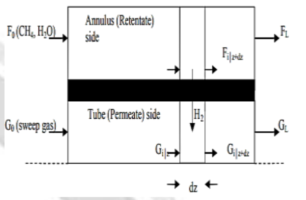
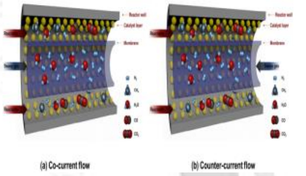
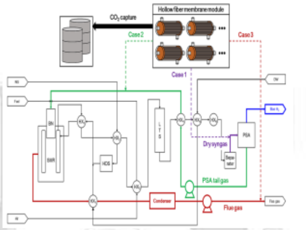
25	[80]	Chemical and physical Absorption	Auto-thermal reforming	T=430-871°C P= 28-33 bar	NG	Ni & MDEA ,Cansolv and Selexol	Numerical study	
26	[81]	sorption-enhanced chemical looping reforming	Steam reforming	T=550-650°C P=1-2 bar S/C=3	Methane	Fe-Ni & K_2CO_3 – Promoted	Experimental study	

Table 5: Summary of technologies for CO_2 capture in hydrogen production from natural gas steam reforming with membrane systems studies.

No.	Ref.	Technique	Condition	Catalyst	Adsorbent	Study type	Configuration
1	[10]	SEMR (Pd)	T=500℃ Poutlet=0.3 MPa S/C =3	Ni /Al_2O_3	Na_2ZrO_3	Numerical study	
2	[13]	SEMR (Pd)	T=773-973K P=3 bar S/C=3	NiO/ Al_2O_3	CaO	Numerical study	
3	[56]	MR (BYS-SDC ceramic-carbonate)	T=700-900 ℃ P= 1 atm S/C=3	Ni /SiO_2	-	Experimental Study	
4	[82]	HSEMR (Pd-Ag)	T=250-300℃ P=3.5-5.5 bar	Cu/ZnO/ Al_2O_3	K_2CO_3 – promoted (MG30-K) hydrotalcite	Experimental Study	

5	[25]	SEMR Tubular(Pd/Ag)	T=(100-550) ℃ P=1 atm	10% CuO/CeO2	A hydrotalcite-derived Mg–Al mixed oxide	Experimental Study	
6	[83]	MR (Polaris thin film composite)	T= 230 ℃ P=13.4 bar	-	-	Experimental Study	
7	[84]	MR (Protonic membrane) +CO2 liquefaction	T=800 ℃ P=26 bar	Ni/ $BaZrO_3$	-	Numerical study	
8	[21]	MR (Pd)	T=673K P=100-400 KPa S/C=3.5	Ni/Al_2O_3	zeolite 13X	Experimental Study	
9	[85]	MR (Pd/PSS)	T= 773K ΔP =500kPa S/C=3	Ru/Al_2O_3	-	Experimental Study	
10	[15]	SE- FBMR	T= 550 ℃ P =0.2-1 MPa S/C=4	-	CaO	Numerical study	

11	[86]	FBMR (Pd)	T= 550-650 °C P =2-4 bar S/C=4	catalyst/ Al_2O_3	-	Experimental Study	
12	[58]	Hybrid VSA-MR (Pd-Au)	T= 550 °C P =30 bar S/C=3	Ni/ $MgAl_2O_3$	-	Numerical study	
13	[59]	CLC-SRM (Pd-Ag)	T= 818°C P =10-20 bar	$NiO_{18}/\alpha Al_2O_3$	-	Numerical study	
14	[87]	MR (Pd-23%Ag) + CO_2 capture system	T= 773K P =9 bar S/C=3/1	Ni/Al_2O_3	-	Numerical study	
15	[88]	SE- FBMR (Pd)	T= 823K P=1000 KPa S/C=3	-	CaO	Numerical study	
16	[89]	MR (a hollow fiber)	T= 313.15 K P=20 bar	-	-	Numerical study	
17	[90]	MR (Pd–23%Ag)	T= 450 °C P =50 barg	-	-	Experimental Study	-

