

Review

Advancements in sorption-enhanced steam reforming for clean hydrogen production: A comprehensive review



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ABSTRACT

The sorption-enhanced steam methane reforming (SE-SMR) process, which integrates methane steam reforming with in situ CO₂ capture, represents a breakthrough technology for clean hydrogen production. This comprehensive review thoroughly explores the SE-SMR process, highlighting its ability to efficiently combine carbon capture with hydrogen generation. The review evaluates the mechanisms of SE-SMR and evaluates a range of innovative sorbent materials, such as CaO-based, alkali-ceramic, hydrotalcite, and waste-derived sorbents. The role of catalysts in enhancing hydrogen production within SE-SMR processes is also discussed, with a focus on bi-functional materials. In addition to examining reaction kinetics and advanced process configurations, this review touches on the techno-economic aspects of SE-SMR. While the analysis does not provide an in-depth economic evaluation, key factors such as potential capital costs (CAPEX), operational expenses (OPEX), and scalability are considered. The review outlines the potential of SE-SMR to offer more efficient hydrogen production, with the added benefit of in situ carbon capture simplifying the process design. Although a detailed economic comparison with other hydrogen production technologies was not the focus, this review emphasizes SE-SMR's promise as a scalable and flexible solution for clean energy. With its integrated design, SE-SMR offers pathways to industrial-scale hydrogen production. This review serves as a valuable resource for researchers, policymakers, and industry experts committed to advancing sustainable and efficient hydrogen production technologies.

1. Introduction

The emission of greenhouse gases (GHG) is a significant global environmental issue due to its impact on climate change. On December 12, 2015, the world witnessed the commitment of 197 countries to address the effects of climate change during the Conference of the Parties of the United Nations Framework Convention on Climate Change (UNFCCC) (COP21), with 189 countries having ratified the Agreement. Under the agreement, the countries are now required to reduce their greenhouse gas GHG emissions to limit the increase in global temperature to a maximum of 2°C, with an aspirational goal of limiting it to 1.5°C by the end of this century (Antar et al., 2021). Also, in November 2022, the Arab

Republic of Egypt hosted the 27th Conference of the Parties (COP27). A key highlight of COP27 was the decision to transition to globally to a low carbon footprint, addressing the significant challenge posed by climate change. Achieving the climate change targets from COP21 to COP27 will require a 60% reduction in carbon emissions from the energy and industrial sectors, especially considering that fossil fuels currently account for 80% of the world's primary energy sources (Masoudi Soltani et al., 2021).

For decades, implementing carbon capture, utilization and storage (CCUS) has been recognized as an effective strategy for mitigating greenhouse gas emissions in various industries (Farooqi et al., 2023). Broadly, there are three primary approaches to capturing carbon from fossil-fuel-fired processes: pre-combustion, oxy-fuel combustion and post-combustion (Chen & Yang, 2021). Among these, post-combustion carbon capture, which employs amine-based solvents is widely utilized in industries to capture CO₂ from flue gas streams (Shahid et al., 2020).

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Nomenclature

List of abbreviations

SE-SMR	Sorption-enhanced steam methane reforming
CCS	Carbon capture and storage
ATR	Autothermal reforming of methane
UNFCCC	United Nations Framework Convention on Climate Change
GHG	Greenhouse gases
CCUS	Carbon capture, utilization and storage
WGS	Water gas shift
SMR	Steam methane reforming
SEP	Sorption enhanced processes
MEA	Monoethanolamine absorption
PSA	Pressure swing adsorption
GTI	Gas Technology Institute
BEIS	Business, Energy and Industrial Strategy
TGA	Thermogravimetric analysis
HTI	Hydrotalcite sorbents
LDH	Layered double hydroxide
PXRD	Powder X-ray diffraction
TEM	Transmission electron microscopy
EDX	Energy-dispersive X-ray spectroscopy
DFT	Density functional theory
WGSr	Water gas shift reaction
CLC	Chemical looping combustion
CLR	Chemical looping reforming
PCC	Post combustion carbon capture
LCOH	Levelized cost of hydrogen

List of symbols

MWth	Megawatt
kWth	Kilowatt
PCH ₄	Partial pressure of methane (kPa)
PH ₂ O	Partial pressure of steam (kPa)
PCO ₂	Partial pressure of CO ₂ (kPa)
PH ₂	Partial pressure of H ₂ (kPa)
ap	Specific surface area (m ² /m ³)
A	Cross sectional area (m ²)
r	Rate of reaction
Ea	Activation energy (kJ/mol)
F	Molar flow rate (kmol/h)
k	Kinetic constant (1/s)
Ni	Moles of species i
Mi	Molecular weight of species i
P	Pressure (Pa)
X _{CH₄}	Conversion of CH ₄
T	Temperature (K)
t	Time (s)
V	Volumetric flowrate (m ³ /h)
ΔH _R	Heat of reaction (kJ/mol)
yi	Mole fraction of gas species
xi	Mole fraction of liquid species
μ	Viscosity (Pa.s)
λ	Thermal conductivity (W/m K)
ρ	Density (kg/m ³)
ε	Volumetric fraction
ω	Mass fraction of component

In pre-combustion CO₂ capture, syngas-composed mainly of CO and H₂ are produced through lean oxygen combustion processes. This syngas is subsequently converted into CO₂ and H₂ via the water gas shift (WGS) reaction (CO+H₂O⇌CO₂+H₂). One key advantage of pre-combustion CO₂ capture is the presence of CO₂ at high partial pressures, which significantly enhance the efficiency of the capture process (Navik et al.,

2024). Hydrogen (H₂) is one of the most environmentally friendly alternatives to fossil fuels for generating heat and energy (Farooqi et al., 2022). It is a highly efficient and environmentally friendly energy source with a high energy density of 120 MJ/kg and a carbon-neutral footprint. This ‘carbon-neutral footprint’ means that the production and use of H₂ do not contribute to the accumulation of greenhouse gases in the atmosphere, making it an excellent alternative to meet the increasing energy demands and combat the climate issues caused by CO₂ emissions (Farooqi, Yusuf, Mohd Zabidi, et al., 2021; Sikarwar et al., 2016). In a perfect scenario, the combustion of hydrogen would only produce water vapor, without any harmful pollutants (Nemitallah et al., 2021; Osman et al., 2022). Although classified as a low-carbon fuel, most hydrogen production methods are associated with substantial carbon emissions. The steam-methane reforming (SMR) process is the primary commercial method for hydrogen production; however, additional methods include electrolysis, thermolysis, biomass gasification, biocatalysis, and fermentative processes (Farooqi, Yusuf, Ishak, et al., 2021; Shamsudin et al., 2019). The hydrogen market is projected to increase from 70 million tons in 2019 to 120 million tons in 2025 (Atilhan et al., 2021; Safari & Dincer, 2020).

Hydrogen production plays a critical role in the transition towards a sustainable and low-carbon energy system. As a promising energy alternative, H₂ has been widely used in fuel cells and iron-making processes due to its high calorific value, good thermal conductivity, high utilization rate and pollutant-free products (Alves et al., 2013; Chen et al., 2020, 2022; Kovač et al., 2021; Liu et al., 2021; Sürer & Arat, 2022). The increasing demand for clean energy sources has led to a growing focus on hydrogen as a viable solution for decarbonization (Oliveira et al., 2021). However, large-scale hydrogen production presents cost, efficiency, and environmental challenges. Hydrogen possesses significant potential as a clean energy source, making it suitable for various applications, including gas turbine combustors where hydrogen can be utilized as a fuel to replace or blend with traditional hydrocarbon fuels (Aliyu et al., 2016). Additionally, hydrogen can be used to enrich oxy-methane premixed flames enhancing the reaction rates (Imteyaz et al., 2018; Nemitallah et al., 2019). These applications highlight the potential of hydrogen to play a vital role in achieving cleaner and more efficient combustion processes, contributing to the transition towards a sustainable energy future.

Several renewable and non-renewable technologies are available for hydrogen production. However, non-renewable technologies such as SMR and coal gasification are the most established technologies on a commercial scale (Shahid & Kim, 2023). The main drawback of these conventional technologies is the high CO₂ emissions. In the SMR process, methane reacts with steam to produce syngas at high temperatures in the reformer. The reformer furnace is typically operated by burning natural gas, resulting in CO₂ emissions. Additionally, more CO₂ is produced as a by-product when the syngas is converted into more hydrogen via a WGS reaction. To reduce CO₂ emissions, amine-based CO₂ capture systems are integrated with the SMR or coal gasification plants to produce blue hydrogen, which significantly increase the cost of hydrogen production (Andrews, 2020; Shahid & Kim, 2023). An alternative approach, sorption enhancement has been identified for capturing CO₂ in the SMR process. This technology offers substantial benefits, allowing a single reactor to perform both SMR and the WGS reaction with in-situ CO₂ capture. This process promotes the WGS reaction and significantly improves the hydrogen yield compared to the conventional method (Sikarwar et al., 2022).

In recent years, extensive research has focused on sorption-enhanced processes (SEP), particularly sorption-enhanced steam methane reforming (SE-SMR), to develop effective sorbents, catalysts, and combined sorbent-catalyst bi-functional materials. Several review articles have discussed the progress on SEP. For instance, Soltani et al. (2021) provided an in-depth review of the SE-SMR process, covering fundamental concepts, kinetics, sorbent development, process configurations, and applications of artificial intelligence. Similarly, Sikarwar et al. (2022) com-

prehensively examined SEP advancements, including adsorbent synthesis, kinetics, pilot scale developments and economic evaluations. Wang et al. (2021) explored various types of sorbents, such as CaO-based, alkali metal-based and hydrotalcite-based materials, while briefly discussing their advantages and limitations. Nevertheless, the present review delves deeper into pivotal aspects of hydrogen production, aiming to enhance understanding and foster innovation within the low-carbon economy. It addresses critical topics such as hydrogen role as a clean energy carrier, the fundamental principles of SE-SMR, an investigation into the different types of sorbents and bifunctional materials to optimize hydrogen production efficiently, reaction kinetics, SE-SMR innovative process configurations, techno-economic analysis and key challenges. Furthermore, it explores future directions, offering valuable insights for this essential field.

2. Low-carbon economy and hydrogen production technologies

Hydrogen has emerged as a crucial component in the quest for a low-carbon economy, offering a versatile and clean energy carrier with the potential to revolutionize multiple sectors. With zero greenhouse gas emissions and high energy density, hydrogen presents a promising solution for reducing carbon emissions and mitigating climate change impacts. Depending on the method of hydrogen production, a commonly used classification of the hydrogen obtained is grey hydrogen, produced by reforming fossil fuels; blue hydrogen, which is produced using CCUS, and green hydrogen, which is produced using renewable energy sources like wind, solar, nuclear, geothermal, biomass, and hydropower (Atilhan et al., 2021; Hasnain et al., 2024). To meet the rising

demand for clean energy, several hydrogen production technologies are available (Yu et al., 2021). These techniques fall into four categories: thermochemical (Guban et al., 2020), electrochemical (Dotan et al., 2019), Biological (Luo et al., 2021), and photocatalytic production (Pal et al., 2022). Fig. 1 illustrates the various methods for hydrogen production systems, including thermochemical, electrochemical, biological, and photocatalytic production. These methods are widely utilized in various sectors, such as petrochemicals, refineries, ammonia production, and fuel cells.

In thermochemical hydrogen generation systems, hydrogen is produced through high-temperature reactions with feedstocks. These techniques include biomass gasification (Mishra et al., 2023), auto thermal reforming (Oni et al., 2022), partial oxidation (Wang et al., 2022), and steam methane reforming (Ben-Mansour et al., 2023) as shown in Fig. 2. The most popular technique for producing hydrogen on a large-scale is SMR. Methane from natural gas is reacted with steam at high temperatures (about 700–1000°C) in the presence of a catalyst, typically nickel-based (Luo et al., 2021).

Hydrogen can be generated via electrochemical water splitting, an environmentally friendly and renewable method. This approach involves using an electric current to separate water molecules into hydrogen and oxygen. The process occurs within an electrolyzer comprising an electrolyte solution and two electrodes—an anode and a cathode. The hydrogen produced through this electrochemical water-splitting process can be classified as “green” hydrogen since it is generated using renewable electricity instead of fossil fuels (Anwar et al., 2021).

Hydrogen can be produced through biological processes using microorganisms or their enzymes. Compared to traditional

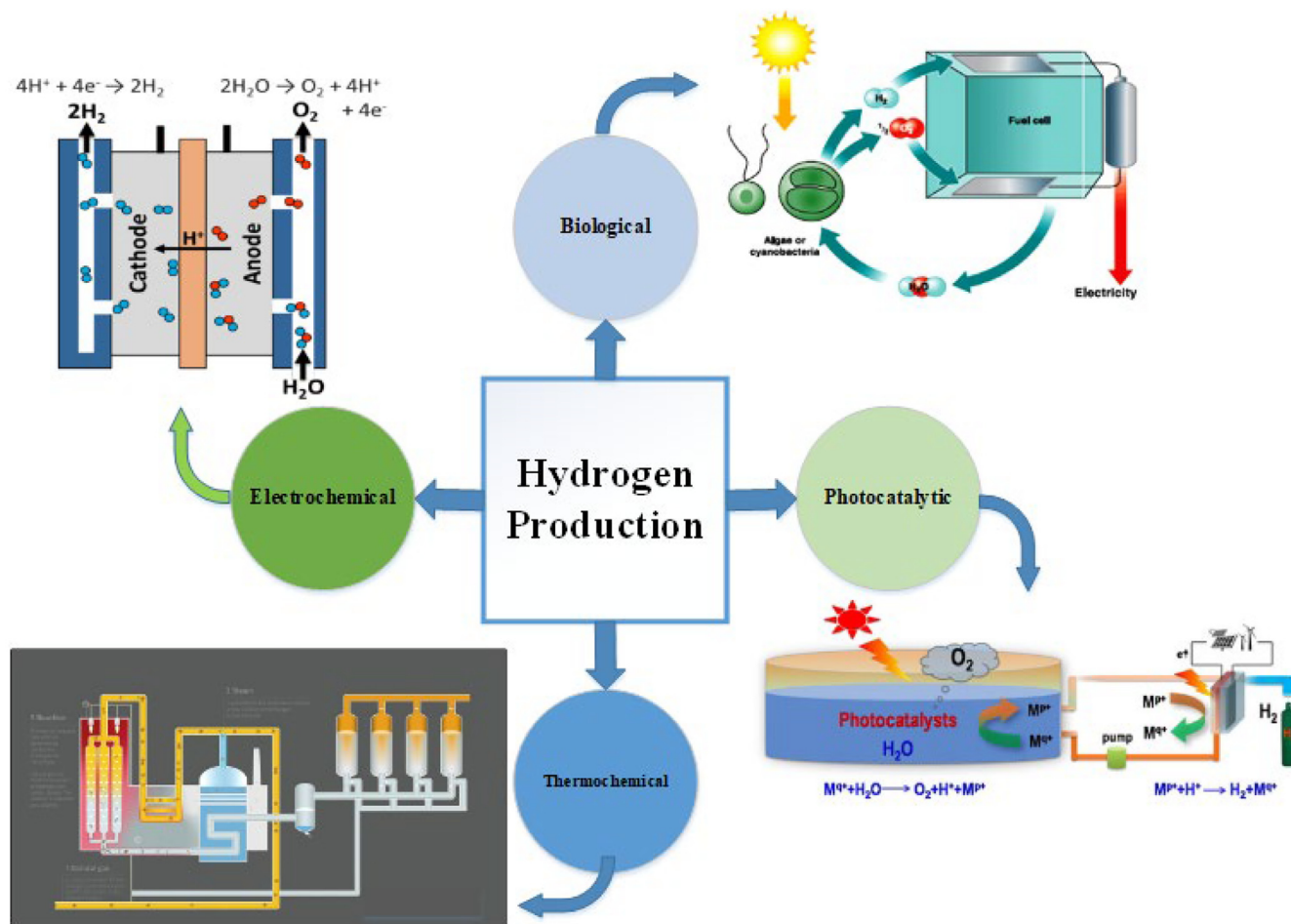


Fig. 1. Methods for hydrogen production systems

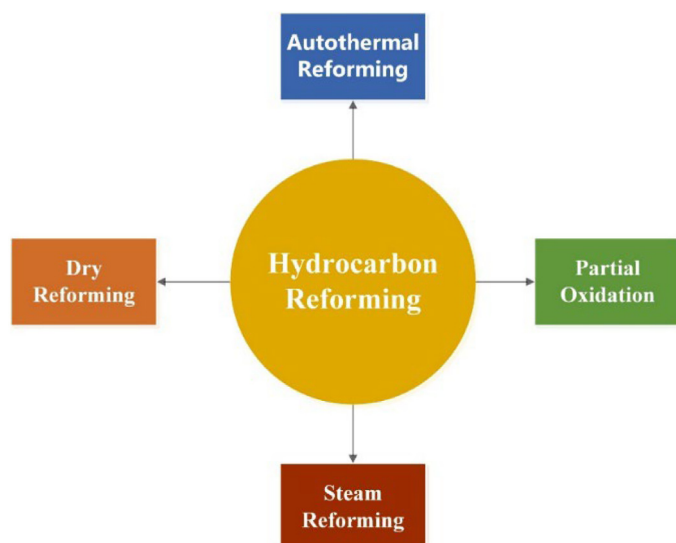


Fig. 2. The thermochemical hydrogen generation systems

thermochemical and electrochemical approaches, these approaches are typically more ecologically friendly and sustainable. The processes of dark fermentation and photo fermentation are frequently used to produce biological hydrogen. For dark fermentation, a variety of organic materials can be employed as substrates, including sugars, wastewater, organic waste, and lignocellulosic biomass (Arun et al., 2022). Volatile fatty acids generated during dark fermentation or other anaerobic processes are frequently used as organic substrates in photo fermentation (Mishra et al., 2019). By converting organic waste or sunshine into hydrogen, biological hydrogen production can contribute to the mix of sustainable energy sources (Gautam et al., 2023). The agriculture sector can use biologically produced hydrogen for power generation or as a feedstock for the creation of biofuels and biofertilizers (Sharma et al., 2020).

Technologies for producing hydrogen through photocatalysis use photocatalysts (materials that absorb light) to facilitate the splitting of water into hydrogen and oxygen when exposed to sunlight. The photocatalyst material should be stable, have a good bandgap energy, and be non-toxic. Water splitting using semiconductor photocatalysts is the most used photocatalytic method for producing hydrogen (Ishaq et al., 2021). By using sunlight to create hydrogen as a clean energy source, photocatalytic hydrogen production can support the renewable energy industry (Hassan et al., 2023; Oh et al., 2022). The generated oxygen and hydrogen gases are kept separate from one another and in the liquid state. It is first purified, compressed, or liquefied to prepare the hydrogen for storage and transportation.

It is important to note that hydrogen production technologies encompass diverse techniques and procedures for generating hydrogen gas. Among the various technologies discussed, thermochemical hydrogen production methods, such as SMR and coal gasification, are the most established. Nevertheless, these technologies require the retrofitting of CO₂ capture plants to reduce CO₂ emissions, significantly increasing the total hydrogen production cost. Therefore, further efforts are required to improve the CO₂ capture processes to reduce the H₂ production cost.

3. Sorption-enhanced steam methane reforming

SE-SMR is an innovative process that combines the principles of SMR with sorption technology to enhance the efficiency and selectivity of hydrogen production. The advanced blue hydrogen production method utilizes sorbents to improve the SMR process by selectively capturing CO₂ and enhancing the overall performance of the reforming reactions (Osman et al., 2021). Compared to traditional hydrogen pro-

duction methods like SMR, this technique offers a reduction in operational complexity and an increase in hydrogen yield, along with a lower cost for gas post-processing. Several earlier reviews have examined SE-SMR from various perspectives. For instance, Harrison (2008) focused on sorbent capacity and durability, while (Voldsund et al., 2016) examined adsorption, absorption, membrane and cryogenic separation technologies for carbon capture in fossil fuel based hydrogen production. Hanak et al. (2018) highlighted advancements in calcium looping technologies and their application in power production systems, including sorption enhanced processes. Similarly, Wang et al. (2014) conducted a techno-economic assessment of these technologies.

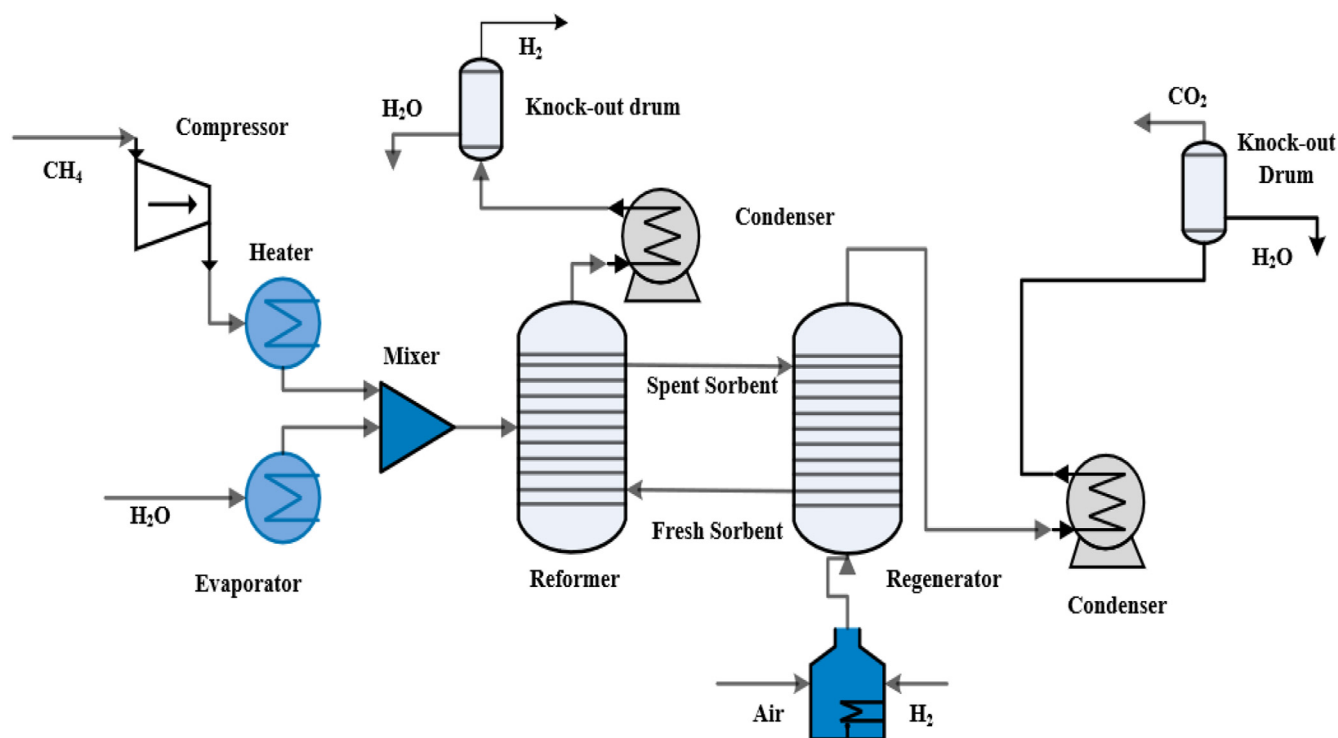
This section provides an extensive overview of SE-SMR. It encompasses the fundamental concepts and principles of SE-SMR, emphasizing the integration of sorbents to enhance hydrogen production. The discussion further delves into the various types of sorbents employed in SE-SMR, namely CaO-based, alkali-ceramic, hydrotalcite, and waste-derived sorbents.

3.1. SE-SMR concept and principles

Fig. 3 shows the conceptual diagram of a SE-SMR process consisting of two interconnected reactors. These reactors operate in two distinct modes. In the swing mode, reactor (i) functions as a reformer, conducting SMR while simultaneously saturating the sorbent with CO₂, and reactor (ii) acts as the regenerator, responsible for regenerating the sorbent. Alternatively, in the configuration of interconnected two fluidized bed reactors, reactor (i) operates as a SE-SMR reformer while reactor (ii) serves as the sorbent/catalyst regenerator. Notably, there is a growing trend in both experimental and modeling studies towards investigating sorption-enhanced processes. The SE-SMR process typically involves three stages: pre-breakthrough, breakthrough, and post-breakthrough. The reaction and adsorption process start with the pre-breakthrough stage, in which the fresh sorbent removes CO₂ from the reaction mixture and significantly promotes the H₂ production reaction. Thereby, the outlet gas contains the least concentration of CO₂. A combination of H₂ and some CO₂ is present in the product stream at the reactor exit when a breakthrough happens, and the rate of CO₂ capture slows down relative to the rate of CO₂ production. The sorbent finally approaches saturation as the CO₂ sorption process progresses, which results in a zero CO₂ capture rate. This step, called the post-breakthrough stage, functions in a manner akin to traditional steam reforming. The process should be kept at the pre-breakthrough stage for effective SE-SMR. The reactor needs to be switched to regeneration mode when a breakthrough happens.

Clough et al. (2018) studied this enhancement by employing an in-situ CO₂ capture method to produce decarbonized, high-purity H₂. This approach involved the reaction of hydrocarbon fuel with steam in the presence of a CO₂ sorbent and a reforming catalyst. Several configurations combined with SE-SMR have been proposed to produce low-carbon, high-purity hydrogen aiming to reduce costs and maximize CO₂ capture efficiency. When SE-SMR and oxy-fuel combustion are combined, Ochoa-Fernández et al. (2007) used HYSYS to simulate the process. The results showed that SE-SMR with oxy-fuel combustion offers advantages over traditional steam reforming with monoethanolamine absorption (MEA) in terms of thermal efficiency, smaller pressure swing adsorption (PSA) unit, and CO₂ capture.

SE-SMR presently occupies a technological readiness level (TRL 4). This is substantiated by the existing literature on process simulations and experimental research (Anderson et al., 2014; Liu et al., 2024; Luo et al., 2024; Ochoa-Fernández et al., 2005). The subsequent stage in elevating the TRL would be pilot-plant studies. Recently, a 1.5 MWth pilot plant being built for hydrogen production by sorbent enhanced steam reforming (HYPER project) at Cranfield University received £7.4 million in funding through the Department for Business, Energy and Industrial Strategy (BEIS), UK. The collaboration includes the US-based research and development company Gas Technology Institute (GTI) and Doosan Babcock, an expert in low-carbon technology implementation.