18	[57]	MR (Pd−Cu)+ 4bed PSA	T=360–380℃ P= 6–10 bar S/C=1-5	Al_2O_3, Cr_2O_3 , CrO_3 and CuO	activated carbon and zeolite 13X	Experimental and Numerical Study	
19	[91]	PBIMR (Pd/Ag)	T= 500 ℃ P =1bar S/C=3	Ni/Al_2O_3	-	Numerical study	
20	[50]	SEMR (Pd−Ru)	T=(673-873) K P=1 bar	Ni/ $MgAl_2O_3$	CaO	Numerical study	
12	[60]	SMR–HFMM (polymer-based membrane)	T=(700-850) ℃ P= 8.8 bar	-	-	Experimental and Numerical Study	

Summary

After reviewing the previously described study, we came to the following conclusions:

- The most widely used and inexpensive method to produce hydrogen from natural gas involves steam methane reforming.
- In addition to discussing new carbon dioxide capture methods and technologies, this study looks at significant technologies that use oxy-, post-, and pre-combustion methods.
- Sorption-enhanced membrane reactor (SEMR) is shown to be the most effective technique, surpassing both standalone membrane and adsorbent reactors in terms of CO_2 capture efficiencies and higher H_2 yield.
- ANSYS, Aspen Plus, MATLAB, and COMSOL These software programs are used to simulate the experimental data, evaluate the fundamental concepts of mass, momentum, and energy in a process, and compare the modeling and simulation results with actual outcomes.

Acronyms list

HSE-MR	Hybrid sorption-enhanced MR
MR	Membrane reactor
SE	Sorption-enhanced
SER	Sorption-enhanced reactor
SMR	Steam methane reforming
POX	Partial oxidation
ATR	Auto-thermal reforming
NG	Natural gas
DACC	Direct Air Carbon Capture
HTSE	High Temperature Steam Electrolysis
CFD	Computational fluid dynamics
SRM	Steam Reformer Assisted by Membranes
MDEA	Methyl-diethanolamine
MEA	Monoethanolamine
PZ	Piperazine
Pd	palladium
MA-GSR	Membrane-assisted gas switching reforming
FBMR	Fluidized bed membrane reactor
PBIMR	Packed bed inert membrane reactor
HFMM	Hollow fiber membrane module
PSS	Porous stainless steel
WGS	Water gas shift
CCS	Carbon capture and storage
CCUS	Carbon capture, utilization, and storage
GHG	Greenhouse gas
ASU	Air separation unit
CMS	Carbon molecular sieves
CLC	Chemical looping combustion
CLR	Chemical looping reforming
LDG	Linz-Donawitz converter gas
PKS	Palm kernel shell

CESAR1	An aqueous blend of 13 wt% of piperazine and 27 wt% of 2-Amino-2- methyl-1-propanol – AMP
BFG	blast furnace gases
S/C	steam to carbon ratio
S/B	steam to biomass ratio

Nomenclature

V_{ij}	Stoichiometric coefficient
m_i	mass fraction of species i
ε	Void fraction of the packed bed
S_i	sink/source that indicating the flux of permeation of the i component through the Membrane.
M_i	Molecular weight of ith compound, g/ mole.
D	Diameter (m)
d_p	Catalyst diameter (m)
R	Gas constant coefficient (8.314 kJ/kmol.k)
T	Temperature (k)
r_j	The reaction rate of j (kmol/m^3.s)
k_1, k_3	Methane Kinetic-constant coefficients (kmol .pa$^{0.5}$ /(kg.s)
k_2	Methane Kinetic-constant coefficient (kmol /(pa.kg.s))
k_4	Carbon dioxide Kinetic-constant coefficient
K_{e1}, K_{e3}	Methane equilibrium constant reactions, (pa $^{-1}$)
K_{e2}	Methane equilibrium constant reaction
$K_{CH4}\ K_{CO}\ K_{H2}$	CH_4 , CO and H_2 constants of adsorption (pa $^{-1}$)
K_{H2O}	H_2O constant of adsorption
u	velocity (m/s)
F_i	Molar flow rate (mol /s)
P	Total pressure (bar)
P_i	Partial pressure of component i (bar)
E_{H2}	the apparent activation energy (kJ/mol)
P_{e0}	the pre-exponential factor (mol/m^2.s .bar$^{0.5}$)
$F_{i.perm}$	Molar flow rate of compound i in the permeate side (mol/s)
$F_{i.ret}$	Molar flow rate of i in the retentate side(mol/s)
φ_i	Stoichiometric coefficient of component i