Fig. 3. Schematic diagram for H₂ production by SE-SMR process

This HyPER project includes a fluidized bed reactor acting as a reformer (concurrently functioning as a carbonator) and an entrained flow reactor for the calciner (Fig. 4). Compared to commercialized processes with a tail-end CCS unit operating at 24 bars absolute (bara), the developed system demonstrated an approximate 20% decrease in the levelized cost of hydrogen (LCOH), alongside a reduction exceeding 50% in both CAPEX and OPEX, while sustaining a CO₂ capture efficiency of around 96% and producing equivalent H₂ purity. Another plant in California, USA constructed by GTI has a capacity of 71kWth, which is

20 times less than the Hyper project pilot plant in the UK. This process has been reported to result in an 18% reduction in CO₂ emissions, 12–40% in CAPEX and 20% in OPEX compared to the conventional SMR process.

Selecting an appropriate CO₂ sorbent is crucial for achieving high-purity hydrogen production in the SE-SMR process. The ideal sorbent should possess sufficient sorption capacity and efficiently capture CO₂ at reforming temperatures. In addition, it must demonstrate stability and robust mechanical strength, even after undergoing multiple

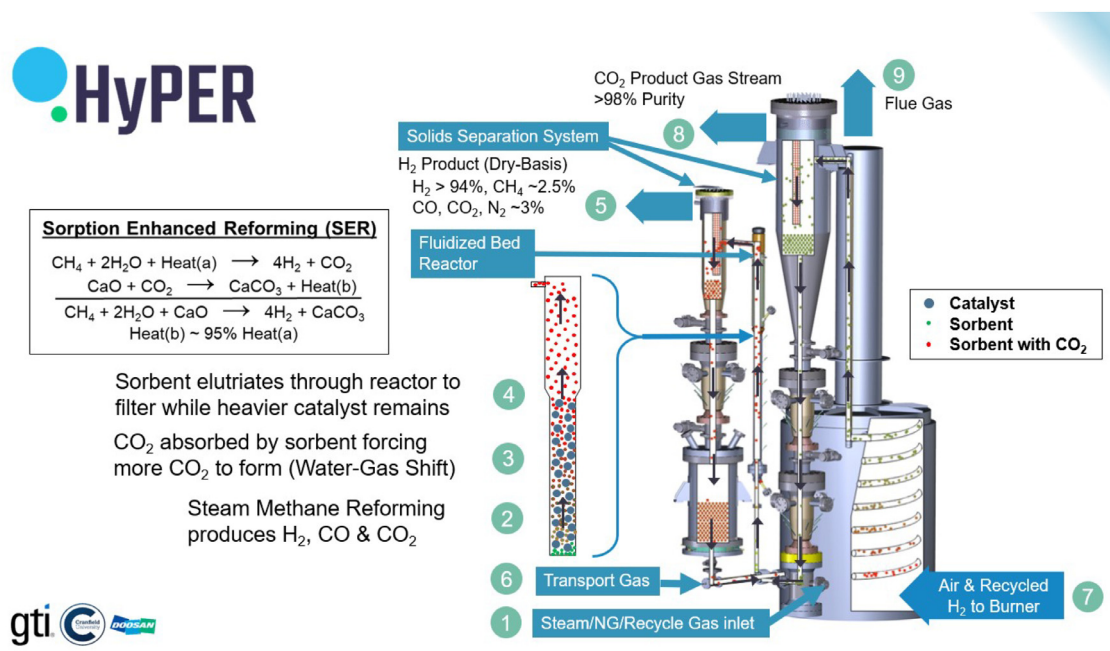
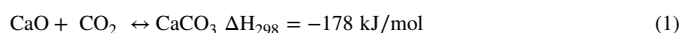


Fig. 4. 1.5MWth pilot plant system for SE-SMR process (Hyper project, n.d.)

carbonization and calcination cycles. Cherbanski & Molga (2018); Ding & Alpay (2000b).

3.2. CaO-based sorbents

Various types of sorbents have been studied and developed to improve the performance of SE-SMR (Karimi et al., 2023). These sorbents play a crucial role in SE-SMR and other hydrogen production methods by enhancing the conversion of feedstock and selectively capturing or removing impurities (Ma et al., 2021). Several types of sorbents have been explored for enhanced hydrogen production. One commonly studied sorbent is calcium oxide (CaO)-based sorbents, which possess high CO₂ capture capacity and can be regenerated through high-temperature release of captured CO₂. CaO offers several advantages, including a high sorption capacity (78.6 wt.%) and fast sorption kinetics (0.1-0.4g-CO₂ g⁻¹ min⁻¹) (Ji et al., 2020; Pecharaumporn et al., 2019). The CO₂ sorption reaction involving CaO is shown below (Eq. 1):



CaO can be obtained from natural materials like limestone and dolomite (Gupta & Fan, 2002; Wang et al., 2016; Yan et al., 2016), as well as from industrial by-products, including marble dust, steel slag, lime mud and carbide slag (Guo et al., 2017; Li, Liu, et al., 2012; Li, Sun, et al., 2012; Sun et al., 2016). Additionally, it can be synthesized from various calcium-based precursors (Martavaltzi & Lemonidou, 2008; Pecharaumporn et al., 2019; Zhou et al., 2012). Nonetheless, there are still issues with the sorbent's conversion and recyclable nature. It has been well-reported that the sorption capacity of CaO decreases during several cycles (Erans et al., 2016; Sun et al., 2007). The high temperatures required for regeneration have a harmful effect on the cyclic stability of the sorbents. The leading cause of this degradation is the low melting point of the CaCO₃, which causes the regenerated CaO particles to aggregate significantly. As Fig. 5 shows, the increased degree of sintering causes a steady reduction of sorption capacity over the course of multicycle operations.

By adopting different strategies, the CaO-based sorbents improve the cyclic stability and initial sorption capacity. These include the application of organic acids like citric, oxalic, formic, and acetic acids (Li et al., 2008; Radfarnia & Iliuta, 2013a; Ridha et al., 2012; Ridha, Manovic, Macchi, et al., 2013; Ridha, Manovic, Wu, et al., 2013), thermal pre-treatment (Manovic and Anthony, 2008; Ozcan et al., 2011) reactivation by water or steam hydration (Shokrollahi Yancheshmeh et al., 2016b), and the integration of thermally resistant inert elements into

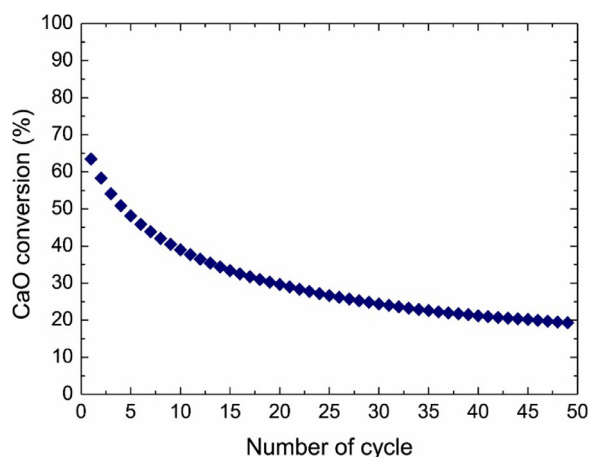


Fig. 5. Behavior of CaO sourced from limestone over repeated sorption/desorption cycles in a thermogravimetric setup (Carbonation: 650°C, 15%CO₂, 30 min; Calcination: 850°C, 100%/N₂, 5 min) (Antzaras & Lemonidou, 2022).

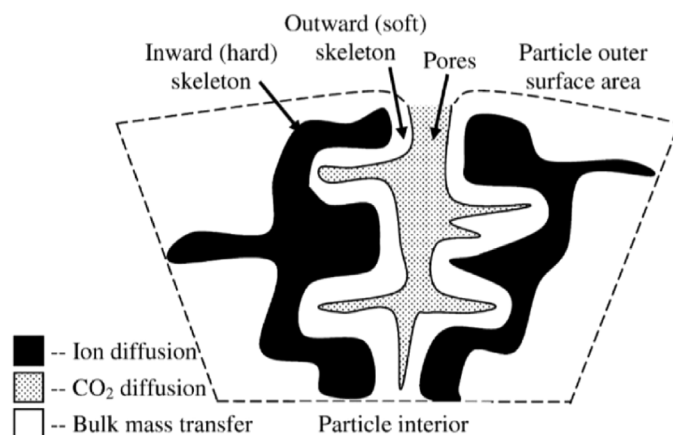


Fig. 6. Schematic representation of proposed pore-skeleton model (Manovic & Anthony, 2008).

the CaO structure (Angeli et al., 2014; Martavaltzi & Lemonidou, 2008; Radfarnia & Iliuta, 2013b; Zhao et al., 2014). Various synthesis techniques have also been explored to enhance the stability of CaO-based sorbents, including precipitation, flame spray pyrolysis, dry and wet mixing, and several modified sol-gel techniques (Angeli et al., 2014; Martavaltzi & Lemonidou, 2008; Reddy et al., 2014). Li et al. (2005) added mayenite to the calcium oxide in a 25 to 75 wt.% ratio to improve the cyclic stability. They tested the prepared material in TGA and found that the CO₂ capture rate increased for the initial three cycles, followed by a minimal enhancement. A model was developed by Manovic and Anthony (2008) to account for the sorbent's structural alterations. They used a TGA to evaluate various limestone samples at temperatures as high as 1300°C. According to their findings, CaO particles calcined at these high temperatures (1300°C) had substantial sintering and always displayed modest carbonation levels of 1-2 %. This suggested that the reaction was confined to the particle surfaces. In contrast, all samples showed a constant rise in conversion when calcination was done at temperatures between 900°C and 1100°C. These results support the suggested hypothesis, which postulates that the internal, unreacted CaO skeleton produced during thermal pre-treatment is responsible for stabilizing and maintaining the porous morphology of the particle inside the sorbent's porous structure. In the meantime, the response happens in the exterior soft skeleton. A schematic depiction of this approach is shown in Fig. 6. Significant carbonation can also occur within the hard-internal skeleton's porous structure. As a result, in the early cycles, part of the less reactive CaO internal hard skeleton can be changed into the more reactive exterior soft skeleton, increasing the pace at which carbonation occurs.

Table 1 provides a comprehensive overview of the various strategies employed in CO₂ capture technologies, focusing on the sorbents used, reaction conditions (temperature and pressure), and key findings. The sorbents reviewed include calcium carbonate (CaCO₃), synthetically produced CaO, calcium-based composites with activated carbon, silica, or alumina and calcium-based sorbents enhanced with promoters such as potassium or magnesium. Additionally, modified CaO sorbents incorporating elements like magnesium or zirconium are highlighted for their enhanced performance.

3.2.1. CaO sorbents from different precursors

Various CaO sorbents derived from different precursors have been extensively investigated. These sorbents play a crucial role in the SE-SMR process, where they capture and release CO₂, a step that enhances the overall efficiency of methane reforming. Different precursors, such as calcium carbonate (CaCO₃), calcium oxide (CaO), and various calcium-containing compounds, have been explored for synthesizing the CaO sorbents. Studies have shown that the choice of

Table 1
CaO-based sorbents used in SE-SMR process

Catalyst/sorbent systems	CaO-sorbent precursor	Feed	Temperature (K)	S/C	Outcome	Ref.
Ca ₁₂ Al ₁₄ O ₃₃ -CaO	CaO commercial	CO ₂	1023	-	The study compares CO ₂ capture kinetics using TGA and a fixed-bed reactor, concluding that the reactor is superior for kinetic studies due to better gas-solid contact and the absence of bypass issues.	(Rout et al., 2014)
Ru/CaAl ₂ O ₆ -CaO	Limestone and Ca(NO ₃) ₂ ·4H ₂ O	CH ₄	823	4	A Ru/Ca ₃ Al ₂ O ₆ -CaO bi-functional catalyst-sorbent was prepared by a citrate sol-gel route and demonstrated superior performance in SE-SMR reaction over Ni-CaO and Ru/limestone. The material's stability, attributed to Ca ₃ Al ₂ O ₆ , ensured prolonged pre-breakthrough and remarkable cyclic stability across multiple regeneration cycles.	(Kim et al., 2019)
Ni/CaZrO ₃ -CaO	Ca(NO ₃) ₂ ·4H ₂ O	CH ₄	873	3	A sol-gel-prepared Ni/CaO-CaZrO ₃ bifunctional catalyst for SE-SMR demonstrated improved stability, CO ₂ uptake, and performance. The catalyst with 15 wt% Ni, around 60 wt% CaO, and 25 wt% CaZrO ₃ presented optimal performance but showed slow deactivation, which was recoverable through additional carbonation steps in prolonged cyclic operation.	(Zhao et al., 2016)
Ni/Ca ₁₂ Al ₁₄ O ₃₃ -CaO	Ca(CH ₃ COO) ₂ ·xH ₂ O	CH ₄	923	3	The study focuses on a Ni/mayenite-CaO combined sorbent-catalyst material optimized for SE-SMR through wet mixing and impregnation methods. The catalyst exhibited stable performance over 205 carbonation/regeneration cycles, demonstrating sustained Ni catalytic activity and CO ₂ sorption capacity without decline in a 15-day continuous operation.	(Di Giuliano et al., 2018)
Ni/hydrotalcite Ni/CaO-Al ₂ O ₃	CaO commercial	CH ₄	673-873	3-9	Ni-CaO/Al ₂ O ₃ in SE-SMR exhibited superior adsorption and longer breakthrough times compared to commercial catalyst-sorbent mixtures. It produced 98.5% H ₂ -rich gas and excellent stability over 16 cycles, highlighting its potential for enhanced hydrogen production.	(Dewoolkar & Vaidya, 2015)
Co ₃ O ₄ /SiO ₂ /CeO ₂ -CaO	Ca(NO ₃) ₂ ·H ₂ O	CH ₄	823-923	-	SESMR using a cobalt-based oxygen carrier and cerium-promoted CaO-based sorbent produced highly pure hydrogen (up to 95% H ₂) at 550°C. The cerium modification improved sorbent morphology, increased CO ₂ sorption capacity, and enhanced thermal resistance, demonstrating the potential for efficient CO ₂ removal and hydrogen production in the SE-SMR process.	(Hafizi et al., 2019)
Ni/Al ₂ O ₃ -CaO	Ca(OH) ₂	CH ₄	873	3	SESMR using CaO as an acceptor achieved H ₂ purity above 95%, surpassing conventional methods (~72% H ₂). The highest H ₂ purity (98.4%) and CH ₄ conversion (95%) occurred at 873K, demonstrating the effectiveness of overcoming equilibrium limitations through in-situ CO ₂ sorption.	(Chen et al., 2020)
Pd/Ni-Co-HT-CaO	Dolomite	Biogas	873-923	3-5	SESR of biogas using a Pd/Ni-Co catalyst and dolomite CO ₂ sorbent achieved high H ₂ purity (98.4%) and yield (91%), demonstrating its potential for efficient H ₂ production from renewable biogas sources. The process effectively removed CO ₂ , maintaining performance comparable to pure methane reforming with dominant SMR and WGS reactions.	(Capa et al., 2020)
Ni-Zr-CaO Ni-Ce-CaO Ni-La-CaO	CaO commercialized	Biogas	873	3	Zr-CaO and Ce-CaO doped sorbents exhibited stable CO ₂ capture activity over ten cycles in sorption-enhanced steam reforming of biogas. However, Ni-Zr-CaO and Ni-Ce-CaO showed declining CH ₄ conversions over five cycles due to pore closure and loss of Ni active sites.	(Phromprasit et al., 2017)
NiO/Al ₂ O ₃ /CaO	CaO commercialized	Shale gas	923	3	SESR of shale gas using CaO and NiO/Al ₂ O ₃ achieved cyclic reduction-oxidation-calcination cycles, producing high-purity H ₂ (92%) with a 31 wt.% yield, presenting an 80% enhancement over conventional SMR. The process demonstrated efficiency in cyclically reducing the oxygen carrier and reforming shale gas at 650°C for 20 cycles.	(Adiya et al., 2019)
Co-CaO-CeO ₂ Co-CaO-ZrO ₂ Co-CaO-MgO	Ca(NO ₃) ₂ ·H ₂ O	Ethanol	773	9	Cobalt-based hybrid materials with CeO ₂ , ZrO ₂ , and MgO-modified Ca-based sorbents enabled efficient SESR of ethanol, producing >85 mol% H ₂ . CeO ₂ and ZrO ₂ based catalyst exhibited superior adsorption capacity and breakthrough time, demonstrating stability over 20 cycles.	(Ghungrud & Vaidya, 2020a)
Co-CaO-Ca ₁₂ Al ₁₄ O ₃₃	Ca(NO ₃) ₂ ·H ₂ O	Glycerol	773	4	A Co-CaO-Ca ₁₂ Al ₁₄ O ₃₃ catalyst for SESR achieved high stability and catalytic activity, producing 96.4% high-purity H ₂ at 525°C during the pre-breakthrough stage. The Ca ₁₂ Al ₁₄ O ₃₃ spacer effectively prevented CaO sintering, and Ca ₃ Co ₂ O ₆ acted as a dynamic Co reservoir, enhancing the catalyst's SESR performance and stability through 50 cycles.	(Dang et al., 2016)
CeNi-ZrO ₂ /CaO	CaO commercialized	Glycerol	923	3	Ni-ZrO ₂ oxygen carriers are used for SESR of glycerol. Overall, CeNi-ZrO ₂ maintained a platelet-stack structure, enhancing metal support interaction and sintering resistance. CeNi@ZrO ₂ exhibited a high H ₂ selectivity of 96.3% H ₂ purity after 50 cycles, demonstrating stability and efficient glycerol conversion.	(Jiang et al., 2018)
Mg-Ni-Al (MNA) HTc	CaO from waste eggshell	CH ₄	923-1123	2	CaO@MNA bifunctional catalyst exhibited the best performance in SESMR, with improved H ₂ purity (80%) and reduced CO ₂ (3%) at 923 K. The catalyst showed excellent regeneration capacity and minimal carbon formation over three cycles.	(Ayesha et al., 2022)

(continued on next page)

Table 1 (continued)

Catalyst/sorbent systems	CaO-sorbent precursor	Feed	Temperature (K)	S/C	Outcome	Ref.
Ni/CaZrO ₃ Ni/Ca ₂ SiO ₄	Ca(NO ₃) ₂ ·H ₂ O	Propane	873	3	The addition of Zr and Si to Ni/CaO catalysts improved thermal stability and minimized CaO sintering, with Ni/CaO-CaZrO ₃ showing the best performance in sorption-enhanced steam propane reforming, achieving over 90% H ₂ yield in the pre-breakthrough period	(Caroline Pereira Oliveira et al., 2024)
Ni/Al ₂ O ₃ -CaO Ni/Al ₂ O ₃ -Na ₂ CO ₃ /CaO	Ca(NO ₃) ₂ ·H ₂ O	CH ₄	823	4	Sodium doping in CaO sorbent reduced its stability during SE-SMR cycles, despite achieving 100% CH ₄ conversion and 93.5% H ₂ yield. The larger crystallite size of Na ₂ CO ₃ -CaO led to increased sintering and lower CO ₂ capture performance compared to pure CaO.	(Santos et al., 2021)
Ni/CaO	CaO commercialize	Ethanol	823-923	4.8	Ni/CaO catalyst showed increased H ₂ production with temperature but CO ₂ capture declined at higher temperatures. After 12 cycles, the catalyst maintained stable CO ₂ capture performance, with only a 7% reduction compared to the fresh catalyst.	(Cortazar et al., 2021)
Ni/Ca ₁₂ Al ₁₄ O ₃₃ -CaO	CaO commercialize	Glycerol	823-923	3-6	Glycerol steam reforming using Ni/CaO-based bifunctional sorbent-catalyst materials enhanced hydrogen yield and purity. These materials exhibited extended pre-breakthrough periods and stable performance over multiple reaction/regeneration cycles.	(Olivier et al., 2024)
Ni/CaZrO ₃ -CaO	Ca(NO ₃) ₂ ·H ₂ O	Ethanol	823	3	The combined catalyst achieved >95% hydrogen purity with a 90-minute pre-breakthrough period during under optimized conditions. The catalyst showed excellent stability, maintaining 90% hydrogen purity over 10 cycles.	(Wang et al., 2024)
Ni-Pb/CaO	Ca(NO ₃) ₂ ·H ₂ O	Bio-gas	823	4	The Ni-Pb/CaO catalyst significantly improved stability in sorption-enhanced biogas steam reforming, maintaining 57.6% of its initial sorption capacity after 20 cycles. It achieved 94.1% hydrogen purity and 95% CH ₄ conversion, outperforming the non-modified catalyst.	(Zhou et al., 2024)
Ni/Al ₂ O ₃ -CaO	CaO commercialize	CH ₄	823	2-4	Granulated Al-modified CaO-based sorbents demonstrated excellent CO ₂ adsorption and mechanical strength, with H ₂ purity reaching nearly 100% during SE-SMR when mixed with catalyst pellets, maintaining stability over 15 cycles having continuous high-purity hydrogen production (>96%) was sustained for 600 minutes.	(Wang et al., 2024)
Ni/Al ₂ O ₃ -CaO	Ca(OH) ₂ and CaCO ₃	Ethanol	823	4	The CaO spherical sorbents significantly enhanced hydrogen purity (>90%) during SESRE, with high stability over repeated cycles. Coupling these sorbents with Ni/Al ₂ O ₃ catalysts demonstrated effective H ₂ production and long-term stability, making SESRE a promising process.	(Xu et al., 2021)

precursor significantly influences the performance of CaO sorbents in SE-SMR (Grasa et al., 2007). For example, CaO derived from CaCO₃ has demonstrated high CO₂ capture capacity due to the decomposition of CaCO₃ during the sorption stage. This decomposition results in the formation of CaO and the release of CO₂, contributing to the overall SE-SMR reaction (Shokrollahi Yancheshmeh et al., 2016a).

Additionally, researchers have explored alternative calcium-containing precursors, including calcium acetate, calcium nitrate, and calcium hydroxide, to tailor the properties of the resulting sorbents. The selection of precursor materials also impacts the structural and chemical characteristics of the CaO sorbents, influencing factors such as surface area, porosity, and reactivity (Hsu et al., 2014). These properties, in turn, affect the sorption-desorption kinetics and the overall efficiency of the SESR process. Natural sources of calcium, such as limestone and dolomite, are widespread and cost-effective. However, the impurities present in natural minerals are challenging to address and cause poor cyclic stability to sorbents due to complex phases and structures. On the other hand, synthetic sorbents can be employed to produce good-quality sorbents due to negligible impurities (Luo et al., 2013; Yang et al., 2013).

Synthetic sources result in sorbents with porous morphologies that enhance anti-sintering performance. Among them, Ca(NO₃)₂, Ca(CH₃COO)₂·H₂O, C₁₂H₂₄O₁₅Ca, Ca(OH)₂, and CaCO₃ are commonly used precursors. Nevertheless, CaO synthesized using calcium acetate precursor exhibits superior CO₂ sorption performance, exhibiting better specific surface area, and larger pore volume in comparison to counterparts derived from Ca(NO₃)₂, Ca(OH)₂, and CaCO₃. Studies have demonstrated that CaO sorbents from calcium acetate promote high-purity hydrogen production in SESMR reactions. For instance, Nimmas et al. (2019) utilized calcium acetate and CO(NH₂)₂ to prepare CaCO₃ sorbents, with CaO_{Ac-urea} exhibiting the highest conversion

rate of 80% at the temperature of 700°C and 15% CO₂ environment. This enhanced performance is attributed to the high specific surface area of 9.83 m²/g, with 0.063 cm³/g pore volume and 27 mm pore size of CaO_{Ac-urea}. Furthermore, researchers also employed CaO_{Ac-urea} sorbent to prepare a Ni/CaO-Ca₁₂Al₁₄O₃₃ bifunctional material through the sol-mixing method. This bifunctional material effectively promoted hydrogen production, with approximately 87% H₂ concentration in the outlet gas during the pre-breakthrough stage over 10 cycles in SE-SMR as depicted in Fig. 7.

Zhang et al. (2019) employed a bi-functional material synthesized using Ni/Hematite catalyst and limestone as a sorbent for tar steam reforming, exploring their applications in biomass gasification and upgrading gasification products. Under specific reaction conditions (500°C ~ 600°C moving bed temperature range, Steam/Biomass ratio of 0.4, and a bed material respectively composed of 20 wt.% Ni/hematite, 60 wt.% calcined limestone, the produced gas exhibited a total content of H₂ and CH₄ exceeding 97%, with H₂ accounting for 71.5% and CH₄ comprising 25.75%. Pecharaumporn et al. (2019) investigated the hydrogen generation efficiency of a Ni-CaO-Ca₁₂Al₁₄O₃₃ bifunctional catalyst in the SE-SMR process. The catalyst was synthesized using calcium nitrate and D-gluconate as precursors, demonstrated exceptional performance at 600°C and S/C ratio of 3. Specifically, the catalyst derived from calcium D-gluconate achieved 88% H₂ purity and exhibited the longest pre-breakthrough period of 60 min reported in their studies. The superior performance was ascribed to the enhanced textural properties of the CaO-Ca₁₂Al₁₄O₃₃ sorbent derived from calcium D-gluconate, which featured a surface area of 13.8 m²/g, a pore volume of 0.04 cm³/g, and an average pore size of 10.7 nm. In contrast, the sorbent derived from calcium nitrate showed a slightly lower surface area of 12.4 m²/g, smaller pore volume of 0.02 cm³/g, and reduce pore size of 9.9 nm.

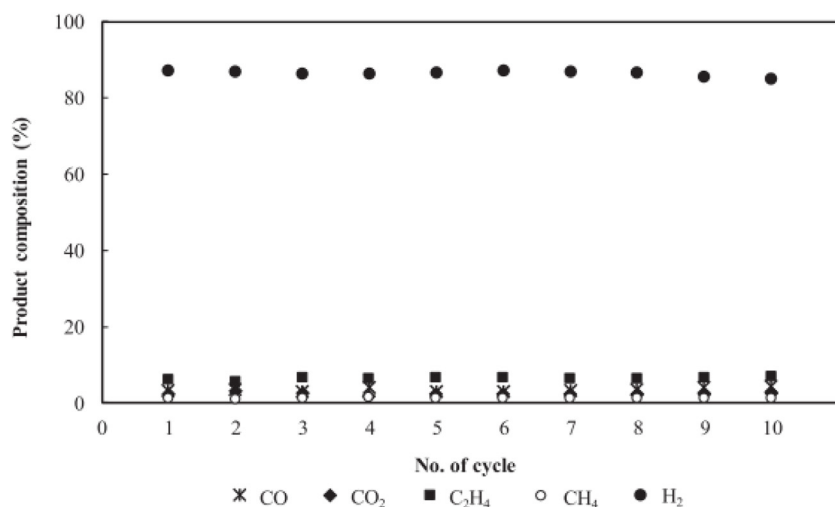


Fig. 7. Composition of product stream after the SESR of ethanol (Nimmas et al., 2019).

3.2.2. CaO sorbents with different morphology

Researchers have developed CaO-based sorbents to improve sorption efficiency by increasing surface area and enhancing diffusion kinetics by improving surface properties and morphology. The hollow spherical structure has proven effective in mitigating the impact of volumetric changes during sorption/desorption cycles. This structure not only alleviates such influences but also facilitates the diffusion of CO₂, thereby enhancing sorption kinetics (Alvarez & Carlos Abanades, 2005). Researchers have explored size control in CaO sorbents, focusing on nano-sized CaO to enhance performance. The transition from the rapid to slow reaction stage during carbonation is observed when the CaCO₃ layer reaches a thickness of approximately 50 nm. Nano-sized CaO sorbents facilitate sustained operation in the rapid reaction phase, thereby accelerating carbonation rates and improving CaO conversion efficiency. Additionally, these nanoscale sorbents exhibit high surface area, providing abundant active sites for CO₂ adsorption and significantly enhancing sorption efficiency (Grasa et al., 2007). Alshafei et al. (2019) prepared different CaO-based sorbents and studied the effect of synthesis techniques on morphology. The TEM images indicate that the CaO sorbent prepared from marble comprises large, closely packed and multi-layered nanoparticles as seen in Fig. 8a. The particle size ranges from approximately 50 to 180 nm. However, the particle size observed was significantly smaller (approximately 25–120 nm) for CaO sorbents derived from calcium nitrate (Fig. 8b) and calcium acetate (Fig. 8d) as compared to those in the CaO-marble sample. The CaO sorbent derived from nanofibers contained nanoparticles with size ranging from 70 to 180 nm; however, they contained microporous intraparticle void volumes that were substantially larger. These intraparticle spaces are depicted as void channels (inset of Fig. 8c) and have diameters of approximately 0.5 μ m.

Wu et al. (2008) conducted a comparative study between nano and micron-sized CaCO₃/Al₂O₃, revealing that nano-sized exhibited better performance in terms of the lower regeneration temperature and demonstrated more stable capacity during cycles. Even after the 50th cycle, it maintained 68.3% of its original capacity, displaying superior performance. Despite the advantages of the hollow structure and nano-sized CaO sorbents, certain drawbacks persist. Because of the hollow spherical structure's fragility and propensity to collapse, nano-CaO often sinters readily during practical use, necessitating intricate preparatory procedures and higher expenses. While morphology-controlled CaO-based sorbents are highly successful at capturing carbon, nothing is known about how well they work to boost hydrogen generation in SE-SMR.

In addition, Alshafei et al. (2019) prepared a CaO-Ca₁₂Al₁₄O₃₃ nanofiber structure using the electrospinning method and evaluated for SE-SMR performance. The sorbent exhibited a high sorption capacity of up to 74 wt.% in the CO₂ sorption test, with rapid sorption kinet-

ics. In the SE-SMR experiment, approximately 100% H₂ selectivity was noted during the pre-breakthrough phase, and the breakthrough time decreased by 6% after ten regeneration cycles. The nanofiber structure, which has a greater specific surface area, a larger pore volume, and a smaller grain size, was attributed to this exceptional performance.

3.2.3. Modified CaO sorbents

Enhancing the effectiveness of CaO-based sorbents offers greater advantages in improving CO₂ capture performance than merely altering calcium sources. Numerous research groups have undertaken studies focusing on the modification of CaO-based sorbents to enhance cyclic stability and adsorption kinetics, aiming for sustained and reliable hydrogen production (Ji et al., 2018; Stendardo et al., 2013; Zhao et al., 2014). Multiple approaches have been reported to improve the performance of CaO-based sorbents such as mixing with alkali metal salts, high Tammann temperatures (e.g., Al, Zr, and Mg, as inert constituents) and CO₂ active support materials (e.g., La₂O₃). These serve to impede or mitigate sintering, thereby improving cycle stability.

Commonly utilized inert components include aluminum, magnesium, zirconia and silica-based stabilizers. Among these, the utilization of Al-based materials to stabilize CaO has garnered the most attention (Caravella et al., 2009; Yan et al., 2016). It is important to highlight that during the modification of CaO-based sorbents, careful consideration must be given to the appropriate amount of the required stabilizer. While an excess of inert components effectively decreases the sintering effect in CaO, it concurrently leads to a dilution of the CaO concentration, resulting in a diminished capacity for CO₂ sorption (Armuthulu et al., 2017). An alternative approach involves introducing the oxides of metal oxides such as Ce and Mn into CaO to improve the diffusion of CO₂ via increasing oxygen vacancies in the sorbent material. It is reported that CaO-based sorbent doped with Ce over varying Ca to Ce ratios and tested for sorption cycles. It was found that the sorbent with Ca to Ce molar ratio of 1:4 exhibited the most consistent cyclic sorption for 18 cycles with a capacity of 59 wt.%. This superior performance was explained based on the anti-sintering properties and the promotion of the carbonation process by the presence of Ce oxide. Appropriately modified CaO-based sorbents demonstrate outstanding hydrogen production capabilities thanks to their enhanced resistance to sintering (Wang et al., 2015).

In another study, Tan and coworkers utilized the co-impregnation method to create a Ni/dolomite/La₂O₃ composite material. They assessed how well this bi-functional material performed in the steam reformation of tar made from gasified biomass. The material performed best at 700°C and a steam-to-carbon (S/C) ratio of 1, with a maximum carbon conversion rate of 77.7 % and a hydrogen yield of 66.2 %. Strong basicity, high reducibility, and mesoporous structure brought about by

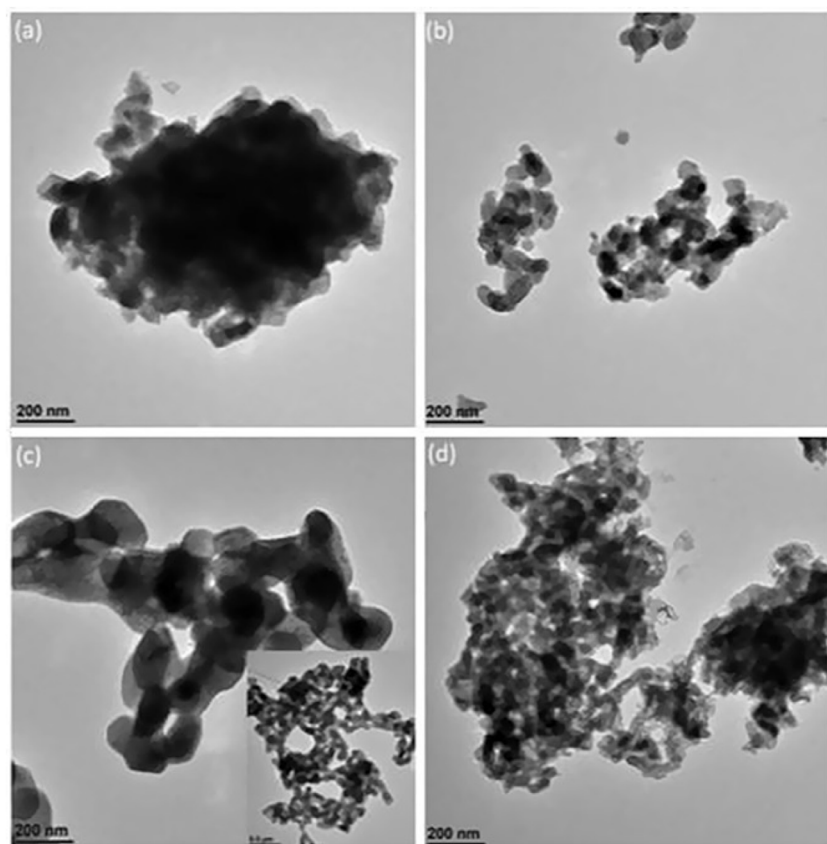


Fig. 8. TEM images of CaO sorbents derived from a) marble, b) calcium nitrate, c) nanofibers, and d) calcium acetate (Alshafei et al., 2019)

La_2O_3 alteration were acknowledged for this increased hydrogen generation (Tan et al., 2019).

Numerous research groups are currently exploring the simultaneous doping of multiple metals into CaO-based sorbents to enhance the diffusion of CO_2 and augment the sorption capabilities of these sorbents. For instance, Rahmanzadeh & Taghizadeh (2019) incorporated Zr and Na metals in CaO-based sorbents using a wet mixing technique, resulting in a Na-Zr-CaO-like structure. The sorbent was tested for stability in more than five sorption-desorption cycles, which indicated good stability with a sorption capacity of 33.6 wt.% in the final cycle. Further, the sorption-enhanced steam reforming of ethanol was tested in a fixed-bed reactor, where the bed contained sequential layers of Na-Zr-CaO sorbent and Ce-Ni/MCM-41 catalyst. The results revealed that 94% pure H_2 was produced in the pre-breakthrough stage, maintaining approximately 80% even after 210 minutes. In another study, Nawar et al. (2021) employed waste eggshells and various organic acids to synthesize structure-modified CaO, with citric acid modification yielding the best stability, sintering resistance, and CO_2 uptake in calcium looping cycles as presented in Fig. 9. The modifications to CaO based sorbents were prepared to improve the stability for multiple cycles which offers a better long-term performance compared to bare CaO.

In addition to utilizing various precursors for CaO-based sorbents, manipulating the morphology of material, and employing high-temperature inert materials for CaO modification, the granulation and reactivation of spent sorbents represent effective strategies for enhancing the cyclic stability of CaO. The inherent susceptibility of CaO to wear and performance deterioration during recycling necessitates effective measures. Granulation emerges as a highly beneficial process, significantly improving the mechanical strength of Ca-based sorbents. This fortification contributes to sustaining a certain level of stability throughout prolonged cycling operations. The granulation process yields multiple advantages; for instance, the incorporation of inert components (such as Al_2O_3 , etc.) stabilizes the structure of the Ca-based sorbent, while doping with porous materials enhances its specific surface area.

The implementation of these measures proves instrumental in effectively enhancing the performance of the sorbents for CO_2 capture (Erans et al., 2016). Furthermore, the regeneration of used CaO sorbent through hydration plays a pivotal role in improving its CO_2 adsorption efficacy. This is attributed to the increase of the sorbent volume due to the formation of $\text{Ca}(\text{OH})_2$ in the hydration process, facilitating the disintegration of CaO particles. Consequently, this process amplifies the pore size and the surface area of the spent sorbent. Simultaneously, hydration engenders the creation of larger pores, promoting CO_2 desorption and preventing pore blockage (Bui et al., 2018; Memon et al., 2017).

3.3. Alkali-ceramic sorbents

Alkali metal-based sorbents are based on alkali metals, such as potassium or sodium. They are used in SE-SMR for CO_2 capture. These sorbents can chemically react with CO_2 to form stable carbonate compounds, capturing and removing CO_2 from the gas stream (Zhao et al., 2020). Alkali-ceramic sorbents typically contain alkali metal particles deposited or dispersed on a porous ceramic support material. The ceramic support provides a high surface area and structural stability, while the alkali metal acts as the active component responsible for capturing the acidic impurities (Memon et al., 2017). Common ceramic support materials include alumina, silica, zeolites, and mixed metal oxides. Even without adding new catalytic sites (like Ni nanoparticles), alkali metal ceramics can function as a dual-purpose catalyst and sorbent for SE-SMR.

Alkali metal ceramics provide mechanical stability at high temperatures without the need for extra refractory support, which is not the case with CaO-based sorbents. For this reason, alkali metal ceramics are appealing as next-generation compounds for bifunctional materials at temperatures higher than 500°C as they can be recycled, have mechanical stability, and are CO_2 selective. Binary-metal oxides, such as Li_2ZrO_3 , Li_4SiO_4 , and Na_2ZrO_3 , possess characteristics that enable them to adsorb CO_2 at low concentrations ($<15\% \text{CO}_2$) and high temperatures

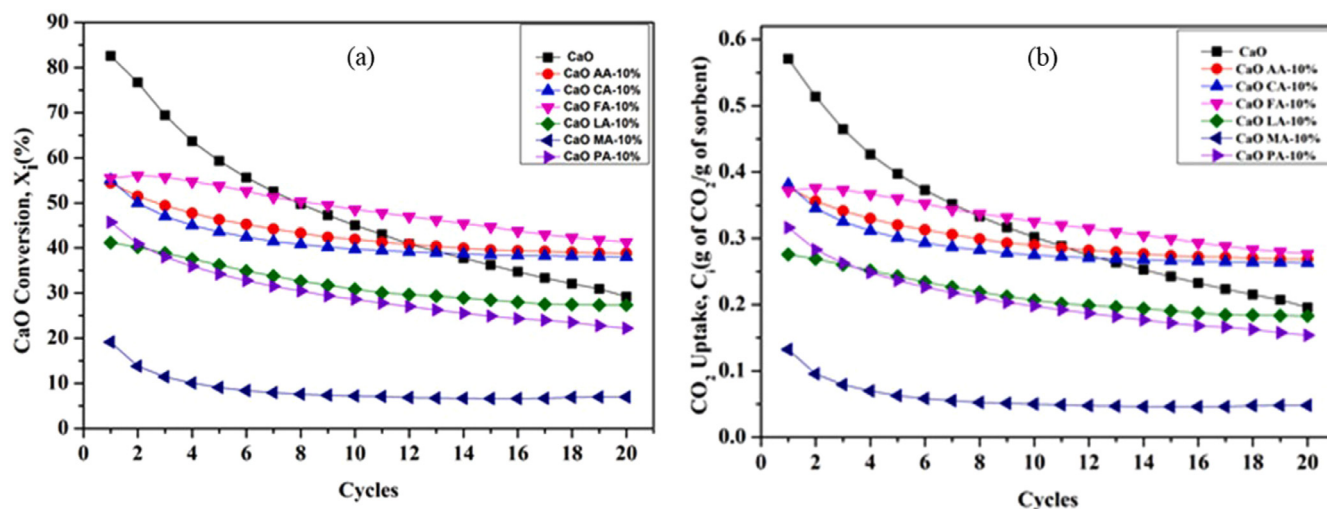
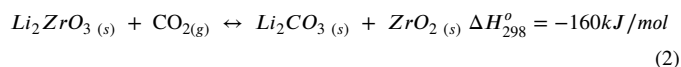
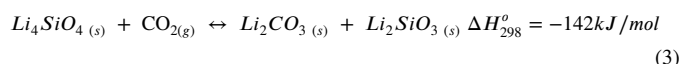
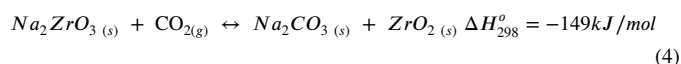


Fig. 9. (a) CaO conversion and (b) CO₂ uptake against number of cycles (Nawar et al., 2021).

(>500°C). According to m studies, these sorbents have the potential to produce up to 95% H₂ in the SESR of ethanol and methane (Aceves Olivares et al., 2014). Their capacity to retain CO₂ as alkali metal carbonates at a variety of temperatures has led to extensive investigation into them as CaO substitute sorbents (Pfeiffer, 2010). Using K₂ZrO₃ as a CO₂ sorbent, (Duan, 2012) conducted first-principal density functional theory (DFT) research. The results indicate that K₂ZrO₃ cannot regenerate economically at temperatures beyond 1000°C. Since CO₂ concentrations in flue gas streams can be as low as 15%, Li₂ZrO₃ and Na₂ZrO₃ are suitable for carbon capture from such streams due to their exceptional selectivity toward CO₂ in gas mixtures. The most studied Eqs. (2)–(4) are those that change with temperature and CO₂ partial pressure throughout the course of multiple cycles of CO₂ capture and release.



Alcántar-Vázquez et al. (2015) reported that alkali metal zirconates, including Na₂ZrO₃, are effective at accelerating the conversion of CO to CO₂. Zhao et al. (2020) explored the use of alkali ceramics as catalyst-sorbent materials to enhance H₂ production during biomass pyrolysis. The results showed that these materials promoted CO₂ capture, leading to increased H₂ production and tar-cracking reactions. The alkali ceramics demonstrated bifunctional activity, making them very promising for renewable energy production from biomass.

A regeneration step is then performed on the alkali-ceramic sorbent to release and recover the component that it has captured. High temperatures are applied to the sorbent to regenerate it and allow it to be utilized again. This process returns the sulfide compounds to their original state. The long-term sustainability and economic feasibility of alkali-ceramic sorbents are enhanced by their regenerability (Lee et al., 2006).

Due to their comparatively excellent cycle stability, alkali-metal-ceramic materials are seen as promising. However, they also have drawbacks like sluggish sorption kinetics and a poor sorption capacity. Recent studies have enhanced the preparation process and doped molten salt to increase the CO₂ sorption performance of alkali-metal-ceramic materials. Alkali-metal ceramics are typically used in reforming reactions at

temperatures between 550 and 600 °C because they can trap CO₂ at a lower temperature range than CaO.

3.4. Hydrotalcite sorbents

Hydrotalcite-like compounds or layered double hydroxides are anionic clays that have been used for more than 150 years for many applications, such as catalysts, ion exchangers, fire retardants, and antacids. Hydrotalcite (HTlc) sorbents can capture CO₂ and improve heat transfer efficiency (Dewoolkar and Vaidya, 2015). It is a commonly utilized CO₂ sorbent in steam reforming reactions because of its attractive properties including distinct layered structure, highly alkaline surface sites, large surface area, reoxidation reduction potential and feasible operating conditions requirements (Xu et al., 2020). HTlc-based sorbents can be operated at broad temperature operating conditions (20 °C - 600 °C) and offer medium CO₂ sorption capacity over appropriate cyclic stability, such as it can retain up to 90% of the original sorption capacity after multiple carbonization/calcination cycles with lower regeneration energy requirements (Aschenbrenner et al., 2011).

According to a study by Yong & Rodrigues (2002), the amount and presence of aluminium in the HTlc sorbent had a significant effect on CO₂ sorption tendency. This is because as its concentration increases in HTlc, the charge density of the HTlc layer increases which accelerates the CO₂ sorption process. Furthermore, because HTlc is a type of medium-temperature sorbent, its commercial application is limited because it will degrade in the reforming reaction of macromolecular hydrocarbons (>500°C) (Sikander et al., 2017). Improved thermal stability and active metal dispersion were achieved with the application of metal salt-modified hydrotalcite materials containing elements such as Ca, Cu, Ce, and Zr (Dębek et al., 2017). The metal-modified hydrotalcite also demonstrated great hydrogen production capacity and improved CO₂ sorption performance because it can prevent the formation of coke. Commercially available LDH materials have been used as a precursor to synthesis for better capacity and kinetics for CO₂ absorption. Years ago, Li et al. introduced a sorbent stearate-pillared layered double hydroxide (LDH) promoted by K₂CO₃ for a CO₂ adsorbent applicable to WGS conditions. This unique precursor is produced by subjecting commercial hydrotalcite, a kind of LDH, to acid-aided anionic exchange and wet impregnation methods. Including the pillared stearate compound in the layered double hydroxide (LDH) structure results in a significant increase in the gallery height extending from 0.28 nm to 3.4 nm when stearate is intercalated into the LDH. This gallery height increase was confirmed by observing distinct peaks of diffrac-

tion in powder X-ray diffraction (PXRD) analysis. Further, the distribution and composition of potassium (K) ions within brucite-like layers was revealed using transmission electron microscopy (TEM) images and energy-dispersive X-ray spectroscopy (EDX) analysis. The experimental results obtained using a thermogravimetric analyzer (TGA) demonstrated a remarkable CO₂ capacity of up to 1.93 mmol/g at 300°C. This capacity is 1.7 times greater than that of a standard K-promoted hydroxalite adsorbent over the enhanced kinetics (Li et al., 2013)

Gungrud & Vaidya (2020b) developed modified HTlc-based sorbents by separately incorporating Ca, Cu, and Zn elements using the co-precipitation technique. The sorbents were then evaluated for their performance in the SESMR process. The findings revealed that among all the metal-HTlc combinations, the Co-Cu-HTlc sorbent demonstrated the highest efficiency in promoting hydrogen production. HTlc material is considered favourable catalyst support, particularly in SE-SMR, where non-noble metal catalysts like Ni and Co are commonly employed, showing promising outcomes. Dang et al. (2016) prepared a range of Co-Ca-Al-HTlc with various Ca/Al ratios by co-precipitation method to produce Co-CaO-Ca₁₂Al₁₄O₃₃ bifunctional material.

Dewoolkar & Vaidya (2017b) studied the performance of Pt and Ru-modified Cu-Al-based HTlc in sorption-enhanced steam reforming. The modified materials achieved high H₂ concentrations and demonstrated stability over multiple cycles, attributed to improved surface area, metal dispersion, and synergistic effects with HTlc support. Gungrud et al. (2019) synthesized and investigated the performance of Ce-HTlc-based bifunctional materials incorporated with Ni and Co contents for SESMR process. The materials (Ce-Ni₁₀Co₃₀/HTlc and Ce-Ni₂₀Co₂₀/HTlc) showed improved performance with longer breakthrough times, higher CO₂ sorption capacities, and >90% H₂ purity. They also demonstrated stability over multiple cycles. Another study by Dewoolkar & Vaidya (2017a) in which they synthesized a hybrid material (Ni-K-CaO/HTlc) by mixing CaO, HTlc, and Ni catalyst and investigated its efficacy in the SESR of butanol. During the pre-breakthrough stage, the material showed stability over 21 cycles, effective synergy among its components, and an H₂ concentration exceeding 95%. Additionally, it demonstrated a high 12.8 mol-CO₂/kg CO₂ sorption capacity. Furthermore, the SESR procedure that encourages hydrogen synthesis uses the majority of HTLC materials made by conventional metal species.

HTlc materials possess distinctive layered structures and strong surface alkalinity, HTlc is well-suited for the sorption of CO₂ from acid gas. Its sorption kinetics are slow, and its sorption capacity is much lower than that of a sorbent based on calcium oxide. Nevertheless, to enhance its sorption ability, it is frequently required to modify the materials. The use of HTlc sorbents in SESR has a temperature range of around 550 °C. The incorporation of metal oxides in HTlc materials improves the sorption-enhanced performance to achieve >90% H₂ purity in SESR with high stability in sorption-desorption cycles. Therefore, to synthesize more effective HTlc sorbent materials in the future, more research on the use of novel metal components in HTlc will be required.

3.5. Waste-derived sorbents

Waste-derived sorbents are derived from biomass, agricultural residues, or industrial by-products. These sorbents provide a sustainable approach to hydrogen production (Wang et al., 2019). In some recent research, solid wastes were recycled to create CO₂ sorbents to cut costs and eliminate waste. Waste-derived CO₂ sorbents provide environmental benefits by recycling solid waste and reducing its impact. Various solid wastes, rich in components like Ca, Si, and Al, can be utilized for low-cost sorbent preparation. In addition, including inert components in some waste materials enhances sorbent performance, making this approach an area of active research.

Extensive research has focused on the synthesis of CO₂ sorbents using solid waste, demonstrating their effectiveness comparable to sorbents

developed based on commercial chemicals. Yan et al. (2015) utilized fly ash from power plants as a modifier and CaO as a calcium precursor to create a sorbent based on CaO in their work. Amazingly, even after 30 cycles of sorption and regeneration, the sorbent exhibited a stable sorption capacity of 38 wt. % at the calcination conditions (920°C in an environment of pure CO₂). The synthesis of an inert component, Ca₂Al₂SiO₇, within the fly ash-modified CaO-based sorbent was responsible for the material's increased sintering resistance. Tian et al. (2015) used Ca-rich scrap steel slag to synthesize a CaO-based sorbent that is more stable than bare CaO. The sorbent showed a maximum sorption capacity of 50 wt.% at the pre-breakthrough stage and held 25 wt.% after 30 cycles. The inclusion of different metal elements such as Al, Mg, and others in the steel slag was the reason for the production of MgO and Al₂O₃ during the sorbent's manufacture, as well as the improvement in sinter resistance and porosity.

In this regard, scientists have attempted to apply CO₂ sorbents made from waste in SESR hydrogen production, with promising outcomes. Wang et al. (2019) utilized rice husk (RH) to prepare a Li₄SiO₄ sorbent (RHLi₄SiO₄) through a solid-state reaction. The sorbent exhibited exceptional CO₂ sorption performance, with a high initial sorption capacity of 36.57 wt.%. This capacity remained stable over 20 subsequent cycles. Additionally, the RHLi₄SiO₄ sorbent was combined with a sol-gel prepared Ni/Al₂O₃ catalyst for the SESR process.

Gao et al. (2020) used a variety of fly ash samples to prepare Ni-CaO-FA bifunctional composites and CaO-FA sorbents. A sorption capacity of 30 wt.% was maintained after 20 cycles by 90 wt.% of CaO-FA₅. It was determined that the stability was caused by the particular surface area of CaO-FA₅ and the presence of inert elements such as SiO₂ and Al₆Si₂O₁₃. The 15-weight percent Ni-CaO-FA₅ bifunctional material demonstrated superior hydrogen production performance in the SESR experiment. Zhang et al. (2020) increased steam reforming in coke ovens by utilizing waste steel slag to generate a CaO sorbent, and then assessed its efficacy and CO₂ sorption performance. The CaO obtained from steel slag showed remarkable CO₂ sorption capabilities, continuing to hold a 48-weight percent sorption capacity even after 35 cycles. Compared to CaO made from calcium acetate, this capacity was 1.37 times more.

Researchers have produced hydrogen by biomass gasification and pyrolysis using waste-derived CO₂ sorbents, with encouraging results. Irfan et al. (2019) examined the effectiveness of waste marble as a bifunctional material in the steam gasification of municipal solid waste. The study showed how well waste marble-derived bifunctional material reforms tar and produces hydrogen-rich synthesis gas. Raheem et al. (2019) employed eggshell waste to prepare a CaO sorbent used to gasify lipid-extracted microalgae biomass (LMB). According to the study, both *Chlorella* and *Spirulina* microalgae performed best when gasified and produced hydrogen at a 50 wt.% concentration of CaO sorbent. In that order, the obtained hydrogen yields were 252 ml.g⁻¹ and 344 ml.g⁻¹.

The utilization of the waste material in producing a sorbent is a promising approach as it simultaneously recycles solid waste and reduces the sorbent production cost. A relatively recent area of research is the use of waste-derived sorbents to increase hydrogen output through SESMR processes.