r_j	Reaction rate of j (mol/m^3.s)
$r_{i.perm}$	Permeation rate of i (mol/m^3.s)
T_a	Wall temperature(K)
$U_{a.C}$	Convection heat transfer coefficient (W/m^2.K)
$U_{a,R}$	Radiation heat transfer coefficient(W/m^2.K)
w	Catalyst weight(g)
υ_{CO2}	Gas phase CO_2 mole fraction
$\upsilon_{CO2\,,eq}$	Equilibrium CO_2 mole fraction
X_{MAX}	Maximum carbonation conversion fraction of adsorbent
ε_{gas}	Emissivity coefficient
η	Effectiveness factor
$C_{p.i}$	Heat capacity of i (J/kg.K)
H_j	Heat of reaction j (kJ/mol).

Greek letter

ε	Porosity of the catalyst
μ	Gas viscosity ($kg \cdot m^{-1} s^{-1}$)
ρ_f	Density of fluid ($kg \cdot m^{-3}$)
δ	Membrane thickness (m)

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مراجعة: تقنيات التقاط ثاني أكسيد الكربون في إنتاج الهيدروجين من الإصلاح البخاري للغاز الطبيعي باستخدام أنظمة الأغشية

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الخلاصة

يُعَدُّ الغاز الطبيعي من أبرز المصادر المستخدمة في إنتاج الهيدروجين. ويشكل إنتاج الهيدروجين من الميثان عبر الإصلاح البخاري باستخدام مفاعل غشائي مع التقاط ثاني أكسيد الكربون طريقة متقدمة تجمع بين إنتاج الهيدروجين وتنقيته، إلى جانب الحصول على وقود نظيف. يمثل الإصلاح البخاري للميثان حوالي 50% من إجمالي إنتاج الهيدروجين عالميًا. يمكن تصنيف تقنيات التقاط ثاني أكسيد الكربون إلى ثلاث فئات رئيسية: التقاط ما بعد الاحتراق، والتقاط ما قبل الاحتراق، والتقاط احتراق الأكسجين. وتشمل طرق التقاط الكربون الامتزاز، والامتصاص، والأغشية، والفصل بالتبريد أو عند درجات الحرارة المنخفضة، والاحتراق الكيميائي الدائري. تُستخدم بعض البرمجيات المتقدمة لحل المعادلات الحاكمة لمفاعل الأغشية المعزز بالممتز، والتي تشمل معادلات الاستمرارية، وانتقال الكتلة، وانتقال الحرارة. تستعرض هذه المراجعة تقنيات التقاط ثاني أكسيد الكربون في إنتاج الهيدروجين، مع التركيز على أنواع المدخلات الهيدروكربونية، وطرق الإنتاج، وأنواع المحفزات، ومواد التقاط ثاني أكسيد الكربون، وظروف التشغيل. كما تلخص أبرز الدراسات حول تقنيات التقاط ثاني أكسيد الكربون في إنتاج الهيدروجين من الإصلاح البخاري للغاز الطبيعي باستخدام أنظمة الأغشية.

الكلمات الدالة:-إنتاج الهيدروجين، التقاط ثاني أكسيد الكربون، مفاعل غشائي، الإصلاح البخاري للغاز الطبيعي، الامتزاز.