3.6. Reforming and regeneration cycles

A key feature of SE-SMR is its cyclic nature, which includes both reforming and regeneration processes. The cyclic process is crucial for improving the overall efficiency of SE-SMR process. By alternating between regeneration and reforming stages, the process optimizes resource utilization and maximizes the production of valuable outputs, such as hydrogen and carbon monoxide. During the regeneration phase, the sorbent material undergoes a critical transformation known as calcination. This process releases the stored CO₂ and prepares the sorbent for the subsequent reforming cycles, which require temperatures exceeding

Table 2
CaO adsorption-desorption capacities of Fe and Ga sorbents

Sorbent	CO ₂ adsorption and desorption capacity (mmol/g)	t _{ads,90%} (min)	t _{des,90%} (min)
Pure CaO	6.9	34	33
1%Fe/CaO	13.0	24	35
5%Fe/CaO	12.8	25	26
10%Fe/CaO	13.7	22	19
15%Fe/CaO	12.2	30	29
1%Ga/CaO	13.0	21	28
5%Ga/CaO	13.0	25	24
10%Ga/CaO	14.2	10	17
15%Ga/CaO	11.1	34	26

700°C, depending on the type of sorbent material. This phase is essential for maintaining the sorbent's efficacy and ensuring a smooth transition to the reforming stage.

de la Cruz-Flores et al. (2020) investigated the regeneration of a deactivated active carbon catalyst using CO₂ as an activating agent under various regeneration conditions. They found that stability was achieved after 480 minutes, with a CH₄ conversion rate of 60% and a H₂ yield of 75%. The reaction was conducted at a temperature of 850°C. It was noted that the textural characteristics of the catalyst decreased with each cycle of deactivation and regeneration, which may be attributed to the formation of graphitic carbon deposited due to the carbon dioxide methanation (CDM) side reaction. This graphitic carbon proved to be resistant to gasification, resulting in the deterioration of the initial catalyst after three regeneration cycles.

Al-Mamoori et al. (2019) investigated the capacities and time required to achieve 90% of the capacity and 90% of the regeneration process of doped materials using TGA. They doped CaO with Fe and Ga to study their effects on the adsorption behaviour compared to bare CaO at different ratios. Their results indicated that metal doping in CaO can significantly reduce the regeneration time as shown in Table 2. Furthermore, stability measurements revealed that the loss of CaO capacity due to particle sintering could be minimized in the presence of the doped metals.

For SE-SMR to be effective, the regeneration and reforming processes must work together harmoniously. This coordinated approach reduces energy losses and maximized the output of CO and H₂. Fan et al. (2012) integrated chemical looping technology with the SE-SMR process to offer a configuration that increased the process energy efficiency. The regeneration step of SE-SMR significantly influences the energy dynamics of the process, as it involves the activation of both catalyst and sorbent material. Activation of the catalyst is necessary to initiate the reforming processes that convert methane and steam into hydrogen and carbon monoxide. Similarly, the activation of the adsorbent material is crucial for releasing trapped CO₂ and preparing the sorbent for the next reforming cycle. To achieve optimal efficiency and minimize energy losses in SE-SMR, it is essential to effectively activate both materials.

4. Bi-functional materials (catalyst/sorbent) for enhanced hydrogen production

Bi-functional materials have become a potentially fruitful direction for improved hydrogen generation. To maximize the processes involved in producing hydrogen, these materials combine catalytic activity with sorption abilities. Bi-functional materials can concurrently promote reforming activities and selectively capture or eliminate reaction by-products like carbon dioxide by combining catalytic and sorption capabilities into a single material (Di Carlo et al., 2017; Zhao et al., 2016).

Le Chatelier's concept is used by SE-SMR to produce high-purity H₂. The generation of hydrogen may be adversely affected by the ineffective removal of CO₂ throughout the reaction. The distance between CO₂

production and capture would be reduced, improving sorption kinetics, by merging catalytic and sorption sites on a smaller scale and attaining more uniform dispersion. In order to solve this, scientists have created bifunctional catalytic materials, which combine adsorption and catalytic active sites. This has led to a recent surge in interest in the field of SESR sorbent research. Additionally, research suggests that these bifunctional materials may maintain a reasonably high partial pressure of CO₂ close to the sorption sites, which improves CO₂ collection and increases the generation of hydrogen. These properties also assist to reduce operating costs. Nickel-based catalysts paired with CO₂ sorbents are one of the most often researched bi-functional materials. The high activity of nickel catalysts in SMR reactions is well known, and CO₂ sorbents capture and remove CO₂ from the reforming process.

There are numerous benefits to incorporating bi-functional materials into SMR operations. Increasing the catalytic activity and selectivity towards hydrogen production increases the process efficiency overall. Simultaneous CO₂ adsorption lowers greenhouse gas emissions, which helps produce hydrogen more cleanly. Ru/Ca₃A₁₂O₆-CaO bifunctional materials were produced by Kim et al. (2019) via the sol-gel technique. The material demonstrated exceptional cyclic stability in CO₂ sorption experiments, maintaining 92% of its initial capacity after 10 carbonation/calcination cycles, with a sorption capacity of 46 wt.%. This stability was ascribed to the formation of a Ca₃A₁₂O₆ stabilizer, which stopped the sintering of CaO particles. The material in SE-SMR studies extracted CO₂ from the product gas, which caused the reaction equilibrium to change in favour of hydrogen generation. The produced gas H₂ purity surpassed 90% during the pre-breakthrough phase throughout ten cycles, demonstrating the system's superior efficacy in boosting hydrogen production.

Ghungrud and Vaidya (2020a) synthesized multiple bifunctional materials using the sorbent materials of CaO, MgO and ZrO₂ along with Co catalyst including, Co-CaO-CeO₂, Co-CaO-ZrO₂, and Co-CaO-MgO using the co-precipitation method and were applied in SESRE to enhance hydrogen production. At 500°C and an S/C ratio of 10, 20 cycles of sorption and desorption were carried out. Throughout 13 cycles, it was shown that Co-CaO/CeO₂ maintained steady sorption performance, yielding more than 85% H₂ with a higher breakthrough time and sorption capacity of 45 min and 24.7 wt.% respectively.

Shokrollahi Yancheshmeh et al. (2017) synthesized the bifunctional material Ca₉A₁₆O₁₈-CaO/NiO-10CeO₂ using a wet mixing technique. Further, the material was evaluated for the performance of CO₂ sorption and the SESR using glycerol. After 15 cycles, the CaO conversion rate declined from 96.5% to 80%. Further, 98% pure H₂ with 91% H₂ yield were obtained from the SESR of glycerol employing this material during 20 cycles (Fig. 10), exhibiting strong hydrogen generation potential.

5. Reaction kinetics in (SE)-SMR

The understanding of catalytic reaction mechanisms along with the kinetics is a highly important aspect of the SMR process, which has not been explored adequately in the existing literature. Different kinetic models are developed for various catalyst systems since the derived mechanism and parameters depend on the catalyst composition.

Akers & Camp (1955) were among the first to investigate the methane and steam reaction rate over a reduced nickel catalyst supported by kieselguhr in 1955. They found that the reaction rate is first-order with respect to methane with the rate determining step is the decomposition of methane. In 1967 and 1968, (Bodrov, 1967, 1968) found that the rate of reaction was inhibited by the presence of hydrogen at 673.15 to 873.15 K and was not inhibited if the temperature was above 973.15 K. They predicted the mechanism for this reaction is based on the surface reaction between a chemisorbed oxygen atom and a chemisorbed CH₂ radical. This also aligned with the study conducted by Temkin (1979), which stated that above 1173.15 K, the reaction rate is simply just a first-order reaction concerning methane; however, be-

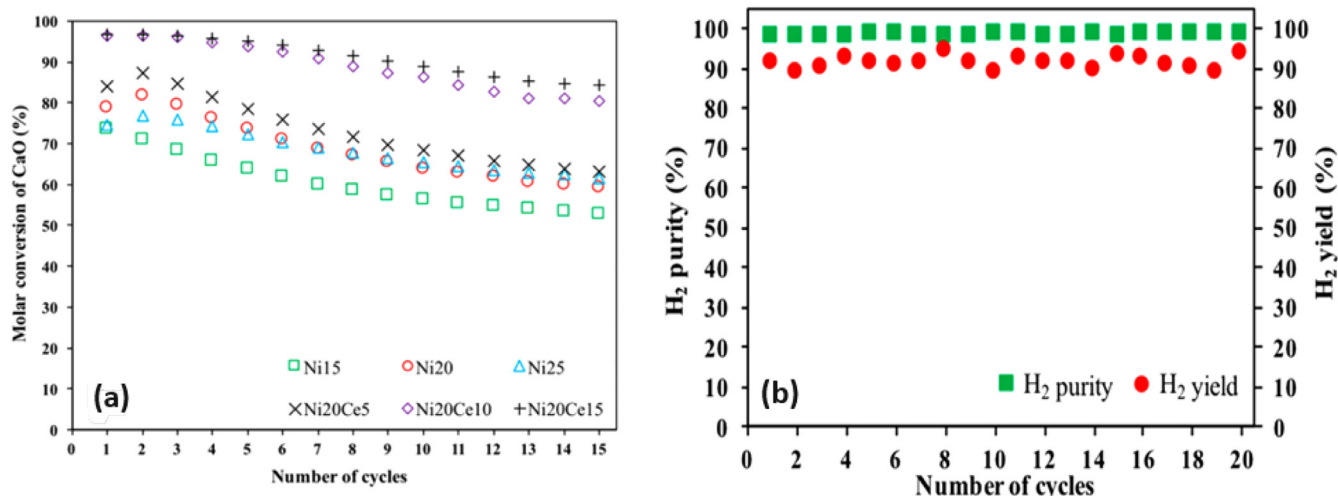


Fig. 10. (a) CaO molar conversion of $\text{Ca}_9\text{Al}_6\text{O}_{18}$ -CaO/NiO-10CeO₂ catalyst vs number of adsorption/desorption cycles, (b) product gas vs time in the first cycle (Shokrollahi Yancheshmeh et al., 2017)

tween 743.15 to 973.15 K, the reaction is limited by the presence of hydrogen.

Allen, Gerhard and Likins (1975) studied the methane–steam reaction using a commercial nickel catalyst at various pressures (1–18 atm). They assumed that the controlling steps were the desorption of carbon monoxide and carbon dioxide. They found that the kinetic models reasonably represented the data at 1 atm.

Numaguchi and Kikuchi (NK) (Numaguchi & Kikuchi, 1988) and (Xu & Froment, 1989) kinetic models are frequently used in SMR process on nickel catalysts. The NK model incorporated the Langmuir-Hinshelwood and power law models to create a combined rate equation for SMR, with the assumption that the surface response is the governing step. The model was analyzed at reaction temperatures up to 1160 K and pressures up to 25 bar. Conversely, Xu & Froment (1989) presented several possible chemical reactions and generated 21 sets of rate equations by considering the Langmuir-Hinshelwood reaction mechanism over the Ni/MgAl₂O₄ catalyst. This became one of the primary references for the reaction rate for the SMR kinetics for industries and other researchers such as Oliveira et al. (2009); Ding & Alpay (2000a); Wei & Iglesia (2004); Abbas et al. (2017); Quirino et al. (2021), among others.

In 2001, Hou & Hughes (2001) developed the kinetics of SMR over a commercial Ni/ α -Al₂O₃ catalyst using the Langmuir-Hinshelwood-Hougen-Watson (LH-HW) approach by considering six possible reactions. The concept of Freundlich's non-ideal adsorption approach was also considered to alter the powers of steam and hydrogen in the rate equations. The comparison between the experimental data and the results from the kinetic model was in good agreement. Another kinetic investigation was also performed by Maestri et al. (2008) on the catalytic mechanism of SMR over Rh/Al₂O₃ catalyst at 673.15 K, 773.15 K, and 873.15 K. The comprehensive and thermodynamically consistent microkinetic model was used to analyze kinetics. Methane activation was considered the rate-limiting step, while all the steps involving the co-reactant were quasi-equilibrated. The kinetic model successfully predicted the most significant aspects of the experiments. At high temperatures, the overall reaction rate was a first-order dependent on CH₄ concentration, while at low temperatures, product inhibition was also predicted.

Wang et al. (2022) studied the reaction processes of SE-SMR catalyzed by Ni-modified CaO using DFT simulations. After Ni alteration, the rate-limiting phase of the SE-SMR process shifted from CH dissociation to CH₃ dissociation. This modification led to a drop in the activation

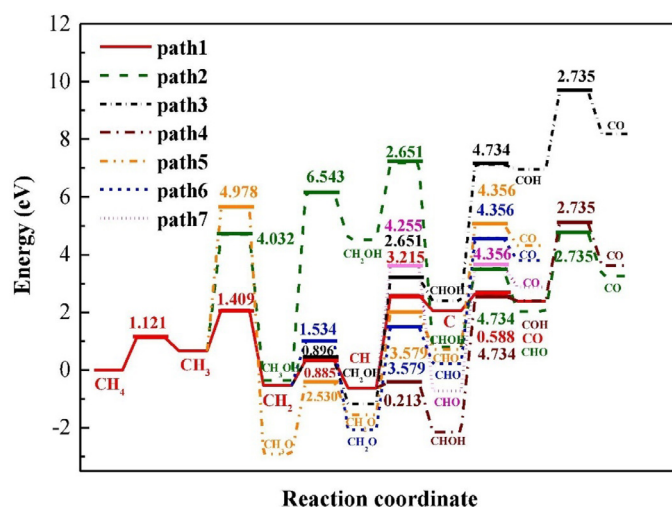


Fig. 11. Potential pathways and relative energy variations of the SE-SMR reaction on a Ni-CaO surface (Wang et al., 2022)

energy barrier from 3.215 to 2.030 eV. Seven potential trajectories of SE-SMR on a Ni-CaO surface for hydrogen production were identified, as shown in Fig. 11. Liu et al. (2019) noted that adding Ni and CaO improved the dissociation of H₂O to produce enough O intermediates for oxidizing C. The presence of Ni and CaO slowed down the diffusion of C and the formation of C-C bonds, which therefore hindered carbon deposition. The microscopic investigation of the reaction mechanism of SESR in the presence of catalysts-modified CaO-based materials has not been thoroughly investigated yet.

Salcedo et al. (2021) demonstrated the impact of the Ni/CeO₂ catalyst on the SMR process. The pathway involving COH intermediates proved effective in preventing carbon build-up and catalytic deactivation. The interactions between nickel and cerium-based support played a key role in ensuring efficient SMR performance while avoiding carbon formation. Niu et al. (2020) evaluated the catalytic performance of core-shell (Ni@Pt) catalysts for SMR through both DFT calculations and experimental kinetics. Their findings revealed that Ni@Pt catalysts facilitated the creation of potent basic surface OH* species, which enhanced reactivity with CH_x and improved resistance to carbon build-up.

Table 3
Overview of reaction kinetics in SMR reaction

Catalyst	Temperature (K)	Rate of reaction	Ref.
Reduced nickel/kieselguhr	609.2–910.9	$r = kP_{CH_4}$	(Akers & Camp, 1955)
Nickel α -alumina	673.15–873.15	$r = k \frac{P_{CH_4}}{P_{H_2}}$	(Bodrov, 1967, 1968)
Nickel α -alumina	>973.15	$r = \frac{kP_{CH_4}}{1 + a \frac{P_{CH_4}}{P_{H_2}} + bP_{CO}}$	
Commercial nickel	910.9	$r_{CO} = \frac{-k_1(P_{CO} - K_{P1} \frac{P_{CH_4}P_{H_2O}}{P_{H_2}})}{1 + K_4P_{H_2O} + K_4K_{S1} \frac{P_{CH_4}P_{H_2O}}{P_{H_2}} + K_4K_{S1}K_{S2} \frac{P_{CH_4}P_{H_2O}^2}{P_{H_2}^2}}$ $r_{CO_2} = \frac{-k_2(P_{CO_2} - K_{P2} \frac{P_{CH_4}P_{H_2O}}{P_{H_2}})}{1 + K_4P_{H_2O} + K_4K_{S1} \frac{P_{CH_4}P_{H_2O}}{P_{H_2}} + K_4K_{S1}K_{S2} \frac{P_{CH_4}P_{H_2O}^2}{P_{H_2}^2}}$	(Allen, Gerhard and Likins, 1975)
Commercial nickel	743.15–973.15	$r = \frac{k_1P_{CH_4}P_{H_2O}(1 - (\frac{P_{CO}}{P_{H_2}})(\frac{P_{CH_4}P_{H_2O}}{P_{H_2}}))}{(P_{H_2O} + k_{-1}/k_2P_{H_2O}P_{H_2} + k_{-1}k_{-2}/k_2k_3P_{H_2}^2 + k_{-1}k_{-2}k_{-3}/k_2k_3k_4P_{H_2}^3)(1 + K_{S1}(\frac{P_{H_2O}}{P_{H_2}}))}$	(Temkin, 1979)
Commercial nickel	>1173.15	$r = kP_{CH_4}$	
Ni/ MgAl ₂ O ₄	773– 848	$r_1 = \frac{k_1/P_{H_2}^{2.5}(P_{CH_4}P_{H_2O} - \frac{P_{H_2}^2P_{CO}}{K_1})}{(1 + K_{CO}P_{CO} + K_{H_2}P_{H_2} + K_{CH_4}P_{CH_4} + K_{H_2O} \frac{P_{H_2O}}{P_{H_2}})^2}$ $r_2 = \frac{k_2/P_{H_2}(P_{CO}P_{H_2O} - \frac{P_{H_2}P_{CO_2}}{K_2})}{(1 + K_{CO}P_{CO} + K_{H_2}P_{H_2} + K_{CH_4}P_{CH_4} + K_{H_2O} \frac{P_{H_2O}}{P_{H_2}})^2}$ $r_3 = \frac{k_3/P_{H_2}^{1.5}(P_{CH_4}P_{H_2O}^2 - \frac{P_{H_2}^3P_{CO_2}}{K_3})}{(1 + K_{CO}P_{CO} + K_{H_2}P_{H_2} + K_{CH_4}P_{CH_4} + K_{H_2O} \frac{P_{H_2O}}{P_{H_2}})^2}$	(Xu & Froment, 1989)
Ni/ α -Al ₂ O ₃	748–823	$r_1 = \frac{k_1(\frac{P_{CH_4}P_{H_2O}^2}{P_{H_2}^2} - \frac{P_{CO}P_{H_2}}{K_{P1}})(1 - \frac{P_{CO}P_{H_2}}{K_{P1}P_{CH_4}P_{H_2O}})}{(1 + K_{CO}P_{CO} + K_{H_2}P_{H_2} + K_{H_2O} \frac{P_{H_2O}}{P_{H_2}})^2}$ $r_2 = \frac{k_2(\frac{P_{CO}P_{H_2O}^2}{P_{H_2}^2} - \frac{P_{CO}P_{H_2}}{K_{P2}})(1 - \frac{P_{CO}P_{H_2}}{K_{P2}P_{CH_4}P_{H_2O}})}{(1 + K_{CO}P_{CO} + K_{H_2}P_{H_2} + K_{H_2O} \frac{P_{H_2O}}{P_{H_2}})^2}$ $r_3 = \frac{k_3(\frac{P_{CH_4}P_{H_2O}^2}{P_{H_2}^2} - \frac{P_{CO}P_{H_2}}{K_{P3}})(1 - \frac{P_{CO}P_{H_2}}{K_{P3}P_{CH_4}P_{H_2O}})}{(1 + K_{CO}P_{CO} + K_{H_2}P_{H_2} + K_{H_2O} \frac{P_{H_2O}}{P_{H_2}})^2}$	(Hou & Hughes, 2001)
Ni/La ₂ O ₃	923.15–1023.15	$r_{CH_4} = \frac{K_1k_2K_3K_4P_{CH_4}P_{CO_2}}{K_1k_2K_3P_{CH_4}P_{CO_2} + K_1k_2P_{CH_4} + K_1k_3P_{CO}}$	(Tspouriari & Verykios, 2001)
Rh/Al ₂ O ₃	673.15–873.15	$r_{SR} = \frac{r_{CH_4}^0}{(1 + \gamma_1C_{H_2}^0)(1 + \gamma_2C_{H_2}^0 + \gamma_3C_{CO}^0)^2} (1 - \eta_{SR})$	(Maestri et al., 2008)

Wang et al. (2017) compared the effects of Ni/Ag alloy and pure Ni catalyst on methane activation in SMR. The substitution of Ag atoms on the Ni surface greatly impacted the active sites close to Ag, with Ag acting as a blocking agent to inhibit C–H activation on the active areas of the Ni surface. As a result, the Ni/Ag alloy successfully limited CH₄ decomposition and reduced carbon formation in the SMR process. Overall, a great deal of research has been done to examine the kinetics of SMR by analyzing various catalysts, supports, and rate-limiting steps. As a result, various kinetic expressions have been discovered, and Table 3 gives an overview of relevant studies.

In the SE-SMR process, the carbonation reaction which is a non-catalytic gas-solid reaction system is also vital to be observed as the process involves a sorbent both in the two-pellet design (2-P) or in one-pellet design (1-P) material. The kinetic rate expression of the carbonation reaction can be expressed generally by a typical model for gas-solid reactions in Eq. 4.

$$\frac{dx}{dt} = Kf(P_a)F(x) \quad (5)$$

Where $f(P_a)$ is the partial pressure of CO₂ and $F(x)$ is a function of conversion based on the shrinking core model, random pore model, grain model, and other particle kinetic models (Rusten et al., 2007; Udemu & Font-Palma, 2023). Johnsen et al. (2006) used the shrinking core model to describe the kinetics of dolomite and introduced a parameter to account for the nonlinear driving force, the carbonation rate (Eq. 6) is as follows.

$$r_c = \frac{\frac{3}{R_p}(1 - X_{CaO})^{\frac{2}{3}} \frac{1}{RT}(P_{CO_2} - P_{CO_2,eq})^n}{\frac{1}{k_4} + \frac{R_p[(1 - X_{CaO})^{\frac{1}{3}} - (1 - X_{CaO})^{\frac{2}{3}}]}{D_e} + \frac{(1 - X_{CaO})^{\frac{2}{3}}}{k_g}} \quad (6)$$

Aloisi et al. (2016) successfully modeled the behavior of 1-P material by combining reaction kinetics developed by NK and a particle grain size model of the sorbent by Stendardo & Foscolo (2009). The model considered the influence of temperature and carbon dioxide concentration in the gas phase on calcium oxide conversion as a function of time, as well as subsequent carbonation cycles. The governing equation of the model is given below (Eq. 7).

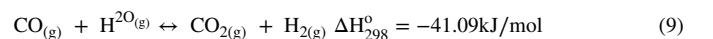
$$\frac{dX}{dt} = \frac{\sigma CaO^0 k_s (1 - X)^{\frac{2}{3}} (C_{CO_2} - C_{CO_2,eq})}{1 + \frac{NCaO^0 k_s}{2D_{PL}} \delta CaO^0 \sqrt{1 - X} - \sqrt{\frac{1 - X}{1 - X + X_Z}}} = \frac{r_{CBN}}{NCaO^0} \quad (7)$$

Regeneration of the sorbent is also a critical process in SE-SMR as the cyclic operation mode is applied in this process. Okunev et al. (2008) approximates the expression for the decarbonation rate of a single particle as a function of temperature, CO₂ pressure, sorbent texture, and Sherwood number as below. This expression predicts the exponential decay of the decarbonation rate with increasing CO₂ pressure by assuming CaO nuclei formation is the rate-limiting step and employing the differential particle model (Eq. 8).

$$r_{decay} = \frac{1}{M_{CO_2}} \frac{2.46 \times 10^4 S_{sp} \exp\left[\frac{-20474}{T}\right]}{\left[16 \frac{d_p^2 S_{sp} \rho_p}{\varepsilon^2 S_h}\right]^{2/3} + \exp\left[7.8 \left(\frac{P_{CO_2}}{P_{CO_2,eq}}\right)\right]} \left(1 - \frac{P_{CO_2}}{P_{CO_2,eq}}\right) \quad (8)$$

5.1. WGS reaction kinetics in (SE)-SMR

WGS reaction is a mildly exothermic reversible reaction to produce hydrogen and carbon dioxide from carbon monoxide and steam, usually assisted by a catalyst (Newsome, 1980). The reaction is given as follows:



Due to the exothermic nature of the reaction and its equilibrium constantly decreasing with increasing temperature, lower temperatures advance higher conversions. Nevertheless, at lower-temperature conditions, the reaction kinetics are slow (Pal et al., 2018; Smith et al., 2010). Hence, to balance between the thermodynamics and kinetics, the WGSR typically is operated as a two-stage process, which is a high-temperature process, 593.15 K to 723.15 K, followed by a low-temperature process, 423.15 K to 523.15 K, with different catalysts (Baraj et al., 2021; Masoudi Soltani et al., 2021).

Principally, there are two types of kinetic expressions for WGSR: a microkinetic approach and a macro kinetic approach. The microkinetic model is employed to recognize critical reaction intermediates and rate-limiting elementary reactions to approximate the reaction order and activation enthalpy theoretically and ultimately predict the possible catalyst to improve the kinetic reactions. On the contrary, the macro kinetic approach is based on experimental outcomes and is normally expressed in the Arrhenius model to predict the rate of reaction (Motagamwala & Dumesic, 2021; Smith et al., 2010).

For the microkinetic approach, the WGSR mechanism for metal oxide catalysts has generally been categorized into regenerative and associative mechanisms. Originally proposed in the late 1940s, the regenerative or redox mechanism is the oxidation-reduction cycle occurring on the surface of the catalyst where the catalyst surface is oxidized by H₂O to produce H₂ and is reduced by CO to produce CO₂ (Baraj et al., 2021; Smith et al., 2010). The reactions below summarize the regenerative mechanism (Choi & Stenger, 2005).



The associative mechanism was first presented earlier than the regenerative mechanism in the 1920s and the surface reaction intermediate was formate (HCOO). Later, another intermediate was introduced, which was the formation of carboxyl (COOH). The associative mechanism, generally represented by Langmuir–Hinshelwood involves an adsorption-desorption process in which adsorbed species interact to create an adsorbed intermediate, which subsequently breaks down to form H₂ and CO₂ (Ebrahimi et al., 2020; Zhu & Wachs, 2016). The associative mechanism is represented by the following reaction :



Generally, the regenerative or redox mechanism is accepted to describe the high-temperature WGSR. However, for the low-temperature WGSR, the mechanism is more challenging due to its unique mechanism for each catalyst. Thus, the associative mechanism is the widely accepted mechanism for the low-temperature WGSR (Ebrahimi et al., 2020; Reddy & Smirniotis, 2015).

For the macro kinetic approach, there are many kinetic equations for the high-temperature WGSR. The most common ones are shown in Table 3. Opinions on the reaction mechanism and the effect of pressure contributed primarily to the difference in the reaction rate. The presence of impurities in the gases and different mass-transfer limitations are also the reasons for the variations in those kinetics (Reddy & Smirniotis, 2015; Twigg & Imperial Chemical Industries, 1989). Podolski & Kim (1974) conducted experiments in a recycle reactor and used statistical techniques to differentiate between those models and they concluded that the Langmuir–Hinshelwood model and the power model are the best models to represent the reaction rate of WGSR that fits with the data from the experiments.

The majority of the kinetic models from the high-temperature WGSR can also be applied to low-temperature WGSR (Reddy & Smirniotis, 2015). For instance, Rhodes et al., (1995) discovered a similarity between high-temperature WGSR and low-temperature WGSR kinetics based on CuO/ZnO/Cr₂O₃ catalysts. However, the low-temperature WGSR also has its specific kinetic expressions, which are the most common ones represented in Table 4 (van Herwijnen & de Jong, 1980).

Table 4

Kinetic expressions for high-temperature and low-temperature water gas shift reaction (WGSR) (Reddy & Smirniotis, 2015)

WGSR stage	Model	Kinetic expressions
High-temperature WGSR (623 – 823 K)	Langmuir–Hinshelwood	$r = \frac{kK_{\text{CO}}K_{\text{H}_2\text{O}}([CO][H_2O] - \frac{[CO_2][H_2]}{K})}{(1 + K_{\text{CO}}[CO] + K_{\text{H}_2\text{O}}[H_2O] + K_{\text{CO}_2}[CO_2] + K_{\text{H}_2}[H_2])^2}$
	Hulburt–Vasan	$r = \frac{k[H_2O]}{1 + k[H_2O]/[H_2]}$
	Kodama	$r = \frac{k([CO][H_2O] - \frac{[CO_2][H_2]}{K})}{1 + K_{\text{CO}}[CO] + K_{\text{H}_2\text{O}}[H_2O] + K_{\text{CO}_2}[CO_2] + K_{\text{H}_2}[H_2]}$
	Oxidation–Reduction	$r = \frac{k_1[CO] + k_2[H_2O] + k_{-1}[CO_2] + k_{-2}[H_2]}{k_1[CO] + k_2([CO][H_2O] - \frac{[CO_2][H_2]}{K})}$
	Power law	$r = kP_{\text{CO}}^a P_{\text{H}_2\text{O}}^b P_{\text{CO}_2}^c P_{\text{H}_2}^d (1 - \beta)$
Low-temperature WGSR (323 – 623 K)	Campbell et al.	$r = k \frac{P_{\text{CO}} P_{\text{H}_2\text{O}}}{(1 + K_{\text{CO}} P_{\text{CO}} + K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}} + K_{\text{CO}_2} P_{\text{CO}_2} + K_{\text{H}_2} P_{\text{H}_2})^2}$
	Shchibrya et al.	$r = \frac{kP_{\text{H}_2\text{O}} P_{\text{CO}} (1 - \beta)}{A P_{\text{H}_2\text{O}} + P_{\text{CO}_2}}$
	Moe	$r = k P_{\text{CO}} P_{\text{H}_2\text{O}} (1 - \beta)$
	Kulkova and Temkin	$r = k P_{\text{CO}} \left(\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} \right)^{0.5} (1 - \beta)$
	Goodgidge and Quazi	$r = k P_{\text{CO}}^a P_{\text{H}_2\text{O}}^b P_{\text{CO}_2}^c P_{\text{H}_2}^d$

where $\beta = P_{\text{CO}_2} P_{\text{H}_2} / P_{\text{CO}} P_{\text{H}_2\text{O}} K$

Several researchers have also utilized the power law to fit the reaction kinetics for different catalysts. The model is also well-suited for the low-temperature WGS for different catalysts with different parameters (Reddy & Smirniotis, 2015). Smith et al. (2010); Reddy & Smirniotis (2015) and Saeidi et al. (2017) combined the more comprehensive kinetic expressions for both microkinetic and macro kinetic models on the high-temperature WGSR, low-temperature WGSR, and noble metal catalysts.

6. Exergy analysis for optimized SE-SMR process configurations

SE-SMR is a promising technology for hydrogen production with simultaneous carbon dioxide capture. As the need for clean and sustainable energy sources increases, researchers have been exploring advanced process configurations to enhance the efficiency and environmental performance of SE-SMR. This section focuses on several advanced process configurations for SE-SMR, including the integration of SE-SMR with chemical looping combustion (CLC), sorption-enhanced chemical looping reforming (SE-CLR) processes, other sorption-enhanced steam reforming processes, and renewable energy integration (Gunawan & Singh, 2022). Exergy analysis is essential to determine the effective thermodynamic limitations of a process. A few studies have reported the exergy analysis of the SE-SMR process to evaluate different process configurations and their performances and compare it to the conventional SMR process (Rahmat et al., 2023). Tzanetis et al. (2012) simulated the conventional SMR and SE-SMR using CaO-based sorbent at 25 bar pressure in Aspen Plus to compute mass and energy balances for the exergy analysis. In comparison to the traditional SMR process, SE-SMR is found to be superior in producing pure hydrogen by 17.3%. The optimal operating temperature for reforming in SE-SMR is found to be 650°C based on the hydrogen yield and reaction enthalpy. The exergy analysis revealed that the SE-SMR process offers 3.2% more exergy benefits. Furthermore, it is reported that the exergy benefit of SE-SMR increased to 10.8% when compared with conventional SMR processes including a similar level of CO₂ capture.

6.1. Integration of SE-SMR with chemical looping combustion

The integration of SE-SMR with CLC is an advanced process configuration that combines the benefits of both technologies. CLC is a combustion process that utilizes oxygen carriers to transfer oxygen from air to the fuel, enabling efficient fuel conversion with inherent CO₂ capture. Fig. 12 shows the schematic diagram of the integrated SE-SMR with CLC process. By integrating SE-SMR with CLC, achieving simultaneous CO₂ capture and hydrogen production. This configuration offers enhanced process efficiency, reduced energy consumption, and improved overall carbon capture performance (Zhu et al., 2015)

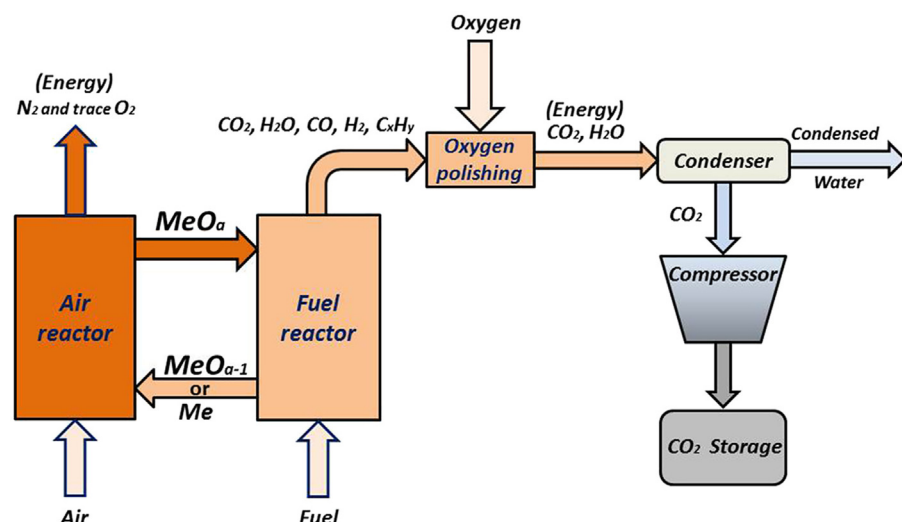


Fig. 12. Schematic diagram of sorption enhanced chemical looping combustion (SE-CLC) process (Abuelgasim et al., 2021).

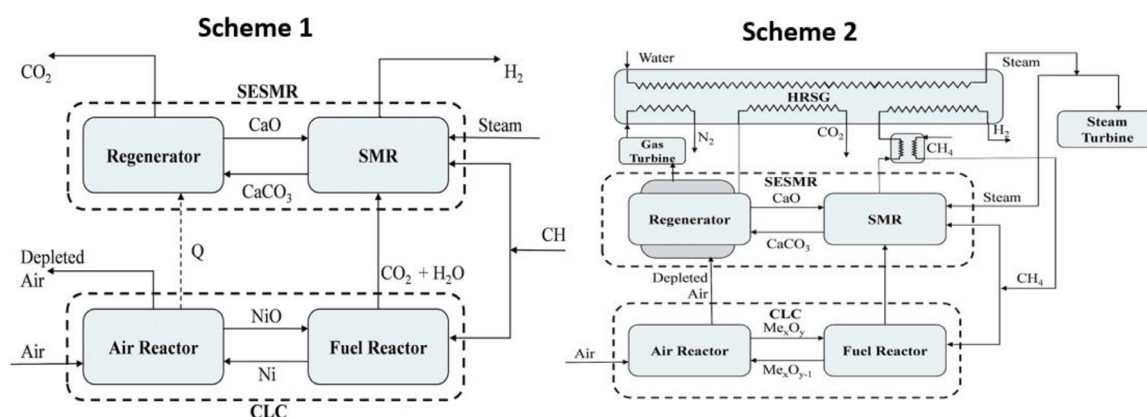


Fig. 13. Scheme 1 and Scheme 2 represent mass and heat-integrated CLC-SESMR and self-sustained CLC-SE-SMR respectively (Alam et al., 2017)

Zhu et al. (2015) performed thermodynamic analysis to evaluate SE-SMR-coupled with chemical looping combustion process and compared it to the conventional SMR-based process at similar conditions using Aspen plus software package. It was found that the SE-SMR base process showed 95% hydrogen yield at a relatively lower reforming temperature (665°C) in comparison to the conventional SMR-based process, which was reported as 77.1% hydrogen yield at 900°C. Alam et al. (2017) also integrated chemical looping with the SE-SMR process and proposed two new schemes as shown in Fig. 13. Scheme 1 included the thermal and mass coupling of the SE-SMR process with a chemical looping system. In Scheme 2, for the thermal coupling additionally, the depleted air from the air reactor was also introduced into the regenerated to utilize the heat in the CaO regeneration process using heat recovery steam generation. The proposed scheme 2 exhibited improved performance with 98% pure hydrogen (3.5% more than the base case) and 95.1% CO₂ capture, respectively energy and exergy efficiencies of 70.3% and 68.24%.

Yan, Thanganadar, et al. (2020) proposed six process configurations for the SE-SMR-based hydrogen production process, simulated in Aspen Plus. The cases were built using the SE-SMR process including the PSA unit integrated with chemical looping, oxy-fired and hydrogen-fired calciners. The detailed modelling of the heat exchanger network was implemented, and thermodynamic analysis was performed to account for the calculations of waste heat recovery. The effect of process variables including S/C ratio, reforming temperature and pressure on process performance was studied and briefly presented in Table 4. The cases were compared using the criteria of H₂ purity, CO₂ capture efficiency, methane conversion, cold gas, and net efficiency of a process. The net efficiency of a process is calculated using equation 13,

where, $H_{2\text{-flow-produced}}$, $CH_{4\text{-flow-in}}$, $CH_{4\text{-flow-in-additional}}$ respectively are the mass flowrate of produced hydrogen, feed methane and the additional methane consumed as a fuel to meet the heating requirements in the boiler and calciner.

$$\eta = \frac{H_{2\text{flow-produced}} \times LH_{H_2}}{(CH_{4\text{flow-in}} + CH_{4\text{flow-in-additional}}) \times LH_{CH_4} + \frac{Utility_{Elec}}{\eta_{Elec}}} \quad (13)$$

It is reported that the SE-SMR system including the PSA unit integrated with chemical looping (Case 4) can provide almost 100% CO₂ removal efficiency, whilst replacing chemical looping with the oxy-fired system (Case 5) can also result in similar CO₂ capture efficiency and hydrogen purity. However, the net process efficiency was reduced by 2.7% compared to case 2. The reduction in net efficiency is observed as the CO₂ capture efficiency and H₂ purity level are increased, this is attributed to the additional consumption of methane as a fuel and the increased penalty of electricity in the air separation unit.

6.2. Integration of SE-SMR with amine-based PCC

Davies et al. (2024) considered Yan et al.'s case 2 (discussed in the previous section) as a base case and modified it by retrofitting it with the amine-based PCC process to capture CO₂ from the combustor. The schematic diagram of the reported process is shown in Fig. 14. Feed gas contains methane, and steam enters the reforming reactor along with CaO and purified hydrogen is produced which is separated using knock-out drums and the PSA unit. The CaO in the reformer converts into CaCO₃, which is regenerated in the calciner. The heat required in the calciner is provided by the combustor unit using methane gas and the

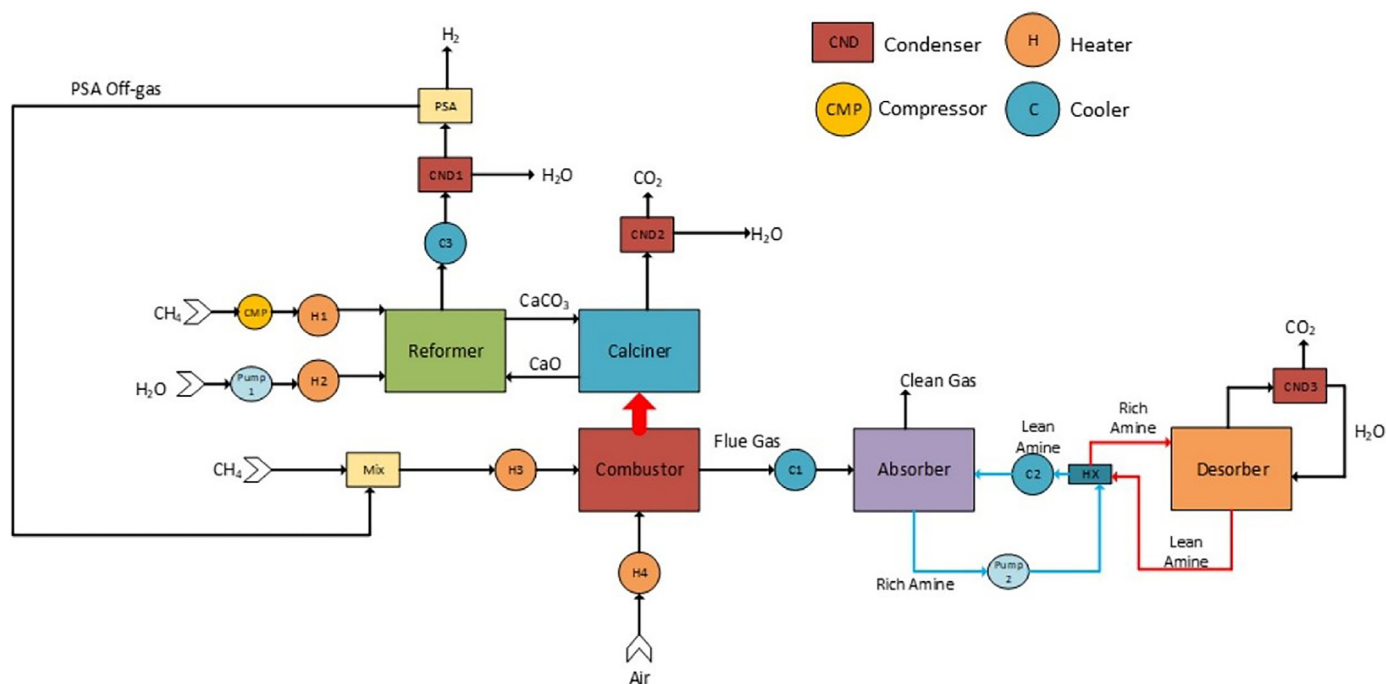


Fig. 14. SESMR Integrated with Amine-based PCC system (Davies et al., 2024)

produced CO_2 is passed to the amine-based PCC system which captures CO_2 , and the loaded amine solvent is further regenerated in the desorber unit. The authors analyzed the process for the exergy evaluation to determine the true thermodynamic potential of the process. The CO_2 capture efficiency and exergy efficiency were respectively determined as 96.04 % and 69.21 %. The results revealed that the combustion process and the PCC system reduce the exergy and process efficiency due to the highly irreversible nature of the combustion and amine absorption process. Furthermore, the process was modified by replacing combustion and PCC systems with chemical looping combustion. The results revealed that the CO_2 capture rate reached around 100 % and exergy efficiency also considerably improved (76.31 %).

6.3. Integration of SE-SMR with chemical looping reforming process

Sorption-enhanced chemical looping reforming (SE-CLR) is an innovative process configuration that combines the principles of SE-SMR and chemical looping reforming (CLR). The schematic diagram of the SE-CLR process is shown in Fig. 15. SE-CLR integrates a CO_2 sorbent into the CLR process, enabling simultaneous CO_2 capture and reforming reactions. The CO_2 sorbent captures CO_2 during the reforming stage, and then, in the reduction stage, the captured CO_2 is released and utilized as an oxygen carrier for fuel conversion. SE-CLR offers several advantages, including improved hydrogen purity, enhanced reforming performance, and efficient CO_2 capture and utilization (Udomchoke et al., 2016).

6.4. Integration of SE-SMR with renewable energy

The integration of renewable energy sources into SE-SMR processes offers opportunities for sustainable hydrogen production. Renewable energy sources such as solar and wind power can provide electricity for operating various components of the SE-SMR system, including pumps, compressors, and CO_2 sorbent regeneration units. The schematic diagram of SE process integrated with solar energy is shown in Fig. 16. The use of renewable energy reduces the carbon footprint of the SE-SMR process and contributes to the decarbonization of the hydrogen production sector. Furthermore, the coupling of renewable energy with SE-SMR can

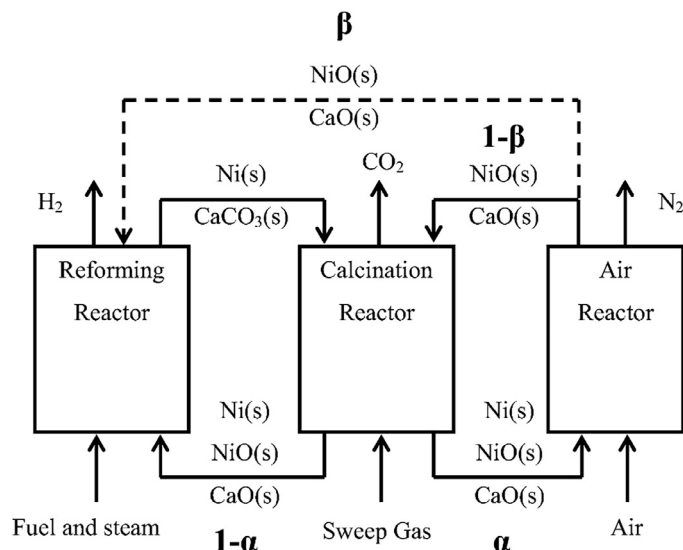


Fig. 15. Schematic diagram of sorption enhanced chemical looping reforming (SE-CLR) process (Udomchoke et al., 2016)

enable the production of "green hydrogen" which has zero or low carbon emissions throughout the entire production process (Song et al., 2022).

6.5. Other sorption-enhanced steam reforming processes

In addition to the integration with CLC and CLR, other sorption-enhanced steam reforming processes have been investigated. These include the integration of SE-SMR with Pressure Swing Adsorption (PSA) (Abd et al., 2023), Membrane Reactors (Anderson et al., 2014), and Hybrid Systems (Faheem et al., 2021). The integration with PSA involves the use of a CO_2 sorbent in the PSA unit to capture CO_2 from the reformate stream, allowing for enhanced hydrogen recovery and reduced CO_2 emissions. Membrane reactors combine catalytic reforming and CO_2 separation in a single unit, enabling in situ CO_2 capture

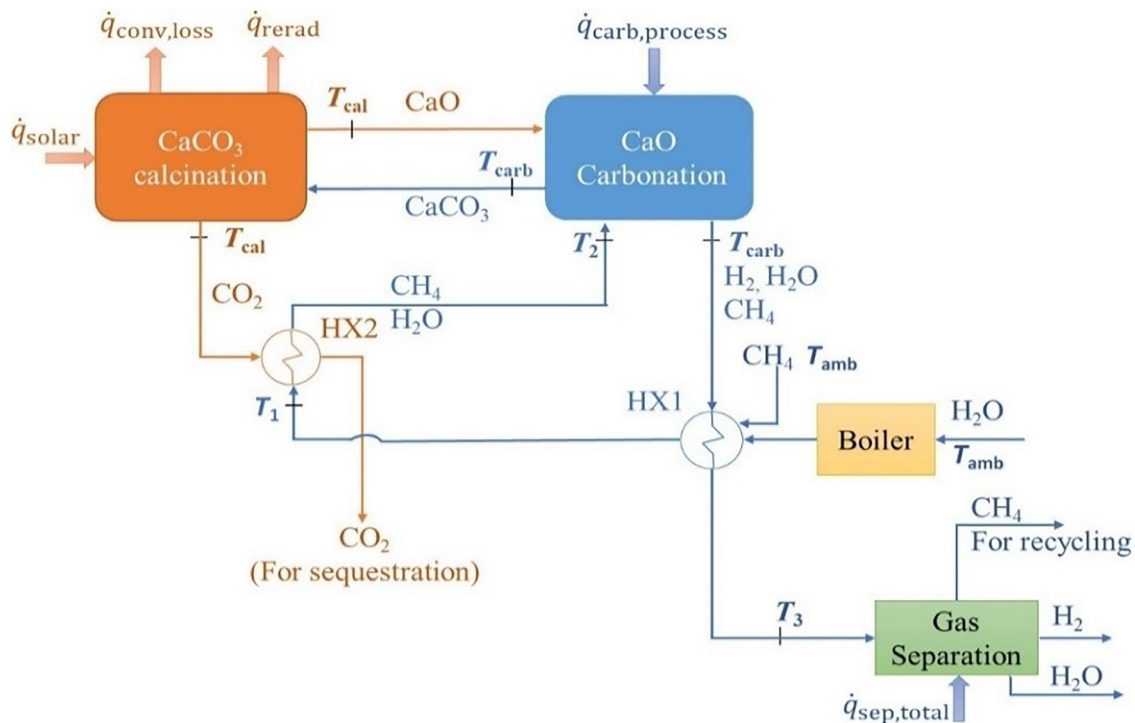


Fig. 16. Schematic diagram of SE + renewable energy process (Gunawan and Singh, 2022).

and high-purity hydrogen production. Hybrid systems integrate multiple technologies, such as SE-SMR, PSA, and/or membrane reactors, to achieve synergistic effects and optimize process performance for enhanced hydrogen production and CO₂ capture.

7. Techno-economics of SE-SMR

SE-SMR is increasingly regarded as a transformative technology for clean hydrogen production, as it integrates hydrogen generation with in situ carbon capture. To evaluate its feasibility and commercial potential, a comprehensive techno-economic assessment is required. This section examines the key factors including the economic viability of SE-SMR, including technical specifications, capital investments (CAPEX), operational costs (OPEX), and potential revenue generation of SE-SMR (Bhandari & Shah, 2021). A detailed analysis is essential to determining whether SE-SMR can be scaled for industrial use and integrated into the global hydrogen economy.

Recent studies have significantly advanced the techno-economic analysis of hydrogen production technologies. For example, Catumba et al. (2023) provided a bibliometric analysis of hydrogen generation, highlighting sustainability challenges, while Garcia & Oliva (2023) evaluated the economic and environmental aspects of green hydrogen produced via solar and wind energy. Other researchers have examined hydrogen production from renewable energy sources, adding valuable insights to the field (Al-Orabi et al., 2023; Hasan & Genç, 2022; Karayel et al., 2023; Kudria et al., 2021).

The primary metric for assessing the techno-economic feasibility of hydrogen facilities is the Levelized Cost of Hydrogen (LCOH). LCOH offers a comprehensive analysis of the total costs incurred over the lifespan of a hydrogen production plant and enables standardized comparisons across hydrogen production methods. It serves as a critical indicator of SE-SMR's long-term financial viability and is a key tool for investors and policymakers in guiding decisions (Parkinson et al., 2019). The LCOH is calculated using Eq. 14:

$$LCOH = \frac{(\text{Net Present Value of Total Cost (CAPEX + OPEX) over the lifetime of the plant } [\$/])}{(\text{Total Hydrogen Production over the lifetime of the plant [kg]})} \quad (14)$$

Several factors influence the cost of hydrogen production, including geographical location, energy source, plant design, raw materials, and capacity. Table 6 provides a comparative analysis of LCOH for various hydrogen production methods, adjusted to 2023 Consumer Price Index (CPI) values to account for inflation. Monte Carlo methods have also been employed to predict future costs based on technological advancements.

The comparative analysis of hydrogen production methods, as indicated in Table 5 highlights a clear cost advantage for blue hydrogen, particularly through SMR and its variants, over green hydrogen production. While SE-SMR, which incorporates in situ carbon capture, incurs slightly higher costs than traditional SMR, it remains competitive due to its dual benefit of hydrogen production and carbon capture, positioning SE-SMR as a viable solution for reducing CO₂ emissions with manageable economic penalties.

The cost difference between blue and green hydrogen can be attributed to several factors. In blue hydrogen production, natural gas prices are a major component, contributing 52-69% of operational expenses (OPEX). This reliance on natural gas prices makes blue hydrogen production more vulnerable to market fluctuations. For SE-SMR, CO₂ storage costs typically range between \$10 and \$20 per tonne of CO₂, adding approximately \$0.09 to \$0.18 per kg of H₂ produced. In analyzed cases, CO₂ storage alone accounts approximately 8% of total operating expenses (OPEX) (Yan, Manovic, et al., 2020). In contrast, green hydrogen production relies heavily on renewable energy sources, such as solar or wind, which have higher CAPEX, contributing to the wider range of LCOH values for green hydrogen.

In SE-SMR, catalysts play an essential role in CO₂ capture, though the costs associated with catalysts, particularly Ni-based catalysts, are relatively minor in comparison to CO₂ capture and storage expenses. For instance, Yan, Manovic, et al. (2020) found that the Ni-based catalyst cost is about 0.5-1.1% of total OPEX in SE-SMR. This modest contribution highlights that while catalysts are indispensable for SE-SMR, their

Table 5
Sensitivity analysis for multiple cases proposed by Yan, Thanganadar, et al. (2020)

No.	Cases	CO ₂ capture (%)	H ₂ purity (%)	Net efficiency (%)	Optimal conditions
1	SE-SMR Air fired calciner	63	98	76	The optimal reforming temperature was found in the range of 600 to 650°C, whilst pressure and S/C were determined as 5 bar and 5 respectively.
2	SE-SMR Pressure swing adsorption	69	100	75	The optimal reforming temperature was below 650°C, and 5 bar pressure was found optimal for maximum CO ₂ capture efficiency, while 25 bar pressure was found for maximum process net efficiency.
3	SE-SMR integrated with chemical looping combustion	95	98	72	Similar conditions as reported for case 1.
4	SE-SMR Pressure swing adsorption integrated with chemical looping combustion	100	100	76	The optimal temperature and pressure were reported as below 650°C and 25 bar respectively.
5	SE-SMR Pressure swing adsorption with oxy-fired calciner	100	100	74	Similar conditions as reported for case 4.
6	SE-SMR Pressure swing adsorption with indirect H ₂ -fired calciner	87	100	62	For pressure and temperature conditions the reported values are similar to case 2. However, an S/C ratio of 5 was found suitable to achieve maximum CO ₂ capture efficiency and S/C of 3 was optimal to achieve maximum process efficiency.

Table 6
Comparative analysis of levelized cost of hydrogen (LCOH) across different hydrogen production methods (adjusted to 2023 consumer price index, CPI).

Hydrogen Production Type	Feed source (Technology)	Levelized Cost of Hydrogen [\$/kg] ^a	Adjusted Cost to 2023[\$/kg] ^a	Reference
Blue	Natural Gas (SMR/ATR)	0.5 - 1.7	0.6 - 1.9	(IEA (2021), Global Hydrogen Review 2021, IEA, Paris https://www.iea.org/reports/global-hydrogen-review-2021 , License: CC BY 4.0, n.d.)
Blue	Natural Gas (SE-SMR)	2.3 - 3.6	2.7 - 4.2	(Yan, Manovic, et al., 2020)
Blue	Natural Gas (SMR)	1.8 - 1.9	2.1 - 2.3	(Nazir et al., 2021)
Blue	Natural Gas (SMR-VPA)	7.4 - 7.9	7.6 - 8.1	(Lee et al., 2023)
Green	Electrolysis (PV/Wind)	3.7 - 4.5	3.7 - 4.6	(Al-Orabi et al., 2023)
Green	Electrolysis (PV ^b /Wind)	7.0 - 14.8	7.7 - 16.3	(Benalcazar & Komorowska, 2022)
Green	Electrolysis (Offshore Wind)	13.8 - 14.6	14.6-15.5	(Jang et al., 2022)
Green	Electrolysis (PV/Wind)	5.0 - 6.1	5.9 - 7.2	(Turkdogan, 2021)

^a Bold text is used to highlight the lower levelized cost of hydrogen (LCOH) for each hydrogen production route.

^b PV refers to Photovoltaic

direct economic impact on operating costs is significantly lower than that of CO₂ capture and storage.

Research into bi-functional materials, such as Ru/Ca₃Al₂O₆-CaO, is gaining attention for its potential to improve SE-SMR performance by reducing solid flux and enhancing intra-particle mass transfer. However, the high cost of ruthenium (approximately \$18,560 per kilogram) (Ruthenium prices, 2024) compared to nickel (around \$16.33 per kilogram) (Nickel prices, 2024) presents a significant challenge. While bi-functional materials show promise in optimizing efficiency, their economic feasibility at scale remains a concern. Furthermore, real-world data on SE-SMR's economic performance with various catalyst-sorbent systems, especially in large-scale applications, is limited.

Another important factor influencing the economic performance of hydrogen production facilities is the CAPEX-to-OPEX ratio. For blue hydrogen, this ratio typically stands at 1:1.15 (Yan, Manovic, et al., 2020), indicating that operational expenses (such as fuel, electricity, and CO₂ management) have a greater impact on overall costs than initial capital investments. This is particularly relevant for technologies like SE-SMR, where ongoing fuel and CO₂ storage costs can significantly affect long-term profitability.

Geographical location also substantially impacts the LCOH, as demonstrated by marked cost differences across countries. For instance, the cost of producing green hydrogen in Egypt is three to four times more expensive than in Poland (Al-Orabi et al., 2023), largely due to disparities in energy infrastructure, renewable resource availability, and electricity costs. This geographical variability underscores the importance of local energy market conditions in determining the economic feasibility of hydrogen production technologies.

8. Challenges and future directions

In this section, we will explore the challenges and future directions of SE-SMR for blue hydrogen production. SE-SMR encounters a range of technical challenges and limitations that need to be addressed. Additionally, environmental and economic considerations play a crucial role in the development and adoption of SE-SMR. Furthermore, policy and regulatory aspects are important factors that shape the implementation and success of SE-SMR technologies.

8.1. Technical challenges and limitations

SE-SMR has the potential for hydrogen production but faces many technical obstacles and restrictions. A key problem involves developing high-performance sorbents that can effectively capture CO₂ and remain stable in the demanding conditions needed for steam methane reforming. Developing and refining the sorbent material requires careful engineering to achieve a balance in adsorption-desorption kinetics, selectivity, and durability. Similarly, development of effective catalyst in the sorption enhanced reforming environment is also challenging as the operating temperature conditions of the SE-SMR process is different to the conventional process. In addition, the understanding of sorbent and catalyst is also crucial and the development of stable bifunctional material that act as both catalyst and sorbent may be the appropriate solution for effective operations of SE-SMR process. Additionally, incorporating sorbent beds into the reformer system increases intricacy and expenses, requiring strong technical solutions to guarantee effective and uninterrupted functioning. The energy needs of the process and their effects on

the efficiency of the reforming process are crucial elements that require in-depth examination and solutions for mitigation. Scalability and cost-effectiveness in large-scale implementations are important areas that need more study and development to promote the broad use of SE-SMR technology.

8.2. Environmental and economic considerations

Implementing SE-SMR has significant effects on environmental sustainability and economic feasibility. SE-SMR shows potential as a method to decrease greenhouse gas emissions linked to hydrogen production from an environmental standpoint. SE-SMR efficiently captures CO₂ during the reforming process, showing promise in reducing CO₂ emissions and aiding in climate change mitigation. Yet, the energy requirements of SE-SMR, especially the regeneration of sorbents and the overall process energy needs, require a thorough life cycle analysis to evaluate its overall environmental impact compared to traditional SMR or other hydrogen production techniques. From an economic perspective, SE-SMR can potentially decrease the expenses related to CO₂ collection by combining it with hydrogen generation. However, obstacles remain in enhancing the cost efficiency of sorbent materials, system integration, and operational costs. The initial expenditure needed to implement SE-SMR technology, which includes research and development expenses for enhanced sorbents and system design, continues to be a key factor affecting its economic viability and general acceptance in the market. Advancements in material research, process optimization, and creative economic models are necessary to improve the competitiveness and appeal of SE-SMR in environmental and economic aspects.

8.3. Policy and regulatory aspects

Policy and regulatory frameworks related to energy generation, emissions reduction, and technology innovation play a crucial role in effectively implementing and accepting SE-SMR. Government regulations that promote clean energy sources and decrease carbon emissions are essential for encouraging the use of SE-SMR. Regulatory mechanisms including carbon pricing, emission reduction objectives, and subsidies for low-carbon technology might affect the economic feasibility and appeal of investments in SE-SMR. Yet, a crucial obstacle is ensuring that these policies are effectively coordinated to promote the advancement and implementation of SE-SMR. The technology's distinctive features, including combining CO₂ capture with hydrogen production, would necessitate customized regulatory frameworks that address its particular qualities while maintaining safety, effectiveness, and environmental sustainability. Collaboration among policymakers, industry stakeholders, and research institutions is crucial to develop supportive policies, offer funding incentives, and establish a regulatory environment that promotes innovation, scalability, and the widespread use of SE-SMR as a viable solution for a sustainable energy future.

9. Conclusions

The progress in research on developing SE-SMR process has been summarized, highlighting the urgent need to mitigate the significant environmental impact associated with conventional SMR methods. These traditional methods contribute to nearly half of global hydrogen production, with approximately 95% of hydrogen worldwide still derived from fossil fuels. This study aims to assess past advancements, current challenges and future prospects in this critical field. The review delves into various aspects of the SE-SMR process, including process analysis, catalyst development, reaction kinetics, CO₂ sorbents, SE-SMR process configurations and techno-economic assessments. Among sorbents, CaO-based materials stand out for their cost-effectiveness and high theoretical CO₂ sorption capacity. However, their efficiency diminishes significantly over repeated carbonization/calcination cycles. Strategies to

enhance their performance include introducing inert components, modifying calcium precursors, and tailoring the microscopic structure. Alkali-metal-ceramic materials exhibit promise because of their stable cyclic performance, but are limited by lower sorption capacity and slow kinetics. Recent efforts have focused on refining their preparation methods and incorporating molten salts to improve CO₂ sorption. Hydrotalcite materials, with their layered structure and high surface alkalinity are also explored for CO₂ sorption. However, their performance in terms of capacity and kinetics lags behind CaO-based sorbents, necessitating modifications to boost efficiency. Additionally, exploring waste derived sorbents offers a promising avenue for reducing costs while recycling solid wastes. Bifunctional catalysts, which combine catalytic and sorptive sites in a single particle, are a key focus of recent SE-SMR research. These bifunctional catalysts improve reaction kinetics and reduce reactor residence time.

SE-SMR technology provides notable benefits, such as a leveled cost of hydrogen that is approximately 25% lower and a carbon footprint that is almost 40% lower than traditional method. Its integrated design enables its scalability to hundreds of megawatts, making it viable for industrial applications. The future of SE-SMR appears bright, with advancements in catalyst and sorbent development continuing to gain momentum. Particularly, the rise in interest around bifunctional materials has spurred innovation, as these materials demonstrate exceptional mass transfer efficiency and outstanding performance in hydrogen production. Waste-derived sorbents also represent a burgeoning area of research, combining sustainability with economic feasibility. This review not only highlights the current state of SE-SMR technology but also paves the way to future advancements in the pursuit of a greener energy landscape.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- Abbas, S.Z., Dupont, V., Mahmud, T., 2017. Kinetics study and modelling of steam methane reforming process over a NiO/Al₂O₃ catalyst in an adiabatic packed bed reactor. *Int. J. Hydrogen. Energy* 42 (5), 2889–2903. doi:10.1016/j.ijhydene.2016.11.093.
- Abd, A.A., Othman, M.R., Majidi, H.S., Helwani, Z., 2023. Green route for biomethane and hydrogen production via integration of biogas upgrading using pressure swing adsorption and steam-methane reforming process. *Renew. Energy* 210, 64–78. doi:10.1016/j.renene.2023.04.041.
- Abuelgasim, S., Wang, W., Abdalazeez, A., 2021. A brief review for chemical looping combustion as a promising CO₂ capture technology: fundamentals and progress. *Sci. Total Environ.* 764, 142892.
- Aceves Olivas, D.Y., Baray Guerrero, M.R., Escobedo Bretado, M.A., Marques da Silva Paula, M., Salinas Gutiérrez, J., Guzmán Velderrain, V., López Ortiz, A., Collins Martínez, V., 2014. Enhanced ethanol steam reforming by CO₂ absorption using CaO, CaO·MgO or Na₂ZrO₃. *Int. J. Hydrogen. Energy* 39 (29), 16595–16607. doi:10.1016/j.ijhydene.2014.04.156.
- Akers, W.W., Camp, D.P., 1955. Kinetics of the methane-steam reaction. *AIChE J.* 1 (4), 471–475. doi:10.1002/aic.690010415.
- Alam, S., Kumar, J.P., Rani, K.Y., Sumana, C., 2017. Self-sustained process scheme for high purity hydrogen production using sorption enhanced steam methane reforming coupled with chemical looping combustion. *J. Clean. Prod.* 162, 687–701. doi:10.1016/j.jclepro.2017.05.136.
- Alcántara-Vázquez, B., Vera, E., Buitron-Cabrera, F., Lara-García, H.A., Pfeiffer, H., 2015. Evidence of CO oxidation–chemisorption process on sodium zirconate (Na₂ZrO₃). *Chem. Lett.* 44 (4), 480–482. doi:10.1246/cl.141134.
- Aliyu, M., Nemtallah, M.A., Said, S.A., Habib, M.A., 2016. Characteristics of H₂-enriched CH₄O₂ diffusion flames in a swirl-stabilized gas turbine combustor: Experimental and numerical study. *Int. J. Hydrogen. Energy* 41 (44), 20418–20432. doi:10.1016/j.ijhydene.2016.08.144.
- Al-Mamoori, A., Lawson, S., Rowanaghi, A.A., Rezaei, F., 2019. Improving adsorptive performance of CaO for high-temperature CO₂ Capture through Fe and Ga Doping. *Energy Fuels* 33 (2), 1404–1413. doi:10.1021/acs.energyfuels.8b03996.
- Aloisi, I., Jand, N., Stendardo, S., Foscolo, P.U., 2016. Hydrogen by sorption enhanced methane reforming: a grain model to study the behavior of bi-functional sorbent-catalyst particles. *Chem. Eng. Sci.* 149, 22–34. doi:10.1016/j.ces.2016.03.042.
- Al-Orabi, A.M., Osman, M.G., Sedhom, B.E., 2023. Evaluation of green hydrogen production using solar, wind, and hybrid technologies under various technical and financial scenarios for multi-sites in Egypt. *Int. J. Hydrogen. Energy* 48 (98), 38535–38556. doi:10.1016/j.ijhydene.2023.06.218.
- Alshafei, F.H., Minardi, L.T., Rosales, D., Chen, G., Simonetti, D.A., 2019. Improved sorption-enhanced steam methane reforming via calcium oxide-based sorbents with targeted morphology. *Energy Technol.* 7 (3), 1800807. doi:10.1002/ente.201800807.
- Alvarez, D., Carlos Abanades, J., 2005. Determination of the critical product layer thickness in the reaction of CaO with CO₂. *Indust. Eng. Chem. Res.* 44 (15), 5608–5615. doi:10.1021/IE050305S/ASSET/IMAGES/LARGE/IE050305SF000008.JPEG.
- Alves, H.J., Bley Junior, C., Niklevicz, R.R., Frigo, E.P., Frigo, M.S., Coimbra-Araújo, C.H., 2013. Overview of hydrogen production technologies from biogas and the applications in fuel cells. *Int. J. Hydrogen. Energy* 38 (13), 5215–5225. doi:10.1016/j.ijhydene.2013.02.057.
- Anderson, D.M., Kottke, P.A., Fedorov, A.G., 2014. Thermodynamic analysis of hydrogen production via sorption-enhanced steam methane reforming in a new class of variable volume batch-membrane reactor. *Int. J. Hydrogen. Energy* 39 (31), 17985–17997. doi:10.1016/j.ijhydene.2014.03.127.
- Andrews, J.W., 2020. Hydrogen production and carbon sequestration by steam methane reforming and fracking with carbon dioxide. *Int. J. Hydrogen. Energy* 45 (16), 9279–9284. doi:10.1016/j.ijhydene.2020.01.231.
- Angeli, S.D., Martavaltzi, C.S., Lemonidou, A.A., 2014. Development of a novel-synthesized Ca-based CO₂ sorbent for multicycle operation: Parametric study of sorption. *Fuel* 127, 62–69. doi:10.1016/j.fuel.2013.10.046.
- Antar, M., Lyu, D., Nazari, M., Shah, A., Zhou, X., Smith, D.L., 2021. Biomass for a sustainable bioeconomy: An overview of world biomass production and utilization. *Renew. Sustain. Energy Rev.* 139, 110691. doi:10.1016/j.rser.2020.110691.
- Antzaras, A.N., Lemonidou, A.A., 2022. Recent advances on materials and processes for intensified production of blue hydrogen. *Renew. Sustain. Energy Rev.* 155, 111917. doi:10.1016/j.rser.2021.111917.
- Anwar, S., Khan, F., Zhang, Y., Djire, A., 2021. Recent development in electrocatalysts for hydrogen production through water electrolysis. *Int. J. Hydrogen. Energy* 46 (63), 32284–32317. doi:10.1016/j.ijhydene.2021.06.191.
- Armutulu, A., Naeem, M.A., Liu, H.J., Kim, S.M., Kierzkowska, A., Fedorov, A., Müller, C.R., 2017. Multishelled CaO microspheres stabilized by atomic layer deposition of Al₂O₃ for enhanced CO₂ capture performance. *Adv. Mater.* 29 (41), 1702896. doi:10.1002/adma.201702896.
- Arun, J., Sasipraba, T., Gopinath, K.P., Priyadharsini, P., Nachiappan, S., Nirmala, N., Dawn, S.S., Thuy Lan Chi, N., Pugazhendhi, A., 2022. Influence of biomass and nanoadditives in dark fermentation for enriched bio-hydrogen production: A detailed mechanistic review on pathway and commercialization challenges. *Fuel* 327, 125112. doi:10.1016/j.fuel.2022.125112.
- Aschenbrenner, O., McGuire, P., Alsamaq, S., Wang, J., Supasitmongkol, S., Al-Duri, B., Styring, P., Wood, J., 2011. Adsorption of carbon dioxide on hydrotalcite-like compounds of different compositions. *Chem. Eng. Res. Design* 89 (9), 1711–1721. doi:10.1016/j.cherd.2010.09.019.
- Atilhan, S., Park, S., El-Halwagi, M.M., Atilhan, M., Moore, M., Nielsen, R.B., 2021. Green hydrogen as an alternative fuel for the shipping industry. *Curr. Opin. Chem. Eng.* 31, 100668. doi:10.1016/j.coche.2020.100668.
- Ayesha, M., Khoja, A.H., Butt, F.A., Sikandar, U., Javed, A.H., Naqvi, S.R., din, I., Mehman, M.T., 2022. Sorption enhanced steam reforming of methane over waste-derived CaO promoted MgNiAl hydrotalcite catalyst for sustainable H₂ production. *J. Environ. Chem. Eng.* 10 (3), 107651. doi:10.1016/j.jece.2022.107651.
- Baraj, E., Ciahotný, K., Hlinčík, T., 2021. The water gas shift reaction: Catalysts and reaction mechanism. *Fuel* 288, 119817. doi:10.1016/j.fuel.2020.119817.
- Benalcazar, P., Komorowska, A., 2022. Prospects of green hydrogen in Poland: a techno-economic analysis using a Monte Carlo approach. *Int. J. Hydrogen. Energy* 47 (9), 5779–5796. doi:10.1016/j.ijhydene.2021.12.001.
- Ben-Mansour, R., Haque, M.A., Habib, M.A., Paglieri, S., Harale, A., Mokheimer, E.M.A., 2023. Effect of temperature and heat flux boundary conditions on hydrogen production in membrane-integrated steam-methane reformer. *Appl. Energy* 346, 121407. doi:10.1016/j.apenergy.2023.121407.
- Bhandari, R., Shah, R.R., 2021. Hydrogen as energy carrier: techno-economic assessment of decentralized hydrogen production in Germany. *Renew. Energy* 177, 915–931. doi:10.1016/j.renene.2021.05.149.
- Bodrov, A. and T. (1967). *Kinet. Katal.* 4(8), 821–823.
- Bodrov, A. and T. (1968). *Kinet. Katal.* 5(9), 1065–1075.
- Bui, M., Adjiman, C.S., Bardow, A., Anthony, E.J., Boston, A., Brown, S., Fennell, P.S., Fuss, S., Galindo, A., Hackett, L.A., Hallett, J.P., Herzog, H.J., Jackson, G., Kemper, J., Krevor, S., Maitland, G.C., Matuszewski, M., Metcalfe, I.S., Petit, C., ... Mac Dowell, N., 2018. Carbon capture and storage (CCS): The way forward. In: *In Energy and Environmental Science*, 11. The Royal Society of Chemistry, pp. 1062–1176. doi:10.1039/c7ee02342a.
- Capa, A., García, R., Chen, D., Rubiera, F., Pevida, C., Gil, M.V., 2020. On the effect of biogas composition on the H₂ production by sorption enhanced steam reforming (SESR). *Renew. Energy* 160, 575–583. doi:10.1016/j.renene.2020.06.122.
- Caravella, A., Barbieri, G., Drioli, E., 2009. Concentration polarization analysis in self-supported Pd-based membranes. *Sep. Purif. Technol.* 66 (3), 613–624. doi:10.1016/j.seppur.2009.01.008.
- Caroline Pereira Oliveira, A., Bruno Lima Santos, D., Gomes Moura, L., Eponina Hori, C., 2024. Sorption-enhanced steam reforming of propane using bifunctional Ni/CaO, Ni/CaO-CaZrO₃, and Ni/CaO-Ca₂SiO₄ catalysts. *Fuel* 358, 130170. doi:10.1016/j.fuel.2023.130170.
- Catumba, B.D., Sales, M.B., Borges, P.T., Ribeiro Filho, M.N., Lopes, A.A.S., Sousa Rios, M.A.de, Desai, A.S., Bilal, M., Santos, J.C.S.dos, 2023. Sustainability and challenges in hydrogen production: an advanced bibliometric analysis. *Int. J. Hydrogen. Energy* 48 (22), 7975–7992. doi:10.1016/j.ijhydene.2022.11.215.
- Chen, C.H., Yu, C.T., Chen, W.H., Kuo, H.T., 2020. Effect of in-situ carbon dioxide sorption on methane reforming by nickel-calcium composite catalyst for hydrogen production. *IOP Conf. Series: Earth Environ. Sci.* 463 (1), 012102. doi:10.1088/1755-1315/463/1/012102.
- Chen, C., Yang, S., 2021. The energy demand and environmental impacts of oxy-fuel combustion vs. post-combustion capture in China. *Energy Strategy Rev.* 38, 100701. doi:10.1016/j.esr.2021.100701.
- Chen, Z., Duan, X., Wei, W., Wang, S., Ni, B.-J., 2020. Electrocatalysts for acidic oxygen evolution reaction: Achievements and perspectives. *Nano Energy* 78, 105392. doi:10.1016/j.nanoen.2020.105392.
- Chen, Z., Wei, W., Song, L., Ni, B.J., 2022. Hybrid water electrolysis: a new sustainable avenue for energy-saving hydrogen production. *Sustainable Horizons* 1, 100002. doi:10.1016/j.horiz.2021.100002.
- Cherbanski, R., Molga, E., 2018. Sorption-enhanced steam methane reforming (SE-SMR) – A review: Reactor types, catalyst and sorbent characterization, process modeling. *Chem. Process Eng.- Inżynieria Chemiczna i Procesowa* 39 (4), 427–448. doi:10.24425/122961.
- Choi, Y., Stenger, H.G., 2005. Kinetics, simulation and optimization of methanol steam reformer for fuel cell applications. *J. Power. Sources* 142 (1), 81–91. doi:10.1016/j.jpowsour.2004.08.058.
- Clough, P.T., Boot-Handford, M.E., Zheng, L., Zhang, Z., Fennell, P.S., 2018. Hydrogen production by sorption enhanced steam reforming (SESR) of biomass in a fluidised-bed reactor using combined multifunctional particles. *Materials* 11 (5). doi:10.3390/ma11050859.
- Cortazar, M., Sun, S., Wu, C., Santamaria, L., Olazar, L., Fernandez, E., Artetxe, M., Lopez, G., Olazar, M., 2021. Sorption enhanced ethanol steam reforming on a bi-functional Ni/CaO catalyst for H₂ production. *J. Environ. Chem. Eng.* 9 (6), 106725. doi:10.1016/j.jece.2021.106725.
- Dang, C., Yu, H., Wang, H., Peng, F., Yang, Y., 2016. A bi-functional Co-CaO-Ca₂Al₂O₃ catalyst for sorption-enhanced steam reforming of glycerol to high-purity hydrogen. *Chem. Eng. J.* 286, 329–338. doi:10.1016/j.cej.2015.10.073.
- Davies, W.G., Babamohammadi, S., Yan, Y., Clough, P.T., Soltani, S.M., 2024. Exergy analysis in intensification of sorption-enhanced steam methane reforming for clean hydrogen production: Comparative study and efficiency optimisation. *Carbon Capture Sci. Technol.* 12, 100202.
- Debek, R., Motak, M., Galvez, M.E., Da Costa, P., Grzybek, T., 2017. Catalytic activity of hydrotalcite-derived catalysts in the dry reforming of methane: on the effect of Ce promotion and feed gas composition. *Reaction Kinetics, Mech. Catal.* 121 (1), 185–208. doi:10.1007/s11144-017-1167-1.
- de la Cruz-Flores, V.G., Martínez-Hernández, A., Gracia-Pinilla, M.A., 2020. Deactivation of Ni-SiO₂ catalysts that are synthesized via a modified direct synthesis method during the dry reforming of methane. *Appl. Catal. A: General* 594, 117455. doi:10.1016/j.apcata.2020.117455.
- Dewoolkar, K.D., Vaidya, P.D., 2015. Improved hydrogen production by sorption-enhanced steam methane reforming over hydrotalcite- and calcium-based hybrid materials. *Energy Fuels* 29 (6), 3870–3878. doi:10.1021/acs.energyfuels.5b00584.

- Dewoolkar, K.D., Vaidya, P.D., 2017a. New hybrid materials for improved hydrogen production by the sorption-enhanced steam reforming of butanol. *Energy Technol.* 5 (8), 1300–1310. doi:10.1002/ente.201600645.
- Dewoolkar, K.D., Vaidya, P.D., 2017b. Sorption-enhanced steam reforming of ethylene glycol over dual functional hydrotalcite materials promoted with Pt and Ru. *ChemistrySelect*. 2 (27), 8326–8336. doi:10.1002/slct.201701007.
- Di Carlo, A., Aloisi, I., Jand, N., Stendardo, S., Foscolo, P.U., 2017. Sorption enhanced steam methane reforming on catalyst-sorbent bifunctional particles: A CFD fluidized bed reactor model. *Chem. Eng. Sci.* 173, 428–442. doi:10.1016/j.ces.2017.08.014.
- Di Giuliano, A., Giancaterino, F., Courson, C., Foscolo, P.U., Gallucci, K., 2018. Development of a Ni-CaO-mayenite combined sorbent-catalyst material for multicycle sorption enhanced steam methane reforming. *Fuel* 234, 687–699. doi:10.1016/J.FUEL.2018.07.071.
- Ding, Y., Alpay, E., 2000a. Adsorption-enhanced steam-methane reforming. *Chem. Eng. Sci.* 55 (18), 3929–3940. doi:10.1016/S0009-2509(99)00597-7.
- Ding, Y., Alpay, E., 2000b. Equilibria and kinetics of CO₂ adsorption on hydrotalcite adsorbent. *Chem. Eng. Sci.* 55 (17), 3461–3474. doi:10.1016/S0009-2509(99)00596-5.
- Dotan, H., Landman, A., Sheehan, S.W., Malviya, K.D., Shter, G.E., Grave, D.A., Arzi, Z., Yehudai, N., Halabi, M., Gal, N., Hadari, N., Cohen, C., Rothschild, A., Grader, G.S., 2019. Decoupled hydrogen and oxygen evolution by a two-step electrochemical-chemical cycle for efficient overall water splitting. *Nat. Energy* 4 (9), 786–795. doi:10.1038/s41560-019-0462-7.
- Duan, Y., 2012. A first-principles density functional theory study of the electronic structural and thermodynamic properties of M₂ZrO₃ and M₂CO₃ (M = Na, K) and their capabilities for CO₂ capture. *J. Renew. Sustain. Energy* 4 (1), 13109. doi:10.1063/1.3683519.
- D. W. Allen, E. R. Gerhard and M. R. Likins, Jr. (1975). *Kinetics of the Methane-Steam Reaction*. 14(3), 256–259.
- Ebrahimi, P., Kumar, A., Khraishah, M., 2020. A review of recent advances in water-gas shift catalysis for hydrogen production. *Emergent. Mater.* 3 (6), 881–917. doi:10.1007/s42247-020-00116-y.
- Erans, M., Manovic, V., Anthony, E.J., 2016. Calcium looping sorbents for CO₂ capture. *Appl. Energy* 180, 722–742. doi:10.1016/J.APENERGY.2016.07.074.
- Faheem, H.H., Tanveer, H.U., Abbas, Syed.Z., Maqbool, F., 2021. Comparative study of conventional steam-methane-reforming (SMR) and auto-thermal-reforming (ATR) with their hybrid sorption enhanced (SE-SMR & SE-ATR) and environmentally benign process models for the hydrogen production. *Fuel* 297, 120769. doi:10.1016/j.fuel.2021.120769.
- Fan, L.-S., Zeng, L., Wang, W., Luo, S., 2012. Chemical looping processes for CO₂ capture and carbonaceous fuel conversion – prospect and opportunity. *Energy Environ. Sci.* 5 (6), 7254–7280. doi:10.1039/C2EE03198A.
- Farooqi, A.S., Yusuf, M., Ishak, M.A.I., Zabidi, N.A.M., Saidur, R., Khan, A., Abdullah, B., 2021. Combined H₂O and CO₂ reforming of CH₄ over Ca promoted Ni/Al₂O₃ catalyst: enhancement of Ni-CaO interactions. In: Awang, M., Emamian, S.S. (Eds.), *Lecture Notes in Mechanical Engineering*. Springer Singapore, pp. 220–229. doi:10.1007/978-981-16-3641-7_26.
- Farooqi, A.S., Yusuf, M., Mohd Zabidi, N.A., Saidur, R., Sanaullah, K., Farooqi, A.S., Khan, A., Abdullah, B., 2021. A comprehensive review on improving the production of rich-hydrogen via combined steam and CO₂ reforming of methane over Ni-based catalysts. *Int. J. Hydrogen. Energy* 46 (60), 31024–31040. doi:10.1016/j.ijhydene.2021.01.049.
- Farooqi, A.S., Yusuf, M., Zabidi, N.A.M., Saidur, R., Shahid, M.U., Ayodele, B.V., Abdullah, B., 2022. Hydrogen-rich syngas production from bi-reforming of greenhouse gases over zirconia modified Ni/MgO catalyst. *Int. J. Energy Res.* 46 (3), 2529–2545. doi:10.1002/er.7325.
- Farooqi, S.A., Farooqi, A.S., Sajjad, S., Yan, C., Victor, A.B., 2023. Electrochemical reduction of carbon dioxide into valuable chemicals: a review. *Environ. Chem. Lett.* doi:10.1007/s10311-023-01565-7.
- Gao, K., Shokrollahi Yancheshmeh, M., Duchesne, J., Iliuta, M.C., 2020. Valorization of coal fly ash as a stabilizer for the development of Ni/CaO-based bifunctional material. *ACS. Sustain. Chem. Eng.* 8 (9), 3885–3895. doi:10.1021/acssuschemeng.9b07360.
- Garcia, G.M., Oliva, H.S., 2023. Technical, economic, and CO₂ emissions assessment of green hydrogen production from solar/wind energy: the case of Chile. *Energy* 278, 127981. doi:10.1016/j.energy.2023.127981.
- Gautam, R., Nayak, J.K., Ress, N.V., Steinberger-Wilckens, R., Ghosh, U.K., 2023. Bio-hydrogen production through microbial electrolysis cell: Structural components and influencing factors. *Chem. Eng. J.* 455, 140535. doi:10.1016/j.cej.2022.140535.
- Ghungrud, S.A., Dewoolkar, K.D., Vaidya, P.D., 2019. Cerium-promoted bi-functional hybrid materials made of Ni, Co and hydrotalcite for sorption-enhanced steam methane reforming (SESME). *Int. J. Hydrogen. Energy* 44 (2), 694–706. doi:10.1016/j.ijhydene.2018.11.002.
- Ghungrud, S.A., Vaidya, P.D., 2020a. Improved hydrogen production from sorption-enhanced steam reforming of ethanol (SESRE) using multifunctional materials of cobalt catalyst and Mg-, Ce-, and Zr-modified CaO sorbents. *Indust. Eng. Chem. Res.* 59 (2), 693–703. doi:10.1021/acs.iecr.9b05472.
- Ghungrud, S.A., Vaidya, P.D., 2020b. Sorption-enhanced reaction process for glycerol-to-hydrogen conversion over cobalt catalyst supported on promoted hydrotalcites. *Int. J. Hydrogen. Energy* 45 (16), 9440–9450. doi:10.1016/j.ijhydene.2020.01.206.
- Grasa, G., González, B., Alonso, M., Abanades, J.C., 2007. Comparison of CaO-based synthetic CO₂ sorbents under realistic calcination conditions. *Energy Fuels* 21 (6), 3560–3562. doi:10.1021/EF0701687/ASSET/IMAGES/LARGE/EF-2007-001687_0004.JPEG.
- Guban, D., Muritala, I.K., Roeb, M., Sattler, C., 2020. Assessment of sustainable high temperature hydrogen production technologies. *Int. J. Hydrogen. Energy* 45 (49), 26156–26165. doi:10.1016/j.ijhydene.2019.08.145.
- Gunawan, A., Singh, A.K., 2022. A solar thermal sorption-enhanced steam methane reforming (SE-SMR) approach and its performance assessment. *Sustain. Energy Technol. Assessments* 52, 102036. doi:10.1016/j.seta.2022.102036.
- Guo, B., Zhao, T., Sha, F., Zhang, F., Li, Q., Zhao, J., Zhang, J., 2017. Synthesis of valterite CaCO₃ micro-spheres by carbide slag and a novel CO₂-storage material. *J. CO₂ Utilization* 18, 23–29. doi:10.1016/j.jcou.2017.01.004.
- Gupta, H., Fan, L.-S., 2002. Carbonation–calcination cycle using high reactivity calcium oxide for carbon dioxide separation from flue gas. *Ind. Eng. Chem. Res.* 41 (16), 4035–4042. doi:10.1021/ie010867l.
- Hafizi, A., Rahimpour, M.R., Heravi, M., 2019. Experimental investigation of improved calcium-based CO₂ sorbent and Co₃O₄/SiO₂ oxygen carrier for clean production of hydrogen in sorption-enhanced chemical looping reforming. *Int. J. Hydrogen. Energy* 44 (33), 17863–17877. doi:10.1016/j.ijhydene.2019.05.030.
- Hanak, D.P., Michalski, S., Manovic, V., 2018. From post-combustion carbon capture to sorption-enhanced hydrogen production: a state-of-the-art review of carbonate looping process feasibility. *Energy Convers. Manage* 177, 428–452. doi:10.1016/j.enconman.2018.09.058.
- Harrison, D.P., 2008. Sorption-enhanced hydrogen production: a review. *Ind. Eng. Chem. Res.* 47 (17), 6486–6501. doi:10.1021/ie800298z.
- Hasan, M.M., Genç, G., 2022. Techno-economic analysis of solar/wind power based hydrogen production. *Fuel* 324, 124564. doi:10.1016/j.fuel.2022.124564.
- Hasnain, S.M.W., Farooqi, A.S., Ayodele, B.V., Farooqi, A.S., Sanaullah, K., Abdullah, B., 2024. Advances in Ni and Co-based catalysts for sustainable syngas production via Bi-reforming of methane: A review of recent advances. *J. Clean. Prod.* 434, 139904. doi:10.1016/j.jclepro.2023.139904.
- Hassan, I.U., Naikoo, G.A., Salim, H., Awan, T., Tabook, M.A., Pedram, M.Z., Mustaqeem, M., Sohani, A., Hoseinzadeh, S., Saleh, T.A., 2023. Advances in photochemical splitting of seawater over semiconductor nano-catalysts for hydrogen production: A critical review. *J. Indust. Eng. Chem.* 121, 1–14. doi:10.1016/j.jiec.2023.01.006.
- Hou, K., Hughes, R., 2001. The kinetics of methane steam reforming over a Ni/α-Al₂O₃ catalyst. *Chem. Eng. J.* 82 (1), 311–328. doi:10.1016/S1385-8947(00)00367-3.
- Hsu, M.J., Lee, K.H., Chyow, Y.P., 2014. CO₂ capture at high temperature using calcium-based sorbents. *J. Chinese Inst. Engineers* 37 (2), 152–164. doi:10.1080/02533839.2012.757045.
- Hyper project. (n.d.). <https://hyperh2.co.uk/the-project/>.
- IEA, 2021. Global Hydrogen Review 2021. IEA, Paris. <https://www.iea.org/reports/global-hydrogen-review-2021> License: CC BY 4.0. (n.d.).
- Imteyaz, B.A., Nemitallah, M.A., Abdelhafez, A.A., Habib, M.A., 2018. Combustion behavior and stability map of hydrogen-enriched oxy-methane premixed flames in a model gas turbine combustor. *Int. J. Hydrogen. Energy* 43 (34), 16652–16666. doi:10.1016/j.ijhydene.2018.07.087.
- Irfan, M., Li, A., Zhang, L., Wang, M., Chen, C., Khushk, S., 2019. Production of hydrogen enriched syngas from municipal solid waste gasification with waste marble powder as a catalyst. *Int. J. Hydrogen. Energy* 44 (16), 8051–8061. doi:10.1016/j.ijhydene.2019.02.048.
- Ishaq, T., Yousaf, M., Bhatti, I.A., Batool, A., Asghar, M.A., Mohsin, M., Ahmad, M., 2021. A perspective on possible amendments in semiconductors for enhanced photocatalytic hydrogen generation by water splitting. *Int. J. Hydrogen. Energy* 46 (79), 39036–39057. doi:10.1016/j.ijhydene.2021.09.165.
- Jang, D., Kim, K., Kim, K.-H., Kang, S., 2022. Techno-economic analysis and Monte Carlo simulation for green hydrogen production using offshore wind power plant. *Energy Convers. Manage* 263, 115695. doi:10.1016/j.enconman.2022.115695.
- Jiang, B., Li, L., Bian, Z., Li, Z., Sun, Y., Sun, Z., Tang, D., Kawi, S., Dou, B., Goula, M.A., 2018. Chemical looping glycerol reforming for hydrogen production by Ni@ZrO₂ nanocomposite oxygen carriers. *Int. J. Hydrogen. Energy* 43 (29), 13200–13211. doi:10.1016/j.ijhydene.2018.05.065.
- Ji, G., Yang, H., Memon, M.Z., Gao, Y., Qu, B., Fu, W., Olguin, G., Zhao, M., Li, A., 2020. Recent advances on kinetics of carbon dioxide capture using solid sorbents at elevated temperatures. *Appl. Energy* 267, 114874. doi:10.1016/j.apenergy.2020.114874.
- Ji, G., Yao, J.G., Clough, P.T., Da Costa, J.C.D., Anthony, E.J., Fennell, P.S., Wang, W., Zhao, M., 2018. Enhanced hydrogen production from thermochemical processes. *Energy Environ. Sci.* 11 (10), 2647–2672. doi:10.1039/C8EE01393D.
- Johnsen, K., Grace, J.R., Elnashaie, S.S.E.H., Kolbeinsen, L., Eriksen, D., 2006. Modeling of sorption-enhanced steam reforming in a dual fluidized bubbling bed reactor. *Ind. Eng. Chem. Res.* 45 (12), 4133–4144. doi:10.1021/ie0511736.
- Karayel, G.K., Javani, N., Dincer, I., 2023. Green hydrogen production potential in Turkey with wind power. *Int. J. Green. Energy* 20 (2), 129–138. doi:10.1080/15435075.2021.2023882.
- Karimi, M., Shirzad, M., Silva, J.A.C., Rodrigues, A.E., 2023. Carbon dioxide separation and capture by adsorption: a review. *Environ. Chem. Lett.* 21 (4), 2041–2084. doi:10.1007/s10311-023-01589-z.
- Kim, S.M., Abdala, P.M., Hosseini, D., Armutulu, A., Margossian, T., Copéret, C., Müller, C., 2019. Bi-functional Ru/Ca₃Al₂O₆-CaO catalyst-CO₂ sorbent for the production of high purity hydrogen: Via sorption-enhanced steam methane reforming. *Catal. Sci. Technol.* 9 (20), 5745–5756. doi:10.1039/c9cy01095e.
- Kovač, A., Paranos, M., Marciš, D., 2021. Hydrogen in energy transition: a review. *Int. J. Hydrogen. Energy* 46 (16), 10016–10035. doi:10.1016/j.ijhydene.2020.11.256.
- Kudria, S., Ivanchenko, I., Tuchynskyi, B., Petrenko, K., Karmazin, O., Riepien, O., 2021. Resource potential for wind-hydrogen power in Ukraine. *Int. J. Hydrogen. Energy* 46 (1), 157–168. doi:10.1016/j.ijhydene.2020.09.211.
- Lee, J., Cho, H., Kim, J., 2023. Techno-economic analysis of on-site blue hydrogen production based on vacuum pressure adsorption: practical application to real-world hydrogen refueling stations. *J. Environ. Chem. Eng.* 11 (2), 109549. doi:10.1016/j.jece.2023.109549.

- Lee, S.C., Choi, B.Y., Lee, T.J., Ryu, C.K., Ahn, Y.S., Kim, J.C., 2006. CO₂ absorption and regeneration of alkali metal-based solid sorbents. *Catal. Today* 111 (3), 385–390. doi:10.1016/j.cattod.2005.10.051.
- Li, S., Shi, Y., Yang, Y., Zheng, Y., Cai, N., 2013. High-Performance CO₂ adsorbent from interlayer potassium-promoted stearate-pillared hydrotalcite precursors. *Energy Fuels* 27 (9), 5352–5358. doi:10.1021/ef400914r.
- Liu, L., Hong, D., Guo, X., 2019. Insight into CaO addition on coking resistance of Ni surface for sorption enhanced methane steam reforming: A density functional study. *Appl. Surf. Sci.* 475, 887–895. doi:10.1016/j.apsusc.2018.12.271.
- Liu, M., Li, Y., Wang, X., Gai, Z., Rao, Q., Yang, T., Zhang, J., Tang, S., Pan, Y., Jin, H., 2024. Synergistic promotions between high purity H₂ production and CO₂ capture via sorption enhanced chemical looping reforming. *Fuel Process. Technol.* 254, 108042. doi:10.1016/j.fuproc.2024.108042.
- Liu, W., Zuo, H., Wang, J., Xue, Q., Ren, B., Yang, F., 2021. The production and application of hydrogen in steel industry. *Int. J. Hydrogen. Energy* 46 (17), 10548–10569. doi:10.1016/j.ijhydene.2020.12.123.
- Li, Y., Liu, C., Sun, R., Liu, H., Wu, S., Lu, C., 2012. Sequential SO₂/CO₂ capture of calcium-based solid waste from the paper industry in the calcium looping process. *Ind. Eng. Chem. Res.* 51 (49), 16042–16048. doi:10.1021/ie301375g.
- Li, Y., Sun, R., Liu, C., Liu, H., Lu, C., 2012. CO₂ capture by carbide slag from chlor-alkali plant in calcination/carbonation cycles. *Int. J. Greenhouse Gas Control* 9, 117–123. doi:10.1016/j.ijggc.2012.03.012.
- Li, Y., Zhao, C., Duan, L., Liang, C., Li, Q., Zhou, W., Chen, H., 2008. Cyclic calcination/carbonation looping of dolomite modified with acetic acid for CO₂ capture. *Fuel Processing Technol.* 89 (12), 1461–1469. doi:10.1016/j.fuproc.2008.07.008.
- Li, Z., Cai, N., Huang, Y., Han, H., Lu, C., 2005. Synthesis, experimental studies, and analysis of a new calcium-based carbon dioxide absorbent. *Energy Fuels* 19 (4), 1447–1452. doi:10.1021/ef0496799.
- Luo, C., Zheng, Y., Zheng, C., Yin, J., Qin, C., Feng, B., 2013. Manufacture of calcium-based sorbents for high temperature cyclic CO₂ capture via a sol-gel process. *Int. J. Greenhouse Gas Control* 12, 193–199. doi:10.1016/j.ijggc.2012.11.011.
- Luo, H., Barrio, J., Sunny, N., Li, A., Steier, L., Shah, N., Stephens, I.E.L., Titirici, M.-M., 2021. Progress and perspectives in photo- and electrochemical-oxidation of biomass for sustainable chemicals and hydrogen production. *Adv. Energy Mater.* 11 (43), 2101180. doi:10.1002/aenm.202101180.
- Luo, Y., Chen, J., Wang, T., 2024. Evaluation of the effect of CaO on hydrogen production by sorption-enhanced steam methane reforming. *ACS. Omega* 9 (5), 5330–5337. doi:10.1021/acsomega.3c05918.
- Maestri, M., Vlachos, D.G., Beretta, A., Groppi, G., Tronconi, E., 2008. Steam and dry reforming of methane on Rh: Microkinetic analysis and hierarchy of kinetic models. *J. Catal.* 259 (2), 211–222. doi:10.1016/j.jcat.2008.08.008.
- Manovic, V., Anthony, E.J., 2008. Thermal activation of CaO-based sorbent and self-reactivation during CO₂ capture looping cycles. *Environ. Sci. Technol.* 42 (11), 4170–4174. doi:10.1021/es800152s.
- Martavaltzi, C.S., Lemonidou, A.A., 2008. Development of new CaO based sorbent materials for CO₂ removal at high temperature. *Microporous Mesoporous Mater.* 110 (1), 119–127. doi:10.1016/j.micromeso.2007.10.006.
- Masoudi Soltani, S., Lahiri, A., Bahzad, H., Clough, P., Gorbounov, M., Yan, Y., 2021. Sorption-enhanced steam methane reforming for combined CO₂ capture and hydrogen production: a state-of-the-art review. *Carbon Capture Sci. Technol.* 1, 100003. doi:10.1016/j.cst.2021.100003.
- Ma, X., Li, Y., Huang, X., Feng, T., Mu, M., 2021. Sorption-enhanced reaction process using advanced Ca-based sorbents for low-carbon hydrogen production. *Process Safety Environ. Protect.* 155, 325–342. doi:10.1016/j.psep.2021.09.009.
- Memor, M.Z., Zhao, X., Sikarwar, V.S., Vuppalladiyam, A.K., Milne, S.J., Brown, A.P., Li, J., Zhao, M., 2017. Alkali metal CO₂ sorbents and the resulting metal carbonates: potential for process intensification of sorption-enhanced steam reforming. *Environ. Sci. Technol.* 51 (1), 12–27. doi:10.1021/ACS.EST.6B04992/ASSET/IMAGES/LARGE/ES-2016-04992Q_0007.JPEG.
- Mishra, K., Singh Siwal, S., Kumar Saini, A., Thakur, V.K., 2023. Recent update on gasification and pyrolysis processes of lignocellulosic and algal biomass for hydrogen production. *Fuel* 332, 126169. doi:10.1016/j.fuel.2022.126169.
- Mishra, P., Krishnan, S., Rana, S., Singh, L., Sakinah, M., Ab Wahid, Z., 2019. Outlook of fermentative hydrogen production techniques: An overview of dark, photo and integrated dark-photo fermentative approach to biomass. *Energy Strategy Rev.* 24, 27–37. doi:10.1016/j.esr.2019.01.001.
- Motaghamwala, A.H., Dumesic, J.A., 2021. Microkinetic modeling: a tool for rational catalyst design. *Chem. Rev.* 121 (2), 1049–1076. doi:10.1021/acs.chemrev.0c00394.
- Navik, R., Wang, E., Ding, X., Qiu, K., Li, J., 2024. Atmospheric carbon dioxide capture by adsorption on amine-functionalized silica composites: a review. *Environ. Chem. Lett.* 22 (4), 1791–1830. doi:10.1007/s10311-024-01737-z.
- Nawar, A., Ali, M., Khoja, A.H., Waqas, A., Anwar, M., Mahmood, M., 2021. Enhanced CO₂ capture using organic acid structure modified waste eggshell derived CaO sorbent. *J. Environ. Chem. Eng.* 9 (1), 104871. doi:10.1016/j.jece.2020.104871.
- Nazir, S.M., Cloete, J.H., Cloete, S., Amini, S., 2021. Pathways to low-cost clean hydrogen production with gas switching reforming. *Int. J. Hydrogen. Energy* 46 (38), 20142–20158. doi:10.1016/j.ijhydene.2020.01.234.
- Nemitalah, M.A., Haque, M.D.A., Hussain, M., Abdelhazef, A., Habib, M.A., 2021. Stratified and hydrogen combustion techniques for higher turndown and lower emissions in gas turbines. *J. Energy Resour. Technol.* 144 (2), 20801. doi:10.1115/1.4052541.
- Nemitalah, M.A., Imteyaz, B., Abdelhazef, A., Habib, M.A., 2019. Experimental and computational study on stability characteristics of hydrogen-enriched oxy-methane premixed flames. *Appl. Energy* 250, 433–443. doi:10.1016/j.apenergy.2019.05.087.
- Newsome, D.S., 1980. The water-gas shift reaction. *Catalysis Reviews* 21 (2), 275–318. doi:10.1080/03602458008067535.
- Nickel prices. (2024). <https://fred.stlouisfed.org/series/PNICKUSD>.
- Nimmas, T., Jamrunroj, P., Wongsakulphasatch, S., Kiatkittipong, W., Laosiripojana, N., Gong, J., Assabumrungrat, S., 2019. Influence of CaO precursor on CO₂ capture performance and sorption-enhanced steam ethanol reforming. *Int. J. Hydrogen. Energy* 44 (37), 20649–20662. doi:10.1016/j.ijhydene.2018.07.095.
- Niu, J., Wang, Y., Qi, Y., Dam, A.H., Wang, H., Zhu, Y.-A., Holmen, A., Ran, J., Chen, D., 2020. New mechanism insights into methane steam reforming on Pt/Ni from DFT and experimental kinetic study. *Fuel* 266, 117143. doi:10.1016/j.fuel.2020.117143.
- Numaguchi, T., & Kikuchi, K. (1988). *Intrinsic Kinetics and Design Simulation in a Complex Reaction Network; Steam-Methane Reforming* (J. R. BOURNE, W. REGENASS, & W. B. T.T. I. S. on C. R. E. RICHARZ, Eds.; pp. 2295–2301). Pergamon. <https://doi.org/10.1016/B978-0-08-036969-3.50086-5>
- Ochoa-Fernández, E., Haugen, G., Zhao, T., Rønning, M., Aartun, I., Børresen, B., Rytter, E., Rønnekleiv, M., Chen, D., 2007. Process design simulation of H₂ production by sorption enhanced steam methane reforming: evaluation of potential CO₂ acceptors. *Green. Chem.* 9 (6), 654–662. doi:10.1039/b614270B.
- Ochoa-Fernández, E., Rusten, H.K., Jakobsen, H.A., Rønning, M., Holmen, A., Chen, D., 2005. Sorption enhanced hydrogen production by steam methane reforming using Li₂ZrO₃ as sorbent: sorption kinetics and reactor simulation. *Catal. Today* 106 (1), 41–46. doi:10.1016/j.cattod.2005.07.146.
- Oh, V.B.Y., Ng, S.F., Ong, W.J., 2022. Is photocatalytic hydrogen production sustainable? – Assessing the potential environmental enhancement of photocatalytic technology against steam methane reforming and electrocatalysis. *J. Clean. Prod.* 379, 134673. doi:10.1016/j.jclepro.2022.134673.
- Okunev, A.G., Nesterenko, S.S., Lysikov, A.I., 2008. Decarbonation rates of cycled CaO absorbents. *Energy Fuels* 22 (3), 1911–1916. doi:10.1021/ef800047b.
- Oliveira, A.M., Beswick, R.R., Yan, Y., 2021. A green hydrogen economy for a renewable energy society. *Curr. Opin. Chem. Eng.* 33, 100701. doi:10.1016/j.coche.2021.100701.
- Oliveira, E.L.G., Grande, C.A., Rodrigues, A.E., 2009. Steam methane reforming in a Ni/Al₂O₃ catalyst: Kinetics and diffusional limitations in extrudates. *Can. J. Chem. Eng.* 87 (6), 945–956. doi:10.1002/cjce.20223.
- Olivier, A., Desgagnés, A., Iluuta, M.C., 2024. Development of a bifunctional material incorporating carbon microspheres for the intensified hydrogen production by sorption-enhanced glycerol steam reforming. *Chem. Eng. Process. - Process Intensification* 200, 109790. doi:10.1016/j.cep.2024.109790.
- Oni, A.O., Anaya, K., Giwa, T., Di Lullo, G., Kumar, A., 2022. Comparative assessment of blue hydrogen from steam methane reforming, autothermal reforming, and natural gas decomposition technologies for natural gas-producing regions. *Energy Convers. Manage.* 254, 115245. doi:10.1016/j.enconman.2022.115245.
- Osman, A.I., Hefny, M., Abdel Maksoud, M.I.A., Elgarhy, A.M., Rooney, D.W., 2021. Recent advances in carbon capture storage and utilisation technologies: a review. *Environ. Chem. Lett.* 19 (2), 797–849. doi:10.1007/s10311-020-01133-3.
- Osman, A.I., Mehta, N., Elgarhy, A.M., Hefny, M., Al-Hinai, A., Al-Muhtaseb, A.H., Rooney, D.W., 2022. Hydrogen production, storage, utilisation and environmental impacts: a review. *Environ. Chem. Lett.* 20 (1), 153–188. doi:10.1007/s10311-021-01322-8.
- Ozcan, D.C., Shanks, B.H., Wheelock, T.D., 2011. Improving the stability of a CaO-based sorbent for CO₂ by thermal pretreatment. *Ind. Eng. Chem. Res.* 50 (11), 6933–6942. doi:10.1021/ie102368g.
- Pal, D.B., Chand, R., Upadhyay, S.N., Mishra, P.K., 2018. Performance of water gas shift reaction catalysts: A review. *Renew Sustain Energy Rev.* 93, 549–565. doi:10.1016/j.rser.2018.05.003.
- Pal, D.B., Singh, A., Bhatnagar, A., 2022. A review on biomass based hydrogen production technologies. *Int. J. Hydrogen. Energy* 47 (3), 1461–1480. doi:10.1016/j.ijhydene.2021.10.124.
- Parkinson, B., Balcombe, P., Speirs, J.F., Hawkes, A.D., Hellgardt, K., 2019. Levelized cost of CO₂ mitigation from hydrogen production routes. *Energy Environ. Sci.* 12 (1), 19–40. doi:10.1039/C8EE02079E.
- Pecharamporn, P., Wongsakulphasatch, S., Glinrun, T., Maneedaeng, A., Hassan, Z., Assabumrungrat, S., 2019. Synthetic CaO-based sorbent for high-temperature CO₂ capture in sorption-enhanced hydrogen production. *Int. J. Hydrogen. Energy* 44 (37), 20663–20677. doi:10.1016/j.ijhydene.2018.06.153.
- Pfeiffer, H., 2010. Advances on alkaline ceramics as possible CO₂ captors. In: *Advances in CO₂ Conversion and Utilization*, 1056. American Chemical Society, pp. 15–233. doi:10.1021/bk-2010-1056.ch015.
- Phromprasit, J., Powell, J., Wongsakulphasatch, S., Kiatkittipong, W., Bumroongsakul-sawat, P., Assabumrungrat, S., 2017. H₂ production from sorption enhanced steam reforming of biogas using multifunctional catalysts of Ni over Zr-, Ce- and La-modified CaO sorbents. *Chem. Eng. J.* 313, 1415–1425. doi:10.1016/j.cej.2016.11.051.
- Podolski, W.F., Kim, Y.G., 1974. Modeling the water-gas shift reaction. *Indust. Eng. Chem. Process Design Develop* 13 (4), 415–421. doi:10.1021/i260052a021.
- Quirino, P.P.S., Amaral, A., Pontes, K.V., Rossi, F., Manenti, F., 2021. Impact of kinetic models in the prediction accuracy of an industrial steam methane reforming unit. *Comput. Chem. Eng.* 152, 107379. doi:10.1016/j.compchemeng.2021.107379.
- Radfarnia, H.R., Iluuta, M.C., 2013a. Limestone acidification using citric acid coupled with two-step calcination for improving the CO₂ sorbent activity. *Ind. Eng. Chem. Res.* 52 (21), 7002–7013. doi:10.1021/ie400277q.
- Radfarnia, H.R., Iluuta, M.C., 2013b. Metal oxide-stabilized calcium oxide CO₂ sorbent for multicycle operation. *Chem. Eng. J.* 232, 280–289. doi:10.1016/j.cej.2013.07.049.
- Raheem, A., Liu, H., Ji, G., Zhao, M., 2019. Gasification of lipid-extracted microalgae biomass promoted by waste eggshell as CaO catalyst. *Algal. Res.* 42, 101601. doi:10.1016/j.algal.2019.101601.
- Rahmanzadeh, L., Taghizadeh, M., 2019. Sorption-enhanced ethanol steam reforming on Ce-Ni/MCM-41 with simultaneous CO₂ adsorption over Na- and Zr- promoted CaO based sorbent. *Int. J. Hydrogen. Energy* 44 (39), 21238–21250. doi:10.1016/J.IJHYDENE.2019.04.289.

- Rahmat, Y., Maier, S., Moser, F., Raab, M., Hoffmann, C., Repke, J.-U., Dietrich, R.U., 2023. Techno-economic and exergy analysis of e-methanol production under fixed operating conditions in Germany. *Appl. Energy* 351, 121738.
- Reddy, G.K., Quillin, S., Smirniotis, P., 2014. Influence of the synthesis method on the structure and CO₂ adsorption properties of Ca/Zr sorbents. *Energy Fuels* 28 (5), 3292–3299. doi:10.1021/ef402573u.
- Reddy, G. K., & Smirniotis, P. G. (2015). *Chapter 1 - Introduction About WGS Reaction* (G. K. Reddy & P. G. B. T.W. G. S. R. Smirniotis, Eds.; pp. 1–20). Elsevier. <https://doi.org/10.1016/B978-0-12-420154-5.00001-2>
- Rhodes, C., Hutchings, G.J., Ward, A.M., 1995. Water-gas shift reaction: finding the mechanistic boundary. *Catal. Today* 23 (1), 43–58. doi:10.1016/0920-5861(94)00135-O.
- Ridha, F.N., Manovic, V., Macchi, A., Anthony, E.J., 2012. The effect of SO₂ on CO₂ capture by CaO-based pellets prepared with a kaolin derived Al(OH)₃ binder. *Appl. Energy* 92, 415–420. doi:10.1016/j.apenergy.2011.11.036.
- Ridha, F.N., Manovic, V., Macchi, A., Anthony, M.A., Anthony, E.J., 2013. Assessment of limestone treatment with organic acids for CO₂ capture in Ca-looping cycles. *Fuel Process. Technol.* 116, 284–291. doi:10.1016/j.fuproc.2013.07.007.
- Ridha, F.N., Manovic, V., Wu, Y., Macchi, A., Anthony, E.J., 2013. Post-combustion CO₂ capture by formic acid-modified CaO-based sorbents. *Int. J. Greenhouse Gas Control* 16, 21–28. doi:10.1016/j.jggc.2013.02.026.
- Rout, K.R., Ferosmo, J., Chen, D., Jakobsen, H.A., 2014. Kinetic rate of CO₂ uptake of a synthetic Ca-based sorbent: Experimental data and numerical simulations. *Fuel* 120, 53–65. doi:10.1016/j.fuel.2013.12.011.
- Rusten, H.K., Ochoa-Fernández, E., Lindborg, H., Chen, D., Jakobsen, H.A., 2007. Hydrogen production by sorption-enhanced steam methane reforming using lithium oxides as CO₂-acceptor. *Ind. Eng. Chem. Res.* 46 (25), 8729–8737. doi:10.1021/ie070770k.
- Ruthenium prices. (2024). <https://strategicmetalsinvest.com/ruthenium-prices/#:text=Ruthenium%20Historical%20Price%20Movement,%20is%20currently%20%2B110.48%25>.
- Saeidi, S., Fazlollahi, F., Najari, S., Iranshahi, D., Klemeš, J.J., Baxter, L.L., 2017. Hydrogen production: Perspectives, separation with special emphasis on kinetics of WGS reaction: a state-of-the-art review. *J. Indust. Eng. Chem.* 49, 1–25. doi:10.1016/j.jiec.2016.12.003.
- Safari, F., Dincer, I., 2020. A review and comparative evaluation of thermochemical water splitting cycles for hydrogen production. *Energy Convers. Manage* 205, 112182. doi:10.1016/j.enconman.2019.112182.
- Salcedo, A., Lustemberg, P.G., Rui, N., Palomino, R.M., Liu, Z., Nemsak, S., Senanayake, S.D., Rodriguez, J.A., Ganduglia-Pirovano, M.V., Irigoyen, B., 2021. Reaction pathway for coke-free methane steam reforming on a Ni/CeO₂ catalyst: active sites and the role of metal-support interactions. *ACS. Catal.* 11 (13), 8327–8337. doi:10.1021/acscatal.1c01604.
- Santos, D.B.L., Oliveira, A.C.P., Hori, C.E., 2021. Performance of Na₂CO₃-CaO sorbent in sorption-enhanced steam methane reforming. *J. CO₂ Utilization* 51, 101634. doi:10.1016/j.jcou.2021.101634.
- S G Adiya, Z.I., Dupont, V., Mahmud, T., 2019. Steam reforming of shale gas with nickel and calcium looping. *Fuel* 237, 142–151. doi:10.1016/j.fuel.2018.09.092.
- Shahid, M.Z., Kim, J.-K., 2023. Design and economic evaluation of a novel amine-based CO₂ capture process for SMR-based hydrogen production plants. *J. Clean. Prod.* 402, 136704.
- Shahid, M.Z., Maulud, A.S., Azmi Bustam, M., Suleman, H., 2020. Modeling of CO₂-MEA absorption system in the packed column using Sulzer DX structured packing. *IOP Conf. Series: Mater. Sci. Eng.* 736 (2), 022059. doi:10.1088/1757-899X/736/2/022059.
- Shamsudin, I.K., Abdullah, A., Idris, I., Gobi, S., Othman, M.R., 2019. Hydrogen purification from binary syngas by PSA with pressure equalization using microporous palm kernel shell activated carbon. *Fuel* 253, 722–730. doi:10.1016/j.fuel.2019.05.029.
- Sharma, P., Gaur, V.K., Kim, S.-H., Pandey, A., 2020. Microbial strategies for bio-transforming food waste into resources. *Bioresour. Technol.* 299, 122580. doi:10.1016/j.biortech.2019.122580.
- Shokrollahi Yancheshmeh, M., Radfarnia, H.R., Iliuta, M.C., 2016a. High temperature CO₂ sorbents and their application for hydrogen production by sorption enhanced steam reforming process. In: *Chemical Engineering Journal*, 283. Elsevier, pp. 420–444. doi:10.1016/j.cej.2015.06.060.
- Shokrollahi Yancheshmeh, M., Radfarnia, H.R., Iliuta, M.C., 2016b. Influence of steam addition during carbonation or calcination on the CO₂ capture performance of Ca9Al6O18CaO sorbent. *J. Nat. Gas. Sci. Eng.* 36, 1062–1069. doi:10.1016/j.jngse.2016.06.009.
- Shokrollahi Yancheshmeh, M., Radfarnia, H.R., Iliuta, M.C., 2017. Sustainable production of high-purity hydrogen by sorption enhanced steam reforming of glycerol over CeO₂-promoted Ca9Al6O18-CaO/NiO bifunctional material. *ACS. Sustain. Chem. Eng.* 5 (11), 9774–9786. doi:10.1021/acssuschemeng.7b01627.
- Sikander, U., Sufian, S., Salam, M.A., 2017. A review of hydrotalcite based catalysts for hydrogen production systems. *Int. J. Hydrogen. Energy* 42 (31), 19851–19868. doi:10.1016/j.ijhydene.2017.06.089.
- Sikarwar, V.S., Pfeifer, C., Ronse, F., Pohorély, M., Meers, E., Kaviti, A.K., Jeremiáš, M., 2022. Progress in in-situ CO₂-sorption for enhanced hydrogen production. *Prog. Energy Combust. Sci.* 91, 101008.
- Sikarwar, V.S., Zhao, M., Clough, P., Yao, J., Zhong, X., Memon, M.Z., Shah, N., Anthony, E.J., Fennell, P.S., 2016. An overview of advances in biomass gasification. *Energy Environ. Sci.* 9 (10), 2939–2977. doi:10.1039/C6EE00935B.
- Smith R J, B., Loganathan, M., & Shantha, M. S. (2010). *A Review of the Water Gas Shift Reaction Kinetics*. 8(1). <https://doi.org/10.2202/1542-6580.2238>
- Soltani, S.M., Lahiri, A., Bahzad, H., Clough, P., Gorbounov, M., Yan, Y., 2021. Sorption-enhanced steam methane reforming for combined CO₂ capture and hydrogen production: a state-of-the-art review. *Carbon Capture Sci. Technol.* 1, 100003.
- Song, H., Liu, Y., Bian, H., Shen, M., Lin, X., 2022. Energy, environment, and economic analyses on a novel hydrogen production method by electrified steam methane reforming with renewable energy accommodation. *Energy Convers. Manage* 258, 115513. doi:10.1016/j.enconman.2022.115513.
- Stendardo, S., Andersen, L.K., Hecce, C., 2013. Self-activation and effect of regeneration conditions in CO₂-carbonate looping with CaO–Ca12Al14O33 sorbent. *Chem. Eng. J.* 220, 383–394. doi:10.1016/J.CEJ.2013.01.045.
- Stendardo, S., Foscolo, P.U., 2009. Carbon dioxide capture with dolomite: A model for gas–solid reaction within the grains of a particulate sorbent. *Chem. Eng. Sci.* 64 (10), 2343–2352. doi:10.1016/J.CES.2009.02.009.
- Sun, J., Liu, W., Hu, Y., Wu, J., Li, M., Yang, X., Wang, W., Xu, M., 2016. Enhanced performance of extruded–spheronized carbide slag pellets for high temperature CO₂ capture. *Chem. Eng. J.* 285, 293–303. doi:10.1016/j.cej.2015.10.026.
- Sun, P., Grace, J.R., Lim, C.J., Anthony, E.J., 2007. The effect of CaO sintering on cyclic CO₂ capture in energy systems. *AIChE J.* 53 (9), 2432–2442. doi:10.1002/aic.11251.
- Sürer, M.G., Arat, H.T., 2022. Advancements and current technologies on hydrogen fuel cell applications for marine vehicles. *Int. J. Hydrogen. Energy* 47 (45), 19865–19875. doi:10.1016/j.ijhydene.2021.12.251.
- Tan, R.S., Tuan Abdullah, T.A., Mahmud, S.A., Md Zin, R., Md Isa, K., 2019. Catalytic steam reforming of complex gasified biomass tar model toward hydrogen over dolomite promoted nickel catalysts. *Int. J. Hydrogen. Energy* 44 (39), 21303–21314. doi:10.1016/j.ijhydene.2019.06.125.
- Temkin, M. I. (1979). *The Kinetics of Some Industrial Heterogeneous Catalytic Reactions* (D. D. Eley, H. Pines, & P. B. B. T.-A. in C. Weez, Eds.; Vol. 28, pp. 173–291). Academic Press. [https://doi.org/10.1016/S0360-0564\(08\)60135-2](https://doi.org/10.1016/S0360-0564(08)60135-2)
- Tian, S., Jiang, J., Yan, F., Li, K., Chen, X., 2015. Synthesis of highly efficient CaO-based, self-stabilizing CO₂ sorbents via structure-reforming of steel slag. *Environ. Sci. Technol.* 49 (12), 7464–7472. doi:10.1021/acs.est.5b00244.
- Tsipouriari, V.A., Verykios, X.E., 2001. Kinetic study of the catalytic reforming of methane with carbon dioxide to synthesis gas over Ni/La₂O₃ catalyst. *Catal. Today* 64 (1), 83–90. doi:10.1016/S0920-5861(00)00511-3.
- Turkdogan, S., 2021. Design and optimization of a solely renewable based hybrid energy system for residential electrical load and fuel cell electric vehicle. *Eng. Sci. Technol. Int. J.* 24 (2), 397–404. doi:10.1016/j.jestech.2020.08.017.
- Twigg, M.V. Imperial Chemical Industries, Ltd A. D. T. A.-T. T.-., 1989. *Catalyst Handbook* (2nd ed NV). Wolfe LK. <https://worldcat.org/title/569523796>.
- Tzanetis, K.F., Martavaltzi, C.S., Lemonidou, A.A., 2012. Comparative exergy analysis of sorption enhanced and conventional methane steam reforming. *Int. J. Hydrogen. Energy* 37 (21), 16308–16320.
- Udemu, C., Font-Palma, C., 2023. Modelling of sorption-enhanced steam reforming (SE-SR) process in fluidised bed reactors for low-carbon hydrogen production: A review. *Fuel* 340, 127588. doi:10.1016/J.FUEL.2023.127588.
- Udomchoke, T., Wongsakulphasatch, S., Kiattitipong, W., Arpornwichean, A., Khaodee, W., Powell, J., Gong, J., Assabumrungrat, S., 2016. Performance evaluation of sorption enhanced chemical-looping reforming for hydrogen production from biomass with modification of catalyst and sorbent regeneration. *Chem. Eng. J.* 303, 338–347.
- van Herwijnen, T., de Jong, W.A., 1980. Kinetics and mechanism of the CO shift on CuZnO: 1. Kinetics of the forward and reverse CO shift reactions. *J. Catal.* 63 (1), 83–93. doi:10.1016/0021-9517(80)90061-5.
- Voldsund, M., Jorlad, K., Anantharaman, R., 2016. Hydrogen production with CO₂ capture. *Int. J. Hydrogen. Energy* 41 (9), 4969–4992. doi:10.1016/j.ijhydene.2016.01.009.
- Wang, C., Liao, M., Jiang, Z., Liang, B., Weng, J., Song, Q., Zhao, M., Chen, Y., Lei, L., 2022. Sorption-enhanced propane partial oxidation hydrogen production for solid oxide fuel cell (SOFC) applications. *Energy* 247, 123463. doi:10.1016/j.energy.2022.123463.
- Wang, F., Li, Y., Wang, Y., Zhang, C., Chu, L., Yang, L., Fan, X., 2022. Mechanism insights into sorption enhanced methane steam reforming using Ni-doped CaO for H₂ production by DFT study. *Fuel* 319, 123849. doi:10.1016/j.fuel.2022.123849.
- Wang, F., Wang, P., Raheem, A., Ji, G., Memon, M.Z., Song, Y., Zhao, M., 2019. Enhancing hydrogen production from biomass pyrolysis by dental-wastes-derived sodium zirconate. *Int. J. Hydrogen. Energy* 44 (43), 23846–23855. doi:10.1016/j.ijhydene.2019.07.095.
- Wang, H., Blaylock, D.W., Dam, A.H., Liland, S.E., Rout, K.R., Zhu, Y.-A., Green, W.H., Holmen, A., Chen, D., 2017. Steam methane reforming on a Ni-based bimetallic catalyst: density functional theory and experimental studies of the catalytic consequence of surface alloying of Ni with Ag. *Catal. Sci. Technol.* 7 (8), 1713–1725. doi:10.1039/C7CY00101K.
- Wang, J., Huang, L., Yang, R., Zhang, Z., Wu, J., Gao, Y., Wang, Q., O'Hare, D., Zhong, Z., 2014. Recent advances in solid sorbents for CO₂ capture and new development trends. *Energy Environ. Sci.* 7 (11), 3478–3518. doi:10.1039/C4EE01647E.
- Wang, K., Hu, X., Zhao, P., Yin, Z., 2016. Natural dolomite modified with carbon coating for cyclic high-temperature CO₂ capture. *Appl. Energy* 165, 14–21. doi:10.1016/j.apenergy.2015.12.071.
- Wang, N., Feng, Y., Chen, Y., Guo, X., 2019. Lithium-based sorbent from rice husk materials for hydrogen production via sorption-enhanced steam reforming of ethanol. *Fuel* 245, 263–273. doi:10.1016/j.fuel.2019.02.048.
- Wang, N., Feng, Y., Guo, X., Ma, S., 2024. Calcium-based pellets for continuous hydrogen production by sorption-enhanced steam methane reforming. *Int. J. Hydrogen. Energy* 49, 897–909. doi:10.1016/j.ijhydene.2023.09.189.
- Wang, S., Fan, S., Fan, L., Zhao, Y., Ma, X., 2015. Effect of cerium oxide doping on the performance of CaO-based sorbents during calcium looping cycles. *Environ. Sci. Technol.* 49 (8), 5021–5027. doi:10.1021/es5052843.
- Wang, Y., Memon, M.Z., Seelro, M.A., Fu, W., Gao, Y., Dong, Y., Ji, G., 2021. A review of CO₂ sorbents for promoting hydrogen production in the sorption-enhanced steam reforming process. *Int. J. Hydrogen. Energy* 46 (45), 23358–23379. doi:10.1016/j.ijhydene.2021.01.206.
- Wang, Y., Zhou, H., Yao, D., Olguin, G., Ding, H., Qu, B., Xie, W., Fu, Z., Guo, Y., Wang, X., Li, A., Ji, G., 2024. Ni-CaO-CaZrO₃ bi-functional materials for high purity hydrogen

- production via sorption enhanced steam reforming of ethanol. *J. Clean. Prod.* 446, 141397. doi:[10.1016/j.jclepro.2024.141397](https://doi.org/10.1016/j.jclepro.2024.141397).
- Wei, J., Iglesia, E., 2004. Isotopic and kinetic assessment of the mechanism of reactions of CH₄ with CO₂ or H₂O to form synthesis gas and carbon on nickel catalysts. *J. Catal.* 224 (2), 370–383. doi:[10.1016/j.jcat.2004.02.032](https://doi.org/10.1016/j.jcat.2004.02.032).
- Wu, S.F., Li, Q.H., Kim, J.N., Yi, K.B., 2008. Properties of a nano CaO/Al₂O₃ CO₂ sorbent. *Indust. Eng. Chem. Res.* 47 (1), 180–184. doi:[10.1021/IE0704748/ASSET/IMAGES/LARGE/IE0704748F00012.JPEG](https://doi.org/10.1021/IE0704748/ASSET/IMAGES/LARGE/IE0704748F00012.JPEG).
- Xu, J., Froment, G.F., 1989. Methane steam reforming, methanation and water-gas shift: I. Intrinsic kinetics. *AIChE J.* 35 (1), 88–96. doi:[10.1002/aic.690350109](https://doi.org/10.1002/aic.690350109).
- Xu, Y., Lu, B., Luo, C., Chen, J., Zhang, Z., Zhang, L., 2021. Sorption enhanced steam reforming of ethanol over Ni-based catalyst coupling with high-performance CaO pellets. *Chem. Eng. J.* 406, 126903. doi:[10.1016/j.cej.2020.126903](https://doi.org/10.1016/j.cej.2020.126903).
- Xu, Z.-X., Song, H., Li, P.-J., Zhu, X., Zhang, S., Wang, Q., Duan, P.-G., Hu, X., 2020. A new method for removal of nitrogen in sewage sludge-derived hydrochar with hydrotalcite as the catalyst. *J. Hazard. Mater.* 398, 122833. doi:[10.1016/j.jhazmat.2020.122833](https://doi.org/10.1016/j.jhazmat.2020.122833).
- Yan, F., Jiang, J., Li, K., Tian, S., Liu, Z., Shi, J., Chen, X., Fei, J., Lu, Y., 2016. Cyclic performance of waste-derived SiO₂ stabilized, cao-based sorbents for fast CO₂ capture. *ACS Sustain. Chem. Eng.* 4 (12), 7004–7012. doi:[10.1021/acssuschemeng.6b01903](https://doi.org/10.1021/acssuschemeng.6b01903).
- Yan, F., Jiang, J., Li, K., Tian, S., Zhao, M., Chen, X., 2015. Performance of coal fly ash stabilized, CaO-based sorbents under different carbonation–calcination conditions. *ACS Sustain. Chem. Eng.* 3 (9), 2092–2099. doi:[10.1021/acssuschemeng.5b00355](https://doi.org/10.1021/acssuschemeng.5b00355).
- Yang, L., Yu, H., Wang, S., Wang, H., Zhou, Q., 2013. Carbon dioxide captured from flue gas by modified ca-based sorbents in fixed-bed reactor at high temperature. *Chin. J. Chem. Eng.* 21 (2), 199–204. doi:[10.1016/S1004-9541\(13\)60459-0](https://doi.org/10.1016/S1004-9541(13)60459-0).
- Yan, Y., Manovic, V., Anthony, E.J., Clough, P.T., 2020. Techno-economic analysis of low-carbon hydrogen production by sorption enhanced steam methane reforming (SE-SMR) processes. *Energy Convers. Manage.* 226, 113530. doi:[10.1016/j.enconman.2020.113530](https://doi.org/10.1016/j.enconman.2020.113530).
- Yan, Y., Thanganadar, D., Clough, P.T., Mukherjee, S., Patchigolla, K., Manovic, V., Anthony, E.J., 2020. Process simulations of blue hydrogen production by upgraded sorption enhanced steam methane reforming (SE-SMR) processes. *Energy Convers. Manage.* 222, 113144.
- Yong, Z., Rodrigues, A.E., 2002. Hydrotalcite-like compounds as adsorbents for carbon dioxide. *Energy Convers. Manage.* 43 (14), 1865–1876. doi:[10.1016/S0196-8904\(01\)00125-X](https://doi.org/10.1016/S0196-8904(01)00125-X).
- Yu, M., Wang, K., Vredenburg, H., 2021. Insights into low-carbon hydrogen production methods: Green, blue and aqua hydrogen. *Int. J. Hydrogen. Energy* 46 (41), 21261–21273. doi:[10.1016/j.ijhydene.2021.04.016](https://doi.org/10.1016/j.ijhydene.2021.04.016).
- Zhang, B., Chen, Y., Kang, B., Qian, J., Chuai, X., Peng, R., Li, Z., Guo, F., Yan, W., Zhang, J., 2020. Hydrogen production via steam reforming of coke oven gas enhanced by steel slag-derived CaO. *Int. J. Hydrogen. Energy* 45 (24), 13231–13244. doi:[10.1016/j.ijhydene.2020.03.061](https://doi.org/10.1016/j.ijhydene.2020.03.061).
- Zhao, C., Zhou, Z., Cheng, Z., 2014. Sol-gel-derived synthetic CaO-based CO₂ sorbents incorporated with different inert materials. *Ind. Eng. Chem. Res.* 53 (36), 14065–14074. doi:[10.1021/ie502559t](https://doi.org/10.1021/ie502559t).
- Zhao, C., Zhou, Z., Cheng, Z., Fang, X., 2016. Sol-gel-derived, CaZrO₃-stabilized Ni/CaO-CaZrO₃ bifunctional catalyst for sorption-enhanced steam methane reforming. *Appl. Catal. B: Environ.* 196, 16–26. doi:[10.1016/j.apcatb.2016.05.021](https://doi.org/10.1016/j.apcatb.2016.05.021).
- Zhang, J., Wang, M., Xu, S., Feng, Y., 2019. Hydrogen and methane mixture from biomass gasification coupled with catalytic tar reforming, methanation and adsorption enhanced reforming. *Fuel Process. Technol.* 192, 147–153. doi:[10.1016/j.fuproc.2019.04.023](https://doi.org/10.1016/j.fuproc.2019.04.023).
- Zhao, M., Bilton, M., Brown, A.P., Cunliffe, A.M., Dvininov, E., Dupont, V., Comyn, T.P., Milne, S.J., 2014. Durability of CaO-CaZrO₃ sorbents for high-temperature CO₂ capture prepared by a wet chemical method. *Energy Fuels* 28 (2), 1275–1283. doi:[10.1021/ef4020845](https://doi.org/10.1021/ef4020845).
- Zhao, M., Memon, M.Z., Ji, G., Yang, X., Vuppuladadiyam, A.K., Song, Y., Raheem, A., Li, J., Wang, W., Zhou, H., 2020. Alkali metal bifunctional catalyst-sorbents enabled biomass pyrolysis for enhanced hydrogen production. *Renew. Energy* 148, 168–175. doi:[10.1016/j.renene.2019.12.006](https://doi.org/10.1016/j.renene.2019.12.006).
- Zhou, D., Li, Z., Deng, Y., Dang, C., Cai, W., 2024. Sorption-enhanced biogas steam reforming over the Pb-modified Ni–CaO bifunctional catalysts. *Fuel* 357, 129851. doi:[10.1016/j.fuel.2023.129851](https://doi.org/10.1016/j.fuel.2023.129851).
- Zhou, Z., Qi, Y., Xie, M., Cheng, Z., Yuan, W., 2012. Synthesis of CaO-based sorbents through incorporation of alumina/aluminate and their CO₂ capture performance. *Chem. Eng. Sci.* 74, 172–180. doi:[10.1016/j.ces.2012.02.042](https://doi.org/10.1016/j.ces.2012.02.042).
- Zhu, L., Li, L., Fan, J., 2015. A modified process for overcoming the drawbacks of conventional steam methane reforming for hydrogen production: Thermodynamic investigation. *Chem. Eng. Res. Design* 104, 792–806. doi:[10.1016/j.cherd.2015.10.022](https://doi.org/10.1016/j.cherd.2015.10.022).
- Zhu, M., Wachs, I.E., 2016. Iron-based catalysts for the high-temperature water–Gas Shift (HT-WGS) reaction: a review. *ACS Catal.* 6 (2), 722–732. doi:[10.1021/acscatal.5b02594](https://doi.org/10.1021/acscatal.5b02594).



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